Mohammad Jawaid
Sarat Kumar Swain *Editors*

Bionanocomposites for Packaging Applications

Springer

Bionanocomposites for Packaging Applications

Mohammad Jawaid · Sarat Kumar Swain
Editors

Bionanocomposites for Packaging Applications

Springer

Editors
Mohammad Jawaid
Laboratory of Biocomposite Technology
Universiti Putra Malaysia
Serdang
Malaysia

Sarat Kumar Swain
Department of Chemistry
Veer Surendra Sai University of Technology
Burla, Odisha
India

ISBN 978-3-319-67318-9 ISBN 978-3-319-67319-6 (eBook)
https://doi.org/10.1007/978-3-319-67319-6

Library of Congress Control Number: 2017951422

© Springer International Publishing AG 2018
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Editors are honoured to dedicate this book to the

Mr. Ziaur Rahman
(Father of Dr. Mohammad Jawaid)

Mr. Rabindra Nath Swain
(Father of Prof. Sarat Kumar Swain)

Preface

This book introduces the current demand of eco-friendly bionanocomposite manufacturing and designing for packaging applications. The focus of this book is about the current demand of the bionanocomposite and their packaging applications. Bionanocomposite materials currently stand best packaging materials among the other materials such as conventional engineering composite materials, because of its outstanding features such as lightweight, low cost, environmentally friendly and sustainability. The specialism in bionanocomposites is inaugurated by its outstanding degradable and sustainable properties. Unlike other composites, this bionanocomposites are prepared with reinforcement of different nanomaterials including natural fibres and biodegradable resins. The unique feature of this book is that it presents a unified knowledge of this eco-friendly biocomposites on the basis of characterization, design, manufacture and applications.

This book assembles the information and knowledge on bionanocomposites and emphasizes the concept of gas barrier properties. This book benefits the lecturers, students, researchers and industrialist who are working in the field of packaging application in particular and material science in general. This book especially on bionanocomposites for packaging purpose is a valuable reference book, handbook and textbook for teaching, learning and research in both academic and industrial interests. This sustainable material for packaging applications penetrates into the market segment and has significant potential in automotive, marine, aerospace, construction, wind energy and consumer goods.

This book contains extensive examples and real-world products that will be suitable as per the need of markets. This book covers versatile topics such as perspectives of bionanocomposites, polymer-based bionanocomposites for future packaging materials, cellulose-reinforced biodegradable polymer composite film, nanohybrid active fillers in food contact biobased materials, oil palm biomass cellulose and polylactic acid/cellulose nanofibre composite, chitosan-based nanocomposite, natural biopolymer-based nanocomposite films, copper-reinforced cellulose nanocomposites, polysaccharides-based bionanocomposites, LDPE/RH/MAPE/MMT nanocomposite films, rubber-based nanocomposites and significance of ionic liquids, proteins as agricultural polymers, and layered double hydroxide reinforced polymer bionanocomposites for packaging applications.

We are highly thankful to contributors of different chapters who provided us their valuable innovative ideas and knowledge in this edited book. We attempt to gather information related to bionanocomposites for packaging applications from diverse fields around the world (Turkey, Italy, Malaysia, India, USA, Pakistan, and Oman) and finally complete this venture in a fruitful way. We greatly appreciate contributor's commitment for their support to compile our ideas in reality.

We are highly thankful to Springer UK team for their generous cooperation at every stage of the book production.

Serdang, Malaysia Mohammad Jawaid
Burla, India Sarat Kumar Swain

Contents

About the Editors

Dr. Mohammad Jawaid is currently working as Fellow Researcher (Associate Professor) at Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, Serdang, Selangor, Malaysia, and also Visiting Professor at the Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia, since June 2013. He is also Visiting Scientist to TEMAG Laboratory, Faculty of Textile Technologies and Design at Istanbul Technical University, Turkey. Previously, he worked as Visiting Lecturer, Faculty of Chemical Engineering, Universiti Teknologi Malaysia (UTM), and also worked as Expatriate Lecturer under UNDP project with Ministry of Education of Ethiopia at Adama University, Ethiopia. He received his Ph.D. from Universiti Sains Malaysia, Malaysia. He has more than 10 years of experience in teaching, research and industries. His area of research interests includes hybrid reinforced/filled polymer composites, advance materials: graphene/nanoclay/fire-retardant, lignocellulosic reinforced/filled polymer composites, modification and treatment of lignocellulosic fibres and solid wood, nanocomposites and nanocellulose fibres, polymer blends. So far, he has published 13 books, 29 chapters, more than 190 international journal papers and five published review papers under top 25 hot articles in science direct during 2013–2015. He is Guest Editor of special issue, Current Organic Synthesis & Current Analytical Chemistry, Bentham Publishers, UK; and Editorial Board Member of Journal of Asian Science Technology & Innovation. Besides that, he is also reviewer of several high-impact ISI journals of Elsevier, Springer, Wiley, Saga, etc. Presently, he is supervising 20 Ph.D. students and eight Master students in the field of hybrid composites, green composites, nanocomposites, natural fibre-reinforced composites, nanocellulose, etc. Nine Ph.D. and five Master students graduated under his supervision in 2014–17. He has several research grants at university, national and international level on polymer composites of around RM 3 Million (USD 700,000). He also delivered plenary and invited talk in international conference related to composites in India, Turkey, Malaysia, Thailand, UK, France, Saudi Arabia, and China. Besides that, he is also member of technical committee of several national and international conferences on composites and material science.

Prof. (Dr.) Sarat Kumar Swain is currently working as a Professor of Chemistry and Dean (Postgraduate Studies and Research) at Veer Surendra Sai University of Technology, Burla, Sambalpur, Odisha, India. Before joining to the present position, he served as an Associate Professor of Chemistry at the North Orissa University, Baripada, India, till September 2011. He was working as Postdoctoral Fellow in the Department of Polymer Engineering, University of Akron, Akron, OH, USA, after receiving his doctoral degree from Utkal University, Bhubaneswar, India. He was also working as a visiting researcher at Indian Association for Cultivation for Science, Kolkata, India, and Jawaharlal Nehru Centre for Advanced and Scientific Research, Bangalore, India, with awarding INSA Fellowship and JNCASR Fellowship. He has more than 20 years of experience in teaching and research in the area of organic chemistry, materials chemistry and polymer chemistry at UG and PG levels. His area of research interests includes: hybrid nanomaterials reinforced polymer nanocomposites, advance materials such as graphene, nanoclay, CNT, CNF for gas barrier and fire-retardant properties. He has designed various nanostructured materials for anti-corrosion performance, superconductor properties and sensor behaviours. So far, he has published two books, 22 chapters and more than 100 international journal papers with inventions of two patents to his credits. Prof. Swain is the regular reviewers of different international journals published by ACS, RSC, Elsevier, Wiley, Springer, Taylor-Francis etc. There are ten scholars who are successfully awarded Ph.D. degree with active supervisions of Prof. Swain along with nine M.Phil., five M.Tech. and 20 M.Sc. students who have completed their thesis in the field of hybrid nanocomposites, nanohydrogels and analysis of polymer-/biopolymer-/protein-based nanostructured materials He has handled several research grants from the Department of Science and Technology, Department of Biotechnology, Council of Scientific & Industrial Research, Department of Atomic Energy, Government of India. He is also the member and fellow of various professional societies such as ACS, ICS, ISTE, MRSI, PSI. He has also delivered several plenary and invited talks in different international conferences in India and abroad. Prof. Swain has received several awards such as BOYSCAST Fellowship, DAE-Young Scientist award, Prof. R.K. Nanda award and Samanta Chandra Sekhar award from Department of Science and Technology, Government of Odisha for outstanding contribution in Science.

Chapter 1
Perspectives of Bio-nanocomposites for Food Packaging Applications

Deniz Turan, Gurbuz Gunes and Ali Kilic

Abstract There is an increasing concern on the environmental issues related to petroleum-based plastics as packaging materials. Therefore, the interest for biodegradable packaging materials from renewable sources (biopolymers) has been increased steadily, particularly for the utilization in short-term packaging and throwaway applications. However, biopolymers have usually low barrier and mechanical characteristics with poor processability resulting in limitations for their scalable production and industrial use. To overcome these limitations, bio-nanocomposites with enhanced packaging characteristics such as mechanical strength, barrier properties against gases and water, and optical clarity have been developed. Moreover, bioactive ingredients can be added to give the targeted functional properties to the subsequent packaging materials. This chapter reviews distinctive sorts of new biobased nanocomposite materials, for example, biodegradable and edible nanocomposite films, and their commercial applications as packaging materials, and relevant regulations.

Keywords Biopolymers · Biodegradable · Bio-nanocomposites · Food packaging

1.1 Introduction

Food packaging acts a critic role in order to maintain the food safety and quality during storage and transport, and to prolong the shelf life of food products via protecting them from microbial, chemical, physical, and environmental hazards. Paper, paperboard, plastic, glass, and metal are mainly used packaging materials for foods. Also, a combination of those materials can be used to fulfill the required

---

D. Turan · G. Gunes
Department of Food Science and Engineering, Istanbul Technical University, Maslak,
Istanbul, Turkey

A. Kilic (✉)
TEMAG Labs, Istanbul Technical University, Taksim, Istanbul, Turkey
e-mail: alikilic@itu.edu.tr

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_1

functions more effectively. There are four basic packaging materials, and among them, plastic materials obtained from petrochemical sources have been more extensively utilized. The greater part of them are utilized in the form of films, cups, sheets, tubes, bottles, trays, and so on (PlasticsEurope 2015). Based on a recent market report published through Persistence Market Research titled ‘Global Market Study on Nano-Enabled Packaging for Food and Beverages: Intelligent Packaging to Witness Highest Growth by 2020,’ the global nanopackaging demand in food and beverages market is supposed to increase annually at a rate of 12.7% from 2014 to 2020, to reach an estimated value of $15 billion in 2020 (CNBC 2014).

Bio-nanocomposites have been noted as a promising alternative in food packaging market. Bio-nanocomposites comprise of a biopolymer framework fortified with particles (nanoparticles) having at least one proportion in the nanometer scale (1–100 nm). In food packaging, nanocomposites usually refer to materials containing 1–7% modified nanoclays (Robertson 2016). However, nanoparticles used in bio-nanocomposites are also classified relying on number of dimensions they have in the nanometer scale (Alexandre and Dubois 2000; De Azeredo 2009).

- Nanoparticles, such as silica, metal, and metal oxide nanoparticles (isodimensional nanoparticles).
- Cellulose nanowhiskers (nanoparticles with two dimensions in the nanometer scale) and carbon nanotubes.
- Layered crystals or clays from silicate (nanoparticles with one dimension in nanometer range).

Despite several nanoparticles potentially recognized as nanocomposite fillers to enhance polymer behavior, the layered clays from silicate, for example, montmorillonite (MMT), hectorite, and saponite, have been most widely investigated because of their availability, low cost, important enhancements, and easiness in processability (Duncan 2011; Silvestre et al. 2011).

In this chapter, recent studies on the bio-nanocomposites for food packaging applications were reviewed. The addition of nanomaterials into packaging materials improves the barrier and mechanical properties abruptly even at very low concentrations. Hence, the addition of such reinforcers will reduce the required weight of raw materials. On the other side due to the use of biopolymers, the total carbon foot print will be minimized. However, there are still ongoing works on reducing the toxicity and cost of nanomaterials.

1.2 Biopolymers

Biopolymers are polymeric materials obtained from renewable biological resources (Rhim et al. 2013). From the aspect of food packaging, biopolymers are expected to exhibit sufficient mechanical and barrier properties and biodegradability at the end of their life in the environment. According to ASTM, the term ***biodegradable*** is defined as ‘capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms that can be measured by standard tests, in a specified period of time, reflecting available disposal condition (ASTM 2005).' Nevertheless, it must be noted that biobased plastics may not necessarily be biodegradable (Iwata 2015). For example, bio-PE is not biodegradable, despite the fact that it is synthesized from bioethanol, delivered by the fermentation of glucose. Recently, bio-PET has additionally been created from biomass by utilizing biobased ethylene glycol, and it is not biodegradable either. There are three main resources for the production of biopolymers (Bordes et al. 2009; Jamshidian et al. 2010; Robertson 2016):

- Bioresources: Protein (gelatin, soy protein, wheat gluten, corn zein, collagen, casein, whey protein, etc.), carbohydrates (alginate, starch, carrageenan, cellulose, agar, chitosan, etc.), and lipids (fatty acids, wax, etc.).
- Chemical synthesis: Source is either from biomass (polylactic acid (PLA)) or from petrochemicals (poly(butylene succinate) (PBS), poly(ε-caprolactone) (PCL), poly(glycolic acid) (PGA), poly(vinyl alcohol) (PVOH), etc.).
- Microbial fermentation: Microbial polyesters, such as poly(hydroxyalkanoates) (PHAs) including poly(β-hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), and microbial polysaccharides (bacterial cellulose).

1.2.1 Bio-nanocomposites

The commercial use of biopolymers is currently limited due to the problems in their performance, processing, and cost. At this point, nanotechnological approaches have opened new ways for the utilization of great performance, reduced weight, green nanocomposite materials making them to supplant traditional non-biodegradable petroleum-based plastic packaging materials. The inclusion of nanoparticles in biopolymers can enhance their mechanical and barrier properties which is associated with high aspect ratio and high surface area of the nanoparticles (Rhim et al. 2013).

1.2.1.1 Natural Bioresources (Edible Packaging Materials)

Edible film (coating) refers to covering surface of a product with a thin layer of material to preserve the quality of the product. Edible films can be applied to products with different techniques including dipping, spraying, brushing. Edible films can potentially scale the shelf life and keep the quality of foods by providing a physical barrier against loss of flavor, moisture, and exchange of gases such as O_2 and CO_2. Therefore, edible films can also be considered as edible packaging for foods. Combination of lipid, polysaccharides, and protein is used in edible films to enhance their barrier and mechanical properties (Abugoch et al. 2016; Ayranci and Tunc 2004; Lee et al. 2003; McHugh and Senesi 2000; Moldao-Martins et al. 2003; Toğrul and Arslan 2004; Zapata et al. 2008).

Proteins

Protein-based edible films from milk, soybeans, corn, wheat, peanut, cotton seed, etc., may exhibit excellent barrier properties against aroma, oil, and oxygen. However, their moisture barrier property is generally weak except zein and gluten which are insoluble in water. The characteristics (barrier, mechanical, thermal) of the protein-based edible films are affected by their molecular structure and origins of the specific proteins (Vargas et al. 2008). The origins of the specific proteins might be either from plant or animal sources. Collagen, gelatin, whey proteins, caseins, plasma proteins, myofibrillar proteins, egg white proteins, soy protein, wheat gluten, and zein are the most widely investigated protein polymers (Lacroix and Vu 2014). Commercialization of protein films has been acknowledged in collagen frankfurter casing, gelatin pharmaceutical capsules, and corn zein protective coatings for nutmeats and candies (Irissin-Mangata et al. 2001). Studies on protein-based biodegradable plastics have also been reported which deals with non-food uses of agricultural feedstock (Swain et al. 2004).

Blending of proteins with nonprotein natural materials, such as chitosan, cellulose, or with synthetic polymer like poly (propylene) (PP), poly(ethylene) (PE), poly(vinyl chloride) (PVC), has been prepared to improve the properties of protein-based polymer for food and non-food packaging. Furthermore, the properties of protein films have also been improved by incorporating nanoclays or other nanoparticles in their structures and application applied in food preservation (Lacroix and Vu 2014). For example, Zhao et al. (2013) obtained nanocomposites based on silver nanoparticles and soy protein isolate. The polymer can potentially be used as a sustainable and active packaging material for foods (Zhao et al. 2013). Bio-nanocomposite films based on soy protein isolate (SPI) mixed with montmorillonite (MMT) were prepared using melt extrusion. It was found that addition of MMT showed significant improvement in mechanical properties such as tensile strength and percent elongation at break, thermal stability, and water vapor permeability of the films. For instance, 16% MMT addition to soy protein-based nanocomposite showed an increase from 8.77 to 15.43 MPa in soy protein/MMT nanocomposite films (Chen and Zhang 2006). These bio-nanocomposite films could conceivably be utilized for packaging of high-moisture foods such as fresh fruits and vegetables to supplant a portion of the current plastics such as low-density polyethylene (LDPE) and polyvinylidene chloride (PVDC) (Kumar et al. 2010a).

Mechanical performance and water vapor permeability of whey protein isolate (WPI) film were enhanced after inclusion of oat husk nanocellulose (ONC). The nanocellulose was obtained from sulfuric acid hydrolysis and the nanocomposite films were prepared using a solution casting method (Qazanfarzadeh and Kadivar 2016). Another WPI-based bio-nanocomposite film is developed by solution casting. The water vapor barrier and mechanical properties of the WPI-based films were improved by blending with zein nanoparticles (ZNP). The water vapor permeability of the film was decreased by 84% at ZNP:WPI (w/w) ratio of 1.2 (Oymaci and Altinkaya 2016; Ozer et al. 2016). The reported improvement was much higher than silica-coated TiO_2 and other clay nanoparticles (Kadam et al. 2013; Zolfi et al. 2014). An antimicrobial nanocomposite film based on fish protein isolate and fish skin gelatin was developed by the addition of zinc oxide nanoparticles in order to be used as an active food packaging to prevent the growth of pathogen and spoilage bacteria in foods (Arfat et al. 2016). Improved thermal properties and mechanical properties with up to 17.76 MPa tensile strength and 70.33% elongation at break were reported, while water vapor permeability was reduced to 2.09×10^{-11} gm^{-1} s^{-1} Pa^{-1} in the films. As an alternative to the synthetic petroleum-based polymers, whey protein isolate (WPI), a by-product of the cheese industry, has quite promising properties for packaging purposes. It exhibited good barrier properties against oxygen, aroma, and oil; however, its water vapor permeability is high. Recently, poly(lactic acid) film coated with WPI resulted in an improvement of about 90% in the oxygen barrier properties and about 27% in the water vapor barrier properties (Weizman et al. 2016).

Carbohydrates

Edible coatings and films have been intensively developed from carbohydrates, such as starch, chitosan, cellulose derivatives, pectin, and galactomannans. The main obstacle is the weak water vapor barrier properties after obtaining mechanically sufficient free-standing films (Zhang et al. 2014). Rhim and Wang (2013) prepared a multicomponent biohydrogel film composed of nanoclay (Cloisite® 30B), agar, konjac glucomannan powder, and κ-carrageenan using solvent casting method. Adding nanoclay increased tensile strength of the ternary blend biohydrogel film from 62 to 76 MPa. Water vapor permeability decreased from 1.25×10^{-9} to 1.05×10^{-9} gm^{-1} s^{-1} Pa^{-1}. Those biohydrogel films showed enormous increase in water holding capacity as from 800 up to 5488%. Therefore, they stated that the developed films have an extreme potency for utilization as an antifog packaging film for highly respiring fresh produce like spinach (Rhim and Wang 2013). Oleyaei et al. (2016) also used solvent casting method to prepare ternary potato starch bio-nanocomposite films containing sodium montmorillonite (MMT) and TiO_2 nanoparticles. A 5% MMT addition to starch-based bio-nanocomposite showed 50% reduction in water vapor permeability. Moreover, those blend nanocomposite films showed an antimicrobial activity against *Listeria monocytogenes* which is a Gram-positive bacterium (Oleyaei et al. 2016). Nearly the same enhancement in water vapor barrier properties and tensile strength was reported with starch-based nanocomposite film incorporated with hydrothermally synthesized zinc oxide nanoparticles (Andiyana and Suyatma 2016). Arfat et al. (2017) investigated the potential of guar gum-based nanocomposite films prepared by incorporating silver–copper alloy nanoparticles (Ag–Cu NPs) through solution casting method as an active food packaging material. Tensile test results showed an improvement in the mechanical strength. Also, the films showed excellent UV light and oxygen barrier capability. Furthermore, a strong antibacterial activity was observed against both Gram-positive and Gram-negative bacteria (Arfat et al. 2017).

Several carbohydrate-based antimicrobial nanocomposite films were developed. Chitosan nanoparticles were incorporated into cellulose films, in which 5% addition of chitosan nanoparticles into cellulose films resulted in 85% inhibition in *Escherichia coli*. Cross-linking of the cellulose films with citric acid reduced water absorbency by 50% the growth of *E. coli* by 3% (Romainor et al. 2014). Ghule et al. (2006) proposed a simple approach to produce a nanoparticle-coated antimicrobial paper. They used an ultrasound-assisted approach to coat the cellulose fibers over the paper surface with zinc oxide nanoparticles. The coated paper showed antimicrobial activity against *E. coli* 11,634 (Ghule et al. 2006). A similar study investigated the antimicrobial effect of copper nanoparticles incorporated into chemically modified cotton cellulose fibers (Mary et al. 2009). Siqueira et al. (2014) analyzed the antimicrobial effect of silver (Ag) nanoparticles incorporated into carboxymethylcellulose (CMC) films. The Ag-CMC nanocomposite inhibited the growth of a Gram-positive bacteria, *Enterococcus faecalis*, and a Gram-negative bacteria, *E. coli,* at a concentration of 0.1 μg cm^{-3} (Siqueira et al. 2014). The nanocomposite was tested on fruits, vegetables, and milk products, and their shelf lives were extended significantly. Table 1.1 summarizes the studies on the synthesized carbohydrate-based bio-nanocomposites and their prospective applications in food packaging area.

Lipids

The lipid-based edible films such as carnauba wax, bees wax, or vegetable oil have good water barrier properties and provide shiny and glossy appearance to food products, particularly to the fruits and vegetables. Entrainment of lipid materials into polysaccharide and protein films in order to produce edible composite films and coatings has the potential to develop barrier properties of film against moisture because proteins and polysaccharides are known to exhibit low moisture barrier properties, because they are hydrophilic (Pérez-Gago and Rhim 2014). Among the lipids, waxes produce edible films with the best water vapor barrier properties, but produce fragile or brittle films. For instance, Saurabh et al. (2016) studied the effects of nanoclay, beeswax, tween-80, and glycerol on physicochemical properties of guar gum films to be used as food packaging. It was ascertained that tensile strength lowered sharply from 86 to 35 MPa by increasing beeswax concentration. However, incorporation of 0.63% of beeswax resulted in a reduction of WVTR of the films from 101 to 85 $g/m^2/d$ as compared to films without beeswax due to the increased hydrophobicity (Saurabh et al. 2016). Starch films incorporated with solid lipid microparticles containing ascorbic acid had lower water vapor permeability as compared to the control film containing no additives (Sartori and Menegalli 2016). Hu et al. (2009) modified the surface of the paper with microsized $CaCO_3$ and fatty

Table 1.1 Various carbohydrate-based bio-nanocomposites (BNC)

Type of BNC film	Observed properties	References
Alginate/clay/essential oil	Inhibitory effect on bacterial growth	Alboofetileh et al. (2014)
κ-carrageenan/chitosan/bioactive compound	Dependent release of bioactive compound (methylene blue) on concentration gradient and polymer relaxation of nanolayers	Pinheiro et al. (2012)
Brucite nanoplate-reinforced starch	Enhanced mechanical properties and thermal stability	Moreira et al. (2013)
Soluble soybean polysaccharide–halloysite nanoclay	Improved heat sealability, mechanical and barrier properties (e.g., decreased oxygen permeability from 202 to 84 cm^3 ($\mu\text{m m}^{-2}$ day^{-1} atm^{-1}))	Alipoormazandarani et al. (2015)
Starch–cellulose nanocrystal	Improvement in 70% of oxygen barrier and mechanical properties	González et al. (2015)
Regenerated cellulose–zeolite	Enhanced thermal and mechanical properties	Soheilmoghaddam et al. (2014)
Agar/carrageenan/CMC–ZnO nanoparticles	UV barrier, surface hydrophobicity, and water vapor barrier properties were increased. Inhibited growth of *L. monocytogenes* and *E. coli*	Kanmani and Rhim (2014)
Savory essential oil–agar–cellulose nanocomposite	Improved antibacterial properties against *Listeria monocytogenes*, *Staphylococcus aureus*, *Bacillus cereus*, and *Escherichia coli*	Atef et al. (2015)
Chitosan and calcium carbonate nanopowder	The oxygen permeability was lowered by 300%	Swain et al. (2014)

acid coating in order to increase the water resistance. It was stated that as the concentration of fatty acid increased, the hydrophobicity of precipitated $CaCO_3$ increased resulting in an increase in the water contact angle (Hu et al. 2009).

Lipid-incorporated edible films were also studied as an antimicrobial agent in order to develop active packaging films. Jo et al. (2014) developed a carnauba wax nanoemulsion coating with lemongrass oil for application onto Fuji apples. The treated fruits were stored at 1 ± 1 °C for 5 months. The apples coated with the nanoemulsion had lower populations of total aerobic bacteria, yeasts, and molds as compared to uncoated apples. The coated samples also maintained sensory quality throughout the storage period (Jo et al. 2014). In another study, Joe et al. (2012a) developed a sunflower oil-based nanoemulsion as edible coating, and it was tested for its antimicrobial properties in vitro. The nanoemulsion exhibited significant antibacterial activity against *Salmonella typhi*, *L. monocytogenes*, and *Staphylococcus aureus* along with antifungal activity against *Rhizopus nigricans*, *Aspergillus niger*, and *Penicillium* spp. The nanoemulsion was also reported to show sporicidal effects against *Bacillus cereus* and *Bacillus circulans*. Besides the in vitro studies on nanocarrier systems, several studies on the application of nanoemulsions as edible coatings on whole, fresh-cut fruits and vegetable commodities and fish products have been reported (Joe et al. 2012a, b; Salvia-Trujillo et al. 2015; Zambrano-Zaragoza et al. 2014).

1.2.1.2 Chemical Synthesis

Biomass

Biomass assets have been used as sustainable fuel substitutes of non-renewable energy sources so as to diminish ozone harming substance or greenhouse gas (GHG) outflows. Since combustion is applied to waste plastic after they have been used as container or packaging material (Kikuchi et al. 2013). Therefore, great majority of studies concentrated on the biobased biodegradable polymer composite films or conventional petrochemical plastic films loaded with common fibers. Fully biobased structural composites can be produced competitive to the traditional plastics. In 2010, first business-scale plant delivering ethylene from sugarcane ethanol was implicit in Brazil and they started the production of biomass-derived polyethylene (bio-PE). In a study of life cycle assessment of bio-PE, Kikuchi et al. (2013) reported that bio-PE can reduce GHG emissions originating from polyethylene production. In addition, a study was reported on mechanical properties and the influence of water absorption on different biocomposites based on biobased polyethylene matrix obtained from sugarcane ethanol filled with lignocellulosic fillers. Composites of biobased HDPE with even low filler content (25%) produced by compounding extrusion followed by injection molding. The samples showed an increase in stiffness, thermal stabilization within the temperatures of usage compared to the neat biopolyethylene. Due to the high water absorption capacity of natural fibers, the modified biobased HDPE showed larger water uptake (Kuciel et al. 2014). Recently, 80% sugarcane-based plastic packaging was patented in order to replace the usage of petroleum-based high-density polyethylene (HDPE) resin packaging for consumer products. Accordingly, there is a need for packaging materials made from renewable materials, which offers the same functionality as HDPE resin, and 100% recyclability (McCarthy 2016). Furthermore, the poly (ethylene glycol) part of PET has also been obtained from biomass. For example, nanoclay was incorporated into biobased PET by twin-screw extruder. The supercritical carbon dioxide injection system was used as an exfoliation agent and connected to extruder. The exfoliated nanocomposite films showed improved mechanical and barrier properties compared to the intercalated films (Jang et al. 2013). The Coca-Cola Company has distributed over 30 trillion plant-based bottles, since they have launched the PlantBottle Packaging program in 2009. Moreover, almost in 40 countries people have been using the present adaptation of PlantBottle Packaging, consisting of 30% plant-based materials. As stated in bio-PE, bio-PET has also shown strong potential to reduce carbon dioxide emission. Therefore, Coca-Cola is developing bio-mono-ethylene glycol conversion technology in order to obtain 100% renewable, fully recyclable PET plastic products (Ren et al. 2015).

Polylactic acid (PLA) is biodegradable aliphatic polyester, obtained from agricultural products, such as corn, or waste products such as molasses. During the process of the sugar fermentation, various monomers are produced. Afterward, polymer structure was obtained from those monomers. The PLA pellets are obtained through direct polycondensation of lactic acid monomers or through ring-opening polymerization of lactide. Considerable efforts have been made by modifying PLA with biocompatible plasticizers or by blending PLA with other polymers in order to improve its properties. Commercial uses of PLA include lunch boxes, fresh produce packaging, bottles for water and juices, and yogurt packages. Mixtures of PLA with starches, proteins, and different biopolymers have additionally been considered to produce completely sustainable and degradable packaging materials. Jin and Gurtler (2011) assessed the antimicrobial activity of a film made up of polylactic acid and antimicrobial compounds such as zinc oxide nanoparticles, allyl isothiocyanate, and nisin that are added individually and in various combinations. The antimicrobial coating was applied onto the inner surface of glass jars containing liquid egg inoculated with a cocktail of three *Salmonella* strains commonly involved in the salmonellosis outbreak. The treatments with combined antimicrobials demonstrated greater antimicrobial activity as compared to individual antimicrobials. Polylactic acid film with allyl isothiocyanate, nisin, and zinc oxide nanoparticles effectively reduced the *Salmonella* population in liquid white albumen from 10^7 CFU/mL to undetectable levels after 28 days of storage, suggesting the potential use of the combined antimicrobials in the films to reduce the required concentrations of individual compound, and to prevent organoleptic degradation (Jin and Gurtler 2011). Another study on PLA/zinc oxide biocomposite film for food packaging application showed good mechanical properties. The elongation to break (ε_b) increased to 40% in machine direction by adding 1% ZnO as shown in Fig. 1.1. The addition of 1% ZnO to PLA caused a decrease in permeability of CO_2 and O_2 of about 17 and 18%, respectively. However, the modification caused a slight increase in water vapor permeability. ZnO addition (5%) to PLA showed a 99.99% reduction for *E. coli* after 24 h (Marra et al. 2016).

Bendahou et al. (2015) developed PLA films with micro- and nanozeolites ($NaAlO_2$, SiO_2) and found antibacterial activity (against *E. coli*) regardless to the zeolite size (Bendahou et al. 2015). In a study, lactic acid-grafted-gum arabic (LA-g-GA) was synthesized by polycondensation reaction in microwave and added into poly(lactic acid) (PLA). Effect of LA-g-GA addition into PLA in terms of improvement in gas barrier properties had been worked. At 5% filler concentration, oxygen permeability was reduced by 10-folds while water vapor transmission rate decreased 27% (Tripathi and Katiyar 2016). PLA and its nanocomposites based on cellulose nanocrystals (CNCs) and chitin nanocrystals (ChNC) were prepared using a twin-screw extruder to improve mechanical and optical properties of plasticized PLA (Herrera et al. 2016a). They also worked on the blown PLA nanocomposite films to be used in packaging applications (Herrera et al. 2016b). In other studies based on PLA and cellulose nanocrystals, improved processability and mechanical

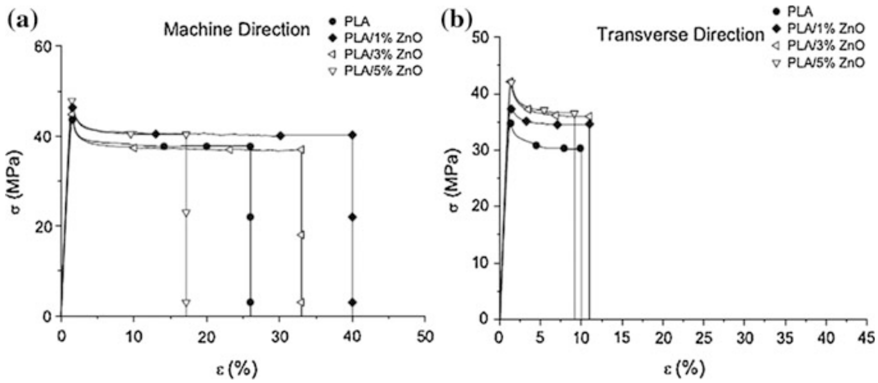


Fig. 1.1 Stress–strain curves of PLA and PLA/ZnO biocomposite films in machine direction (**a**) and in transverse direction (**b**) (Marra et al. 2016)

properties for packaging applications were reported (Lizundia et al. 2016). PLA/cellulose nanowhisker was mixed in twin-screw extruder, and then nanocomposite was prepared by injection molding (Moran et al. 2016). PLA as a food packaging material has low barrier properties against oxygen and water vapor in comparison with traditional petroleum-derived materials. To deal with this problem, a sandwich-architectured PLA–graphene oxide composite film was designed (Goh et al. 2016). PLA was used as outer protective encapsulation material, and graphene oxide was used as the core barrier. The protective encapsulation resulted in 87.6% reduction in the water vapor permeability. Moreover, twofold reduction in the oxygen permeability was observed under both dry and humid conditions. Studies on using the PLA–graphene oxide composite film for edible oil and potato chips also showed at least eightfold extension in the shelf life (Goh et al. 2016). Salvatore et al. (2016) investigated the effect of montmorillonite addition to PLA and the effect of electron beam radiation on the properties of PLA nanocomposite. An increase in the mechanical and oxygen barrier properties compared to neat PLA was reported for all nanocomposites. This study also demonstrated that PLA nanocomposite films are suitable materials for irradiation processing of prepacked food at the realistic doses (1–10 kGy) (Salvatore et al. 2016). Regarding PLA, different nanomaterials including nanoclays, cellulose nanocrystals, and eugenol-loaded chitosan nanoparticles have been used in nanocomposites formulation (Moreno-Vásquez et al. 2016; Rhim et al. 2009; Salmieri et al. 2014a, b).

Another pattern for biobased polymers is the improvement of methods to deliver basic plastics, for example, PE, PP, or PET from biomass. Bio-PE has already been produced from bioethanol in Brazil. Besides, the poly(ethylene glycol) which contents some portion of PET has additionally been acquired from biomass. For these plastics, biomass was utilized as the crude material rather than oil; however, the final material has an indistinguishable structure from the oil-based plastics.

Petrochemicals

Recently, a broad range of synthetic biodegradable resins based on aliphatic polyesters and aliphatic-aromatic copolyesters have been commercialized by global suppliers to be used as food packaging. Polymers such as poly(ε-caprolactone) (PCL), poly(esteramides) (PEA), aliphatic copolyesters (e.g., PBSA), and aromatic copolyesters (e.g., PBAT) have monomers obtained by chemical synthesis from fossil resources (Ikada and Tsuji 2000). PCL is an aliphatic polyester obtained by chemical synthesis from crude oil or even from renewable resources, such as polysaccharides (Ortega-Toro et al. 2015, 2016). It has good water, oil, solvent, and chlorine resistance, a low melting point (58–60 °C) and low viscosity, and hence, it is easy to process. However, PCL packaging applications were restricted in processing due to its low degradation temperatures and the relatively high cost. Therefore, many researchers have developed blended PCL polymers. For example, Cabedo et al. (2006) developed nanocomposites of biodegradable blends of amorphous PLA and PCL by melt blending. Blending amorphous PLA with PCL led to improvement in mechanical properties, thermal stability, and the increase in gas barrier properties. This is expected to result in better processability of the material (Cabedo et al. 2006). Another biodegradable nanocomposite based on starch/PCL/montmorillonite was prepared by melt intercalation at 110 °C followed by compression molding for packaging application (Guarás et al. 2015). A total of 101% increase in Young´s modulus was reported. Due to the addition of hydrophilic groups into polymer structure, water absorption has increased in compatible polymer matrix compared to incompatible polymer matrix. Besides, a slight reduction in the biodegradation rate of polymer was observed when nanoclay has added into the polymer (Guarás et al. 2016). In addition, polyethylene/PCL nanocomposite films modified with magnetite and casein for food packaging applications were developed. Significant enhancements were observed with in terms of mechanical (tensile strength, elongation at break) and thermal properties, while gas barrier (O_2 permeability) properties were improved to a minor scale (Rešček et al. 2016a, b).

Poly(vinyl alcohol) (PVOH) is also widely used because of its biocompatibility and interesting physical properties. It is obtained by polymerization of vinyl acetate which is converted into PVOH later (Cano et al. 2015). Due to the cost advantage, sodium MMT clay was also incorporated into PVOH and effect of clay concentration on the oxygen permeability and optical properties of PVOH was investigated. Reduction in oxygen permeability at elevated humidity might provide advantages in food packaging applications (Grunlan et al. 2004). Thermoplastic starch and polyvinyl alcohol blends have been subject of a particular interest due to excellent compatibility of these components. The major outcome of these studies was that the degradation of the starch in blend was restrained by PVOH (Russo et al. 2009). In another study, PVOH/clay composite blended with starch and nanocomposites were prepared via melt extrusion method. Type of clay cation, content of clay, and PVOH affected the mechanical properties of composites. The water content factor was not significant in terms of mechanical property improvement. Better tensile strength and modulus were reported with 4% CMMT nanocomposite. Nanocomposites including CMMT have shown better tensile strength and modulus (σ = 65.4 MPa and E = 6856 MPa) compared to values in other studies (Majdzadeh-Ardakani and Nazari 2010). Recently, polymeric films based on PVOH, chitosan (CH), and lignin nanoparticles (LNP) were produced by solvent casting. The addition of LNP reinforced the tensile strength of PVOH from 45.8 to 51.5 MPa compared to pure PVOH. Moreover, Young's modulus increased from 1100 to 2100 MPa when 3% of LNP was incorporated in PVOH matrix. LNP addition also improved the thermal stability of the nanocomposites. By increasing the proportion of LNP from 0 to 3%, thermal degradation point shifted from 85 up to 95.3 °C for PVOH/LNP binary films, from 59.2 to 79.4 °C for CH/LNP binary films, and from 82.3 to 98.4 °C for PVOH/CH/LNP ternary films. Antimicrobial studies showed an inhibition against Gram-negative *Erwinia carotovora* subsp. *carotovora* and *Xanthomonas arboricola* pv. *pruni* bacteria growth over the time, which is important for bacterial plant/fruit pathogens (Yang et al. 2016).

In addition, poly(butylene succinate) (PBS) and poly(butylene succinate-co-adipate) (PBSA) are aliphatic biodegradable polyesters to be used in the food packaging (Siracusa et al. 2015). A composite film based on PBS/zinc oxide (ZnO) was successfully prepared by using a blown film extruder. Antimicrobial activity against *E. coli* and *S. aureus* growths was observed with the clear zone of 1.31 and 1.25 cm, respectively (Petchwattana et al. 2016). In order to prepare novel bioactive food packaging material, PBS-based composites containing β-cyclodextrin/ᴅ-limonene inclusion complex were studied. ᴅ-limonene was efficiently encapsulated within β-cyclodextrin (β-CD) and thermal analysis showed that addition of this complex into the polymeric matrix represented a crucial strategy to preserve ᴅ-limonene from evaporation during melt processing of the composites. Therefore, polymeric films were expected to be used as active food packaging due to the slow release of antibacterial ᴅ-limonene from β-CD cages (Mallardo et al. 2016). In order to improve the physical/mechanical properties of PBS, cellulose nanocrystals (CNC) were added to polymer based on PBS/poly (ethylene-glycol) (PEG)/CNC. The samples containing 4% CNC showed the highest mechanical performance among the nanocomposites due to the combination of high modulus and elongation at break compared with the PBS/PEG blend (Ludueña et al. 2016). PBS was also blended with PLA, and bio-nanocomposite films were prepared by solvent casting method after addition of 1 or 3% of cellulose nanocrystals (CNC). Mechanical analysis showed increased values of Young's modulus. The presence of both CNC and the addition of PBS to PLA matrix provoked an improvement of barrier properties (Luzi et al. 2016). Recently, water-assisted extrusion was used to prepare poly[(butylene succinate)-co-(butylene adipate)] (PBSA) and montmorillonite (MMT) nanocomposites. This process consisted of mixing inorganic platelets with water. By this way, the risks of gel formation and of the polymer chain degradation were consequently limited. Then, water was removed by vacuum degassing during extrusion process. The best performance in barrier properties against gases and water was obtained with the PBSA matrix loaded with 10% MMT which was extruded via water injection (Charlon et al. 2016).

Poly(butylene adipate-co-terephthalate) (PBAT) is a petroleum-based biodegradable copolyester. It has high barrier property against water vapor; it is a flexible biodegradable thermoplastic and shows great processability. Therefore, it is a great alternative beside compost bags and agricultural film materials (Witt et al. 2001). However, the high cost of PBAT limits its extensive applications in replacing non-biodegradable plastics (Mekonnen et al. 2016). Therefore, recently PBAT has been blended with several materials in order to be used in food packaging applications. For instance, inexpensive fermented soy meals (SM) were blended with PBAT. Fermentation was run to decompose some carbohydrates that are deterrent to plastic making. The resulting low-cost blended materials exhibited better tensile properties, thermal stability, and moisture resistance (Mekonnen et al. 2016). In another study, blend films of PBAT with PLA were prepared using a solvent casting method. It was found that PLA was highly compatible with PBAT. In the packaging of potatoes and green onion, the blend films prevented greening of packaged potatoes and also showed antifogging effect with reduced quality changes. The blend films have high potential for being used as UV screening without sacrificing transparency and antifogging behaviors (Wang et al. 2016a, b). Moreover, nanofibril form of PBAT was blended with PLA. The oxygen permeability coefficient of PLA/PBAT (85/15 w/w) was measured to be as low as $2 \times 10^{-15}\ \mathrm{cm^3\ cm^{-2}\ s^{-1}\ Pa^{-1}}$. The blend films combined high strength and modulus (104.5 and 3484 MPa, respectively) which can be comparable to the excellent barrier films obtained from petroleum-based polymers (e.g., PET). The study provided an industrially scalable processing method for environmentally friendly food packaging material by forming unique matrix to improve the gas barrier and mechanical property (Zhou et al. 2016a, b). Recently, PBAT bio-nanocomposites were also studied as active packaging film with antimicrobial property. For example, SiO_2 nanoparticles filled in PBAT composites were prepared by a solvent casting method. Antimicrobial activity by the well diffusion assay method was followed against *S. aureus* and *E. coli* which were found to have good inhibition zones: 17.2 and 16.7 mm, respectively (Venkatesan and Rajeswari 2016). Furthermore, PLA/PBAT/nanocrystal cellulose-silver nanohybrids were synthesized. Antimicrobial activity against both Gram-negative *E. coli* and Gram-positive *S. aureus* cells was achieved (Ma et al. 2016). In addition, PBAT/silver nanoparticle composite films exhibited strong antibacterial activity against *E. coli* and *L. monocytogenes* (Shankar and Rhim 2016). In another study, PBAT reinforced with organomodified montmorillonite was blended with poly (3-hydroxybutyrate-co23-hydroxyvalerate). Moreover, two natural propolis additives and an industrial antimicrobial were added to the materials in order to give them antimicrobial properties. However, weak biocidal activities were observed against *S. aureus* and *E. coli*. By contrast, samples containing the industrial additive exhibited antimicrobial effect (Bittmann et al. 2016). Zinc oxide (ZnO)/PBAT nanocomposite films were investigated in terms of packaging properties such as barrier, thermal, and mechanical properties beside biological activity. The resulting

PBAT/ZnO nanofilms exhibited a significant increase in the mechanical and thermal stability. It also showed superior antimicrobial activity against *E. coli* and *S. aureus* (Venkatesan and Rajeswari 2017).

Poly(propylene carbonate) (PPC) is a copolymer of carbon dioxide and propylene oxide, and another biodegradable polymer with potential for commercialization due to its excellent tensile toughness (Zhou et al. 2016a, b). Nonetheless, PPC additionally has a few drawbacks that confine the scope of its large-scale modern application; for example, it has a non-crystalline structure and force between subatomic chains is weak. Moreover, it has weak mechanical properties, low glass transition temperature, and poor thermal stability. Therefore, cellulose nanowhiskers (CNWs) were added to PPC through simple solution technique in order to increase the tensile strength and storage modulus of PPC. The elongation at break of PPC/CNW nanocomposite films was reported above 900%. Besides, increase in thermal stability by addition of CNWs was also reported (Wang et al. 2013). In another study, PPC/ZnO nanocomposite films with different compositions were prepared via solution blending method. The enhanced water/oxygen barrier properties and good antibacterial properties of PPC/ZnO nanocomposite films were reported as potential candidates for versatile packaging applications (Seo et al. 2011). Recently, Wang et al. (2016b) chemically modified PPC with a chain extender to improve its thermal, barrier, and mechanical properties. While thermal degradation temperature of PPC was increased from 177.3 to 240.6 °C, the tensile strength of the modified PPC was improved from 3.3 to 20.7 MPa (Wang et al. 2016a, b). In another study, in order to enhance the gas barrier and mechanical properties of PPC, organic modified filler hydroxide (OLDH) was added to the composite. Oxygen permeability coefficient was 54% lower than neat PPC, while water vapor permeability coefficient was reduced by 17%. Also, the tensile strength of the PPC bio-nanocomposite was 83% higher than that of pure PPC. As shown in Fig. 1.2, OLDH was well dispersed within the composites. On the other hand, there were some cracks between OLDH filler and polymer in 3% OLDH-added PPC composite (Fig. 1.2d). Those cracks might decrease the tensile strength and gas barrier performance of the composite films (Li et al. 2016).

Polyurethanes (PU) have been broadly utilized as a part of numerous areas, for example, therapeutic, textile, automotive, and chemical industry. Beforehand, the side chain crystallizable polymers were outlined, and polyurethane packaging films including a block copolyether ester or a block copolyether amide were defined for breathing produces (Hodson and Perre 2006; Stewart 1993). Recently, castor oil-based polyurethane film has been reported as intelligent packaging material with increased thermally responsive gas permeability for fresh fruit and vegetables. Films showed maximum 67% increase in temperature sensitivity (Q_{10}) for oxygen permeability and had at least a twofold increase in O_2 permeability compared to the traditional films, including LDPE, HDPE and oriented polypropylene (Turan et al. 2016, 2017). In another study, carbon nanotubes (CNTs) were utilized as reinforcing agent in castor oil-based polyurethane. Nanocomposites were thermally stable up to 305 °C (Huo et al. 2016). In another study, cellulose nanocrystals (CNC) were used for reinforcement. Similarly, increase in modules and stress at

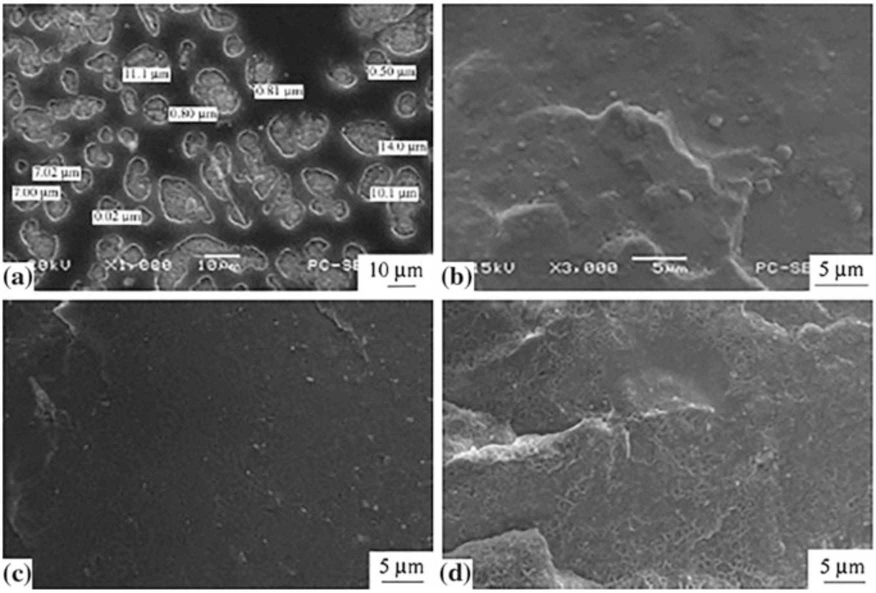


Fig. 1.2 SEM images of OLDH and PPC/OLDH composite films: **a** OLDH, **b** pure PPC, **c** PPC/2% OLDH, and **d** PPC/3% OLDH (Li et al. 2016)

yield besides increased thermomechanical stability were reported (Santamaria-Echart et al. 2016). Another PU/CNC composite was reported with increased tensile strength over 200% compared to the neat matrix without degradation of elongation at break (Girouard et al. 2016). Besides, nanocomposite scatterings from polyester sort of polyurethane and blends of the polyurethane with different biopolymers, for example, hydrolyzed collagen, k-elastin, chondroitin sulfate, or hyaluronic acid containing diverse concentrations of in situ produced silver nanoparticles (Ag NPs), were arranged and considered for application as antimicrobial materials. Rheological properties of Ag NPs scatterings were examined with a specific end goal to give profitable data on the viscosity and stability of the suspension. Complex viscosity values step-by-step expanded as the substance of Ag NPs increased at all considered frequencies. Polymer demonstrated shear thinning behavior at expanding frequency and encourage the flow (Dumitriu et al. 2016).

1.2.1.3 Microorganisms

Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) belong to a family of completely biodegradable and biocompatible polyesters synthesized by bacteria from renewable substrate resources such as sugarcane. Several types of PHAs consisting of various monomers have been reported so far. The PHA biopolymer can be applied in the fields of medicine, agriculture as well as packaging (Díez-Pascual and Díez-Vicente 2014). For example, poly(3-hydroxybutyrate)-co-(3-hydroxyvalerate) (PHBV) is 100% biodegradable and can be synthesized by bacteria. Recently, functionalized multiwalled carbon nanotube (MWCNT) was used to improve the properties of the PHBV matrix as a novel bio-nanocomposite for food packaging. Compared to neat PHBV, the tensile strength and Young's modulus of the nanocomposite film containing 7% MWCNT were enhanced by 88 and 172%, respectively. Moreover, the nanocomposites exhibited a wider melt-processing temperature range and reduced water absorption and water vapor permeability. Furthermore, the migration levels to simulants for all of the nanocomposites were below the overall migration limits determined by legislative standards for food packaging materials (Yu et al. 2014). In another study, PHBV was modified with zinc oxide (ZnO) nanoparticles for antimicrobial food packaging application. It exhibited stronger antibacterial activity against *E. coli* than *S. aureus*. PHBV/ZnO films also showed reduced water absorption, oxygen, and water vapor permeability in comparison with pure biopolymer. The overall migration levels of the nanocomposites in simulants were below the permitted limits for food packaging materials (Díez-Pascual and Díez-Vicente 2014).

In another study, natural clay and organophilic clay were added to PHBV matrix by melt intercalation technique. The total migration results were within the maximum allowable limit for food packages (da Costa Reis et al. 2016). Antimicrobial bio-nanocomposites based on PHBV with silver nanoparticles (AgNPs) were also successfully synthesized and characterized. Beside enhancement in oxygen barrier properties, the antimicrobial performance of the PHBVs–AgNPs films against two of the most common food-borne pathogens, *Salmonella enterica* and *L. monocytogenes*, showed a strong (even after seven months) antibacterial activity. This study provided a potential renewable and biodegradable way in order to obtain active food packaging material (Castro-Mayorga et al. 2016).

Polyhydroxybutyrate (PHB) is the other regular PHA and generally deliberated because of its predominant biodegradability, biocompatibility, and processability, yet its high cost and fragility confine its applications. Seoane et al. (2016) prepared PHB-based bio-nanocomposites using various percentages of cellulose nanocrystals (CNCs) by a solution casting method. The resulted bio-nanocomposites showed enhanced tensile strength and Young's modulus. In addition, the PHB/CNC bio-nanocomposites showed decreased water vapor permeability contrasted with pure PHB and improved barrier properties against UV light than traditional polymers, for example, polypropylene. It was found that nanocomposites with 6% of CNCs were the best for thermal, mechanical, and barrier properties (Seoane et al. 2016).

Bacterial Cellulose

Cellulose may be delivered by microorganisms and in addition by plants and different living beings. Bacterial cellulose can be created in generally expansive amounts by microbial fermentation of different substrates by *Gluconacetobacter xylinus* strains. Bacterial cellulose-based films have remarkable qualities contrasted with different sources of cellulose, for example, high quality, high crystallinity, high rigidity, and high water holding limit, and subsequently indicate great potential for utilization (Iguchi et al. 2000). In addition, these polysaccharides are economical and widely used in food and pharmaceutical industries (Desai 2007). The use of nisin containing bacterial cellulose reported to inhibit *L. monocytogenes* on processed meats. Films produced using high concentration of nisin (2500 IU ml^{-1}) with exposure time (6 h) resulted in 2 log CFU g^{-1} after 14 days of storage compared to control samples (Nguyen et al. 2008). In another study, Gao et al. (2014) explored the feasibility of using bacterial cellulose cross-linked with ε-polylysine nanoparticles to form composite nanofibers with antimicrobial properties as active packaging material. The developed nanocomposite was reported to exhibit antibacterial activity against *S. aureus* and *E. coli* (Gao et al. 2014).

1.2.2 Nanofillers and Bio-nanocomposite Production

There are 3 sorts of conceivable biopolymer–clay nanocomposite configurations, specifically (1) tactoid, (2) intercalated, and (3) exfoliated (Rhim et al. 2013). If the clay's interlayer space does not scale, tactoid structures stay within the polymer, because generally clay has poor chemical attraction for the polymer. However, it is not a common method in nanocomposite formation. For example, when a polymer and silicate are immiscible, the layers do not separate and exist as agglomerates or tactoids (Tang et al. 2012). Intercalated structures are gained at direct extension of the clay interlayer. For this situation, interlayer spaces scale marginally as polymer chains enter into the primary clay space. On account of exfoliated structures, clay groups lose their layered structure and are very much isolated into single sheets inside the constant polymer phase. This is because of a high chemical attraction among polymer and clay. It is fundamental that the clay ought to be exfoliated into single platelet and appropriated homogeneously all through the polymer matrix to take full favorable position of nanoclays with high surface region (Sorrentino et al. 2007; Torre et al. 2003). Moreover, in order to obtain active nanoparticles, different chemical or physical methods have been used. For example, more classical methods such as acid hydrolysis are commonly used to obtain cellulose nanoparticles (Peponi et al. 2014). Likewise, nanostructures as carriers of active compounds have also been obtained by different techniques such as electrospinning and electrospraying. Nanofiber and other nanoparticle formation via electrospinning and electrospraying requires dispersing the biopolymer in a liquid medium, and thus, both the process of electrospinning and the shape and size of the obtained materials depend on solvent related properties like pH, conductivity, and surface tension (Bhushani and Anandharamakrishnan 2014).

For the case of antimicrobial biodegradable food packaging production, the incorporation of biocidal additives into a biopolymer matrix is a challenge because most natural antimicrobials are sensitive to heat. Electrospinning can be carried out at room temperature, and thus, it allows such molecules to be incorporated by nanoencapsulating them in nanofibers of proteins such as zein or biopolymers like PLA. With this approach, the antimicrobial activity of chitosan was used to produce zein/chitosan electrospun insoluble fiber materials with biocide properties (Torres-Giner et al. 2009).

1.2.3 Commercial Bio-nanocomposites in Food Packaging Applications

With the advances in production techniques and lowered nanoreinforce costs, there are various commercial bio-nanocomposites used in food packaging. Studies on food materials were summarized in Table 1.2. A nylon 6 nanocomposite film with silicate nanoparticles has been commercialized by Bayer under the name ‘Durethan® KU2-2601.’ This nanocomposite film was claimed to have better transparency and gas and moisture barrier properties than simple polyamide 6. The beer industry is actively exploring the use of polymers enhanced with nanocomposites in an effort to complement or replace costly and fragile glass. In this regard, Honeywell claims that their nanocomposite PET bottle offers a 100-fold reduction in OTR compared to nylon 6, reducing oxygen ingress near to zero. In the ‘Aegis OX’ beer bottle produced by Honeywell, the nanolayers act as the passive barrier and nylon-specific oxygen scavengers act as the active agents. These beer bottles provide a shelf life of 6–12 months, which is comparable to that of glass bottles (Reig et al. 2014). Another multilayer PET bottle was produced by Nanocor Inc. with the name ‘Imperm.’

Frito-Lay has launched one of its product, Sun Chips, in a 100% compostable PLA bag consisting of a six-layer, 20-μm-thick film which was 90% PLA by weight. However, after consumer complaints about PLA bags that they were too loud and made noise, they were withdrawn in October 2010. The bags were relaunched in February 2011 after a different adhesive, which absorbed some of the noise, was used. Again in 2010, Metabolix, Inc., launched a thermoformed package called ‘Mirel’ for non-alcoholic food packages such as yogurt containers, meat and vegetable trays, and single-served and disposable packaging materials. However, to date, no peer-reviewed publications on food with ‘Mirel’ packaging have appeared (Robertson 2016). In addition, a company, Nanobiomatters, in Spain launched solutions for food packaging in terms of barrier improvement with O_2Block® additives dispersed on PHB polymer system and antibacterial properties with BactiBlock® (NBM 2017).

Table 1.2 Bio-nanocomposites for food packaging applications

Type of BNC film	Product	Observed properties/Results	References
Poly(glycidyl methacrylate-covinylferrocene)/graphene oxide/iron oxide nanoparticle, and poly(glycidyl methacrylate-covinylferrocene)/MWCNT	Fish	Bio-nanocomposite xanthine biosensor showed excellent detection limit as 0.12 μM in 4 s for fish meat freshness control	Dervisevic et al. (2015)
Soy protein isolate–MMT (protein)	Fresh fruits and vegetables	Improvement in mechanical properties, thermal stability, and water vapor permeability with the addition of MMT	Kumar et al. (2010b)
Tilapia skin gelatin–hydrophilic–hydrophobic nanoclays (protein)	–	Improved barrier and mechanical properties	Nagarajan et al. (2014)
Wheat gluten–lignin NPs (protein)	–	Decreased water uptake of gluten and improved thermal stability and tensile strength	Yang et al. (2015)
Starch/halloysite/nisin	Soft cheese	Improved mechanical properties with halloysite addition; antimicrobial activity against *Listeria monocytogenes*, *Clostridium perfringens*, and *Staphylococcus aureus*	Meira et al. (2016)
Pectin/nanohybrid-layered double-hydroxide salicylate	Fresh apricot	Improved elongation at break point for pectin; improved water vapor barrier properties; extended shelf life	Gorrasi and Bugatti (2016)
Corn starch/talc nanoparticles	Tomato	Water vapor and oxygen permeability were reduced 54 and 26%, respectively, by talc addition (3% w/w) to thermoplastic starch; increased Young's modulus and yield stress	López et al. (2015)
Gelatin/ethanolic extract from coconut husk/Cloisite Na+ nanoclay	Meat powder	Lower lipid oxidation products, increased moisture barrier properties, extended shelf life	Nagarajan et al. (2015)

(continued)

Table 1.2 (continued)

Type of BNC film	Product	Observed properties/Results	References
Nanozinc oxide–neem oil–chitosan	Carrot	Good inhibition effect as antibacterial activity against *Escherichia coli*	Sanuja et al. (2015)
Alginate/nano-Ag	Shiitake mushroom	Spoilage reduction, improvement of sensory attributes, lower weight loss	Jiang et al. (2013)
Edible coating of polyvinylpyrrolidone (PVP) containing silver nanoparticle	Asparagus	Inhibited growth of psychrotrophic microorganisms during the storage period, lower weight loss, greener color, and tender textures were observed in the nanocoated samples, ensuring good quality for 25 days at 2 °C and 20 days at 10 °C	An et al. (2008)
Sodium alginate solution containing silver nanoparticles	Carrot and pear	Antibacterial film effective against the test strains, *E. coli* ATCC 8739 and *S. aureus* ATCC 6538, reduced the weight loss and soluble protein loss, thereby increasing the shelf life of carrots and pears	Mohammed Fayaz et al. (2009)
Calcium alginate film loaded with zinc oxide nanoparticles	Ready-to-eat poultry meat	Reduced microbial load of *Salmonella typhimurium* and *E. coli* by 7-log within 10 days when stored at 8 ± 1 °C	Akbar and Anal (2014)
Silver nanoparticle-based cellulose absorbent pads	Beef meat	Migrated 60 ppm silver ions from bio-nanocomposite caused significant reduction in the population of total aerobic bacteria, *Pseudomonas* spp. and *Enterobacteriaceae*, without causing any change in the properties of the food product	Fernandez et al. (2010a)

(continued)

Table 1.2 (continued)

Type of BNC film	Product	Observed properties/Results	References
Silver nanoparticle-based cellulose absorbent pads	Fresh-cut melons	Antimicrobial activity by 3-log reduction; retarded the senescence rate of the fresh-cut melons and gave juicier appearance after 10 days of storage	Fernández et al. (2010b)
Nanoemulsion coating of chitosan and mandarin essential oil	Green beans	Reduction in the population of *L. monocytogenes* of less than 1-log; combined with high pressure processing caused 4-log reduction	Donsì et al. (2015)
Chitosan/poly(vinyl alcohol)/ titanium nanoparticles	Soft white cheese	Antibacterial activity against Gram-positive (*Staphylococcus aureus*), Gram-negative (*Pseudomonas aeruginosa*, *Escherichia coli*) bacteria and fungi (*Candidia albicans*), and extended shelf life	Youssef et al. (2015)
Whey protein isolate (WPI)/ MMT	Food models (water, 3% acetic acid, 15% ethanol, olive oil)	Increased tensile strength of the WPI film and the swelling of the WPI film was reduced by 35% in food model systems	Wakai and Almenar (2015)

1.3 Legal and Ethical Barriers

One of the most critical drawbacks for nano-biocomposite application in food packaging is the lack of regulation in some fields, mostly for those with food contact. In fact, most of the studies are performed with biodegradable materials, which may be edible or even biocompatible (Jimenez et al. 2016). Regarding the potential toxicity of the nanocomposites, the principle danger of purchaser exposure to nanoparticles from food packaging is probably going to be through potential migration of nanoparticles into the foodstuffs (Han et al. 2011). Any packaging material intended to be used in USA must comply with those requirements included in the Title 21 of the Code of Federal Regulations (CFR). Although this regulation does not specify any requirements directly for nanocomposites, each component has to be authorized for its use in food contact materials (FDA 2015). In the European

Union, some regulations apply directly for all food contact materials. Regulation (EC) No. 1935/2004 on materials and articles intended to come into contact with food and Commission Regulation (EC) No. 2023/2006 on good manufacturing practice for materials and articles intended to come into contact with food apply for any packaging intended to be used in the European Union, including nanocomposites. Furthermore, Commission Regulation (EC) on active and intelligent materials and articles intended to come into contact with food applies also to antimicrobial nanocomposites since they are considered as active packaging.

Besides cited regulations, Commission Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food establishes the conditions to determine the migration from packaging to foodstuffs and distinguish between overall and specific migration. Therefore, this regulation presents a positive list of substances authorized in the formulation of plastic packaging as well as the maximum migration limit for each substance. Other nanospecific legislations were listed below;

- Regulation (EC) No. 1333/2008 on food additives.
- Regulation (EU) No. 10/2011 on plastic materials and articles intended to come into contact with food.
- Regulation (EC) No. 450/2009 on active and intelligent materials and articles intended to come into contact with food.
- Regulation (EU) No. 1169/2011 on the provision of food information to consumers (FIC) indicates.
- Regulation (EU) No. 2283/2015 on novel foods and novel food ingredients.

It was stated that ‘All ingredients present in the form of engineered nanomaterials shall be clearly indicated in the list of ingredients. The names of such ingredients shall be followed by the word “nano” in brackets.’ Designed nanomaterial implies any purposefully created material that has at least one measurement in the dimension of 100 nm or less. Besides, designed material may make out of discrete practical parts, either inside or at the surface, including structures, agglomerates, or aggregates, which may have a size over the dimension of 100 nm but hold properties that are acceptable for the nanoscale. From one aspect, nanomaterials in the food sector are the drivers for further developments in terms of:

- Food processing: Coatings for food production machinery, nanostructured filters and nanostructured/nanoscale adsorbents and catalysts.
- Food safety: Nanosensors for detecting pathogens and contaminants.
- Food quality/shelf life improvement: Packaging (barrier, active, smart) for better preservation.
- Food traceability: Tracking and monitoring.
- New food: Creating novel textures, flavors, and tastes, changing sensation.
- Nutritional quality improvement: Lower amount of fat, salt, sugar, and preservatives.
- Functional foods: Efficient delivery of bioactives and nutrients.

On the other side, nanomaterials in the food sector are also the barriers to further development in terms of:

- Technical issues: Particle size and size distribution differences (polydispersity and irregular shape).
- Safety issues.
- Analytical challenges: Nanomaterials chemical composition challenging.
- Regulatory challenges.
- Public perception: Lack of transparency, risks to health and the environment, unfair distribution of risks to the consumers and benefits to the industry, lack of socially useful application if consumers have any advantages, free choice about exposure by labeling.

There are major gaps in knowledge with regard to the behavior, fate, and effects of nanosized material via the gastrointestinal route. Properties of nanomaterials are significantly different from their bulk material and molecular forms. Oral exposure studies in rodents were carried out only for some inorganic nanoparticles. There are still problems in quantifying the amount of nanomaterial stuck in the animal. While accurately predict toxicity has been reported for some nanoparticles (silver, gold, titanium dioxide, silica, copper, carbon nanotubes, etc.) at high dose oral exposure, no information on accurate toxicity after low dose oral exposure is available (Bergin and Witzmann 2013). Most of the concerns are for insoluble, indigestible, and biopersistant nanoparticles used in the food area.

1.4 Future Trends and Concluding Remarks

In food packaging industry, a major emphasis is the use of proper packaging materials with improved mechanical, thermal, and barrier properties to minimize food losses and provide food safety. Also, a few nanostructures can be valuable to give dynamic or potentially intelligent properties to food packaging, as demonstrated by antimicrobial properties, oxygen scavenging capacity, enzyme immobilization, or sign of the level of exposure to some hindering elements, for example, improper temperatures or oxygen levels. Challenges stay in expanding the similarity among clays and polymers and achieving complete scattering of the nanoparticles in the polymer network. Properties of bio-nanocomposites were discussed in Sect. 4.2.1. There are many examples on petrochemical-based nanocomposite applications for food, while bio-nanocomposite applications in food packaging are still rare at commercial scale. More or less similar composite designs were preferred that are modified with active materials. Table 1.2 summarizes the materials used in the reviewed studies together with their packaging performances. It can be clearly seen that bio-nanocomposite packaging materials seem to have a brilliant future for an extensive variety of utilizations in inventive dynamic and smart food packaging with practical properties. On the other hand, there are some security worries about utilization of nanocomposites as food contact materials since there is constrained scientific observations or logical information about the migration of nanostructures from packaging materials into food. Subsequently, huge measure of further study is needed to assess the potential danger of nanocomposite materials.

References

Abugoch L, Tapia C, Plasencia D, Pastor A, Castro-Mandujano O, López L, Escalona VH (2016) Shelf-life of fresh blueberries coated with quinoa protein/chitosan/sunflower oil edible film. J Sci Food Agric 96(2):619–626

Akbar A, Anal AK (2014) Zinc oxide nanoparticles loaded active packaging, a challenge study against *Salmonella typhimurium* and *Staphylococcus aureus* in ready-to-eat poultry meat. Food Control 38:88–95

Alboofetileh M, Rezaei M, Hosseini H, Abdollahi M (2014) Antimicrobial activity of alginate/clay nanocomposite films enriched with essential oils against three common foodborne pathogens. Food Control 36(1):1–7

Alexandre M, Dubois P (2000) Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater Sci Eng R Rep 28(1):1–63

Alipoormazandarani N, Ghazihoseini S, Nafchi AM (2015) Preparation and characterization of novel bionanocomposite based on soluble soybean polysaccharide and halloysite nanoclay. Carbohydr Polym 134:745–751

An J, Zhang M, Wang S, Tang J (2008) Physical, chemical and microbiological changes in stored green asparagus spears as affected by coating of silver nanoparticles-PVP. LWT-Food Sci Technol 41(6):1100–1107

Andiyana Y, Suyatma NE (2016) Physico-mechanical properties of starch-based nanocomposite film incorporated with hydrothermally synthesized zinc oxide nanoparticles. In: Materials science forum. Trans Tech Publications, pp 162–167

Arfat YA, Benjakul S, Prodpran T, Sumpavapol P, Songtipya P (2016) Physico-mechanical characterization and antimicrobial properties of fish protein isolate/fish skin gelatin-zinc oxide (ZnO) nanocomposite films. Food Bioprocess Technol 9(1):101–112

Arfat YA, Ejaz M, Jacob H, Ahmed J (2017) Deciphering the potential of guar gum/Ag-Cu nanocomposite films as an active food packaging material. Carbohydr Polym 157:65–71

ASTM (2005) Standard terminology of packaging and distribution environments, D996-04. In: Annual book of ASTM. American Society for Testing and Material, Philadelphia, PA

Atef M, Rezaei M, Behrooz R (2015) Characterization of physical, mechanical, and antibacterial properties of agar-cellulose bionanocomposite films incorporated with savory essential oil. Food Hydrocolloids 45:150–157

Ayranci E, Tunc S (2004) The effect of edible coatings on water and vitamin C loss of apricots (*Armeniaca vulgaris* Lam.) and green peppers (*Capsicum annuum* L.). Food Chem 87(3):339–342

Bendahou D, Bendahou A, Grohens Y, Kaddami H (2015) New nanocomposite design from zeolite and poly (lactic acid). Ind Crops Prod 72:107–118

Bergin IL, Witzmann FA (2013) Nanoparticle toxicity by the gastrointestinal route: evidence and knowledge gaps. Int J Biomed Nanosci Nanotechnol 3(1–2):163–210

Bhushani JA, Anandharamakrishnan C (2014) Electrospinning and electrospraying techniques: potential food based applications. Trends Food Sci Technol 38(1):21–33

Bittmann B, Bouza R, Barral L, Bellas R, Cid A (2016) Effect of environmental factors on Poly (3-hydroxybutyrate-co−3-hydroxyvalerate)/Poly (butylene adipate-co-terephthalate)/montmorillonite nanocomposites with antimicrobial agents. Polym Compos

Bordes P, Pollet E, Avérous L (2009) Nano-biocomposites: biodegradable polyester/nanoclay systems. Prog Polym Sci 34(2):125–155

Cabedo L, Luis Feijoo J, Pilar Villanueva M, Lagarón JM, Giménez E (2006) Optimization of biodegradable nanocomposites based on aPLA/PCL blends for food packaging applications. In: Macromolecular symposia. Wiley Online Library, pp 191–197

Cano AI, Cháfer M, Chiralt A, González-Martínez C (2015) Physical and microstructural properties of biodegradable films based on pea starch and PVA. J Food Eng 167:59–64

Castro-Mayorga J, Fabra M, Lagaron J (2016) Stabilized nanosilver based antimicrobial poly (3-hydroxybutyrate-co-3-hydroxyvalerate) nanocomposites of interest in active food packaging. Innovative Food Sci Emerg Technol 33:524–533

Charlon Sb, Follain Ng, Dargent E, Soulestin Jrm, Sclavons M, Marais Sp (2016) Poly [(butylene succinate)-co-(butylene adipate)]-montmorillonite nanocomposites prepared by water-assisted extrusion: role of the dispersion level and of the structure-microstructure on the enhanced barrier properties. J Phys Chem C 120(24):13234–13248

Chen P, Zhang L (2006) Interaction and properties of highly exfoliated soy protein/montmorillonite nanocomposites. Biomacromol 7(6):1700–1706

CNBC (Consumer News and Business Channel) (2014) Global nano-enabled packaging market for food and beverages industry will reach $15.0 billion in 2020. Persistence market research. http://www.cnbc.com/id/102011212. Accessed 26 Feb 2017

da Costa Reis DC, Lemos Morais AC, de Carvalho LH, Alves TS, Barbosa R (2016) Assessment of the morphology and interaction of PHBV/clay bionanocomposites: uses as food packaging. In: Macromolecular symposia. Wiley Online Library, pp 113–118

De Azeredo HM (2009) Nanocomposites for food packaging applications. Food Res Int 42 (9):1240–1253

Dervisevic M, Custiuc E, Çevik E, Durmus Z, Şenel M, Durmus A (2015) Electrochemical biosensor based on REGO/Fe 3 O 4 bionanocomposite interface for xanthine detection in fish sample. Food Control 57:402–410

Desai KG (2007) Properties of tableted high-amylose corn starch–pectin blend microparticles intended for controlled delivery of diclofenac sodium. J Biomater Appl 21(3):217–233

Díez-Pascual AM, Díez-Vicente AL (2014) ZnO-reinforced poly (3-hydroxybutyrate-co-3-hydroxyvalerate) bionanocomposites with antimicrobial function for food packaging. ACS Appl Mater Interfaces 6(12):9822–9834

Donsì F, Marchese E, Maresca P, Pataro G, Vu KD, Salmieri S, Lacroix M, Ferrari G (2015) Green beans preservation by combination of a modified chitosan based-coating containing nanoemulsion of mandarin essential oil with high pressure or pulsed light processing. Postharvest Biol Technol 106:21–32

Dumitriu RP, Sacarescu L, Macocinschi D, Filip D, Vasile C (2016) Effect of silver nanoparticles on the dispersion, rheological properties and morphological aspect of solvent cast polyurethane/biopolymers bionanocomposite membranes. J Adhes Sci Technol 30(16): 1716–1726

Duncan TV (2011) Applications of nanotechnology in food packaging and food safety: barrier materials, antimicrobials and sensors. J Colloid Interface Sci 363(1):1–24

European Commission (2004) European Commission, Community Health and Consumer Protection. Nanotechnologies: a preliminary risk analysis on the basis of a workshop organized in Brussels on 1–2 Mar 2004 by the Health and Consumer Protection Directorate General of the European Commission. http://europa.eu.int/comm/health/ph_risk/events_risk_en.htm Accessed 2 Oct 2016

FDA (Food and Drug Administration) (2015) Packaging & food contact substances (FCS). http://www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/ucm2006853.htm. Accessed 25 Feb 2017

Fernandez A, Picouet P, Lloret E (2010a) Reduction of the spoilage-related microflora in absorbent pads by silver nanotechnology during modified atmosphere packaging of beef meat. J Food Prot 73(12):2263–2269

Fernández A, Picouet P, Lloret E (2010b) Cellulose-silver nanoparticle hybrid materials to control spoilage-related microflora in absorbent pads located in trays of fresh-cut melon. Int J Food Microbiol 142(1):222–228

Gao C, Yan T, Du J, He F, Luo H, Wan Y (2014) Introduction of broad spectrum antibacterial properties to bacterial cellulose nanofibers via immobilising ε-polylysine nanocoatings. Food Hydrocolloids 36:204–211

Ghule K, Ghule AV, Chen B-J, Ling Y-C (2006) Preparation and characterization of ZnO nanoparticles coated paper and its antibacterial activity study. Green Chem 8(12):1034–1041

Girouard NM, Xu S, Schueneman GT, Shofner ML, Meredith JC (2016) Site-selective modification of cellulose nanocrystals with isophorone diisocyanate and formation of polyurethane-CNC composites. ACS Appl Mater Interfaces 8(2):1458–1467

Goh K, Heising JK, Yuan Y, Karahan HE, Wei L, Zhai S, Koh J-X, Htin NM, Zhang F, Wang R (2016) Sandwich-architectured poly (lactic acid)–graphene composite food packaging films. ACS Appl Mater Interfaces 8(15):9994–10004

González K, Retegi A, González A, Eceiza A, Gabilondo N (2015) Starch and cellulose nanocrystals together into thermoplastic starch bionanocomposites. Carbohydr Polym 117: 83–90

Gorrasi G, Bugatti V (2016) Edible bio-nano-hybrid coatings for food protection based on pectins and LDH-salicylate: preparation and analysis of physical properties. LWT-Food Sci Technol 69:139–145

Grunlan JC, Grigorian A, Hamilton CB, Mehrabi AR (2004) Effect of clay concentration on the oxygen permeability and optical properties of a modified poly (vinyl alcohol). J Appl Polym Sci 93(3):1102–1109

Guarás M, Alvarez V, Ludueña L (2015) Processing and characterization of thermoplastic starch/polycaprolactone/compatibilizer ternary blends for packaging applications. J Polym Res 22(9):165

Guarás M, Alvarez V, Ludueña L (2016) Biodegradable nanocomposites based on starch/polycaprolactone/compatibilizer ternary blends reinforced with natural and organo-modified montmorillonite. J Appl Polym Sci 133(44)

Han W, Yu Y, Li N, Wang L (2011) Application and safety assessment for nano-composite materials in food packaging. Chin Sci Bull 56(12):1216–1225

Herrera N, Roch H, Salaberria AM, Pino-Orellana MA, Labidi J, Fernandes SC, Radic D, Leiva A, Oksman K (2016a) Functionalized blown films of plasticized polylactic acid/chitin nanocomposite: preparation and characterization. Mater Des 92:846–852

Herrera N, Salaberria AM, Mathew AP, Oksman K (2016b) Plasticized polylactic acid nanocomposite films with cellulose and chitin nanocrystals prepared using extrusion and compression molding with two cooling rates: effects on mechanical, thermal and optical properties. Compos A Appl Sci Manuf 83:89–97

Hodson JD, Perre CM (2006) Film structures and packages therefrom useful for packaging respiring food products. U.S. Patent No. 7,008,677, 7 Mar 2006

Hu Z, Zen X, Gong J, Deng Y (2009) Water resistance improvement of paper by superhydrophobic modification with microsized $CaCO_3$ and fatty acid coating. Colloids Surf A 351(1):65–70

Huo L, Wang D, Liu H, Jia P, Gao J (2016) Cytoxicity, dynamic and thermal properties of bio-based rosin-epoxy resin/castor oil polyurethane/carbon nanotubes bio-nanocomposites. J Biomater Sci Polym Ed 27(11):1100–1114

Iguchi M, Yamanaka S, Budhiono A (2000) Bacterial cellulose—a masterpiece of nature's arts. J Mater Sci 35(2):261–270

Ikada Y, Tsuji H (2000) Biodegradable polyesters for medical and ecological applications. Macromol Rapid Commun 21(3):117–132

Irissin-Mangata J, Bauduin G, Boutevin B, Gontard N (2001) New plasticizers for wheat gluten films. Eur Polym J 37(8):1533–1541

Iwata T (2015) Biodegradable and bio-based polymers: future prospects of eco-friendly plastics. Angew Chem Int Ed 54(11):3210–3215

Jamshidian M, Tehrany EA, Imran M, Jacquot M, Desobry S (2010) Poly-lactic acid: production, applications, nanocomposites, and release studies. Compr Rev Food Sci Food Saf 9(5): 552–571

Jang K, Lee JW, Hong I-K, Lee S (2013) Effect of supercritical carbon dioxide as an exfoliation aid on bio-based polyethylene terephthalate glycol-modified/clay nanocomposites. Korea-Aust Rheol J 25(3):145–152

Jiang T, Feng L, Wang Y (2013) Effect of alginate/nano-Ag coating on microbial and physicochemical characteristics of shiitake mushroom (*Lentinus edodes*) during cold storage. Food Chem 141(2):954–960

Jimenez A, Vargas M, Chiralt A (2016) Chapter 11—Antimicrobial nanocomposites for food packaging applications: novel approaches. In: Grumezescu A (ed) Novel approaches of nanotechnology in food, vol 1. Academic Press

Jin T, Gurtler J (2011) Inactivation of Salmonella in liquid egg albumen by antimicrobial bottle coatings infused with allyl isothiocyanate, nisin and zinc oxide nanoparticles. J Appl Microbiol 110(3):704–712

Jo W-S, Song H-Y, Song N-B, Lee J-H, Min SC, Song KB (2014) Quality and microbial safety of 'Fuji' apples coated with carnauba-shellac wax containing lemongrass oil. LWT-Food Sci Technol 55(2):490–497

Joe MM, Bradeeba K, Parthasarathi R, Sivakumaar PK, Chauhan PS, Tipayno S, Benson A, Sa T (2012a) Development of surfactin based nanoemulsion formulation from selected cooking oils: evaluation for antimicrobial activity against selected food associated microorganisms. J Taiwan Inst Chem Eng 43(2):172–180

Joe MM, Chauhan PS, Bradeeba K, Shagol C, Sivakumaar PK, Sa T (2012b) Influence of sunflower oil based nanoemulsion (AUSN-4) on the shelf life and quality of Indo-Pacific king mackerel (*Scomberomorus guttatus*) steaks stored at 20 °C. Food Control 23(2):564–570

Kadam DM, Thunga M, Wang S, Kessler MR, Grewell D, Lamsal B, Yu C (2013) Preparation and characterization of whey protein isolate films reinforced with porous silica coated titania nanoparticles. J Food Eng 117(1):133–140

Kanmani P, Rhim J-W (2014) Properties and characterization of bionanocomposite films prepared with various biopolymers and ZnO nanoparticles. Carbohydr Polym 106:190–199

Kikuchi Y, Hirao M, Narita K, Sugiyama E, Oliveira S, Chapman S, Arakaki MM, Cappra CM (2013) Environmental performance of biomass-derived chemical production: a case study on sugarcane-derived polyethylene. J Chem Eng Jpn 46(4):319–325

Kuciel S, Jakubowska P, Kuźniar P (2014) A study on the mechanical properties and the influence of water uptake and temperature on biocomposites based on polyethylene from renewable sources. Compos B Eng 64:72–77

Kumar P, Sandeep K, Alavi S, Truong V-D, Gorga R (2010a) Effect of type and content of modified montmorillonite on the structure and properties of bio-nanocomposite films based on soy protein isolate and montmorillonite. J Food Sci 75(5):N46–N56

Kumar P, Sandeep K, Alavi S, Truong V-D, Gorga R (2010b) Preparation and characterization of bio-nanocomposite films based on soy protein isolate and montmorillonite using melt extrusion. J Food Eng 100(3):480–489

Lacroix M, Vu KD (2014) Edible coating and film materials: proteins. In: Han JH (ed) Innovations in food packaging. Academic Press, San Diego, CA, USA, pp 277–294

Lee J, Park HJ, Lee C, Choi W (2003) Extending shelf-life of minimally processed apples with edible coatings and antibrowning agents. LWT-Food Sci Technol 36(3):323–329

Li G-f, Luo W-h, Xiao M, Wang S-j, Meng Y-z (2016) Biodegradable poly (propylene carbonate)/ layered double hydroxide composite films with enhanced gas barrier and mechanical properties. Chin J Polym Sci 34(1):13–22

Lizundia E, Fortunati E, Dominici F, Vilas JL, León LM, Armentano I, Torre L, Kenny JM (2016) PLLA-grafted cellulose nanocrystals: role of the CNC content and grafting on the PLA bionanocomposite film properties. Carbohydr Polym 142:105–113

López OV, Castillo LA, García MA, Villar MA, Barbosa SE (2015) Food packaging bags based on thermoplastic corn starch reinforced with talc nanoparticles. Food Hydrocolloids 43:18–24

Ludueña LN, Fortunati E, Morán JI, Alvarez VA, Cyras VP, Puglia D, Manfredi LB, Pracella M (2016) Preparation and characterization of polybutylene-succinate/poly (ethylene-glycol)/cellulose nanocrystals ternary composites. J Appl Polym Sci 133(15)

Luzi F, Fortunati E, Jiménez A, Puglia D, Pezzolla D, Gigliotti G, Kenny J, Chiralt A, Torre L (2016) Production and characterization of PLA_PBS biodegradable blends reinforced with cellulose nanocrystals extracted from hemp fibres. Ind Crops Prod 93:276–289

Ma P, Jiang L, Yu M, Dong W, Chen M (2016) Green antibacterial nanocomposites from poly (lactide)/poly (butylene adipate-co-terephthalate)/nanocrystal cellulose-silver nanohybrids. ACS Sustain Chem Eng 4(12):6417–6426

Majdzadeh-Ardakani K, Nazari B (2010) Improving the mechanical properties of thermoplastic starch/poly (vinyl alcohol)/clay nanocomposites. Compos Sci Technol 70(10):1557–1563

Mallardo S, De Vito V, Malinconico M, Volpe MG, Santagata G, Di Lorenzo ML (2016) Poly (butylene succinate)-based composites containing β-cyclodextrin/d-limonene inclusion complex. Eur Polym J 79:82–96

Marra A, Silvestre C, Duraccio D, Cimmino S (2016) Polylactic acid/zinc oxide biocomposite films for food packaging application. Int J Biol Macromol 88:254–262

Mary G, Bajpai S, Chand N (2009) Copper (II) ions and copper nanoparticles-loaded chemically modified cotton cellulose fibers with fair antibacterial properties. J Appl Polym Sci 113 (2):757–766

McCarthy A (2016) Sugarcane-based packaging for consumer products. In: Google patents

McHugh T, Senesi E (2000) Apple wraps: a novel method to improve the quality and extend the shelf life of fresh-cut apples. J Food Sci 65(3):480–485

Meira SMM, Zehetmeyer G, Scheibel JM, Werner JO, Brandelli A (2016) Starch-halloysite nanocomposites containing nisin: characterization and inhibition of *Listeria monocytogenes* in soft cheese. LWT-Food Sci Technol 68:226–234

Mekonnen T, Misra M, Mohanty AK (2016) Fermented soymeals and their reactive blends with poly (butylene adipate-co-terephthalate) in engineering biodegradable cast films for sustainable packaging. ACS Sustain Chem Eng 4(3):782–793

Mohammed Fayaz A, Balaji K, Girilal M, Kalaichelvan P, Venkatesan R (2009) Mycobased synthesis of silver nanoparticles and their incorporation into sodium alginate films for vegetable and fruit preservation. J Agric Food Chem 57(14):6246–6252

Moldao-Martins M, Beirao-da-Costa S, Beirao-da-Costa M (2003) The effects of edible coatings on postharvest quality of the “Bravo de Esmolfe” apple. Eur Food Res Technol 217(4): 325–328

Moran JI, Ludueña LN, Phuong VT, Cinelli P, Lazzeri A, Alvarez VA (2016) Processing routes for the preparation of poly (lactic acid)/cellulose-nanowhisker nanocomposites for packaging applications. Polym Polym Compos 24(5):341

Moreira FK, Pedro DC, Glenn GM, Marconcini JM, Mattoso LH (2013) Brucite nanoplates reinforced starch bionanocomposites. Carbohydr Polym 92(2):1743–1751

Moreno-Vásquez MJ, Plascencia-Jatomea M, Sánchez-Valdes S, Castillo-Yáñez FJ, Ocaño-Higuera VM, Rodríguez-Félix F, Rosas-Burgos EC, Graciano-Verdugo AZ (2016) Preparation and characterization of films made of poly (l-lactic acid)/poly (l-lactic acid) grafted maleic anhydride/epigallocatechin gallate blends for antibacterial food packaging. J Plastic Film Sheeting 8756087916631602

Nagarajan M, Benjakul S, Prodpran T, Songtipya P (2014) Characteristics of bio-nanocomposite films from tilapia skin gelatin incorporated with hydrophilic and hydrophobic nanoclays. J Food Eng 143:195–204

Nagarajan M, Benjakul S, Prodpran T, Songtipya P (2015) Properties and characteristics of nanocomposite films from tilapia skin gelatin incorporated with ethanolic extract from coconut husk. J Food Sci Technol 52(12):7669–7682

NBM (Nanobiomatters) (2017) What is O2Block® additives for barrier applications? http://www.nanobiomatters.com/wordpress/products/barrier-and-mechanical-additives. Accessed 26 Feb 2017

Nguyen VT, Gidley MJ, Dykes GA (2008) Potential of a nisin-containing bacterial cellulose film to inhibit *Listeria monocytogenes* on processed meats. Food Microbiol 25(3):471–478

Oleyaei SA, Almasi H, Ghanbarzadeh B, Moayedi AA (2016) Synergistic reinforcing effect of TiO_2 and montmorillonite on potato starch nanocomposite films: thermal, mechanical and barrier properties. Carbohydr Polym 152:253–262

Ortega-Toro R, Contreras J, Talens P, Chiralt A (2015) Physical and structural properties and thermal behaviour of starch-poly (ε-caprolactone) blend films for food packaging. Food Packag Shelf Life 5:10–20

Ortega-Toro R, Muñoz A, Talens P, Chiralt A (2016) Improvement of properties of glycerol plasticized starch films by blending with a low ratio of polycaprolactone and/or polyethylene glycol. Food Hydrocolloids 56:9–19

Oymaci P, Altinkaya SA (2016) Improvement of barrier and mechanical properties of whey protein isolate based food packaging films by incorporation of zein nanoparticles as a novel bionanocomposite. Food Hydrocolloids 54:1–9

Ozer BBP, Uz M, Oymaci P, Altinkaya SA (2016) Development of a novel strategy for controlled release of lysozyme from whey protein isolate based active food packaging films. Food Hydrocolloids 61:877–886

Peponi L, Puglia D, Torre L, Valentini L, Kenny JM (2014) Processing of nanostructured polymers and advanced polymeric based nanocomposites. Mater Sci Eng R Rep 85:1–46

Pérez-Gago MB, Rhim JW (2014) Chapter 13-edible coating and film materials: lipid bilayers and lipid emulsions. In: Han JH (ed) Innovations in food packaging. Academic Press, London, pp 325–350

Petchwattana N, Covavisaruch S, Wibooranawong S, Naknaen P (2016) Antimicrobial food packaging prepared from poly (butylene succinate) and zinc oxide. Measurement 93:442–448

Pinheiro AC, Bourbon AI, Medeiros BGdS, da Silva LH, da Silva MC, Carneiro-da-Cunha MG, Coimbra MA, Vicente AA (2012) Interactions between κ-carrageenan and chitosan in nanolayered coatings—structural and transport properties. Carbohydr Polym 87(2):1081–1090

PlasticsEurope (2015) Plastics–the facts 2014/2015 an analysis of European plastics production, demand and waste data. http://www.plasticseurope.org/documents/document/20150227150049-final_plastics_the_facts_2014_2015_260215.pdf. Accessed 25 Feb 2017

Qazanfarzadeh Z, Kadivar M (2016) Properties of whey protein isolate nanocomposite films reinforced with nanocellulose isolated from oat husk. Int J Biol Macromol 91:1134–1140

Reig CS, Lopez AD, Ramos MH, Ballester VAC (2014) Nanomaterials: a map for their selection in food packaging applications. Packag Technol Sci 27(11):839–866

Ren H, Qiao F, Shi Y, Knutzen MW, Wang Z, Du H, Zhang H (2015) PlantBottle™ packaging program is continuing its journey to pursue bio-mono-ethylene glycol using agricultural waste. J Renew Sustain Energy 7(4):041510

Reščček A, Katančić Z, Kratofil Krehula L, Ščetar M, Hrnjak-Murgić Z, Galić K (2016a) Development of double-layered PE/PCL films for food packaging modified with zeolite and magnetite nanoparticles. Adv Polym Technol

Reščček A, Ščetar M, Hrnjak-Murgić Z, Dimitrov N, Galić K (2016b) Polyethylene/polycaprolactone nanocomposite films for food packaging modified with magnetite and casein: oxygen barrier, mechanical, and thermal properties. Polym-Plast Technol Eng 55(14):1450–1459

Rhim J-W, Wang L-F (2013) Mechanical and water barrier properties of agar/κ-carrageenan/konjac glucomannan ternary blend biohydrogel films. Carbohydr Polym 96(1):71–81

Rhim J-W, Hong S-I, Ha C-S (2009) Tensile, water vapor barrier and antimicrobial properties of PLA/nanoclay composite films. LWT-Food Sci Technol 42(2):612–617

Rhim J-W, Park H-M, Ha C-S (2013) Bio-nanocomposites for food packaging applications. Prog Polym Sci 38(10):1629–1652

Robertson GL (2016) Food packaging: principles and practice. CRC Press

Romainor ANB, Chin SF, Pang SC, Bilung LM (2014) Preparation and characterization of chitosan nanoparticles-doped cellulose films with antimicrobial property. J Nanomater 2014:130

Russo MA, O'Sullivan C, Rounsefell B, Halley PJ, Truss R, Clarke WP (2009) The anaerobic degradability of thermoplastic starch: polyvinyl alcohol blends: potential biodegradable food packaging materials. Biores Technol 100(5):1705–1710

Salmieri S, Islam F, Khan RA, Hossain FM, Ibrahim HM, Miao C, Hamad WY, Lacroix M (2014a) Antimicrobial nanocomposite films made of poly (lactic acid)-cellulose nanocrystals (PLA-CNC) in food applications: part A—effect of nisin release on the inactivation of *Listeria monocytogenes* in ham. Cellulose 21(3):1837–1850

Salmieri S, Islam F, Khan RA, Hossain FM, Ibrahim HM, Miao C, Hamad WY, Lacroix M (2014b) Antimicrobial nanocomposite films made of poly (lactic acid)–cellulose nanocrystals (PLA–CNC) in food applications—part B: effect of oregano essential oil release on the inactivation of *Listeria monocytogenes* in mixed vegetables. Cellulose 21(6):4271–4285

Salvatore M, Marra A, Duraccio D, Shayanfar S, Pillai SD, Cimmino S, Silvestre C (2016) Effect of electron beam irradiation on the properties of polylactic acid/montmorillonite nanocomposites for food packaging applications. J Appl Polym Sci 133(2)

Salvia-Trujillo L, Rojas-Graü MA, Soliva-Fortuny R, Martín-Belloso O (2015) Use of antimicrobial nanoemulsions as edible coatings: impact on safety and quality attributes of fresh-cut Fuji apples. Postharvest Biol Technol 105:8–16

Santamaria-Echart A, Ugarte L, García-Astrain C, Arbelaiz A, Corcuera MA, Eceiza A (2016) Cellulose nanocrystals reinforced environmentally-friendly waterborne polyurethane nanocomposites. Carbohydr Polym 151:1203–1209

Sanuja S, Agalya A, Umapathy M (2015) Synthesis and characterization of zinc oxide–neem oil–chitosan bionanocomposite for food packaging application. Int J Biol Macromol 74:76–84

Sartori T, Menegalli FC (2016) Development and characterization of unripe banana starch films incorporated with solid lipid microparticles containing ascorbic acid. Food Hydrocolloids 55:210–219

Saurabh CK, Gupta S, Variyar PS, Sharma A (2016) Effect of addition of nanoclay, beeswax, tween-80 and glycerol on physicochemical properties of guar gum films. Ind Crops Prod 89:109–118

Seo J, Jeon G, Jang ES, Bahadar Khan S, Han H (2011) Preparation and properties of poly (propylene carbonate) and nanosized ZnO composite films for packaging applications. J Appl Polym Sci 122(2):1101–1108

Seoane IT, Fortunati E, Puglia D, Cyras VP, Manfredi LB (2016) Development and characterization of bionanocomposites based on poly (3-hydroxybutyrate) and cellulose nanocrystals for packaging applications. Polym Int 65(9):1046–1053

Shankar S, Rhim J-W (2016) Tocopherol-mediated synthesis of silver nanoparticles and preparation of antimicrobial PBAT/silver nanoparticles composite films. LWT-Food Sci Technol 72:149–156

Silvestre C, Duraccio D, Cimmino S (2011) Food packaging based on polymer nanomaterials. Prog Polym Sci 36(12):1766–1782

Siqueira MC, Coelho GF, de Moura MR, Bresolin JD, Hubinger SZ, Marconcini JM, Mattoso LH (2014) Evaluation of antimicrobial activity of silver nanoparticles for carboxymethylcellulose film applications in food packaging. J Nanosci Nanotechnol 14(7):5512–5517

Siracusa V, Lotti N, Munari A, Dalla Rosa M (2015) Poly (butylene succinate) and poly (butylene succinate-co-adipate) for food packaging applications: gas barrier properties after stressed treatments. Polym Degrad Stab 119:35–45

Soheilmoghaddam M, Wahit MU, Yussuf AA, Al-Saleh MA, Whye WT (2014) Characterization of bio regenerated cellulose/sepiolite nanocomposite films prepared via ionic liquid. Polym Testing 33:121–130

Sorrentino A, Gorrasi G, Vittoria V (2007) Potential perspectives of bio-nanocomposites for food packaging applications. Trends Food Sci Technol 18(2):84–95

Stewart RF (1993) Food package comprised of polymer with thermally responsive permeability. U.S. Patent No. 5,254,354, 19 Oct 1993

Swain S, Biswal S, Nanda P, Nayak PL (2004) Biodegradable soy-based plastics: opportunities and challenges. J Polym Environ 12(1):35–42

Swain SK, Dash S, Kisku SK, Singh RK (2014) Thermal and oxygen barrier properties of chitosan bionanocomposites by reinforcement of calcium carbonate nanopowder. J Mater Sci Technol 30(8):791–795

Tang X, Kumar P, Alavi S, Sandeep K (2012) Recent advances in biopolymers and biopolymer-based nanocomposites for food packaging materials. Crit Rev Food Sci Nutr 52 (5):426–442

Toğrul H, Arslan N (2004) Extending shelf-life of peach and pear by using CMC from sugar beet pulp cellulose as a hydrophilic polymer in emulsions. Food Hydrocolloids 18(2):215–226

Torre L, Frulloni E, Kenny J, Manferti C, Camino G (2003) Processing and characterization of epoxy–anhydride-based intercalated nanocomposites. J Appl Polym Sci 90(9):2532–2539

Torres-Giner S, Ocio MJ, Lagaron JM (2009) Novel antimicrobial ultrathin structures of zein/chitosan blends obtained by electrospinning. Carbohydr Polym 77(2):261–266

Tripathi N, Katiyar V (2016) PLA/functionalized-gum Arabic based bionanocomposite films for high gas barrier applications. J Appl Polym Sci

Turan D, Gunes G, Seniha Güner F (2016) Synthesis, characterization and O_2 permeability of shape memory polyurethane films for fresh produce packaging. Packag Technol Sci 29(7): 415–427

Turan D, Sängerlaub S, Stramm C, Gunes G (2017) Gas permeabilities of polyurethane films for fresh produce packaging: response of O 2 permeability to temperature and relative humidity. Polym Testing 59:237–244

Vargas M, Pastor C, Chiralt A, McClements DJ, González-Martínez C (2008) Recent advances in edible coatings for fresh and minimally processed fruits. Crit Rev Food Sci Nutr 48(6): 496–511

Venkatesan R, Rajeswari N (2016) Preparation, mechanical and antimicrobial properties of SiO_2/ poly (butylene adipate-co-terephthalate) films for active food packaging. Silicon 1–7

Venkatesan R, Rajeswari N (2017) ZnO/PBAT nanocomposite films: investigation on the mechanical and biological activity for food packaging. Polym Adv Technol 28(1):20–27

Wakai M, Almenar E (2015) Effect of the presence of montmorillonite on the solubility of whey protein isolate films in food model systems with different compositions and pH. Food Hydrocolloids 43:612–621

Wang D, Yu J, Zhang J, He J, Zhang J (2013) Transparent bionanocomposites with improved properties from poly (propylene carbonate)(PPC) and cellulose nanowhiskers (CNWs). Compos Sci Technol 85:83–89

Wang L-F, Rhim J-W, Hong S-I (2016a) Preparation of poly (lactide)/poly (butylene adipate-co-terephthalate) blend films using a solvent casting method and their food packaging application. LWT-Food Sci Technol 68:454–461

Wang X-y, Weng Y-x, Wang W, Huang Z-g, Wang Y-Z (2016b) Modification of poly (propylene carbonate) with chain extender ADR-4368 to improve its thermal, barrier, and mechanical properties. Polym Testing 54:301–307

Weizman O, Dotan A, Nir Y, Ophir A (2016) Modified whey protein coatings for improved gas barrier properties of biodegradable films. Polym Adv Technol

Witt U, Einig T, Yamamoto M, Kleeberg I, Deckwer W-D, Müller R-J (2001) Biodegradation of aliphatic–aromatic copolyesters: evaluation of the final biodegradability and ecotoxicological impact of degradation intermediates. Chemosphere 44(2):289–299

Yang W, Kenny JM, Puglia D (2015) Structure and properties of biodegradable wheat gluten bionanocomposites containing lignin nanoparticles. Ind Crops Prod 74:348–356

Yang W, Owczarek J, Fortunati E, Kozanecki M, Mazzaglia A, Balestra G, Kenny J, Torre L, Puglia D (2016) Antioxidant and antibacterial lignin nanoparticles in polyvinyl alcohol/chitosan films for active packaging. Ind Crops Prod 94:800–811

Youssef AM, El-Sayed SM, Salama HH, El-Sayed HS, Dufresne A (2015) Evaluation of bionanocomposites as packaging material on properties of soft white cheese during storage period. Carbohyd Polym 132:274–285

Yu H-Y, Qin Z-Y, Sun B, Yang X-G, Yao J-M (2014) Reinforcement of transparent poly (3-hydroxybutyrate-co-3-hydroxyvalerate) by incorporation of functionalized carbon nanotubes as a novel bionanocomposite for food packaging. Compos Sci Technol 94:96–104

Zambrano-Zaragoza M, Mercado-Silva E, Gutiérrez-Cortez E, Cornejo-Villegas M, Quintanar-Guerrero D (2014) The effect of nano-coatings with α-tocopherol and xanthan gum on shelf-life and browning index of fresh-cut “Red Delicious” apples. Innovative Food Sci Emerg Technol 22:188–196

Zapata PJ, Guillén F, Martínez-Romero D, Castillo S, Valero D, Serrano M (2008) Use of alginate or zein as edible coatings to delay postharvest ripening process and to maintain tomato (Solanum lycopersicon Mill) quality. J Sci Food Agric 88(7):1287–1293

Zhang Y, Rempel C, McLaren D (2014) Edible coating and film materials: carbohydrates. Innovations Food Packag 305–323

Zhao S, Yao J, Fei X, Shao Z, Chen X (2013) An antimicrobial film by embedding in situ synthesized silver nanoparticles in soy protein isolate. Mater Lett 95:142–144

Zhou L, Zhao G, Jiang W (2016a) Effects of catalytic transesterification and composition on the toughness of poly (lactic acid)/poly (propylene carbonate) blends. Ind Eng Chem Res 55 (19):5565–5573

Zhou S-Y, Huang H-D, Ji X, Yan D-X, Zhong G-J, Hsiao BS, Li Z-M (2016b) Super-robust polylactide barrier films by building densely oriented lamellae incorporated with ductile in situ nanofibrils of poly (butylene adipate-co-terephthalate). ACS Appl Mater Interfaces 8 (12):8096–8109

Zolfi M, Khodaiyan F, Mousavi M, Hashemi M (2014) The improvement of characteristics of biodegradable films made from kefiran–whey protein by nanoparticle incorporation. Carbohydr Polym 109:118–125

Chapter 2
Polymer-Based Bionanocomposites for Future Packaging Materials

Sarat K. Swain, Niladri Sarkar, Bhagyashree Patra and Gyanaranjan Sahoo

Abstract Packaging technology is mainly dealing with the safety storage and hygienic handling of daily needs and undergoes in continuous modification with time as per the choice of the consumers. With the ever-increasing market race, psychological aspect of the consumer behavior is also reflected in the packaging technology. For easy production and low cost of synthetic plastic materials, it has won the prime interest in packaging field. But, environmental issues lead the system to run behind the fabrication of eco-friendly bionanocomposites with incorporation of nanomaterials in renewable, biodegradable polymers in order to obtain bionanocomposites with improved fire retardant, oxygen barrier, thermal and mechanical properties. This chapter focusses some important basics of polymer-based bionanocomposites for packaging applications. The mechanical, fare retardant, thermal and gas barrier properties are improved substantially with incorporation of nanomaterials with biopolymers. Herein, the commercial, physiological and safety aspects of packaging materials are also discussed for the promotion of polymer-based nanocomposite as a future smart material for packaging products.

Keywords Packaging · Psychological aspect · Plastics · Bionanocomposites
Fire retardant · Oxygen barrier

2.1 Introduction

The term packaging is not a word of today's generation; it has taken birth in ancient. In ancient age, packages were made of natural materials like baskets of reeds, botal bags, wooden boxes, pottery vases, wooden barrels, woven bags,

---

S. K. Swain (✉) · N. Sarkar · B. Patra
Department of Chemistry, Veer Surendra Sai University of Technology,
Sambalpur 768018, Odisha, India
e-mail: swainsk2@yahoo.co.in

G. Sahoo
Department of Chemistry, Veer Surendra Sai University of Technology,
Burla, Sambalpur 768018, Odisha, India

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_2

ceramic amphorae, etc. In current age, when someone mentions packaging, what is the first thing that comes to mind? Possibly, brightly colored cereal boxes designed to entice children, or may be the impenetrable plastic cage. Packaging, itself represents a technology dealing with the distribution of products from industry to market zone to consumer's house. Packaging technology is all about the process of designing, evaluating and production of packages. Packaging plays a pivotal role in marketing, safety storage and hygienic handling of daily needs (Coles et al. 2003). The application of packaging is not limited to a single sectors. It spreads its wings to several sectors like bulk chemical packaging, medical-device packaging, retail-food packaging, pharmaceutical packaging, military packaging and so on. As it is related with the safety storage, it is also categorized by the layer of function. In many countries, it is fully integrated into business, government, institutional, industrial and personal use. In marketing, packaging is used to add more importance to motivate the consumers by notifying the product details, including composition and branding context, called package labeling. Package labeling is any written, electronic and graphic communication on the package. Packaging is used for convenience and information transmission. On the other hand, package labels communicate how to use, transport, recycle or dispose of package or product. The package and package labeling are highly used by the marketers to encourage potential buyers to purchase the product. Many types of symbols for package labeling are nationally and internationally standardized. For consumer packaging, symbol exists for product certification (such as TUV and FCC marks), trademarks, proof of purchase, etc. Recently, a great effort has been done on motivational research, color testing and physiological manipulation of the daily products to draw the consumer's attention to new package. Based on the results of this research, past experience, and the current and anticipated decisions of competitors, the marketer will initially determine the primary role of the package relative to the product. The things that we really need to address that what is the purpose of packaging and how this technology is evolving over the year with respect to the consumer's needs.

2.1.1 The Main Aspect of Product Packaging

The main purpose of packaging is to transport the products from the manufacturing industry to the customer's house with its original form, i.e., keeping its freshness, form, function and composition throughout the transit. The most important aspect essentially followed by the marketers during the designing of packages is that the transfer of product must be maximally efficient in terms of time and cost.

Packaging has its own brand value and it is maintained by the industrialists. As we know, coke is a worldwide recognized brand; industrialist will not prefer to make a huge change in their brand. Minor changes can be made without modifying the original look so that it could be recognizable with its brand success. Therefore, one can easily say that packaging has created brand recognition.

2.1.2 Safety Maintenance in Product Packaging

Depending on the type of product, package designing firstly ensures the protection of products from external factors like vibration, compression, electrostatic discharge, mechanical shock, temperature, etc. In case of food items, packaging protects and preserves food items purchased by consumers. It retains product freshness and prevents risk of cross-contamination with other food items, pesticides and harmful pathogens. During processing and transportation, foods can be exposed to chemical, biological and physical risks. Hence, proper packaging can only save the food and drinking items from damage by blocking the exposure of hazardous chemicals, sunlight, gases and moistures. Permeation is a critical factor in package designing. Some packages contain desiccants or oxygen absorbency to extend shelf life. Modified atmospheres or controlled atmospheres are also maintained in some food packages. Keeping the contents clean, fresh, sterile and safe for the intended shelf life is a primary function. Packaging materials made of glass and metal shield foods from pathogens and chemicals.

2.1.3 Commercialization of Product Through Packaging

The second purpose of packaging is related to the commercialization of product and its brand visibility. Being a marketer everyone has the desire to be on the top as compared to their other competitors. Everyone provides the best product in their category and wants to make best selling product. In order to achieve the dream, creative food packaging with information transmission is a necessary one.

The last purpose of packaging is related to its security. On shelling product without packaging, there is a high probability that the retailer does not give the right amount to the customer and saves some part for himself. Packaging reduces the security risk during shipment. For better security, packages are made up with improved temper resistant material and also bearing some features to indicate tampering. Packages can be engineered to reduce the risks of package pilferage.

The choice of color in package designing is also play an important role in commercialization of products. Our brain has different thoughts regarding different colors. For example, products with white cover convey safety, purity and simplicity whereas; black color keeps the secrecy, and the complexity in thoughts. In the same way, a light sky blue reflects the playful mood, while dark navy color is considered as much professional. If you think of baby, then the things should be colorful. It is important to study the target demographic before deciding on a color scheme for your product packaging.

There are several reasons for doing packaging such as safety, brand visibility, theft prevention, etc. Packages can have features that add convenience in distribution, handling, stacking, display, sale, opening, reclosing, use, dispensing, reuse, recycling and ease of disposal. The packaging technology we have today has evolved over the time to better perform the function under the specified aspects. With the development of new marketers and ever-increasing market race, advertisement of the product through attractive and unique packages has opened up a new era in packaging technology. As the paper worker revealed that one-third of consumer has taken up their decision on packaging to purchase their product, marketers are devoted to make the product packages distinguishable and unique in look from other available products. For example, Captain Morgans has recently created a new product, “Cannon blast” in a container shaped like a cannon ball which has grabbed a huge attention due to relevant designing of product package with the name of the product. It is also eye catching and highly distinct from what many of its competitors offer.

2.2 Psychological Aspect of Product Packaging

In packaging technology, manipulation of consumer behavior is one of the main criteria for marketing of the products. It relates with the thought and action process of the consumer, i.e., ultimate end users. The whole thinking process of consumer is related to several factors, such as money, time, energy to select, use and disposal of product goods, services and anything else that satisfies the customer’s personal desire. Therefore, marketers should have knowledge of consumer’s desire, so that a proper product designing and development, marketing communication, pricing and placement in distribution channels could be established. Although the physiologist, Ivan Pavlov had demonstrated his theory in 1870s by the name of “theory of conditioning.” But with the progress of time, Pavlov theory has entered into the market place to analyze the consumer’s buying behaviors (Pachauri 2001). According to this theory, consumer is represented as subject, whereas product package is represented as stimuli. In the store, packaging acts as the gate way of product. Therefore, product packages are heavily cultured to influence the consumer’s buying behavior or subject’s response. This interrelated phenomenon is represented in Fig. 2.1. The first way of purchase along the decision-making pathway is to recognize the need by consumer. In second stage, they actively verified the product look and product information available across various channels and comparing their needs with product information. In the final stage, they decide to purchase the product that satisfies their needs. According to classical conditioning theory, product packaging directly influences a consumer’s perception of the product. Consumer’s perception is directly related to their assessment that what they receive (quality) versus what they give (price). Consumer has a high tendency to compare directly the price with quality. A normal expectation that comes into mind before buying a high-price product that it should offer a high quality. Throughout the decision-making process, they are searching for the cues that satisfy their own expectations. Consumers are generally interested to spend their time and involving themselves into the whole process of ensuring the best choice under the given circumstances. Spending time and involvement in product purchasing are the

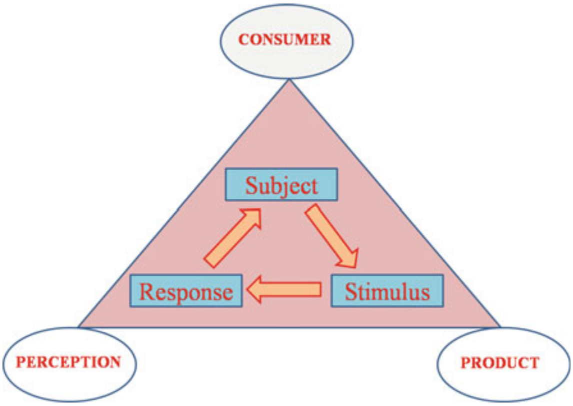


Fig. 2.1 Ian Pavlov's stimulus response theory explains the consumer buying behavior

different emotion. For product purchasing, spending time is necessary, whereas involvement is an optional one. The degree of involvement is related to consumer's psychological, personal and social context. Before making any decision to buy the product, a consumer has gone through several mental stages and these are attention, comprehension, attitude and intent. A simplified modeling of consumer's path of purchases is schematized in Fig. 2.2a, b. Social media such as reference groups, family, colleagues, friends, online review forums have a great impact on the attitude and perception of consumer's buying behavior. Each of these inputs acts as signal to affect the buying decision. Among all input signals, only certain signals have strong impact on the consumer's attitude that are either appeal emotionally or strengthen their beliefs. Various aspects that affect the consumer's perceptions during the progress through different stages of decision-making pathway can be explored through "Tarben Hansens conceptual frame-work" and shown in Fig. 2.3.

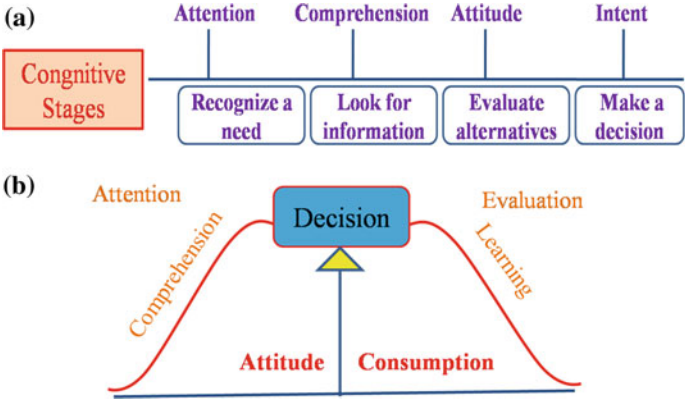


Fig. 2.2 **a** Different cognitive stages of decision-making pathway of consumers; **b** A simplified modeling of consumer's path to purchase

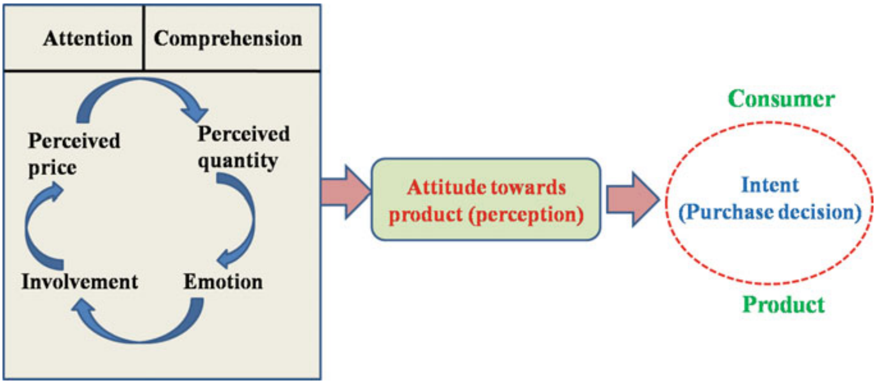


Fig. 2.3 The conceptual framework is adapted from perspectives on consumer decision making: An integrated approach

Sometimes, consumers are not gone through the well-known framework of mental stages and instantly take the decision, known as impulsive decisions. As in case of impulsive buying, consumers appear to skip most stages of decision-making pathway, cognitively they are responding to visceral cues from product packaging. This type of purchasing behavior is observed for 70% purchases of supermarkets. Hence, no doubt in the display of product and product information through packages is of great importance in product marketing.

2.3 Revolution in Packaging

As we discussed earlier, the main role of packaging is to protect or safety storage of products. Depending on the type of product, packaging has been introduced in several ways. Product information is related with the content, storage condition and nutrition value of the product. For food packaging, i.e., packaging related with food and drinking items, packaging continues to protect the items once they are in the home and can extend the period when they are safe to eat and of their best. For the packaging of vegetable items, freshness of the items should be guaranteed. Therefore, green vegetables such as root vegetables and cucumbers are restored in the packages that do not allow the loss of water. This helps to keep them fresh for a longer period of time. Recently, as packaging material, plastic products have won the primary interest and the use of plastics for food packaging is increasing day by day. This fact is attributed by the low cost of production. With the progress of time, a huge research effort has been dedicated to the formulation of new plastic materials with improved thermal, mechanical and fire retardant properties. The oxygen barrier performance is another important property that influences the characteristics of packaging materials. When we make our first choice "plastic," unknowingly we bring some problems to our society. No doubt, the petroleum-based plastic materials are light in weight and therefore, easy to handle. They can be made of various colors and shapes. But these are non-biodegradable in nature and lead to the unwanted pollution to our nearby surroundings. That is why, we are moving toward the age of “green revolution” by replacing commercial polymers with biopolymers.

2.4 Environmental Aspect of Product Packaging

To avoid the environmental pollution, the use of different biodegradable synthetic polymers, particularly aliphatic polyesters, such as poly (ethylene succinate) (PES) (Oishi et al. 2006), poly (L-lactide) (PLA) (Wee et al. 2006), poly (p-dioxanone) (PPDO) (Sabino et al. 2000), poly (butylenesuccinate) (PBS) (Carroccio et al. 2004), poly (€-caprolactone) (PCL) (Kai et al. 2006) are used with nanoparticles to fabricate bionanocomposites with superior properties. But the source of synthetic polymer is limited. Polymers obtained from the natural resources are of great interest in packaging industry due to their low cost, renewability, ease of surface modification and high compatibility with inorganic fillers. Starch, chitin, chitosan, cellulose, lignin and proteins are the name of few widely used biopolymers. But they have some drawbacks like high hydrophilicity, poor processability and low-mechanical strength. The integrating combination of biopolymers and nano fillers has recently grabbed the light as nano fillers and its efficiency to overcome these drawbacks. Manufacturing of starch nanocomposites has become of growing interest as a promising option toward enhancing the mechanical and barrier property.

2.5 Role of Starch in Packaging Application

Among different biopolymers, starch is a highly abundant polysaccharides and biodegradable in nature. It is composed of two structural units and these are amylose (linear) and amylopectin (branched) (Fig. 2.4). Each unit consists with the repetition

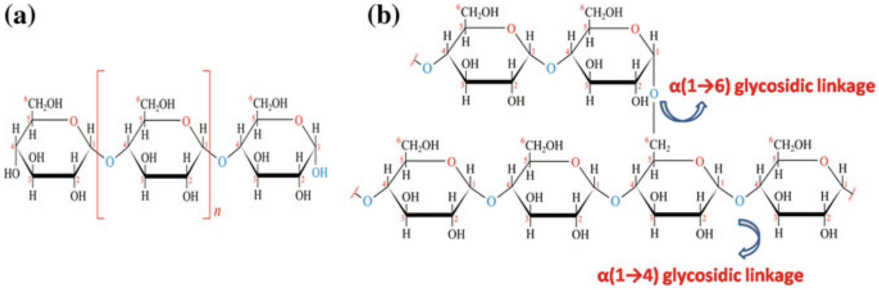


Fig. 2.4 **a** Amylose and **b** amylopectin: Two structural units of starch

of 1,4-α-D-glucopyranosyl units. Starch is stored as granules in plants for future food source. Starch has lot of uses such as thickener, water binder, emulsion stabilizer, gelling agent, coating sizing in paper, textile, adhesives, adsorbents, encapsulates and so many. Starch is a suitable option to substitute petroleum-based plastics for the fabrication of short-term packaging materials. The high sensitivity of starch toward moisture has limited their practical application. To introduce biodegradability into synthetic polymers, starch is blended with various polymers like polyethylene (PE), low-density polyethylene (LDPE) (Psomiadou et al. 1997), polystyrene (PS), poly (ethylene-vinyl alcohol) (EVA) and poly (ethylene-co-acrylic acid) (EAA). But the attempt fails to show the biodegradable response.

Therefore, starch is allowed to blend with various biodegradable synthetic polymers like poly (lactic acids) (PLA) (Zhang and Sun 2004), poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) (Willett and Shogren 2002; Rosa et al. 2004b), polycaprolactone (PCL) (Rosa et al. 2004a), poly (glycolic acids) (PGA) (Kong et al. 2011) and PHB (Rosa et al. 2004b). Starch has also been blended with PCL, PHB (Godbole et al. 2003) and PHBV (Avella and Errico 2000) showing a dramatic change in their properties. We have studied the oxygen permeability and flame retardant of Polymethylmethacrylate/starch composite in our earlier report (Kisku and Swain 2012).

2.6 Polymer Nanocomposites: An Alternative to Non-Biodegradable Plastics

Due to high surface area to volume ratio, unique physical and chemical properties, nanoparticles are widely used with polymers to fabricate polymer nanocomposites with improved properties. High surface area is a critical factor for the performance of catalysis and electrochemical performance in fuel cells and batteries. Nanocomposites exhibit excellent flexibility, low density and easy processability in connection with the high strength, rigidity and heat resistance. The enhancement was observed on mechanical properties, thermal stability, gas barrier properties, electric properties, even on biodegradation rates. The enhancement of different physical properties in polymer nanocomposites is highly dependent on the nature of nano filler and the nature of interfacial adhesion.

2.7 Nanomaterials as Promising Filler in Polymer Based Bionanocomposites

2.7.1 Nanoclay

There are many inorganic nano fillers which are widely used in different industrial and biomedical application, but the use of nanoclays with polymers is huge in literature to enhance the mechanical and gas barrier performance of the material. Nanoclays are layered silicate materials with thickness ~ 1 nm and the lateral dimension ranging from 30 nm to several microns. The basic building blocks of nanoclays are octahedral and tetrahedral sheets. In tetrahedral sheet, the silicon–oxygen tetrahedra are linked to neighboring tetrahedra by sharing three corners while the fourth corner of each tetrahedron forms a part to adjacent octahedral sheet (Fig. 2.5a). The octahedral sheet is usually composed of aluminum or magnesium in six fold coordination with oxygen from the tetrahedral sheet and with hydroxyl. Interlayer possesses net negative charge which is due to the ionic substitutions in the sheets of clay minerals. The layer charge is neutralized by cations which occupy the interlamellar. These interlamellae cations can be easily replaced by other cations or molecules as per required surface chemistry and hence called exchangeable cations. Na^+, K^+, Mg^{2+} and Ca^{2+} are among common exchangeable cations present in the interlayer which are exchanged with other required cations. The clay has immense use in architecture, in industry and in agriculture. It is used for the preparation of bricks and for the manufacturing of tile for wall and floor coverings. Due to high aspect ratio and layered structure of nanoclay, they are chosen as a good candidate for reinforcement in polymer nanocomposites (Zhang et al. 2017). Depending on the synthetic route of polymer/clay nanocomposites, they have shown different structural arrangement between clay platelets and polymeric chains. These structures are named intercalated and exfoliated structures (Fig. 2.5b). Exfoliation refers the high degree of dispersion of clay platelets within polymeric phase and shows better mechanical performances as compared to the conventional and intercalated structures.

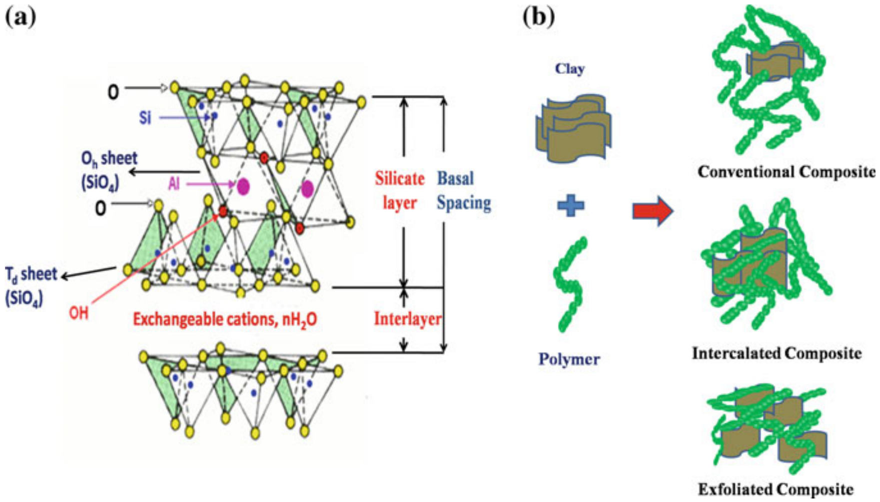


Fig. 2.5 **a** Structure of clay and **b** Structural arrangement of clay within polymer nanocomposites

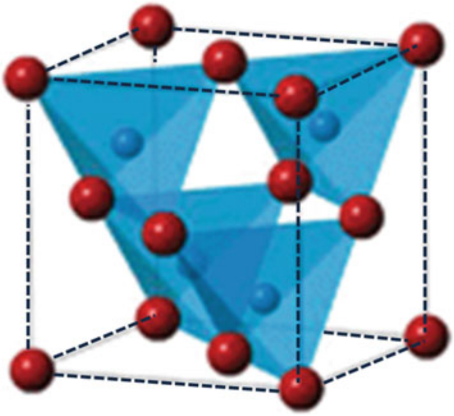


Fig. 2.6 Structure of silicon carbide

2.7.2 Nano Silicon Carbide

Nano silicon carbide is an important non-oxide ceramic material (Fig. 2.6) having diversified industrial applications due to its exclusive properties such as, high melting point, oxidation resistance, high erosion resistance, high hardness and strength, chemical and thermal stability, etc. (Benea et al. 2001). Silicon carbide can occur in more than 250 crystalline forms called polytypes and are widely used in making of polymer nanocomposites.

2.7.3 Nano Calcium Carbonate

Calcium carbonate is one of the most abundant biomaterials and one that can be grown easily under laboratory condition. The thermodynamically stable form of $CaCO_3$ under normal conditions is hexagonal β-$CaCO_3$ (calcite) (Fig. 2.7). Other forms can be prepared, the denser, (2.83 g/cc) orthorhombic λ-$CaCO_3$ (aragonite) and μ-$CaCO_3$, occurring as the mineral vaterite. It is one of the most commonly used inorganic filler for thermoplastics, such as poly (vinyl chloride) (Xie et al. 2004) and polypropylene (PP) (Lin et al. 2008). A lot of efforts have been devoted to surface-modified $CaCO_3$ particles to increase the polymer–filler interactions and reported enhancement of mechanical properties. The introduction of above-cited nanoparticles, i.e., nanoclay, nano SiC and nano $CaCO_3$ into starch matrix are found to improve the fire retardant, oxygen barrier, thermal and mechanical properties.

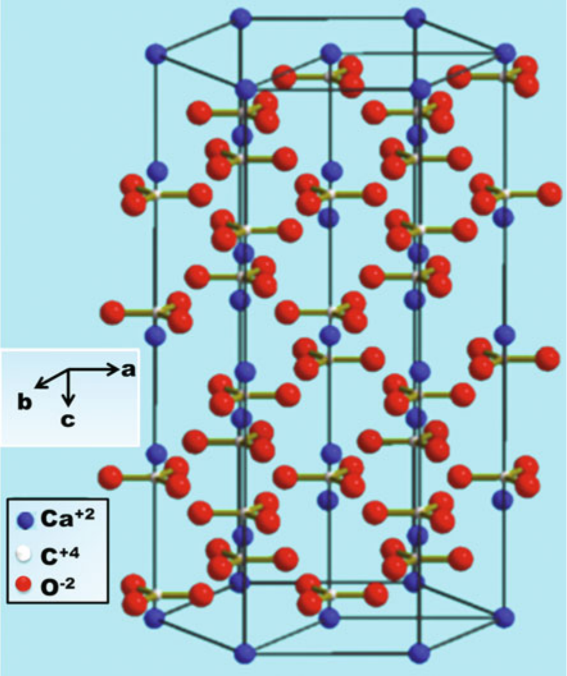


Fig. 2.7 Crystal structure of calcite (most stable polymorph of calcium carbonate)

2.8 Responsible Properties of Bionanocomposites for Packaging Applications

2.8.1 *Fire Retardant Properties*

Fire retardant properties of packaging materials are simply related to their ability of protecting the packed items from fire. Some materials like benzene, cyclohexane, acetone, alcohols are highly flammable. On the other hand, diesel, fuels, motor oils, kerosene are also combustible liquids. Therefore, these types of materials should be packed with the fire retardant materials. Limiting oxygen index (LOI) is a parameter that is used to compare the fire retardant properties of the materials. Higher the value of limiting oxygen index, higher will be the amount of oxygen requires burning the sample. In order to develop the fire retardant property in biopolymer starch, different wt% of nanoclay is incorporated within starch matrix through simple solution casting technique (Swain et al. 2014).The exfoliation of clay platelets within starch is achieved through the ultrasonication technique. The parametric estimation of LOI of nanoclay reinforced starch bionanocomposites of different composition and virgin starch is calculated and compared to understand the fire retardant nature of the materials. From Fig. 2.8, it is observed that with increasing the clay content in starch matrix, the value of LOI % increases. At 10 wt% of loading, the value of LOI is

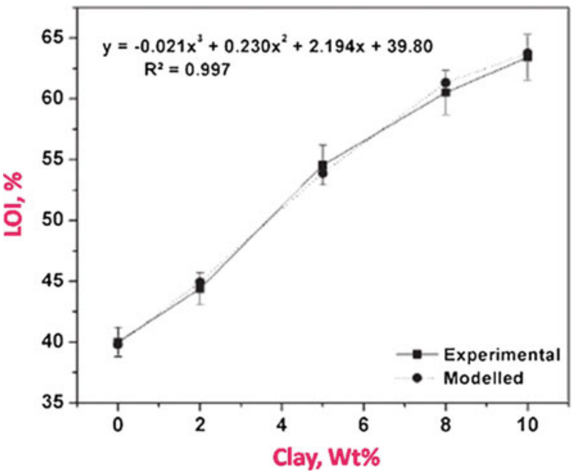


Fig. 2.8 Limiting oxygen index of starch/clay bionanocomposites as a function of wt% of clay (Swain et al. 2014)

increased 58.5% more as compared to the virgin starch. At high loading of clay and the effect of ultrasound leads to the effective dispersion of the layered clays within starch, so that a strong barrier is formed due to the tacoid orientation of the clay platelets. Uniformly, dispersed clay platelets also insulate the underlying polymer from heat source.

2.8.2 Oxygen Barrier Properties

As it is observed that due to the incorporation of clay platelets within starch, the fire retardant property is developed, it must be correlated with the oxygen barrier performance of the materials (Swain et al. 2014). The oxygen barrier property is measured in terms of the oxygen permeability value. Lower the value of oxygen permeability, higher will be the barrier performance. Figure 2.9 represents the oxygen permeability plots of starch bionanocomposites with different wt% of nanoclay loading. With increasing the clay content, the oxygen permeability is found to fall, and at 10 wt% of clay loading, the oxygen permeability is reduced to 69% more than virgin starch. Due to the porous structure and highly hydrophilic nature of starch, starch itself shows a very high value of oxygen permeability. But when organically modified nanoclays are inserted within starch, porous structure is eliminated and a torturous path is generated. Generally, the torturous path is created for the high degree of exfoliation of clay platelets in starch. The torturous path in highly exfoliated nanocomposite forces the gas to permeate through a longer path than conventional composites. To enhance the oxygen barrier performance, the increase in path length is a critical factor that depends upon the high aspect ratio of clay platelets and volume fraction of the filler in bionanocomposites. To ensure the

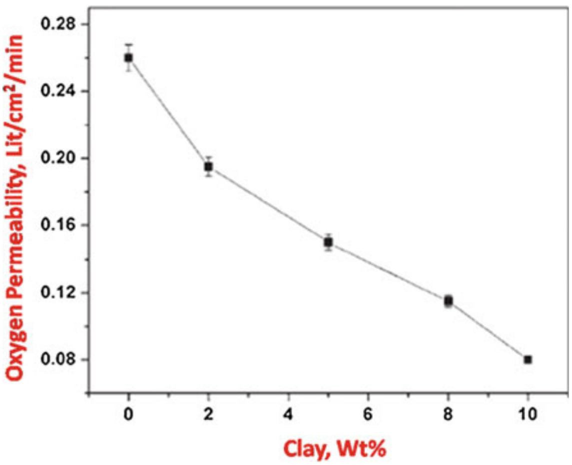


Fig. 2.9 Oxygen permeability of starch and Starch/clay bionanocomposites as a function of wt% of clay (Swain et al. 2014)

accuracy of the experimental data, a model regression is drawn and it is observed that experimental values are well fitted with third-order polynomial equation ($R^2 = 0.997$).

2.8.3 Thermal Properties

Thermal stability of the packaging material is another important issue that should be taken into account during the development of packages for the better safety of the products. If the packages are not enough thermally stable, then they may degrade and make contamination of the product. Thermally stable nano SiC reinforced starch bionanocomposites are synthesized through simple solution casting method in aqueous medium (Dash and Swain 2013). Nano SiC is introduced in the starch solution as aqueous suspension and allowed to disperse through simple stirring and sonication. Nano SiC is a non-oxide ceramic material and is highly thermally stable. Nano SiC remains in its initial form in the temperature range of 30–800 °C. Due to incorporation of nano SiC in starch, the thermal stability of starch/SiC bionanocomposites is enhanced (Fig. 2.10). With increasing the nano SiC, thermal stability of starch/SiC bionanocomposites increases and at 10 wt% of nano SiC, the char residue is increased to 40%. From the TGA profile, it has been observed that all starch/SiC bionanocomposites including virgin starch show three-step decomposition patterns. In first step, at about 100 °C all materials are gone through the loss of surface water. In second step, partial thermal decomposition of the bionanocomposite is occurred, whereas, in third step, complete decomposition and oxidation are occurred. The final degradation of starch is occurred at 330 °C, whereas, in bionanocomposites the final degradation is occurred at higher temperature as compared to virgin starch.

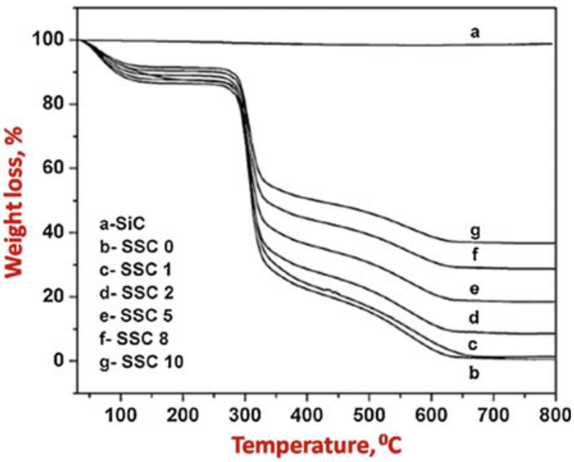


Fig. 2.10 Thermo gravimetric analysis curves of starch, SiC and Starch/SiC bionanocomposites at different weight % of Silicon Carbide (Dash and Swain 2013)

2.8.4 *Mechanical Properties*

Starch films are brittle in nature and, therefore, cannot be processed as film. But the incorporation of poly vinyl alcohol (PVA) in starch is a well-known way to obtain the films (Majdzadeh-Ardakani and Nazari 2010). As PVA is a highly hydrophilic in nature with numerous number of hydroxyl (–OH) groups, it has wide applicability as binder and adhesives. But the combination of starch and PVA is not enough to obtain the thin films with high-mechanical strength. Due to enhance the mechanical strength of starch/PVA thin film, nano calcium carbonate ($CaCO_3$) particles are incorporated through simple solution casting technique in aqueous medium (Kisku et al. 2014). The plot of tensile strength of starch/PVA/$CaCO_3$ nanocomposite thin films with various wt% nano $CaCO_3$ is shown in Fig. 2.11. The tensile strength of

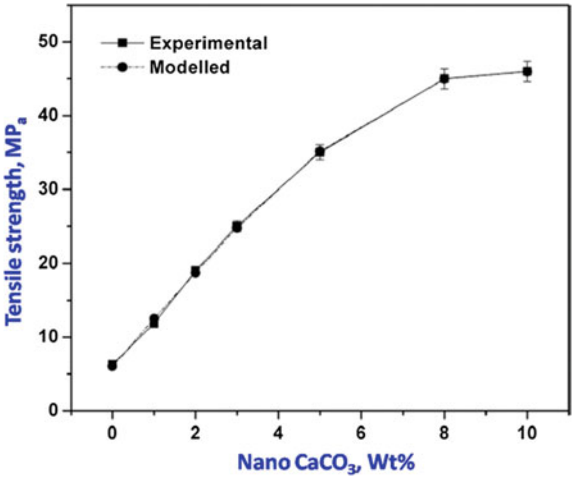


Fig. 2.11 Tensile properties of starch/Polyvinyl alcohol/Calcium Carbonate nanobiocomposite films and its modeled graph (Kisku et al. 2014)

starch/PVA thin film is 6 MPa. It is due to the strong intermolecular hydrogen bonding between starch and PVA. With incorporation of nano $CaCO_3$, the tensile strength of starch/PVA/$CaCO_3$ is increased and at 10 wt% of nano $CaCO_3$, the tensile strength is increased to above 40 MPa. It is due to the strong interfacial adhesion between uniformly distributed nano $CaCO_3$ and starch/PVA co-polymeric matrix. Similar explanations are also reported of the earlier study during the enhancement of tensile properties of polymers due to incorporation of nano $CaCO_3$.

2.9 Concluding Remarks

Packaging is a well-groomed technology dealing with the safety storage and handling of daily needs. Packaging technology is mainly divided into three sectors and these are process of designing, evaluation and production of packages. Depending on the type of product, packaging has been introduced in several ways. Different types of packaging are included bulk chemical packaging, medical device packaging, pharmaceutical packaging and retail food packaging. There are several reasons for doing packaging and these are safety, brand visibility, theft prevention, etc. Some packages contain oxygen absorbency to extend the self-life of packed items. Packages should have the features that can add convenience in distribution, handling, stacking, display, sale, opening, reclosing, use, dispensing, reuse, recycling and ease of disposal. With the ever-increasing market race, advertisement of the products through attractive and unique packages has opened a new age of packaging technology. Package labeling includes product specification, storing condition and the method of use. Labeling is highly used by the marketers to encourage potential buyers to purchase the product. In packaging technology, manipulation of consumer's behavior is one of the main issues that should be taken into account during the designing of product packages. The well-known "theory of conditioning" of Ivan Pavlov is widely used into the market place to control the consumer's choice. Although we cannot avoid the demand of plastics in food packaging, simultaneously we cannot deny the problem of environmental pollution. Therefore, researchers are running behind to fabricate the bionanocomposite-based packaging materials. Some essential features of packaging material like fire retardant, oxygen barrier, thermal and mechanical properties are introduced in highly biodegradable polysaccharide starch through simple solution casting techniques by the dispersion of nanoclay, nano SiC and nano $CaCO_3$.

References

Avella M, Errico ME (2000) Preparation of PHBV/starch blends by reactive blending and their characterization. J Appl Polym Sci 77:232–236

Benea L, Bonora PL, Borello A, Martelli S (2001) Wear corrosion properties of nano-structured SiC–nickel composite coatings obtained by electroplating. Wear 249:995–1003

Carroccio S, Rizzarelli P, Puglisi C, Montaudo G (2004) MALDI investigation of photooxidation in aliphatic polyesters: poly (butylene succinate). Macromolecules 37:6576–6586

Coles R, McDowell D, Kirwan MJ (eds) (2003) Food packaging technology. CRC Press. Taylor and Francis Group, London

Dash S, Swain SK (2013) Synthesis of thermal and chemical resistant oxygen barrier starch with reinforcement of nano silicon carbide. Carbohydr Polym 97:758–763

Godbole S, Gote S, Latkar M, Chakrabarti T (2003) Preparation and characterization of biodegradable poly-3-hydroxybutyrate–starch blend films. Biores Technol 86:33–37

Kai W, Hua L, Zhao L, Inoue Y (2006) Synthesis of novel star shaped poly (ε-caprolactone) utilizing fullerene as the molecular core. Macromol Rapid Commun 27:1702–1706

Kisku SK, Swain SK (2012) Study of oxygen permeability and flame retardancy properties of biodegradable polymethylmethacrylate/starch composites. Polym Compos 33:79–84

Kisku SK, Sarkar N, Dash S, Swain SK (2014) Preparation of starch/PVA/$CaCO_3$ nanobiocomposite films: study of fire retardant, thermal resistant, gas barrier and biodegradable properties. Polym Plast Technol Eng 53:1664–1670

Kong W, Wang W, Gao J, Liu T, Liu Y (2011) Oxidized starch films reinforced with natural halloysite. J Mater Res 26:2938–2944

Lin Y, Chen H, Chan CM, Wu J (2008) High impact toughness polypropylene/$CaCO_3$ nanocomposites and the toughening mechanism. Macromolecules 41:9204–9213

Majdzadeh-Ardakani K, Nazari B (2010) Improving the mechanical properties of thermoplastic starch/poly (vinyl alcohol)/clay nanocomposites. Compos Sci Technol 70:1557–1563

Oishi A, Zhang M, Nakayama K, Masuda T, Taguchi Y (2006) Synthesis of poly (butylenes succinate) and poly (ethylene succinate) including diglycollate moiety. Polym J 38:710–715

Pachauri M (2001) Consumer behaviour: a literature review. Mark Rev 2:319–355

Psomiadou E, Arvanitoyannis I, Biliaderis CG, Ogawa H, Kawasaki N (1997) Biodegradable films made from low density polyethylene (LDPE), wheat starch and soluble starch for food packaging applications. Part 2. Carbohydr Polym 33:227–242

Rosa DS, Guedes CGF, Pedroso AG, Calil MR (2004a) The influence of starch gelatinization on the rheological, thermal, and morphological properties of poly (ε-caprolactone) with corn starch blends. Mater Sci Eng C 24:663–670

Rosa DS, Lotto NT, Lopes DR, Guedes CGF (2004b) The use of roughness for evaluating the biodegradation of poly-β-(hydroxybutyrate) and poly-β-(hydroxybutyrate-co-β-valerate). Polym Test 23:3–8

Sabino MA, Feijoo JL, Muller AJ (2000) Crystallisation and morphology of poly (p-dioxanone). Macromol Chem Phys 201:2687–2698

Swain SK, Patra SK, Kisku SK (2014) Study of thermal, oxygen-barrier, fire-retardant and biodegradable properties of starch bionanocomposites. Polym Compos 35:1238–1243

Wee YJ, Kim JN, Ryu HW (2006) Biotechnological production of lactic acid and its recent applications. Food Technol Biotechnol 44:163–172

Willett JL, Shogren RL (2002) Processing and properties of extruded starch/polymer foams. Polymer 43:5935–5947

Xie XL, Liu QX, Li RKY, Zhou XP, Zhang QX, Yu ZZ, Mai YW (2004) Rheological and mechanical properties of PVC/$CaCO_3$ nanocomposites prepared by in situ polymerization. Polymer 45:6665–6673

Zhang JF, Sun X (2004) Mechanical properties of poly (lactic acid)/starch composites compatibilized by maleic anhydride. Biomacromolecules 5:1446–1451

Zhang G, Wu T, Lin W, Tan Y, Chen R, Huang Z, Qu J (2017) Preparation of polymer/clay nanocomposites via melt intercalation under continuous elongation flow. Compos Sci Technol 145:157–164

Chapter 3
Cellulose Reinforced Biodegradable Polymer Composite Film for Packaging Applications

H.P.S. Abdul Khalil, Ying Ying Tye, Cheu Peng Leh, C.K. Saurabh, F. Ariffin, H. Mohammad Fizree, A. Mohamed and A.B. Suriani

Abstract This chapter provides a broad overview of bionanocomposite film prepared from various biodegradable polymers reinforced with nanocellulose. In nature, biodegradable polymer exhibits relatively weaker properties than the synthetic polymers. Incorporation of cellulose into the biopolymer matrix has improved the mechanical, thermal, and barrier properties of the resulting biopolymer film significantly. This achievement has encouraged their application as packaging material. Since they have a huge potential in the future, further investigation of this composite material is crucial.

Keywords Cellulose · Biodegradable polymer · Composite film · Reinforcement · Packaging

3.1 Introduction

"Packaging" can be described as a material that uses to protect the packed products against any physical, chemical, or biological hazards. Plastic is among the materials (i.e., wood, paper, metals, and glass) that commonly used in packaging due to its softness, lightness, and transparency. Petrochemical-based plastics such as polyethylene terephthalate (PET), polyvinylchloride (PVC), polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyamide (PA) are the common materials for manufacturing packaging films. These materials are chosen probably due to their abundant availability, low cost, excellent mechanical, and barrier properties. However, the increase of using these synthetic packaging films has led

---

H.P.S. Abdul Khalil (✉) · Y.Y. Tye · C.P. Leh · C.K. Saurabh · F. Ariffin
H. Mohammad Fizree
School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia
e-mail: akhalilhps@gmail.com

A. Mohamed · A.B. Suriani
Faculty of Science and Mathematics, Nanotechnology Research Centre,
Universiti Pendidikan Sultan Idris, 35900, Tanjung Malim, Perak, Malaysia

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_3

to serious municipal waste disposal problem, which attributed by the materials' non-degradable characteristic (Siracusa et al. 2008). Therefore, the biodegradable polymer becomes more attention as green materials for packaging applications.

Biodegradable polymers can be derived from renewable resources (biomass) and microorganisms or synthesized from bio-derived monomers (Vieira et al. 2011). Polymers from biomass such as polysaccharides, proteins, and lipids are the most basic (common) materials utilized to form edible and/or biodegradable films. Polysaccharides have good film forming properties, but their moisture barriers are weak, while the protein-based films usually have better mechanical and barrier properties than that of the polysaccharide-based films. Although lipid films exhibit good moisture barrier properties, they can cause textural and organoleptic problems (Vieira et al. 2011). Since these biodegradable polymer films possess certain unfavorable physicochemical properties, which may restrict their applicability and feasibility on edible or non-edible packaging applications, development of composite film is an alternative approach to solving this issue.

Cellulose is one of the polysaccharides that largely available in the world. In comparison with other biopolymers, cellulose is neither meltable nor soluble in water or any common organic solvents. Thus, chemical modification of cellulose surface is generally required to form soluble cellulose (i.e., cellulose derivatives), which is suitably used as film-forming materials for packaging. Since cellulose exhibits excellent mechanical performance, it has gained more significant interest and attention as reinforcement in the biodegradable polymer film. It is well known that incorporation of cellulose into a biodegradable polymer film can be an effective way to overcome the poor properties of the biodegradable polymer and meanwhile, obtain desired function and properties (Hu et al. 2016; Phan The et al. 2009).

This chapter highlights the important role of cellulose used as reinforcement material in packaging applications. Literature review on cellulose reinforced biopolymer-based biodegradable packaging film is the main focus in this chapter. Hence, the first section of this chapter briefly summarizes the chronological events of cellulose fiber as reinforcement in composite materials, whereas the second section describes the characteristics and properties of different (micro-/nanoscale) cellulose as reinforcing materials. Thereafter, the following section comprehensively discusses the preparation and properties of the composite film with cellulose reinforced plastics by using the biodegradable polymer as a matrix. The criteria of this composite film as packaged material are also highlighted in the last section of this chapter.

3.2 Chronological Events of Cellulose Fiber as Reinforcement in Composite Materials

Since cellulosic fiber consists of specific benefits over the synthetic fibers (i.e., carbon and glass fibers) such as renewability, abundant availability, inexpensive and acceptable specific strength, as well as non-hazardous, cellulosic natural fiber as

Table 3.1 Chronological events of the development of cellulose fiber as reinforcement in composite materials

Year	Progress and development	References
1838	First introduction of cellulose	Bledzki and Gassan (1999)
1908	Cellulose from paper or cotton reinforced phenol or melamine formaldehyde matrix as sheet for electronic purpose	Bledzki and Gassan (1999)
1978	Jute fiber reinforced polyester as construction material for building	Bledzki and Gassan (1999)
1987	Cellulosic pulp fiber reinforced thermoplastic composite	Boldizar et al. (1987)
1995	First introduction of “all-organic” nanocomposite: cellulose whickers from sea animal reinforced polymer nanocomposite film	Favier et al. (1995)
1996	Cellulose whickers from wheat straw reinforced thermoplastic nanocomposite film	Helbert et al. (1996)
1999	Green composite: cellulosic pineapple leaf fiber reinforced Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) biodegradable composite film	Luo and Netravali (1999)
2000	Cellulose microfibrils from potato tuber cells reinforced starch film for packaging	Dufresne et al. (2000)
2001	Cellulose fiber reinforced starch composite film for thermoforming packaging	Moroa (2001)
2004–2005	First introduction of “all-cellulose” composite: native cellulose fiber reinforced cellulose matrix	Nishino et al. (2004), Gindl and Keckes (2005)
2005	Microcrystalline cellulose (MCC) reinforced Polylactic acid (PLA) biodegradable composite film for packaging	Mathew et al. (2005)
2007	MCC reinforced hydroxypropyl methylcellulose (HPMC, a cellulose derivative) film for food packaging	Dogan and McHugh (2007)
2008	Carboxymethyl cellulose (CMC) reinforced pea starch composite film for food and biodegradable packaging	Ma et al. (2008)
2009	Cellulose whiskers reinforced chitosan composite film for food packaging	Li et al. (2009)
2009	Cellulose nanofiber reinforced mango puree composite film for food packaging	Azeredo et al. (2009)
2009	Microfibrillated cellulose reinforced PLA composite film for packaging applications	Suryanegara et al. (2009)
2010	Cellulose nanofiber reinforced PLA composite film for packaging applications	Jonoobi et al. (2010)
2010	Bamboo cellulosic crystal reinforced starch composite film for packaging applications	Liu et al. (2010)
2010	Bagasse cellulose whickers reinforced natural rubber composite for packaging films and tapes	Bras et al. (2010)

(continued)

Table 3.1 (continued)

Year	Progress and development	References
2011	Different cellulose nanoparticles reinforced HPMC composite film for packaging	Bilbao-Sainz et al. (2011)
2011	Nanocrystalline cellulose reinforced xylan composite film for packaging applications	Saxena et al. (2011)
2012	Nanocrystalline cellulose reinforced chitosan composite film for food packaging	Khan et al. (2012)
2013	Cellulose nanowhiskers reinforced cellulose acetate composite film for packaging	Yang et al. (2013)
2014	Cellulose reinforced alginate composite film for packaging	Sirviö et al. (2014)
2015	Recycle cellulose reinforced starch–gelatin composite film for packaging	Rodríguez-Castellanos et al. (2015)
2016	Bacterial cellulose nanowhiskers reinforced thermoplastic corn starch nanocomposite film for food packaging	Fabra et al. (2016a)
2016	MCC reinforced polypropylene composite for microwavable packaging	Ummartyotin and Pechyen (2016)

reinforcement for composite material and their utilization in various applications have been widely studied in the past few years (Jawaid and Khalil 2011). Table 3.1 illustrates the chronological events of the development of cellulose fiber as reinforcing materials including its modification and applications. As can be seen, cellulose as filler in the composite material is mainly focused on the field of packaging. Since the year 1999, researchers are started paying attention to renewable and sustainable packaging materials.

3.3 Cellulose: A Biodegradable Polymer Reinforcement

Cellulose can be obtained from wood or non-wood plant biomasses. It is a linear carbohydrate polymer chain that consists of units of glucose connected through (1,4)-β-D linkages (Tye et al. 2016). Moreover, it is among the constituents (i.e., hemicellulose and lignin) of lignocellulose biomass that largely available with a content approximately about 45%. In the plant cell wall, the crystalline fraction of the plant is contributed only by cellulose, whereas hemicellulose and lignin are amorphous. Since a lot of hydroxyl groups in the crystalline phase of cellulose form many hydrogen bonds, and these hydrogen bonds construct a huge network that directly contributes the compact and highly ordered crystal cellulose structure, cellulose is very stable and difficult to break apart. Therefore, with this crystalline part, cellulose has outstanding mechanical properties, which is interesting to be used as reinforcement in polymer composite (Zimmermann et al. 2010). Nevertheless, the mechanical properties of cellulose are strongly depended on the cellulose type (Brinchi et al. 2013). Cellulose fibers are assembled in a hierarchical and multi-level ordered structure, where microfibrils (basic fibrils) in the nano-sized scale formed by the cellulose chains are packed into larger units called macrofibrils. Therefore, different kinds of nanocellulose fillers can be extracted such as cellulose nano-structured materials (i.e., microcrystalline cellulose and microfibrillated cellulose) and cellulose nanofibers (i.e., nanocrystalline cellulose and nanofibrillated cellulose) (Osong et al. 2016).

3.3.1 Cellulose Nano-structured Materials

Within the microfibrils in the plant cell wall, cellulose exhibits both crystalline and amorphous regions. Since it is known that crystalline cellulose is much stronger and stiffer than the amorphous cellulose and cellulose itself, the production of microcrystalline cellulose (MCC) can be a better reinforcing agent than cellulose (Ashori and Nourbakhsh 2010). Microcrystalline cellulose (MCC) or known as cellulose microcrystal is a crystalline cellulose. It is generally produced from the acid hydrolysis of cellulosic pulp fiber to remove the amorphous region of cellulose (Ashori and Nourbakhsh 2010; Siqueira et al. 2010). The resulting particles are porous, insoluble in water, possess high cellulose content, high aspect ratio (>1000), and high crystallinity (Moon et al. 2011; Osong et al. 2016). In comparison with other synthetic polymers such as glass fiber, MCC is cheap, has low density, and is renewable as well as biodegradable. Moreover, the high crystallinity of MCC delivers a strong reinforcing ability due to the high modulus. The longitudinal modulus for MCC is about 150 GPa, which is capable of improving the mechanical properties of the resulting biocomposites. Therefore, MCC has been widely used as fillers in various polymers composite (Ashori and Nourbakhsh 2010; Rico et al. 2016).

Microfibrillated cellulose (MFC) is cellulose microfibrils that can be extracted by a mechanical disintegration process (consisting of refining and high-pressure homogenizing) with or without chemical/enzymatic pretreatment from cellulosic pulp fiber (Siró and Plackett 2010). Besides, there are also several kinds of mechanical treatment such as microfluidization, super-grinding, cryo-crushing, steam explosion, and high-intensity ultrasonication (HIUS), which can be used to reduce the particle size of fibers to micro- or nanoscale (Osong et al. 2016). The resulting particles are spaghetti-like in shape, long, flexible, and composed of more or less individualized cellulose microfibrils (width: 10–100 nm, length: 0.5–10 mm) and pure cellulose that contains both crystalline and amorphous regions (Moon et al. 2011; Siqueira et al. 2010). Moreover, MFC has a very good ability to form the web-like network and high elastic modulus ($\sim$150 GPa), which is attracted to be used as reinforcement materials in composite films (Siqueira et al. 2010).

3.3.2 Cellulose Nanofibers

Nanofibrillated cellulose (NFC) is cellulose nanofibrils or finer cellulose fibrils produced by high shearing forces of disintegration leading to a high degree of fibrillation from cellulosic pulp fiber. Similar to MFC, the resulting NFC particles consist of pure cellulose from both crystalline and amorphous regions and have the ability to create entangled networks (Kalia et al. 2014). However, NFC has a relatively high aspect ratio (width: 4–20 nm wide, length: 500–2000 nm) than MFC (Moon et al. 2011). The wide range of size distribution for NFC usually dependent on the energy input to disintegrate the cellulose fibers and on the pretreatment utilized to facilitate the disintegration process (Kalia et al. 2014). Besides, nanocrystalline cellulose or known as cellulose nanocrystal is stiff-rod ('rice-like') or whisker-shaped particles produced after acid hydrolysis of MCC or cellulose fiber (Siqueira et al. 2010). Similar to MCC, the resulting particles are crystalline cellulose with a high crystallinity of 54–88%. Nevertheless, NCC has a relatively higher aspect ratio than MCC (width: 3–5 nm, length: 50–500) (Moon et al. 2011).

3.4 Cellulose Reinforced Biodegradable Polymer Composite Film

The reason for using biodegradable polymers is to reduce the amount of synthetic polymer required for packaging applications, but not to completely replace the synthetic plastic. Nevertheless, the commercial use of biodegradable polymer films has been limited due to their poor mechanical and barrier properties when compared to synthetic polymers. The incorporation of reinforcing component to polymer has recently proposed to improve the poor properties of this biopolymer film. However, many reinforced materials especially the macroscopic reinforcing components present poor interfacial adhesion with the polymer matrix (Azeredo et al. 2009). Therefore, there has been a growing interest from industry to use nano-sized cellulose as reinforcement materials in packaging applications. Nanocellulose materials are usually having a high aspect ratio, which is capable of providing better reinforcing effects. Hence, a high strength, stiffness, and transparency film can be produced due to the uniform dispersion of nanoparticles in a polymer matrix (Besbes et al. 2011).

3.4.1 Types and Properties of Biodegradable Polymer

Unlike non-renewable petroleum-based biodegradable polymer, biodegradable polymers can be naturally derived from renewable resources. The renewable biodegradable polymer can be categorized into three groups depending on the

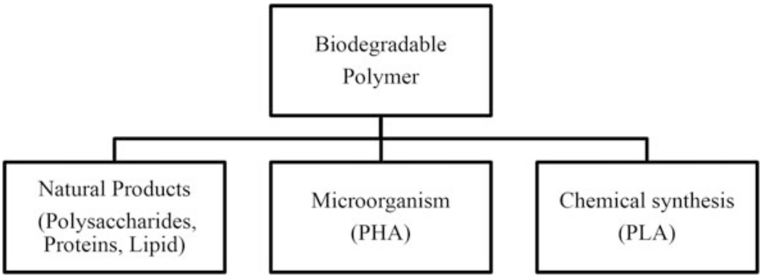


Fig. 3.1 Classification of renewable biodegradable polymers (Othman 2014)

origin of the biopolymers: (1) natural biopolymers extracted from natural products, (2) synthetic biopolymers from microbial production or fermentation, and (3) synthetic biopolymers conventionally and chemically synthesized from biomass (Fig. 3.1).

3.4.1.1 Polysaccharides

Polysaccharides, proteins, and lipid are the common biodegradable polymer that extracted from plants or animals. Among the biopolymers, polysaccharides such as starch, cellulose, seaweed, and chitosan are widely used as polymer film in packaging applications due to they are typically cheap and abundantly available.

Starch is derived from cereal grains and tubers like corn, wheat, potato, tapioca, and rice. Generally, it consists of two kinds of molecules such as amylose (about 20–30%) and amylopectin (about 70–80%), in which amylose was the primary molecule for filmmaking. The edible film with high amylose content is flexible, oxygen impermeable, oil resistant, heat sealable, and water soluble. Moreover, starch is extensively used as a replacement for plastic polymer due to both having similar characteristics, which are transparent, odorless, tasteless, colorless, non-toxic, biologically absorbable, semipermeable to CO_2, and resistant to the passage of O_2. In addition, edible starch-based films can hinder microbial growth by lowering the water activity within the package (Shit and Shah 2014). Although starch is edible, safe, and degradable, it has low mechanical properties. Therefore, previous studies have proposed that starch mechanical properties can be improved by incorporation with plasticizer and/or nanofillers (Jiménez et al. 2012; Othman 2014).

Cellulose and starch are two very similar polymers. Both of them are made from glucose and have the same glucose-based repeat units. The main difference between cellulose and starch is that cellulose contains beta glucose, while starch is made of alpha glucose. Because of this difference, both differ in their chemical and physical properties. In comparison with starch, cellulose from lignocellulosic biomass is a more sustainable material as it does not disturbs the food sources such as wheat, maize, and potatoes, which are mainly used to derive the starch. Unlike starch, only cellulose-derived polymers (cellulose derivatives) have the film-forming ability because native cellulose is water-insoluble compound. Hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC), carboxymethylcellulose (CMC), and methylcellulose (MC) are the common cellulose derivatives that used for polymer coatings or films. The cellulose derivatives' films exhibit moderate strength, flexibility, transparency, flavorless, colorless, tasteless, and moderate barriers to oxygen as well as resistant to oils and fats. Nevertheless, similar to starch, they possess poor mechanical and water vapor barrier properties. A way to improve weak properties would be the addition of filler to develop a composite film (Shit and Shah 2014).

Besides plant-derived polysaccharides, marine-derived polysaccharides such as alginate, carrageenan, and agar have a potential to form biopolymer film because of their unique colloidal properties, which commonly used as a thickening, stabilizing, and suspending agent in food industry. Alginate, carrageenan, and agar are seaweed derivatives. Agar and carrageenan can be extracted from red seaweed, while alginate from brown seaweed. Since seaweed derivatives are a water-soluble polymer, they exhibit poor water resistance because of their hydrophilic nature. Although edible films prepared from these seaweed-derived polymers have strong potential to be used in wide range of applications, they usually lack the desired mechanical properties, such as high strength that are needed for certain packaging application (Joye and McClements 2014; Shit and Shah 2014).

Chitin is a linear polysaccharide comprised of β-1,4-N-acetylglucosamine, which is extracted from shells of crustaceans and cell walls of fungi. Similar to cellulose, chitin is insoluble in common solvents because of its high crystalline structure and hydrogen bonding between carbonyl, hydroxyl, and acetamide groups. Therefore, chitin is generally used for the production of chitosan by deacetylation (Abdul Khalil et al. 2016). Chitosan is biodegradable, non-toxic, and low-cost as well as has good film-forming properties. The edible film prepared from chitosan exhibits excellent O_2 and CO_2 permeability and antimicrobial activity against bacteria, yeasts, and molds (Shit and Shah 2014). However, similar to other polysaccharides, their poor mechanical and thermal properties have restricted its widespread applications. Thus, the chitosan film properties can be improved by reinforcement of nano-sized cellulose (Abdul Khalil et al. 2016).

3.4.1.2 Proteins

Proteins used to produce edible film can be divided into animal- and plant-derived proteins. Plant origin proteins are corn zein, wheat gluten, soy protein, pea protein, sunflower protein, peanut protein, and cotton protein, whereas animal origin proteins are keratin, collagen, gelatin, fish myofibrillar protein, egg white protein, and casein as well as whey protein (Ogur and Erkan 2015). Generally, animal-derived protein (the fibrous protein) is water insoluble, while plant-derived protein (the globular protein) can soluble in water or aqueous solutions of acids, bases, or salts. The chemical and physical properties of these proteins are highly depending on the relative amounts of component amino acid residues and their placement along the protein polymer chain (Wittaya 2012).

Among the biodegradable polymer films, protein-based films are the most attractive. It has the impressive gas barrier and better mechanical properties as compared with other biodegradable polymer films due to proteins have a unique structure (based on 20 different monomers), which can form bonds at different positions and offer high potential for forming numerous linkages. However, similar to other biodegradable polymers, the protein-based film has a poor water vapor barrier (contain predominantly hydrophilic amino acid residues) and mechanical strength as compared with synthetic polymers, which limits its application. These properties can be improved by modifying properties of the protein by chemical and enzymatic methods, combining with the hydrophobic material or some polymers, or by using a physical method (Bourtoom 2009).

3.4.1.3 Lipid

Lipid compound consists of acetylated monoglycerides, natural wax, and surfactants. Parrafin wax and beeswax are the lipid substances that widely used as edible film. Although lipid-based film is capable of inhibiting the passage of moisture, its hydrophobic character usually forms thicker and brittle film. Therefore, it usually mixes with other film-forming agents such as polysaccharides, to provide mechanical strength, while maintaining its characteristics (Shit and Shah 2014).

3.4.1.4 Polyhydroxyalkanoates (PHA)

Different from other biodegradable polymers, polyhydroxyalkanoates (PHA) is a family of bio-polyesters, which derived from the microorganism. PHA is biodegradable. However, it is costly (Yang et al. 2002). Since PHA presents a relatively wide range of properties depending on the hydroxyvalerate (HV)-to-hydroxybutyrate (HB) ratio, several studies were conducted using homopolymer polyhydroxy butyrate (PHB), the most common member of the PHA family, as a biomaterial for in vitro and in vivo studies (Martínez-Sanz et al. 2016). Although it presents mechanical properties similar to those synthetic thermoplastics such as polyethylene and polypropylene, it has relatively high glass transition and melting temperatures, leading to excessive brittleness due to its highly crystalline characteristics. In order to reduce the excessive brittleness and low thermal stability, copolymers of PHB with hydroxyvalerate, which commonly known as PHBV, have been developed to enhance the properties of this bio-polyester. Nevertheless, they still present an insufficient barrier to substitute other synthetic polymers commonly used for food packaging applications. Hence, the addition of fillers is an alternative way in order to make this biopolymer more suitable for food packaging applications (Yang et al. 2002; Fabra et al. 2016b).

3.4.1.5 Polylactic Acid (PLA)

Polylactic acid (PLA) is among the most common synthetic biopolymers. PLA is produced from lactic acid through fermentation of carbohydrate from plant resources, for instance, sugar beet and corn. It is biodegradable and offers good stiffness and strength. However, it possesses low heat distortion temperature, low resistance to extreme heat and humidity, and low flexibility (Mathew et al. 2005; Othman 2014). Therefore, PLA mainly used in products with not very high performance such as plastic bags for household wastes, barriers for sanitary products and diapers, planting, and disposable cups and plates. Hence, the incorporation of renewable reinforcement can be of great interest in order to enhance some limitation of PLA (i.e., low toughness and thermal stability) while maintaining their transparency and biodegradability properties (Mathew et al. 2005; Haafiz et al. 2016).

3.4.2 Properties of Biodegradable Polymer-Cellulose Composite Film

To understand the performance of cellulose fiber reinforced biopolymer film, it becomes necessary to determine the mechanical, physical, and chemical properties of this developed composite film. According to Table 3.2, biopolymers, which derived from natural products (i.e., polysaccharides and proteins), are among widely used with cellulose as reinforcement material in packaging applications.

Although amylose from starch can form gels and films, starch has poor mechanical, thermal, and barrier properties when compared with petroleum-based polymers. The dispersion of filler reinforcement from micro- or nanoscale such as microcrystalline cellulose (MCC), cellulose nanoparticles (CN), and microfibrillated cellulose (MFC) into a starch biopolymer matrix has been reported as one of the most promising approaches for improving the mechanical and water vapor barrier properties of the starch film (Table 3.2). However, the starch bionanocomposite films increased in tensile strength but decreased in elongation at breaks of composites. The increase in tensile strength is directly related to the hydrogen bonds formed between the starch and cellulose structures. A good interfacial interaction between cellulose and starch matrix is most probably due to their chemical similarity (both are polysaccharides). Moreover, the presence of these micrometric or nanometric particles also is capable of reducing the water vapor diffusion through the matrix and thus, decreasing the water vapor permeability of the starch films (Guimarães et al. 2016).

In general, the native starch in a granular structure can be processed into thermoplastic materials for expanding starch processability and applications. Thermoplastic starch (TPS) usually formed when the presence of a suitable plasticizer (i.e., water, polyols, and amides), temperature, and shear. Then, the starch

Table 3.2 Properties of cellulose reinforced biopolymer film by casting method

Biodegradable polymer (matrix)	Type of cellulose (reinforcement)	Film characteristics and improvement	References
Starch	MCC	Addition of MCC improved tensile strength and water resistance of starch film	Wittaya (2009)
	Cellulose nanoparticles (CN)	Addition of CN improved the tensile strength, thermal stability, and water vapor barrier of starch film	Chang et al. (2010)
	MFC	Addition of MFC increased the tensile strength and decreased the water vapor permeability	Guimarães et al. (2016)
Thermoplastic Starch (TPS)	MCC	Addition of MCC improved the thermal stability, tensile strength, dynamic mechanical and water vapor barrier properties of TPS film	Ma et al. (2008), Rico et al. (2016)
	Cellulose nanocrystals (CNC)	Addition of CNC improved the tensile strength and water vapor permeability of TPS film	González et al. (2015)
	Cellulose nanofiber (CNF)	Addition of CNF improved the mechanical and water vapor barrier properties as well as storage modulus and degradation rate of TPS film	Babaee et al. (2015)
Alginate	NCC	Incorporation of NCC improved film mechanical (except elongation), water vapor permeability, and thermal properties	Huq et al. (2012)
	NFC	Incorporation of CNF improved film water resistance and mechanical properties as well as decreased biodegradation time	Deepa et al. (2016)
Kappa-carrageenan	NCC	Incorporation of NCC showed good dispersion, superior mechanical properties, and thermal stability of film	Zarina and Ahmad (2015)
	NFC	Addition of CNF improves the tensile strength, water vapor transmission rate, and oxygen transmission rate of film	Savadekar et al. (2012)
Agar	NCC	Film transparency decreased. Addition of NCC improved film mechanical, thermal, and water vapor barrier properties	Rhim et al. (2015), Shankar and Rhim (2016)

(continued)

Table 3.2 (continued)

Biodegradable polymer (matrix)	Type of cellulose (reinforcement)	Film characteristics and improvement	References
Chitosan	Cellulose nanoparticles (CN)	Chitosan/CN indicated excellent antimicrobial properties and thermal stability	Dehnad et al. (2014)
	Cellulose whiskers (CW)	Addition of CW increased tensile strength of chitosan film. This nanocomposite film displayed excellent thermal stability and water resistance	Li et al. (2009)
	Nanocrystalline cellulose (NCC)	Addition of NCC improved the tensile strength water vapor barrier properties of chitosan film	Khan et al. (2012)
	MFC	Addition of MFC increased the tensile strength, storage modulus and glass transition temperature of chitosan film	Hassan et al. (2011)
Protein	Cellulose pulp fiber	Cellulosic pulp fiber as reinforcement improved mechanical properties (except elongation at breaks) of castor bean cake protein film	Oliveira et al. (2015)
	MCC	Addition of MCC improved the tensile strength, oxygen, and water barrier properties of soy protein isolate (SPI) film	Wang et al. (2013)
	CW	CW/SPI composite film showed greater tensile strength, young modulus, and water resistance as well as thermal stability	Wang et al. (2006)
	CW	CW/fish gelatin composite film exhibits good mechanical properties (except elongation) and water vapor barrier	Santos et al. (2014)
	MFC	Addition of MFC improved the mechanical strength and reduced the water vapor permeability (WVP) and water absorption of gelatin film	Fadel et al. (2012)
	Bacterial cellulose nanocrystal (BCNC)	Addition of BCNC improved the moisture sorption, WVP behavior, mechanical and thermal properties of gelatin film	George and Siddaramaiah (2012)

(continued)

Table 3.2 (continued)

Biodegradable polymer (matrix)	Type of cellulose (reinforcement)	Film characteristics and improvement	References
PHB	CNC	Addition of CNC improved gas barrier and migration properties of PHB film	Dhar et al. (2015)
PHBV	MCC or ultrasound modified bacterial cellulose (us-BC)	Us-BC/PHBV show higher tensile strength and modulus than MCC/PHBV	Panaitescu et al. (2013)
	CW	CW/PHBV exhibit good mechanical and thermal properties	Ten et al. (2010, 2012)
PLA	MCC	Addition of MCC improved the thermal stability and young modulus, but decreased the tensile strength and elongation of PLA film	Mathew et al. (2005), Haafiz et al. (2013)
	Cellulose nanofibril	The mechanical properties of cellulose nanofibril/PLA are lower than poly (ethylene glycol)/PLA film	Qu et al. (2010)

granules can be fragmented, swelled, and melted, and consequently, the hydrogen bonds among the starch molecules can be disrupted. This modified starch is capable of being processed and with similar applications as conventional thermoplastic materials (Rico et al. 2016). Nevertheless, TPS still exhibits problems such as high water absorption and low mechanical properties, which are highly affected by the relative humidity. Previous studies have reported that the incorporation of natural bio-fillers such as MCC, cellulose nanofiber (CNF), and cellulose nanocrystals (CNC) is one of the methods to enhance the performance of TPS films and develop inexpensive starch biocomposite (Table 3.2). Similar to native starch film, TPS film reinforced with these cellulosic fibers, whiskers, and nanofibers is capable of enhancing the tensile strength and water vapor permeability of TPS film. Surprisingly, in an addition of these cellulose reinforcement materials to TPS matrix, other properties like thermal stability, storage modulus, and degradation rate of TPS films are improved as well (Table 3.2).

Similar to starch, seaweed derivatives (alginate, carrageenan, and agar) are ideal film-forming materials. It also lacks sufficient mechanical and water vapor properties. Since cellulose possesses outstanding characteristics and properties, the incorporation of cellulose reinforcing materials such as NCC and NFC into seaweed matrix is capable of increasing the seaweed derivatives' film mechanical properties and water resistance as well as thermal properties of the seaweed film remarkably (Table 3.2). This phenomenon is actually expected due to both seaweed and cellulose are a chemical similarity. Hence, the improvement in mechanical strength and water vapor barrier properties are largely due to strong hydrogen bond networks between cellulose and seaweed and good dispersion of cellulose in the seaweed film (Deepa et al. 2016; Huq et al. 2012).

Different from starch and seaweed, chitosan is natural antimicrobial polysaccharides that can fight against a wide variety of microorganisms (i.e., bacteria, yeast, and molds), and thus, it has been successfully used as packaging material for the preservation of food quality (Dehnad et al. 2014). However, the inherent water sensitivity and relatively low mechanical properties of chitosan have restricted it applications especially in the wet or moist conditions (Li et al. 2009). To solve these problems, chitosan is mixed with nanoparticles, which having at least one dimension in nanoscale (i.e., CN, CW, NCC, and MFC) to prepare composite materials with improved properties. Since chitosan and cellulose are structural similarities, they are compatible, and thus, the composite film exhibits excellent mechanical, thermal, and water vapor barrier properties as well as the capability for further extending the food shelf-life (Table 3.2).

Soy protein isolate (SPI) is one of the proteins that often used to develop edible materials for diverse applications. However, SPI application is limited by poor mechanical properties (especially flexibility) and the water sensitivity of soy protein-based materials. Although the brittleness of SPI film can be reduced by employing plasticizer, this phenomenon will lead to a significant decrease in the tensile strength and increase in the water sensibility as well (Wang et al. 2006, 2013). Therefore, to obtain flexible SPI plastic with an acceptance tensile strength, several kinds of reinforcement materials such as cellulosic pulp fiber, MCC, and CW have been studied (Table 3.2). Surprisingly, these reinforcement materials improve the tensile strength and water resistance as well as the thermal stability of SPI films. However, the incorporation of cellulosic pulp fiber in the SPI matrix is less effective as compare to the nanocellulose materials (MCC and CW) due to the load with cellulosic pulp fiber is not able to transform the composite film in a high water vapor barrier (Oliveira et al. 2015). Therefore, it is believed that nanoscale cellulose, which contained smaller particle size, larger surface area, and more free hydroxyls on the surface, is capable of forming a crosslinking network by hydrogen bonds between the nanocellulose materials and the SPI matrix. Hence, this phenomenon improved the film's abilities as a water vapor and oxygen barrier (Wang et al. 2006, 2013).

Besides, gelatin is another protein that is widely used as a food ingredient. It can be extracted from collagen, which exists in skin, bones, and animal tissue, by boiling them after alkali or acid pretreatment. However, the source, age of the animal, and type of collagen will affect the properties of the gelatin. Therefore, most of the gelatin exhibits poor mechanical properties and water sensitivity. Studies have reported that the use of nanocellulose materials as reinforcement has markedly improved the moisture sorption, water vapor permeability behavior, and mechanical as well as thermal properties of gelatin film, as shown in Table 3.2.

PHA (polyhydroxyalkanoates) and PLA (polylactic acid) are both bio-polyesters that have attracted special interest recently due to they are synthesized from renewable resources and possess excellent properties. For PHA, the homopolymer poly(3-hydroxybutyrate) (PHB) has been more extensively studied since it presents mechanical properties similar to those of conventional petroleum-based polymers. Although PHB exhibits a relatively high melting and glass transition temperature as well as great stiffness, it presents some drawbacks like brittleness and low thermal stability and thus, making it unstable during melt processing and limiting its applicability (Martínez-Sanz et al. 2014). The reinforcement of PHB with CNC has further improved the properties like a gas barrier of PHB film as crystalline cellulose has the capability to form a network-like structure within biopolymer matrix (Table 3.2). Besides, the toughness of PHB can be enhanced by forming a copolymer of hydroxybuterate and hydroxyvalerate (HV)—PHBV. Although PHBV exhibits low stiffness, low brittleness, and low melting temperature without reducing the thermal stability of the material, it rather low crystallinity due to the present of HV content will impair the barrier properties of the polymeric materials. Recent studies have reported that MCC, ultrasound modified bacterial cellulose (us-BC), and CW are capable of enhancing this limitation (Table 3.2). This is due to the strong interaction between the nanocellulose materials and their high aspect ratio.

Similar to other biopolymers, PLA has its own drawbacks such as low thermal stability, low water vapor, and gas barrier properties, as well as it possesses limited use in the high-temperature environment. Reinforcing fillers such as MCC and cellulose nanofibrils are capable of improving PLA properties (Table 3.2). However, the mechanical properties decreased with increasing MCC content due to poor dispersion of MCC in PLA matrix and subsequent chain restriction movement, respectively (Haafiz et al. 2013). In contrast, the mechanical properties are increased when the cellulose nanofibrils and poly(ethylene glycol) (PEG) are added to the PLA matrix. This phenomenon shows that addition of PEG gives positive effects to the mechanical properties of the composite film. Besides using as a plasticizer, PEG also acts as a compatibilizer between PLA matrix and cellulose nanofibrils to improve their interaction and prevent the aggregation of nanofibrils (Qu et al. 2010).

3.5 Packaging Applications

Today, biopolymer films, which derived from renewable resources, have been increasingly used as packaging materials, because of their great advantages as follows (Ogur and Erkan 2015):

- edible and biodegradable
- supplement the nutritional value of foods
- enhance organoleptic characteristics of food, such as appearance, odor, and flavor
- reducing packaging volume, weight, and waste
- incorporate antimicrobial agents and antioxidants
- extended shelf-life and improved quality of usually non-packed items
- control over inter-component migration of moisture, gases, lipids, and solutes
- individual packaging of small particulate foods (i.e., nuts and raisins)
- function as carriers for antimicrobial and antioxidant agents
- for microencapsulation and controlled release of active ingredients
- have a possible utilization in multilayer food packaging materials together with non-edible film
- low cost and abundant.

Moreover, a good packaging film for food, pharmaceutical, and electronic device packaging applications should meet below criteria (Tharanathan 2003):

- allow for a slow but controlled respiration (reduced O_2 absorption) of the commodity
- allow for a selective barrier to gases (i.e., CO_2) and water vapor
- creation of a modified atmosphere with respect to internal gas composition, thus regulating the ripening process and leading to shelf-life extension
- lessening the migration of lipids in confectionery industry
- maintain structural integrity (delay loss of chlorophyll) and improve mechanical handling
- serve as a vehicle to incorporate food additives (flavor, color, antioxidant, antimicrobial agent)
- prevent or reduce microbial spoilage during extended storage.

All the above criteria can be met with by biopolymers from agricultural feedstocks and other resources providing they mixed with other materials such as other biopolymers, plasticizer, and additives due to their uncertain limitations. Owing to the advantages of nano-sized cellulose, these bio-nanocomposites packaging materials have great potential in enhancing the food quality, safety, and stability as an innovative packaging and processing technology. The unique benefits of the natural biopolymer packaging may open a new possibility product development in various edible and non-edible packaging industries.

3.6 Conclusion and Future Perspective

This chapter shows that nanocellulose reinforced biodegradable polymer-based film is of great potential and benefit to use as packaging material. Nevertheless, the development of bionanocomposite film is still at the initial stage. In order to widen the application of bio-nanocellulose composite packaging films across various industries, several aspects regarding their quality, cost, and utility must be considered for future development and application.

Acknowledgements All the authors are gratefully acknowledged Ministry of Higher Education for the Fundamental Research Grant Scheme—*Malaysia's Rising Star Award 2015* (FRGS-203/PTEKIND/6711531).

References

Abdul Khalil HPS, Saurabh CK, Adnan AS et al (2016) A review on chitosan-cellulose blends and nanocellulose reinforced chitosan biocomposites: Properties and their applications. Carbohydr Polym 150:216–226

Ashori A, Nourbakhsh A (2010) Performance properties of microcrystalline cellulose as a reinforcing agent in wood plastic composites. Compos Part B Eng 41(7):578–581

Azeredo H, Mattoso LHC, Wood D et al (2009) Nanocomposite edible films from mango puree reinforced with cellulose nanofibers. J Food Sci 74(5):N31–N35

Babaee M, Jonoobi M, Hamzeh Y et al (2015) Biodegradability and mechanical properties of reinforced starch nanocomposites using cellulose nanofibers. Carbohydr Polym 132:1–8

Besbes I, Alila S, Boufi S (2011) Nanofibrillated cellulose from TEMPO-oxidized eucalyptus fibres: effect of the carboxyl content. Carbohydr Polym 84(3):975–983

Bilbao-Sainz C, Bras J, Williams T et al (2011) HPMC reinforced with different cellulose nano-particles. Carbohydr Polym 86(4):1549–1557

Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. Prog Polym Sci 24(2):221–274

Boldizar A, Klason C, Kubat J et al (1987) Prehydrolyzed cellulose as reinforcing filler for thermoplastics. Int J Polym Mater 11(4):229–262

Bourtoom T (2009) Edible protein films: properties enhancement. Int Food Res J 16(1):1–9

Bras J, Hassan ML, Bruzesse C et al (2010) Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. Ind Crops Prod 32 (3):627–633

Brinchi L, Cotana F, Fortunati E (2013) Production of nanocrystalline cellulose from lignocellulosic biomass: technology and applications. Carbohydr Polym 94(1):154–169

Chang PR, Jian R, Zheng P et al (2010) Preparation and properties of glycerol plasticized-starch (GPS)/cellulose nanoparticle (CN) composites. Carbohydr Polym 79(2):301–305

Deepa B, Abraham E, Pothan LA et al (2016) Biodegradable nanocomposite films based on sodium alginate and cellulose nanofibrils. Mater 9:1–11

Dehnad D, Mirzaei H, Emam-Djomeh Z et al (2014) Thermal and antimicrobial properties of chitosan–nanocellulose films for extending shelf life of ground meat. Carbohydr Polym 109:148–154

Dhar P, Bhardwaj U, Kumar A et al (2015) Poly (3-hydroxybutyrate)/cellulose nanocrystal films for food packaging applications: Barrier and migration studies. Polym Eng Sci 55(10):2388–2395

Dogan N, McHugh TH (2007) Effects of microcrystalline cellulose on functional properties of hydroxy propyl methyl cellulose microcomposite films. J Food Sci 72(1):E016–E022

Dufresne A, Dupeyre D, Vignon MR (2000) Cellulose microfibrils from potato tuber cells: processing and characterization of starch–cellulose microfibril composites. J Appl Polym Sci 76(14):2080–2092

Fabra MJ, López-Rubio A, Ambrosio-Martín J et al (2016a) Improving the barrier properties of thermoplastic corn starch-based films containing bacterial cellulose nanowhiskers by means of PHA electrospun coatings of interest in food packaging. Food Hydrocolloid 61:261–268

Fabra MJ, Pardo P, Martínez-Sanz M et al (2016b) Combining polyhydroxyalkanoates with nanokeratin to develop novel biopackaging structures. J Appl Polym Sci 133(2):1–12

Fadel SM, Hassan M, Oksman K (2012). Improving tensile strength and moisture barrier properties of gelatin using microfibrillated cellulose. J Compos Mater 47(16):1977–1985

Favier V, Chanzy H, Cavaille JY (1995) Polymer nanocomposites reinforced by cellulose whiskers. Macromolecules 28(18):6365–6367

George J, Siddaramaiah (2012) High performance edible nanocomposite films containing bacterial cellulose nanocrystals. Carbohydr Polym 87(3):2031–2037

Gindl W, Keckes J (2005) All-cellulose nanocomposite. Polym 46(23):10221–10225

González K, Retegi A, González A et al (2015) Starch and cellulose nanocrystals together into thermoplastic starch bionanocomposites. Carbohydr Polym 117:83–90

Guimarães IC, dos Reis KC, Menezes EGT et al (2016) Cellulose microfibrillated suspension of carrots obtained by mechanical defibrillation and their application in edible starch films. Ind Crops Prod 89:285–294

Haafiz MM, Hassan A, Zakaria Z et al (2013) Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose. Carbohydr Polym 98(1):139–145

Haafiz MM, Hassan A, Khalil HA et al (2016) Exploring the effect of cellulose nanowhiskers isolated from oil palm biomass on polylactic acid properties. Int J Biol Macromolec 85:370–378

Hassan ML, Hassan EA, Oksman KN (2011) Effect of pretreatment of bagasse fibers on the properties of chitosan/microfibrillated cellulose nanocomposites. J Mater Sci 46(6):1732–1740

Helbert W, Cavaille JY, Dufresne A (1996) Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: processing and mechanical behavior. Polym Compos 17(4):604–611

Hu D, Wang H, Wang L (2016) Physical properties and antibacterial activity of quaternized chitosan/carboxymethyl cellulose blend films. LWT—Food Sci Technol 65:398–405

Huq T, Salmieri S, Khan A et al (2012) Nanocrystalline cellulose (NCC) reinforced alginate based biodegradable nanocomposite film. Carbohydr Polym 90:1757–1763

Jawaid MHPS, Khalil HA (2011) Cellulosic/synthetic fibre reinforced polymer hybrid composites: a review. Carbohydr Polym 86(1):1–18

Jiménez A, Fabra MJ, Talens P et al (2012) Edible and biodegradable starch films: a review. Food Bioprocess Tech 5(6):2058–2076

Jonoobi M, Harun J, Mathew AP et al (2010) Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. Compos Sci Technol 70(12):1742–1747

Joye IJ, McClements DJ (2014) Biopolymer-based nanoparticles and microparticles: fabrication, characterization, and application. Curr Opin Colloid Interface Sci 9(5):417–427

Kalia S, Boufi S, Celli A et al (2014) Nanofibrillated cellulose: surface modification and potential applications. Colloid Polym Sci 292(1):5–31

Khan A, Khan RA, Salmieri S et al (2012) Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films. Carbohydr Polym 90(4):1601–1608

Li Q, Zhou J, Zhang L (2009) Structure and properties of the nanocomposite films of chitosan reinforced with cellulose whiskers. J Polym Sci Part B Polym Phys 47(11):1069–1077

Liu D, Zhong T, Chang PR et al (2010) Starch composites reinforced by bamboo cellulosic crystals. Bioresour Technol 101(7):2529–2536

Luo S, Netravali AN (1999) Interfacial and mechanical properties of environment-friendly "green" composites made from pineapple fibers and poly (hydroxybutyrate-co-valerate) resin. J Mater Sci 34(15):3709–3719

Ma X, Chang PR, Yu J (2008) Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. Carbohydr Polym 72(3):369–375

Martínez-Sanz M, Villano M, Oliveira C et al (2014) Characterization of polyhydroxyalkanoates synthesized from microbial mixed cultures and of their nanobiocomposites with bacterial cellulose nanowhiskers. N Biotechnol 31(4):364–376

Martínez-Sanz M, Lopez-Rubio A, Villano M et al (2016) Production of bacterial nanobiocomposites of polyhydroxyalkanoates derived from waste and bacterial nanocellulose by the electrospinning enabling melt compounding method. J Appl Polym Sci 133(2):1–14

Mathew AP, Oksman K, Sain M (2005) Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). J Appl Polym Sci 97(5):2014–2025

Moon RJ, Martini A, Nairn J et al (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 40(7):3941–3994

Moroa L (2001) Starch-based biodegradable materials suitable for thermoforming packaging. Starch/Stärke 53:368–371

Nishino T, Matsuda I, Hirao K (2004) All-cellulose composite. Macromolecules 37(20):7683–7687

Ogur S, Erkan N (2015) The physicochemical properties of edible protein films. Ital J Food Sci 27 (1):1F

Oliveira TG, Makishi GLA, Chambi HNM et al (2015) Cellulose fiber reinforced biodegradable films based on proteins extracted from castor bean (Ricinus communis L.) cake. Ind Crops Prod 67:355–363

Osong SH, Norgren S, Engstrand P (2016) Processing of wood-based microfibrillated cellulose and nanofibrillated cellulose, and applications relating to papermaking: a review. Cellulose 23 (1):93–123

Othman SH (2014) Bio-nanocomposite materials for food packaging applications: types of biopolymer and nano-sized filler. Agric Agric Sci Procedia 2:296–303

Panaitescu DM, Casarica A, Stanescu PO et al (2013) Comparative analysis of bacterial and microcrystalline celluloses as reinforcements for poly (3-hydroxybutyrate-co-3-hydroxyvalerate). Mater Plast 50(4):236–240

Phan The D, Debeaufort F, Voilley A et al (2009) Biopolymer interactions affect the functional properties of edible films based on agar, cassava starch and arabinoxylan blends. J Food Eng 90:548–558

Qu P, Gao Y, Wu G et al (2010) Nanocomposites of poly (lactic acid) reinforced with cellulose nanofibrils. BioResources 5(3):1811–1823

Rodríguez-Castellanos W, Flores-Ruiz FJ, Martínez-Bustos F et al (2015) Nanomechanical properties and thermal stability of recycled cellulose reinforced starch–gelatin polymer composite. J Appl Polym Sci 132(14):1–7

Rhim JW, Reddy JP, Luo X (2015) Isolation of cellulose nanocrystals from onion skin and their utilization for the preparation of agar-based bio-nanocomposites films. Cellulose 22:407–420

Rico M, Rodríguez-Llamazares S, Barral L et al (2016) Processing and characterization of polyols plasticized-starch reinforced with microcrystalline cellulose. Carbohydr Polym 149:83–93

Santos TM, de Sá Men, Filho MS, Caceres CA et al (2014) Fish gelatin films as affected by cellulose whiskers and sonication. Food Hydrocoll 41:113–118

Savadekar NR, Karande VS, Vigneshwaran N et al (2012) Preparation of nano cellulose fibres and its application in kappa-carrageenan based film. Int J Biol Macromolec 51:1008–1013

Saxena A, Elder TJ, Ragauskas AJ (2011) Moisture barrier properties of xylan composite films. Carbohydr Polym 84(4):1371–1377

Shankar S, Rhim JW (2016) Preparation of nanocellulose from micro-crystalline cellulose: the effect on the performance and properties of agar-based composite films. Carbohydr Polym 135:18–26

Shit SC, Shah PM (2014). Edible polymers: challenges and opportunities. J Polym 2014:1–13

Siqueira G, Bras J, Dufresne A (2010) Cellulosic bionanocomposites: a review of preparation, properties and applications. Polym 2(4):728–765

Siracusa V, Rocculi P, Romani S et al (2008) Biodegradable polymers for food packaging: a review. Trends Food Sci Tech 19(12):634–643

Siró I, Plackett D (2010) Microfibrillated cellulose and new nanocomposite materials: a review. Cellulose 17(3):459–494

Sirviö JA, Kolehmainen A, Liimatainen H et al (2014) Biocomposite cellulose-alginate films: promising packaging materials. Food Chem 151:343–351

Suryanegara L, Nakagaito AN, Yano H (2009) The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites. Compos Sci Technol 69(7):1187–1192

Ten E, Turtle J, Bahr D et al (2010) Thermal and mechanical properties of poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskers composites. Polym 51 (12):2652–2660

Ten E, Bahr DF, Li B et al (2012). Effects of cellulose nanowhiskers on mechanical, dielectric, and rheological properties of poly (3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhisker composites. Ind Eng Chem Res 51(7):2941–2951

Tharanathan RN (2003) Biodegradable films and composite coatings: past, present and future. Trends Food Sci Technol 14(3):71–78

Tye YY, Lee KT, Abdullah WNW et al (2016) The world availability of non-wood lignocellulosic biomass for the production of cellulosic ethanol and potential pretreatments for the enhancement of enzymatic saccharification. Renew Sustain Energy Rev 60:155–172

Ummartyotin S, Pechyen C (2016) Microcrystalline-cellulose and polypropylene based composite: a simple, selective and effective material for microwavable packaging. Carbohydr Polym 142:133–140

Vieira MGA, da Silva MA, dos Santos LO et al (2011) Natural-based plasticizers and biopolymer films: a review. Eur Polym J 47(3):254–263

Wang Y, Cao X, Zhang L (2006) Effects of cellulose whiskers on properties of soy protein thermoplastics. Macromol Biosci 6(7):524–531

Wang Z, Sun XX, Lian ZX et al (2013) The effects of ultrasonic/microwave assisted treatment on the properties of soy protein isolate/microcrystalline wheat-bran cellulose film. J Food Eng 114 (2):183–191

Wittaya T (2009) Microcomposites of rice starch film reinforced with microcrystalline cellulose from palm pressed fiber. Int Food Res J 16(4):493–500

Wittaya T (2012) Protein-based edible films: characteristics and improvement of properties. INTECH Open Access Publisher, Rijeka, pp 44–46

Yang X, Zhao K, Chen GQ (2002) Effect of surface treatment on the biocompatibility of microbial polyhydroxyalkanoates. Biomaterials 23(5):1391–1397

Yang ZY, Wang WJ, Shao ZQ et al (2013) The transparency and mechanical properties of cellulose acetate nanocomposites using cellulose nanowhiskers as fillers. Cellulose 20(1):159–168

Zarina S, Ahmad I (2015) Biodegradable composite films based on k-carrageenan reinforced by cellulose nanocrystal from kenaf fibres. BioResources 10:256–271

Zimmermann T, Bordeanu N, Strub E (2010) cellulose). Properties of nanofibrillated from different raw materials and its reinforcement potential. Carbohydr Polym 79(4):1086–1093

Chapter 4
Nanohybrid Active Fillers in Food Contact Bio-based Materials

Giuliana Gorrasi, Valeria Bugatti and Andrea Sorrentino

Abstract Nanohybrid active fillers are gaining interest from basic and applied research, due to their potential to provide quality and safety benefits. Great attention has been devoted in the last decade to the hybrid organic–inorganic systems, in particular to those in which inorganic materials are dispersed at a nanometric level in polymeric matrices. This review presents some important examples of the most used inorganic nanometric fillers, with antimicrobial activity for potential active packaging applications. Particular emphasis is given to biodegradable polymer matrices such as aliphatic polyesters, polysaccharides, proteins, and their blends. As food contact materials, they present the possibility of being carriers of different additives, such as antioxidant, antimicrobial, nutraceuticals, and flavoring agents. Current regulation issues are also reported and discussed and possible trends and perspectives in the food contact field shortly commented.

Keywords Nanohybrid fillers · Food contact · Antimicrobials · Active packaging

4.1 Introduction

Food contact materials, such as food containers and packaging, can be defined as the means of achieving safe handling and delivery of products in sound condition (Yam 2009; Soroka 1999; Baldwin et al. 2011; Khan and Abourashed 2011). It generally provides a barrier between the food and the environment by controlling contamination, rate of transfer of heat, moisture and gases, and light transmission (Coles et al. 2003; Ensminger et al. 1995; Brody 1997). The ideal food contact

---

G. Gorrasi · V. Bugatti
Department of Industrial Engineering, University of Salerno, via Giovanni Paolo II 132,
84084 Fisciano, SA, Italy

A. Sorrentino (✉)
Institute for Polymers, Composites and Biomaterials (IPCB),
National Research Council (CNR), via Previati n. 1/E, 23900 Lecco, Italy
e-mail: andrea.sorrentino@cnr.it

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_4

materials should be easy for handling, efficient and economic on the production line, resistant to damage, safe and healthy to human (Hotchkiss 1997). In the last decade, food contact materials using nanotechnology (or containing part of the material in the nanoscale dimension) were proposed and in some cases applied with success (Imran et al. 2010; Silvestre et al. 2011; Duncan 2011). Several inorganic nanostructured materials were incorporated into food contact materials to enhance mechanical and barrier properties and to prevent the photodegradation of plastics (Chaudhry et al. 2008; Hatzigrigoriou and Papaspyrides 2011; Sorrentino et al. 2007). Nanoparticles are present in certain active and intelligent materials and articles, polymeric containers, ceramic coatings, nanocoatings on paper and board. A well-known example is represented by the new types of nonsticking coatings on cookware containing embedded inorganic particles (Risch 2009). The European Institute for Health and Consumer Protection revealed that the use of nanomaterials in the food packaging market is expected to reach several billions of Euros by 2020.

Nanoparticles have proven also to be good carriers for antimicrobials in the form of organic salts, oxides, and colloids (Hajipour et al. 2012; Llorens et al. 2012). They can effectively prevent from the invasion of bacteria and microorganism and ensure the product safety (Rashidi and Khosravi-Darani 2011). The efficiency of nanobased antimicrobial systems is mainly due to the high surface to volume ratio and enhanced surface reactivity of the nanosized antimicrobial agents (Farokhzad and Langer 2009; Hughes 2005). This makes them able to inactivate microorganisms more effectively than their micro- or macroscale counterparts (Damm et al. 2008). Furthermore, these materials are excellent vehicles for incorporating a wide variety of additives, such as antioxidants, antifungal agents, colors, and other nutrients (Imran et al. 2010; Sung et al. 2013). They can be used for food preservation purposes and help to protect and hold safe surfaces in industrial environments (Dingman n.d.). Other relevant properties, such as the capability for ethylene oxidation or oxygen scavenging, can be introduced in active food packaging to extend food shelf life (Cruz et al. 2012; Llorens et al. 2012). The use of nanoparticles will allow to obtain controlled gas/water vapor permeability, and the resulting packaging will be lighter and stronger with better thermal performance (de Azeredo 2009; Augustin and Sanguansri 2009). Embedded nanosensors allow the consumers to control the exact status of the contents (Pérez-Esteve et al. 2013). The amazing properties of these nanomaterials have the capability to transform the nature of conventional of food contact materials, to give the materials new and multifunctional properties (Sozer and Kokini 2009; Sekhon 2010). Commonly used or tested inorganic nanofillers to prepare food contact materials include organically modified montmorillonite (MMT) or cationic clays, layered double hydroxydes or hydrotalcite-like compounds (LDHs) (anionic clays), halloysite, talc, zeolites, metal ions (copper, silver, platinum, gold), metal oxide (TiO_2, MgO, ZnO).

The present work is an overview of some of these inorganic nanofillers with potential use in food contact applications. Particular attention was devoted to the so-called nano-biocomposites." This new class of material is the last answer to the growing problems related to urban waste management and disposal. As a matter of fact, requests for continuous enhancement of food quality and extend of its shelf life, while reducing environmental impact, have encouraged the research in biodegradable and edible films from renewable resources. The right combination of these materials with new nanohybrid systems can allow to obtain biodegradable materials with a variety of structural and amazing functional properties.

4.2 Inorganic Fillers with Potential Use in Food Contact

4.2.1 Clays

The clays most commonly used in the field of food contact materials belong to the family of 2:1 layered silicates, also called 2:1 phyllosilicates (montmorillonite, saponite). As shown in Fig. 4.1, their structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide (Giannelis et al. 1999). Montmorillonite, in particular, is naturally occurring as micron-sized tactoids, consisting of several hundred platelets held together by electrostatic forces (Uddin 2008; LeBaron et al. 1999). The individual platelets have thicknesses of 1 nm and surface lengths on the order of 100–1000 nm (Alexandre and Dubois 2000). Isomorphic substitution may occur inside the stacked structure since Al^{3+} can be replaced by Mg^{2+} or Fe^{2+}, and Mg^{2+} by Li^{+}. Globally, negatively charged platelets are counterbalanced by alkali

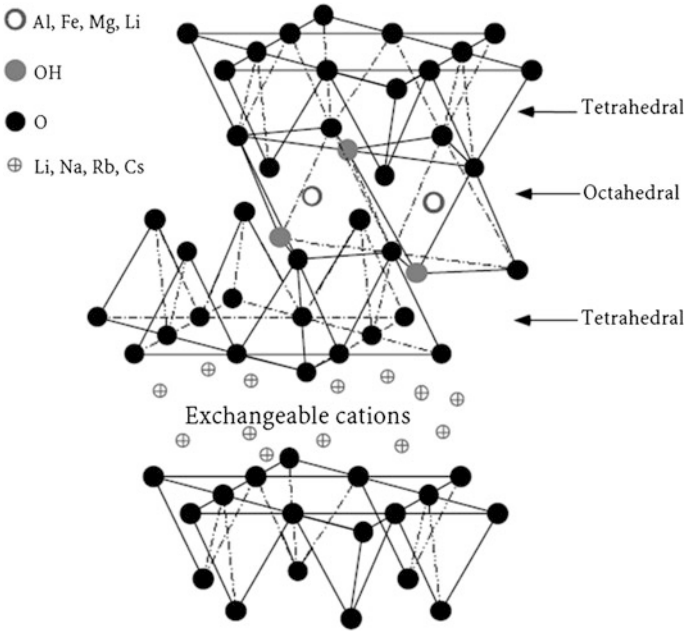


Fig. 4.1 Structure of 2:1 layered silicates. Reproduced from Giannelis et al. (1999)

and alkali earth cations (Na^+, Ca^{2+}, etc.) located in the galleries, which increases the clay hydrophilic character.

The natural as well as the synthetic clays are hydrophilic, which makes proper exfoliation and dispersion into conventional organic materials difficult (Sinha Ray and Okamoto 2003). Thus, they must be modified through substitution of their sodium ions with organic ammonium ions, resulting in an organoclay complex (Qutubuodin and Fu 2002). The modification procedure expands the spacing between individual clay layers and improves the compatibility of the complex with hydrophobic materials so that individual platelets can be more easily separated in an organic matrix (Sinha Ray and Okamoto 2003). The ability to modify the surface of smectite clay minerals by means of a cation exchange with organic cations has been recognized for a long time (Gieseking 1938). The quantity of exchangeable cations available on the clay mineral surfaces can be characterized by the cation exchange capacity (C.E.C.), which has units of milliequivalents (meq)/100 g of clay. The C.E.C. of smectite clays typically varies between approximately 50 and 150 meq/100 g.

The mechanical incorporation of the modified clay into the polymer matrix can leave to the separation and the dispersion of the individual clay particles in the matrix (Lefebvre 2002). The degree of exfoliation of the clay in single layers critically depends upon the processing conditions as well as the matrix characteristics (Pavlidou and Papaspyrides 2008; Hussain 2006).

The addition of these nanoclay sheets has proven to improve the mechanical, gas barrier, and thermal properties of several synthetic and bio-based polymers (Lange and Wyser 2003). The enhancement is a result of well-dispersed and uniform distribution of single layer of nanoclay sheets in polymer matrices (Alexandre and Dubois 2000; Ajayan et al. 2003). Up to now, this approach has been used in several commercially available packaging products such as plastic wraps and bottles for carbonated beverages (Raheem 2012; Collister 2001).

A number of investigations have shown that polymers filled with clay have a lower permeability than that of the corresponding virgin polymer (Sorrentino et al. 2006a, b). In particular, the clay sheets have shown to have different influence on the diffusion and the solubility of the resulting nanocomposites. Often, it has been found that the decrease of the diffusion parameter in the nanocomposites is the most relevant effect in the decrease of permeability, even when the solubility is similar or higher (Sorrentino et al. 2012). This phenomenon has traditionally been explained by considering the clay sheets as impermeable obstacles in the path of the diffusion process. The clay sheets act like barriers, which makes it difficult for gases or vapor to pass through the bulk material (Fig. 4.2).

The impermeable clay increases the distance the gas molecules have to travel by causing those molecules to zigzag around the silicate plates (Fig. 4.2). Obviously, in the fully exfoliated state, the number of obstacles as well as the aspect ratios is the highest possible, and thus, the highest barrier improvement is expected (Sorrentino et al. 2006a, b). In addition, to the sinuous pathway formation, the development of interface regions between polymer bulk and clay sheets can influence the barrier properties of the composite. As observed in some experiments,

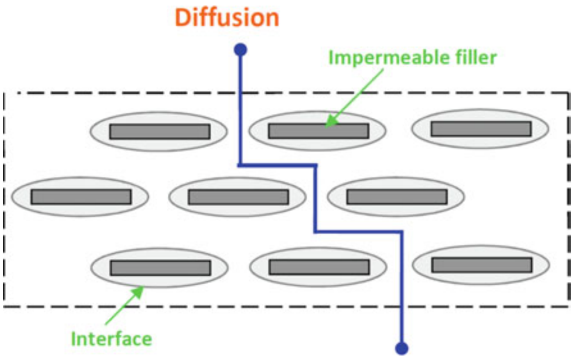


Fig. 4.2 Models of aligned mono-disperse flakes in a periodic arrangement

the presence of these regions around the single slabs can be occasionally responsible for a diffusional enhancement (Petersen et al. 1999). Interface regions can be due to either the surface modifiers utilized to compatibilize the inorganic sheets with the polymer or to microvoids formation between the different phases (Sorrentino et al. 2006a, b). The presence of these regions is responsible, for example, for the different behaviors shown by the nanocomposites treated with different surface modifiers, and/or different behaviors shown by the same nanocomposites with respect to different permeant molecules. Conceptually, the higher diffusion coefficient, in these zones, will compensate some of the increase in tortuosity of the diffusional path (Lu and Mai 2005, 2007; Xu et al. 2006).

The quality of the interface regions and their dimensions depends of the organoclay type and dispersion. Some applications can be important to have controlled microporous voids that allow permeation of gas (oxygen and carbon dioxide) without losing the barrier to water vapor molecules. In that case, a correct choice of the organoclay to be blended into the hydrophobic polymer matrix can allow the production of breathable films. Films with well-distributed elongated, narrow shaped voids can be obtained by uniaxial stretching. The resulting microstructure can allow the deferring respiratory anaerobiosis in modified atmosphere packaged fresh fruit and vegetables.

The utility of organoclay as antimicrobial compounds has been pointed out by several workers (Ōya et al. 1991, 1992; Ohashi and Oya 1996). These materials were fabricated by treating the smectite clay mineral with an organic cation or a metal chelated with an organic cation. In food packaging field, the use of mineral clays as biocide has the principal application as carriers of metals such as Ag, Cu, Zn, Mg. (Ohashi and Oya 1996; Ohashi et al. 1998; Li et al. 2011; Patakfalvi and Dékány 2004; Whilton et al. 1998; Patil et al. 2005). Metals, having biocidal properties, can be incorporated into the clay structure via ion exchange, as charge compensating ions. Nanoparticles of neutral metals can also be formed inside the clay gallery by the reduction on metal salts previously loaded into the clay (Rhim et al. 2000). Synthetic clays have been functionalized to provide antimicrobial functions (Thostenson et al. 2005). Aminopropyl-functionalized magnesium phyllosilicate (AMP) produced by sol-gel process strongly inhibited the growth of microorganisms such as *E. coli*, *S. aureus*, *and Candida albicans* (Chandrasekaran et al. 2011). The inhibition of microbial growth by AMP clay was attributed to the amino propyl groups and their charge interactions with the cell membrane.

Silver–silicate nanocomposites were produced using a flame spray pyrolysis process and incorporated into polystyrene, which showed significant antibacterial activity against both *Escherichia coli* and *Staphylococcus aureus* (Egger et al. 2009). Ag-MMT nanoparticles, obtained by exchanging the Na^+ of natural MMT with Ag ions from silver nitrate solution, exhibited high antimicrobial activity against *Pseudomonas* spp. when they were embedded in agar film (Valodkar et al. 2010).

Bio-nanocomposite films prepared with some organically modified nanoclay have been demonstrated to show antimicrobial activity (Rhim et al. 2006; Wang et al. 2006). Rhim et al. (2006) prepared chitosan/clay nanocomposite films with two different types of nanoclay (i.e., a natural MMT and an organophilic MMT (OMMT), Cloisite 30B) and tested the antimicrobial activity of the films against pathogenic microorganisms, *Listeria monocytogenes* and *Staphylococcus aureus*, while the natural MMT did not show any antimicrobial activity. They confirmed the result using a total colony count method, which showed clear antimicrobial activity of Cloisite 30B-incorporated chitosan films against *Staphylococcus aureus* (Fig. 4.3). They proposed that the antimicrobial activity was due to the quaternary ammonium salt of organically modified nanoclay (Cloisite 30B), although it is partly attributed to the chitosan itself, which has long been demonstrated as an antimicrobial activity against a wide variety of microorganisms (Tripathi et al. 2011; Helander et al. 2001; Wang et al. 2007). Hong and Rhim (2008) reported that some organically modified clays, such as Cloisite 30B and 20A, have strong antimicrobial activity against both Gram-positive and Gram-negative pathogenic bacteria by using agar diffusion method and the total colony count method. They

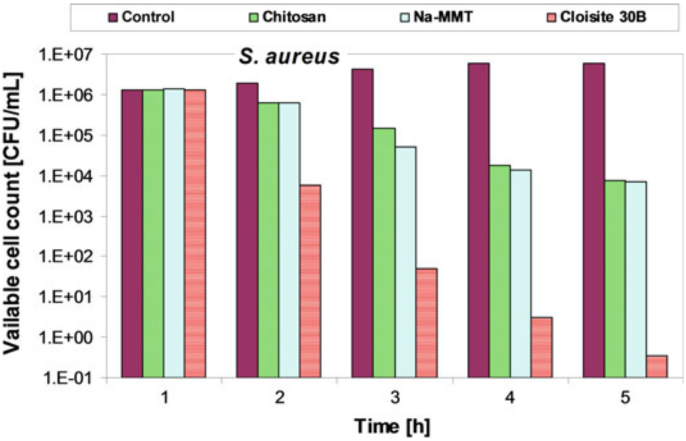


Fig. 4.3 Effect of antimicrobial activity of chitosan and chitosan-based nanocomposite films on broth cultures of *S. aureus*. Data adapted from Rhim et al. (2006)

concluded that the antimicrobial activity of the chitosan/clay nanocomposite was mainly due to the quaternary ammonium salt of the organophilic nanoclay (Cloisite 30B). The antimicrobial function of the quaternary ammonium cations in the organoclays was attributed to the positively charged ammonium group which interacts with the predominantly anionic molecules at the cell surface. This interaction could change the permeability of the cell membrane of the microorganisms, resulting in a leakage of intercellular components, and then the death of cell (Helander et al. 2001). Wang et al. (2006, 2007, 2009) performed a series of antimicrobial studies with chitosan/unmodified Ca^{2+}-rectorite (REC) and chitosan/organic modified rectorite with cetyltrimethyl ammonium bromide (OREC) nanocomposite films prepared by a solution intercalation method. They evaluated the antibacterial activity of the nanocomposites by determining the minimum inhibition concentration (MIC) and the relative inhibition time (RIT) and found that although the pristine REC did not inhibit the growth of bacteria, both chitosan-based nanocomposites showed higher antimicrobial activity than pure chitosan, particularly against Gram-positive bacteria, showing the strongest activity by the chitosan/OREC nanocomposite (Wang et al. 2006). They also found that the antibacterial activity of the nanocomposites increased with the increase of the amount of clay and the interlayer distance of the layered silicates in the nanocomposite. They confirmed the result by using the total colony count method for testing the antimicrobial activity (Wang et al. 2007). They suggested two stages of antibacterial mechanism of the nanocomposites: (i) adsorption of the bacteria and immobilization on the clay surface and (ii) accumulation of chitosan on the clay surface and inhibition of bacterial growth. Antimicrobial activity was also evaluated on different bio-nanocomposite films composed of agar and PLA filled with Cloisite 30B (Rhim et al. 2009, 2011; Sothornvit et al. 2009). Bio-nanocomposites with antimicrobial function are highly useful to minimize the growth of post-processing contaminant microorganisms, extending shelf life of food and improving food safety.

4.2.2 Hydrotalcites

Layered double hydroxides (LDHs) represent another interesting class of inorganic nanomaterials for food contact materials [61]. LDH particles are constituted by magnesium aluminum hydroxide layers (Fig. 4.4) (Tronto et al. 2013). In contrast to layered silicates, the hydroxide layers display a positive surface charge which is counterbalanced by anions located in the domains between adjacent layers (Sorrentino et al. 2005). Their structure is similar to that of brucite mineral, magnesium hydroxide, easy to find in nature. In this mineral, Mg atoms are octaedrically coordinated to six oxygen atoms belonging to six groups of –OH; each –OH group is, in turn, shared by three octaedrical cations and points the hydrogen atom to the interlayer space. When some of Mg(II) cations are isomorphously replaced by Al(III) cations, the substitution generates positive charges that are counterbalanced

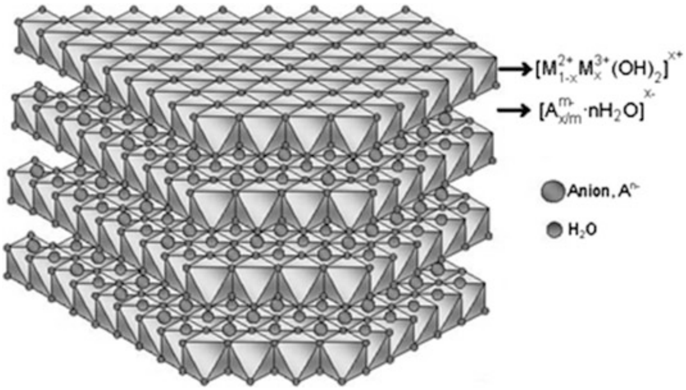


Fig. 4.4 Schematic representation of the layered double hydroxide structure. Reproduced from Tronto et al. (2013)

by the presence of counter ions located in the interlamellar regions. The possibility to substitute these anions by simple ionic exchange procedure makes the hydrotalcites ideal solids to be used as host of potentially active molecules having a negative charge. LDHs can be prepared with simple procedures and high level of purity; they are also economic and eco-compatible. For these reasons, they are excellent as fillers for active food contact materials (Rives 2001).

Benzoate (Bz), 2,4-dichlorobenzoate (BzDC), and para- and ortho-hydroxybenzoate (p- and o-BzOH) anions with antimicrobial activity were intercalated into $[Zn_{0.65}Al_{0.35}(OH)_2](NO_3)_{0.35} \times 0.6H_2O$, layered double hydroxide (LDH), via anion exchange reactions (Costantino et al. 2009; Bugatti et al. 2010, 2011). Such nanohybrids were dispersed into a poly(ε-caprolactone) biodegradable matrix, through high-energy ball milling, at different concentrations. Composites have been considered for “active packaging” applications because of the antimicrobial properties of the anions anchored to the LDH layer. X-ray diffraction analysis and optical and scanning electron microscopy of the composites indicate that the LDH samples containing BzDC anions were delaminated into the polymeric matrix, whereas those containing p-BzOH anions maintained, for the most part, the crystal packing and gave rise to microcomposites. Intermediate behavior was found for LDH modified with Bz and o-BzOH anions because exfoliated and partly intercalated composites were obtained. Mechanical and barrier properties to water vapor were also investigated and correlated to the chemical structure of the host active molecule and to the nanohybrid loading into the composites. An improvement in mechanical properties, due to the inorganic part reinforcement, was observed. The barrier properties to water vapor were also investigated. The improvement in the barrier properties, as a result of the decrease of diffusion, was maximum for samples with dichlorobenzoate anions, in the entire composition range. It was concluded that it is not the content of inorganic phase alone, but the type of dispersion (exfoliation and/or partial exfoliation) of the inorganic

Table 4.1 Antimicrobial activity of LDH-p-BzOH/PCL composite with 10 wt% of nanohybrid (data from Costantino et al. 2009)

Sample	CFU (*S. cerevisiae*)/cm^3
Unfilled PCL	248 ± 10
PCL filled with LDH- p-BzOH (10 wt%)	150 ± 8

component in the polymer phase that is important for improving the barrier properties of the samples. Table 4.1 reports the bacterial growth for unfilled PCL, composite with PCL/ZnAl-p-BzOH10 film (nanohybrid with 10 wt% of LDH and p-Bz OH molecule) (Costantino et al. 2009). The polymer does not show antimicrobial activity, with the *S. cerevisiae* concentration being very close to that of the yeasts in a pure culture medium (250 CFU/cm^3). The presence of p-BzOH in the composite film inhibited the microbial growth by 40%.

The release of the benzoate molecules from the lamellar solid incorporated into the polymeric matrix is much slower than the release of the same molecule simply blended to the PCL. Consequently, such systems are very promising in the active packaging field (Bugatti et al. 2010).

Nanocomposites of apple peel pectin with 5 wt% of nanohybrid fillers based on a Zn/Al layered double hydroxide (LDH) with anchored molecules having antimicrobial activity, [benzoate (Bz), 2,4-dichlorobenzoate (DCBz), para-hydroxybenzoate (p-OHBz), and ortho-hydroxybenzoate (o-OHBz)], were prepared through high-energy ball milling (HEBM) in the presence of water (Gorrasi et al. 2012). Milled composites were cast from water and films obtained analyzed. X-ray diffractometric analysis showed a complete destruction of all nanohybrids in the pectin matrix. Mechanical properties displayed an improvement in elastic modulus in particular for LDH-para-hydroxybenzoate nanohybrid, due probably to a better interaction between the pectin matrix and nanohybrid layers. Barrier properties to water vapor [sorption at R.H. = 20% and the diffusion coefficient, D_0 (cm^2/s)] showed improvement dependent on the intercalated active molecule. The best improvement was achieved for composites containing para-hydroxybenzoate molecules, suggesting that the interaction between the filler and the pectin plays an important role in sorption and diffusion phenomena. Incorporation of these active molecules gave antimicrobial properties to the composite films giving opportunities in the field of active packaging (Fig. 4.5).

4.2.3 Halloysites

Natural halloysites are two-layered aluminosilicate clay, $Al_2Si_2O_5(OH)_4 \times nH_2O$, which exhibit a predominant form of hollow tubes, and are chemically similar to kaolin (Fig. 4.6) (Yah et al. 2012). They present an external diameter of 50–80 nm, lumen of 10–15 nm, and length of about 1000 nm (Joussein et al. 2005; Kautz and Ryan 2003; Hillier and Ryan 2002). Due to the tubular shape and less abundant

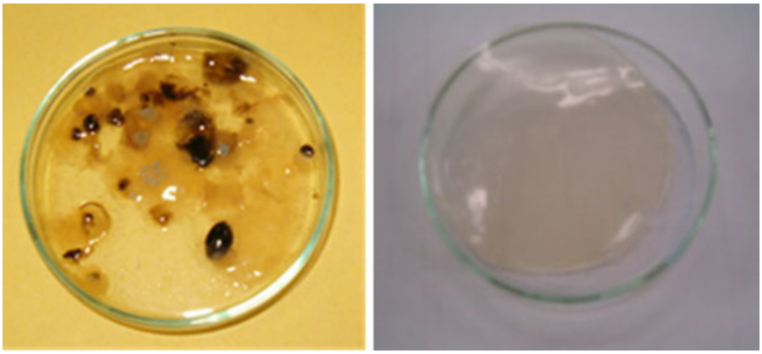
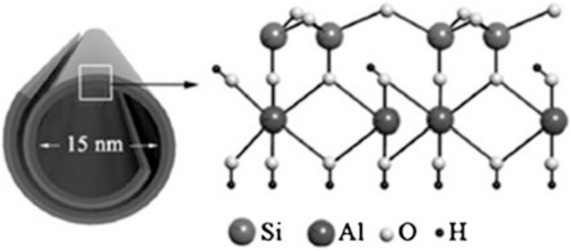


Fig. 4.5 Pictures of film of pure pectin and composite with 5 wt% of LDH-p-OHBz after 12 months of storage at ambient temperature (from Gorrasi et al. 2012)

Fig. 4.6 Schematic illustration of crystalline structure of halloysite. Reproduced from Yah et al. (2012)



surface hydroxyl groups, halloysites can be readily dispersed in polymers without need for the exfoliation, as in the case of layered silicates (Du et al. 2010). Polymeric composite materials may be filled with these tubule containers that are able to release specific active molecules (antimicrobials, oxygen scavengers, etc.) in a sustained fashion. Halloysite lumen loading capacity is 15–20 wt%, and chemical agents release time may vary from 5–10 h to several days (Lvov and Abdullayev 2013; Liu et al. 2014). Halloysite has found application in the areas of bio-sorbents for heavy metal ions and dyes and nanofillers in biopolymer matrices. These nanotubes were functionalized with amylose, resulting in an increase in dispersion of the halloysite in a hydrophilic substrate, enabling compatibility with several kinds of hydrophilic polymers (Chang et al. 2011). Gorrasi (2014) reported the preparation of green nanocomposites based on pectin and a nanohybrid composed of natural halloysite (HNTs) and rosemary oil. Essential oils, applied to the formulation of edible films, provide them additional antioxidant and/or antimicrobial properties. X-ray analysis on the composites showed that pure pectin presents an amorphous structure, which is retained in all the composites. The basal peak of dehydrated HNTs tends to disappear and/or to be expanded after the intercalation of essential oil, and the ball milling assisted mixing with pectin in the presence of water. Mechanical properties showed an improvement in all the mechanical parameters. In particular, the elongation at break point reached values up to 50%.

Fig. 4.7 Rosmarinic acid released fraction (wt/wt%) as function of contact time (h)$^{1/2}$ for pectin and 15 wt% of rosemary oil directly dispersed into pectin (*open square*), and HNTs loaded (*open diamond*)

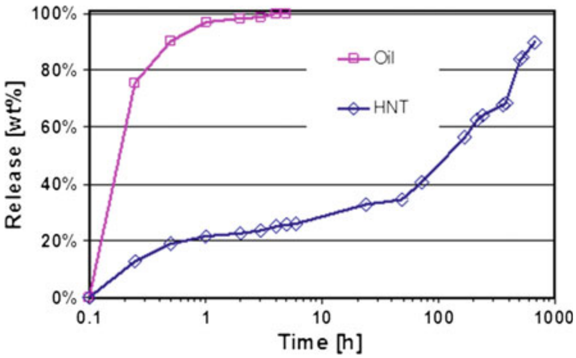
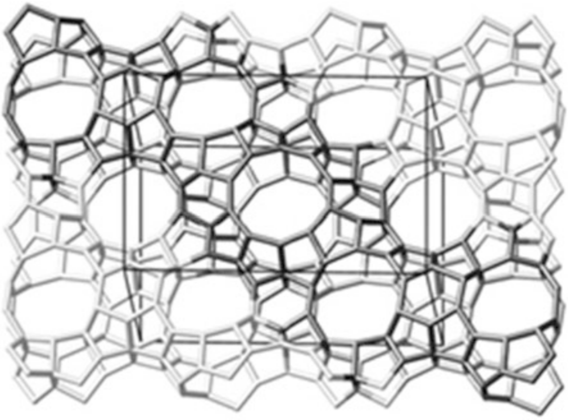


Fig. 4.8 Example of zeolite structure



Barrier properties to water vapor, in terms of diffusion, resulted improved. The thermodynamic diffusion coefficient decreased on increasing the nanohybrid loading. The presence of the filler increased the tortuosity of the system, leading to a decrease in the value of the diffusion coefficient. A comparison of the molecular release of the rosmarinic acid molecules directly dispersed in pectin and in the nanohybrid was shown, indicating the much slower release in the latter case (Fig. 4.7).

4.2.4 Zeolites

Zeolites are natural porous aluminosilicates which have a crystalline structure. In these crystalline materials, the metal atoms (classically, silicon, or aluminum) are surrounded by four oxygen anions to form an approximate tetrahedron consisting of a metal cation at the center and oxygen anions at the four apexes (Fig. 4.8)

(Corma and Martinez 1995; Wong 2009). The main reason for the zeolites' interest lies in their crystalline structure with microscopic channels, which have a negative charge (Willhammar et al. 2012; Corma et al. 2003). The size and shape of the channels have extraordinary effects on the properties of these materials for adsorption processes, and this property leads to their use in separation processes (Smit and Maesen 2008a). Molecules can be separated via shape and size effects related to their possible orientation in the pore, or by differences in strength of adsorption (Smit and Maesen 2008b). Zeolites are characterized by the ability to lose and gain water reversibly and to exchange constituent cations without major changes of structure (Inglezakis and Zorpas 2012). Natural zeolites are the main absorptive, low-cost material used in agriculture and industry (Bailey et al. 1999; Kurniawan et al. 2006; Babel 2003). There is a favorable situation for potential applications of zeolite in industrial and agricultural wastewater purification, aquaculture, animal feeding, agriculture, and horticulture (Auerbach et al. 2003). Zeolite is important in medicine as they have a positive effect on detoxification of the body (Genuis 2011; Genuis et al. 2010), removal of pollutants and capture of free radicals, increasing the stability of the immune system, controlling mineral metabolism, increasing mental and physical performance, inhibition of the aging process, and stress-reducing effect (Auerbach et al. 2003; Pavelić et al. 2001; Grancaric et al. 2009). Synthetic silver zeolite hybrids, which are produced by substituting the Na^+ ion in the mineral zeolites with Ag^+ ion, are one of the most widely used antimicrobial agents since it possesses a broad antimicrobial spectrum of microorganisms such as bacteria, yeast, and mycelium fungi (Fernández et al. 2010). They have been incorporated into food contact packaging film because of their role in allowing slow release of antimicrobial silver ions into the surface of food products (Hrenović et al. 2003; Joseph Kerry 2008). Ag-zeolites did not show any antimicrobial activity against spores of heat-resistant bacteria, but rather only against vegetative cells (Fernández et al. 2010). Ag-zeolites incorporated into chitosan showed strong antimicrobial activity against both Gram-positive and Gram-negative bacteria (Rhim et al. 2006).

The efficiency of antimicrobial function of these polymeric nanocomposites is greatly influenced by many factors such as silver content, particle size, size distribution, degree of particle agglomeration, interaction of silver surface with the base polymer (Kim et al. 2007). Zeolite containing copper ions exhibits good antibacterial activity for both Gram-negative and Gram-positive bacteria and the effect developed in a short period of time (Auerbach et al. 2003).

4.2.5 Mica and Talc

Mica represents a group of phyllosilicate minerals having close to perfect basal cleavage (Mineral Information Institute 2008; Dietrich 2013). It means that mica separates easily into small flat planar surfaces as determined by the structure of its crystal lattice. These two-dimensional surfaces, often used to make electrical insulator, are caused by the alignment of weaker bonds between atoms in the crystal lattice. The general formula for the mica minerals is $XY_{2\text{-}3}[(Si,Al)_4O_{10}](OH,F)_2$, where X = K,Na,Ca and Y = Mg,Fe,Li,Al. Their structure consists of double sheets of strongly joined silica units (SiO_4) that sandwich between them a sheet of hydroxyl (OH) plus Y cations. The X cations lie between these sandwiches and bind them loosely.

The mica sheets are chemically inert, dielectric, elastic, flexible, hydrophilic, insulating, lightweight, platy, reflective, refractive, resilient, and range in opacity from transparent to opaque (Kauffman et al. 1974). Mica is stable when exposed to electricity, light, moisture, and extreme temperatures (Murray 2000).

The term talc refers to a naturally occurring mineral with chemical formula $Mg_3Si_4\ O_{10}(OH)_2$ and a platelike structure composed of a layer of magnesium–oxygen/hydroxyl octahedra, sandwiched between two layers of tetrahedral silica (Deer et al. 1996). In nature, it is found as steatite or soapstone, which is composed of varying proportions of the mineral talc, often combined with other minerals such as chlorite and carbonate. Highly lamellar talc will have large individual platelets, whereas microcrystalline talc will have small platelets. It is odorless, insoluble in water but slightly soluble in dilute mineral acids. It is neither explosive nor flammable. Although talc has a marked affinity for certain organic chemicals, it generally has very little chemical reactivity (Giese and van Oss 2002). Its color ranges from white to gray or green, and it has a distinctly greasy feel. Talc material is irreplaceable in a large number of industrial applications such as ceramics manufacturing, paints, rubber, cables, paper, lead, pharmaceutical products, insecticides and herbicides, civil engineering, military industry (McCarthy 2000). In medicine, talc is used as a pleurodesis agent to prevent recurrent pleural effusion or pneumothorax (Sahn 2000). Talc is used as food additive or in pharmaceutical products as a glidant. It is also used as an antisticking agent, an anticaking agent, a lubricant, a carrier, a thickener, strengthening filler, smooth filler, surface-finishing, and texturizing agent (Burdock 1997; Zazenski et al. 1995).

Talc is used as filler in polymeric matrix to improve mechanical properties, thermal resistance, and dimensional stability, all at a low cost (Sakthivel and Pitchumani 2011; Ewen et al. 1988; Setz et al. 1996; Maiti and Sharma 1992; Denault and Vu-Khanh 1992; Stricker et al. 1997). The performance of polymer/inorganic composites is strongly related to the interfacial adhesion between the polymer and the filler.

Mica and talc have high surface energy and inherently poor interactions with nonpolar materials. In order to increase the interaction with chemically inert polymer, a variety of coupling agents, including silanes (Alonso et al. 1997), titanium esters (Ai Wah et al. 2000), phosphate, aluminate, and zirconate, have been adopted to modify the interfacial structure. Talc and Mica-filled polymer composite has low specific gravity and combine excellent chemical resistance with low cost (Zihlif and Ragosta 2003; Tripathi et al. 2011; Mahmoud 2012; Chen 2004).

4.3 Regulation Issues

Several studies have been carried out to identify any regulatory gap in the field of nanotechnology (Wyser et al. 2016). They cover different countries, such as the European Union (EU), United States (USA), and Australia, and concluded that existing frameworks are broad enough to deeply regulate nanotechnology applications for food and food packaging (Magnuson et al. 2013; Chaudhry et al. 2008; Sonkaria et al. 2012). Following this, we aim to describe the relevant regulatory frameworks in EU and in USA, and the current regulatory position regarding the applications of nanotechnologies for food packaging.

4.3.1 European Union

Food contact materials (FCMs) are regulated by regulation (EC) No. 1935/2004 on materials and articles intended to come into contact with food (Benckiser 2012; EC 2004). This regulation sets the general rules for FCM with regard to their safety, labeling, and traceability. Specific measures have been adopted for plastics (EU 2011), ceramics (EU 1984), regenerated cellulose film (EC 2007), recycled plastics (EC 2008a), and active and intelligent materials and articles (EC 2009). Materials not covered by the EU-harmonized specific measures are subject to national legislations. Some EU regulations include requirements for nanomaterials; however, no definition is reported. For this reason, it is usually accepted the Recommendation 696/2011 (EC 2011) for a definition of nanomaterial is adopted by the European Commission in 2011 which reports "*Nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100* nm. *In specific cases and where warranted by concerns for the environment, health, safety or competitiveness, the number size distribution threshold of 50% may be replaced by a threshold between 1 and 50%.*" The Recommendation also contains a deadline for its revision by December 2014, which up to now (2016) was not achieved. Nevertheless, the Joint Research Center of the European commission recently completed a series of three reports that evaluate the current definition and present options in view of its revision (Wyser et al. 2016). It can therefore be reasonably expected that the definition contained in Recommendation 696/2011 might evolve in the forthcoming months. Polymeric materials are covered by Regulation 10/201132 and its amendments. Natural macromolecules not chemically modified are not within the scope of the plastics regulation. The use of additives to modify the macromolecule's properties is not considered a chemical modification. Only authorized nanoparticles specifically mentioned in the specification of Annex I of the above-mentioned regulation can be used in plastic packaging. This applies also to nanoparticles intended to be used as functional barrier. The Annex has been amended on the basis of several opinions published by the European Food Safety Authority (EFSA) on nanomaterial for use in FCM, and other materials have been added with specific conditions of use (EFSA 2012a, b, 2014, 2015). Active packaging, which covers also some reported in this chapter, is covered by Regulation 450/2009 (EC 2009). They represent materials and articles to extend the shelf life or to improve the condition of packed food. They are projected to deliberately incorporate components that would release or absorb substances into or from the packed food or the environment surrounding the food. Substances released into food to become a component of the food must comply with food legislation (EC 2008b). Currently, no nanoparticles have been authorized as food preservatives or antioxidants in the EU. If such nanoparticles are to be used in active materials, then an application for authorization would need to be submitted under the authorization scheme for food additives. For substances forming part of the active or intelligent component, and which are not intentionally released, the Regulation (EU) No. 450/200936 provides the authorization scheme. Currently, EU is developing a list of authorized substances for use in active and intelligent packaging applications. Once completed, only those substances listed will be authorized for use in active and intelligent packaging components.

All other materials have to comply with the general safety requirements of the Framework Regulation and specific national legislation. The Framework Regulation requires, in particular, that materials and articles should not release its constituents in concentrations that could:

- cause deterioration in the organoleptic characteristics of the packed food
- cause an unacceptable change in the composition of the packed food
- be harmful for human health.

4.3.2 United States (USA)

The Food and Drug Administration (FDA), the agency within the US Department of Health and Human Services, is responsible for protecting the public health by assuring the safety, efficacy, and security of human and veterinary drugs, biological products, medical devices, USA's food supply, cosmetics, and products that emit radiation. FDA is also responsible for the advancement of the public health speeding the innovations that make medicines more effective, safer, and more affordable (www.fda.gov). A new food contact substance (FCS) must be the subject of a food contact notification (FCN) to be lawfully used. For a new FCS authorization, FDA focuses on particle size when it is important for the identity of the food contact substance, when it impacts the functionality of the food substance, or when it impacts the intended technical effect. The FDA offers guidance to the regulated industry on the submission of new FCMs. While the current guidance documents for FCNs (FDA 2007) do not presently make specific recommendations regarding nanomaterials, the chemistry guidance does address the issue of properties that are specific to particle size (FDA 2014). More specific requirements will be addressed in future revisions of the guidance documents. At moment, the FDA offers informal advice on the issues of interest when evaluating these materials. The regulatory status of nanoscale versions of FCSs is a questioned issue. In the absence of formal guidance, FDA has been addressing these questions on a case-by-case basis. For currently approved direct and indirect food additives, and food contact substances, the use of the additive is no longer in compliance with an existing regulation if the change in manufacturing practice alters the chemical such that the chemical identity and composition are no longer the same as the approved compound (FDA 2014). Ultimately, the manufacturer has the responsibility to ensure that the foods and food components that they bring to market are safe and lawful. Thus, the manufacturer or user has an obligation to take all appropriate steps to ensure that the substance as manufactured is safe and lawful under the conditions of its intended use. FDA encourages food manufacturers to conduct a thorough safety assessment of all manufacturing changes. As earlier mentioned, a guidance document has been published in June 2014 to address the impact of manufacturing changes, including nanotechnology, on the regulatory status of FCSs (FDA 2014). The FDA encourages manufacturers to consult with this guidance document, as well as other relevant guidance documents (FDA 2016), and also to consult with the FDA before undertaking any experimental activities in support of submission of a future FCN, in order to discuss pertinent issues for the achievement of a mutual understanding.

4.4 Conclusions and Future Perspectives

Nanotechnology offers new opportunities in projecting and formulating novel, food contact materials. They will allow to obtain smart and intelligent packaging and able to considerably enhance the shelf life of many types of food. This can lead to lower weight packages because less material is needed to obtain the same or even better barrier properties. A general reduction in package cost and waste is expected. Furthermore, a complete transition from packaging with metal layers and glass containers to flexible packaging will be possible when the control of the physical properties of these materials will be enough to compete in all environmental conditions. Therefore, science and technology are called to further improve the nanoparticle properties, including the development of the optimum formulation for the polymer and processing method to obtain desired properties. In addition, there are some safety concerns about the use of nanocomposites as food contact materials. There is a limited scientific database about the migration of nanostructures from packaging materials into packed products. Significant research effort is still required to evaluate the potential toxicity of nanocomposite materials, as well as the environmental safety of their use. However, nanomaterials appear to have a bright future for a wide range of applications in the food and biomedical industries, as well as innovative active and intelligent food packaging with structural and bio-functional properties. Furthermore, it is clear that the enthusiasm with respect to such nanohybrid systems must be accompanied with a critical attention to the safety of the consumers and the healthcare workers in the context of stringent regulatory approval perspectives.

Acknowledgement A. Sorrentino acknowledges financial support from the "FHfFC" (Future Home for Future Communities) project, D.R. Lombardia n. 7784 del 05/08/2016, CUP:B16J16001430002.

References

Ai Wah C, Yub Choong L, Seng Neon G (2000) Effects of titanate coupling agent on rheological behaviour, dispersion characteristics and mechanical properties of talc filled polypropylene. Eur Polym J 36(4):789–801. http://www.sciencedirect.com/science/article/pii/S0014305799001238. Accessed 9 Sept 2014

Ajayan PM, Schadler LS, Braun PV (eds) (2003) Nanocomposite science and technology. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG. http://doi.wiley.com/10.1002/3527602127. Accessed 26 Mar 2014

Alexandre M, Dubois P (2000) Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater Sci Eng R Rep 28(1–2):1–63. http://www.sciencedirect.com/science/article/pii/S0927796X00000127. Accessed 13 Apr 2014

Alonso M, Velasco J, de Saja J (1997) Constrained crystallization and activity of filler in surface modified talc polypropylene composites. Eur Polym J 33(3):255–262. http://linkinghub.elsevier.com/retrieve/pii/S0014305796001590. Accessed 9 Sept 2014

Auerbach SM, Carrado KA, Dutta PK (2003) Handbook of zeolite science and technology. CRC Press. http://books.google.com/books?id=onSMvcjgB1YC&pgis=1. Accessed 10 Sept 2014

Augustin MA, Sanguansri P (2009) Nanostructured materials in the food industry. Adv Food Nutr Res 58:183–213. http://www.ncbi.nlm.nih.gov/pubmed/19878860. Accessed 10 Sept 2014

Babel S (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater 97(1–3):219–243. http://www.sciencedirect.com/science/article/pii/S0304389402002637. Accessed 11 Sept 2014

Bailey SE et al (1999) A review of potentially low-cost sorbents for heavy metals. Water Res 33(11):2469–2479. http://www.sciencedirect.com/science/article/pii/S0043135498004758. Accessed 11 Sept 2014

Baldwin EA, Hagenmaier R, Bai J (2011) Edible coatings and films to improve food quality. CRC Press

Benckiser G (2012) Nanotechnology and patents in agriculture, food technology, nutrition and medicine—advantages and risks: worldwide patented nano- and absorber particles in food nutrition and agriculture. Recent Pat Food Nutr Agric 4(3):171–175. http://www.ncbi.nlm.nih.gov/pubmed/23061649

Brody AL (1997) Packaging, food. Wiley Online Library

Bugatti V et al (2010) Nano-hybrids incorporation into poly(ε-caprolactone) for multifunctional applications: mechanical and barrier properties. Eur Polym J 46(3):418–427. http://www.sciencedirect.com/science/article/pii/S0014305709004601. Accessed 30 Nov 2012

Bugatti V et al (2011) Modified layered double hydroxides in polycaprolactone as a tunable delivery system: in vitro release of antimicrobial benzoate derivatives. Appl Clay Sci 52(1–2):34–40. http://www.sciencedirect.com/science/article/pii/S016913171100041X. Accessed 29 Oct 2012

Burdock GA (ed) (1997) Encyclopedia of food and color additives, vol 1. CRC Press. http://books.google.com/books?id=vxtxWneRBN4C&pgis=1. Accessed 11 Sept 2014

Chandrasekaran G et al (2011) Antimicrobial activity of delaminated aminopropyl functionalized magnesium phyllosilicates. Appl Clay Sci 53(4):729–736. http://www.sciencedirect.com/science/article/pii/S0169131711002407. Accessed 9 Sept 2014

Chang PR et al (2011) Amylose wrapped halloysite nanotubes. Carbohydr Poly 84(4):1426–1429. http://linkinghub.elsevier.com/retrieve/pii/S0144861711000713. Accessed 11 Sept 2014

Chaudhry Q et al (2008) Applications and implications of nanotechnologies for the food sector. Food Addit Contam Part A 25(3):241–258. http://www.ncbi.nlm.nih.gov/pubmed/18311618. Accessed 10 Sept 2014

Chen B (2004) Polymer–clay nanocomposites: an overview with emphasis on interaction mechanisms. Br Ceram Trans 103(6):241–249. http://www.maneyonline.com/doi/abs/10.1179/096797804X4592. Accessed 4 Sept 2014

Coles R, McDowell D, Kirwan MJ (2003) Food packaging technology. CRC Press

Collister J (2001) Commercialization of polymer nanocomposites. In: Polymer nanocomposites. ACS Symposium Series. American Chemical Society, pp 2–7. doi:10.1021/bk-2002-0804.ch002

Corma A, Martinez A (1995) Zeolites and zeotypes as catalysts. Adv Mater 7(2):137–144. http://doi.wiley.com/10.1002/adma.19950070206. Accessed 11 Sept 2014

Corma A et al (2003) A zeolite with interconnected 8-, 10- and 12-ring pores and its unique catalytic selectivity. Nat Mater 2(7):493–497. http://www.ncbi.nlm.nih.gov/pubmed/12819773. Accessed 11 Sept 2014

Costantino U et al (2009) New polymeric composites based on poly(-caprolactone) and layered double hydroxides containing antimicrobial species. ACS Appl Mater Interfaces 1(3):668–677. http://www.ncbi.nlm.nih.gov/pubmed/20355989. Accessed 10 Nov 2012

Cruz RS, Camilloto GP, dos Santos Pires AC (2012) Oxygen scavengers: an approach on food preservation. In: Amer Eissa A (ed) Structure and function of food engineering. InTech, pp 21–42. http://www.intechopen.com/books/structure-and-function-of-food-engineering. Accessed 10 Sept 2014

Damm C, Münstedt H, Rösch A (2008) The antimicrobial efficacy of polyamide 6/silver-nano- and microcomposites. Mater Chem Phys 108(1):61–66. http://www.sciencedirect.com/science/article/pii/S0254058407005524. Accessed 5 Aug 2014

de Azeredo HMC (2009) Nanocomposites for food packaging applications. Food Res Int 42(9):1240–1253. http://linkinghub.elsevier.com/retrieve/pii/S096399690900091X. Accessed 11 July 2014

Deer WA, Howie RA, Zussman J (1996) An introduction to the rock-forming minerals, 2nd edn. Prentice Hall. http://www.amazon.com/Introduction-Rock-Forming-Minerals-2nd-Edition/dp/0582300940. Accessed 11 Sept 2014

Denault J, Vu-Khanh T (1992) Crystallization behavior and effect of thermal treatment on fracture performance of glass flake reinforced polypropylene. Polym Compos 13(5):372–379. http://doi.wiley.com/10.1002/pc.750130506. Accessed 9 Sept 2014

Dietrich RV (2013) Mica (mineral). Encyclopedia Britannica. http://www.britannica.com/EBchecked/topic/379747/mica. Accessed 11 Sept 2014

Dingman J., Nanotechnology: its impact on food safety. J Environ Health 70(6):47–50. http://www.ncbi.nlm.nih.gov/pubmed/18236938. Accessed 10 Sept 2014

Du M, Guo B, Jia D (2010) Newly emerging applications of halloysite nanotubes: a review. Polym Int 59:574–582. http://doi.wiley.com/10.1002/pi.2754. Accessed 11 Sept 2014

Duncan TV (2011) Applications of nanotechnology in food packaging and food safety: barrier materials, antimicrobials and sensors. J Colloid Interface Sci 363(1):1–24. http://www.ncbi.nlm.nih.gov/pubmed/21824625. Accessed 11 July 2014

EC (2004) Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004 on materials and articles intended to come into contact with food and repealing

EC (2007) Commission directive 2007/42/EC of 29 June 2007 relating to materials and articles made of regenerated cellulose film intended to come into contact with foodstuffs (codified version) text with EEA relevance

EC (2008a) Commission Regulation (EC) No 282/2008 of 27 March 2008 on recycled plastic materials and articles intended to come into contact with foods and amending Regulation (EC) No 2023/2006

EC (2008b) Regulation (EC) No 1333/2008 of the European Parliament and of the Council of 16 December 2008 on food additives

EC (2009) Commission Regulation (EC) No 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food

EC (2011) Commission recommendation of 18 October 2011 on the definition of nanomaterial

EFSA (2012a) Scientific Opinion on the safety evaluation of the active substance iron (II) modified bentonite as oxygen absorber for use in active food contact materials. EFSA J 10(10):2906. http://doi.wiley.com/10.2903/j.efsa.2012.2906

EFSA (2012b) Scientific Opinion on the safety evaluation of the substance, titanium nitride, nanoparticles, for use in food contact materials. EFSA J 10(3):2641. http://doi.wiley.com/10.2903/j.efsa.2012.2641

EFSA (2014) Scientific Opinion on the safety assessment of the substances, kaolin and polyacrylic acid, sodium salt, for use in food contact materials. EFSA J 12(4):3637. http://doi.wiley.com/10.2903/j.efsa.2014.3637

EFSA (2015) Scientific Opinion on the safety evaluation of the substance zinc oxide, nanoparticles, uncoated and coated with [3-(methacryloxy)propyl] trimethoxysilane, for use in food contact materials. EFSA J 13(4):4063. http://doi.wiley.com/10.2903/j.efsa.2015.4063

Egger S et al (2009) Antimicrobial properties of a novel silver-silica nanocomposite material. Appl Environ Microbiol 75(9):2973–2976. http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=2681698&tool=pmcentrez&rendertype=abstract. Accessed 9 Sept 2014

Ensminger AH et al (1995). The concise encyclopedia of foods & nutrition. CRC Press Inc

EU (1984) Council Directive of 15 October 1984 on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with foodstuffs

EU (2011) Commission Regulation (EU) No. 10/2011 of 14 January 2011 on plastic materials intended to come into contact with food

Ewen JA et al (1988) Syndiospecific propylene polymerizations with Group IVB metallocenes. J Am Chem Soc 110(18):6255–6256. http://www.ncbi.nlm.nih.gov/pubmed/22148816. Accessed 9 Sept 2014

Farokhzad OC, Langer R (2009) Impact of nanotechnology on drug delivery. ACS Nano 3(1): 16–20. http://www.ncbi.nlm.nih.gov/pubmed/19206243. Accessed 26 Aug 2014

FDA (2007) https://www.fda.gov/Food/GuidanceRegulation/GuidanceDocumentsRegulatoryInformation/IngredientsAdditivesGRASPackaging/ucm081818.htm

FDA (2014) https://www.fda.gov/RegulatoryInformation/Guidances/ucm300661.htm

FDA (2016) http://www.fda.gov/food/IngredientsPackagingLabeling/default.htm

Fernández A et al (2010) Migration of antimicrobial silver from composites of polylactide with silver zeolites. J Food Sci 75(3):E186–E193. http://www.ncbi.nlm.nih.gov/pubmed/20492293. Accessed 9 Sept 2014

Genuis SJ (2011) Elimination of persistent toxicants from the human body. Hum Exp Toxicol 30 (1):3–18. http://het.sagepub.com/content/early/2010/04/20/0960327110368417.short. Accessed 4 Sept 2014

Genuis SJ et al (2010) Human detoxification of perfluorinated compounds. Public Health 124 (7):367–375. http://www.sciencedirect.com/science/article/pii/S0033350610000600. Accessed 11 Sept 2014

Giannelis EP, Krishnamoorti R, Manias E (1999) Polymer-silicate nanocomposites: model systems for confined polymers and polymer brushes. In: Granick S et al (eds) Polymers in confined environments SE-3. Advances in polymer science. Springer, Berlin, pp 107–147. doi:10.1007/3-540-69711-X_3

Giese RF, van Oss CJ (2002) Colloid and surface properties of clays and related minerals. CRC Press. http://books.google.com/books?hl=it&lr=&id=vUuYfFQkX40C&pgis=1. Accessed 11 Sept 2014

Gieseking JE (1938) The mechanism of cation exchange in the montmorillonite-beidellite-nontronite type of clay minerals. Soil Sci 47(1):1–14

Gorrasi G (2014) Dispersion of halloysite loaded with natural antimicrobials into pectins: characterization and controlled release analysis. Carbohydrate Polymers (In press)

Gorrasi G, Bugatti V, Vittoria V (2012) Pectins filled with LDH-antimicrobial molecules: preparation, characterization and physical properties. Carbohydr Polym 89(1):132–137. http://www.sciencedirect.com/science/article/pii/S0144861712001981. Accessed 30 Nov 2012

Grancaric A, Tarbuk A, Kovacek I (2009) Nanoparticles of activated natural zeolite on textiles for protection and therapy. Chem Ind Chem Eng Q 15(4):203–210. http://www.doiserbia.nb.rs/Article.aspx?ID=1451-93720904203G. Accessed 11 Sept 2014

Hajipour MJ et al (2012) Antibacterial properties of nanoparticles. Trends Biotechnol 30(10):499–511. http://www.ncbi.nlm.nih.gov/pubmed/22884769. Accessed 12 July 2014

Hatzigrigoriou NB, Papaspyrides CD (2011) Nanotechnology in plastic food-contact materials. J Appl Polym Sci 122(6):3719–3738. http://doi.wiley.com/10.1002/app.34786. Accessed 10 Sept 2014

Helander I et al (2001) Chitosan disrupts the barrier properties of the outer membrane of Gram-negative bacteria. Int J Food Microbiol 71(2–3):235–244. http://www.sciencedirect.com/science/article/pii/S0168160501006092. Accessed 28 Aug 2014

Hillier S, Ryan PC (2002) Identification of halloysite (7 Å) by ethylene glycol solvation: the "MacEwan effect." Clay Miner 37(3):487–496. http://www.ingentaselect.com/rpsv/cgi-bin/cgi?ini=xref&body=linker&reqdoi=10.1180/0009855023730047. Accessed 11 Sept 2014

Hong S-I, Rhim J-W (2008) Antimicrobial activity of organically modified nano-clays. J Nanosci Nanotechnol 8(11):5818–5824. http://www.ncbi.nlm.nih.gov/pubmed/19198311. Accessed 9 Sept 2014

Hotchkiss JH (1997) Food-packaging interactions influencing quality and safety. Food Addit Contam 14(6–7):601–607. http://www.ncbi.nlm.nih.gov/pubmed/9373524. Accessed 8 Sept 2014

Hrenović J, Büyükgüngör H, Orhan Y (2003) Use of natural zeolite to upgrade activated sludge process. Food Technol Biotechnol 41(2):157–165. http://hrcak.srce.hr/index.php?show=clanak&id_clanak_jezik=163976. Accessed 10 Sept 2014

Hughes GA (2005) Nanostructure-mediated drug delivery. Nanomed Nanotechnol Biol Med 1(1):22–30. http://www.ncbi.nlm.nih.gov/pubmed/17292054. Accessed 29 July 2014

Hussain F (2006) Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. J Compos Mater 40(17):1511–1575. http://jcm.sagepub.com/cgi/doi/10.1177/0021998306067321. Accessed 25 Mar 2014

Imran M et al (2010) Active food packaging evolution: transformation from micro- to nanotechnology. Crit Rev Food Sci Nutr 50(9):799–821. http://www.ncbi.nlm.nih.gov/pubmed/20924864. Accessed 28 Aug 2014

Inglezakis VJ, Zorpas AA (eds) (2012) Handbook of natural zeolites. Bentham Science Publishers. http://books.google.com/books?id=p88zmymzTMUC&pgis=1. Accessed 10 Sept 2014

Joseph Kerry PB (ed) (2008) Smart packaging technologies for fast moving consumer goods. Wiley. http://books.google.com/books?id=XKeW-I1rVTIC&pgis=1. Accessed 10 Sept 2014

Joussein E et al (2005) Halloysite clay minerals—a review. Clay Miner 40(4):383–426. http://claymin.geoscienceworld.org/content/40/4/383.abstract. Accessed 15 Aug 2014

Kauffman SH et al (1974) The preparation and classification of high aspect ratio mica flakes for use in polymer reinforcement. Powder Technol 9(2–3):125–133. http://linkinghub.elsevier.com/retrieve/pii/0032591074850175. Accessed 11 Sept 2014

Kautz CQ, Ryan PC (2003) The 10 Å to 7 Å halloysite transition in a tropical soil sequence, Costa Rica. Clays Clay Miner 51(3):252–263. http://www.ingentaselect.com/rpsv/cgi-bin/cgi?ini=xref&body=linker&reqdoi=10.1346/CCMN.2003.0510302. Accessed 11 Sept 2014

Khan IA, Abourashed EA (2011) Leung's encyclopedia of common natural ingredients: used in food, drugs and cosmetics. Wiley

Kim JS et al (2007) Antimicrobial effects of silver nanoparticles. Nanomed Nanotechnol Biol Med 3(1):95–101. http://www.nanomedjournal.com/article/S1549-9634(06)00346-7/abstract. Accessed 9 July 2014

Kurniawan TA et al (2006) Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. Sci Total Environ 366(2–3):409–426. http://www.sciencedirect.com/science/article/pii/S004896970500728X. Accessed 24 Aug 2014

Lange J, Wyser Y (2003) Recent innovations in barrier technologies for plastic packaging? A review. Packag Technol Sci 16(4):149–158. http://doi.wiley.com/10.1002/pts.621. Accessed 10 Sept 2014

LeBaron P, Wang Z, Pinnavaia T (1999) Polymer-layered silicate nanocomposites: an overview. Appl Clay Sci. http://www.sciencedirect.com/science/article/pii/S0169131799000174. Accessed 11 Sept 2014

Lefebvre J-M (2002) Nanocomposites, polymer–clay. In: Encyclopedia of polymer science and technology. Wiley. doi:10.1002/0471440264.pst210

Li KS, Chen YH, Niu HM, Chen JJ (2011) Preparation of PVC/Kaolin nanocomposites through solid state shear compounding based on pan-milling. Mater Sci Forum 694:350–354. http://www.scientific.net/MSF.694.350. Accessed 24 Nov 2012

Liu M et al (2014) Recent advance in research on halloysite nanotubes-polymer nanocomposite. Prog Polym Sci 39(8):1498–1525. http://www.sciencedirect.com/science/article/pii/S0079670014000483. Accessed 30 July 2014

Llorens A et al (2012) Metallic-based micro and nanocomposites in food contact materials and active food packaging. Trends Food Sci Technol 24(1):19–29. http://linkinghub.elsevier.com/retrieve/pii/S0924224411002184. Accessed 10 July 2014

Lu C, Mai Y (2005) Influence of aspect ratio on barrier properties of polymer-clay nanocomposites. Phys Rev Lett. http://journals.aps.org/prl/abstract/10.1103/PhysRevLett.95.088303. Accessed 11 Sept 2014

Lu C, Mai Y (2007) Permeability modelling of polymer-layered silicate nanocomposites. Compos Sci Technol. http://www.sciencedirect.com/science/article/pii/S0266353807001819. Accessed 11 Sept 2014

Lvov Y, Abdullayev E (2013) Functional polymer–clay nanotube composites with sustained release of chemical agents. Prog Polym Sci 38(10–11):1690–1719. http://www.sciencedirect.com/science/article/pii/S0079670013000506. Accessed 28 Aug 2014

Magnuson B et al (2013) Review of the regulation and safety assessment of food substances in various countries and jurisdictions. Food Addit Contam Part A 30(7):1147–1220. http://www.tandfonline.com/doi/abs/10.1080/19440049.2013.795293

Mahmoud WE (2012) The physical properties of carbon nanoparticles dispersed into NBR/LLDPE nanocomposites for corrosion protection applications. J Appl Polym Sci 123(5):2667–2675. http://doi.wiley.com/10.1002/app.34665. Accessed 7 Jan 2014

Maiti SN, Sharma KK (1992) Studies on polypropylene composites filled with talc particles. J Mater Sci 27(17):4605–4613. http://link.springer.com/10.1007/BF01165994. Accessed 9 Sept 2014

McCarthy EF (2000) Talc. In: Kirk-Othmer encyclopedia of chemical technology. Wiley. doi:10.1002/0471238961.2001120313030301.a01.pub2

Mineral Information Institute (2008) Mica. http://www.eoearth.org/view/article/154599/. Accessed 11 Sept 2014

Murray HH (2000) Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. Appl Clay Sci 17(5–6):207–221. http://linkinghub.elsevier.com/retrieve/pii/S0169131700000168. Accessed 12 Aug 2014

Ohashi F, Oya A (1996) Antimicrobial and antifungal agents derived from clay minerals. J Mater Sci 31(13):3403–3407. http://link.springer.com/article/10.1007/BF00360741. Accessed 9 Sept 2014

Ohashi F et al (1998) Structural model calculation of antimicrobial and antifungal agents derived from clay minerals. Appl Clay Sci 12(6):435–445. http://www.sciencedirect.com/science/article/pii/S0169131798000088. Accessed 9 Sept 2014

Ōya A et al (1991) An antimicrobial and antifungal agent derived from montmorillonite. Appl Clay Sci 6(2):135–142. http://www.sciencedirect.com/science/article/pii/016913179190003R. Accessed 9 Sept 2014

Ōya A, Banse T, Ohashi F (1992) Antimicrobial and antifungal agents derived from clay minerals (III): control of antimicrobial and antifungal activities of Ag+-exchanged montmorillonite by intercalation of polyacrylonitrile. Appl Clay Sci 6(4):311–318. http://www.sciencedirect.com/science/article/pii/S0169131709900060. Accessed 9 Sept 2014

Patakfalvi R, Dékány I (2004) Synthesis and intercalation of silver nanoparticles in kaolinite/DMSO complexes. Appl Clay Sci 25(3–4):149–159. http://www.sciencedirect.com/science/article/pii/S0169131703002230. Accessed 22 Aug 2014

Patil AJ, Muthusamy E, Mann S (2005) Fabrication of functional protein–organoclay lamellar nanocomposites by biomolecule-induced assembly of exfoliated aminopropyl-functionalized magnesium phyllosilicates. J Mater Chem 15(35–36):3838. http://pubs.rsc.org/en/content/articlehtml/2005/jm/b504288g. Accessed 9 Sept 2014

Pavelić K et al (2001) Natural zeolite clinoptilolite: new adjuvant in anticancer therapy. J Mol Med 78(12):708–720. http://link.springer.com/10.1007/s001090000176. Accessed 26 Aug 2014

Pavlidou S, Papaspyrides CD (2008) A review on polymer–layered silicate nanocomposites. Prog Polym Sci 33(12):1119–1198. http://linkinghub.elsevier.com/retrieve/pii/S0079670008000701. Accessed 11 July 2014

Pérez-Esteve E et al (2013) Nanotechnology in the development of novel functional foods or their package. An overview based in patent analysis. Recent Pat Food Nutr Agric 5(1):35–43. http://www.ncbi.nlm.nih.gov/pubmed/22963076. Accessed 10 Sept 2014

Petersen K et al (1999) Potential of biobased materials for food packaging. Trends Food Sci Technol 10(2):52–68. http://www.sciencedirect.com/science/article/pii/S0924224499000199. Accessed 9 Sept 2014

Qutubuodin S, Fu X (2002) Polymer-clay nanocomposites: synthesis and properties. Marcel Dekker, Inc, 270 Madison Avenue, New York, …. http://scholar.google.it/scholar?q=related:JbulUlQhIBUJ:scholar.google.com/&hl=it&as_sdt=0,5&as_vis=1#4. Accessed 11 Sept 2014

Raheem D (2012) Application of plastics and paper as food packaging materials—an overview. Emirates J Food Agric 25(3). http://ejfa.info/index.php/ejfa/article/view/11509. Accessed 23 Aug 2014

Rashidi L, Khosravi-Darani K (2011) The applications of nanotechnology in food industry. Crit Rev Food Sci Nutr 51(8):723–30. http://www.ncbi.nlm.nih.gov/pubmed/21838555. Accessed 10 Sept 2014

Rhim J-W et al (2000) Solubility, tensile, and color properties of modified soy protein isolate films. J Agric Food Chem 48(10):4937–4941. http://www.ncbi.nlm.nih.gov/pubmed/11052759. Accessed 7 Jan 2014

Rhim J-W et al (2006) Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity. J Agric Food Chem 54(16):5814–5822. doi:10.1021/jf060658h. Accessed 9 Sept 2014

Rhim J-W, Hong S-I, Ha C-S (2009) Tensile, water vapor barrier and antimicrobial properties of PLA/nanoclay composite films. LWT Food Sci Technol 42(2):612–617. http://www.sciencedirect.com/science/article/pii/S0023643808000613. Accessed 9 July 2014

Rhim J-W, Lee S-B, Hong S-I (2011) Preparation and characterization of agar/clay nanocomposite films: the effect of clay type. J Food Sci 76(3):N40–N48. http://www.ncbi.nlm.nih.gov/pubmed/21535851. Accessed 9 Sept 2014

Risch SJ (2009) Food packaging history and innovations. J Agric Food Chem 57(18):8089–8092

Rives V (2001) Layered double hydroxides: present and future. In: Rives V (ed) Nova Publishers. http://books.google.com/books?id=U5c5zzqjthgC&pgis=1. Accessed 9 Sept 2014

Sahn SA (2000) Talc should be used for pleurodesis. Am J Respir Crit Care Med 162(6):2023–2024

Sakthivel S, Pitchumani B (2011) Production of nano talc material and its applicability as filler in polymeric nanocomposites. Part Sci Technol 29(5):441–449. http://www.tandfonline.com/doi/abs/10.1080/02726351.2010.510166. Accessed 9 Sept 2014

Sekhon BS (2010) Food nanotechnology—an overview. Nanotechnol Sci Appl 3:1–15. http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=3781769&tool=pmcentrez&rendertype=abstract. Accessed 9 Sept 2014

Setz S et al (1996) Morphology and mechanical properties of blends of isotactic or syndiotactic polypropylene with SEBS block copolymers. J Appl Polym Sci 59(7):1117–1128. http://doi.wiley.com/10.1002/%28SICI%291097-4628%2819960214%2959%3A7%3C1117%3A%3AAID-APP8%3E3.0.CO%3B2-H. Accessed 9 Sept 2014

Silvestre C, Duraccio D, Cimmino S (2011) Food packaging based on polymer nanomaterials. Prog Polym Sci 36(12):1766–1782. http://linkinghub.elsevier.com/retrieve/pii/S0079670011000311. Accessed 18 July 2014

Sinha Ray S, Okamoto M (2003) Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog Polym Sci 28(11):1539–1641. http://linkinghub.elsevier.com/retrieve/pii/S0079670003000790. Accessed 23 Mar 2014

Smit B, Maesen TLM (2008a) Molecular simulations of zeolites: adsorption, diffusion, and shape selectivity. Chem Rev 108(10):4125–4184. http://www.ncbi.nlm.nih.gov/pubmed/18817356. Accessed 11 Sept 2014

Smit B, Maesen TLM (2008b) Towards a molecular understanding of shape selectivity. Nature 451(7179):671–678. http://www.ncbi.nlm.nih.gov/pubmed/18256663. Accessed 1 Aug 2014

Sonkaria S, Ahn S-H, Khare V (2012) Nanotechnology and its impact on food and nutrition: a review. Recent Pat Food Nutr Agric 4(1):8–18. http://www.ncbi.nlm.nih.gov/pubmed/22316269

Soroka W (1999) Fundamentals of packaging technology. Institute of Packaging Professionals, Herndon

Sorrentino A et al (2005) Incorporation of Mg–Al hydrotalcite into a biodegradable Poly (ε-caprolactone) by high energy ball milling. Polymer 46(5):1601–1608. http://www.scopus.com/inward/record.url?eid=2-s2.0-12944268753&partnerID=tZOtx3y1. Accessed 24 Nov 2012

Sorrentino A et al (2006a) Polymer nanocomposites. Elsevier. http://www.scopus.com/inward/record.url?eid=2-s2.0-84904143329&partnerID=tZOtx3y1. Accessed 2 Sept 2014

Sorrentino A, Tortora M, Vittoria V (2006b) Diffusion behavior in polymer-clay nanocomposites. J Polym Sci Part B Polym Phys 44(2):265–274. http://doi.wiley.com/10.1002/polb.20684. Accessed 10 Sept 2014

Sorrentino A, Gorrasi G, Vittoria V (2007) Potential perspectives of bio-nanocomposites for food packaging applications. Trends Food Sci Technol 18(2):84–95. http://linkinghub.elsevier.com/retrieve/pii/S092422440600272X. Accessed 19 Mar 2014

Sorrentino A, Gorrasi G, Vittoria V (2012) Environmental silicate nano-biocomposites. In: Avérous L, Pollet E (eds). Springer, London. http://www.scopus.com/inward/record.url?eid=2-s2.0-84883142116&partnerID=tZOtx3y1. Accessed 11 Sept 2014

Sothornvit R, Rhim J-W, Hong S-I (2009) Effect of nano-clay type on the physical and antimicrobial properties of whey protein isolate/clay composite films. J Food Eng 91(3):468–473. http://www.sciencedirect.com/science/article/pii/S0260877408004858. Accessed 6 Aug 2014

Sozer N, Kokini JL (2009) Nanotechnology and its applications in the food sector. Trends Biotechnol 27(2):82–89. http://www.ncbi.nlm.nih.gov/pubmed/19135747. Accessed 10 July 2014

Stricker F, Bruch M, Mülhaupt R (1997) Mechanical and thermal properties of syndiotactic polypropene filled with glass beads and talcum. Polymer 38(21):5347–5353. http://www.sciencedirect.com/science/article/pii/S0032386197000657. Accessed 9 Sept 2014

Sung S-Y et al (2013) Antimicrobial agents for food packaging applications. Trends Food Sci Technol 33(2):110–123. http://www.sciencedirect.com/science/article/pii/S092422441300160X. Accessed 15 July 2014

Thostenson E, Li C, Chou T (2005) Nanocomposites in context. Compos Sci Technol 65(3–4):491–516. http://www.sciencedirect.com/science/article/pii/S0266353804003008. Accessed 9 July 2014

Tripathi S, Mehrotra GK, Dutta PK (2011) Chitosan–silver oxide nanocomposite film: preparation and antimicrobial activity. Bull Mater Sci 34(1):29–35. http://link.springer.com/10.1007/s12034-011-0032-5. Accessed 9 Sept 2014

Tronto J et al (2013) Conducting polymers/layered double hydroxides intercalated nanocomposites. In: Materials science—advanced topics. http://www.intechopen.com/books/materials-science-advanced-topics/conducting-polymers-layered-double-hydroxides-intercalated-nanocomposites

Uddin F (2008) Clays, nanoclays, and montmorillonite minerals. Metall Mater Trans A 39(12):2804–2814. http://link.springer.com/10.1007/s11661-008-9603-5. Accessed 9 Sept 2014

Valodkar M et al (2010) Morphology and antibacterial activity of carbohydrate-stabilized silver nanoparticles. Carbohydr Res 345(12):1767–1773. http://www.sciencedirect.com/science/article/pii/S0008621510001916. Accessed 9 Sept 2014

Wang X et al (2006) Preparation, characterization and antimicrobial activity of chitosan/layered silicate nanocomposites. Polymer 47(19):6738–6744. http://www.sciencedirect.com/science/article/pii/S003238610600855X. Accessed 9 Sept 2014

Wang X et al (2007) Chitosan/organic rectorite nanocomposite films: structure, characteristic and drug delivery behaviour. Carbohydr Polym 69(1):41–49. http://www.sciencedirect.com/science/article/pii/S0144861706004644. Accessed 9 Sept 2014

Wang X et al (2009) A novel biopolymer/rectorite nanocomposite with antimicrobial activity. Carbohydr Polym 77(3):449–456. http://www.sciencedirect.com/science/article/pii/S0144861709000460. Accessed 9 Sept 2014

Whilton NT, Burkett SL, Mann S (1998) Hybrid lamellar nanocomposites based on organically functionalized magnesium phyllosilicate clays with interlayer reactivity. J Mater Chem 8(8):1927–1932. http://pubs.rsc.org/en/content/articlehtml/1998/jm/a802120a. Accessed 9 Sept 2014

Willhammar T et al (2012) Structure and catalytic properties of the most complex intergrown zeolite ITQ-39 determined by electron crystallography. Nat Chem 4(3):188–194. http://www.ncbi.nlm.nih.gov/pubmed/22354432. Accessed 11 Sept 2014

Wong TW (2009) Handbook of zeolites: structure, properties and applications (Materials science and technologies). Nova Science Publishers, Inc. http://www.amazon.com/Handbook-Zeolites-Properties-Applications-Technologies/dp/160741046X. Accessed 11 Sept 2014

Wyser Y et al (2016) Outlook and challenges of nanotechnologies for food packaging. Packag Technol Sci. http://doi.wiley.com/10.1002/pts.2221

Xu B et al (2006) Calculating barrier properties of polymer/clay nanocomposites: effects of clay layers. Polymer. http://www.sciencedirect.com/science/article/pii/S0032386106002333. Accessed 11 Sept 2014

Yah WO et al (2012) Biomimetic dopamine derivative for selective polymer modification of halloysite nanotube lumen. J Am Chem Soc 134(29):12134–12137. http://www.ncbi.nlm.nih.gov/pubmed/22765271. Accessed 12 Sept 2014

Yam KL (ed) (2009) The Wiley encyclopedia of packaging technology. Wiley, Hoboken. http://doi.wiley.com/10.1002/9780470541395. Accessed 8 Sept 2014

Zazenski R et al (1995) Talc: occurrence, characterization, and consumer applications. Regul Toxicol Pharmacol 21(2):218–229. http://linkinghub.elsevier.com/retrieve/pii/S027323008571032X. Accessed 11 Sept 2014

Zihlif AM, Ragosta G (2003) A study on the physical properties of rock wool fiber—polystyrene composite. J Thermoplast Compos Mater 16(3):273–283. http://jtc.sagepub.com/content/16/3/273.abstract. Accessed 9 Sept 2014

Chapter 5
Oil Palm Biomass Cellulose-Fabricated Polylactic Acid Composites for Packaging Applications

**Hidayah Ariffin, Mohd Nor Faiz Norrrahim,
Tengku Arisyah Tengku Yasim-Anuar, Haruo Nishida,
Mohd Ali Hassan, Nor Azowa Ibrahim and Wan Md Zin Wan Yunus**

Abstract The use of biodegradable polymers for food packaging material is favorable due to its ability to degrade after use. Nevertheless, the real application of the polymers is still limited due to its poor physical properties. Polylactic acid (PLA) is one of the biodegradable polymers commonly used for packaging. Recently, there have been reports on the use of nanocellulose as filler in polylactic acid (PLA) for improving the mechanical properties of PLA; however, it has limitation in which non-uniform dispersion of nanocellulose is formed within the polymer during melt-blending. Uniform dispersion can be obtained through solvent casting method; nevertheless, it is not industrially applicable. In this study, a one-pot process was developed where nanofibrillation of cellulose and subsequently melt-blending of the nanocellulose with PLA were conducted in a twin-screw extruder. Results showed that nanocomposite reinforced with 3 and 5 wt% cellulose nanofiber (CNF) exhibited higher tensile strength and Young's modulus compared

---

H. Ariffin (✉) · M.N.F. Norrrahim · M.A. Hassan
Department of Bioprocess Technology, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
e-mail: hidayah@upm.edu.my

H. Ariffin · T.A.T. Yasim-Anuar
Laboratory of Biopolymer and Derivatives, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

H. Nishida
Department of Biological Functions and Engineering, Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu-Ku, Kitakyushu, Fukuoka 808-0196, Japan

N.A. Ibrahim
Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

W.M.Z.W. Yunus
Department of Chemistry, Centre for Defence Foundation Studies, Universiti Pertahanan Nasional Malaysia, Kem Perdana Sungai Besi, 57000 Kuala Lumpur, Malaysia

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_5

to neat PLA. Crystallinity of the polymer increased by 43% with the addition of 5 wt% CNF. Meanwhile, wettability of the polymer was also improved as seen by the reduction in contact angle value. Results obtained exhibited the potential of the composite films to be used in packaging material, especially for high respiration products.

Keywords One-pot process · Twin-screw extruder · Cellulose nanofiber · Oil palm biomass · Polylactic acid · Reinforcement · Packaging

5.1 Introduction

Polylactic acid (PLA) is a biodegradable polymer with high mechanical strength and easy processability compared to other biopolymers. It is thermoplastic and aliphatic polyester which can be derived from renewable resources and is a sustainable alternative to petrochemical-derived products. Studies have shown that PLA is economically feasible to be used packaging material, with low amount of lactic acid (LA) leaching (Auras et al. 2004) making it an advantageous material for food packaging. However, improvements can be done in order to increase the properties of this PLA used in several applications. This could be done by reinforcing other polymers or fibers to PLA.

Cellulose nanofibers (CNF) from renewable biomass have attracted much interest as an alternative to micro-sized reinforcements in composite materials. There have been significant advances in the development of plant–plastic composites (Iwamoto et al. 2014). One challenge when using CNF in composites is due to its non-uniform dispersion. This is contributed by their polar surfaces which is difficult to disperse uniformly in a nonpolar medium. This might be the reason why the processing of CNF composites was first limited to solvent casting, where water-soluble or dispersive polymers were the most common matrices (Oksman et al. 2016). However, the development of other, more flexible, and industrially viable processing techniques is necessary to promote commercialization of these materials. Therefore, several interesting processing methods have been recently reported for these materials. One of the developed processing methods is melt compounding (Ho et al. 2015). Melt compounding of cellulose nanocomposites presents several challenges (Oksman et al. 2016). Extensive studies of CNF as reinforcement in PLA also have been carried out and prepared by solvent casting as well as melt compounding (Jonoobi et al. 2010). The major difficulties in melt compounding are to feed the CNF into the extruder and achieve uniform dispersion in the polymer matrix. The CNF has high surface area and has tendency to aggregate when dried. This is expected to be avoided by firstly mixing them in a suitable medium, which is then fed into the extruder. Another method to provide uniform dispersion of nanocellulose in polymer matrix is by using solvent casting; nevertheless, the process is not industrially applicable.

One-pot nanofibrillation of cellulose and compounding process for composite production could be done by extrusion. The advantage of this processing method would lie on efficient production of CNF composites due to fewer processing steps involved. In this study, nanofibrillation of cellulose from oil palm mesocarp fiber (OPMF) for the production of CNF and subsequently melt compounding of the CNF with PLA was taken place in the same twin-screw extruder. The composites produced were characterized for their mechanical, morphological, thermal stability, and wettability properties.

The ability to nanofibrillate cellulose from OPMF and subsequently melt compounding the produced CNF with PLA in the same extruder would be advantageous for large-scale nanocomposite production since extrusion will allow for high solid content processing and provide a continuous process.

5.2 Materials and Methods

5.2.1 Materials

OPMF was collected from Seri Ulu Langat Palm Oil Mill, Selangor, Malaysia. The fiber was disintegrated, washed, and dried. Sodium chlorite ($NaClO_2$) and potassium hydroxide (KOH) were obtained from ACROS ORGANICS and J.T Baker Neutracit, respectively. PLA used was provided by TOYOTA Eco-Plastic (U'z S-09).

5.2.2 Oil Palm Mesocarp Fiber Pretreatment

OPMF was pretreated chemically to isolate cellulose fraction from the material. Pretreatment of the fiber involved two steps; which were hemicellulose and lignin removal. Delignification was conducted by treating the fiber with 5 wt% of sodium chlorite ($NaClO_2$) aqueous solution with pH adjusted to pH 4–5. The fiber was soaked in this solution at 70 °C for 1.5 h. Then, fiber was washed and filtered with deionized water until the pH became neutral. Subsequently, hemicellulose removal was done by soaking the fiber in 6 wt% of potassium hydroxide (KOH) for 24 h with constant stirring rate. Sample was then filtered and rinsed with deionized water until the pH reached pH 7.

5.2.3 One-Pot Nanofibrillation and Nanocomposite Production in a Twin-screw Extruder

Fibrillation and melt compounding were carried out using a twin-screw extruder (Imoto machinery Co. Limited: Model IMO-160B). The extruder consisted of two major parts: fibrillation and mixing. Fibrillation of cellulose was conducted with a specially designed screw for nanofibrillation at 120 °C, with screw speed of 100 rpm for 1 h. After nanofibrillation was completed, the rotational speed was reduced to 25 rpm. This is to allow the movement of the fibrillated cellulose into mixing part. PLA was fed through a hopper in between fibrillation and mixing sections with the ratio of PLA to cellulose of 97:3 and 95:5. For melt compounding, temperature used was 180 °C and screw speed was set at 25 rpm for 30 min. PLA/CNF-OPMF composites were then pressed at the same temperature in an electrically heated platen press for 5 min under a pressure of 10 atm to form composite sheets.

5.2.4 Analyses

5.2.4.1 Visual Examination

The dispersion of CNF in composite samples was observed. Pictures were taken in order to investigate the distribution of CNF in PLA matrix.

5.2.4.2 Morphological Analysis

The morphology of the CNF and the fracture surfaces of the PLA/CNF-OPMF composite samples were observed using a scanning electron microscopy, SEM (FE-SEM S-3400 N, Hitachi, Japan). Composites fracture surfaces were obtained through flexural tests. The dried CNF and fracture surfaces were coated with Pt-Pd for 100 s (Ion sputter: Hitachi, Japan) prior to the observations.

5.2.4.3 Mechanical Properties

Tensile tests were performed to determine the mechanical properties of the composites using a mechanical tester (AGS-5kNG, Autograph, Shimadzu Co, Kyoto, Japan). The dumbbell-like composites samples were subjected to tensile tests. The tensile tests were performed at a crosshead speed of 10 mm/min. Results of tensile strength (MPa), Young's modulus (MPa), and elongation at break (%) were recorded.

5.2.4.4 Crystallinity

X-ray diffraction (XRD) pattern was recorded using an X-ray powder diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with nickel-filtered Cu Ka radiation (k = 0.1542 nm) at 40 kV and 25 mA. The diffractograms were detected in the range 2θ = 2–50° at a scan rate of 2°/min.

5.2.4.5 Thermal Properties

Differential scanning calorimetry (DSC): Measurements were performed using a Pyris 1 DSC calorimeter (Perkin–Elmer Co., Waltham, MA, USA). The samples were first heated from 30 to 200 °C at a rate of 10 °C/min and held at 200 °C for 1 min. They were then cooled to 50 °C at a rate of 10 °C/min and held at 50 °C for 1 min. Next, they were again heated to 200 °C at a rate of 10 °C/min and held at 200 °C for 1 min. Finally, they were quenched to 135 °C at a rate of 50 °C/min. The temperatures corresponding to the exothermic and endothermic peaks in the first heating step and the cooling step were called T_m and T_c, respectively.

Thermal stability of the composite samples was determined by using a thermogravimetry analyzer, TGA (TGA–9, Perkin Elmer, USA) under nitrogen flow. Sample (5–11 mg) was placed on a ceramic pan and set on the TGA. The sample was heated at heating rate of 10 °C min^{-1} within the temperature range of 50–500 °C.

5.2.4.6 Contact Angle

Contact angle (CA) of 0.5 μL water droplets on the film surfaces originally attached to the Petri dishes in the film preparation was measured for five times for different parts of each film at 23 °C and 50% RH using a FAMAS DM500 apparatus (Kyowa Interface Science).

5.3 Results and Discussion

5.3.1 Nanofibrillation of Cellulose by Extrusion

In order to evaluate the effectiveness of OPMF cellulose nanofibrillation by extrusion, fibrillated cellulose was evaluated morphologically by FE-SEM and the micrograph is depicted as in Fig. 5.1. Based on the FE-SEM micrograph, it is seen that fibrillation of cellulose occurred completely, giving CNF with diameter of about 80–100 nm.

5.3.2 Mechanical Properties

Mechanical properties of PLA/CNF-OPMF composites and neat PLA are shown in Table 5.1. Based on the results, it is seen that the addition of 3 and 5 wt%

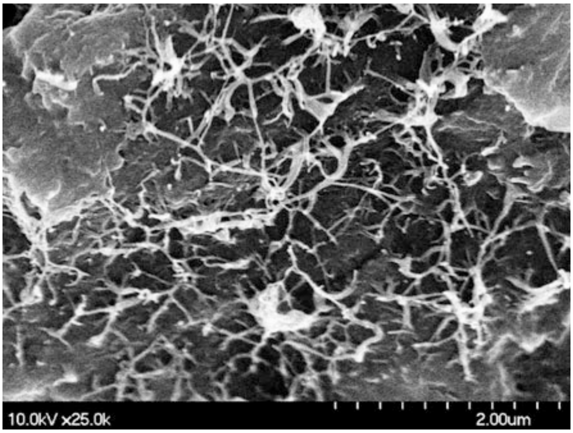


Fig. 5.1 Morphology of OPMF cellulose nanofiber obtained by extrusion

Table 5.1 Tensile properties of neat PLA and PLA/CNF-OPMF composites

Composition	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
Neat PLA	54.7 ± 0.2	933 ± 12	105.0 ± 3
PLA/CNF-OPMF (3%)	61.9 ± 0.9	1280 ± 41	105.0 ± 0
PLA/CNF-OPMF (5%)	56.1 ± 0.5	1067 ± 52	106.0 ± 3

CNF-OPMF to PLA markedly increased the tensile properties of the composites as compared to neat PLA. Similar observation was seen for Young's Modulus. Meanwhile, elongation at break was consistent even with the addition of 5 wt% CNF.

The value for both tensile strength and Young's modulus dropped when 5 wt% of CNF-OPMF was used in the composites compared to 3 wt%. The reduction can be explained by the distribution of CNF within PLA matrix as shown in the next section.

5.3.3 *Visual Appearance of Composite Samples*

Visual appearance of the biocomposite samples was observed to determine dispersion characteristic of CNF in the PLA matrix. It was seen that CNF in both PLA/CNF-OPMF (3%) and PLA/CNF-OPMF (5%) was well dispersed as shown in Fig. 5.2b, c. However, aggregation of CNF was observed in some parts of PLA/CNF-OPMF (5%) composite (Fig. 5.2c). The aggregated CNF in PLA matrix could be correlated to the decrement of the mechanical properties when CNF

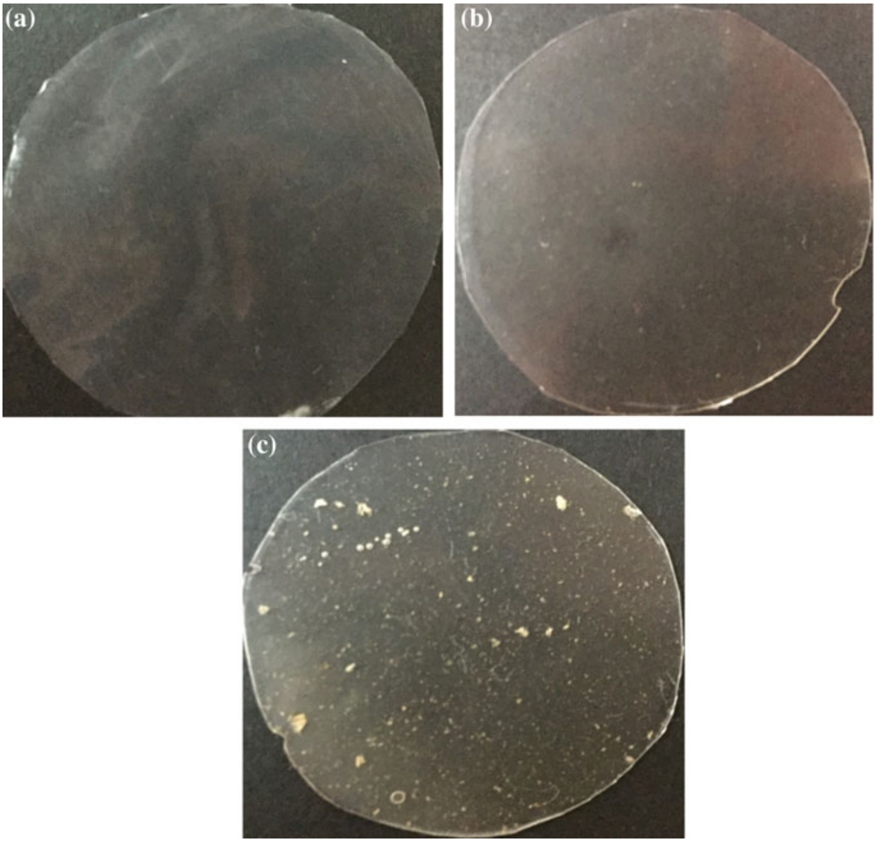


Fig. 5.2 Visual appearance of neat PLA and PLA/CNF-OPMF composites prepared by extrusion. **a** neat PLA. **b** PLA/CNF-OPMF (3%). **c** PLA/CNF-OPMF (5%)

amount was increased. In order to support this finding, morphological analysis of composites by SEM was also evaluated.

5.3.4 Morphological Analysis

SEM micrographs of fractured surfaces of the PLA and its nanocomposites are presented in Fig. 5.3. Generally, good dispersion of nanocellulose can be observed in PLA/CNF-OPMF (3%) (Fig. 5.3b). However, aggregation of CNF was occurred at some parts for PLA/CNF-OPMF (5%) (Fig. 5.3c). As the amount of CNF increased, the degree of aggregation was increased. This aggregation could be due to limited chemical interaction between hydroxyl group of cellulose and PLA when

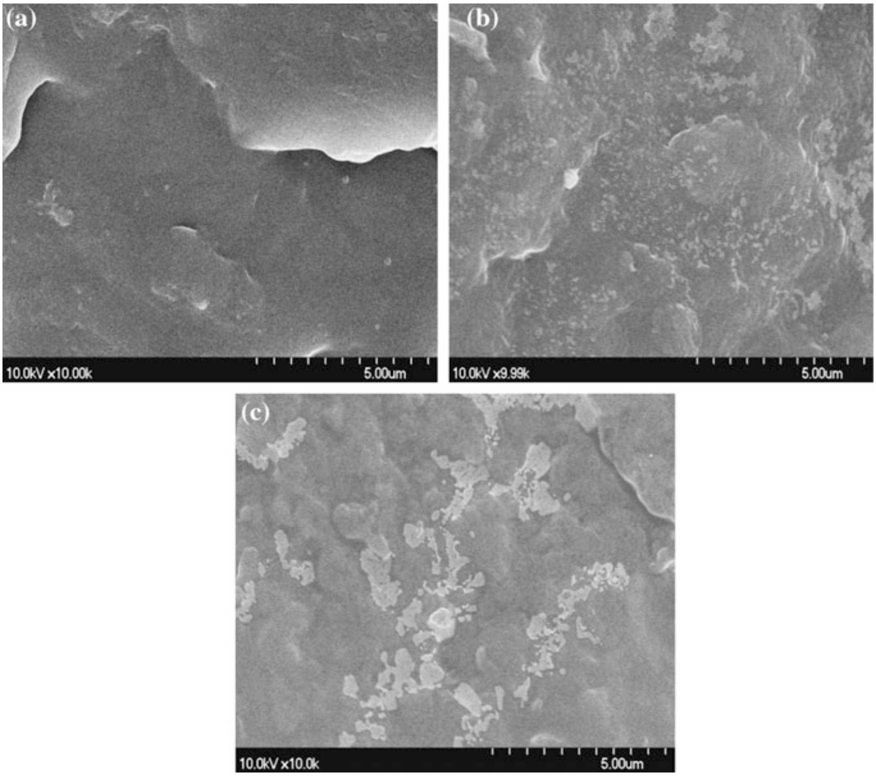


Fig. 5.3 SEM micrographs of neat PLA and PLA/CNF-OPMF composites. **a** neat PLA. **b** PLA/CNF-OPMF (3%). **c** PLA/CNF-OPMF (5%)

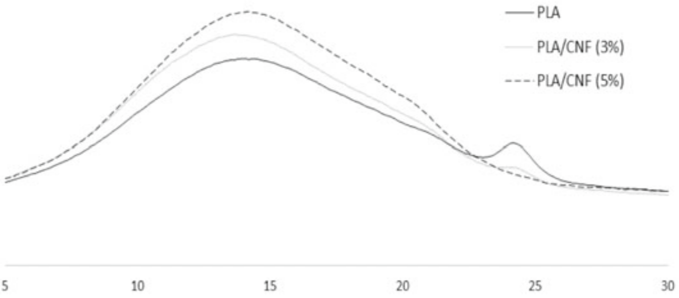
higher amount of CNF was added. These findings were also correlated to the mechanical properties of the composite as discussed before. Aggregation of nanocellulose may result in a low stress transfer in the composite matrix which may lead to the low mechanical performance of composites.

5.3.5 Crystallinity Properties

Crystallinity of PLA/CNF-OPMF composite samples is shown in Fig. 5.4. As the amount of CNF increased, the crystallinity of the composites was also increased. The crystallinity of PLA/CNF-OPMF (3%) and PLA/CNF-OPMF (5%) were 62.6 and 78.5%, respectively, as compared to neat PLA (54.9%). Composites samples had higher crystallinity than neat PLA which resulted in better mechanical properties as discussed before. Nevertheless, even though PLA/CNF-OPMF (5%) had the highest crystallinity, the tensile strength and Young's modulus of the composite sample were lower compared to PLA/CNF-OPMF (3%), which could be explained by the aggregation of CNF in the composites and hence resulted in low stress transfer and eventually affected the mechanical properties.

5.3.6 Thermal Properties

Table 5.2 lists the thermal properties of PLA/CNF-OPMF composites. The T_m values were almost similar in all samples, indicating that the CNF blended well with the polymer matrix. ΔH_m of composites for both PLA/CNF-OPMF (3%) and PLA/CNF-OPMF (5%) were slightly higher than that of the neat PLA, inferring that the crystallinity of the PLA matrix in the composites was higher. This is in correlation with the crystallinity values presented earlier (Fig. 5.4). Thermal stability of the samples is shown by $T_{d50\%}$ values in Table 5.2. Overall, neat PLA had the highest thermal stability. Cellulose is known to have degradation temperature lower than PLA. Similar result was published by Guan (2012), in which PLA/CNF composites had degradation temperature in between that of PLA and cellulose.



Composition	Crystallinity (%)
Neat PLA	54.9
PLA/CNF-OPMF (3%)	62.6
PLA/CNF-OPMF (5%)	78.5

Fig. 5.4 Crystallinity of neat PLA and PLA/CNF-OPMF composites

Table 5.2 Thermal properties of neat PLA and PLA/CNF-OPMF composites

Composition	T_m (°C)	ΔH_m (°C)	$T_{d50\%}$ (°C)
Neat PLA	178.4	114.0	366.5
PLA/CNF-OPMF (3%)	175.7	115.3	354.9
PLA/CNF-OPMF (5%)	175.7	116.9	340.3

Table 5.3 Contact angle of neat PLA and PLA/CNF-OPMF composites

Composition	CA(°)
Neat PLA	74.7 ± 0.6
PLA/CNF-OPMF (3%)	71.9 ± 0.9
PLA/CNF-OPMF (5%)	64.7 ± 2.3

5.3.7 Contact Angle Analysis

CA is a parameter used to evaluate the relationships between solid surfaces and water. When a solid surface is wetted with a water droplet, the droplet competes with the surrounding air to occupy a larger contact area with the solid surface. The surface of PLA is strongly hydrophobic, and CNF used to have ionic groups on their surfaces and have no hydrophobic surface. The addition of CNF could enhance the hydrophilicity property of the composite samples. Table 5.3 shows the CA value for PLA and PLA/CNF-OPMF composites. The presence of CNF decreased the CA value of the PLA/CNF-OPMF composites as compared to neat PLA. Addition of 3 and 5 wt% CNF in composites decreased the CA value to 71.9 ± 0.9° and 64.7 ± 2.3°, respectively, as compared to neat PLA at 74.7 ± 0.6°. Due to the aggregation of CNF in PLA/CNF-OPMF (5%) as shown in Figs. 5.2c and 5.3c, the standard deviation of CA value for this composite was higher.

5.4 Conclusions

One-pot process for nanofibrillation of OPMF cellulose and melt-blending of PLA and CNF-OPMF composites was successfully developed by using a twin-screw extruder. The advantage of using a twin-screw extrusion process is that it allows for the processing and fibrillation of cellulose at high solid content. To the best of our knowledge, there is lack of research on one-pot nanofibrillation of cellulose and nanocomposite production by extrusion, and this report provides extensive information on the potential use of the method for PLA/CNF composite production. From our results, the morphological observation of PLA and its composites showed that a relatively good dispersion of CNF was achieved as no CNF aggregates were visible in the fractured surfaces of the PLA/CNF-OPMF (3%). CNF started to aggregate at higher concentration (5 wt%). Evaluation of the mechanical properties of the PLA/CNF-OPMF composites showed that the composite samples had higher tensile strength and Young's modulus compared to neat PLA. The improvement in mechanical properties of the composite samples could be related to the high crystallinity of PLA/CNF-OPMF. Nevertheless, despite of steady increment in crystallinity with the increased amount of CNF, the mechanical properties of the composite samples with higher CNF content reduced slightly, mainly due to the CNF aggregation which resulted in low stress transfer. Meanwhile, CA analysis of the composite samples showed that PLA/CNF-OPMF had lower CA value compared to neat PLA, indicating that inclusion of CNF in the composite samples improved the hydrophilicity property of the material. Increased hydrophilicity of PLA composite films could be advantageous in packaging particularly for highly respiration products such as fresh fruits and vegetables. Additionally, improving surface wetting may lead to a significant improvement in material biocompatibility and functionality such as in antimicrobial active packaging (Hendrick and Frey 2014). Overall, this study shows that one-pot nanofibrillation and nanocomposite production by extrusion is a promising method to achieve good processability of PLA/CNF-OPMF composites. Improvement on mechanical and wettability properties of the composite films makes it suitable to be used as packaging material.

Acknowledgements This work is a part of Science and Technology Research Partnership for Sustainable Development (SATREPS) project. We would like to thank the Ministry of Higher Education Malaysia (MOHE) for funding this research (SATREPS) and for the provision of MyBrain 15 scholarship to the authors. Part of this work was conducted at INTROP Tropical Wood and Fibre Research Centre, a Higher Institution Centre of Excellence (HICoE) under the Ministry of Higher Education, Malaysia. Authors also would like to thank Seri Ulu Langat Palm Oil Mill for the provision of oil palm mesocarp fiber.

References

Auras R, Harte B, Selke S (2004) An Overview of Polylactides as Packaging Materials. Macromol Biosci 4(9):835–864

Guan X (2012) Fabrication of poly-lactic acid (PLA) composite films and their degradation properties. Thesis Dissertation, The University of Toledo

Hendrick E, Frey M (2014) Increasing Surface Hydrophilicity in Poly (Lactic Acid) Electrospun Fibers by Addition of Pla-b-Peg Co-Polymers. J Eng Fibers Fabr 9:153–164

Ho TTT, Abe K, Zimmermann T, Yano H (2015) Nanofibrillation of pulp fibers by twin-screw extrusion. Cellulose 22:421–433

Iwamoto S, Yamamoto S, Lee SH, Endo T (2014) Solid-state shear pulverization as effective treatment for dispersing lignocelluloses nanofibers in polypropylene composites. Cellulose 21:1573–1580

Jonoobi M, Harun J, Mathew AP, Oksman K (2010) Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. Compos Sci Technol 70:1742–1747

Oksman K, Aitomäki Y, Mathew AP, Siqueira G, Qi Zhou, Butylina S, Tanpichai S, Zhou X, Hooshmand S (2016) Review of the recent developments in cellulose nanocomposite processing. Composites Part A: Appl Sci Manufact 83:2–18

Chapter 6
Chitosan-Based Bionanocomposite for Packaging Applications

Sarat K. Swain and Kalyani Prusty

Abstract Concerns on environmental waste problems caused by non-biodegradable petrochemical-based plastic packaging materials as well as the consumers demand for high-quality food products have caused an increasing interest in developing biodegradable packaging materials like polysaccharides. Out of these polysaccharides, Chitosan has created its greater interest due to non-toxic, antibacterial behaviour, film-forming abilities and low permeability to oxygen, poor thermal and mechanical properties restricted its wide spread applications for packaging. However, reinforcement of various nanostructured materials shall increase the mechanical, thermal and gas barrier properties of chitosan without disturbing the biodegradable behaviour. This chapter summarizes different characterization techniques such as Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) of chitosan-based bionanocomposites. For keeping on the packaging applications of the materials, the important properties such as thermal and mechanical gas barrier and antimicrobial properties of chitosan-based bionanocomposites are discussed. The main focus of this chapter is to establish the packaging applications of chitosan-based bionanocomposites.

Keywords Chitosan · Oxygen barrier · Antibacterial · Packaging applications

6.1 Introduction

Chitosan is composed of arbitrarily dispersed α-(1-4)-linked N-acetyl-D-glucosamine (acetylated unit) and D-glucosamine (deacetylated unit). Chitosan derivatives are arising from partial deacetylation of chitin. Chitins are the best abundant

---

S.K. Swain (✉) · K. Prusty
Department of Chemistry, Veer Surendra Sai University of Technology,
Sambalpur 768018, Odisha, India
e-mail: swainsk2@yahoo.co.in

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_6

nitrogen-bearing organic compound. These biopolymers are formed by a huge number of living organisms. Chitins are mostly crystalline microfibrils structural components in nature, and it can be found from exoskeleton of arthropods or in the cell walls of fungi and yeast. Generally, it is insoluble in common solvents due to their hydrogen bonding between acetamide, carbonyl and hydroxyl groups. Hence, chitin and chitosan are same polymers but different degree of deacetylation (DD). However, the degrees of deacetylation are main factors to determining the characteristics of chitosan. Chitosan is mainly used if DD is more than 40%. These chains are completely insoluble in water when DD is less than 40% due to H-bonds between amide, ether and alcohol functionalities dispersed on the repeating units along the polymer chains and hydrophobic interactions and also due to the presence of methyl groups of the acetamide functions and to the –CH and –CH_2 of the glucosidic rings (Dumitriu 2002; Chung et al. 2003; Kurita 2006). If DD is more than 40%, then chitosan becomes soluble in acidic solution. Chitosan is a bio-macromolecule having good porous, environmental friendly and non-toxic in nature. The strength and stability of chitosan are a drawback of using chitosan as alone; while chitosan was reinforced with other nanomaterials, its strength (Kisku et al. 2014), stability (Swain et al. 2014a), barrier (Swain et al. 2014b) and resistance (Swain et al. 2014a) are enhanced. Chitosan has been broadly investigated for different applications due to their biodegradability, biocompatibility, mucoadhesiveness and derivability produced by abundant and an inexpensive biomass (Szymanska et al. 2015). It exhibits antibacterial behaviour, wound healing properties and homeostatic behaviour which make chitosan-based biocomposites very useful in biomedical area. Furthermore, it has been applied in agriculture field as a fertilizer and in water treatment as ion exchange (Yen et al. 2008). When the units of N-glucosamine is more than 50%, it is known as chitosan and when amount of N-acetyl glucosamine is higher than 50%, it is known as chitin (Croisier et al. 2013; Tsigos et al. 2000).

A potential amount of research works have been dedicated in last few decades to replace fossil fuel-based polymers with biodegradable ones, originated from renewable resources, in food packaging applications (Kumar et al. 2011; Petersen et al. 1999; Rhim et al. 2013; Siracusa et al. 2008; Sorrentino et al. 2007). Chitosan is the second most abundant polysaccharide which is derived from chitin (Muzzarelli et al. 2012) and has been predictable as a strong candidate due to their antimicrobial behaviour, non-toxicity, selective permeability to gases (CO_2 and O_2) and excellent film-forming properties (Aider 2010; Dutta et al. 2009; Leceta et al. 2013a, b; Tripathi et al. 2008). But, chitosan is relatively brittle and hydrophilic in nature with moisture barrier capabilities.

Nowadays, biopolymeric materials have involved great consideration due to their environmental concerns of consumption of petrochemical-based materials in the packaging industry. Chitosan is an alternative to replace "Environment threatening" materials because of important properties like good biodegradability, biocompatibility, non-toxicity, antimicrobial and antifungal properties (Aider 2010; Van den Broek et al. 2015). The poly cationic nature of chitosan can neutralize the bacterial metabolism (antimicrobial property), making it an excellent material to be applied in the food packaging application (Leceta et al. 2013a, b). Chitosan is found to be non-toxic and exhibit antibacterial behaviour, film-forming abilities and low permeability to oxygen. That is why it is suitable candidates for packaging applications (Kanatt et al. 2012). The presence of amino group in C_2 position of chitosan and hydroxyl groups of the C_3 and C_6 positions provides major functionality towards biotechnological needs, typically in food industry (Imam et al. 2012). The antimicrobial behaviour of chitosan in various forms i.e. films, composites or solutions have been well predictable for many years, and it has been studied as an antimicrobial material against a broad range of target organisms like bacteria, fungi, algae and yeasts (Benhabiles et al. 2012). The antimicrobial effect of chitosan is found to be dependent on its characteristics, most notably molecular weight (M_w), DD (degree of deacetylation), p^H, temperature, concentration and bacteria type.

Although a number of reports are available in the literature regarding chitosan and its film as food packaging applications, however, the chitosan-based bionanocomposites for packaging applications are scanty and important in present area of investigation. Present chapter focuses on the chitosan-based bionanocomposites for packaging applications. The different characterization techniques for chitosan-based bionanocomposites are elaborated in the present chapter. The important properties responsible for packaging materials are mechanical, thermal, antibacterial and barrier properties.

6.2 Characterization of Chitosan-Based Nanocomposites

6.2.1 *Fourier Transform Infrared Spectroscopy (FTIR) of Chitosan-Based Nanocomposites*

FTIR of films based on chitosan, nanocrystaline cellulose ans chitosan with 5% nnaocrystaline cellulose is represented in Fig. 6.1 (Khan et al. 2012). In FTIR spectra of chitosan films, the peak of 3500–3250 cm^{-1} corresponds to stretching of intermolecular O-H and intra and –CH_2OH vibrations, and 3300–3280 cm^{-1} corresponds to –NH secondary amides vibration (Fig. 6.1a). Further, 2960–2870 cm^{-1} related to asymmetric and symmetric C–H vibrations. Neat nanocrystalline cellulose films show the FTIR peaks of 3600 and 3200 cm^{-1} correspond to the O–H stretching vibrations (Fig. 6.1b). Here, in this Fig., broad peak of 3337 cm^{-1} might be ascribed to the O–H vibrations because of their intramolecular hydrogen bonding (Li et al. 2011). But the broad peaks of 3000–2800 cm^{-1} and 1500–1250 cm^{-1} arise from the C-H and bending vibrations and CH_2 stretching, respectively (Nikonenko et al. 2000; Wang et al. 2011). The absorption band of 1160 cm^{-1} corresponds to C–O–C stretching motion. The strongest bands across nanocrystalline cellulose spectra of 1054 and 1032 cm^{-1} correspond to C–O stretching. Other bands between 800 and

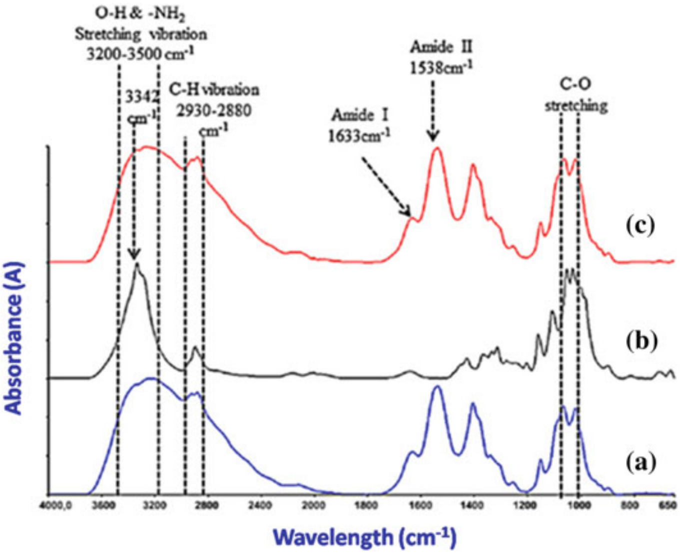


Fig. 6.1 Fourier Transform Infrared spectroscopy spectra of films based on chitosan (**a**), Nanocrystalline cellulose (**b**) and chitosan +5% nanocrystalline cellulose (**c**). Reproduced with permission from Elsevier science, Ltd. (Khan et al. 2012)

650 cm^{-1} correspond to O–H out of plane bending vibrations (Kondo et al. 1996; Nikonenko et al. 2005). In addition, the FTIR peak of chitosan and nanocrystalline cellulose is 3342 cm^{-1}, which is not present in the control chitosan films (Fig. 6.1c). This increase peak may be due to hydrogen bonding between neat chitosan and nanocrystalline cellulose (Khan et al. 2010). Furthermore, there is a severe increase in the intensity of the absorption bands of 1054 and 1032 cm^{-1} due to reinforcement of nanocrystalline cellulose.

6.2.2 X-ray Diffraction (XRD) Analysis of Chitosan-Based Nanocomposites

XRD pattern of neat chitosan films and nanocrystalline cellulose containing chitosan films is compared in Fig. 6.2 (Khan et al. 2012). XRD of nanocrystalline cellulose films shows crystalline peaks of $2\theta = 16.8°$, and $2\theta = 22.4°$ may be due to the 110 and 220 planes of cellulose I, respectively. Chitosan films exhibited a characteristics diffraction sharp peak of $2\theta = 13°$ may be due to hydrated crystalline structure, and a broad halo of $2\theta = 20–23°$ may be due to amorphous structure of

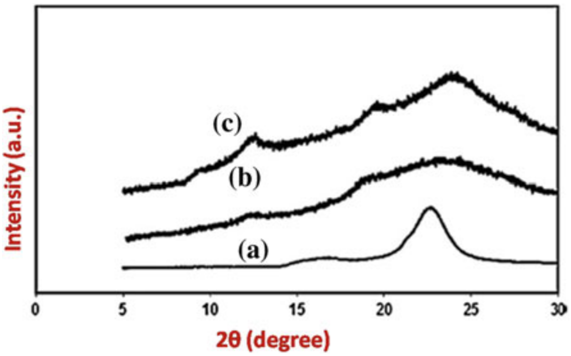


Fig. 6.2 X-ray diffractogram of films based on Nano crystalline cellulose (**a**), chitosan (**b**) and chitosan +5% nanocrystalline cellulose (**c**). Reproduced with permission from Elsevier science, Ltd. (Khan et al. 2012)

chitosan (Ogawa et al. 1994; Wang and Shen 2005). In addition to XRD peak of neat chitosan and incorporation of crystalline cellulose into neat chitosan, the diffraction peak of 2θ = 13° is found. Further, the diffraction sharp halo of amorphous chitosan of 2θ = 20–23° super positioned with the broad peak of nanocrystalline cellulose of 2θ = 22° and 2θ = 25° is observed. As a result, incorporation of nanocrystalline cellulose into chitosan films shows a combination of crystalline and amorphous peaks (Bodin et al. 2007). These increases in peak intensity of the neat chitosan may be due to transcrystallization effect. This effect means orientation of crystals of a semi-crystalline matrix perpendicular to the cellulose nanocrystals (Helbert et al. 1994).

6.2.3 Scanning Electron Microscopy (SEM) Analysis of Chitosan-Based Nanocomposites

The micro- and nanostructure of neat chitosan, neat nanocrystalline cellulose and reinforcement of nanocrystalline cellulose into pure chitosan films are studied from SEM as Fig. 6.3 (Khan et al. 2012). It is noticed that the presence of voids, the dispersion level of the nanoparticles within the continuous matrix, the presence of aggregates and the possible orientation of nanoparticles are shown in Fig. 6.3. Figure 6.3 represents scanning electron microscopy micrographs of the fractured surface of the nanocrystalline cellulose (NCC) (a), Chitosan (b), chitosan with 5% nanocrystalline films (c) and chitosan with 10% nanocrystalline films (d). It is noticed that Quito smooth surface is found which shows excellent film homogenization of chitosan in aqueous medium (Fig. 6.3b). By relating the micrographs of chitosan to that of the nanocomposite films, cellulose nanocrystals appeared like white dots in the chitosan with 5 and 10% nanocrystalline cellulose films. These shiny dots could relate to the transversal sections of the cellulose nanocrystals. Nanocomposite films with 5% nanocrystalline cellulose loading can be ascribed to this homogeneous structure of the films. But, the surface became rougher with the

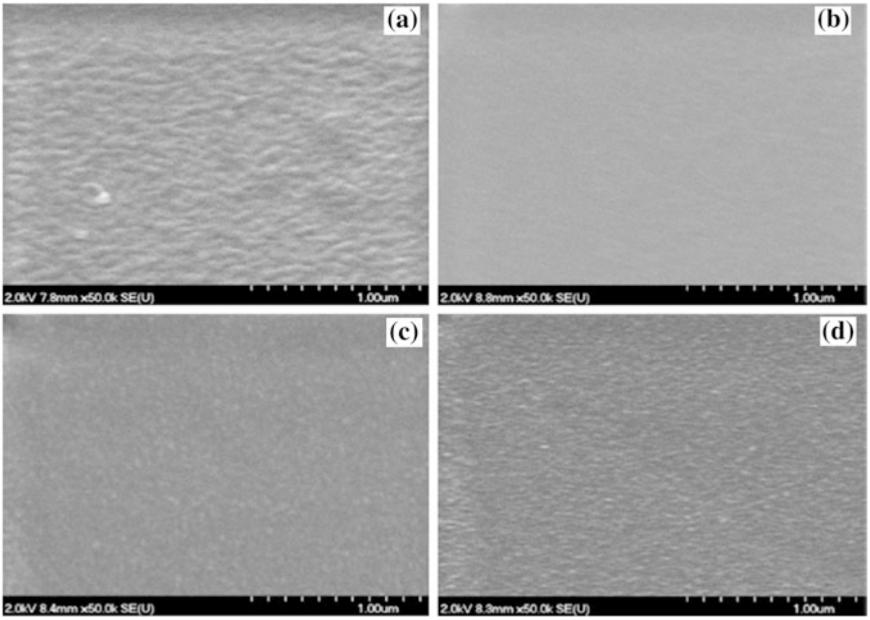


Fig. 6.3 Scanning Electron Microscopy image of the surface of nanocrystalline cellulose (**a**), chitosan (**b**), Chitosan +5% nanocrystalline cellulose (**c**) and Chitosan +5% nanocrystalline cellulose films (**d**). Reproduced with permission from Elsevier science, Ltd. (Khan et al. 2012)

increase in nanocrystalline cellulose amount (Fig. 6.3d). It is noticed that concentration of white dots is increased. Azizi Samir et al. (2005) also observed that the content of the white dots is a direct function of the cellulose nanocrystals composition in the composite.

6.2.4 *Transmission Electron Microscopy (TEM) Analysis of Chitosan-Based Nanocomposites*

TEM micrographs of the synthesized chitosan/silver microspheres (CAgMs) are represented in Fig. 6.4 (Youssef et al. 2014). It is noticed that silver nanoparticles show a spherical shape, and particle size is 10–20 nm (Fig. 6.4a, b). But in Fig. 6.4c and d, the silver nanoparticles are uniformly distributed in chitosan microspheres and have no change in size distribution, shape and particle size than those in the colloidal sol i.e. chitosan acts as a good stabilizing agent to avoid the agglomeration of silver nanoparticles and make them have a narrow size distribution in the cross-linking process (An et al. 2010). As a result, silver ions have been decreased to n Ag^0 and then found in silver nanoparticles both in the cellulose microspheres and chitosan/Ag colloidal sol.

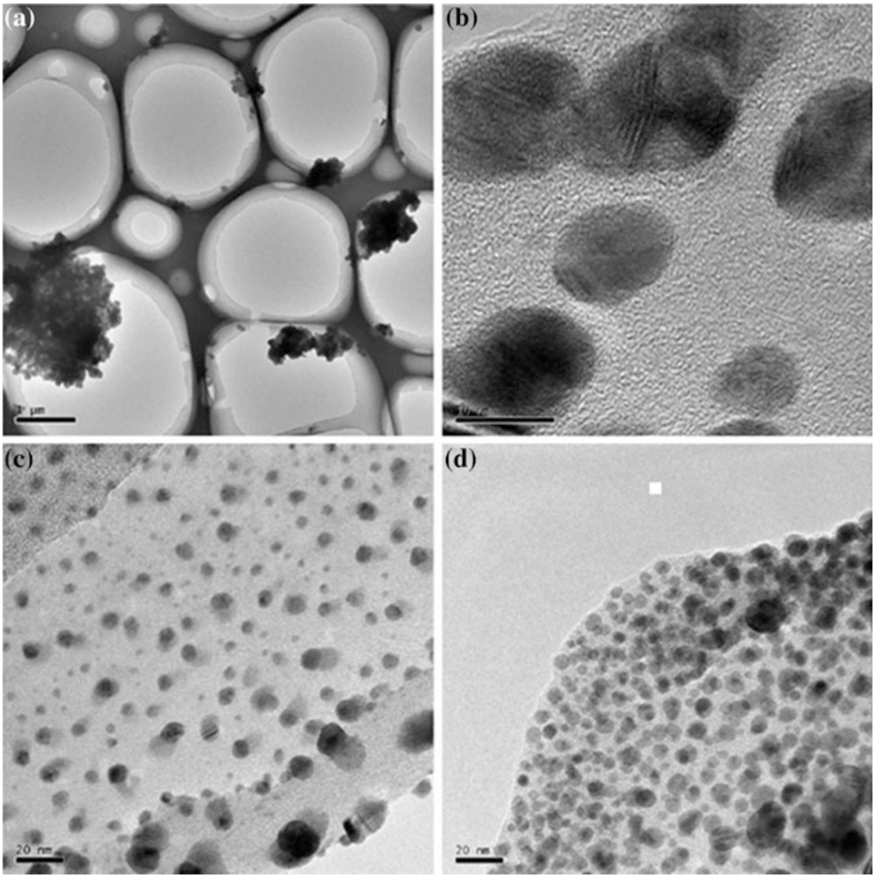


Fig. 6.4 TEM micrographs of chitosan/silver microspheres **a**, **b** and **c** and chitosan/silver colloidal sol (**d**). Reproduced with permission from Elsevier science, Ltd. (Youssef et al. 2014)

6.2.5 X-ray Photoelectron Spectroscopy (XPS) Analysis of Chitosan-Based Nanocomposites

The surface state of the chitosan/silver microspheres and elemental composition is examined by x-ray photoelectron spectroscopy as shown in Fig. 6.5 (Youssef et al. 2014). Here, in this Figure, Fig. 6.5a represents the presence of nitrogen, oxygen, carbon and silver with the relating molar ratios of 2.05, 20.87, 77.05 and 0.03%, respectively. Figure 6.5b represents chemical states of O1s, Ag3d and N1s core levels in the microsphere. But a strong Ag signal peaks of a binding energy of about 373.5 and 368.0 eV, indicating Ag^+ and Ag^0, respectively. The $Ag3d^{5/2}$ peak of silver nanoparticles in the microsphere matrix shows the presence of silver nanocrystalline on the surface of the microspheres. Because no other impurities are

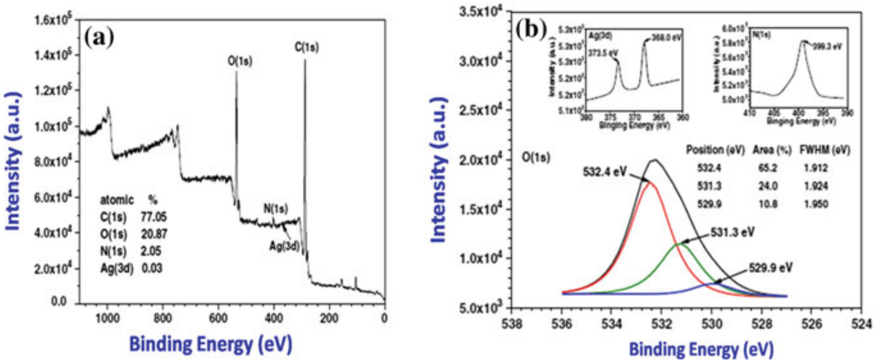


Fig. 6.5 X-ray photoelectron spectroscopy spectra as prepared chitosan/silver microspheres: survey spectrum O1s (**a**), Ag3d (**b**) and N1s (*inset*). Reproduced with permission from Elsevier science, Ltd. (Youssef et al. 2014)

detected within the sensitivity of the technique, it can be drawn a conclusion that the signal of O1s of 529.9 eV could be the Ag–O bond existing in the microspheres, which leads to the tight combination between silver nanoparticles and chitosan molecules. Another two spectrums of O1s of 531.3 and 532.4 eV can be ascribed to C–O and O–H bands, respectively. The spectrum of N1s of 399.3 eV shifts to a higher binding energy implies the decrease of electron density probably due to the existing of the bond linkage between the silver nanoparticles and chitosan molecules.

6.3 Properties of Chitosan-Based Nanocomposites

6.3.1 Thermal Properties of Chitosan-Based Nanocomposites

Thermal stability of pure nanocrystalline cellulose, pure chitosan, chitosan 10% NCC and chitosan 5% NCC is investigated by thermo gravimetric analysis (TGA) and are represented in Fig. 6.6 (Khan et al. 2012). Nanocrystalline cellulose films are very stable during the heating range 50–275 °C, losing only 4.2% of its initial weight. The weight loss for the chitosan, chitosan with 5 and 10% nanocrystalline cellulose are 26.7, 27.6 and 27.8%, respectively. Out of all these films, major weight loss is observed around at 280 °C which is combined to fast volatilization of polymer segments may be due to thermal scission of the polymer backbone. All chitosan samples (Control, chitosan with 5 and 10% nanocrystalline

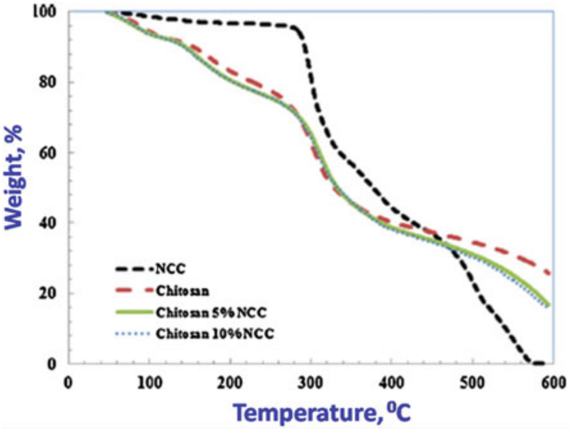


Fig. 6.6 Thermo gravimetric analysis curves for nanocrystalline cellulose, chitosan and chitosan with 5 and 10% nanocrystalline cellulose films. Reproduced with permission from Elsevier science, Ltd. (Khan et al. 2012)

cellulose films) exhibited a similar thermal behaviour of the temperature range 280–460 °C, and the influence of nanocrystalline cellulose on the thermal stability is observed to be negligible.

6.3.2 Mechanical Properties of Chitosan-Based Nanocomposite

Stress-strain curves of chitosan oil blends and chitosan/oil/organic montmorillonite nanocomposite films are illustrated in Fig. 6.7 (Giannakas et al. 2017). Here, in this Fig, addition of ethyl alcohol does not alter the elastic region of neat chitosan films; it leads, however, to a significant reduction of the strain of break from 11 to 8% (Fig. 6.7a). But in Fig. 6.7b, curves 1 and 2 result in small reduction of all mechanical properties, including strain of break. Similar results are also obtained in the earlier literature (Sánchez-González et al. 2010a, b, 2011). Though in Fig. 6.3b and c, addition of oils and ethyl alcohol result in a significant increase of the elongation of break. These behaviours are better prominent in films synthesized with olive oil (Fig. 6.7c), which shows strain of break values up to approximately 22%, of 20 wt% oil content. Corn oil-based films present lower strain of break, but higher amounts of oil (20 wt% corn oil) result in small reduction of the strain values. Furthermore, synthesized films using ethyl alcohol and oil present a widespread deformation strengthening region, indicative of the presence of a dense network of intermolecular hydrogen bonds (Petrova et al. 2012), but those synthesized through aquatic solutions present limited plastic flow. The observed differences in the plasticization efficiency and deformation strengthening region of olive and corn oil can be associated with the binding capacity of the different fatty acids with chitosan. In addition, the interactions of both olive and corn oil with chitosan chains are not interrupted by unbound water molecules. The combined effects of oil addition with organic montmorillonite are represented in Fig. 6.8 (Giannakas et al. 2017). Here, in this Figure, curve 1 and curve 2 represents the stress-strain behaviour of chitosan/organic montmorillonite samples is almost identical before and after the addition of ethyl alcohol. The addition of organic montmorillonite in chitosan improves the elastic modulus and decreases the tensile strength and strain of break

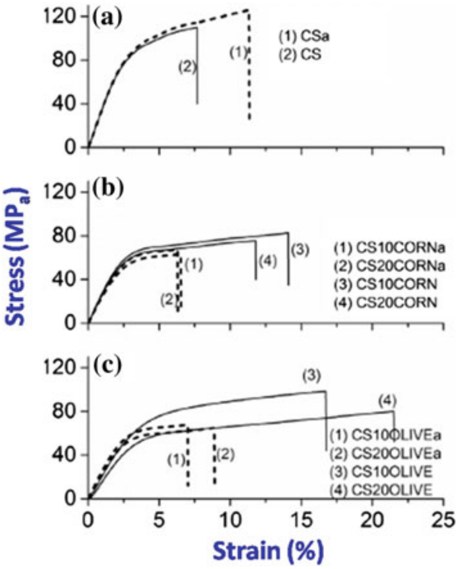


Fig. 6.7 Effect of Ethyl alcohol addition on the stress-strain behaviour of chitosan (**a**); chitosan/corn oil (**b**); and chitosan/olive oil films (**c**) (subscript a aquatic solution). Reproduced with permission from Elsevier science, Ltd. (Giannakas et al. 2017)

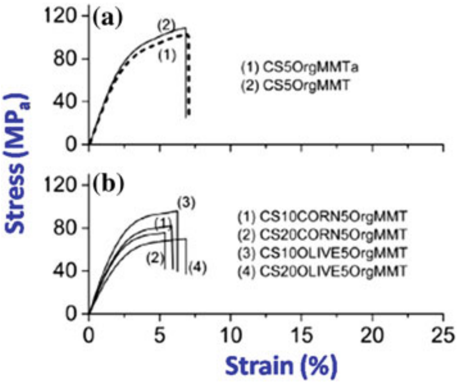


Fig. 6.8 Stress-strain behaviour of chitosan/organic MMT with/without EtOH (**a**), and chitosan/corn oil/organic MMT and chitosan/olive oil/organic MMT films. Note that all oil-containing nanocomposites are prepared from EtOH-based solutions (*subscript a* = aquatic solution). Reproduced with permission from Elsevier science, Ltd. (Giannakas et al. 2017)

values of chitosan films. Similar results are also obtained in the earlier literature (Barkoula et al. 2016). The addition of organic montmorillonite in oil-containing films (Fig. 6.8b) results in stiffening of the films (up to app. 25%); however, the strain of break is considerably decreased and in most cases is even lower than that of chitosan/organic montmorillonite. It is demonstrated that the intercalation of chitosan chains inside the organic montmorillonite platelets hinders the direct interaction of the chitosan chains with oils and obstructs the plasticization of the chitosan matrix. Another reason is that organic-modified montmorillonite platelets anchor between chitosan and oil chains, and these points act as stress concentrations resulting in reduced elongation of break.

6.3.3 Oxygen Barrier Properties

Composite materials which avoid oxygen permeation are being investigated for applying in packaging applications. Chitosan/calcium carbonate bionanocomposites are the kind of biodegradable material of bio origin and are essential for manufacturing of packaging films. The incorporation of calcium carbonate nanopowders provides the huddles to oxygen entrance, but pristine chitosan may have voids for oxygen permeation. Oxygen permeability of chitosan/calcium carbonate bionanocomposites is conducted to determine the effect of calcium carbonate loading on the chitosan matrix. The oxygen permeability of chitosan/calcium carbonate and chitosan bionanocomposites is represented in Fig. 6.9 (Das et al. 2014). As a result, the oxygen flow rate through all the chitosan/calcium carbonate bionanocomposites is found to be less than pristine chitosan at constant pressure (Fig. 6.9a) (Dash and Swain 2013a, b). It is observed that the flow rate is decreased with increasing percentage of $CaCO_3$ concentration. This remarkable reduction in oxygen permeability may be due to nanostructure incorporation of calcium carbonate particles within the matrix at different pressure up to 13.79 kPa (Fig. 6.9b).

6.3.4 Antibacterial Properties

Different microbial population grew in the chitosan matrix with silver montmorillinite are represented in Fig. 6.10 (Lavorgna et al. 2014). Here, in this Fig, Fig. 6.10b represents the different microbial population grew in the different samples. After 48 h, in all the broths the bacteria, the bacteria reached the maximum load. The same result is confirmed after 72 h of monitoring. The effects of silver-montmorillonite nanoparticles are developed in another scientific literature (Costa et al. 2011; Gammariello et al. 2011; Incoronato et al. 2010, 2011), where nanoparticles are incorporated in different polymeric matrices than chitosan and also applied to fresh food products. The hydrophilic cell wall structure of gram-negative bacteria as pseudomonas spp. is essentially constituted of lipopolysaccharides that

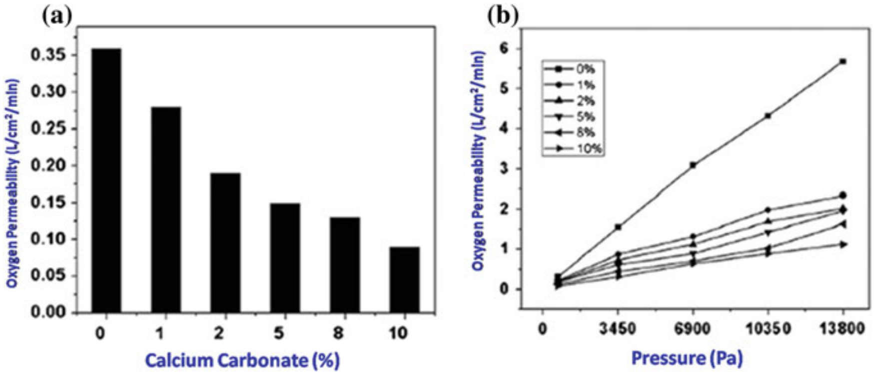


Fig. 6.9 Oxygen permeability of chitosan and chitosan/CaCO$_3$ bionanocomposites at constant pressure (**a**) and at different pressure (**b**). Reproduced with permission from Elsevier science, Ltd. (Das et al. 2014)

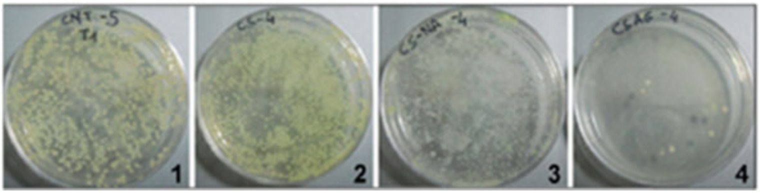


Fig. 6.10 Microbial population growth after 24 h in the different samples: *1* Control (CNT); *2* Neat Chitosan; *3* Chitosan/10NaMMT and *4* Chitosan/10AgMMT. Reproduced with permission from Elsevier science, Ltd. (Lavorgna et al. 2014)

attract towards the weak positive charge available on Ag ions, thus allowing the Ag-based antimicrobial nanoparticles to be effective (Bezic et al. 2003). The effect recorded after 24 h is followed by an increasing cell loads despite the Ag$^+$ released is still increasing over time. This is ascribable to a reversible stress of the cells. It is wide recognized that silver nanocomposite can cause reversible damages to the outer membrane that compromises microbial proliferation, but within a prolonged stress condition, the cell would repair the damages, re-acquiring the growth ability (Bezic et al. 2003; Johnston and Brown 2002).

6.4 Chitosan-Based Nanocomposite for Packaging Applications

Research efforts and enhancement of nanocomposite materials for packaging industry and other food contact surfaces are conventional to develop in the next decade with the introduction of new polymeric materials and composites with inorganic nanoparticles and their commercial applications as packaging materials (Youssef 2013, 2014, Youssef et al. 2013; Alam et al. 2008; Coma et al. 2002). Out of these biodegradable polymeric materials, chitosan has the potential and an excellent property for the application in packaging field. Further the intrinsic biodegradability of these materials, there are other important properties such as low cost, transparency, antibacterial properties and good film-forming properties through casting process. Rao et al. (2010) synthesized films using guar gum and chitosan during casting process in variation ratios. In this literature, the chitosan and guar gum can be applied to make a composite film having attractive packaging characteristics. In addition, these composite films attained from chitosan and guar gum might decrease environmental problems along with synthetic packaging.

The quality improvement and retardation in detrimental deterioration of food can be done by the protective coating during processing, storage and handling. Normally, appropriate packaging can slow deterioration rate, and hence, extend the shelf life of food. Nowadays, various types packages and processes have been working to interact with the food to provide desirable effects incorporating oxygen, moisture and ethylene scavengers for sensitive foods, respectively.: Physical reinforcement of these chemicals or other agents may be made into the package material, on or between the package and the food. That approaches, designed to perform some desirable function other than providing an inert barrier, refer to concepts called “active packaging”, “interactive packaging”, and “intelligent packaging” (Jiang 2001). Active packaging technologies are a relatively novel concept designed to provide interaction between food and packaging material. Although in the recent years, the moisture absorption packaging and antibacterial packaging are high commercial for oxygen scavenging. It is well known that plastic packaging films, produce a good quality results when combined with biopolymer coatings and films made from polysaccharides, proteins and lipids (Li et al. 2011; Szymanska et al. 2015). The marketing of environmentally friendly packaging that uses biodegradable materials has the greatest potential in countries where landfill is the main waste management tool. Caner et al. (1998) developed the effects of acid concentrations, plasticizer concentrations, and storage time on the mechanical and permeation properties of chitosan films. Jiang (2001) reported that the chitosan coating is extending the past-harvest life and maintaining the quality of longan fruit during storage at a low temperature. Chen et al. (1996) developed that chitosan films made in dilute acetic acid solutions are capable of inhibiting the growth of rhodotorula rubra and pencillium notatum by direct applications of the film on the colony-forming organism. Smart packagings are deliberate to monitor and give information about the quality of the packaged food (Suppakul et al. 2003; Appendini et al. 2002).

Antibacterial packaging is another field with high-potential applications by using bionanocomposites technology to control adverse microorganisms on foods by means of the inclusion of active molecules like antimicrobial compounds in or coated on to the packaging materials (Nigmatullin et al. 2008; Persico et al. 2009;

Vartiainen et al. 2010; Travan et al. 2011). Nanocomposite antimicrobial systems are particularly effective due to their high surface-to-volume ratio and the improved surface reactivity of the nano-sized antimicrobial agents: make them able to control microorganisms more effectively than higher scale counterparts. Bio-hybrid nanocomposite i.e. chitosan and bentonite nanoclay coated on argon-plasma-activated low-density polyethylene coated paper had enhanced barrier properties against water vapour, oxygen, grease and ultra violet light transmission (De Silva et al. 2017). The antibacterial behaviour of silver nanoparticles has been exploited by developing non-cytotoxicity coating for methacrylic thermo sets by means of a nanocomposite material based on a lactose-modified chitosan and silver nanoparticles (Rhim et al. 2006). Those biocompatible antimicrobial polymeric films containing antimicrobial silver nanoparticles may show excellent promising properties for antimicrobial packaging material. But, the antibacterial functions of chitosan are limited because amino groups on chitosan molecule backbone can only be protonated as relatively weak positive charge centres, which cannot bind strongly to negatively charged surface of bacterium cell walls. Different method- and different filler-incorporated chitosan-based nanocomposites are represented in Table 6.1.

Table 6.1 Different method- and different filler-incorporated chitosan-based nanocomposite

Material	Name of the filler	Method	Reference
Chitosan	Organo clay	Solution blending	Giannakas et al. (2017)
Chitosan	Nano-MgO	In-situ	De Silva et al. (2017)
Chitosan	Na-MMT, Closite 30B, a Nano-silver and an Ag-Zeolites (Ag-Ion)	Solvent casting	Rhim et al. (2006)
Chitosan	Nanocrystalline cellulose	Solution casting	Khan et al. (2012)
Chitosan	Nanomatric graphene stacks	Schiff base formation for chitosan functionalized	Demitri et al. (2016)
Chitosan	ZnO-NPs	Model system to better estimation of staling rate and microbial growth	Noshirvani et al. (2017)
Chitosan	Clay platelets	Electron beam irradiation	Shahbazi et al. (2017)
PVA/Chitosan	Closite 30B	Freeze/thawing	Butnaru et al. (2016)
Chitosan	Fish gelatin	Solution casting	Hosseini et al. (2015)
Chitosan	Ag NPs and AU NPs	Simple chemical	Youssef et al. (2014)
Chitosan	Chitosan-tripolyphosphate-thymol	Thermal Ink-jet printing	Caro et al. (2016)

6.5 Concluding Remarks

Non-biodegradable petrochemical-based plastic packaging materials as well as the consumers demand for high-quality food products have caused an increasing interest in developing biodegradable packaging materials using renewable natural biopolymers like polysaccharides and proteins. Out of these biodegradable polymeric materials, chitosan has potential and an excellent property for the application in packaging field. In this chapter, different characterization technique, properties are explained along with the applications of chitosan-based nanocomposites for packaging purpose. The dispersion of nanomaterials in the chitosan matrix creates huddles in penetration of gas with improving barrier property which is an important property for enabling the materials for packaging applications.

Acknowledgements Authors express their thanks to Department of Science and Technology, Government of India for awarding Inspire Fellowship to Kalyani Prusty for carrying out her doctoral degree.

References

Aider M (2010) Chitosan application for active bio-based films production andpotential in the food industry: review. LWT Food Sci Technol 43:837–842

Alam R, Khan MA et al (2008) Study on the physico-mechanical properties of photo-cured chitosan films with oligomer and acrylate monomer. J Polym Environ 16:213–219

An J (2010) Preparation of chitosan-*graft*-(methyl methacrylate)/Ag nanocomposite with antimicrobial activity. Polym Int 59:62–70

Appendini P et al (2002) Review of antimicrobial food packaging. Innovative Food Sci Emerg Technol 3:113–126

Azizi Samir MAS et al (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. Biomacromol 6:612–626

Barkoula NM et al (2016) Mechanical and thermomechanicalproperties of nanocomposites. In Jyotishkumar Parameswaranpillai NH, Kurian T, Yu Y (eds) Nanocomposite materials: synthesis, properties andapplications. CRC Press, Boca Raton

Benhabiles MS, Salah R, Lounici H et al (2012) Antibacterial activity of chitin, chitosan and its oligomers prepared from shrimp shell waste. Food Hydrocolloid 29:48–56

Bezic N et al (2003) Composition and antimi-crobial activity of *Achillea clavennae* L. essential oil. Phytotherapy Research. 17:1037–1040

Bodin A, Ahrenstedt L et al (2007) Modification of nanocellulose with a xyloglucan–RGD conjugate enhances adhesion and proliferation of endothelial cells: implications for tissue engineering. Biomacromol 8:3697–3704

Butnaru E et al (2016) Poly (Vinyl alcohol) chitosan/Montmorillonite nanocomposites for food packaging applications: Influence of Montmorillonite content. High Perform Polym 28: 1124–1138

Caner C et al (1998) Chitosan film mechanical and permeation properties as affected by acid, plasticizer, and storage. J Food Sci 63:1049–1053

Caro N et al (2016) Novel active packaging based on films of chitosan and chitosan/quinoa protein printed with chitosan-tri polyphosphate-thymal nanoparticles via thermal ink-jet printing. Food Hydrocolloids 52:520–532

Chen MC et al (1996) G.H.C. Yeh, B.H. Chiang, Antimicrobial and physicochemical properties of methylcellulose and chitosan films containing a preservative. J. Food Proc Preserv 20:379–390

Chung TW, Lu YF, Wang HY et al (2003) Growth of human endothelial cells on different concentrations of Gly-Arg-Asp grafted chitosan surface. Artif Organs 27:155–161

Coma V, MartiaL-Gros R et al (2002) Edible antimicrobial films based on chitosan matrix. J Food Sci 67:1162–1169

Costa C et al (2011) Bio-based nanocom-posite coating to preserve quality of Fiordilatte cheese. Int J Food Microbiol 148:164–167

Croisier F et al (2013) Chitosan-based biomaterials for tissue engineering. Eur Polymer J 49: 780–792

Das S, Kisku SK et al (2014) Thermal and oxygen barrier properties of chitosan bionanocomposites by reinforcement of calcium carbonate nanopowder. J. Mater Sci. Techn. 30:791–795

Dash S, Swain SK (2013a) Effect of nanoboron nitride on the physical and chemical properties of soy protein. Compos Sci Technol 84:39–43

Dash S, Swain SK (2013b) Synthesis of thermal and chemical resistant oxygen barrier starch with reinforcement of nano silicon carbide. Carbohydr Polym 97:758–763

De Silva RT et al (2017) Nano-MgO reinforced chitosan nanocomposites for high performance packaging applications with improved mechanical, thermal and barrier properties. Carbohydr Polym 157:739–747

Demitri C et al (2016) Nanostructured active chitosan-based films for food packaging applications: Effect of graphene stacks on mechanical properties. Measurement 90:418–423

Dumitriu S. (2002). Polymeric biomaterials. Marcel Dekker, Inc, New York

Dutta K, Tripathi S et al (2009) Perspectives for chitosanbased antimicrobial films in food applications. Food Chem 114:1173–1182

Gammariello D et al (2011) Bio-basednanocomposite coating to preserve quality of Fior di latte cheese. J Dairy Sci 94:5298–5304

Giannakas A et al (2017) A novel solution blending method for using olive oil and corn oil as plastisizers in chitosan based organo clay nanocomposites. Carbohydr Polym 157:550–557

Helbert W et al (1994) Oriented growth of V amylase n-butanol crystals on cellulose. Carbohydr Polym 24:119–122

Hosseini SF et al (2015) Fabrication of bionanocomposites films based on fish gelatin reinforced with chitosan nanoparticles. Food Hydrocolloids 44:172–182

Imam SH et al (2012) Utilization of biobased polymers in food packaging: assessment of materials, production and commercialization. In: Yam KL, Lee DS (eds) Emerging food packaging technologies principles and practice. Wood head Publishing Limited, Cambridge, pp 435–468

Incoronato AL et al (2010) Active systems based on silver/montmorillonite nanoparticles embedded intobio-based polymer matrices for packaging applications. J Food Prot 73: 2256–2262

Incoronato AL et al (2011) Agar hydrogel with silver nanoparticles to prolong the shelf life of Fior di Latte cheese. J Dairy Sci 94:1697–1704

Jiang Y et al (2001) Effects of chitosan coating on postharvest life and quality of long an fruit. Food Chem 73:139–143

Johnston MD, Brown MH (2002) An investigation into the changed physiological state of Vibrio bacteria as a survival mechanism in response to coldtemperatures and studies on their sensitivity to heating and freezing. J Appl Microbiol 92:1066–1077

Kanatt SR, Rao MS et al (2012) Active chitosan polyvinyl alcohol films with natural extracts. Food Hydrocolloid 29:290–297

Khan RA et al (2010) Production and properties of nanocellulose reinforced methylcellulose based biodegradable films. J Agric Food Chem 58:7878–7885

Khan A, Khan RA et al (2012) Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films. Carbohydr Polym 90:1601–1608

Kisku SK, Das S et al (2014) Dispersion of sic nanoparticles in cellulose for study of tensile, thermal and oxygen barrier properties. Carbohydr Polym 99:306–310

Kondo T et al (1996) The assignment of IR absorption bands due to free hydroxyl groups in cellulose. Polymer 37:393–399

Kumar MNS, Yaakob Z et al (2011). Biobased materials in foodpackaging applications. In Handbook of bioplastics and biocompositesengineering applications. Wiley, New York, pp 121–159

Kurita K (2006) chitin and chitosan: functional biopolymers from marine crustaceans. Mar Biotechnol 8:203–226

Lavorgna M et al (2014) MMT-supported Ag nanoparticles for chitosan nanocomposites: structural properties and antibacterial activity. Carbohydr Polym 102:385–392

Leceta I, Guerrero P et al (2013a) Characterization and antimicrobial analysis of chitosan-based films. J Food Eng 116:889–899

Leceta I, Guerrero P, Ibarburu I et al (2013b) Characterization and antimicrobial analysis of chitosan-based films. J Food Eng 11:889–899

Li Q et al (2011) Supramolecular structure characterization of molecularly thin cellulose I nanoparticles. Biomacromol 12:650–659

Muzzarelli RAA, Boudrant J et al (2012) Current views on fungal chitin/chitosan, human chitinases, foodpreservation, glucans, pectins and inulin: a tribute to Henri Braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial. Carbohydr Polym 87:995–1012

Nigmatullin R et al (2008) Polymer-layered silicate nanocomposites in the design of antimicrobial materials. J Mater Sci 43:5728–5733

Nikonenko NA et al (2005) Spectroscopic manifestation of stretching vibrations of glycosidic linkage in polysaccharides. J Mol Struct 752:20–24

Nikonenko NA, Buslov DK et al (2000) Investigation of stretching vibrations of glycosidic linkages in disaccharides and polysaccharides with use of IR spectra deconvolution. Biopolymers 57:257–262

Noshirvani N et al (2017) Novel active packaging based on carboxymethyl cellulose-chitosan-ZnO NPs nanocomposite for increasing the shelf life of bread. 11:106–114

Ogawa K et al (1994) New polymorph of chitosan. Macromolecules 17:973–975

Persico P et al (2009) Nanocomposite polymer films containing carvacrol for antimicrobial active packaging. Polym Eng Sci 49:1447–1455

Petersen K, Nielsen P, Bertelsen G, Lawther M, Olsen MB et al (1999) Potential of biobased materials for food packaging. Trends Food Sci Technol 10:52–68

Petrova VA et al (2012) Specific features of chitosan-montmorillonite interaction in anaqueous acid solution and properties of related composite films. Polyme Sci Ser A 54:224–230

Rao MS, Kanatt SR et al (2010) Chitosan and guar gum composite films: preparation, physical, mechanical and antimicrobial properties. Carbohydr Polym 82:1243–1247

Rhim JW et al (2006) Preparation and characterization of chitosan-based nanocomposite films with antimicrobial activity. J Agric Food Chem 54:5814–5822

Rhim JW, Park HM et al (2013) Bio-nanocomposites for food packaging applications. Prog Polym Sci 38:1629–1652

Sánchez-González L et al (2010a) Physical properties of edible chitosan films containing bergamot essential oiland their inhibitory action on Penicillium italicum. Carbohyd Polym 82:277–283

Sánchez-González L et al (2010b) Physical properties of edible chitosan films containing bergamot essential oiland their inhibitory action on Penicillium italicum. Carbohydr Polym 82:277–283

Sánchez-González L (2011) Effect of essential oils on properties of film forming emulsions and films based on hydroxypropylmethylcellulose and chitosan. J Food Eng 105:246–253

Shahbazi M et al (2017) Characterization of nanocomposite film based on chitosan intercalated in clay platelets by electron beam irradiation. Carbohydr Polym 157:226–235

Siracusa V, Rocculi P, Romani S et al (2008) Biodegradable polymers for food packaging: a review. Trends Food Sci Technol 19:634–643

Sorrentino A, Gorrasi G et al (2007) Potential perspectives of bio-nanocomposites for food packaging applications. Trends Food Sci Technol 18:84–95

Suppakul MJ et al (2003) Active packaging technologies with an emphasis on antimicrobial packaging and its applications. J Food Sci 68:408–420

Swain SK, Dash S et al (2014a) Effect of zirconium oxide nanopowders on the thermal, chemical and gas barrier properties of starch. Mater Sci Semicond Process 23:115–121

Swain SK, Patra SK et al (2014b) Study of thermal, oxygen-barrier, fire-retardant and biodegradable properties of starch bionanocomposites. Polyme Compos 35:1238–1243

Szymanska E et al (2015) Stability of chitosan—a challenge for pharmaceutical and biomedical applications. Marine Drugs 13:1819–1846

Travan A et al (2011) Silver-polysaccharide nanocomposite antimicrobial coatings for methacrylic thermosets. Acta Biomater 7:337–346

Tripathi S, Mehrotra GK et al (2008) Chitosan based antimicrobial films for food packaging applications. E-Polymers 8:1082–1088

Tsigos I, Martinou A et al (2000) Chitin deacetylases: new: versatile tools in biotechnology. Trends Biotechnol 18:305–312

Van den Broek LA, Knoop RJ et al (2015) Chitosan films and blends for packaging material. Carbohyd Polym 116:237–242

Vartiainen J et al (2010) Bio-hybrid nanocomposite coatings from sonicated chitosan and nanoclay. J Appl Polym Sci 116:3638–3647

Wang SF, Shen L (2005) Preparation and mechanical properties of chitosan/carbon nanotubes composites. Biomacromol 6:3067–3072

Wang H et al (2011) Formation and properties of chitosan cellulose nanocrystal polyelectrolyte macroion complexes for drug delivery applications. Biomacromol 12:1585–1593

Yen MT, Yang JH et al (2008) Antioxidant properties of chitosan from crab shells. Carbohyd Polym 74:840–844

Youssef AM (2013) Polymer Nanocomposites as a new trend for packaging applications. Polym Plastic Technol Eng 52:635–660

Youssef AM (2014) Chitosan nanocomposite films based on Ag-NP and AU-NP biosynthesis by Bacillus subtilis as packaging materials. International J Biological Macromol 69:185–191

Youssef AM et al (2013) Morphological and antibacterial properties of modified paper by PS nanocomposites for packaging applications. Carbohydr Polym 98:1166–1172

Youssef AM et al (2014) Morphological studies of polyaniline nanocomposite based mesostructured TiO 2 nanowires as conductive packaging materials. RSC Adv 4:6811–6820

Chapter 7
Sugar Palm Starch-Based Composites for Packaging Applications

M.L. Sanyang, R.A. Ilyas, S.M. Sapuan and R. Jumaidin

Abstract Non-biodegradable petroleum-based plastics are still the most dominant material used by the food industry for packaging applications. Consequently, the widespread usage of these conventional plastics has led to serious negative environmental impacts. Numerous studies were conducted over the years to substitute these packaging plastics with eco-friendly materials in order to arrest the ongoing plastic waste disposal problems. Against this background, the current chapter presents a review of recent works on sugar palm starch-based films and different modification techniques employed to improve their performance as effective biopackaging material.

Keywords Sugar palm starch · Packaging · Blend · Biocomposites · Nanocomposites

7.1 Introduction

The predominant purpose of food packaging is to retain the safety and quality of food products during transportation and storage as well as to preserve the lifetime of food product by avoiding undesired conditions such as moisture, external force, spoilage microorganism, mechanical shock and vibration, odor, gases, oxygen, and

---

M.L. Sanyang (✉) · R.A. Ilyas · S.M. Sapuan
Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products,
Universiti Putra Malaysia, UPM Serdang, 43400 Selangor, Malaysia
e-mail: sanyang.abuhamza@gmail.com

S.M. Sapuan · R. Jumaidin
Department of Mechanical and Manufacturing Engineering, Universiti Putra Malaysia,
UPM Serdang, 43400 Selangor, Malaysia

R. Jumaidin
Department of Structure and Material, Faculty of Mechanical Engineering,
UniversitiTeknikal Malaysia Melaka, Durian Tunggal, 76100 Melaka,
Hang Tuah Jaya, Malaysia

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_7

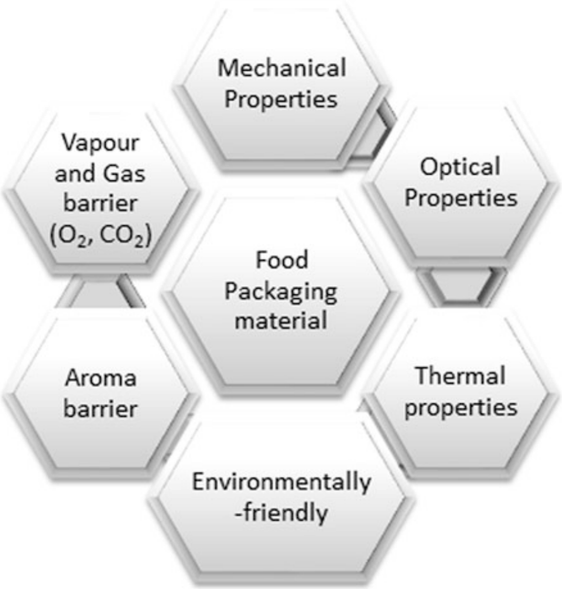


Fig. 7.1 Common features required for food packaging materials

chemical contamination, etc. (Fang and Fowler 2003; Mihindukulasuriya and Lim 2014). Besides that, other functions of packaging are to provide crucial information about the product to customers as well as to advertise and promote the product.

Nowadays, food producers are struggling to improve food packaging system by enhancing the end use convenience features due to active lifestyle in modern society. Packaging materials are not only use as a packaging bag, but they also act as a protective barrier with some established functions. Apparently, due to their safety aspects and relatively temporary use, food packaging materials are entirely different from other sturdy goods such as furniture, home appliances, and electronics. Figure 7.1 shows the common features necessary for food packaging materials.

Overall, this chapter highlights the significance of utilizing bio-based plastics such as thermoplastic starch in place of conventional packaging plastics. Furthermore, the current chapter introduces sugar palm starch as a relatively novel starch for the development of bio-based packaging materials.

7.2 Types of Packaging Materials

In older time, glass, plastic, metal, and paper are used for numerous packaging application as shown in Fig. 7.2. Among these basic packaging types, petroleum-based plastics have been ubiquitously used due to their good processing properties, good physicochemical and good esthetic feature (Rhim et al. 2013). Plastic is preferred as food packaging material over glass and metal owing to their

Fig. 7.2 Different types of materials for food packaging

flexibility, lightweight, portability, and affordability. Though glass and metal are easier to be reused, they are quite expensive to recycle, whereas, it is much more easier and cheaper to completely recycle plastics for reuse. In case of paper, the raw material for making paper is dominantly wood from various species of trees. The increasing use of paper to meet the high demand for packaging will lead to huge deforestation. Moreover, paper packaging materials are less durable, highly sensitive to water, and recycling them is difficult and inefficient compared to plastics in terms of energy and water consumption. Hence, plastic packaging continues to dominate over paper in the packaging market.

According to Fang and Fowler (2003), in a year, it is estimated that over 30 million tons of petroleum-based plastics are utilized for packaging purpose such as gardening supplies, blood platelets bag, food packing, agricultural mulch films, waste disposal bags, woven plastic fibers bags used for sand or plastic shopping bag. In which, this is approximately equivalent to 25% of plastic produced around the globe and their consumption is still growing continuously (Fang and Fowler 2003). In actual fact, it is estimated that by 2015, the worldwide plastic manufacturing is expected to surpass 300 million tons (Arvanitoyannis 1999; Rhim et al. 2013).

7.2.1 Bio-Based Plastics

There are two main types of plastics depending on the source, namely petroleum-based and bio-based plastics (see Fig. 7.3). Despite countless advantages

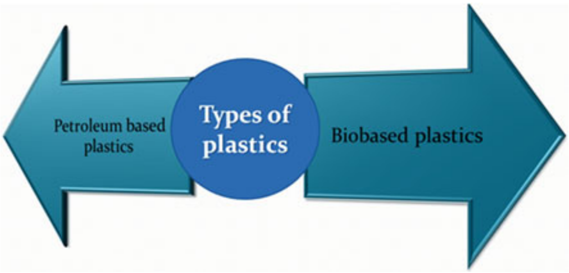


Fig. 7.3 Two main types of plastics

of petroleum-based plastics, they are synthesized to be resistance to microbial attack and recalcitrant to degrade and thus give rise to serious environmental impact allied with the accumulation of disposed plastic waste into the environment. Consequently, numerous researches have been conducted recently for developing new thermoplastic material that is bio-based plastic from renewable sources. Hence recently, green polymers with controllable lifetimes have become increasingly significant for various applications in the field of biomedical implants, wild life conservation, drug release, agriculture, forestry, and waste management (Fang and Fowler 2003). The starch-based packaging material is one of the alternatives to replace synthetic plastic market, which to date; their utilization is estimated to surpass 30,000 tons/annual within the following years ahead (Sreekala et al. 2001). The bio-based packaging usage is on the hike, particularly in countries where land field is used as primary waste management (Cha and Chinnan 2004). According to Tang et al. (2012), from 1988 to 2005, the municipal solid waste generation increased by 37% which 31.2% of the solid waste is contributed by packaging materials, with two-thirds of the total packaging waste by volume are covered alone by food packaging (Cha and Chinnan 2004; Weber et al. 2002).

7.3 Starch

Starch is a cheap, abundant, renewable, sustainable, edible, and biodegradable polymer. It is mostly extracted from the roots, stalks, and seeds of staple crops such as rice, potato, tapioca, wheat, corn (Fig. 7.4). Starch is considered as the main form of stored carbohydrate in these crops. It safely contributes 50–70% of the energy in the human diet. Glucose which can be directly obtained from starch is a vital source of substrate for the brain and red blood cells to produce metabolic energy (Srikaeo et al. 2016). After cellulose, starch is the most abundant natural polymer. USA and Europe were reported as the largest producers of starch in the entire world; they contribute almost half of produced commercial starch (Imam et al. 2012). The annual global production of starch from different cereal, tubers, and root crops is about 60 million tonnes, 60% of which are utilized in food (i.e., ice cream, bakery products, baby foods etc), whereas the remaining 40% is used in pharmaceuticals

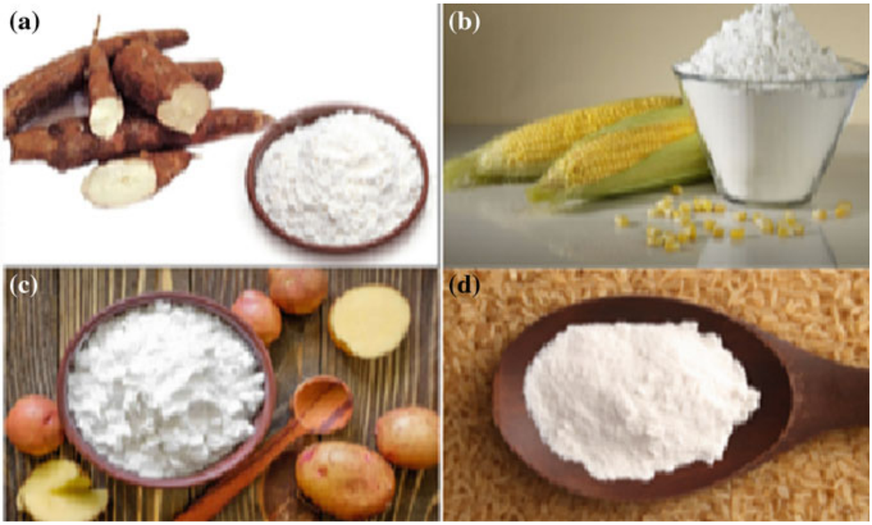
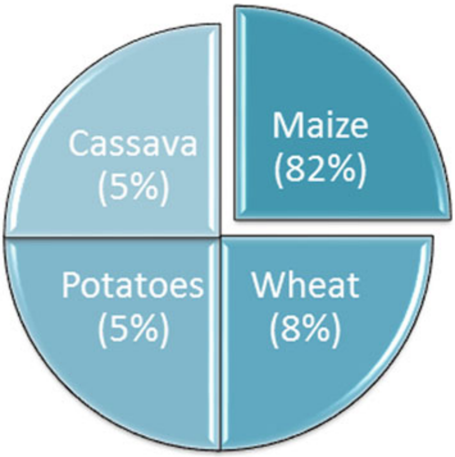


Fig. 7.7 Starch from different sources **a** cassava, **b** corn, **c** potato, **d** rice

Fig. 7.5 The main source of starch worldwide (Angellier et al. 2004)



and non-edible applications (i.e., fertilizers, paper, cardboard, diapers, adhesives etc.). Figure 7.5 shows the distribution of the main source of starch worldwide.

7.3.1 Starch Structure

Starch is a polysaccharide which consists of D-glucose units, known as homoglucan or glucopyranose. The D-glucopyranose polymers in starch are connected together by α-(1 → 4) and α-(1 → 6) glycosidic bonds. The C1 on a D-glucopyranose molecule reacts with C4 or C6 from a nearby D-glucopyranose molecule in the process of forming α-(1 → 4) and α-(1 → 6) glycosidic bonds. The glycosidic linkages in starch are primarily in the α configuration, whereas the development of the α linkages depends on the orientation of the hydroxyl group (–OH) ON C1 of the pyranose ring. Some starch polymers form helical structures due to the existence of α linkages, which contribute to its extraordinary properties and enzyme digestibility (Srikaeo et al. 2016).

7.3.1.1 Amylose

Chemically, starch consists of two different types of anhydroglucose polymers, regardless of botanical origins. These macromolecules are referred to as amylose and amylopectin, which embody approximately 98–99% of the dry weight (Tester et al. 2004). Amylose and amylopectin have varying structures (as shown in Fig. 7.6) and properties. The ratio of these two anhydroglucose polymers differs based on botanical origin of the starch. Starches with amylose content greater than 40% are considered as 'high' amylose starches, whereas 'waxy' starches contain below 15% amylose. Generally, the amylose-to-amylopectin ratio in most starches ranges from 15:85 to 35:65 (Cano et al. 2014; Liu and Han 2005). Both amylose and amylopectin contribute to the crystallization of starches which affect the mechanical behavior of starch-based products (Cano et al. 2014; Talja et al. 2007).

Amylose is a macromolecule found in starches with relatively long, slightly branched or essentially linear α-glucan containing approximately 99% α-(1 → 4) and α-(1 → 6) linkages. The amylose content in starches varies in structure and size according to the botanical origin of starches. The molecular weight of amylose is as high as 10^6 g mol^{-1}. Its degree of polymerization (DP) by number (DP_n) is 324–4920, which comprises of about 9–20 branch points corresponding to 3–11

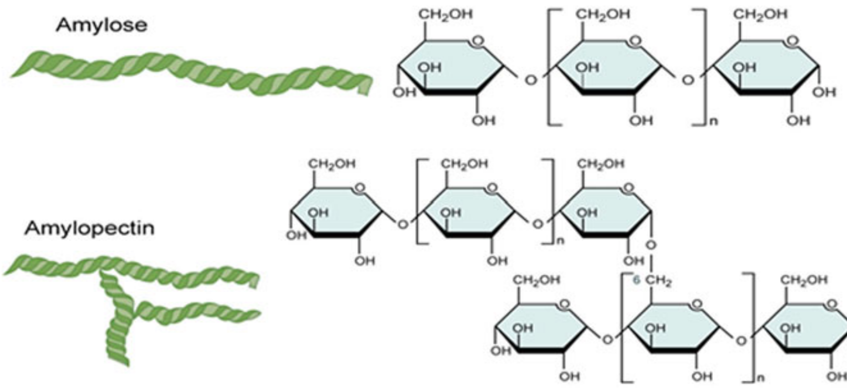


Fig. 7.6 Starch amylose and amylopectin structure

chains per molecule (Yoshimoto et al. 2002). The quantity of glucose residues of each chain ranges from 200 to 700, which in turn is equivalent to a molecular weight of 32400–113400 (Srikaeo et al. 2016). Owing to the low degree of branching, amylose has the affinity to form insoluble semicrystalline aggregates when dissolved. The position of the branches in the amylose structure also plays significant role in the formation of such insoluble semicrystalline aggregates.

7.3.1.2 Amylopectin

The major component of starches is amylopectin, which consists of a large number of relatively shorter chains but highly branched. The shorter chains of amylopectin are compelled together at their reducing end side by α-(1 → 6) linkages (Wittaya 2012). The aldehyde group on one end of starch polymers is free, which is referred to as the reducing end. Whereas, the other end of the polymer is denoted as the non-reducing end (Chap. 2). The α-(1 → 6) linkages serve as the branching point of the α-(1 → 4) linear chains, resulting in the highly branched structure of amylopectin. However, these α-(1 → 6) linkages constitute only about 5% of the amylopectin structure. Amylopectin has larger molecular weight (as high as 10^9 g mol^{-1}) compared to the amylose molecule. Similar to amylose, the size, shape, and structure of amylopectin vary with botanical origin. Morphologically, the amylopectin component consists of crystalline areas which make it insoluble even in hot water, unlike the linear amylose which is mostly amorphous or semicrystalline (Tester et al. 2004).

Basically, amylopectin chain length is considered as the main factor for crystalline polymorphism (Hizukuri et al. 1983). However, it is worth noting that the short-branched chains in amylopectin are the main crystalline component of native starch granules, whereas amylose and the branching chains of amylopectin form amorphous regions. Thus, an organization of amylopectin side chains clustered together is responsible for the partial crystallinity of native starch granules. The source, age, and a times the employed extraction process of the starch determine the amylose and amylopectin ratio of the starch (Koshy et al. 2013).

7.4 Sugar Palm Starch

Nowadays, the expanding of human population as well as depletion of non-renewable sources of raw material such as petroleum-based polymer caused the shift in food packaging industry from conventional material to biopolymers. One of the efforts to resolve this problem is by alternating the production of petroleum-based food packaging material to natural biopolymers such as sugar palm starch. Utilization of biopolymer such as sugar palm starch for the formation of packaging films is advantageous because they are biodegradable, environmental friendly polymer, and originated from renewable resources. Sugar palm also known as *Arenga pinnate* is mostly found in humid tropics and considered to be a good source of brown sugar (Sanyang et al. 2016a, b, c, d). Besides the production of brown sugar, numerous other products are obtained from sugar palm tree (Ishak et al. 2013). It also serves as a potential source of starch and fibers for developing green composite materials. Sugar palm tree takes around fifteen years or more to reached maturity, and its physical height is from twelve to fifteen meter with diameter around 40 cm (Florido 2003). Around 50–100 kg of starch can be obtained from a single sugar palm tree (Sahari et al. 2012).

7.4.1 Extraction and Preparation of Sugar Palm Starch

Sugar palm starch is extracted from the trunk of sugar palm tree. In the sugar palm plantation, there are some trees that are unproductive in terms of fruits and cannot produce sap as well. Hence, such trees are utilized for the extraction of starch. The starch is obtained from the inner soft core of the trunk, and the age of the tree affects the quality and quantity of starch present in the trunk. Typical traditional technique of starch extraction from the tree is normally employed to obtain sugar palm starch with some innovative modifications. The technique is similar to that of sago starch extraction. Basically, the tree is cut down and split open with the help of a mechanized chain saw to access the inner core of the tree as shown in Fig. 7.7. The chain saw is further used for grinding and removing the soft inner core of the trunk which contains short fibers and starch (see Fig. 7.7).

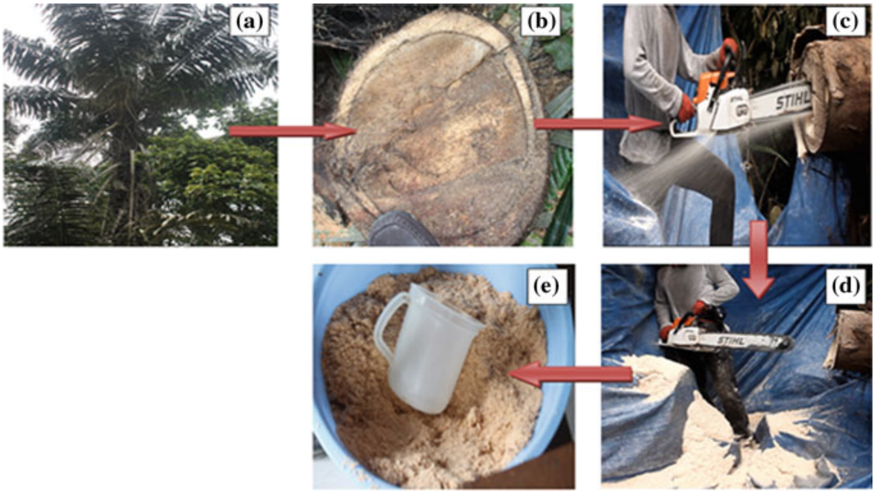


Fig. 7.7 Process of removing starch from the inner core of the tree trunk

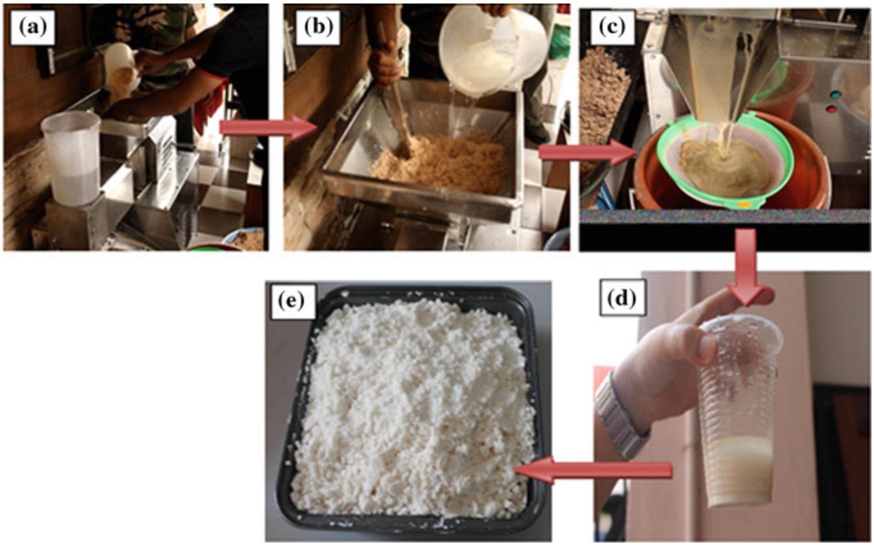


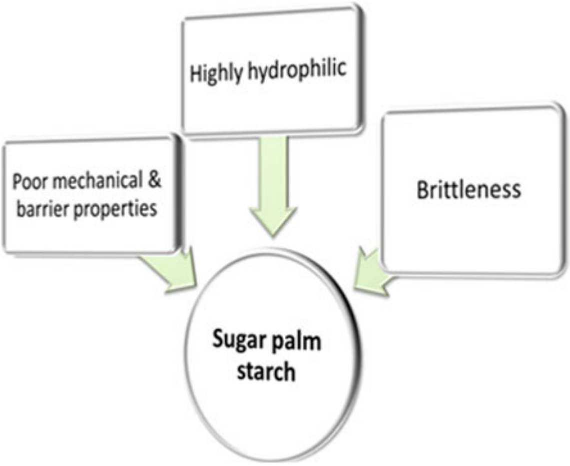
Fig. 7.8 Process of sugar palm starch extraction using starch extracting machine

> The olden method of separating starch from the grinded soft short fibers is to gradually pour water into the mixture and thoroughly knead by hand to squeeze out the starch. This technique is extremely tedious, time consuming and the starch yield is quite low. Moreover, this technique is not favorable for large scale extraction of starch. Hence, starch extracting machine is currently utilized for effective separation of starch. This innovative method enhances the quantity of starch obtained as well as lessens the labor intensity of the process. To separate the starch, the mixture is inserted in the open mouth of the machine and water is also introduced so that the starch will be flush and flow out with the added water via the machine outlet. Thereafter, the mixture of starch and water passes a sieve to filter possible impurities. The starch suspended in the water is allowed to completely settle down with time before the water is finally decanted. The obtained starch is first dried in open air prior to its drying in an air circulating oven at 120°C. On the other hand, the soft short fibers are isolated and removed from the machine as waste (Fig. 7.8).

7.5 Modification of Sugar Palm Starch Films

Sugar palm starch like most other biopolymers is hydrophilic in nature due to either their hydroxyl or polar groups. The major challenges for the development of starches as packaging films are the shortcomings related to brittleness, processability, high moisture sensitivity, quick retrogradation, poor mechanical and barrier properties (Fig. 7.9). In order to transform native sugar palm starch into high-performance thermoplastic starch for packaging application, the aforementioned drawbacks should be addressed. Some of the approaches employed to tackle these roadblocks are; (1) the addition of different types and concentrations of plasticizer(s) into the

Fig. 7.9 Main drawbacks of sugar palm starch films



starch matrix, (2) the combination of sugar palm starch with other polymers that possess better functional properties, and (3) the incorporation of natural fibers, cellulose, and nanocellulose. The implementation of such modifications on the sugar palm starch contributes to the improvement of its functional properties as well as helps in optimizing its full potential as an effective food packaging material.

7.5.1 Plasticization of Sugar Palm Starch Films

In the last few decades, there is an accelerating demand for starch-based materials for numerous packaging applications. The increasing growth of starch-based materials in the packaging industry can be ascribed to their abundant availability, affordability, renewability, and biodegradability. Besides, they can be utilized to prepare transparent films which are odorless, tasteless, and non-toxic. Numerous researchers developed biodegradable packaging products from various starches such as tapioca (Edhirej et al. 2017; Villacrés et al. 2014; Klein et al. 2014), yam (Gutiérrez et al. 2015), maize (Wu et al. 2013; Xie et al. 2014), pea (Li et al. 2015), rice (Wittaya 2009), agar (Tian et al. 2011), sago (Arockianathan et al. 2012), corn (Dai et al. 2015; Moreno et al. 2014), potato (Fonseca et al. 2015; da Rosa Zavareze et al. 2012). Over the years, sugar palm starch, a novel biopolymer, has received considerable attention as a potential film-forming material (Sahari et al. 2013a; Sanyang et al. 2015a, b; 2016a, b, c). This novel biopolymer has demonstrated higher amylose content (i.e., 37%) which is somehow responsible for its outstanding properties as compared to many other starches (Sanyang et al. 2016c).

It is a known fact that native starches are brittle and they do not behave like thermoplastic materials. Therefore, native starches are difficult to process due to the strong intermolecular bonding that exists between the amylose and amylopectin macromolecular network chains. Consequently, products developed using native starches are inherently brittle and fragile (Ma and Yu 2004; Zhang and Rempel 2012). The introduction of plasticizers together with elevated temperatures and shear increases the flexibility of native starches similar to conventional thermoplastic polymers. The process of overcoming the brittleness of native starches is known as the plasticization of starch. Glycerol had been used in previous studies for sugar palm starch plasticization (Sahari et al. 2012; 2013a, b, 2014).

Sahari et al. (2012, 2013a, b, 2014) have extensively reported the effect of glycerol concentration on the physicochemical, mechanical, thermal, and degradability properties of plasticized sugar palm starch. In order to further explore the potentiality of sugar palm starch, (Sanyang et al. 2015a, b, 2016b). Sanyang et al. (2015a, b) investigated the influence of various plasticizer types (glycerol, sorbitol, and glycerol: sorbitol) and concentration (0, 15, 30, and 45%) on the physical, mechanical, thermal, and water vapor permeability properties of sugar palm starch films.

The incorporation of plasticizers to SPS films produces flexible films with smooth and homogeneous surface. The authors reported that SPS films with 45% plasticizers were more flexible and the flexibility reduces as the plasticizer content decreases, irrespective of the plasticizer type. Meaning, the increase of plasticizer concentration improves flexibility of SPS plasticized films. The introduced plasticizers creep within the intermolecular spaces of the SPS polymer chains, reducing the intermolecular hydrogen bond strength. Hence, increasing the molecular mobility which enhances the flexibility of the films. It was observed that the intermolecular hydrogen bond of SPS films weakened as the plasticizer concentration increased from 15 to 45%. It was also noted that different plasticizer type significantly affected the flexibility of the plasticized films at the same plasticizer concentration. Films containing the combination of glycerol and sorbitol (GS) demonstrated higher flexibility, followed by glycerol (G) plasticized films.

Figure 7.10 presents the photographic images of SPS films with different plasticizer type and concentration. The transparency of all the films increases as the concentration of plasticizer increases. It was noticed that SPS films with sorbitol exhibited better transparency than films containing other plasticizer types at the same concentration. On the other hand, the brittleness and fragile feature of films significantly decreased with the increase of plasticizer concentration, irrespective of plasticizer type. This is so because the molecular network structure of the starch weakens as more plasticizers interpose themselves within the intra/intermolecular spaces of the matrix. Thus, the molecular free volume in the starch increases. Glycerol-plasticized SPS films were easily peeled from the casting surface, unlike films containing sorbitol.

Incorporating plasticizer into polymer matrix disrupts and restructures the intermolecular polymer chain networks, subsequently, keeping the strongly bond intermolecular chains apart. Hence, it was observed that the thickness of plasticized

Fig. 7.10 SPS films prepared using different plasticizer type and concentration (Sanyang et al. 2016b)

SPS films increased in response to the increase in plasticizer concentration regardless of plasticizer type. However, glycerol-plasticized SPS films presented lower film thickness which was attributed to the smaller molar mass of glycerol compared to sorbitol. Similar finding regarding the effect of plasticizers on film thickness was reported by many other researchers (Ahmadi et al. 2012; Ghasemlou et al. 2011; Imranet al. 2010; Jouki et al. 2013; Razavi et al. 2015).

The density of all plasticized SPS films was lower than the unplasticized SPS film. This indicates that the addition of plasticizers (G, S and GS) reduces the density of SPS films. However, different types of plasticizer reflect unequal degree of density reduction at the same plasticizer concentration. It was reported that G provided the lowest density value followed by GS and then S. This trend was attributed to the differences in molecular weight and density of the plasticizers. Razavi et al. (2015) also reported similar finding, in which glycerol-plasticized sage seed gum films gave lower density than sorbitol (below 60% plasticizer content).

The moisture content of SPS films containing glycerol significantly increased as plasticizer content increases. The addition of glycerol multiples the hydrophilicity of the starch-based films. The hydroxyl groups in glycerol exhibit strong affinity with water molecules. This enables glycerol-plasticized films to easily hold on water within their matrix and form hydrogen bond. On the other hand, the addition of sorbitol into SPS films does not increase the moisture content of sorbitol-plasticized starch films. Several other authors (Aguirre et al. 2013; Arvanitoyannis 1999; Ghasemlou et al. 2011; Osés et al. 2009) reported similar findings regarding the effect of sorbitol on the moisture content of various starch-based films. The high molecular structure of sorbitol which resembles that of the glucose units in the starch structure is believed to create strong molecular interactions between the former and intermolecular polymer chains of the latter. Hence, water molecules have slim chances of interacting with the sorbitol molecules.

In terms of solubility in water, glycerol-plasticized SPS films demonstrated the highest solubility in water compared to its counterparts with equal concentration. Plasticization of SPS films significantly increases film solubility in water. Regardless of the plasticizer type, the solubility of plasticized SPS films in water increased with increased plasticizer concentration. Similar trend was reported in previous studies, regarding the effect of plasticizer concentration on biodegradable film solubility in water (Aguirre et al. 2013; Chiumarelli and Hubinger 2014; Maran et al. 2013). Due to the hydrophilic nature of plasticizers, most especially glycerol, they perform essential role in weakening the interaction between polymer molecular chains, increasing the free space volumes between the chains. This in turn promotes water diffusion into the film matrix and, consequently, increasing the solubility of plasticized films.

Regardless of plasticizer types, the tensile strength of plasticized SPS films decreased, whereas their elongation at break (E%) increased as the plasticizer concentrations were raised. However, the E% for G and GS-plasticized films significantly decreased at higher plasticizer concentration (45% w/w) due to anti-plasticization effect of plasticizers. It was observed that the storage (E’) and loss modulus (E”) of the plasticized SPS films decrease as plasticizer concentration increase from 15 to 45%. S-plasticized films showed higher storage modulus (1000 MPa) over G (880 MPa) and GS (920 MPa) plasticized films, irrespective of plasticizer concentration. Overall, the study manifested that plasticizer type and concentration significantly improve film properties and enhance their suitability for food packaging applications.

7.5.2 Sugar Palm Starch Blend

Polymer blending is another type of polymer modification by combining two or more polymers in order to achieve the desired properties. Apart from using synthetic polymer, blending of starch with another biopolymer is a promising approach since the resulting materials will be able to sustain the biodegradable and renewable aspects of starch. Modification of thermoplastic sugar palm starch through incorporation with agar has been conducted in previous studies (Jumaidin et al. 2016, 2017). In this study, the sugar palm starch was pre-mixed with glycerol (30 wt% starch-based) in order to produce the thermoplasticity behavior of the material. The thermoplastic sugar palm starch was then incorporated with agar at 10 to 40 wt% by using internal mixer Brabender Plastograph at 140 °C for 10 min. Consequently, these mixtures were granulated and thermo-pressed at 140 °C for 10 min in order to obtain laminate plate with 3 mm thickness. In these processes, the presence of plasticizer and heat has transformed the starch and agar into thermoplastic polymer

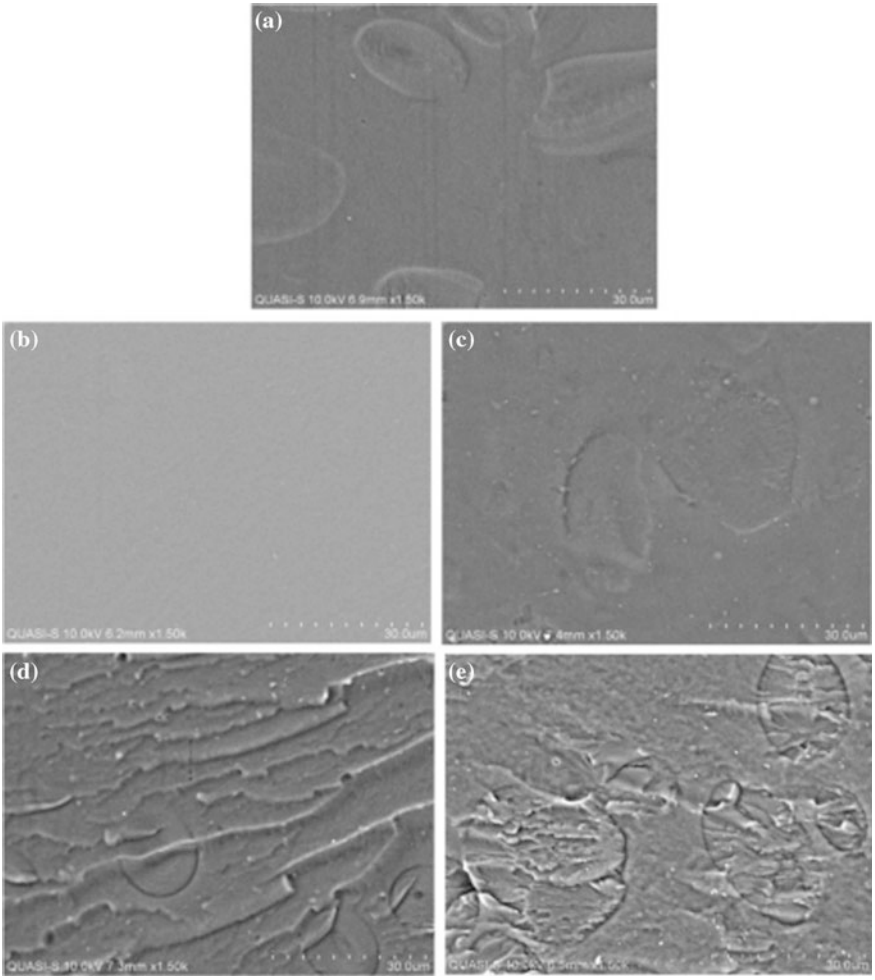


Fig. 7.11 SEM micrograph of fracture surface of thermoplastic SPS blended with different ratio of agar **a** 0 wt% **b** 10 wt% **c** 20 wt% **d** 30 wt% **e** 40 wt% (Jumaidin et al. 2016)

blend. The results show that incorporation of agar has increased the mechanical properties of the material, i.e., tensile, flexural, and impact strength. The authors attributed the properties enhancement of thermoplastic sugar palm starch/agar blend to several reasons. Firstly, chemical similarity between starch and agar has led to good miscibility and good phase compatibility between them. This finding was supported by the homogenous surface of the tensile fracture (Fig. 7.11). Furthermore, FTIR analysis indicates the formation of new hydrogen bonding between starch and agar following the blending process. Finally, the enhancement in the mechanical properties of thermoplastic sugar palm starch/agar blend was attributed to more entangled network structure of agar which provides strengthening effect to the polymer blend.

In addition, the enhancement in the thermal stability of the polymer blend was reported. Incorporation of agar has increased the glass transition temperature and melting temperature of thermoplastic sugar palm starch blend. This improvement was associated to higher melting temperature of native agar than the sugar palm starch. Moreover, increase in the intermolecular hydrogen bonding has decreased the mobility of matrix chain, hence, increasing the glass transition temperature. TGA results show that thermoplastic sugar palm starch/agar blend has higher char residual content than the neat thermoplastic sugar palm starch. This was clearly attributed to higher ash content of agar than the sugar palm starch.

Furthermore, incorporation of agar into thermoplastic sugar palm starch has increased the moisture absorption and thickness swelling ratio of the material. This was associated to the fact that agar is sulfated polysaccharide and the presence of charged groups resulted in more extended chains with a higher hydrophilicity than starch. Nevertheless, the increment was insignificant (3 wt%) with regards to the amount of agar (30 wt%) incorporated into the material. Overall, blending of sugar palm starch with agar has led to significant improvement in the mechanical and thermal properties of the material which was accompanied with slight increment in the moisture sensitivity.

7.5.3 Sugar Palm Starch Bilayer Films

The widespread application of SPS can be delimited by resolving the demerits associated with SPS-based products such as high water or moisture sensitivity, high brittleness, poor water vapor barrier, and mechanical properties. Hence, incorporation of PLA with SPS to form a fully biodegradable bilayer films could significantly enhance the functional properties of SPS-based products and boost their acceptability in the market. Many studies reported the use of PLA in developing outstanding bilayer or multilayer films with other biopolymers besides starch, to upgrade the performance of those biopolymers. In this respect, the preparation and characterization of isolated soy protein (SPI) and PLA biodegradable bilayer films were reported by González and Igarzabal (2013). The authors expounded on the significant contribution of PLA in improving the mechanical properties of the bilayer films as well as arresting the issue of high moisture sensitive attributed to the use of SPI films. There were another separate studies conducted by Rhim et al. (2013) on the development of multilayer films from plasticized soybean protein isolate combined with PLA films. Their findings strongly concur with that of González and Igarzabal (2013), in the sense that both studies reported the positive impact of PLA in improving the mechanical and barrier properties of the multilayer films as compared to those of SPI. Elsewhere, Martucci and Ruseckaite (2010) developed a three-layer sheet with glycerol-plasticized gelatin as the inner layer while PLA function as the outer layers to serve as a good barrier for the moisture penetration.

Although PLA/starch blend has been extensively reported, limited works are so far carried out on PLA—starch bilayer or multilayer films. Interestingly, a current study by Sanyang et al. (2016a) was conducted to enhance the functional properties of SPS films by combining different proportions of PLA layers with SPS films. The prepared SPS-PLA bilayer films were free of any compatibilizer, adhesives, or chemical modification to maintain low preparation cost. Bilayer films with SPS-to-PLA ratio of 50:50 (SPS50-PLA50) manifested significant improvement in physical, mechanical, and water barrier properties. In comparison to SPS100, SPS50-PLA50 showed 76.36% increase in tensile strength and 96.70 decreased in water vapor permeability as well as 65.89% decrease in water absorption. The scanning electron microscope (SEM) images revealed a distinct gap between the two layers of the film. This implies that SPS and PLA layers were immiscible, resulting to poor interfacial adhesion between the two layers which in turn might affect the mechanical behavior of the films. Against this basis, it is imperative for the surface of the two films to be somehow modified for better performance.

7.5.4 Sugar Palm Fiber Reinforced Sugar Palm Starch Biocomposites

The incorporation of natural fibers into biopolymer matrix such as starch has attracted numerous attention their superior environmental profile as green biocomposites. Thus, Sahari et al. (2013a) fabricated and characterized a fully renewable and biodegradable biocomposite derived from sugar palm starch (SPS) and sugar palm fiber (SPF). The most attractive aspect of their study is that both the biopolymer matrix and the natural fiber reinforcement material originated from a single source (sugar palm tree). Meaning, SPS and SPF should share similar functional groups to enable SPF/SPS biocomposite and form strong interfacial bonding. This argument was supported by the FTIR results of neat SPS and SPF/SPS biocomposite with different SPF loading presented by the authors (Fig. 7.12). As observed in the Figure … all the various samples demonstrated the same peaks, since they all originate from one botanical source. Consequently, the good interfacial bonding between SPS and SPF significantly contributed to the improvement of the mechanical behavior and the reduction of the water uptake of SPF/SPS biocomposite. The intrinsic adhesion feature between SPS and PSF was also supported by the SEM as shown in Fig. 7.13.

The reinforcement of SPS with varying loading concentration of SPF remarkably improved the properties of the resultant biocomposite samples. Increasing the SPF content enhanced the load-bearing capacity of the biocomposite as well as its stiffness. It was further reported that the flexural strength and modulus of SPF/SPS biocomposite increased as a result of adding more SPF to a constant SPS matrix. On

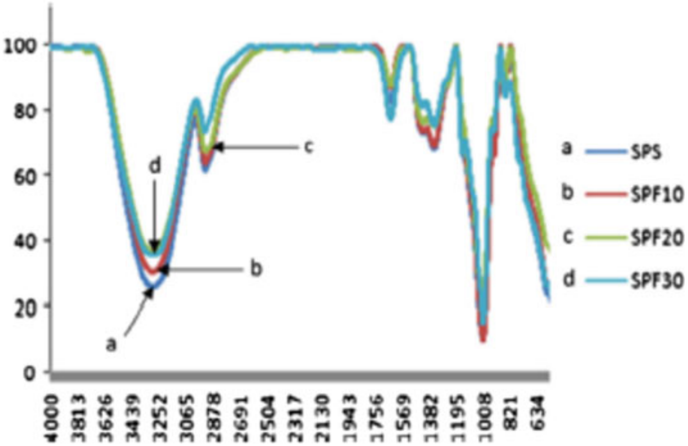


Fig. 7.12 FTIR results of neat SPS and SPF/SPS biocomposite with different SPF loading (Sahari et al. 2013a)

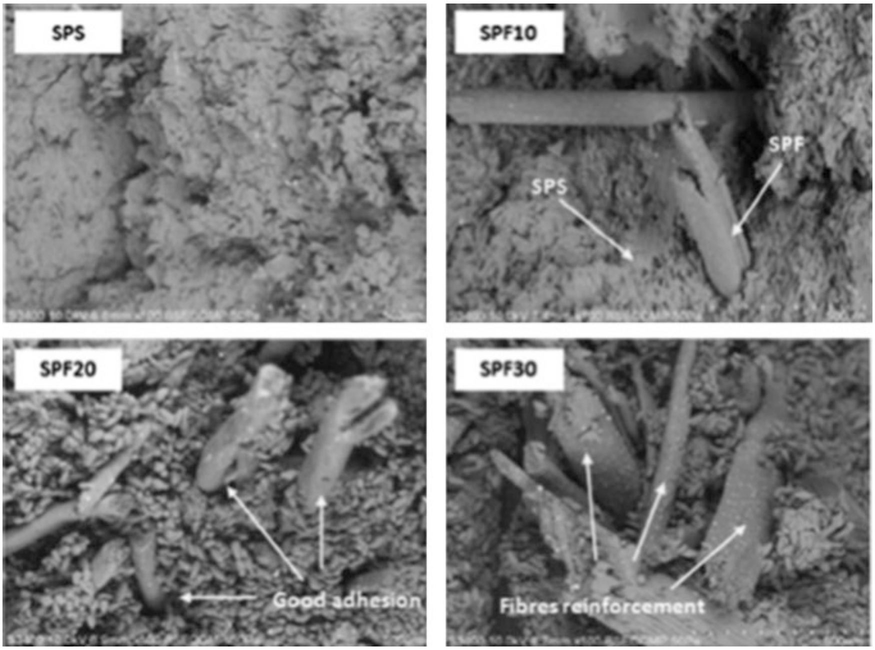


Fig. 7.13 SEM images of neat SPS and SPF/SPS biocomposite with different SPF loading (Sahari et al. 2013a)

top of that, SPF loading improved the thermal stability of the biocomposite due to the presence of lignin and other inorganic materials such as silica which only decompose at higher temperatures (Sahari et al. 2013a).

7.5.5 Sugar Palm Cellulose Reinforced Sugar Palm Starch Biocomposites

Numerous investigations were performed by researcher to enhance the functional properties of products made from starch; Müller et al. 2009; Sanchez-garcia et al. 2008). The incorporation of cellulose fibers in the matrix of starch composite films improves the properties of the starch-based product for better packaging application as reported by many authors (Slavutsky and Bertuzzi 2014; Teac et al. 2013; Teixeira et al. 2009). Thus, eco-friendly cellulose reinforced starch films are potential promising packaging materials for better sustainable future.

In a recent study, Sanyang et al. (2016a, b, c, d) extracted sugar palm-derived cellulose (SPC) and utilized it as reinforcement material to improve the mechanical and water vapor barrier properties of sugar palm starch (SPS)-based films. Cellulose reinforced SPS composite films (SPS-C) were prepared with different SPC loadings (1–10 wt%) using a solution casting method. The incorporation of SPC significantly increased the tensile strength and tensile modulus but decreased the elongation at break of composite films. Hence, the composite films became more resistant to break, more stiff, and less flexible. Overall, the FESEM images manifest good dispersion of cellulose fiber in the starch matrix without any visible clusters. This indicates the compatibility between the two components (cellulose and starch) which originated from the same source (sugar palm tree). Hence, the good random distribution of SPC in the composite films contributes to the decrease of water vapor permeability and increase of mechanical strength of composite films.

7.5.6 Microcrystalline Cellulose (MCC) Reinforced Sugar Palm Starch

MCC is a white, odorless and tasteless crystalline powder in the form of porous particles. It is a purified non-fibrous form of cellulose extracted from the indigestible portion of plant material via the partial acid hydrolysis of quality wood pulp (Głowińska and Datta 2015; Kiziltas et al. 2014; Reis et al. 2014). High crystallinity index cellulose is obtained after the hydrolysis process, which occurs in the amorphous regions of the polymer chain leaving behind the more resistant crystalline areas. Owing to the source of cellulose and the processing variables such as chemical concentration, reaction time, and temperature during hydrolysis as well as drying conditions, the crystallinity index of MCC often ranges 55–80% (Haafiz et al. 2013).

The crystallinity degree of MCC affects their performance to a great extent. MCC is considered as a good reinforcement material for bio-based polymers due to their similar chemical composition and the high specific surface area of MCC.

MCC as a reinforcement material for various polymer matrices has been well-documented in the open literature (Haafiz et al. 2013; Reis et al. 2014). However, little known investigation was found on cellulose reinforced SPS bio-composite at the moment of compiling this chapter. Sapuan and Sanyang (2016) evaluated the effect of MCC on the mechanical, thermal, and water barrier properties of MCC-reinforced SPS composite films. The incorporation of MCC improved the tensile strength, storage modulus, and the glass transition temperature of the composite films as compared to the neat SPS films. MCC also increased the barrier of water vapor which was associated with the good interaction between MCC and SPS. The authors concluded that the introduction of MCC enhanced the suitability of SPS-based composite films for food packaging to enhance shelf-life of food products.

7.5.7 Sugar Palm Nanocellulose Reinforced Sugar Palm Starch

The growing interest in eco-friendly materials due to the environmental and society health concern has motivated both industrial and academic researchers in the evolution and utilization of biopolymers for application in which mineral and synthetic petroleum-based polymer filler are traditionally used. Therefore, to overcome it, nanocellulose crystalline from bio-based plant became a preferred substitution. Based on previous studies, NCC has revealed momentous advancements in mechanical, thermal, and barrier properties compared to neat polymer and conventional composites (Hietala et al. 2013; Ng et al. 2015; Siqueira et al. 2010). NCC is broadly used as filler in thermoplastic polymeric matrices to manufacture durable and cost-effective nanocomposite materials. The property of NCC is relevant for load-bearing and stress transfer in thermoplastic polymeric matrix including thermoplastic starch. Some research had been done on the modification of nanocellulose surfaces in order to improve the compatibility of NCC with hydrophobic matrices. Over the past two decade, many researches are covering nanocellulosic material with thermoplastic in various applications.

As the main function of food packaging is to preserve the food from any contaminations as well to maintain the quality of food product from the processing and manufacturing through handling and storage and finally consumption, thus the selection of the suitable food packaging materials is very important. The innovation of sugar palm starch-based film reinforced with sugar palm nanocellulose crystal to form bio-based plastic is a huge promising candidate to substitute petroleum-based plastics. At this point in time, there is an ongoing extensive work on sugar palm NCC-reinforced SPS nanocomposites.

7.6 Conclusion

This chapter presents the current status of sugar palm starch-based films research for packaging application. Sugar palm starch is a suitable biopolymer that can be utilize for packaging film development to substitute problematic non-biodegradable packaging materials. In order to overcome the inherent defaults in the properties of starch-based films due to their high hydrophilic nature, various modification methods were employed. The new trend in improving the functional properties of sugar palm starch-based films is the use of nanotechnology which is a promising approach for packaging films. Nanocrystalline cellulose from sugar palm fibers and nanocrystals from sugar palm starch are prospective nano-reinforcement or nano-filler to enhance the properties of sugar palm starch-based films as a high-performance packaging material.

References

Aguirre A, Borneo R, León AE (2013) Properties of triticale protein films and their relation to plasticizing–antiplasticizing effects of glycerol and sorbitol. Ind Crops Prod 50:297–303

Ahmadi R, Kalbasi-Ashtari A, Oromiehie A, Yarmand MS, Jahandideh F (2012) Development and characterization of a novel biodegradable edible film obtained from psyllium seed (Plantago ovata Forsk). J Food Eng 109(4):745–751

Angellier H, Choisnard L, Molina-Boisseau S, Ozil P, Dufresne A (2004) Optimization of the preparation of aqueous suspensions of waxy maize starch nanocrystals using a response surface methodology. Biomacromol 5(4):1545–1551

Arockianathan PM, Sekar S, Sankar S, Kumaran B, Sastry TP (2012) Evaluation of biocomposite films containing alginate and sago starch impregnated with silver nano particles. Carbohyd Polym 90(1):717–724

Arvanitoyannis IS (1999) Totally and partially biodegradable polymer blends based on natural and synthetic macromolecules: preparation, physical properties, and potential as food packaging materials. Mater Chem Phys C 39(2):205–271

Cano A, Jiménez A, Cháfer M, Gónzalez C, Chiralt A (2014) Effect of amylose: amylopectin ratio and rice bran addition on starch films properties. Carbohyd Polym 111:543–555

Cha DS, Chinnan MS (2004) Biopolymer-based antimicrobial packaging: a review. Crit Rev Food Sci Nutr 44(4):223–237

Chiumarelli M, Hubinger MD (2014) Evaluation of edible films and coatings formulated with cassava starch, glycerol, carnauba wax and stearic acid. Food Hydrocolloids 38:20–27

da Rosa Zavareze E, Pinto VZ, Klein B, El Halal SLM, Elias MC, Prentice-Hernández C, Dias ARG (2012) Development of oxidised and heat–moisture treated potato starch film. Food Chem 132(1):344–350

Dai L, Qiu C, Xiong L, Sun Q (2015) Characterisation of corn starch-based films reinforced with taro starch nanoparticles. Food Chem 174:82–88

Dias AB, Müller CM, Larotonda FD, Laurindo JB (2010) Biodegradable films based on rice starch and rice flour. J Cereal Sci 51(2):213–219

Edhirej A, Sapuan SM, Jawaid M, Zahari NI (2017) Effect of various plasticizers and concentration on the physical, thermal, mechanical, and structural properties of cassava-starch-based films. Starch-Stärke 69(1–2)

Fang J, Fowler P (2003) The use of starch and its derivatives as biopolymer sources of packaging materials. J Food Agric Environ 1:82–84

Florido HB, de Mesa PB (2003) Sugar palm [Arenga Pinnata (Wurmb.) Merr.]. Res Info Ser Ecosyst 15(2):1–7

Fonseca LM, Gonçalves JR, El Halal SLM, Pinto VZ, Dias ARG, Jacques AC, da Rosa Zavareze E (2015) Oxidation of potato starch with different sodium hypochlorite concentrations and its effect on biodegradable films. LWT-Food Sci Technol 60(2):714–720

Ghasemlou M, Khodaiyan F, Oromiehie A (2011) Physical, mechanical, barrier, and thermal properties of polyol-plasticized biodegradable edible film made from kefiran. Carbohyd Polym 84(1):477–483

Głowińska E, Datta J (2015) Structure, morphology and mechanical behaviour of novel bio-based polyurethane composites with microcrystalline cellulose. Cellulose 22(4):2471–2481

González A, Igarzabal CIA (2013) Soy protein–Poly (lactic acid) bilayer films as biodegradable material for active food packaging. Food Hydrocolloids 33(2):289–296

Gutiérrez TJ, Morales NJ, Pérez E, Tapia MS, Famá L (2015) Physico-chemical properties of edible films derived from native and phosphated cush-cush yam and cassava starches. Food Packag Shelf Life 3:1–8

Haafiz MM, Hassan A, Zakaria Z, Inuwa IM, Islam MS, Jawaid M (2013) Properties of polylactic acid composites reinforced with oil palm biomass microcrystalline cellulose. Carbohydr Polym 98(1):139–145

Hietala M, Mathew AP, Oksman K (2013) Bionanocomposites of thermoplastic starch and cellulose nanofibers manufactured using twin-screw extrusion. Eur Polymer J 49(4):950–956

Hizukuri S, Kaneko T, Takeda Y (1983) Measurement of the chain length of amylopectin and its relevance to the origin of crystalline polymorphism of starch granules. Biochim Biophys Acta (BBA) Gen Subj 760(1):188–191

Imam SH, Wood DF, Abdelwahab MA, Chiou BS, Williams TG, Glenn GM, Orts WJ (2012) Chemistry, microstructure, processing, and enzymatic degradation. In: Ahmed J, Tiwari BK, Imam SH, Rao MA (eds) Starch-based polymeric materials and nanocomposites: chemistry, processing, and applications, CRS Press, Boca Raton, pp 5–32

Imran M, El-Fahmy S, Revol-Junelles AM, Desobry S (2010) Cellulose derivative based active coatings: effects of nisin and plasticizer on physico-chemical and antimicrobial properties of hydroxypropyl methylcellulose films. Carbohydr Polym 81(2):219–225

Ishak MR, Sapuan SM, Leman Z, Rahman MZA, Anwar UMK, Siregar JP (2013) Sugar palm (Arenga pinnata): its fibres, polymers and composites. Carbohydr Polym 91(2):699–710

Jouki M, Khazaei N, Ghasemlou M, HadiNezhad M (2013) Effect of glycerol concentration on edible film production from cress seed carbohydrate gum. Carbohydr Polym 96(1):39–46

Jumaidin R, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2016) Characteristics of thermoplastic sugar palm Starch/Agar blend: thermal, tensile, and physical properties. Int J Biol Macromol 89:575–581

Jumaidin R, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2017) Effect of agar on flexural, impact, and thermogravimetric properties of thermoplastic sugar palm starch. Curr Org Synth 14: 200–205

Kiziltas A, Gardner DJ, Han Y, Yang HS (2014) Mechanical properties of microcrystalline cellulose (MCC) filled engineering thermoplastic composites. J Polym Environ 22(3):365–372

Klein B, Vanier NL, Moomand K, Pinto VZ, Colussi R, da Rosa Zavareze E, Dias ARG (2014) Ozone oxidation of cassava starch in aqueous solution at different pH. Food Chem 155: 167–173

Koshy RR, PothAn LA, Thomas S (2013) Starch-based bionanocomposite: processing techniques. In: Dufresne A, Thomas S, Pothen LA (eds) Biopolymer nanocomposites: processing, properties, and applications. Wiley, Hoboken, NJ, pp 203–226

Li M, Li D, Wang LJ, Adhikari B (2015) Creep behavior of starch-based nanocomposite films with cellulose nanofibrils. Carbohydr Polym 117:957–963

Liu Z, Han JH (2005) Film-forming characteristics of starches. J Food Sci 70(1)

Ma X, Yu J (2004) The plastcizers containing amide groups for thermoplastic starch. Carbohydr Polym 57(2):197–203

Maran JP, Sivakumar V, Sridhar R, Thirugnanasambandham K (2013) Development of model for barrier and optical properties of tapioca starch based edible films. Carbohydr Polym 92 (2):1335–1347

Martucci JF, Ruseckaite RA (2010) Three-layer sheets based on gelatin and poly (lactic acid), part 1: preparation and properties. J Appl Polym Sci 118(5):3102–3110

Mihindukulasuriya SDF, Lim LT (2014) Nanotechnology Development in food packaging: a review. Trends Food Sci Technol 40:149–167

Moreno O, Pastor C, Muller J, Atarés L, González C, Chiralt A (2014) Physical and bioactive properties of corn starch–Buttermilk edible films. J Food Eng 141:27–36

Müller CM, Laurindo JB, Yamashita F (2009) Effect of cellulose fibers addition on the mechanical properties and water vapor barrier of starch-based films. Food Hydrocolloids 23(5):1328–1333

Ng HM, Sin LT, Tee TT, Bee ST, Hui D, Low CY, Rahmat AR (2015) Extraction of cellulose nanocrystals from plant sources for application as reinforcing agent in polymers. Compos B Eng 75:176–200

Osés J, Fernández-Pan I, Mendoza M, Maté JI (2009) Stability of the mechanical properties of edible films based on whey protein isolate during storage at different relative humidity. Food Hydrocolloids 23(1):125–131

Razavi SMA, Amini AM, Zahedi Y (2015) Characterisation of a new biodegradable edible film based on sage seed gum: Influence of plasticiser type and concentration. Food Hydrocolloids 43:290–298

Reis MO, Zanela J, Olivato J, Garcia PS, Yamashita F, Grossmann MVE (2014) Microcrystalline cellulose as reinforcement in thermoplastic starch/poly (butylene adipate-co-terephthalate) films. J Polym Environ 22(4):545–552

Rhim JW, Park HM, Ha CS (2013) Bio-nanocomposites for food packaging applications. Prog Polym Sci 38(10):1629–1652

Sahari J, Sapuan SM, Zainudin ES, Maleque MA (2012) A new approach to use Arenga pinnata as sustainable biopolymer: effects of plasticizers on physical properties. Procedia Chemistry 4:254–259

Sahari J, Sapuan SM, Zainudin ES, Maleque MA (2013a) Mechanical and thermal properties of environmentally friendly composites derived from sugar palm tree. Mater Des 49:285–289

Sahari J, Sapuan SM, Zainudin ES, Maleque MA (2013b) Thermo-mechanical behaviors of thermoplastic starch derived from sugar palm tree (Arenga pinnata). Carbohydr Polym 92 (2):1711–1716

Sahari J, Sapuan SM, Zainudin ES, Maleque MA (2014) Physico-chemical and thermal properties of starch derived from sugar palm tree (Arenga pinnata). Asian J Chem 26(4):955

Sanchez-Garcia MD, Gimenez E, Lagaron JM (2008) Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. Carbohydr Polym 71(2):235–244

Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2015a) Effect of plasticizer type and concentration on dynamic mechanical properties of sugar palm starch-based films. Int J Polym Anal Charact 20(7):627–636

Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2015b) Effect of plasticizer type and concentration on tensile, thermal and barrier properties of biodegradable films based on sugar palm (Arenga pinnata) starch. Polymers 7(6):1106–1124

Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2016a) Development and characterization of sugar palm starch and poly (lactic acid) bilayer films. Carbohydr Polym 146:36–45

Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2016b) Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (Arenga pinnata) starch for food packaging. J Food Sci Technol 53(1):326–336

Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2016c) Recent developments in sugar palm (Arenga pinnata) based biocomposites and their potential industrial applications: a review. Renew Sustain Energy Rev 54:533–549

Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J (2016d) Effect of sugar palm-derived cellulose reinforcement on the mechanical and water barrier properties of sugar palm starch biocomposite films. BioResources 11(2):4134–4145

Siqueira G, Bras J, Dufresne A (2010) Cellulosic bionanocomposites: a review of preparation, properties and applications. Polymers 2(4):728–765

Slavutsky AM, Bertuzzi MA (2014) Water barrier properties of starch films reinforced with cellulose nanocrystals obtained from sugarcane bagasse. Carbohydr Polym 110:53–61

Sreekala MS, Kumaran MG, Joseph R, Thomas S (2001) Stress-relaxation behaviour in composites based on short oil-palm fibres and phenol formaldehyde resin. Compos Sci Technol 61(9):1175–1188

Srikaeo K, Boonrod C, Rahman MS (2016) Effect of storage temperatures on the head rice yield in relation to glass transition temperatures and un-freezable water. J Cereal Sci 70:164–169

Talja RA, Helén H, Roos YH, Jouppila K (2007) Effect of various polyols and polyol contents on physical and mechanical properties of potato starch-based films. Carbohydr Polym 67(3): 288–295

Tang XZ, Kumar P, Alavi S, Sandeep KP (2012) Recent advances in biopolymers and biopolymer-based nanocomposites for food packaging materials. Crit Rev Food Sci Nutr 52(5): 426–442

Teacă CA, Bodîrlău R, Spiridon I (2013) Effect of cellulose reinforcement on the properties of organic acid modified starch microparticles/plasticized starch bio-composite films. Carbohydr Polym 93(1):307–315

Teixeira EDM, Pasquini D, Curvelo AA, Corradini E, Belgacem MN, Dufresne A (2009) Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch. Carbohydr Polym 78(3): 422–431

Tester RF, Karkalas J, Qi X (2004) Starch—composition, fine structure and architecture. J Cereal Sci 39(2):151–165

Tian H, Xu G, Yang B, Guo G (2011) Microstructure and mechanical properties of soy protein/ agar blend films: effect of composition and processing methods. J Food Eng 107(1):21–26

Villacrés RAE, Flores SK, Gerschenson LN (2014) Biopolymeric antimicrobial films: study of the influence of hydroxypropyl methylcellulose, tapioca starch and glycerol contents on physical properties. Mater Sci Eng C 36:108–117

Weber CJ, Haugaard V, Festersen R, Bertelsen G (2002) Production and applications of biobased packaging materials for the food industry. Food Addit Contam 19(S1), 172–177

Wittaya T (2009) Microcomposites of rice starch film reinforced with microcrystalline cellulose from palm pressed fiber. Int Food Res J 16(4):493–500

Wittaya T (2012) Rice starch-based biodegradable films: properties enhancement. INTECH Open Access Publisher

Wu M, Wang LJ, Li D, Mao ZH, Adhikari B (2013) Effect of flaxseed meal on the dynamic mechanical properties of starch-based films. J Food Eng 118(4):365–370

Xie F, Flanagan BM, Li M, Sangwan P, Truss RW, Halley PJ et al (2014) Characteristics of starch-based films plasticised by glycerol and by the ionic liquid 1-ethyl-3-methylimidazolium acetate: a comparative study. Carbohydr Polym 111:841–848

Yoshimoto Y, Takenouchi T, Takeda Y (2002) Molecular structure and some physicochemical properties of waxy and low-amylose barley starches. Carbohydr Polym 47(2):159–167

Zhang Y, Rempel C (2012) retrogradation and antiplasticization of thermoplastic starch. Thermoplast Elastomers 118–19

Chapter 8
Natural Biopolymer-Based Nanocomposite Films for Packaging Applications

Tahrima B. Rouf and Jozef L. Kokini

Abstract Recent interest in environmentally friendly bio-based polymers coupled with an increased food safety awareness has resulted in various packaging technology advances, including the incorporation of different kinds of nanofillers into biodegradable biopolymers to improve their overall properties for improving shelf life and preventing microbial growth. Among the different nanofillers that have recently emerged, graphene's invention has catalyzed a multitude of novel material applications in different fields. Graphene has functionalized different biopolymers and has improved their mechanical, thermal, electrical, as well as, gas, and water vapor barrier properties, for potentially replacing petrochemical-based packaging materials that pose a great threat to the environment. The objective of this chapter is to provide comprehensive understanding of the different types of nanoreinforcement that are available for biodegradable packaging application, especially focusing on graphene oxide (GO), a graphene derivative nanofiller that is being extensively studied for packaging reinforcement. This chapter aims to draw a clear picture of synthesis and chemistry of bonding between graphene derivatives and biodegradable biopolymers suitable for packaging applications, like starch, cellulose, poly (lactic acid), and others. The methodology behind the chemical and physical changes during synthesis will be discussed, based on different spectroscopic characterization techniques, and the influence of chemical changes on resulting properties will also be highlighted. This chapter will also briefly go over other nanomaterials like clay, cellulose nanofibers, starch nanocrystals, and their usage in different biopolymers for packaging application. This will help to explain the synergy resulting from addition of nanomaterials, the use of different characterization techniques as well as the improvement in different properties.

T. B. Rouf
Department of Food Science, Purdue University, West Lafayette, Indiana 47907, USA
e-mail: trouf@purdue.edu

J. L. Kokini (✉)
Department of Food Science, Purdue University, 745 Agricultural Mall Drive,
West Lafayette, Indiana 47907, USA
e-mail: jkokini@purdue.edu

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_8

Keywords Biopolymer · Smart packaging · Graphene · Spectroscopic characterizations · Nanoclay · Packaging sensors

8.1 Introduction

Biopolymers can be divided into three different classes based on their production method, as shown in Fig. 8.1 (Petersen et al. 1999). Starch and cellulose derivatives, as well as, polylactic acid (PLA), and polyhydroxy alkanoates (PHA), are some of the most studied biopolymers suitable for packaging. The inferior property profiles of biopolymers compared to commercial thermoplastic polymers urge the need for property enhancements for various applications. A notable increase in the mechanical, thermal, rheological, and gas barrier properties of biopolymers have resulted from inclusion of a large variety of fillers like layered silicates, nanotubes, etc. (Mark 1996; Favier et al. 1997; Ray et al. 2003, 2007; Mittal 2007; Mittal 2008; Luecha et al. 2010). Different functional groups in biopolymers have distinct and divergent properties which affect the interaction with different nanofillers, and in turn results in different levels of property enhancements and diverse applications. The high surface area, high aspect ratio, and high strength of graphene provide it with the superior ability to surpass other fillers and significantly improve the functional properties of polymers.

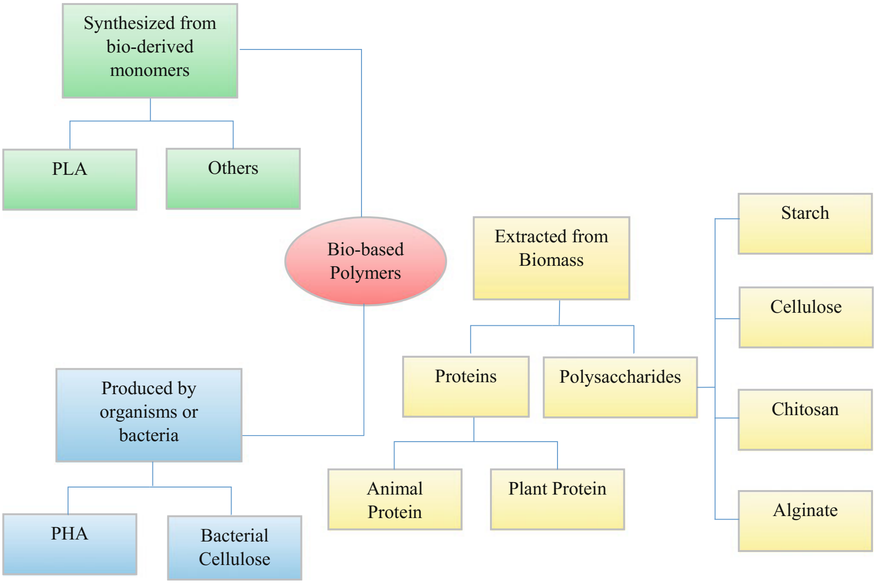


Fig. 8.1 Schematic overview of classification of biopolymers

Therefore, the focus of this chapter will be to discuss the different aspects of biopolymer-graphene nanocomposite fabrication, characterization, and property enhancement for biodegradable packaging applications. In addition, in this chapter, there will be a brief overview of the different clay, polysaccharide-based nanoparticles, and antimicrobial nanoparticles, and how their addition and interaction contribute in improving the different properties of biopolymers. This chapter will help the readers by comparing all relevant information encompassing the complete dimension of research on biopolymer functionalization and will contribute in understanding the basics for smart, biodegradable environment-friendly packaging.

8.2 Basic Principles of Reinforcement

The basic principle of effective polymer nanocomposite fabrication and reinforcement lies in good geometrical and aspect ratio, abundant functional groups in the filler, matching polarity between polymer and filler, in addition to, optimal interfacial interaction (Terzopoulou et al. 2015). The method of nano-functionalization of biopolymers can be classified into three categories, and these are (1) solution intercalation, (2) melt intercalation, and (3) in situ polymerization. For solvent casting, the dispersibility of the nanofiller in the solvent is equally important as the compatibility of the functional groups of the nanofillers and the matrix. Uniform dispersion during fabrication is very important, and it is dependent on proper interaction and interfacial bonding between the nanomaterial and the biopolymer. During composite formation, nanomaterials undergo three different types of dispersions in the polymer matrix, which can be labeled as (i) Tactoid dispersion, (ii) Intercalated dispersion, and (iii) Exfoliated dispersion. The tactoid dispersion is mainly observed in macrocomposites, where the polymer and the filler remain immiscible, and thus, clusters of fillers distribute throughout the polymer matrix, which ultimately results in little or no improvement of properties of the macrocomposites (Luduena et al. 2007; Alexandre et al. 2009). Nanofillers and polymer matrices usually undergo the two other types of interaction. In the intercalated dispersion, the interlayer spacing of the nanofiller (clay, carbon nanotubes graphene derivative, etc.) is penetrated by the polymer chain during composite formation, by means of mixing or sonication, creating an alternating layer of polymer/inorganic layer maintaining a distance of a few nanometers (Weiss et al. 2006). The third type of interaction "Exfoliation" is rather an extreme type of intercalation where the nanofiller layers are completely separated and distributed throughout the polymer matrix, as shown in Fig. 8.2 (Luduena et al. 2007). Exfoliation results in the best property reinforcement as the nanofiller distributed throughout the matrix forms a continuous network, which enables it to transfer its mechanical energy to the

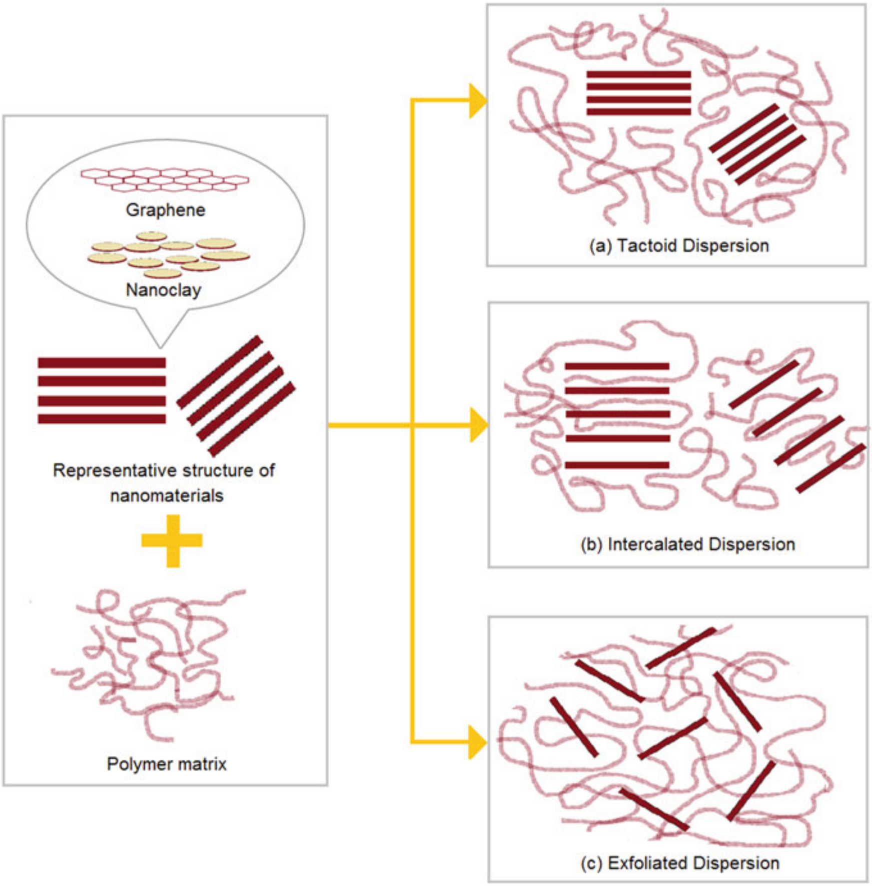


Fig. 8.2 Types of composite derived from interaction between nanomaterials and polymers: **a** tactoid dispersion creating phase-separated microcomposite; **b** intercalated dispersion; and **c** exfoliated dispersion

polymer and prevent rupture. In addition to this, the network formed creates a barrier against volatile components during thermal combustion and delays the escape of gases like oxygen, nitrogen, and water vapor (Fig. 8.3) and thus improves mechanical, thermal, and permeability properties.

Depending on origin, function, and properties, the nanomaterial used for reinforcement of biopolymer used in packaging can be divided into four categories as shown in Fig. 8.4. Each category with fabrication, reaction mechanism, characterization will be briefly discussed in the following sections.

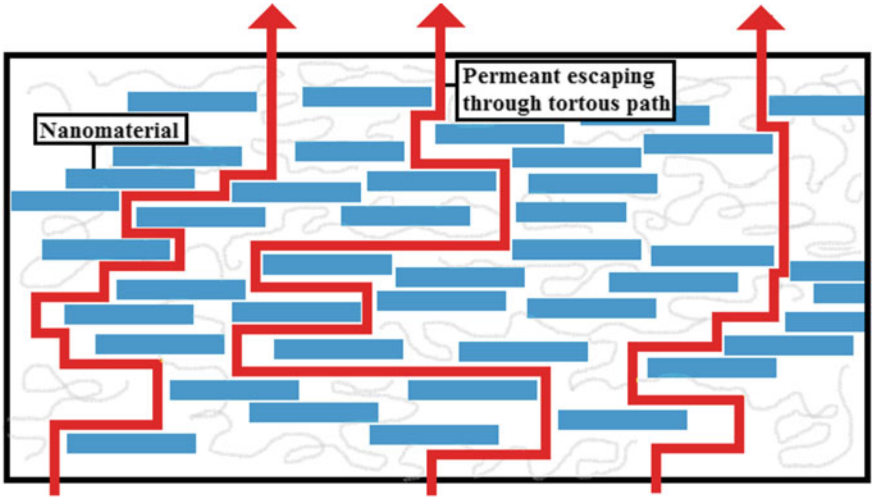


Fig. 8.3 Schematic representation of tortuous pathway created by dispersion of nanofillers in polymer matrix and the delayed escape of water vapor from the nanocomposite film. Adapted from Adame and Beall (2009)

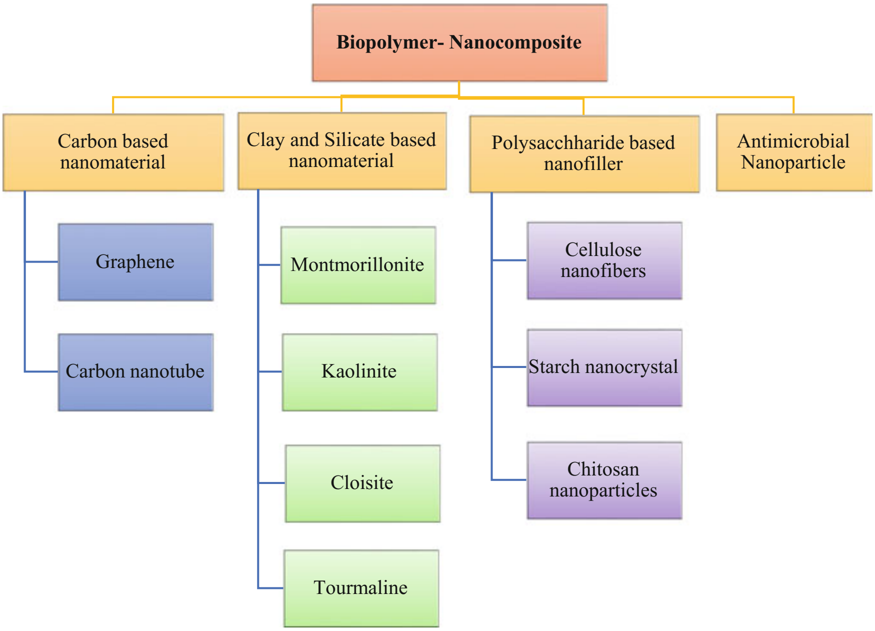


Fig. 8.4 Classification of nanomaterials used for biopolymer nanocomposite fabrication for packaging application

8.3 Carbon Nanomaterial-Based Reinforcement

8.3.1 Graphene-Based Functionalization

Despite the fact that the historical backdrop of graphene follows back to 1840, room temperature stable graphene did not come into existence until 2004, when Geim and Novoselov produced room temperature stable graphene (Novoselov et al. 2004) using the simple scotch tape method, for the first time which led to a Nobel Prize in 2010. A comparison among the different derivatives of graphene like graphene oxide (GO), reduced graphene oxide (RGO), graphene nanoplatelets (GNP); GO has found more application in biopolymer nanocomposite fields, due to the rich number of functional groups like carboxyl, epoxide, hydroxyl, etc.

The unit structure of graphene consists of a hexagonal cell, and a repeating pattern of these hexagonal cells creates a honeycomb structure. Graphene was originally defined as a single carbon atom thick sheet (Boehm 2010), but now the definition has been expanded to include up to 10 carbon layers. However, when more than 10 layers of carbon atoms are stacked on top of each other, it is known as graphite nanoplatelet (GNP) or exfoliated graphite nanoplatelet (xGNP) (Chung 2016). There are also graphene nanosheets (GNS), which are a slightly thinner version of GNP (Shokrieh et al. 2013). GNP or GNS has a low number of carboxyl, epoxy, and hydroxyl groups and therefore do not participate in polar interactions or hydrogen bonding and therefore they are considered to be hydrophobic.

GO has proven to be very useful due to its numerous and diverse functional groups that easily bond with other materials, and therefore find numerous applications in nanocomposites. The Lerf–Klinowski model for the structure of GO shows that the hydroxyl and epoxy (1,2-ether) functional groups in the carbon plane of GO enable hydrogen bonding with hydrophilic polymers (Lerf et al. 1998). Aside from the Lerf–Klinowski model, there are other models like the Hoffman model, Ruess model, Nakajima–Matsuo model, etc., which describe the structure of GO, as depicted in Fig. 8.5.

8.3.1.1 Synthesis of Graphene Oxide and Derivatives

The fabrication techniques for pristine graphene include chemical vapor deposition (CVD) (Dervishi et al. 2011), adhesion tape assisted repeated peeling of graphene layers from graphite (Singh et al. 2011), unzipping of multi-wall carbon nanotubes (MWCNTs), micro-mechanical exfoliation (Jayasena et al. 2013), mechanical exfoliation with ultrasonication (Guan et al. 2016), growth on crystalline silicon carbide, etc. The two major processes for fabrication of graphene-based nanofillers are (i) Exfoliation of graphite (ii) Oxidation of graphite.

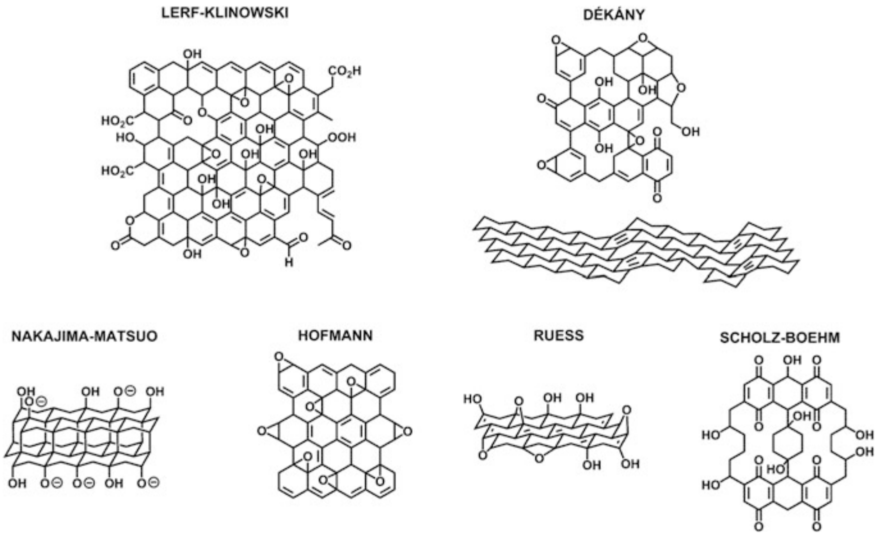


Fig. 8.5 Summary of proposed structural models of GO, including recent examples (*top* Lerf–Klinowski and Dékány models) as well as earlier examples (*bottom* Nakajima–Matsuo, Hofmann, Ruess, and Scholz–Boehm models). Reprinted with permission from Szabó et al. (2006). Copyright 2006, American Chemical Society

Exfoliation of Graphite

The first step includes increasing the interlayer spacing between graphite using a mixture of sulfuric and nitric acid. This step is called intercalation, and the product of this step is called graphite intercalated compound (GIC). The next step of intercalation includes accelerated heating or treatment with microwave, producing even larger interlayer spacing and creating expanded graphite (EG), which contains barely attached thin graphite platelets (30–80 nm) (Chen et al. 2004). But further exfoliation of EG is necessary as the layered structure and relatively low specific surface area (below 40 m^2/g) (Celzard et al. 2000) prevent efficient performance as a composite filler (Zheng et al. 2004; Yasmin et al. 2006; Pötschke et al. 2009). Higher degree of exfoliation of EG produces GNP with thickness of 5 nm or lower (Jang and Zhamu 2008; Potts et al. 2011) (Fig. 8.6).

Oxidation of Graphite

The first step involves an oxidizing agent like potassium permanganate (William et al. 1958) or a combination of $KClO_4$ with HNO_3 (Brodie 1859; Staudenmaier 1898). The oxidation level of graphite with the different oxidants are very similar (C:O = 2:1 approx.) (Dreyer et al. 2010), and they all result in the destruction of the π-conjugation of the stacked graphene sheets, producing nanoscale graphitic

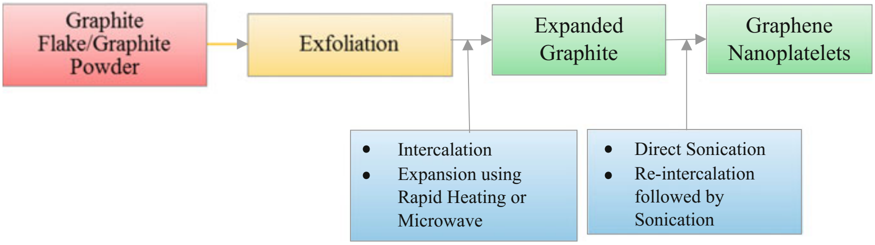


Fig. 8.6 Schematic representation of the steps for exfoliation of graphite to obtain GNP. Adapted from Rouf and Kokini (2016)

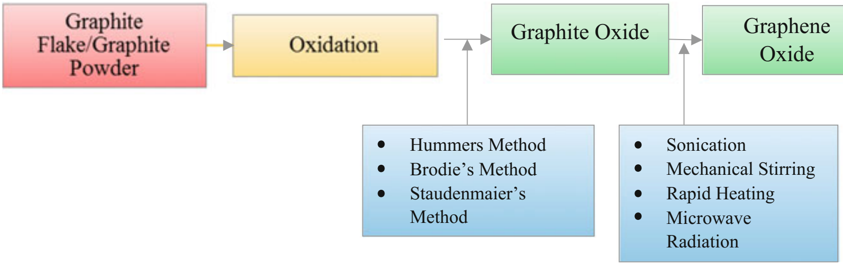


Fig. 8.7 Schematic representation of the steps for oxidation of graphite to obtain GO. Adapted from Rouf and Kokini (2016)

sp^2 domains, which are surrounded by highly disorganized oxidized domains (sp^3 C\C) (Krishnan et al. 2012).

Hummer's method is a very well-known technique for synthesis of GO, in order to use it in biopolymer nanocomposite fabrication (Yang et al. 2012; Yadav et al. 2013, 2014; He et al. 2014; Huang et al. 2014; Stanier et al. 2014; Nie et al. 2015); modified Hummer's method (Pan et al. 2011; Wang and Qiu 2011; Yoon et al. 2011; He et al. 2012; Ma et al. 2013; Pinto et al. 2013a, b; Thakur and Karak 2013; Faghihi et al. 2014; Liu et al. 2014; Si et al. 2014; Stanier et al. 2014; Tian et al. 2014), the Staudenmaier's method has also been used in some studies (Cao et al. 2010; Kim and Jeong 2010; Wang and Qiu 2012) as well as Brodie's method (Tian et al. 2014).

During further exfoliation of the oxidized graphite, the phenol, hydroxyl, and epoxy groups are formed at the basal plane and carboxylic acid groups are formed at the edges, and GO is synthesized (Singh et al. 2011). GO, in spite of being chemically similar to graphite oxide, is structurally different due to its quasi-infinite interlayer spacing (Fig. 8.7).

Mechanical stirring of graphite oxide to produce GO is very time consuming; however, it results in large lateral dimensions (several hundred nanometers). On the other hand, ultrasonication offers fast yield but often fractures the GO sheets into smaller pieces (Park and Ruoff 2009).

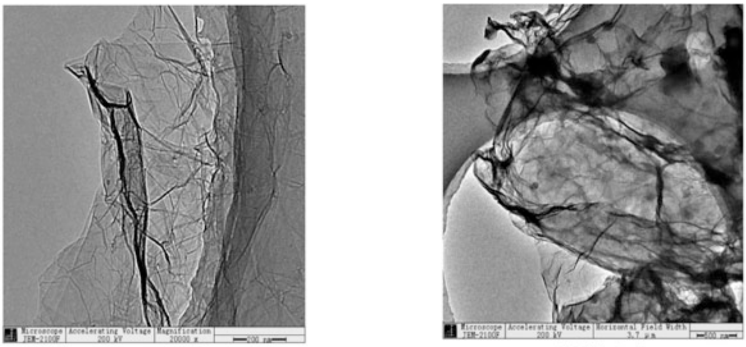
8.3.1.2 Biopolymer-Graphene Nanocomposites for Packaging

Uniform dispersion of the nanoparticles is necessary to optimize functionalization of the polymer nanocomposite. Particle characterization is therefore a very important aspect of nanocomposite fabrication for understanding the internal changes of the nanocomposites as well as for quality assurance. Distribution of nanofillers in polymer matrix, substantial changes in bulk matrix, and any changes in the interface of polymer and particle are some of the main aspects of characterization. Spectroscopic techniques including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM) have been used in different studies to understand the mechanism of enhancement of functional properties. Therefore, different graphene-biopolymer nanocomposites that are appropriate for packaging applications will be discussed, where the fabrication, different types of characterization, the synergy resulting from the use of different spectroscopic techniques as well as the different property enhancement will be explained.

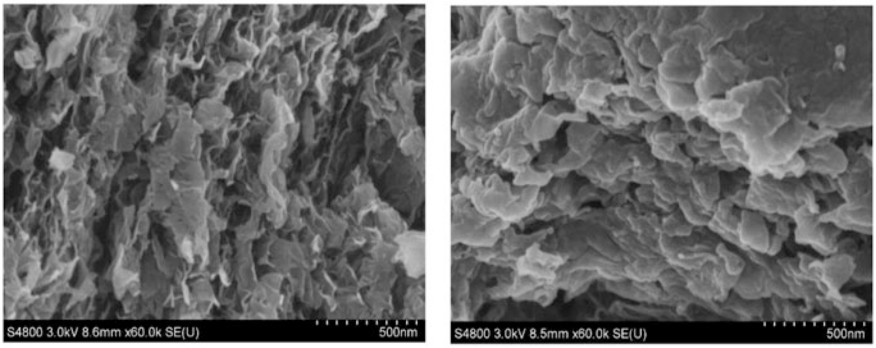
Starch

Starch-based materials have shown the most potential to replace synthetic plastics as packaging materials because of their biodegradability, low cost, abundance, and renewability. However, starch suffers from inferior mechanical strength and thermal stability which have been reinforced with various derivatives of graphene like GO, RGO, and GNP. Polarity of solvents, plasticizer addition, temperature, etc., affects the degree of property improvement by graphene nanofillers in the biopolymer nanocomposites. Since starch is soluble in water, in most of the studies water is used as a solvent, but since it is a polar protic solvent, samples with more polar groups would have higher dispersibility, meaning that GO would have higher degree of dispersion than RGO (Dai et al. 2015). This was observed in a study of glycerol plasticized starch (PS), where better overall property improvement was observed for starch-GO nanocomposites, as compared to starch-RGO nanocomposites (Ma et al. 2013). Tensile strength increase for starch-GO nanocomposite was 66% at 2wt% GO loading and water vapor permeability improved for PS-4wt% GO nanocomposite. On the other hand, tensile strength improvement for starch-RGO nanocomposite was 67% for 6wt% addition of RGO; however, noticeable improvement for PS-RGO was not achieved even at 8wt% RGO loading. This comparative improvement of starch properties with GO over RGO is due to the comparatively larger number of polar groups for GO leading to better compatibility with PS. In addition, this resulted in better mechanical and water vapor barrier properties of starch-GO nanocomposites compared with starch-RGO composites, which may ultimately result in an advanced packaging material.

To study the other forms of graphene as well as effect of plasticizers on tensile strength and water vapor permeability improvement of starch nanocomposites,



(a) GN (b) GN-starch



(c) GN (d) GN-starch

Fig. 8.8 TEM images of **a** Graphene **b** GN-Starch; SEM images of **c** Graphene, and **d** GN-Starch. Reprinted with permission from Zheng et al. (2013). Copyright 2013, American Chemical Society

glycerol was used as a plasticizer for starch, and starch-grafted graphene (GN-Starch) was used as a nanofiller to prepare PS-graphene nanocomposites (Zheng et al. 2013). TEM images, as shown in Fig. 8.8a, b, confirmed successful conversion GO to GN-Starch. Oxidized graphite was observed to have a flat, transparent, and wrinkled structure, while GN-Starch had a darker appearance due to the presence of starch. On the other hand, the presence of starch component in the GN-Starch nanofiller was confirmed from the FTIR spectra of GN-Starch. Figure 8.9a shows peaks corresponding to C–O bond stretching of the C–O–H group, and the two peaks from C–O bond stretching of the C–O–C group, which are also seen at the fingerprint region of starch. The comparison of Raman spectra (Fig. 8.9b) of GO and GN-Starch showed that GN-Starch had higher intensity peaks corresponding to a disordered structure (D mode), this disorder was a result of creation of new graphitic domain in GN-Starch. GN-Starch loading of 0.28–1.7wt%, was enough to make significant improvements in mechanical and WVP properties, proving its efficiency as a nanofiller for starch to be used for packaging. The improvement in mechanical properties and barrier properties are summarized in Tables 8.1 and 8.2.

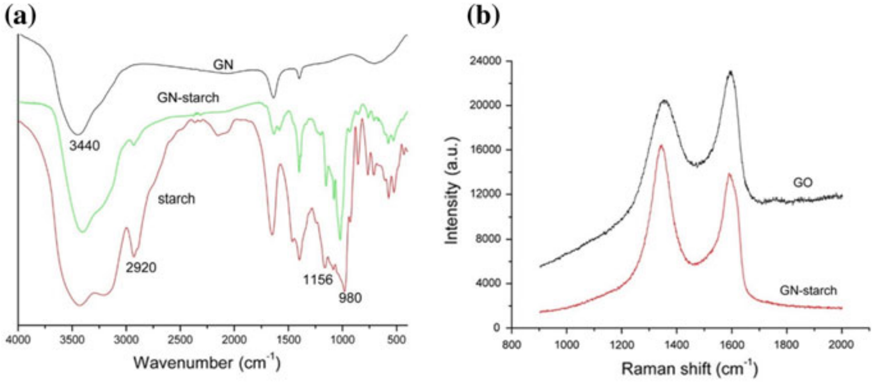


Fig. 8.9 **a** FTIR spectra of starch, GO, and GN-Starch. **b** Raman spectra of GO and GN-Starch. Reprinted with permission from Zheng et al. (2013). Copyright 2013, American Chemical Society

In another study on GO-functionalized-glycerol plasticized pea starch (Li et al. 2011), morphological tests conducted on the nanocomposites showed that hydrogen bonding occurs as a result of the solution casting between starch and GO. FTIR spectra of pea starch-GO nanocomposite shows gradual shifting of characteristic peaks of starch with gradual addition of GO, which is an indication of hydrogen bond formation. Similarly, XRD of starch-GO nanocomposites showed decrease in intensity of starch-GO nanocomposites compared to the intensity of characteristic starch peak offering another proof of H-bonding. Moreover, AFM images (Fig. 8.10) showed that plasticized pea starch-1% GO nanocomposites have lower roughness than pristine starch, but above 2% GO, blisters start to form indicating aggregate formation (Li et al. 2011). The uniform dispersion positively affected the overall properties of starch and only a loading of 2wt% GO was sufficient to effectively improve the tensile strength from 4.56 to 13.79 MPa, and the young's modulus from 0.11 to 1.05 GPa. In addition, significant improvement in moisture uptake was observed at 1.5wt% GO, indicating good potential for packaging application.

Starch-GNS and chitosan-GNS nanocomposites (Ashori 2014) showed similar results to the previous study on pea starch-GO (Li et al. 2011), where smoother surface was observed on addition of GNS to both starch and chitosan. However, above 3% GNS loading, significant roughness coupled with phase separation were observed, with starch showing a higher percentage of aggregation than chitosan. These findings also explain the comparatively better water vapor barrier properties of chitosan-GNS nanocomposites compared to starch-GNS. Also, a blend of chitosan and starch with graphene nanofiller gave a higher tensile strength increase compared to starch and chitosan individually (Ashori and Bahrami 2014), due to which much stronger hydrogen bonding is observed between NH_3 of the chitosan backbone and OH of the starch. The blend also showed improved water vapor barrier properties, over the previous study (Ashori 2014), with a WVTR drop from 44.3 to 38.7 g/m^{2}h, at only 2.5wt% graphene addition.

Table 8.1 The effects of graphene on mechanical properties of different biopolymers that are suitable for packaging application

Matrix	Graphene	Young's modulus (%)	Tensile strength (%)	Ref.
Pea starch	2wt% GO	↑854	↑202	Li et al. (2011)
PS	2wt% GO	–	↑92	Ma et al. (2013)
PS	6wt% RGO	–	↑54	
CS-Tap-S	3wt% GNS	–	↑37.5	Ashori and Bahrami (2014)
CS	1.5wt% G	–	↑45	Ashori (2014)
RC	3wt% GNP	↑56	↑34	Mahmoudian et al. (2012)
RC	1.6vol% GONS	↑68	↑67	Huang et al. (2014)
RC	1.6wt% GNP	↑111	↑66	Zhang et al. (2012)
PLA	0.3wt% GO	↑115	↑95 (YS)	(Pinto et al. (2013a)
PLA	0.4wt% GNP	↑156	↑129 (YS)	
PHO	2.5wt% TRG	↑590	↑9	Barrett et al. (2014)
PHD	2.5wt% TRG	↑200	↑16	
PHOe	2.5wt% TRG	↑280	↑2	
PLA	0.3wt% RGO	–	↑3.4	Chieng et al. (2014)
PLA-EPO	0.3wt% RGO	–	↓32	
PLA-PEG	0.3wt% RGO	–	↓43	
PLA	0.3wt% GNP	–	↑1.7	
PLA-EPO	0.3wt% xGNP	–	↓34	
PLA-PEG	0.3wt% xGNP	–	↓49	
PLA-PEG	0.3wt% xGNP	↑69.5	↑32.7	Chieng et al. (2013)

CS = Chitosan; EPO = Epoxide; PEG = Poly Ethylene Glycol; PFG = PMMA Functionalized Graphene; PHO = Poly(hrydroxyoctanoate); PHD = Poly(hydroxydecanoate); PHOe = Poly (hydroxyoctenoate); PLA = Poly(lactic acid); PPC = Polypropylene Carbonate; PS = Plasticized Starch; RC = Regenerated Cellulose; Tap-S = Tapioca Starch; YS = Yield Strength

Cellulose

Cellulose has also gained popularity as an industrial biopolymer that offers biodegradable packaging opportunities. Some forms of cellulose like cellophane which is a regenerated form of cellulose has been commercially used for decades. However, cellulose's limited mechanical property and thermal stability hinder its performance and limits its application. Therefore, different graphene nanomaterials have been applied to different forms of cellulose in various studies to see how graphene interacts with cellulose and reinforces it to enhance its various properties.

Table 8.2 The effects of graphene on gas and vapor barrier properties of candidate biopolymers for packaging applications

Matrix–Graphene derivative	Permeability	Ref.
1. RC-GNP	P_{CO_2} ↓ 35% at 3wt% P_{O_2} ↓ 27% at 3wt%	Mahmoudian et al. (2012)
2. RC-GONS	P_{O_2} ↓ 98% at 1.64vol%	Huang et al. (2014)
3. PLA-GNP; PLA-GO	P_{O_2} ↓ 67.3% at 0.4wt% for GO P_{O_2} ↓ 68.1% at 0.4wt% for GNP P_{N_2} ↓ 75.4% at 0.2wt% for GO P_{N_2} ↓ 78.5% at 0.6wt% for GNP	Pinto et al. (2013a)
4. PS-GO, PS-RGO	WVP ↓ 43.7% at 4wt% GO WVP ↓ 34.9% at 8wt% RGO	Ma et al. (2013)
5. Pea starch-GO	WVP ↓ 39.4% at 1.5wt% GO at 98% RH	Li et al. (2011)

GONS = Graphene Oxide Nanosheets, P_{CO_2} = Permeability of CO_2, P_{O_2} = Permeability of O_2, P_{N_2} = Permeability of N_2

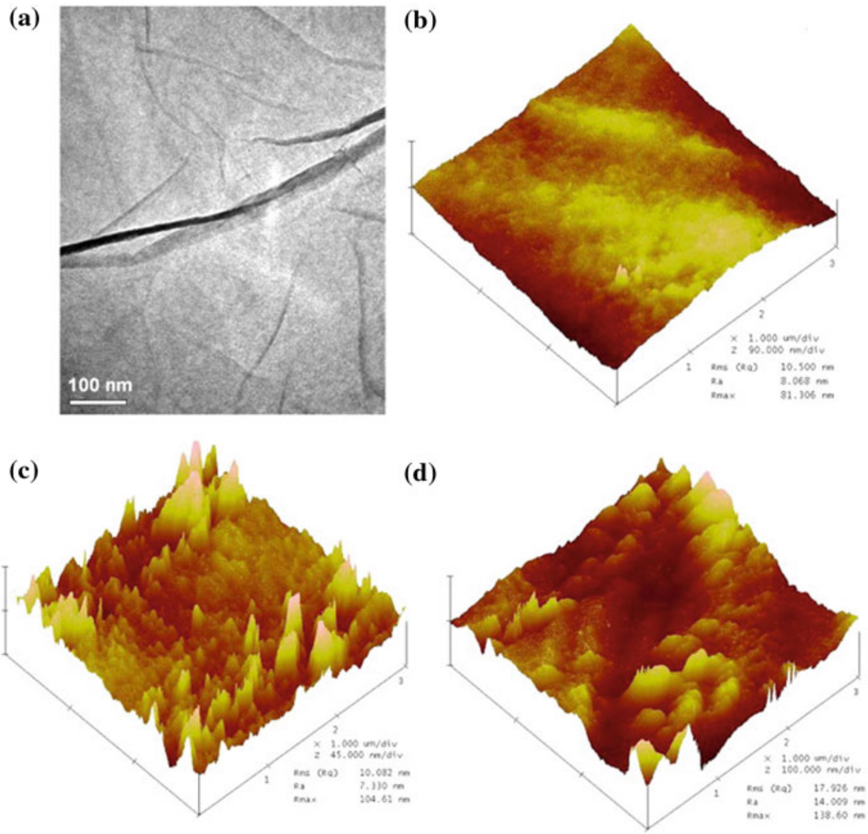


Fig. 8.10 **a** TEM images of pea starch-GO nanocomposite; AFM images of **b** pea starch, **c** pea starch-1wt% GO nanocomposite, and **d** pea starch-2wt% GO nanocomposites. Reprinted with permission from Li et al. (2011). Copyright 2011, Elsevier

Solubilization of natural cellulose and subsequent regeneration, using electrospinning or solution casting, is called regenerated cellulose (RC). RC-graphene oxide nanosheets (GONS) nanocomposites were also investigated for packaging application (Huang et al. 2014), where NaOH–urea was used as a solvent that efficiently dissolved GONS throughout RC matrix. TEM images confirmed the complete exfoliation of GONS into individual nanosheets and ensured homogeneous dispersion. In addition, two-dimensional wide-angle X-ray diffraction (2D-WAXD) showing disappearance of the regular and periodic structure of graphite oxide was a clear indication that characteristic diffraction ring of GONS was absent in the cellulose nanocomposite. The efficient dispersion and subsequent reinforcement by only 1.64vol% GONS increased tensile strength by 67% and Young's modulus by 68%, relative to the pristine RC (Fig. 8.11). The authors were able to prove, using the Halpin–Tsai model (Affdl and Kardos 1976), that GONSs were more parallelly aligned to the film surface, as result of gravitational forces and hot pressing during fabrication (Fig. 8.11). GONS also improved the barrier properties of RC as evidenced by the three times decrease in O_2 permeability of the nanocomposite compared to the control, as shown in Table 8.2.

There were two different studies focusing on RC–GNP nanocomposites, but with two different solvents 1-ethyl-3-methylimidazolium acetate (EMIMAc) solvent (Mahmoudian et al. 2012) and the other used N,N-dimethylacetamide (DMAC)–LiCl (Zhang et al. 2012) solvent. DMAC–LiCl solvent proved to be a better option for solvent casting of cellulose and graphene, as tensile strength and thermal decomposition temperature increased substantially compared to the study with EMIMAc solvent. The tensile strength improvement, thermal stability improvement, and gas barrier property enhancement found in this study as well as other studies are shown in Tables 8.1, 8.2, and 8.3.

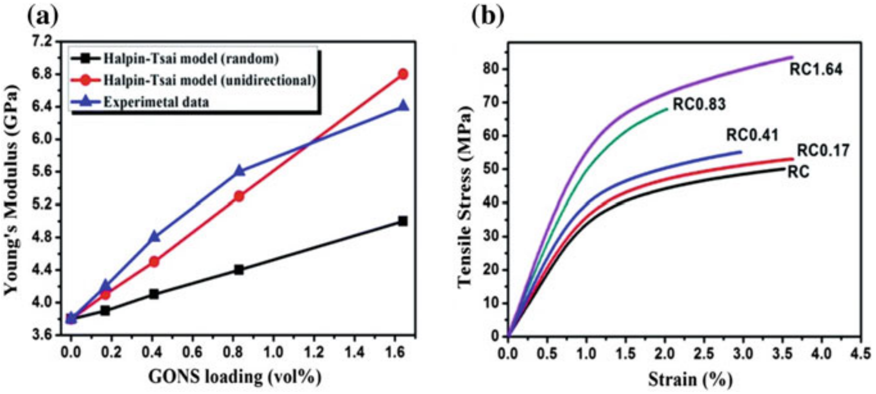


Fig. 8.11 **a** Typical stress–strain curves of RC and the cellulose nanocomposite films with different GONS loadings **b** Young's modulus of the samples as determined experimentally and the theoretical values obtained by Halpin–Tsai models based on the hypothesis that GONSs are randomly or unidirectionally distributed in the cellulose matrix. Reprinted with the permission from Huang et al. (2014). Copyright 2014, Royal Society of Chemistry

Table 8.3 The effects of graphene on thermal properties of different biopolymers

Matrix–Graphene	Thermal property	Ref.
RC-GNP	$T_{20\%}(\uparrow)$ 20 °C at 0.25wt%	Mahmoudian et al. (2012)
RC-Graphene	$T_{10\%}(\uparrow)$ 20 °C at 0.4wt%	Zhang et al. (2012)
Pea starch-GO	$T_{onset}(\uparrow)$ 10.2 °C at 2wt% $T_{end}(\uparrow)$ 7.4 °C at 2wt%	Li et al. (2011)
CAP-EG	$T_{50\%}(\uparrow)$ 29 °C at 10wt%	Jeon et al. (2012)

EG = Expanded Graphite, T_{onset} = Onset Temperature for Thermal Decomposition, T_{end} = End Temperature for Thermal Decomposition, T_g = Glass Transition Temperature, T_{50} = 50% Decomposition Temperature

Melt blending, which is another well-known biopolymer-graphene nanocomposite fabrication technique, has also been used to make cellulose-graphene nanocomposite. In a study to improve the properties of cellulose acetate propionate (CAP), EG nanoplatelets were melt blended with CAP (Jeon et al. 2012), which resulted in strong interlocked network between graphene and CAP. This lowered oxygen permeation, improved dynamic storage modulus, and increased thermal degradation temperature of the CAP–EG nanocomposite. Electrical volume resistivity of CAP–EG composites declined from 10^{15} to 10^{6} Ωcm, at only 5–7wt% loading.

Poly(Lactic Acid)

Another highly known biodegradable and biocompatible polymer is PLA, which has shown its versatile application as a packaging material. With the objective to overcome its poor mechanical property, low crystallization rate, and thermal resistance, different studies have graphene nanofiller in PLA matrix. Property enhancement of the pristine PLA, plasticized PLA nanocomposite, and unplasticized PLA nanocomposites were compared, where the plasticized nanocomposites showed 100% increase in tensile strength and Young's modulus, but unplasticized nanocomposite films showed only a 15% increase in tensile strength and 85% increase in Young's modulus at the same concentration of graphene (Pinto et al. 2013a). With increasing filler loading, glass transition temperature increased and permeability decreased, and maximum glass transition and lowest permeability were observed at for 0.4wt% loading of GO and 0.4wt% of GNP, in the PLA-graphene nanocomposites. Their oxygen and nitrogen permeability decrease were threefold and fourfold higher compared to pristine PLA. GNP was assumed to show better performance due to its planar configuration, which would ideally create a tortuous path and delay the process of escape of various gases, but due to the disordered orientation of GNP along the film plane, it was unable to create an efficient tortuous path and resulted in permeability similar to GO.

Poly(Hydroxyalkanoate)

Recently medium-chain-length poly(hydroxyalkanoate)s (PHA_{mcl}), a new class of renewable and biodegradable biopolymers have emerged, and has shown great promise in packaging applications. With the objective of producing biodegradable packaging sensors and charge dissipating applications, three different types of PHA_{mcl} polymers: poly(hrydroxyoctanoate) (PHO), poly(hydroxydecanoate) PHD, and poly(hydroxyoctenoate) (PHOe) were functionalized with thermally reduced graphene (TRG) nanoparticles, using solution casting technique, (Barrett et al. 2014; Barrett 2014), which showed that efficacy of reinforcement was affected by the chain packing length, ability of non-covalent interaction with TRG and covalent crosslinking. The results showed that the addition of up to 2.5vol% TRG to PHA_{mcl} increased the Young's modulus of PHO by 590%, PHD by 200%, and PHOe by 280%. The extent of hydrogen bonding was directly related to the length of the aliphatic extensions from the polyester backbone. Steric hindrance was a result of longer chains, which reduced the intensity of hydrogen bonding between the PHA_{mcl} and TRG. PHO, which is the shortest chain PHA_{mcl} polymer out of the three biopolymers, had the least hindrance to hydrogen bonding and therefore the highest modulus enhancement. TEM and SEM images of the PHA_{mcl} showed TRG had the best dispersion in PHO, but experienced entanglement at only 0.5% loading, on the other hand, TRG had the worst dispersion in PHOe, but entanglements did not occur until 2.5% loading of TRG. The thermal properties of the PHA polymers were increased by TRG, as melting temperature improved by 1−3 °C, and an increase over 7 orders of magnitude of the electrical conductivity was attained.

8.3.2 Carbon Nanotube-Based Functionalization

Carbon nanotubes (CNTs) are another member of the carbon family similar to graphene. Carbon nanotubes are one atom thick nano-sized tubes that may exist as a single unit, which is referred as single-wall nanotube (SWNT) or it may consist of a number of concentric tubes defined as multi-walled nanotubes (MWNT). CNTs have astonishingly high aspect ratio, with tensile strength as high as 200 GPa and elastic modulus of 1 TPa (Lau and Hui 2002; Zhou et al. 2004). CNTs have been used in various types of synthetic polymer nanocomposites, like poly (ethylene-2,6-naphtalene) (PEN) (Kim et al. 2008), PVA (Chen et al. 2005; Bin et al. 2006), and polyamide (Zeng et al. 2006) for packaging application. These nanocomposites showed remarkable improvements in mechanical, thermal, and barrier properties. CNTs have also been coupled with different biopolymers like PLA (Kuan et al. 2008; Chiu et al. 2008; Villmow et al. 2008; Yoon et al. 2009), starch (Ma et al. 2008), etc., for improving their mechanical, thermal, and electrical properties. They have shown great promise for being used as reinforcement for biodegradable packaging application, as they increased the flexural and tensile strength of PLA, by 17.5 and 27.2%, respectively, at only 4 phr (parts of CNT per hundred parts of PLA) loading (Kuan et al. 2008) and has decreased PLA's WVTR by 200% (Brody 2006). MWNTs have also been used with PLA to fabricate conductive biopolymer vapor sensor which can act as a smart packaging material (Kumar et al. 2012).

8.4 Clay and Silicate Nanoclay-Based Reinforcement

The widely available, inexpensive, and relatively simple processing of layered inorganic solids like clays and silicates garnered a lot of attention as a filler material to improve polymer performance in the packaging industry. Nanoclays usually have a thickness of 1 nm and length of several microns, and when nanoclays are introduced to nanocomposite formulations, it results in increased tortuosity of the diffusive path for a penetrant molecule (Fig. 8.2), providing excellent barrier properties (Bharadwaj et al. 2002; Cabedo et al. 2004; Mirzadeh and Kokabi 2007).

Montmorillonite (MMT), which is a hydrated alumina-silicate-layered clay (Weiss et al. 2006), is most well-known clay filler in polymer-nanoclay research. The high specific surface area and large aspect ratio (50–100), makes MMT an exceptionally effective nanofiller for various polymers (Uyama et al. 2003). For the purpose of improving the food packaging application of various biopolymers, MMT has been investigated, especially for starch (Park et al. 2002; Avella et al. 2005; Huang et al. 2005; Chen and Evans 2005; Yoon and Deng 2006; Cyras et al. 2008). At only 5wt% addition, MMT has been reported to improve the tensile strength and strain of corn starch by 450 and 20%, respectively (Huang et al. 2006). MMT has even been used for reinforcing PLA (Sinclair 1996; Thellen et al. 2005) and various types of proteins (Dean and Yu 2005; Rhim et al. 2005; Chen and Zhang 2006; Yu et al. 2007). Zein, a protein extract from corn with, film-forming ability, biodegradability, and biocompatibility, finds application as a coating agent in food industry (Shukla and Cheryan 2001; Liu et al. 2005; Luecha et al. 2010, 2011). However, due to its high water vapor permeability and low tensile strength, it has been functionalized with MMT and has shown tensile strength increase of 150% using only 5wt% clay, and the water vapor permeability drop from 11.58 to 4.56 g mm/days m^2 KPa at only 3wt% MMT loading (Luecha et al. 2010).

Kaolinite [$Al_2Si_2O_5(OH)_4$] is a layered silicate mineral, mainly used in the production of paper, ceramics, and cosmetics. Nanocomposites of thermoplastic starch and kaolin clay showed that at a loading of 50 phr, tensile strength increased up to 135% and Young's modulus increased up to 50% (de Carvalho et al. 2001). Moreover, water vapor resistance significantly increased up to 20 phr loading of kaolinite, but no improvement in thermal stability was observed with increasing kaolinite concentration. In another study, chemically modified kaolinite was used to reinforce amorphous PLA (Cabedo et al. 2006), where kaolinite successfully improved the oxygen barrier property by 50%.

Another widely known form of MMT is Cloisite (Na-MMT), which has also been used in different biopolymer nanocomposite research for improved packaging application. A research has been conducted on reinforcement of plasticized starch using four different types of Cloisite (natural Cloisite: Na-MMT, and organically modified Cloisite: Cloisite 30B, Cloisite 10A, and Cloisite 6A) (Park et al. 2002), at 5% loading. XRD and TEM characterization of the four types of TPS-Cloisite nanocomposite showed 20% increase in tensile strength and 30% in Young's modulus, as well as significant reduction in water vapor permeability. Compared to the thermal property of pristine TPS, all four nanocomposites showed notable enhancement. Four different organoclays Cloisite 30B, 10A, 25A, and 20A were used as filler for starch acetate, using melt blending, which resulted in substantial improvement in mechanical and thermal stability as the glass transition temperature increased by 6–14 °C and onset temperature for thermal decomposition increased by 15–25 °C (Xu et al. 2005).

Another notable hydrous silicate mineral, Tourmaline, $[Na(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OHF)_4]$ was also tested to examine its reinforcing capabilities on RC. Unfortunately, it did not show any significant mechanical or thermal property improvement over pristine RC (Ruan et al. 2004). However, it showed great promise as a filler for functional packaging material because of its antibacterial property against *Staphylococcus aureus*, a common food-borne pathogen.

8.5 Cellulose Nanofiber, Starch Nanocrystal, and Chitosan Nanoparticle-Based Reinforcements

A popular polysaccharide-based nanomaterial, cellulose nanofiber (CNF), has garnered a lot of attention, due to their inexpensive pricing, biodegradability, high strength, and renewability (Helbert et al. 1996; Podsiadlo et al. 2005). The type of CNF consisting of elongated molecule bundles, stabilized by hydrogen bonding, is called cellulose nanofibers (Azizi Samir et al. 2005; Wang and Sain 2007), and the other type, which consists of the crystalline part of microfibrils, called cellulose whiskers, is obtained using acid hydrolysis (Dujardin et al. 2003; Samir et al. 2004). A more commercially available alternative of cellulose whiskers is microcrystalline cellulose (MCC), obtained from particles of hydrolyzed cellulose microcrystals (Petersson and Oksman 2006).

One of the governing factors that influence the final property of the nanocomposite of reinforced cellulose nanofibers is the aspect ratio of the fiber, which is a direct consequence of type of cellulose and fabrication conditions (Azizi Samir et al. 2005). The other governing factors are the dimensions of the fiber as well as the geometrical and mechanical percolation effects (Dubief et al. 1999; Hubbe et al. 2008), including the orientation distribution of the fillers (Jiang et al. 2007; Kvien and Oksman 2007). According to the percolation theory, properly dispersed filler that is present in sufficient number to create continuous network is the primary condition for maximum improvement by the nanofiller (Helbert et al. 1996; Ljungberg et al. 2005).

Different types of biopolymers have been considered with CNF, like fruits and vegetable puree (Azeredo et al. 2009), poly(styrene-co-butyl acrylate) (Helbert et al. 1996), poly(vinyl alcohol) (PVOH) (Zimmermann et al. 2004), starch (Angles and Dufresne 2000, 2001; de Souza Lima and Borsali 2004; Alemdar and Sain 2008). Mango puree films have been functionalized with cellulose nanofibers, to create highly efficient edible packaging films (Azeredo et al. 2009), and showed an increase in tensile strength from 4.09 to 8.76 MPa at 36% loading and decrease in water vapor permeability from 2.66 to 1.67 g mm/kPa h m^2 at 10wt% loading. A study on straw cellulose whiskers showed that addition of the nanofiller at 30wt% with poly(styrene-co-butyl acrylate) latex film resulted in modulus improvements three orders of magnitude over control (Helbert et al. 1996). Compatible geometry and whisker stiffness, effective linkage of cellulose fibers through hydrogen bonds, fibril network formation within the polymer matrix, are some of the key elements for such an impressive reinforcing effect. The reinforcing capabilities of cellulose fibers are somewhat temperature dependent, especially at temperatures above the glass transition temperature (T_g) of the matrix polymer, when CNF has noticeably improved strength and modulus of polymers (Dufresne and Vignon 1998; Dufresne et al. 2000). CNF has also been reported to decrease water uptake in starch (Dufresne and Vignon 1998; Dufresne et al. 2000) and has improved moisture barrier properties of many other biopolymers (Paralikar et al. 2008; Sanchez-Garcia et al. 2008; Svagan et al. 2009).

Some other notable biopolymer-based nanofillers are starch nanocrystals, which have reportedly improved the mechanical properties of PVOH (Chen et al. 2008), by adding up to 10wt%. Another nanoreinforcement is chitin whiskers or chitosan nanoparticles, which have successfully improved tensile strength and water resistance of soy protein isolates (SPI) (Lu et al. 2004), tensile strength and barrier properties of chitosan films (Sriupayo et al. 2005), and hydroxypropyl methyl cellulose (HPMC) (de Moura et al. 2009) and has proven to be a potential food packaging material for elongated storage stability.

8.6 Antimicrobial Nanomaterial

Nano-sized antimicrobial filler-functionalized food packaging materials have gained a lot of popularity, as they can reduce, obstruct, or defer the growth of pathogenic and spoilage microorganisms (Rhim and Ng 2007). Antimicrobial compounds in nanoscale range have proven to be superior to the micro-sized compounds as the larger surface area increased adhesion to biological materials (Luo and Stutzenberger 2008). Silver-based antimicrobial packaging materials are well known for their application as they have significant toxicity toward various microorganisms and have excellent thermal stability and minimal volatility (Liau et al. 1997). Silver-based nanocompounds act as an antimicrobial agent by releasing silver ions, which binds to the electron donor group from the pathogenic molecule (Kumar and Münstedt 2005). Poly(Amide 6)-2wt% Ag-NP has shown antimicrobial activity against *E. coli*, even after 100 days of storage (Damm et al. 2007). Moreover, Ag-NPs have shown promise in elongation of shelf stability of fruits and vegetables (Hu and Fu 2003), jujube (a Chinese fruit) (Li et al. 2009), asparagus (An et al. 2008), etc. Another notable antimicrobial nanomaterial is chitosan nanoparticles, which, in the presence of protonated amino groups, interact with the oppositely charged cell membranes of the pathogenic molecule causing leakage and eventual rupture of intracellular material (Qi et al. 2004). CNTs have also shown antibacterial properties, as aggregates of CNT, using its long and thin structure can puncture the microbial cells of pathogens like *E. coli*, (Kang et al. 2007). Also, water dispersible GO and RGO paper have shown significant antibacterial activity against *E. coli*, while showing very little cytotoxicity (Hu et al. 2010). Graphene has also shown antibacterial activity against *Staphylococcus aureus* (Akhavan and Ghaderi 2010).

8.7 Future Perspective and Limitations

There are several forms of graphene, but only the GO or RGO powder forms have been explored for packaging application. So other forms like graphene aerogel, CVD graphene can also be explored, where CVD graphene or graphene aerogel can be used in biopolymer-graphene sandwich structure to make smart biodegradable packaging that ensures quality control and elongated and safe storage for food and pharmaceuticals. Biopolymer-graphene nanocomposites can also be used as a mechanically strong yet flexible, biodegradable platform for antibody-antigen or synthetic detecting element (liposome, aptamer, and peptide)-based FET biosensors (Guo et al. 2015; Qian et al. 2015). Moreover, different biopolymer-graphene nanocomposites can function as a gate dielectric for enhanced current modulation throughout FET biosensors (Qian et al. 2015), for a more efficient recognition of different food toxins, allergen, and pathogenic bacteria.

Nowadays, advanced chemical sensors made of chemical selective coating use the principle of surface adsorption to detect a particular chemical or gas (Vanderroost et al. 2014). Various kinds of carbon nanomaterials like graphene, graphite, and nanotubes can be used as transducers in various chemical sensors, where it is used as a transducer as well as mechanical reinforcement for the biodegradable packaging material, thus detects various pathogenic and spoilage microorganisms to ensure product integrity, and tracks ingredients or products through the processing chain (Nachay 2007; De Azeredo 2009).

Another revolutionary technique in the area of smart packaging is the radiofrequency identification (RFID), which is an programmable recognition technique that applies wireless sensors to detect items and collect data, for application in quality control and supply chain management, classify and handle the flow of goods (Jones et al. 2004; Sarac et al. 2010; Ruiz-Garcia and Lunadei 2011). Commercially available RFID with tags can track the temperature, relative humidity, light exposure, pressure, and pH of products. "Water-based, inkjet-printed GO ink" has been successfully applied to develop used as the basis for design and development of inexpensive, autonomous, wireless sensor, which has good response to spoilage gases like ammonia gas (NH_3) (Le et al. 2012). Graphene-based RFID tags can also be used, coupled with the biopolymer-graphene nanocomposite packaging, to ensure food quality and food safety.

For long term packaging application and shelf life stability, a massive challenge would be the intrinsic biodegradability of biopolymers, as controlled environment, like control of moisture, nutrients, or microorganisms, as well as temperature during various experimentation becomes a great hindrance (Kaplan 1998). In addition, "more random configuration of the repeating units in biopolymers and the resulting steric hindrance" (Rouf and Kokini 2016) experienced by the nanofillers, as compared to the more controlled and organized configurations of synthetic polymers, ultimately result in the weaker performance of biopolymers compared to synthetic polymers when different nanomaterials like graphene is added. Table 8.4 shows comparison of the young's modulus of biopolymer-graphene nanocomposite with synthetic polymer-graphene nanocomposites which provide a clear difference between biopolymer and synthetic polymer-graphene nanocomposites.

Another challenging aspect of nanomaterial functionalization in biopolymer is the release of the nanomaterial from the host matrix. Some studies have reported release of silver (Ag), Cu, Ag-zeolites, montmorillonite nanoclay, from its host polymer matrix in some applications (Duncan and Pillai 2014); however, the release of graphene from its polymer/biopolymer host matrix has not yet been reported, so more investigation is required in this regard. The nanomaterial release can be prevented by adding an extra layer of biopolymer that comes in contact with the

Table 8.4 Comparison of highest reported young's modulus increase of some common biopolymer-graphene and synthetic polymer-graphene nanocomposites

Biopolymer				Synthetic polymer			
Polymer	Graphene	YM (%)	Ref.	Polymer	Graphene	YM (%)	Ref.
Starch	2wt% GO	854	(Li et al. 2011)	PVA	2.5vol% GO	128	(Xu et al. 2009)
CS	6wt% RGO	170	(Wang et al. 2010)	NR	1.2vol% TRG	750	(Prud'Homme et al. 2010)
PLA	0.4wt% GNP	156	(Pinto et al. 2013a)	PDMS	2.2vol% TRG	1100	(Prud'Homme et al. 2010)
PHO	2.5wt% TRG	590	(Barrett et al. 2014)	TPU	2.4vol% GO	900	(Kim et al. 2010)
RC	1.6wt% GNP	111	(Zhang et al. 2012)	SBR	0.8% TRG	390	(Prud'Homme et al. 2010)

NR = Natural Rubber; PCL = Poly(ε-caprolactone); PDMS = Polydimethylsiloxane; PVA = Poly(vinyl alcohol); SBR = Styrene-Butadiene Rubber; SF = Silicone Foam; TPU = Tetra Polyurethane; YM = Young's Modulus

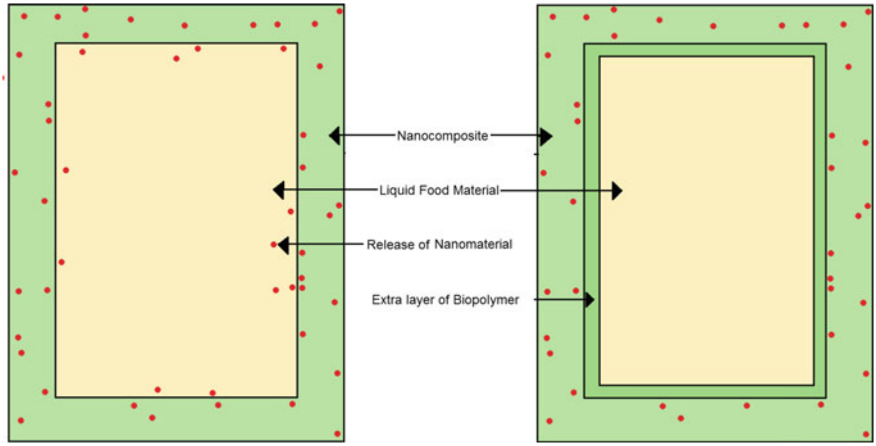


Fig. 8.12 ENM release from nanocomposite into food material [Adapted from Duncan and Pillai (2014)]

food material, as shown in Fig. 8.12. This will not only provide a barrier to the nanomaterial release (if any) but will also improve the permeability property of the packaging and provide extra mechanical support.

8.8 Conclusion

The need for high quality, long lasting, and safe food supply has catalyzed various novel techniques in packaging systems, with smart biodegradable packaging being the latest and most promising addition. From this chapter, it is clear that usually a very small amount (<5%) of graphene and carbon nanotubes is used in biodegradable packaging for improvement of their various properties as packaging material, compared to other nanomaterials like kaolinite (up to 50% loading), CNF (up to 36% loading), and therefore, these graphene nanocomposites have more eco-friendly impact in the various novel packaging applications. The property improvement of various biodegradable packaging materials using graphene derivatives depends on not only the form of nanofiller but also the reaction condition and fabrication technique, which is clearly noticeable from the comparison of the improvement in mechanical property of all the biopolymer nanocomposites. There has been extensive research for packaging application with polysaccharides, PLAs, and other biopolymers as discussed above but when it comes to packaging research, the field of proteins has been neglected. Solution casting and melt blending technique have been the major fabrication technique for biopolymer nanocomposite fabrication, whereas grafting technique has shown great potential for synthetic polymers (Fang et al. 2010; Song et al. 2013); therefore, grafting techniques for combining different nanomaterials to biopolymers require much consideration. In conclusion, nanomaterial-based biodegradable packaging has great potential as smart packaging to further consumer benefits and convenience, as well as ensures a healthier environment.

References

Affdl JCH, Kardos JL (1976) The Halpin-Tsai equations: a review. Polym Eng Sci 16:344–352. doi:10.1002/pen.760160512

Akhavan O, Ghaderi E (2010) Toxicity of graphene and graphene oxide nanowalls against bacteria. ACS Nano 4:5731–5736

Alemdar A, Sain M (2008) Biocomposites from wheat straw nanofibers: morphology, thermal and mechanical properties. Compos Sci Technol 68:557–565

Alexandre B, Langevin D, Médéric P et al (2009) Water barrier properties of polyamide 12/montmorillonite nanocomposite membranes: structure and volume fraction effects. J Membr Sci 328:186–204

An J, Zhang M, Wang S, Tang J (2008) Physical, chemical and microbiological changes in stored green asparagus spears as affected by coating of silver nanoparticles-PVP. LWT-Food Sci Technol 41:1100–1107

Angles MN, Dufresne A (2000) Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. Macromolecules 33:8344–8353

Angles MN, Dufresne A (2001) Plasticized starch/tunicin whiskers nanocomposite materials. 2. Mechanical behavior. Macromolecules 34:2921–2931

Ashori A (2014) Effects of graphene on the behavior of chitosan and starch nanocomposite films. Polym Eng Sci 54:2258–2263

Ashori A, Bahrami R (2014) Modification of physico-mechanical properties of chitosan-tapioca starch blend films using nano graphene. Polym-Plast Technol Eng 53:312–318

Avella M, De Vlieger JJ, Errico ME et al (2005) Biodegradable starch/clay nanocomposite films for food packaging applications. Food Chem 93:467–474

Azeredo H, Mattoso LHC, Wood D et al (2009) Nanocomposite edible films from mango puree reinforced with cellulose nanofibers. J Food Sci 74:N31–N35

Azizi Samir MAS, Alloin F, Dufresne A (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. Biomacromolecules 6:612–626

Barrett J (2014) Physical and biochemical strategies for improving the yield and material properties of Polyhydroxyalkanoate Biopolymers

Barrett JSF, Abdala AA, Srienc F (2014) Poly(hydroxyalkanoate) Elastomers and their Graphene nanocomposites. Macromolecules 47:3926–3941. doi:10.1021/ma500022x

Bharadwaj RK, Mehrabi AR, Hamilton C et al (2002) Structure–property relationships in cross-linked polyester–clay nanocomposites. Polymer 43:3699–3705

Bin Y, Mine M, Koganemaru A et al (2006) Morphology and mechanical and electrical properties of oriented PVA–VGCF and PVA–MWNT composites. Polymer 47:1308–1317

Boehm H-P (2010) Graphene—how a laboratory curiosity suddenly became extremely interesting. Angew Chem Int Ed 49:9332–9335

Brodie BC (1859) On the atomic weight of graphite. Philos Trans R Soc Lond 149:249–259

Brody AL (2006) Nano and food packaging technologies converge

Cabedo L, Giménez E, Lagaron JM et al (2004) Development of EVOH-kaolinite nanocomposites. Polymer 45:5233–5238. doi:10.1016/j.polymer.2004.05.018

Cabedo L, Luis Feijoo J, Pilar Villanueva M et al (2006) Optimization of biodegradable nanocomposites based on a PLA/PCL blends for food packaging applications. In: Macromolecular Symposia. Wiley Online Library, pp 191–197

Cao Y, Feng J, Wu P (2010) Preparation of organically dispersible graphene nanosheet powders through a lyophilization method and their poly(lactic acid) composites. Carbon 48:3834–3839

Celzard A, Mareche JF, Furdin G, Puricelli S (2000) Electrical conductivity of anisotropic expanded graphite-based monoliths. J Phys D Appl Phys 33:3094

Chen B, Evans JRG (2005) Thermoplastic starch–clay nanocomposites and their characteristics. Carbohyd Polym 61:455–463. doi:10.1016/j.carbpol.2005.06.020

Chen P, Zhang L (2006) Interaction and properties of highly exfoliated soy protein/montmorillonite nanocomposites. Biomacromolecules 7:1700–1706

Chen G, Weng W, Wu D et al (2004) Preparation and characterization of graphite nanosheets from ultrasonic powdering technique. Carbon 42:753–759

Chen W, Tao X, Xue P, Cheng X (2005) Enhanced mechanical properties and morphological characterizations of poly(vinyl alcohol)–carbon nanotube composite films. Appl Surf Sci 252:1404–1409

Chen Y, Cao X, Chang PR, Huneault MA (2008) Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/native pea starch. Carbohyd Polym 73:8–17

Chiu W-M, Chang Y-A, Kuo H-Y et al (2008) A study of carbon nanotubes/biodegradable plastic polylactic acid composites. J Appl Polym Sci 108:3024–3030. doi:10.1002/app.27796

Chung DDL (2016) A review of exfoliated graphite. J Mater Sci 51:554–568

Cyras VP, Manfredi LB, Ton-That M-T, Vázquez A (2008) Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films. Carbohyd Polym 73:55–63. doi:10.1016/j.carbpol.2007.11.014

Dai J, Wang G, Ma L, Wu C (2015) Study on the surface energies and dispersibility of graphene oxide and its derivatives. J Mater Sci 50:3895–3907

Damm C, Münstedt H, Rösch A (2007) Long-term antimicrobial polyamide 6/silver-nanocomposites. J Mater Sci 42:6067–6073

De Azeredo HMC (2009) Nanocomposites for food packaging applications. Food Res Int 42:1240–1253. doi:10.1016/j.foodres.2009.03.019

de Carvalho AJF, Curvelo AAS, Agnelli JAM (2001) A first insight on composites of thermoplastic starch and kaolin. Carbohyd Polym 45:189–194. doi:10.1016/S0144-8617(00)00315-5

de Moura MR, Aouada FA, Avena-Bustillos RJ et al (2009) Improved barrier and mechanical properties of novel hydroxypropyl methylcellulose edible films with chitosan/tripolyphosphate nanoparticles. J Food Eng 92:448–453

de Souza Lima MM, Borsali R (2004) Rodlike cellulose microcrystals: structure, properties, and applications. Macromol Rapid Commun 25:771–787

Dean K, Yu L (2005) Biodegradable protein-nanoparticles composites. Biodegradable polymers for industrial applications. Woodhead Publishing Ltd, Cambridge, UK, pp 289–312

Dervishi E, Biris AR, Watanabe F et al (2011) Few-layer nano-graphene structures with large surface areas synthesized on a multifunctional Fe:Mo:MgO catalyst system. J Mater Sci 47:1910–1919. doi:10.1007/s10853-011-5980-z

Dreyer DR, Park S, Bielawski CW, Ruoff RS (2010) The chemistry of graphene oxide. Chem Soc Rev 39:228–240

Dubief D, Samain E, Dufresne A (1999) Polysaccharide microcrystals reinforced amorphous poly(β-hydroxyoctanoate) nanocomposite materials. Macromolecules 32:5765–5771

Dufresne A, Dupeyre D, Vignon MR (2000) Cellulose microfibrils from potato tuber cells: processing and characterization of starch–cellulose microfibril composites. J Appl Polym Sci 76:2080–2092

Dufresne A, Vignon MR (1998) Improvement of starch film performances using cellulose microfibrils. Macromolecules 31:2693–2696

Dujardin E, Blaseby M, Mann S (2003) Synthesis of mesoporous silica by sol–gel mineralisation of cellulose nanorod nematic suspensions. J Mater Chem 13:696–699

Duncan TV, Pillai K (2014) Release of engineered nanomaterials from polymer nanocomposites: diffusion, dissolution, and desorption. ACS Appl Mater Interfaces 7:2–19

Faghihi S, Gheysour M, Karimi A, Salarian R (2014) Fabrication and mechanical characterization of graphene oxide-reinforced poly(acrylic acid)/gelatin composite hydrogels. J Appl Phys 115:083513

Fang M, Wang K, Lu H et al (2010) Single-layer graphene nanosheets with controlled grafting of polymer chains. J Mater Chem 20:1982–1992

Favier V, Cavaille JY, Canova GR, Shrivastava SC (1997) Mechanical percolation in cellulose whisker nanocomposites. Polym Eng Sci 37:1732–1739

Guan G, Lu J, Jiang H (2016) Preparation, characterization, and physical properties of graphene nanosheets and films obtained from low-temperature expandable graphite. J Mater Sci 51:926–936

Guo J, Liu J, Yang B et al (2015) Biodegradable junctionless transistors with extremely simple structure. Electron Device Lett IEEE 36:908–910

He L, Wang H, Xia G et al (2014) Chitosan/graphene oxide nanocomposite films with enhanced interfacial interaction and their electrochemical applications. Appl Surf Sci 314:510–515

He Y, Zhang N, Gong Q et al (2012) Alginate/graphene oxide fibers with enhanced mechanical strength prepared by wet spinning. Carbohyd Polym 88:1100–1108

Helbert W, Cavaille JY, Dufresne A (1996) Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: processing and mechanical behavior. Polym Compos 17:604–611

Hu AW, Fu ZH (2003) Nanotechnology and its application in packaging and packaging machinery. Packag Eng 24:22–24

Hu W, Peng C, Luo W et al (2010) Graphene-based antibacterial paper. ACS nano 4:4317–4323

Huang H-D, Liu C-Y, Li D et al (2014) Ultra-low gas permeability and efficient reinforcement of cellulose nanocomposite films by well-aligned graphene oxide nanosheets. J Mater Chem A 2:15853–15863

Huang L, Li D-Q, Lin Y-J et al (2005) Controllable preparation of Nano-MgO and investigation of its bactericidal properties. J Inorg Biochem 99:986–993

Huang M, Yu J, Ma X (2006) High mechanical performance MMT-urea and formamide-plasticized thermoplastic cornstarch biodegradable nanocomposites. Carbohyd Polym 63: 393–399

Hubbe MA, Rojas OJ, Lucia LA, Sain M (2008) Cellulosic nanocomposites: a review. BioResources 3:929–980

Jang BZ, Zhamu A (2008) Processing of nanographene platelets (NGPs) and NGP nanocomposites: a review. J Mater Sci 43:5092–5101

Jayasena B, Reddy CD, Subbiah S (2013) Separation, folding and shearing of graphene layers during wedge-based mechanical exfoliation. Nanotechnology 24:205301. doi:10.1088/0957-4484/24/20/205301

Jeon GW, An J-E, Jeong YG (2012) High performance cellulose acetate propionate composites reinforced with exfoliated graphene. Compos B Eng 43:3412–3418

Jiang B, Liu C, Zhang C et al (2007) The effect of non-symmetric distribution of fiber orientation and aspect ratio on elastic properties of composites. Compos B Eng 38:24–34

Jones P, Clarke-Hill C, Shears P et al (2004) Radio frequency identification in the UK: opportunities and challenges. Int J Retail Distrib Manag 32:164–171

Kang S, Pinault M, Pfefferle LD, Elimelech M (2007) Single-walled carbon nanotubes exhibit strong antimicrobial activity. Langmuir 23:8670–8673

Kaplan DL (1998) Introduction to biopolymers from renewable resources. In: Kaplan DDL (ed) Biopolymers from renewable resources. Springer, Berlin Heidelberg, pp 1–29

Kim I-H, Jeong YG (2010) Polylactide/exfoliated graphite nanocomposites with enhanced thermal stability, mechanical modulus, and electrical conductivity. J Polym Sci, Part B: Polym Phys 48:850–858

Kim JY, Han SI, Hong S (2008) Effect of modified carbon nanotube on the properties of aromatic polyester nanocomposites. Polymer 49:3335–3345

Krishnan D, Kim F, Luo J et al (2012) Energetic graphene oxide: challenges and opportunities. Nano today 7:137–152

Kuan C-F, Kuan H-C, Ma C-CM, Chen C-H (2008) Mechanical and electrical properties of multi-wall carbon nanotube/poly(lactic acid) composites. J Phys Chem Solids 69:1395–1398. doi:10.1016/j.jpcs.2007.10.060

Kumar R, Münstedt H (2005) Silver ion release from antimicrobial polyamide/silver composites. Biomaterials 26:2081–2088

Kumar B, Castro M, Feller JF (2012) Poly(lactic acid)–multi-wall carbon nanotube conductive biopolymer nanocomposite vapour sensors. Sens Actuators B: Chem 161:621–628. doi:10.1016/j.snb.2011.10.077

Kvien I, Oksman K (2007) Orientation of cellulose nanowhiskers in polyvinyl alcohol. Appl Phys A 87:641–643

Lau AK-T, Hui D (2002) The revolutionary creation of new advanced materials—carbon nanotube composites. Compos B Eng 33:263–277

Le T, Lakafosis V, Lin Z et al (2012) Inkjet-printed graphene-based wireless gas sensor modules. In: 2012 IEEE 62nd electronic components and technology conference, 1003–1008

Lerf A, He H, Forster M, Klinowski J (1998) Structure of graphite oxide revisited||. J Phys Chem B 102:4477–4482

Liau SY, Read DC, Pugh WJ et al (1997) Interaction of silver nitrate with readily identifiable groups: relationship to the antibacterialaction of silver ions. Lett Appl Microbiol 25:279–283

Li H, Li F, Wang L et al (2009) Effect of nano-packing on preservation quality of Chinese jujube (Ziziphus jujuba Mill. var. inermis (Bunge) Rehd). Food Chem 114:547–552

Li R, Liu C, Ma J (2011) Studies on the properties of graphene oxide-reinforced starch biocomposites. Carbohyd Polym 84:631–637

Liu X, Sun Q, Wang H et al (2005) Microspheres of corn protein, zein, for an ivermectin drug delivery system. Biomaterials 26:109–115. doi:10.1016/j.biomaterials.2004.02.013

Liu L, Shen Z, Liang S et al (2014) Graphene for reducing bubble defects and enhancing mechanical properties of graphene/cellulose acetate composite films. J Mater Sci 49:321–328

Ljungberg N, Bonini C, Bortolussi F et al (2005) New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: effect of surface and dispersion characteristics. Biomacromolecules 6:2732–2739

Lu Y, Weng L, Zhang L (2004) Morphology and properties of soy protein isolate thermoplastics reinforced with chitin whiskers. Biomacromolecules 5:1046–1051

Luduena LN, Alvarez VA, Vazquez A (2007) Processing and microstructure of PCL/clay nanocomposites. Mater Sci Eng, A 460:121–129

Luecha J, Hsiao A, Brodsky S et al (2011) Green microfluidic devices made of corn proteins. Lab Chip 11:3419–3425

Luecha J, Sozer N, Kokini JL (2010) Synthesis and properties of corn zein/montmorillonite nanocomposite films. J Mater Sci 45:3529–3537. doi:10.1007/s10853-010-4395-6

Luo PG, Stutzenberger FJ (2008) Nanotechnology in the detection and control of microorganisms. Adv Appl Microbiol 63:145–181

Ma X, Yu J, Wang N (2008) Glycerol plasticized-starch/multiwall carbon nanotube composites for electroactive polymers. Compos Sci Technol 68:268–273. doi:10.1016/j.compscitech.2007.03.016

Ma T, Chang PR, Zheng P, Ma X (2013) The composites based on plasticized starch and graphene oxide/reduced graphene oxide. Carbohyd Polym 94:63–70

Mahmoudian S, Wahit MU, Imran M et al (2012) A facile approach to prepare regenerated cellulose/graphene nanoplatelets nanocomposite using room-temperature ionic liquid. J Nanosci Nanotechnol 12:5233–5239

Mark JE (1996) Ceramic-reinforced polymers and polymer-modified ceramics. Polym Eng Sci 36:2905–2920

Mirzadeh A, Kokabi M (2007) The effect of composition and draw-down ratio on morphology and oxygen permeability of polypropylene nanocomposite blown films. Eur Polymer J 43:3757–3765. doi:10.1016/j.eurpolymj.2007.06.014

Mittal V (2007) Polypropylene-layered silicate nanocomposites: filler matrix interactions and mechanical properties. J Thermoplast Compos Mater 20:575–599

Mittal V (2008) Mechanical and gas permeation properties of compatibilized polypropylene–layered silicate nanocomposites. J Appl Polym Sci 107:1350–1361

Nachay K (2007) Analyzing nanotechnology. Food Technol 61:34–36

Nie L, Liu C, Wang J et al (2015) Effects of surface functionalized graphene oxide on the behavior of sodium alginate. Carbohyd Polym 117:616–623

Novoselov KS, Geim AK, Morozov SV et al (2004) Electric field effect in atomically thin carbon films. Science 306:666–669

Pan Y, Wu T, Bao H, Li L (2011) Green fabrication of chitosan films reinforced with parallel aligned graphene oxide. Carbohyd Polym 83:1908–1915

Paralikar SA, Simonsen J, Lombardi J (2008) Poly(vinyl alcohol)/cellulose nanocrystal barrier membranes. J Membr Sci 320:248–258

Park S, Ruoff RS (2009) Chemical methods for the production of graphenes. Nat Nanotechnol 4:217–224

Park H-M, Li X, Jin C-Z et al (2002) Preparation and properties of biodegradable thermoplastic starch/clay hybrids. Macromol Mater Eng 287:553–558

Petersson L, Oksman K (2006) Preparation and properties of biopolymer-based nanocomposite films using microcrystalline cellulose. In: ACS symposium series. Oxford University Press, pp 132–150

Petersen K, Væggemose Nielsen P, Bertelsen G et al (1999) Potential of biobased materials for food packaging. Trends Food Sci Technol 10:52–68. doi:10.1016/S0924-2244(99)00019-9

Pinto AM, Cabral J, Tanaka DAP et al (2013a) Effect of incorporation of graphene oxide and graphene nanoplatelets on mechanical and gas permeability properties of poly(lactic acid) films. Polym Int 62:33–40

Pinto AM, Moreira S, Gonçalves IC et al (2013b) Biocompatibility of poly(lactic acid) with incorporated graphene-based materials. Colloids Surf, B 104:229–238

Podsiadlo P, Choi S-Y, Shim B et al (2005) Molecularly engineered nanocomposites: layer-by-layer assembly of cellulose nanocrystals. Biomacromol 6:2914–2918

Pötschke P, Abdel-Goad* M, Pegel S et al (2009) Comparisons among electrical and rheological properties of melt-mixed composites containing various carbon nanostructures. J Macromol Sci Part A 47:12–19

Potts JR, Dreyer DR, Bielawski CW, Ruoff RS (2011) Graphene-based polymer nanocomposites. Polymer 52:5–25

Qi L, Xu Z, Jiang X et al (2004) Preparation and antibacterial activity of chitosan nanoparticles. Carbohyd Res 339:2693–2700

Qian C, Sun J, Yang J, Gao Y (2015) Flexible organic field-effect transistors on biodegradable cellulose paper with efficient reusable ion gel dielectrics. RSC Adv 5:14567–14574

Ray SS, Bandyopadhyay J, Bousmina M (2007) Thermal and thermomechanical properties of poly [(butylene succinate)-co-adipate] nanocomposite. Polym Degrad Stab 92:802–812

Ray SS, Yamada K, Okamoto M, Ueda K (2003) New polylactide-layered silicate nanocomposites. 2. Concurrent improvements of material properties, biodegradability and melt rheology. Polymer 44:857–866

Rhim J-W, Ng PKW (2007) Natural biopolymer-based nanocomposite films for packaging applications. Crit Rev Food Sci Nutr 47:411–433. doi:10.1080/10408390600846366

Rhim J-W, Lee J-H, Kwak H-S (2005) Mechanical and water barrier properties of soy protein and clay mineral composite films. Food Sci Biotechnol 14:112–116

Rouf TB, Kokini JL (2016) Biodegradable biopolymer–graphene nanocomposites. J Mater Sci 51:9915–9945

Ruan D, Zhang L, Zhang Z, Xia X (2004) Structure and properties of regenerated cellulose/tourmaline nanocrystal composite films. J Polym Sci Part B: Polym Phys 42:367–373

Ruiz-Garcia L, Lunadei L (2011) The role of RFID in agriculture: applications, limitations and challenges. Comput Electron Agric 79:42–50

Samir MASA, Alloin F, Sanchez J-Y, Dufresne A (2004) Cellulose nanocrystals reinforced poly (oxyethylene). Polymer 45:4149–4157

Sanchez-Garcia MD, Gimenez E, Lagaron JM (2008) Morphology and barrier properties of solvent cast composites of thermoplastic biopolymers and purified cellulose fibers. Carbohyd Polym 71:235–244

Sarac A, Absi N, Dauzère-Pérès S (2010) A literature review on the impact of RFID technologies on supply chain management. Int J Prod Econ 128:77–95

Shokrieh MM, Esmkhani M, Shahverdi HR, Vahedi F (2013) Effect of graphene nanosheets (GNS) and graphite nanoplatelets (GNP) on the Mechanical properties of epoxy nanocomposites. Sci Adv Mater 5:260–266

Shukla R, Cheryan M (2001) Zein: the industrial protein from corn. Ind Crops Prod 13:171–192

Si H, Luo H, Xiong G et al (2014) One-step in situ biosynthesis of graphene oxide-bacterial cellulose nanocomposite hydrogels. Macromol Rapid Commun 35:1706–1711

Sinclair RG (1996) The case for polylactic acid as a commodity packaging plastic. J Macromol Sci Part A 33:585–597. doi:10.1080/10601329608010880

Singh V, Joung D, Zhai L et al (2011) Graphene based materials: past, present and future. Prog Mater Sci 56:1178–1271

Song K, Zhao X, Xu Y, Liu H (2013) Modification of graphene oxide via photo-initiated grafting polymerization. J Mater Sci 48:5750–5755

Sriupayo J, Supaphol P, Blackwell J, Rujiravanit R (2005) Preparation and characterization of α-chitin whisker-reinforced chitosan nanocomposite films with or without heat treatment. Carbohyd Polym 62:130–136

Stanier DC, Patil AJ, Sriwong C et al (2014) The reinforcement effect of exfoliated graphene oxide nanoplatelets on the mechanical and viscoelastic properties of natural rubber. Compos Sci Technol 95:59–66

Staudenmaier L (1898) Verfahren zur darstellung der graphitsäure. Ber Dtsch Chem Ges 31:1481–1487

Svagan AJ, Hedenqvist MS, Berglund L (2009) Reduced water vapour sorption in cellulose nanocomposites with starch matrix. Compos Sci Technol 69:500–506

Szabó T, Berkesi O, Forgó P et al (2006) Evolution of surface functional groups in a series of progressively oxidized graphite oxides. Chem Mater 18:2740–2749. doi:10.1021/cm060258

Terzopoulou Z, Kyzas GZ, Bikiaris DN (2015) Recent advances in nanocomposite materials of graphene derivatives with polysaccharides. Materials 8:652–683

Thakur S, Karak N (2013) Bio-based tough hyperbranched polyurethane–graphene oxide nanocomposites as advanced shape memory materials. RSC Adv 3:9476–9482

Thellen C, Orroth C, Froio D et al (2005) Influence of montmorillonite layered silicate on plasticized poly(l-lactide) blown films. Polymer 46:11716–11727. doi:10.1016/j.polymer.2005.09.057

Tian M, Qu L, Zhang X et al (2014) Enhanced mechanical and thermal properties of regenerated cellulose/graphene composite fibers. Carbohyd Polym 111:456–462

Uyama H, Kuwabara M, Tsujimoto T et al (2003) Green nanocomposites from renewable resources: plant oil-clay hybrid materials. Chem Mater 15:2492–2494

Vanderroost M, Ragaert P, Devlieghere F, De Meulenaer B (2014) Intelligent food packaging: the next generation. Trends Food Sci Technol 39:47–62

Villmow T, Pötschke P, Pegel S et al (2008) Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix. Polymer 49:3500–3509. doi:10.1016/j.polymer.2008.06.010

Wang B, Sain M (2007) Isolation of nanofibers from soybean source and their reinforcing capability on synthetic polymers. Compos Sci Technol 67:2521–2527

Wang H, Qiu Z (2011) Crystallization behaviors of biodegradable poly(l-lactic acid)/graphene oxide nanocomposites from the amorphous state. Thermochim Acta 526:229–236

Wang H, Qiu Z (2012) Crystallization kinetics and morphology of biodegradable poly(l-lactic acid)/graphene oxide nanocomposites: influences of graphene oxide loading and crystallization temperature. Thermochim Acta 527:40–46

Weiss J, Takhistov P, McClements DJ (2006) Functional materials in food nanotechnology. J Food Sci 71:R107–R116. doi:10.1111/j.1750-3841.2006.00195.x

William S, Hummers JR, Offeman RE, others (1958) Preparation of graphitic oxide. J Am Chem Soc 80:1339

Xu Y, Zhou J, Hanna MA (2005) Melt-intercalated starch acetate nanocomposite foams as affected by type of organoclay 1. Cereal Chem 82:105–110

Yadav M, Rhee KY, Jung IH, Park SJ (2013) Eco-friendly synthesis, characterization and properties of a sodium carboxymethyl cellulose/graphene oxide nanocomposite film. Cellulose 20:687–698

Yadav M, Rhee KY, Park SJ (2014) Synthesis and characterization of graphene oxide/carboxymethylcellulose/alginate composite blend films. Carbohyd Polym 110:18–25

Yang J-H, Lin S-H, Lee Y-D (2012) Preparation and characterization of poly(l-lactide)–graphene composites using the in situ ring-opening polymerization of PLLA with graphene as the initiator. J Mater Chem 22:10805–10815

Yasmin A, Luo J-J, Daniel IM (2006) Processing of expanded graphite reinforced polymer nanocomposites. Compos Sci Technol 66:1182–1189

Yoon JT, Jeong YG, Lee SC, Min BG (2009) Influences of poly(lactic acid)-grafted carbon nanotube on thermal, mechanical, and electrical properties of poly(lactic acid). Polym Adv Technol 20:631–638. doi:10.1002/pat.1312

Yoon S-Y, Deng Y (2006) Clay–starch composites and their application in papermaking. J Appl Polym Sci 100:1032–1038

Yoon OJ, Jung CY, Sohn IY et al (2011) Nanocomposite nanofibers of poly(d, l-lactic-co-glycolic acid) and graphene oxide nanosheets. Compos A Appl Sci Manuf 42:1978–1984

Yu J, Cui G, Wei M, Huang J (2007) Facile exfoliation of rectorite nanoplatelets in soy protein matrix and reinforced bionanocomposites thereof. J Appl Polym Sci 104:3367–3377. doi:10.1002/app.25969

Zeng H, Gao C, Wang Y et al (2006) In situ polymerization approach to multiwalled carbon nanotubes-reinforced nylon 1010 composites: mechanical properties and crystallization behavior. Polymer 47:113–122

Zhang X, Liu X, Zheng W, Zhu J (2012) Regenerated cellulose/graphene nanocomposite films prepared in DMAC/LiCl solution. Carbohyd Polym 88:26–30

Zheng W, Lu X, Wong S-C (2004) Electrical and mechanical properties of expanded graphite-reinforced high-density polyethylene. J Appl Polym Sci 91:2781–2788

Zheng P, Ma T, Ma X (2013) Fabrication and properties of starch-grafted graphene nanosheet/plasticized-starch composites. Ind Eng Chem Res 52:14201–14207

Zhou X, Shin E, Wang KW, Bakis CE (2004) Interfacial damping characteristics of carbon nanotube-based composites. Compos Sci Technol 64:2425–2437. doi:10.1016/j.compscitech.2004.06.001

Zimmermann T, Pöhler E, Geiger T (2004) Cellulose fibrils for polymer reinforcement. Adv Eng Mater 6:754–761

Chapter 9
Green Synthesis of Copper-Reinforced Cellulose Nanocomposites for Packaging Applications

P. Sivaranjana, E.R. Nagarajan, N. Rajini, A. Varada Rajulu and Suchart Siengchin

Abstract In the present work, cellulose nanocomposites dispersed with copper nanoparticles (CuNPs) were prepared using $CuSO_4 \cdot 5H_2O$ as the source and Cassia alata leaf extract as the reducing agent. These nanocomposites were prepared by regeneration method using ethanol as the coagulant. The morphology of generated CuNPs was viewed by SEM and TEM. The cellulose/CuNPs composite films showed good antibacterial activity against E-coil. The interaction between cellulose matrix and CuNPs was examined by FTIR and XRD. The changes in the thermal and tensile properties were examined with TGA and tensile tests. All these studies revealed that cellulose/CuNPs composites have enhanced thermal stability, tensile strength by the addition of CuNPs. These biodegradable cellulose/CuNPs composites films can be used for packaging and biomedical applications.

Keywords Biodegradable composites · CuNPs · Cassia alata leaves · Antibacterial activity

---

P. Sivaranjana · E.R. Nagarajan
Department of Chemistry, Kalasalingam University, Krishnankoil, Tamil Nadu 626126, India

N. Rajini
Department of Mechanical Engineering, Centre for Composite Materials, Kalasalingam University, Krishnankoil, Tamil Nadu 626126, India

N. Rajini (✉) · A.V. Rajulu
Centre for Composite Materials, International Research Center, Kalasalingam University, Krishnankoil, Tamil Nadu 626126, India
e-mail: rajiniklu@gmail.com

S. Siengchin
Graduate School of Engineering (TGGS), King Mongkut's University of Technology North Bangkok, 1518 Wongsawang Road, Bangsue, Bangkok 10800, Thailand

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_9

9.1 Introduction

Nowadays, it is becoming very popular developing green composites, to minimize pollution, (Abdul Khalil et al. 2012). Various natural biodegradable fibres from different parts of the variety of plants were also used in this attempt. These natural fibres lack behind the synthetic fibres in terms of performance (Abdul Khalil et al. 2007), and so as to enhance the performance, several attempts of (Dufresne 2010; Chen et al. 2011; Deep et al. 2011) chemical modifications of natural fibres were done, which again eliminates wastes in another way. Bioreduction of metal nanoparticles was done by so many researchers using various plant extracts (Ahmed et al. 2016). In this study, methodology as well as the material used for developing the composites were also been checked for its environmental compatibility. The cellulose used as the matrix is an organic compound, highly crystalline, and can be made into transparent films, with high performance due to the presence of intermolecular hydrogen bonding. The performance of the composite is further enhanced by the addition of CuNPs as fillers into the cellulose matrix, which is synthesized by using the Cassia alata leaf extract as reducing agent, and copper sulphate pentahydrate as the source of metal particles. The raw materials used in this synthesis were eco-friendly, low cost, biodegradable, and process is also easy, economic, energy efficient and reproducible. Further, the reinforcement effect of Cu nanoparticle obtained from the leaf extract reducing agent is expected to produce good thermal stability, antibacterial activity and biodegradable.

9.2 Materials and Methods

9.2.1 Materials

In this present work, cotton linters (with a degree of polymerization Dp of 620) supplied by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China) were used. LiOH, $CuSO_4 \cdot 5H_2O$ and Urea supplied by Hi Media laboratories pvt. Ltd (India) were used without purification. Ethyl alcohol was supplied by Ganesh Scientific (India). The *Cassia alata* leaves were collected locally and washed thoroughly with distilled water before preparing the extract.

9.2.2 Cassia alata Leaf Extraction

The Cassia alata leaves were collected, washed and cut into small pieces of even size. 10 wt% *Cassia alata* leaves by 10% the weight of distilled water maintained at 80 °C were taken and the mixture was kept for about 20 min. Then, the solution was cooled, filtered and the supernatant liquid was stored in the refrigerator.

9.2.3 Synthesis of Copper Nanoparticles

250 mM of aqueous copper sulphate solution was prepared using $CuSO_4 \cdot 5H_2O$ as the source. 10 ml of Cassia alata leaf extract was added to 100 ml of aqueous copper sulphate solution and kept under magnetic stirrer for uniform mixing for about 6 h. At once, the extract was introduced into the copper sulphate solution, and the colour of the solution changes gradually, indicating the reduction of copper to its nano form. The CuNPs formed were separated from the solution by repeated centrifugation at 12,000 rmp. Then, the CuNPs were washed repeatedly with distilled water and dried in hot air oven at 75 °C for about 2 h.

9.2.4 Dissolution of Cellulose

The aqueous solution of 8 wt% of LiOH and 15 wt% of urea was prepared and refrigerated to −12.5 °C, 4 wt% of cotton linters were added into the solution and stirred under mechanical stirrer and within 2 min the cellulose (cotton linters) got dissolved completely. The residues remaining undissolved were removed by centrifugation 7200 rpm at 5 °C. The clear stock solution was stored at 5 °C.

9.2.5 Preparation of Cellulose Wet Films with CuNPs

0.5, 1, 1.5, 2, 2.5 wt% of CuNPs were sonicated in 1 ml of water each to ensure uniform dispersion, and then it was added to the cellulose solutions under mechanical stirrer. The cellulose solutions with CuNPs were casted over glass plates and regenerated in alcohol bath for about 24 h, and then it was immersed in distilled water bath for about 3 h for the removal of alcohols and dissolved salts if any. Then, the films were dried over a smooth surface at room temperature.

9.2.6 FTIR Spectroscopic Analysis

The FTIR spectra of cellulose (matrix) and the composite films were recorded on a spectrum RXI Perkin Elmer FTIR spectrophotometer. All the spectra were recorded from 4000 to 500 cm^{-1} range with 45 scans in each case, at a resolution of 4 cm^{-1}.

9.2.7 Morphology

The presence of CuNPs in the nanocomposite films and the size distributions of CuNPs were examined by Carl Zeiss EVO 18 electron microscope. The copper element presence was confirmed by the EDX spectra using ESPIRIT software. The nanoparticles formed outside the film in solution were examined for their particle size distribution with Joel model JEM 210 transmission electron microscope.

9.2.8 Thermogravimetric Analysis

The primary and derivative thermograms of matrix and cellulose/CuNP composite films were recorded using TGA Q500 TA Instruments, USA, in the temperature range of 50–600 °C in nitrogen atmosphere at a heating rate of 10 °C/min.

9.2.9 Antibacterial Testing

200 ml of LB and agar containing medium was prepared and sterilized for 20 min, and the prepared medium was immediately transferred into sterile Petri plates. The plate was left for 15 min to solidify. After solidification, overnight cultured *E. coli* was taken in sterile buds and was swapped on the surface of the agar plates. Wells were punched on each plate using gel puncture. The circular discs of the matrix and the cellulose/CuNPs composite films with 0.5, 1, 1.5, 2, 2.5 wt% CuNPs were tested against pathogenic *E. coli* bacteria. The zones of clearance formed were recorded, and the diameter of zones was measured.

9.3 Result and Discussion

9.3.1 Appearance of Matrix and Cellulose/CuNPs Composite Film

In order to examine the effect of CuNPs on the appearance of the nanocomposite films prepared, the photographs of the matrix and the nanocomposites prepared using 0.5, 1, 1.5, 2, 2.5 wt% of CuNPs using aqueous $CuSO_4 \cdot 5H_2O$ solution as the source for CuNPs were regarded and are presented in Fig. 9.1.

From Fig. 9.1, it is evident the matrix and composite films were transparent, and with increase in the wt% of CuNPs the colour becomes brownish, but the intensity

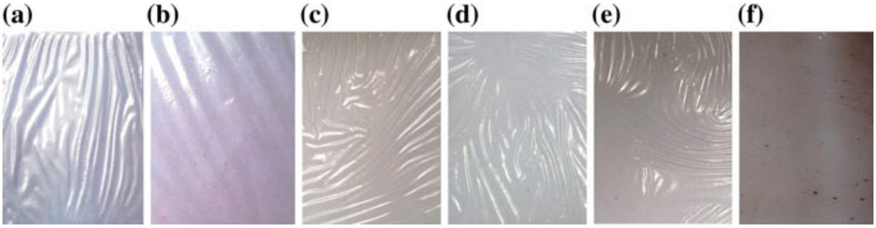


Fig. 9.1 Photographs of matrix and cellulose/CuNP composite films

of the colour was not uniform, even brown spots are viewed at higher concentration of 2.5 wt% of CuNPs due to the agglomeration of nanoparticles, as its concentration increases. Whereas in the case of newly generated systems, the intensity of colour change was uniform (Sadanand et al. 2016), indicating the even distribution of nanoparticles inside the film.

9.3.2 *Size of the CuNPs Formed by Using the Cassia alata Leaf Extract as Reducing Agent*

The CuNPs formed were separated by series of centrifugation and dried. To examine the nature of CuNPs formed, the TEM and SEM micrographs were recorded and are presented in Fig. 9.2. Using SEM micrograph, the particle size of one hundred CuNPs was measured and the particle size distribution is also presented in the same Fig. 9.2. The EDX spectrum of the particles is also presented in Fig. 9.2.

From Fig. 9.2, it is evident that the CuNPs formed were spherical in nature, and further the average size of one hundred particles selected was 71 nm. The presence of CuNPs was confirmed by EDX spectrum. Further, most of the CuNPs produced have the size in the 60–69 nm range.

9.3.3 *Distribution of Ex situ Generated CuNPs Inside the Matrix*

The distribution of ex situ generated CuNPs inside the cellulose/CuNPs composite films was recorded as an example; the fractrographs of the composite films prepared with 0.5–2.5 wt% CuNPs are presented in Fig. 9.3. From fig (a) and (b), it is evident that as the concentration of CuNPs increases the agglomeration occurs. The corresponding EDX spectra are also presented in Fig. 9.3c and d which confirms the presence of CuNPs inside the composite films.

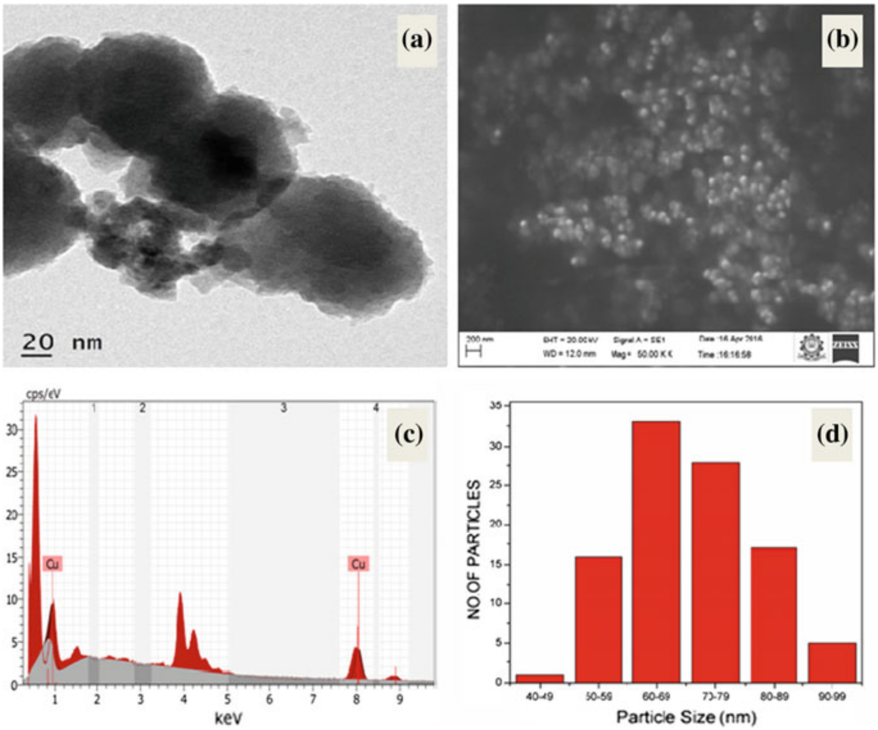


Fig. 9.2 **a** and **b** TEM and SEM image of CuNPs, **c** EDX of reduced CuNPs, **d** particle size distribution of reduced CuNPs

9.3.4 Interaction Between Matrix and CuNPs

In order to prove the interactions between matrix and CuNPs, the FTIR spectra of the matrix and the composites were regarded and are presented in Fig. 9.4.

From Fig. 9.4, it is evident that the spectrum of matrix is similar to that of the composites except, an increase in the intensity of all the bands in the case of the composites. It implies that the dispersed CuNPs did not change the chemical structure of cellulose matrix (Tsurumi et al. 1990) and were held within the cellulose matrix by electrostatic forces.

The common bands observed at 3344 cm^{-1} belong to –OH group of the cellulose; the other band 2901 and 1021 cm^{-1} was due to the vibrations of $–CH_2$ and –C–OH groups of cellulose. The peak observed at 1651 cm^{-1} was due to crystallization of water.

The bands observed at 1424 and 1365 cm^{-1} were due to C–CH asymmetric deformation and C–CH scissoring `modes of cellulose. The other bands obtained at 1260 and 1158 cm^{-1} were due to the –COO vibration of acetyl groups present in hemicelluloses and antisymmetric bridge stretching vibrations of cellulose in the

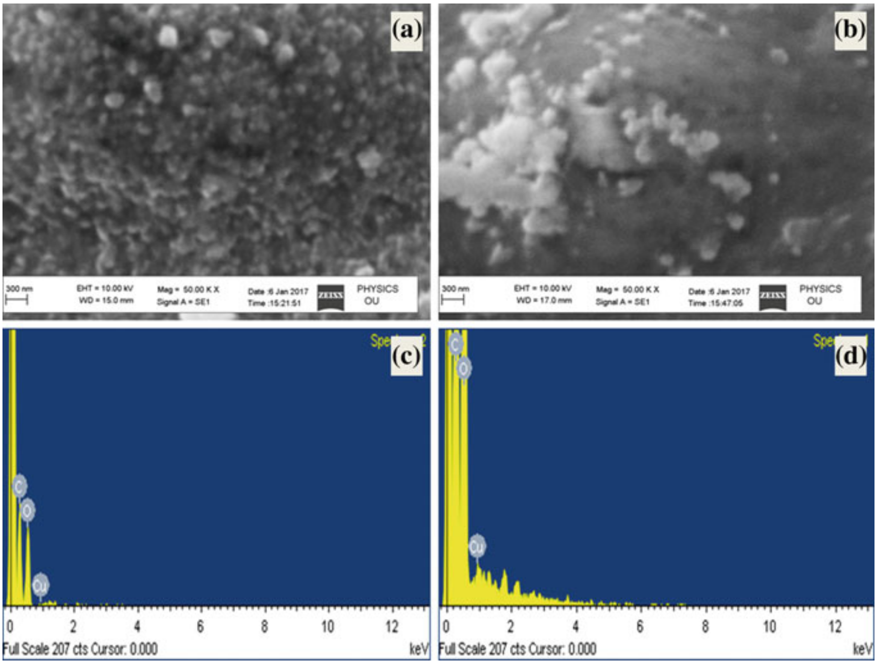


Fig. 9.3 **a** and **b** SEM images of composite films with 5 and 2.5 wt% of CuNPs, **c** and **d** EDX spectra of composite films with 5 and 2.5 wt% of CuNPs

leaf extract. Further, the bands at 895, 710 and 677 cm^{-1} were due to = C–H stretching and bending in cellulose.

9.3.5 Antibacterial Activity

As CuNPs possess antibacterial activity, the antibacterial activity of cellulose nanocomposite films with dispersed CuNPs was examined. For this, the antibacterial activity test was conducted against *E.coil* bacteria, by disc method. The clear zones observed for the matrix, and composites were photographed and are presented in Fig. 9.5. In each case, the diameter of clear zone was measured and shown in Fig. 9.5.

From Fig. 9.5, it is evident that the matrix does not show any antibacterial activity against *E. coli* bacteria, whereas on increase in the wt% of CuNPs in the cellulose/CuNPs composites films the antibacterial activity against *E. coli* bacteria increases.

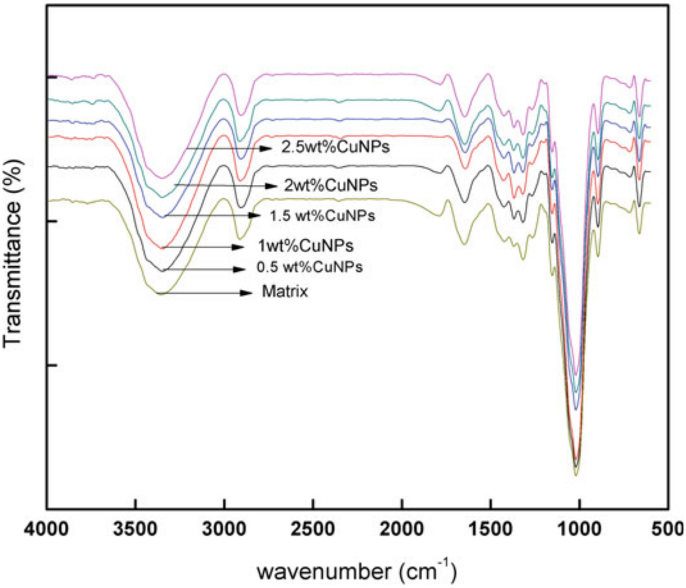


Fig. 9.4 FTIR spectra of matrix and cellulose/CuNPs composites

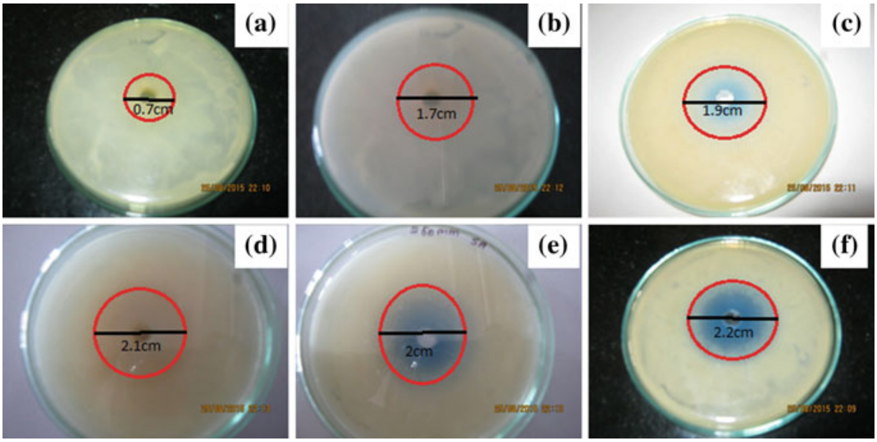


Fig. 9.5 **a** Antibacterial activity of matrix cellulose, **b** cellulose/0.5% CuNPs composites, **c** cellulose/1% CuNPs composites, **d** cellulose/1.5% CuNPs composites, **e** cellulose/2% CuNPs composites, **f** cellulose/2.5% CuNPs composites

9.3.6 X-Ray Diffraction Analysis

In order to study the effect of dispersed CuNPs on the crystallinity nanocomposite films, the X-ray diffractograms of matrix and cellulose/CuNPs composites dispersed with different wt% of CuNPs were recorded and are presented in Fig. 9.6.

From Fig. 9.6, it is evident that there are two main peaks similar in the case of matrix and the composite 2θ = 12.8° and 21.9° corresponding to reflections from (1–10) to (200) planes of cellulose II (Zhang et al. 2001). On close examination of the diffractogram corresponding to the composites made with different wt% of CuNPs, some additional peaks were observed at 2θ = 23.3, 32.3, 33.1, 35.6, 38.4, 46.5, 54.6 and 57.9, which are comparable to JCPDS standards of CuO particles (Kulkarni et al. 2015); further, the peaks at 39.7 and 68.7 correspond to the cubic-centred CuNPs (Alekseeva et al. 2011). Of these, the peaks observed at 32.3° and 36.8° were assigned to Cu_2O nanoparticles arising from diffractions from (002) and (111) planes respectively weres as the other two peaks at 43.9° and 50.8° were assigned to CuNPs resulting from the diffractions by (111) and (200) planes respectively. Similar observation was made by Sadanand et al. (2016) in case of cellulose/CuNP composite films reduced by ocimum sanctum leaf extract. X-ray diffractograms of the composites clearly indicate the presence of the both CuNPs and Cu_2NPs as a mixture.

The broadening of the XRD peaks in the cellulose/CuNPs composites indicates the decrease in the crystallinity of the cellulose by the filling up of biointerfaces by CuNPs.

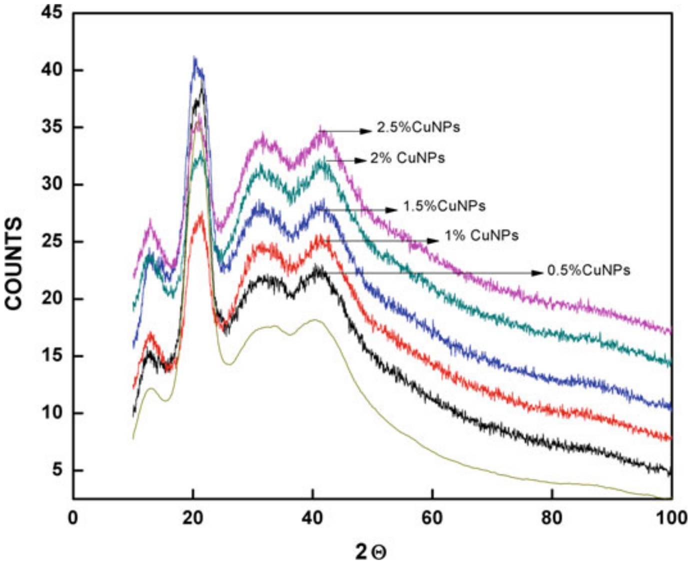


Fig. 9.6 X-ray diffractograms of matrix and cellulose/CuNPs composites

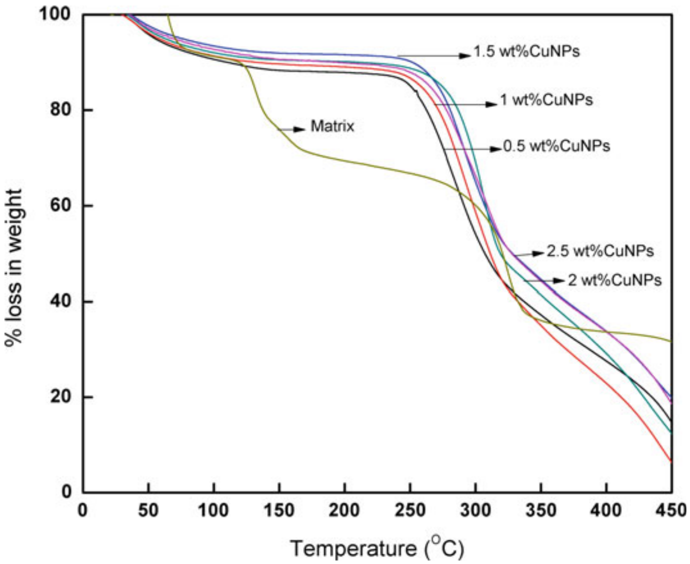


Fig. 9.7 Primary thermogram of matrix and cellulose/CuNPs composites

9.3.7 Thermal Properties

To investigate the effect of CuNPs on the thermal stability of the composites, the authors carried the thermogravimetric analysis of the matrix and the composites. The primary thermogram for the matrix and composites with different wt% of CuNPs are presented in Fig. 9.7. The thermal stability of the composites was greater than the matrix due to the addition of CuNPs which prolonged the degradation process.

9.4 Conclusions

The cellulose-based CuNPs-reinforced composite films were synthesized using Cassia alata leaf extract as reducing agent to enhance the properties of cellulose film. The nanolevel particles size range of 60–69 nm was noticed with the aid of transmission electron microscope and scanning electron microscope. A significant improvement in the increase of crystallinity was observed in the newly generated CuNPs-reinforced composite films. The enhanced thermal stability of around 57% of increase was found in the case particle-reinforced films compared to the pure matrix. However, no liner trend in the increase of thermal stability of the nanocomposites was observed with increasing CuNPs content. Regarding to the antibacterial activity, the increase in particle content exhibits gradual improvement in resistance property. Among various concentrations, the 2.5 wt% Cu showed maximum antibacterial activity of 68% improvement which could be the good sign to propose this material to microbial applications. Based on the thermal stability and the antibacterial activity, the cellulose/CuNPs composites can be considered for usage in packaging and biomedical applications.

References

Abdul Khalil HPS, Hanida S, Kang CW, Nik Fuaad NA (2007) Agro-hybrid composite: the effects on mechanical and physical properties of oil palm fiber (EFB)/glass hybrid reinforced polyester composites. J Reinf Plast Compos 26:203–218

Abdul Khalil HPS, Bhat AH, Yusra AFI (2012) Green composites from sustainable cellulose nanofibrils: a review. Carbohyd Polym 87(2012):963–979

Ahmed Shakeel, Ahmad Mudasir, Swami Babu Lal, Ikram Saiqa (2016) A review on plants extract mediated synthesis of silver nanoparticles for antimicrobial applications: a green expertise. J Adv Res 7:17–28

Alekseeva O, Chulovskaya S, Bagrovskaya N (2011) Copper nanoparticle composites based on cellulose derivatives. Chem Chem Technol 5:447–450

Chen WY, Liu H, Chen Y, Zhang P, Hai M, Parfenyuk YV (2011) Individualization of cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments. Carbohyd Polym 83:1804–1811

Deepa B, Abraham E, Cherian BM, Bismarck A, Blaker JJ, Pothan LA, Leao AL, de Souza SF, Kottaisamy M (2011) Structure, morphology and thermal characteristics of banana nano fibers obtained by steam explosion. Biores Technol 102:1988–1997

Dufresne A (2010) Processing of polymer nanocomposites reinforced with polysaccharide nanocrystals. Molecules 15(6):4111–4128

Kulkarni V, Suryawanshi S, Kulkarni P (2015) Biosynthesis of copper nanoparticles using aqueous extract of Eucalyptus sp. plant leaves. Curr Sci 109(2):25

Sadanand V, Rajini N, Satyanarayana B, Varada Rajulu A (2016) Preparation of cellulose composites with in situ generated copper nanoparticles using leaf extract and their properties. Carbohyd Polym 150:32–39

Tsurumi T, Osawa N, Hitaka H, Hirasaki T, Yamaguchi K, Manabe S, Yamashiki T (1990) Structure of cuprammonium regenerated cellulose hollow fiber (BMM Hollow fiber) for virus removal. Polym J 22(8):751–758

Zhang L, Ruan D, Zhoul J (2001) Structure and properties of regenerated cellulose films prepared from cotton linters in NaOH/Urea aqueous solution. Ind Eng Chem Res 40:5923–5928

Chapter 10
Polysaccharides-Based Bionanocomposites for Food Packaging Applications

Sarat K. Swain and Fanismita Mohanty

Abstract The use of plastic packaging material goes on increasing due to its high mechanical, oxygen barrier, and water vapor barrier properties. However, it lacks biodegradability and environmental compatibility. Biopolymers like polysaccharides can be used to solve such environmental hazards due to their non-biodegradability and toxicity. Besides these advantages, polysaccharides also have some disadvantages such as poor mechanical properties and low resistance to water. Hence, nanomaterials are promising reinforcing candidates to enhance the mechanical, thermal, and gas barrier properties without hampering their biodegradable and non-toxic characters. In the present chapter, different explanations are included to improve the properties responsible for packaging applications of these biopolymers. The focus of this chapter highlights the use of various polysaccharides-based bionanocomposites for food packaging applications. The combining study of different plant- and animal-based bionanocomposites in one chapter may explore a new idea for eco-friendly and future materials for food packaging.

Keywords Food packaging · Polysaccharides · Bionanocomposites · Nanomaterials

10.1 Introduction

Packaging of food is necessary as it provides protection to food against tampering, chemicals, and different physical and biological conditions. The basic need of food packaging is reduction in food spoilage and retention of food hygiene and quality. The main objective of packaging is to increase the shelf life of food (Rashidi and Khosravi-Darani 2011; Zhang et al. 2013a). Almost 40% of

---

S.K. Swain (✉) · F. Mohanty
Department of Chemistry, Veer Surendra Sai University of Technology, Burla,
Sambalpur 768018, Odisha, India
e-mail: swainsk2@yahoo.co.in

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_10

the plastics of the European plastic market are used in plastic packaging for processing, protecting, storing, transporting, and preserving food (Siracusa et al. 2008; Dainelli et al. 2008). The characteristics such as strength, stability, flexibility, impermeability, lightness, and ease of sterilization have made plastic packaging material an ideal candidate for packaging material (Genovese et al. 2016). Polymers like polyethylene (PE), polyethylene terephthalate (PET), and polypropylene (PP) are used in packaging sector (Novák et al. 2015). But polystyrene (PS) and polyvinyl chloride (PVC) are used in food packaging sector due to their excellent water vapor barrier and biological resistance properties (Plackett 2011). The use of plastic packaging materials is helpful to control humidity and extend shelf life. These materials also have mechanical and barrier properties to maintain and different gases (Plackett 2011). The postconsumer waste of plastics is the largest contributor of (63%) plastic wastes (Brems et al. 2012). Most of these materials are non-reusable, and around 14% of packaging materials are recyclable (Tumwesigye et al. 2016).

The high use of plastic packaging material has caused severe environmental risk (Cushen et al. 2014). Researches are done for the eco-friendly alternative of packaging material. Biodegradable biopolymer-based nanocomposites packaging materials are supposed to be the new generation packaging materials due to their improved packaging properties such as mechanical, thermal, biodegradable, chemical resistance, antimicrobial properties, gas barrier property (toward oxygen, moisture, flavors, and lipid), food quality sensor, and intelligent (Rhima et al. 2013). These materials also have low cost and easy processibility and are able to increase the shelf of foods. The use of polysaccharides-based packaging materials and coatings is reported in various studies which indicate the promising applications of these materials in packaging industry (Alcântara et al. 2016; Ghanbarzadeh et al. 2010; Versino et al. 2016). Polysaccharides-based packaging films possess strong hydrophilic character and stiff in comparison with synthetic packaging films. Different plasticizers (usually polyols) are added to these films in order to avoid the brittleness and to improve flexibility and workability. The addition of correct amount of glycerol (most commonly used plasticizer) with respect to biopolymer content reduces the intermolecular force of attraction and is able to increase the mobility of polymer chain. This property is commonly used to enhance the mechanical properties of edible films (Khan et al. 2014; Mihindukulasuriya and Lim 2014). Researchers obtained a new polysaccharide (Soluble Soybean Polysaccharide (SSPS)) from cell wall materials of soybean cotyledon. SSPS consists of backbone of homogalacturonan and rhamnogalacturonan branched by β-1, 4-galactan and α-1, 3 or α-1,5-arabianan chains (Salarbashi et al. 2014; Yin et al. 2015). It is reported that SSPS has the ability to reduce the risk of diabetes, lower blood cholesterol, and improve laxation in human being (Tajik et al. 2013; Slavin 2013). Besides this, it also has good adhesive, dispersive, emulsifying, and stabilizing property (Chawla and Patil 2010). According to previous study, SSPS can act as a functional ingredient in fortified foods (Chawla and Patil 2010). The films prepared by SSPS have satisfactory mechanical property.

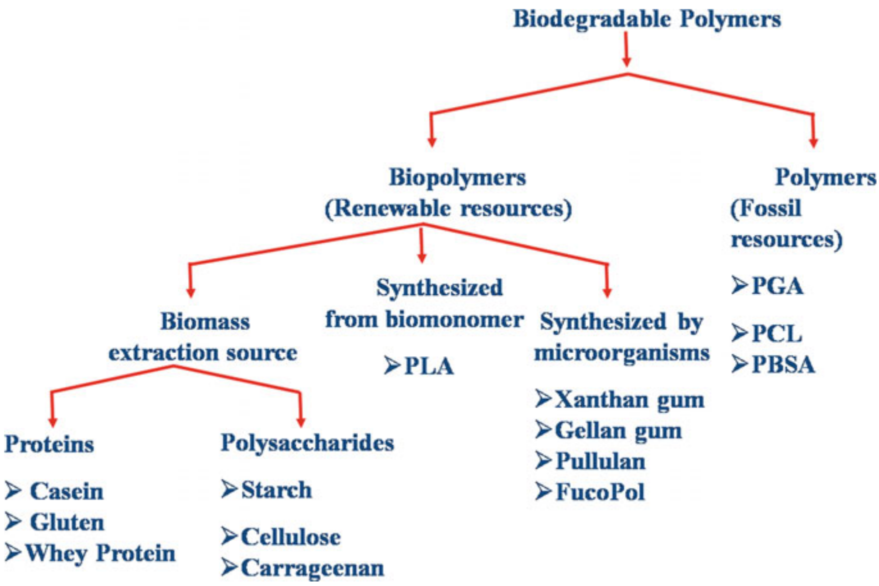


Fig. 10.1 Classification of biodegradable polymers (Ferreira et al. 2016a)

10.2 Biodegradable Polymers

Based on the statement of American society for Testing and Materials (ASTM) standard D-5488-94d, Material capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds or biomass in which the predominant mechanism is the enzymatic action of microorganisms that can be measured by standardized tests in a specific period of time reflecting available disposal condition. All biodegradable substances may not be biopolymer, but all biopolymers undergo biodegradation. For example, polyglycolide (PGA), polybutylene succinate adipate (PBSA), and polyglycolide (PGA) can undergo biodegradation. Still, these polymers are not included in the list of biopolymers as they have non-renewable origin (fossil-sourced chemicals) (Plackett 2011) (Fig. 10.1). Based on origin, biopolymers are categorized as (i) polymers having direct biological origin, e.g., proteins (gluten and casein) and polysaccharides (cellulose, starch, galactomannans, dextran, etc.), (ii) polymers having bio-derived monomer unit, e.g., polylactic acid produced from lactic acid which is originated by the fermentation of carbohydrate material, and (iii) polymers having microbial origin, e.g., polyhydroxyalkanoates (PHA) and some polysaccharides (pullulan and gellan gum) (Mensitieri et al. 2011; Galgano 2015). Biopolymer derived from renewable resources must be biodegradable and compostable resulting in the disposal of package in soil. As a result, these can be used as soil conditioner and fertilizers (Mensitieri et al. 2011; Siracusa et al. 2008). A fine balance among economic, environment, and social concern is required to maintain material supply and waste product generation which are the criteria for sustainability of biopolymer. Human resources, technology development, and product viability should be considered to draw conclusion about sustainability. Petrochemicals-based polymers are much cheaper in comparison with biodegradable product from different points of view such as collection of materials, processing, conversion of materials and economic value.

The anxiety about eco-friendly packaging material was developed from the toxic effect of non-biodegradable product from different points of view such as collection of materials, processing and conversion, and economic value. The eco-friendly packaging material was developed from the toxic effect of non-biodegradable polymer packaging material on environment. The biodegradable packaging materials.

10.3 Polysaccharides in Food Packaging

Polysaccharides are abundantly available in nature. These are the complex carbohydrates formed by the glycosidic linkage of simple sugars. The polysaccharides like cellulose act as primary structural element of plant. Similarly, chitin is the major component of exoskeleton of arthropods, and cell wall of fungi and starch is the source of energy storage in plant (Thakur and Thakur 2016). Biodegradable thin membranes and films are produced using varieties of polysaccharides. These films are used for different purposes like pharmaceutical, food, medical, and also in industrial processes like pervaporation (Freitas et al. 2014). In food industry, these are used for packaging and coating of food materials. These membranes have good mechanical and barrier (carbon dioxide and oxygen barrier at low and moderate humidity) properties. The low water vapor barrier property is considered as the main drawback of these membranes (Galgano 2015; Rhim et al. 2013). Several attempts have been taken to improve the packaging properties of biopolymer-based membranes for their industrial applications (Rhim et al. 2013). Polysaccharide materials originated from diverse sources have been used in packaging sector.

10.3.1 Plant-Based Polysaccharides for Food Packaging

10.3.1.1 Starch

It is abundantly found as a reserve polysaccharide in plants. It belongs to renewable resource. Besides this, it has low cost, easy processibility, and biodegradability, and also possesses thermoplastic behavior. There are a number of extraction sources of starch such as grain (e.g., amaranth), cereals (e.g., rice, wheat, or corn), nuts (e.g., cashew), and tubers (e.g., tapioca, potato, or manioc) (Thakur and Thakur 2016; Babu et al. 2013). Starch is insoluble in cold water. It comprises of 20% linear and branched amylopectin polymeric units. The properties of starch vary with variation in genotype, morphology, distribution of granule size, ratio of amylase to amylopectin, chemical modifications, composition, p^H, and also on source of extraction (Cruz-Romero and Kerry 2008; Babu et al. 2013). The coating and films produced using starch have high oxygen barrier property, low mechanical properties, high hydrophilicity, and increase in crystallinity over time (retrogradation) (Jiménez et al. 2012; Souza et al. 2012). The high oxygen barrier property makes these films suitable for packaging whereas other properties deteriorating the packaging property. Researchers have been trying to improve the packaging properties. Plasticizers are used to enhance flexibility and mobility of chain which develop the plastic starch with improved mechanical properties in comparison with polyolefin-derived one. Sorbitol, glycerol, and glycol are commonly used plasticizers (Souza et al. 2012; Müller et al. 2008; Isotton et al. 2015; Abdorreza et al. 2011). The packaging properties of starch can also be improved by other techniques like blending, chemical modification, and composite formation along with the retention of biodegradability of packaging materials. Generally, blends of starch are prepared with more hydrophobic polymer like polycaprolactone (PCL) or polylactic acid (PLA) (Sarazin et al. 2008; Gupta and Kumar 2007). Nanocomposites are also formed by taking these materials with nanoparticles (Souza et al. 2012; Dufresne 2010). Novamont is a plastic based on a plastic based on starch (Mater-Bi®). It is compostable and biodegradable bioplastic available in granualar form (Satyanarayana and Prasad. 2016). Eco-Go, Bangkok, Thailand, developed sells finished packaging products (e.g., food containers, food trays, and bowls) from corn and cassva starch (Ferreira et al. 2016a). A high barrier packaging sheet (PLANTC™) is prepared by Plantic Technologies Ltd, Altona, Australia, from corn starch, polypropylene (PP), and polyethylene (PE) (Ferreira et al. 2016a).

10.3.1.2 Cellulose

It is the most abundantly available natural polymer on earth's surface. The cell walls of all plants are made up of cellulose. It consists of β-D-glucopyranose form of glucose (Credou and Berthelot 2014). Cellulose can combine with crystalline micro-fibrils and fibers through hydrogen bond due to the presence of regular structure and a number of hydroxyl groups (Cruz-Romero and Kerry 2008; Babu et al. 2013). It possesses high mechanical strength, low density, non-toxicity, low cost, renewability, durability, biodegradability, good film-forming ability, chemical derivative forming ability, etc. (Credou and Berthelot 2014; Duan et al. 2016).

Mostly cellulose is produced from cotton fibers, wood, and sugarcane bagasse. The water insolubility, crystallinity, and hydrophilic nature of natural cellulose fibers have good mechanical properties, low cost, and biodegradability (Thakur and

Thakur 2016; Cruz-Romero and Kerry 2008). Generally, there are two kinds of cellulose used in industrial sector (packaging, fibers, and textiles). These are modified and regenerated cellulose. Different chemical modifications like esterification and etherifications are employed to enhance the thermoplastic behavior of cellulose. There are various modified cellulose available in commercial market. Mainly, cellulose acetate, regenerated cellulose, and cellulose esters are used in industrial sector. Use of plasticizer and blending (of cellulose with other biopolymers) is also helpful to overcome the hard mechanical properties of cellulose. In addition to these, chemical modifications are also used to enhance the mechanical property of cellulose. Aggressive and toxic solutions are used to dissolve cellulose followed by recasting in sulfuric acid during the synthesis of cellophane membrane. All these procedures improve the mechanical properties of cellulose, making it hydrophilic. This membrane cannot be heat sealed and lack thermoplastic behavior (Thakur and Thakur 2016). Cellulosic membranes are widely available in commercial market. Two compostable and biodegradable films, namely Naturflex$^{\text{TM}}$ and cellophane$^{\text{TM}}$, are widely used for food packaging.

10.3.1.3 Galactomannans

The endosperm of some dicotyledon plants' seed (especially leguminosae) contains neutral polysaccharides known as galactomannans (Cerqueira et al. 2011). These heterogenous polysaccharides are gum-like and consist of β-(1-4)-D mannan as backbone with α-(1-6)-D galactose branch chain link. Different galactomannans differ from one another by the presence of mannose and galactose (M/G) ratio, e.g., Tara gum (M/G ratio = 3:1, *Caesalpinia spinosa*), locust bean gum (M/G ratio = 3.5:1, *Ceratonia siliqua*), and guar gum (M/G ratio = 2:1, *Cyamopsis tetragonolobo*). Among these, the latter two have commercial importance because of their price and availability (Prajapati et al. 2013a).

10.3.2 Animal-Based Polysaccharides for Food Packaging

10.3.2.1 Chitosan

The second most plenty available agro-polymer present in nature is Chitin. The cell walls of yeasts and fungi and exoskeleton of arthropods contain chitin. It is commercially extracted from crab and prawn shells. It is nothing but an acetylated polysaccharide consisting of *N*-acetyl-D-glucosamine. Other processes like fermentation or enzyme hydrolysis are able to prepare chitin, but these processes are not suitable economically (Cruz-Romero and Kerry 2008; Babu et al. 2013). Norlife is a commercially available chitin which is reported by Klofta, Norway (Ferreira et al. 2016b).

Chitosan is nothing but the deacetylated product obtained from chitin. The factor employed during deacetylation such as incubation time, alkali concentration, chitin source, chitin to alkali ratio, and temperature are responsible for the properties of chitosan. It is water insoluble, but easily soluble in acidic solutions. Presence of a cationic group in chitosan makes it different from other polysaccharides. It also possesses antimicrobial property against yeasts, fungi, and bacteria (Thakur and Thakur 2016; Babu et al. 2013; Van den Broek et al. 2015; Dutta et al. 2009). It is also used for synthesis of film of thickness >30 μm and coating of thickness <30 μm due to its good film-forming capacity. Chitosan films have biocompatibility, renewability, non-toxicity, biodegradability, semipermeability toward gas but having low oxygen permeability, and moderate water vapor permeability (Van den Broek et al. 2015; Pereda et al. 2009; Elsabee and Abdou 2013; Fajardo et al. 2010; Epure et al. 2011). Attempts have been taken in order to improve the properties of chitosan membranes. The thermoplastic properties and mechanical properties of chitosan membrane can be enhanced by the use of plasticizer and thermochemical treatments like mechanical kneading (Thakur and Thakur 2016; Epure et al. 2011). The addition of hydrocolloids to chitosan-based membranes results in the enhancement of functional properties. Blendings of chitosan with anionic polymers are also able to enhance the barrier and mechanical properties of chitosan. This is due to the formation of electrostatic interactions between protonated amine group of chitosan and negatively charged side chain of anionic polymer (Elsabee and Abdou 2013; Luo and Wang 2014). Mechanical properties and water vapor barrier properties of chitosan films are enhanced by combing it with alginate, starch, pectin, whey protein, and gelatin (Jindal et al. 2013; Luo and Wang 2014; Sun et al. 2014; Kurek et al. 2014; Rivero 2009) in comparison with virgin chitosan films. The hydrophobicity of films is increased by adding lipids (such as fatty acids, natural waxes, resins, and vegetable oils) into the films (Galus and Kadzińska 2015). Beeswax is able to decrease the water susceptibility of chitosan-based membranes (Hromiš et al. 2015). The addition of neem oil (Sanuja et al. 2015), oleic acid (Vargas et al. 2011), and cinnamom essential oil (Ojagh et al. 2010) reduces the water vapor permeabilities. Commercially available Chitoclear® (a purest chitosan-based product) is widely used in food packaging (Ferreira et al. 2016a). Kitoflokk™ is the commercially available chitosan by Norwegian chitosan (Klofta, Norway) (Ferreira et al. 2016b). Table 10.1 summarizes the properties and applications of animal-based polysaccharides and plant-based polysaccharides.

10.3.3 Algae-Based Polysaccharides for Food Packaging

10.3.3.1 Alginate

It is an abundantly occurring linear polysaccharide derived from brown seaweeds (e.g., *Ascophyllum nodosum* and *Laminaria digitata*) and some soil bacteria. It is composed of 1-4 linked mannuronate (M block) and β-L-guluronate (G-block) and

Table 10.1 Properties and application of plant-based polysaccharides and animal-based polysaccharides

Polysaccharide	Composition	Film properties	Role in food packaging	Reference
Chitin	*N*-acetylglucosamine	Transparent Antifungal and antibacterial in nature Non-toxicity and biocompatibility Biodegradable	Coffee capsules Packaging films Food bags	Ferreira et al. (2016b)
Chitosan	D-glucosamine *N*-acetyl-D-glucosamine	Biodegradable Antibacterial and antifungal in nature Non-toxicity and biocompatibility Good mechanical Barrier to gases and water vapor (high) Brittle—need to use plasticizer	Packaging membranes for vegetables and fruit Edible membranes and coatings (Strawberries, cherries, mango, guava, among others)	Galgano (2015), Epure et al. (2011), Campos et al. (2011)
Starch	Glucose	Transparent Tasteless and odorless Retrogradation High elongation and tensile strength Biodegradable	Flexible packaging: Extruded bags Nets for fresh fruit and vegetables Rigid packaging Thermoformed trays and containers for fresh food	Cruz-Romero and Kerry (2008), Campos et al. (2011)
Cellulose	Glucose	Biodegradable Good mechanical Transparent Highly sensitive to water Need to perform modification, use of plasticizer or polymer blend	Cellophane membranes	Cruz-Romero and Kerry (2008), Campos et al. (2011)
Galactomannans	Galactose, Mannose	Edible Biodegradable Semi-permeable barrier to gases	Edible membranes and coatings Fruits and Cheese	Galgano (2015), Cerqueira et al. (2011)

Reproduced with permission from Elsevier Science Ltd. (Ferreira et al. 2016a) β-L-guluronate as well as chain of alternating mannuronic acid and guluronic acids (MG block). The relative percentage of these three blocks affects the physical properties of alginate which varies according to the source of extraction (Pawar and Edgar 2012). Low cost, non-toxic nature, biocompatibility, and biodegradability have made alginate attractive component for film formation. It also has other properties like stabilizing, gel-producing, suspending, and thickening (Babu et al. 2013; Tavassoli-Kafran et al. 2016; Vu and Won 2013). Sodium alginate is the by-product produced from algal purification. Alginate has a wide range of application in industrial sector like medical, food packaging, pharmaceutical, paper and release agents due to its biological origin, i.e., from brown seaweed extract (Tavassoli-Kafrani et al. 2016). The linear structure of alginate gives adequate fibrous structure and support to the film in solid state (Blanco-Pascual et al. 2014). Different companies are selling alginate in commercial market. These are Cargill (Minneapolis, MN, USA), DuPont (Danisco) (Copenhagen, Denmark), and FMC (Philadelphia, PA, USA). The price of alginate was increased from 2009 to 2013 due to high demand. However, the price became stable in 2014 (11€/Kg) (Ferreira et al. 2016a).

10.3.3.2 Carrageenan

It is a linear polysaccharide derived from red seaweed (Rhodophyceae family, e.g., *Kappaphycus spp*., *Gigartina stellata*, *Chonarus cripus*, and *Eucheuma spp*.) (Prajapati et al. 2014; Tavassoli-Kafrani 2016). It contains anionic sulfur and hydrophilic in nature. It comprises of α-D-1, 3 and β-D-1, 4 galactose residues which are sulfated around 40% of total weight. Carrageenans are divided into different types depending on their solubility in potassium chloride such as λ, κ, t, $\mathcal{E}$, and μ carrageenans (Necas and Bartosikova 2013). κ-Carrageenans have fewest negative charge per disaccharide along with excellent membrane and gel-forming capacity. It also provides better mechanical properties in comparison with λ and t-carrageenans (Necas and Bartosikova 2013; Blanco-Pascual et al. 2011; Khan et al. 2017). Carrageenan is a certified food grade additive basically used for emulsifying and stabilizing purposes (flavored milks, pet food, dairy products, infant formulas, and dietetic formulas) (Necas and Bartosikova 2013; Khan et al. 2017). Edible films and coating prepared from carrageenan and their blends (with other polymers) have been used to reduce moisture and gas exchange of food, preserve fresh cut fruits, maintain texture, and prevent decoloration (Bico et al. 2009; Plotto et al. 2010). It is also used as encapsulated membrane for aromatic compounds (Tavassoli-Kafrani 2016; Hambleton et al. 2009; Fabra et al. 2012). Most experienced producer of carrageenan is FMC (Philadelphia, PA, USA). Film-forming carrageenan trade name is Gelcarin® (Prajapati et al. 2013a). Other companies like Danisco (Copenhagen, Denmark), Quest International (Naarden, Netherlands), Ceamsa (Porrino, Spain), and CP kelco (Atlanta, GA, USA) are selling carrageenan in global market. Neutrafilm™ is a packaging film of carrageenan by JetNet corporation (Sewickley, PA, USA). This film has been poultry and meat packaging and is available over 300 different sizes of elastic netting and styles (Satyanarayana and Prasad 2016).

10.3.4 Microorganism-Based Polysaccharides for Food Packaging

These are several polysaccharides obtained by microbes like fungus, yeast, or bacteria. These include xanthan gum, Pullan, gellan gum, FucoPol, bacterial alginate, and bacterial cellulose.

10.3.4.1 Xanthan Gum

It is a kind of exopolysaccharide synthesized by *Xanthomonas campestris*. Northern Regional Research Laboratories (Peoria, IL, USA) first discovered xanthan gum in microbial polysaccharide. This microbial polysaccharide is largely studied and widely accepted exopolysaccharide (Palaniraj and Jayaraman 2011; Freitas et al. 2011a). It is composed of glucuronic acid, glucose, and mannose in 1:2:2 ratio. In addition to these, acetyl and pyruvate substituents are also present (Pooja et al. 2014). It is non-toxic and water soluble in nature. It possesses very strong shear-thinning behavior by imparting high viscosity in aqueous solution even in low concentration. Its solutions also have very stable rheological properties in different temperature, ionic strength and wide range of pH (Freitas et al. 2013; Faria et al. 2011). Different industries like pharmaceutical, food, textile, cosmetic, slurry explosives, and petroleum have used xanthan gum for different purposes. It is used as a thickening and suspending agent (Palaniraj and Jayaraman 2011; Sworn et al. 2016). It is less used in packaging sector probably due to its high cost (Palaniraj and Jayaraman 2011). The application of xanthan coating to acerola reduces not only the weight loss but also respiration process which leads to increase in shelf life and retention of color (Quoc et al. 2015). Commercially, xanthan of different purity grades are available. Merck (Kenilworth, NJ, USA), Jungbunzlauer (Basel, Switzerland), Danisco (Copenhagen, Denmark), and Sanofi-Elf (Gentilly, France) are the producers of xanthan gum.

10.3.4.2 Gellan Gum

This anionic exopolysaccharide is derived by *Sphingomonas elodea*. It is water soluble in nature and possesses high molecular weight. It contains a repeating trisaccharide unit of β-D-glucose, β-D-glucuronic acid, and α-L-rhamnose in 2:1:1 ratio (Morris et al. 2012). Gellan gum contains two acyl substituents (Morris et al. 2012; Kirchmajer et al. 2014). Gel prepared from high acyl gelan is firm, brittle, thermostable, and non-elastic in nature. Gel prepared from high acyl gelan is soft, non-brittle, thermo-reversible, and elastic in nature (Kirchmajer et al. 2014; De Filpo et al. 2015). Gel prepared from high acyl gelan is soft, non-brittle, thermo-reversible, and elastic in nature, whereas the gel prepared from low acyl gelan is firm, brittle, thermostable, and non-elastic in nature (Kirchmajer et al. 2014; De Filpo et al. 2015). Basically, food industries use gellan gum as a gelling, stabilizing, and thickening agent. The coating and membrane of gellan gum may be used in food industries. These coatings and membranes have high barrier and less oil absorption ability. Gellan gum provides crispiness to food even long time after baking or frying (when used in batter) and thus helps in maintaining product quality (Brannan et al. 2014).

The leading supplier of gellan gum is CP Kelco (Atlanta, GA, USA) in two trade names Kelcogel™ (high acyl) and Gelrite™ (low acyl). Dancheng Caixin Sugar Industry Co.Ltd. (Zhoukou, China) also supplies gellan gum global market.

10.3.4.3 FucoPol

This high molecular weight exopolysaccharide is synthesized by *Enterobacter* A47 (DSM23139). This bacterium utilizes the by-product obtained from biodiesel (i.e., glycerol) for the synthesis of FucoPol. This heteropolysaccharide is anionic, water soluble, and biodegradable in nature. It consists of fucose, galactose, glucose, and glucuronic acid inb 36–38% mol, 22–24% mol 27–33% mol, and 9–10% mol, respectively. It also has acyl group such as acetate, pyruvate, and succinate (Torres et al. 2011; Alves et al. 2010; Torres et al. 2014). FucoPol production in laboratory is more in comparison with gellan and xanthan (Freitas et al. 2013). However, it is not commercialized yet. It has flocculating and emulsion stabilizing capacity (Freitas et al. 2011b). It forms thick aqueous solution in different ionic strength and pH (Torres et al. 2015). All these above properties make it suitable for food, textile, cosmetic, petroleum, pharmaceutical, and paper industries. FucoPol produces brownish, transparent, water soluble, ductile high gas (particularly O_2 and CO_2) barrier, and low water vapor barrier membrane. These properties enable FucoPol as the inner layer of multilayer packaging material (Ferreira et al. 2014). The properties of membrane have enhanced by adding chitosan to FucoPol membrane. The properties of membrane have enhanced by adding chitosan into FucoPol membrane. Specially, these FucoPol–chitosan bilayers have lower water solubility and enhanced mechanical and gas barrier properties which increase the suitability of this membrane in food packaging sector (for storing low moisture content food) (Ferreira et al. 2016).

10.3.4.4 Pullulan

This water soluble, neutral, linear exopolysaccharide is composed of maltotriose unit. It is synthesized by fungus *Aureobasidium pullulans* from simple sugars (Babu

Table 10.2 The source, properties, and application of algae-based polysaccharides and microorganism-based polysaccharides

Polysaccharide	Microorganism or algae	Composition	Film properties	Role in food packaging	Reference
Alginate	Brown sea weed (e.g. *A. nodosum* and *L. digitata*)	Mannuronic Glucuronic acid	Biodegradable High water vapor permeability Cross-link with calcium Strong and brittle membranes	Coatings prevents water loss in fresh cut fruits (apple, pear, melon, and papaya) Inhibits microbial growth	Galgano (2015), Campos et al. (2011)
Carrageenan	Red seaweed (e.g., *Kappaphycus* spp., *G. stellata*, and *Eucheuma* spp.)	Galactose	Biodegradable Fragile and ductile	Coatings of Fruits Encapsulation of aroma Compounds	Campos et al. (2011)
Xanthan gum	*Xanthomonas campestris*	Glucose Mannose Glucuronic acid AcetatePyruvate	Biodegradable Edible	Edible coating Meat (prevent moisture migration during frying) Fruit (extend shelf life)	Quoc et al. (2015)
Gellan gum	*Sphingomonas elodea*	Glucose Rhamnose Glucuronic acid	Biodegradable Edible Lipid barrier Excellent gas barrier Good tensile strength	Edible Coatings in breading and batters for chicken, fish, cheese, vegetables and potatoes. Encapsulation of flavor and bioactive ingredients	Freitas et al. (2014), Ferreira et al. (2016a)
FucoPol	*Enterobacter* A47	Fucose Galactose Glucose Glucuronic acid Acetate Succinate Pyruvate	Biodegradable Transparent High gas barrier Poor water resistance	Possible application as inner layer in multilayer packaging	Ferreira et al. (2014), (2016b)

(continued)

Table 10.2 (continued)

Polysaccharide	Microorganism or algae	Composition	Film properties	Role in food packaging	Reference
Pullulan	*A. pullulans*	Maltotriose (three glucose)	Biodegradable Transparent Edible Oil and grease resistant Heat sealable High water solubility Barrier to oxygen	Coating material Wrapping material Blends with other polymers to improvement of mechanical properties Inner package Seasoning bag of instant noodles Instant coffee	Cheng et al. (2011), Zhang et al. (2013a)

Reproduced with permission from Elsevier Science Ltd. (Ferreira et al. 2016a)

et al. 2013). Different cultivation parameters such as carbon source, temperature, types of nitrogen source, and pH affect the molecular weight of pullulan (4.5×10^4 Da to 6×10^5 Da).

Hayashibara company (Okayama, Japan) is the first commercial supplier of pullulan. The work on commercialization of pullulan membrane was started in 1982 by Hayashibara (Cheng 2011; Prajapati et al. 2013a). It is non-toxic, odorless, tasteless, and biodegradable in nature. It also possesses film forming, flocculent, food additive ability. The membranes produced from pullulan have flexibility, transparency, homogeneity, heat resistance, good oxygen barrier, and antifungal properties (Freitas et al. 2014; Kristo and Biliaderis 2007; Gniewosz and Synowiec 2011). These membranes have weak mechanical properties and water sensitivity (Shih et al. 2011, 2015). The high cost of pullulan and its membrane limits their use. These membranes have weak mechanical properties and water sensitivity (Shih et al. 2011; Singh et al. 2015). The high cost of pullulan and its membrane limits their use. Researchers have been working to improve mechanical and physico-chemical properties of pullulan membranes. Low water absorption and water vapor permeability, enhanced mechanical and thermal properties of membranes are achieved by blending pullulan with chitosan, starch, alginate, and cellulose (Wu et al. 2013; Trovatti et al. 2011; Kanmani and Lim, 2013; Kim et al. 2014; Zhang et al. 2013a). The composites of pullulan with proteins and lipids also exhibit enhanced properties. Reduction in oxygen permeability with high tensile strength is achieved by incorporation of gelatin into pullulan membranes (Zhang et al. 2013b). The addition of rice wax to pullulan membranes showed a significant enhancement in vapor barrier properties (water) (Shih et al. 2011). Shandong Jinmei Biotechnology Co.Ltd. (Zhucheng, China) and Hayashibara corporation are the commercial supplier of pullulan (Ferreira et al. 2016b). Table 10.2 gives a hint about the use of microbial polysaccharide in food packaging sector.

10.4 Conclusion

This work includes the source, origin, and utility of polysaccharides in food packaging sector. Researches are taking place to find out polymers with enhanced properties. This paper indicates that polysaccharides-based nanocomposites have biodegradability, renewability, and non-toxic nature and also possess improved mechanical and barrier properties toward oxygen and moisture. Certain polysaccharides like chitosan have antimicrobial property. Continuous researches are going on to prepare environmental free alternative of non-biodegradable packaging materials. The industrial development of these products and reduction in price is required in future. Complete study of life cycle of polysaccharides-based materials (starting from production to disposal of waste) is necessary for calculation of efficiency of these films in comparison with plastic packaging material. The properties of polysaccharides-based packaging films are generally improved by blending with other polymers and making composites with lipids and other nanoparticles. Table 10.2 describes the source, properties, and applications of algae-based polysaccharides and microorganism-based polysaccharides.

References

Abdorreza MN, Cheng LH, Karim AA (2011) Effects of plasticizers on thermal properties and heat sealability of sago starch films. Food Hydrocoll 25:56–60

Alcântara ACS, Darder M, Aranda P, Ayral A, Ruiz-Hitzky E (2016) Bionanocomposites based on polysaccharides and fibrous clays for packaging application. J Appl Polym Sci 133. doi:10.1002/app.42362

Alves VD, Freitas F, Torres CAV, Cruz M, Marques R, Grandfils C, Gonçalves MP, Oliveira R, Reis MAM (2010) Rheological and morphological characterization of the culture broth during exopolysaccharide production by *Enterobacter sp*. Carbohydr Polym 81:758–764

Babu R, O'Connor K, Seeram R (2013) Current progress on bio-based polymers and their future trends. Prog Biomater 2:1–16

Bico SLS, Raposo MFJ, Morais RMSC, Morais AMMB (2009) Combined effects of chemical dip and/or carrageenan coating and/or controlled atmosphere on quality of fresh-cut banana. Food Control 20:508–514

Blanco-Pascual N, Montero MP, Gómez-Guillén MC (2014) Antioxidant film development from unrefined extracts of brown seaweeds laminaria digitata and ascophyllum nodosum. Food Hydrocoll 37:100–110

Brannan RG, Mah E, Schott M, Yuan S, Casher KL, Myers A, Herrick C (2014) Influence of ingredients that reduce oil absorption during immersion frying of battered and breaded foods. Eur J Lipid Sci Technol 116:240–254

Brems A, Baeyens J, Dewil R (2012) Recycling and recovery of post-consumer plastic solid waste in a European context. Therm Sci 16:669–685

Campos CA, Gerschenson LN, Flores SK (2011) Development of edible films and coatings with antimicrobial activity. Food Bioprocess Technol 4:849–875

Cerqueira MA, Bourbon AI, Pinheiro AC, Martins JT, Souza BWS, Teixeira JA, Vicente AA (2011) Galactomannans use in the development of edible films/coatings for food applications. Trends Food Sci Technol 22:662–671

Chawla R, Patil GR (2010) Soluble Dietary Fiber. Compr Rev Food Sci Food Saf 9:178–196

Cheng KC, Demirci A, Catchmark JM (2011) Pullulan: biosynthesis, production, and applications. Appl Microbiol Biotechnol 92:29–44

Credou J, Berthelot T (2014) Cellulose: from biocompatible to bioactive material. J Mater Chem B 2:4767–4788

Cruz-Romero M, Kerry JP (2008) Crop-based biodegradable packaging and its environmental implications. CAB rev. Perspect Agric Vet Sci Nutr Nat Resour 3:1–25

Cushen M, Kerry J, Morris M, Cruz-Romero M, Cummins E (2014) Evaluation and simulation of silver and copper nanoparticle migration from polyethylene nanocomposites to food and an associated exposure assessment. J Agric Food Chem 62:1403–1411

Dainelli D, Gontard N, Spyropoulos D, Beuken EZ, Tobback P (2008) Act intell food packag: leg asp saf concern Trends Food Sci Technol 19:S103–S112

De Filpo G, Palermo AM, Munno R, Molinaro L, Formoso P, Nicoletta FP (2015) Gellan gum/titanium dioxide nanoparticle hybrid hydrogels for the cleaning and disinfection of parchment. Int Biodeterior Biodegrad 103:51–58

Duan J, Reddy KO, Ashok B, Cai J, Zhang L, Rajulu AV (2016) Effects of spent tea leaf powder on the properties and functions of cellulose green composite films. J Environ Chem Eng 4:440–448

Dufresne A (2010) Processing of polymer nanocomposites reinforced with polysaccharide nanocrystals. Molecules 15:4111–4128

Dutta PK, Tripathi S, Mehrotra GK, Dutta J (2009) Perspectives for chitosan based antimicrobial films in food applications. Food Chem 114:1173–1182

Elsabee MZ, Abdou ES (2013) Chitosan based edible films and coatings: a review. Mater Sci Eng C 33:1819–1841

Epure V, Griffon M, Pollet E, Avérous L (2011) Structure and properties of glycerol-plasticized chitosanobtained by mechanical kneading. Carbohydr Polym 83:947–952

Fabra MJ, Chambin O, Voilley A, Gay JP, Debeaufort F (2012) Influence of temperature and nacl on the release in aqueous liquid media of aroma compounds encapsulated in edible films. J Food Eng 108:30–36

Fajardo P, Martins JT, Fuciños C, Pastrana L, Teixeira JA, Vicente AA (2010) Evaluation of a chitosan-based edible film as carrier of natamycin to improve the storability of saloio cheese. J Food Eng 101:349–356

Faria S, de Oliveira Petkowicz CL, de Morais SAL, Terrones MGH, de Resende MM, de França FP, Cardoso VL (2011) Characterization of xanthan gum produced from sugar cane broth. Carbohydr Polym 86:469–476

Ferreira ARV (2016) Design of microbial polysaccharide films for food packaging. Universidade de Lisboa, Diss

Ferreira ARV, Torres CAV, Freitas F, Reis MAM, Alves VD, Coelhoso IM (2014) Biodegradable films produced from the bacterial polysaccharide fucopol. Int J Biol Macromol 71:111–116

Ferreira ARV, Alves VD, Coelhoso IM (2016a) Polysaccharide-based membranes in food packaging applications. Membranes 6:1–17

Ferreira ARV, Torres CAV, Freitas F, Sevrin C, Grandfils C, Reis MAM, Alves VD, Coelhoso IM (2016b) Development and characterization of bilayer films of FucoPol and chitosan. Carbohydr Polym 147:8–15

Freitas F, Alves VD, Coelhoso I, Reis MAM (2013) Production and food applications of microbial biopolymers. In: Teixeira JA, Vicente AA (eds) Engineering aspects of food biotechnology, CRC Press, Boca Raton

Freitas F, Alves VD, Reis MA, Crespo JG, Coelhoso IM (2014) Microbial polysaccharide-based membranes: current and future applications. J Appl Polym, Sci, 131:40047-40058.

Freitas F, Alves VD, Reis MAM (2011a) Advances in bacterial exopolysaccharides: from production to biotechnological applications. Trends Biotechnol 29:388–398

Freitas F, Alves VD, Torres CAV, Cruz M, Sousa I, Melo MJ, Ramos AM, Reis MAM (2011b) Fucose-containing exopolysaccharide produced by the newly isolated *enterobacter* strain A47 DSM 23139. Carbohydr Polym 83:159–165

Galgano F (2015) Biodegradable packaging and edible coating for fresh-cut fruits and vegetables. Ital J Food Sci 27:1

Galus S, Kadzińska J (2015) Food applications of emulsion-based edible films and coatings. Trends Food Sci Technol 45:273–283

Genovese L, Lotti N, Gazzano M, Siracusa V, Rosa MD, Munari (2016) A Novel biodegradable aliphatic copolyesters based on poly(butylene succinate) containing thioether-linkages for sustainable food packaging applications. Polym Degrad Stabil 132:191–201

Ghanbarzadeh B, Almasi H, Entezami AA (2010) Physical properties of edible modified starch/carboxymethyl cellulose films. Innov food sci emerg technol 11:697–702

Gniewosz M, Synowiec A (2011) Antibacterial activity of pullulan films containing thymol. Flavour Fragr J 26:389–395

Gupta AP, Kumar V (2007) New emerging trends in synthetic biodegradable polymers—polylactide: a critique. Eur Polym J 43:4053–4074

Hambleton A, Fabra MJ, Debeaufort F, Dury-Brun C, Voilley A (2009) Interface and aroma barrier properties of iota-carrageenan emulsion–based films used for encapsulation of active food compounds. J Food Eng 93:80–88

Hromiš NM, Lazić VL, Markov SL, Vaštag ŽG, Popović SZ, Šuput DZ, Džinić NR, Veli´canski AS, Popović LM (2015) Optimization of chitosan biofilm properties by addition of caraway essential oil and beeswax. J Food Eng 158:86–93

Isotton FS, Bernardo GL, Baldasso C, Rosa LM, Zeni M (2015) The plasticizer effect on preparation and properties of etherified corn starchs films. Ind Crops Prod 76:717–724

Jiménez A, Fabra MJ, Talens P, Chiralt A (2012) Effect of sodium caseinate on properties and ageing behavior of corn starch based films. Food Hydrocoll 29:265–271

Jindal M, Kumar V, Rana V, Tiwary AK (2013) An insight into the properties of aegle marmelos pectin-chitosan cross-linked films. Int J Biol Macromol 52:77–84

Kanmani P, Lim ST (2013) Development and characterization of novel probiotic-residing pullulan/starch edible films. Food Chem 141:1041–1049

Khan A, Huq T, Khan RA, Riedl B, Lacroix M (2014) Nanocellulose-based composites and bioactive agents for food packaging. Crit Rev Food Sci Nutr 54:163–174

Khan AK, Saba AU, Nawazish S, Akhtar F, Rashid R, Mir S, Nasir B, Iqbal F, Afzal S, Pervaiz F, Murtaza G (2017) Carrageenan based bionanocomposites as drug delivery tool with special emphasis on the influence of ferromagnetic nanoparticles. Oxid Med Cell Longev:1–13

Kim JY, Choi YG, Byul Kim SR, Lim ST (2014) Humidity stability of tapioca starch–pullulan composite films. Food Hydrocoll. 41(140–145):92

Kirchmajer DM, Steinhoff B, Warren H, Clark R, in het Panhuis M (2014) Enhanced gelation properties of purified gellan gum. Carbohydr Res 388:125–129

Kristo E, Biliaderis CG (2007) Physical properties of starch nanocrystal-reinforced pullulan films. Carbohydr Polym 68:146–158

Kurek M, Galus S, Debeaufort F (2014) Surface, mechanical and barrier properties of bio-based composite films based on chitosan and whey protein. Food Packag Shelf Life 2014:56–67

Luo Y, Wang Q (2014) Recent development of chitosan-based polyelectrolyte complexes with natural polysaccharides for drug delivery. Int J Biol Macromol 64:353–367

Mensitieri G, di Maio E, Buonocore GG, Nedi I, Oliviero M, Sansone L, Iannace S (2011) Processing and shelf life issues of selected food packaging materials and structures from renewable resources. Trends Food Sci Technol 22:72–80

Mihindukulasuriya SDF, Lim LT (2014) Nanotechnology development in food packaging: a review. Trends Food Sci Technol 40:149–167

Morris ER, Nishinari K, Rinaudo M (2012) Gelation of gellan—a review. Food Hydrocoll 28:373–411

Müller CMO, Yamashita F, Laurindo JB (2008) Evaluation of the effects of glycerol and sorbitol concentration and water activity on the water barrier properties of cassava starch films through a solubility approach. Carbohydr Polym 72:82–87

Necas J, Bartosikova L (2013) Carrageenan: a review. Vet Med 58:187–205

Novák I, Popelka A, Špitalský Z, Krupa I, Tavman S (2015) Polyolefin in packaging and food industry. Polym Compos Mater 181-199, doi:10.1007/978-3-319-25-982-6_7

Ojagh SM, Rezaei M, Razavi SH, Hosseini SMH (2010) Development and evaluation of a novel biodegradable film made from chitosan and cinnamon essential oil with low affinity toward water. Food Chem 122:161–166

Palaniraj A, Jayaraman V (2011) Production, recovery and applications of xanthan gum by *X. campestris*. J Food Eng 106:1–12

Pawar SN, Edgar KJ (2012) Alginate derivatization: a review of chemistry, properties and applications. Biomaterials 33:3279–3305

Pereda M, Aranguren MI, Marcovich NE (2009) Water vapor absorption and permeability of films based on chitosan and sodium caseinate. J Appl Polym Sci 111:2777–2784

Plackett D (2011) Introductory overview. In: Biopolymers: new materials for sustainable films and coatings; Wiley, Chichester, pp 1–14

Plotto A, Narciso JA, Rattanapanone N, Baldwin EA (2010) Surface treatments and coatings to maintain fresh-cut mango quality in storage. J Sci Food Agric 90:2333–2341

Pooja D, Panyaram S, Kulhari H, Rachamalla SS, Sistla R (2014) Xanthan gum stabilized gold nanoparticles: characterization, biocompatibility, stability and cytotoxicity. Carbohyd Polym 110:1–9

Prajapati VD, Jani GK, Khanda SM (2013a) Pullulan: an exopolysaccharide and its various applications. Carbohydr Polym 95:540–549

Prajapati VD, Jani GK, Moradiya NG, Randeria NP, Nagar BJ, Naikwadi NN, Variya BC (2013b) Galactomannan: a versatile biodegradable seed polysaccharide. Int J Biol Macromol 60:83–92

Prajapati VD, Maheriya PM, Jani GK, Solanki HK (2014) Carrageenan: A natural seaweed polysaccharide and its applications. Carbohydr Polym 105:97–112

Quoc LPT, Hoa DP, Ngoc HTB, Phi TTY (2015) Effect of xanthan gum solution on the preservation of acerola. Cercet Agron Mold 48:89–97

Rashidi L, Khosravi-Darani K (2011) The applications of nanotechnology in food industry crit. Rev Food Sci Nutr 51:723–730

Rhim JW, Park HM, Ha CS (2013) Bio-nanocomposites for food packaging applications. Prog Polym Sci 38:1629–1652

Rhima JW, Park HM, Hac CS (2013) Bio-nanocomposites for food packaging applications. Prog Polym Sci 38:1629–1652

Rivero S, García MA, Pinotti A (2009) Composite and bi-layer films based on gelatin and chitosan. J Food Eng 90:531–539

Salarbashi D, Tajik S, Shojaee-Aliabadi S, Ghasemlou M, Moayyed H, Khaksar R, Noghabi MS (2014) Development of new active packaging film made from a soluble soybean polysaccharide incorporated *Zataria* multiflora Boiss and *Mentha pulegium* essential oils. Food Chem 146:614–622

Sanuja S, Agalya A, Umapathy MJ (2015) Synthesis and characterization of zinc oxide–neem oil–chitosan bionanocomposite for food packaging application. Int J Biol Macromol 74:76–84

Sarazin P, Li G, Orts WJ, Favis BD (2008) Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. Polymer 49:599–609

Satyanarayana KG, Prasad VS (2016) Starch-based green composites. Biodegradable green composites p 199

Shih FF, Daigle KW, Champagne ET (2011) Effect of rice wax on water vapour permeability and sorption properties of edible pullulan films. Food Chem 127:118–121

Singh RS, Kaur N, Kennedy JF (2015) Pullulan and pullulan derivatives as promising biomolecules for drug and gene targeting. Carbohydr Polym 123:190–207

Siracusa V, Rocculi P, Romani S, Rosa MD (2008) Biodegradable polymers for food packaging: a review. Trends Food Sci Technol 19:634–643

Slavin J (2013) Fiber and prebiotics: mechanisms and health benefits Nutrients 5:1417–1435. doi:10.3390/nu5041417

Souza AC, Benze R, Ferrão ES, Ditchfield C, Coelho ACV, Tadini CC (2012) Cassava starch biodegradable films: influence of glycerol and clay nanoparticles content on tensile and barrier properties and glass transition temperature. LWT-Food Sci Technol 46:110–117

Sun X, Wang Z, Kadouh H, Zhou K (2014) The antimicrobial, mechanical, physical and structural properties of chitosan–gallic acid films. LWT-Food Sci Technol 57:83–89

Sworn G, Kerdavid E, Chevallereau P, Fayos J (2016) Natural suspending agent including a synergistic blend of xanthan gum and konjac powder for oral pharmaceutical suspensions. US 20160051684 A1

Tajik S, Maghsoudloua Y, Khodaiyanb F, Jafari SM, Ghasemloub M, Aalami M (2013) Soluble soybean polysaccharide: a new carbohydrate to make a biodegradable film for sustainable green packaging. Carbohyd Polym 97:817–824

Tavassoli-Kafrani E, Shekarchizadeh H, Masoudpour-Behabadi M (2016) Development of edible films and coatings from alginates and carrageenans. Carbohydr Polym 137:360–374

Thakur VK, Thakur MK (2016) Handbook of sustainable polymers: processing and applications. Pan Stanford Publishing, Singapore

Tong Q, Xiao Q, Lim LT (2008) Preparation and properties of pullulan–alginate–carboxymethylcellulose blend films. Food Res Int 41:1007–1014

Torres CAV, Marques R, Antunes S, Alves VD, Sousa I, Ramos AM, Oliveira R, Freitas F, Reis MAM (2011) Kinetics of production and characterization of the fucose-containing exopolysaccharide from *enterobacter* A47. J Biotechnol 156:261–267

Torres CAV, Marques R, Ferreira ARV, Antunes S, Grandfils C, Freitas F, Reis MAM (2014) Impact of glycerol and nitrogen concentration on *enterobacter* A47 growth and exopolysaccharide production. Int J Biol Macromol 71:81–86

Torres CAV, Ferreira ARV, Freitas F, Reis MAM, Coelhoso I, Sousa I, Alves VD (2015) Rheological studies of the fucose-rich exopolysaccharide fucopol. Int J Biol Macromol 79:611–617

Trovatti E, Fernandes SCM, Rubatat L, Perez DDS, Freire CSR, Silvestre AJD, Neto CP (2011) Pullulan–nanofibrillated cellulose composite films with improved thermal and mechanical properties. Compos Sci Technol 72:1556–1561

Tumwesigye KS, Oliveira JC, Sousa-Gallagher MJ (2016) New sustainable approach to reduce cassava borne environmental waste and develop biodegradable materials for food packaging applications. Food Packag 7:8–19

Van den Broek LAM, Knoop RJI, Kappen FHJ, Boeriu CG (2015) Chitosan films and blends for packaging material. Carbohydr Polym 116:237–242

Vargas M, Perdones Á, Chiralt A, Cháfer M, González-Martínez C (2011) Effect of homogenization conditions on physicochemical properties of chitosan-based film-forming dispersions and films. Food Hydrocoll 25:1158–1164

Versino F, Lopez OV, Garcia MA, Zaritzky NE (2016) Starch-based films and food coatings: an overview. Starch 68:1026–1037

Vu CHT, Won K (2013) Novel water-resistant uv-activated oxygen indicator for intelligent food packaging. Food Chem 140:52–56

Wu J, Zhong F, Li Y, Shoemaker CF, Xia W (2013) Preparation and characterization of pullulan–chitosan and pullulan–carboxymethyl chitosan blended films. Food Hydrocoll 30:82–91

Yin B, Zhang R, Yao P (2015) Influence of pea protein aggregates on the structure and stability of pea protein/soybean polysaccharide complex emulsions. Molecules 20:5165–5183

Zhang C, Gao D, Ma Y, Zhao X (2013a) Effect of gelatin addition on properties of pullulan films. J Food Sci 78:C805–C810

Zhang Y, Butelli E, De Stefano R, Schoonbeek H, Magusin A, Pagliarani C, Wellner N, Hill L, Orzaez D, Granell A, Jones JDG (2013b) Anthocyanins double the shelf life of tomatoes by delaying overripening and reducing susceptibility to gray mold. Curr Biol 23:1094–1100

Chapter 11
LDPE/RH/MAPE/MMT Nanocomposite Films for Packaging Applications

Khaliq Majeed, Reza Arjmandi and Azman Hassan

Abstract The ever-growing demand for the development of high-performance packaging films and the equally growing need to protect our environment has led to intense research in the manufacture of eco-friendly films with good mechanical and barrier properties. Rice husk (RH)/montmorillonite (MMT) filled and maleic anhydride-grafted polyethylene (MAPE) compatibilized LDPE films were prepared by extrusion blown film. MAPE, RH and MMT were used in various loading to study their effect on the mechanical, oxygen barrier and morphological properties. Results revealed that MAPE helped LDPE chains to delaminate MMT platelets and distribute RH/MMT uniformly in the LDPE matrix. In addition, mechanical and barrier properties of nanocomposite films prepared by MAPE as compatibilizer are better than those without compatibilizer. Increasing RH content in RH/MMT filler deteriorated mechanical and barrier properties. Increasing MMT content into RH/MMT filler-filled LDPE nanocomposite films improved the tensile and barrier properties significantly, and the films containing 4 phc MMT, 3wt% RH and 6wt% MAPE are the optimum formulation as evidenced by mechanical properties and oxygen permeability. The unique combination of mechanical properties and oxygen permeability for RH/MMT filler-filled LDPE composite films shows that these nanocomposite films are potential candidate for a variety of packaging applications.

Keywords Montmorillonite · Rice husk · Maleic anhydride-grafted polyethylene · Low-density polyethylene · Nanocomposites · Mechanical properties · Barrier properties

---

K. Majeed · R. Arjmandi · A. Hassan (✉)
Department of Bioprocess and Polymer Engineering, Universiti Teknologi Malaysia,
Skudai 81310 Johor Bahru, Malaysia
e-mail: azmanh@cheme.utm.my

K. Majeed
Department of Chemical Engineering, COMSATS Institute of Information Technology,
Lahore, Pakistan

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_11

11.1 Introduction

In recent years, the growing interest in the development of superior materials has led to intense research in the production of polymer biocomposites. Packaging perishable plant products are one of the most important steps in the long and complicated journey from grower to consumer. In addition, packaging plays a crucial role in shelf-life extension of vegetables and fresh fruits. It is well known that the plastics are permeable to gases at different degrees, and their permeability depends on internal structure of the polymer such as crystallinity, crystalline to amorphous ratio, degree of crosslinking, molecular mass and glass transition temperature (Siracusa et al. 2012).

Polyolefins such as polyethylene and polypropylene are the most prominent plastics due to their light weight, excellent water and gas barrier properties, high mechanical performance and low cost. Polyolefins have greatly contributed to develop superior materials in which their usage and production have been significantly increased (Kayaisang et al. 2013). Low-density polyethylene (LDPE) is the most promising polyolefin in flexible films due to its good mechanical properties and easy processibility, which extensively used for food packaging, agriculture and merchandising (Zhong et al. 2007a, b).

Incorporation of clay into polymers has shown increasing attention over the past few decades. Polymer/clay nanocomposites are developed to reduce carbon dioxide, organic vapours and permeability of gases such as oxygen (O_2) that are hazardous to packaged materials (Silvestre et al. 2011). Montmorillonite (MMT) is one of the commercial clays which must be exfoliated and distributed homogeneously in the polymer matrix to provide its excellent properties in polymer nanocomposites (Youssef 2013). Surface modification of MMT enhanced the compatibility between the MMT and polymer matrix (Merinska et al. 2012; Mittal 2013). Previous studies have shown that the use of nanoparticles as fillers improved the barrier properties of the nanocomposites (Merinska et al. 2012; Mittal 2013; Horst et al. 2014).

In the last decade, the use of agricultural waste to produce composite materials has increased due to their relative low abrasiveness, high stiffness, low densities and low cost (Feng et al. 2011). Rice husk (RH) is a widely available biomass material which produced during rice milling. The main components of RH are lignin (26–31%), hemicellulose (18–21%), cellulose (25–35%), silica (15–17%) and solubles (2–5%) (Majeed et al. 2015a, b). RH is currently burned for power generation and used as a bedding material for animals. The industrial applications of RH are very limited like many other agricultural by-products. It is reported that about 0.23 tons of RH are generated for every ton of rice produced, which means millions of tons of RH are produced every year (Majeed et al. 2015a, b). It is clear that the continuous generation of RH leads to a major disposal problem due to its limited commercial application. RH has been successfully used to improve the mechanical performance of composite materials because of its silica component (Kumagai and Matsuo 2013). Therefore, utilisation of RH as filler to develop environmentally friendly composite materials will not only resolve their disposal issue but also added value to this underutilized renewable material.

In general, the properties of the composites are mainly influenced by the dispersion of the fillers in the polymer matrix and interfacial adhesion between the fillers and the matrix (Gwon et al. 2010; Dadfar et al. 2011; Sliwa et al. 2012). Polyolefins are faced difficulty in establishing a well-bonded structure with lignocellulosic fillers and MMT due to its nonpolar hydrophobic nature. The uniform dispersion of the fillers and their adhesion with polymer matrix are very important in order to make a composite with balance properties. The uniform filler dispersion and good interfacial adhesion between the fillers and the matrix are usually accomplished through reagents. Azizi et al. (2011) studied the effect of maleic anhydride-grafted polyethylene (MAPE) on the properties of high-density polyethylene/polystyrene/MMT nanocomposites and found encouraging results; better adhesion between the fillers and matrix which resulted in improved mechanical properties. Najafi et al. (2012) found that the mechanical properties of the polypropylene/reed flour/MMT composites improved by incorporation of maleated polypropylene. Similar findings have also been reported by Hemmasi et al. (2010) for the polypropylene/wood flour/MMT composites.

Incorporation of two different fillers into a matrix is receiving significant attention because it offers superior properties that can be difficult to obtain using single filler. The properties of the polymer composites can be significantly enhanced at a moderate cost by carefully selecting the reinforcing fillers. The present chapter focuses on the effects of MMT, RH and MAPE on the mechanical and barrier properties of LDPE/RH/MAPE/MMT nanocomposite films prepared using extrusion blown film. The main reason for hybridization of the RH and MMT fillers is to enhance the mechanical and barrier properties, which are the main properties for packaging applications.

11.2 Materials and Methods

11.2.1 Materials

LDPE with density of 0.922 g/cm^3 and melt flow index of 2 g/10 min (Titan® LDF200GG;) was used as the polymer matrix. Naturally modified MMT (Nanomer® 1.44P) with quarternary ammonium salt with an average dry particle size of 15–20 µm was used as reinforcing filler. RH was obtained from BERNAS (Padiberas Nasional Berhad, Malaysia), and it was washed and dried in oven at 100 °C for 24 h before processing. After that, RH was ground using a grinder and sieved (Retsch test sieve, Model AS200) to obtain a particle size of <75 µm. MAPE with density of 0.916 g/cm^3 and melt flow index of 2.5 g/10 min (OREVAC® 18365) was used as compatibilizing agent.

11.2.2 Preparation of Nanocomposite Films

Three different series of the MAPE compatibilized and LDPE/RH/MMT composite films with variations in terms of MAPE loading, RH addition and MMT concentration were prepared using melt blending in a co-rotating twin-screw extruder followed by blown to prepare thin films. Detailed compositions of the composite films are tabulated in Tables 11.1, 11.2 and 11.3. The temperature setting from the hopper to the die was 160/170/170/180 °C and the screw speed was 50 rpm. After reached to the set temperatures, LDPE and MAPE were fed through the side hoppers, whereas MMT and RH were fed manually throughout the extrusion process. Consequently, the extruded strands were pelletized and then dried at 100 °C before blown process. Lastly, the composite pellets were blown into the films using a blown film extrusion machine (model: TK/HD) manufactured by Tai King Machinery Factory, Taiwan. The target film gauge was 80 μm and a 2.5 blow-up ratio (bubble diameter to die diameter ratio) was used.

Table 11.1 Formulations to study the effect of MAPE loadings on composite film properties

Sample Designation	LDPE (wt%)	RH (wt%)	MMT (wt%)	MAPE (phc)[a]
LRMC-0	92	5	3	0
LRMC-2	92	5	3	2
LRMC-4	92	5	3	4
LRMC-6	92	5	3	6
LRMC-8	92	5	3	8

[a] Parts per hundred parts of the composite

Table 11.2 Formulations to study the effect of RH loadings on composite film properties

Sample Designation	LDPE (wt%)	MMT (wt%)	MAPE (wt%)	RH (phc)
LMCR-2	92	2	6	2
LMCR-3	92	2	6	3
LMCR-4	92	2	6	4
LMCR-5	92	2	6	5
LMCR-7	92	2	6	7

Table 11.3 Formulations to study the effect of MMT loadings on composite film properties

Sample Designation	LDPE (wt%)	RH (wt%)	MAPE (wt%)	MMT (phc)
LRCM-2	90	4	6	2
LRCM-3	90	4	6	3
LRCM-4	90	4	6	4
LRCM-5	90	4	6	5
LRCM-6	90	4	6	6

11.3 Characterizations

11.3.1 X-Ray Diffraction

X-ray diffraction (XRD) analysis was used to investigate the intercalation of LDPE chains into the MMT layers and their degree of delamination. The *d*-spacing of the LDPE nanocomposites was measured by a Bruker D8 Advance diffractometer. The X-ray beam Cu Kα radiation ($\lambda = 0.154$ nm) operated at 30 kV and 10 mA. The diffraction patterns were obtained at ambient temperature in the range $2\theta = 2$–10° with step size of 0.02°. The interlayer distance (*d*-spacing) of MMT was calculated using the following equations:

$$D_{001} = \frac{\lambda}{2\sin\theta}$$

Where, D_{001} is interlayer distance between clay layers, λ is wavelength of the X-ray beam and θ is half of the diffraction angle at the first peak.

11.3.2 Mechanical Measurements

The neat LDPE and its composite films were cut into rectangular-shaped specimen (102 × 15 mm) along with their longitudinal direction. Micrometre (Mitutoyo, Japan, precision of ±0.001 mm) was used to measure the thickness of the composite films. The mechanical measurements and tensile and tear properties were carried out by Lloyd's universal testing machine according to ASTM D882 and D1938, respectively. Minimum of seven different specimens was tested for each formulation, and the average values were reported.

11.3.3 Oxygen Barrier Analysis

The oxygen (O_2) permeability coefficient measurement of the composite films was carried out at ambient temperature in a constant pressure/variable volume-type permeation cell designed according to ASTM D1434-82. Circular film samples (4.4 cm diameter) were used to investigate the oxygen transmission rate (OTR, mL/m2-24 h). Micrometre (Mitutoyo, Japan, precision of ± 0.001 mm) was used to measure the thickness of film samples. Permeability coefficient was calculated using following the equation:

$$P = t\frac{OTR}{\Delta p}$$

where, P is permeability coefficient (mL-mm/m^2-24hr-atm), t is the film thickness (mm) and Δp is O_2 partial pressure difference on two sides of the film (atm).

11.3.4 Morphological Analysis

Scanning electron microscopy (SEM) was carried out to investigate the fillers dispersion in the composite films. The composite films were frozen in liquid nitrogen and fractured to view filler-matrix interface. In addition, the composite films were mounted onto copper stubs, and their surface was coated with a thin gold layer (BIO-RAD SEM-coating system) to investigate the surface topography. The composite films were examined using a scanning electron microscope (Philips XL 40) at an accelerating voltage of 30 kV.

11.4 Results and Discussion

11.4.1 X-Ray Diffraction

Uniform dispersion of nanoclay in polymer matrix and increase in its interlayer spacing due to insertion of polymer chains into the nanoclay structure is a good evidence that indicates the development of nanocomposites. Based on the increase in interlayer spacing of nanoclays and their ultimate delamination, X-ray diffraction (XRD) patterns exhibit the formation of intercalated or semi-exfoliated composite. Increase in the interlayer spacing which is due to the movement of characteristic peak towards lower angle is measured by using Brags formula while receding of this characteristic peak could be due to delamination of nanoclay platelets (Majeed et al. 2014, 2015a, b, 2016). XRD diffractograms of the MMT and nanocomposite films having varying contents of MAPE compatibilizer and RH/MMT filler are shown in Fig. 11.1. The figure compares the influence of varying compatibilizer, RH and MMT in delaminating the MMT platelets due to the intercalation of LDPE chains into the galleries.

Movement of the characteristic peak position of MMT due to adding varying amounts of MAPE compatibilizer in RH/MMT-filled LDPE system is compared in Fig. 11.1a. As the pattern shows, the peak of virgin MMT is at about 3.45°, corresponding to interlayer spacing of 2.56 nm. The corresponding peak position moved slightly towards lower angle for composite film without compatibilizer (LRMC-0). Concerning MAPE compatibilzed system, for composites with MAPE loadings ranging from 2 to 8 phc, characteristic peak shifted towards lower 2θ as compared to uncompatibilized composite. Movement of the characteristic peak towards lower 2θ resulted in an increase in the interlayer spacing which could be due to the intercalation of the LDPE chains between the MMT platelets. An

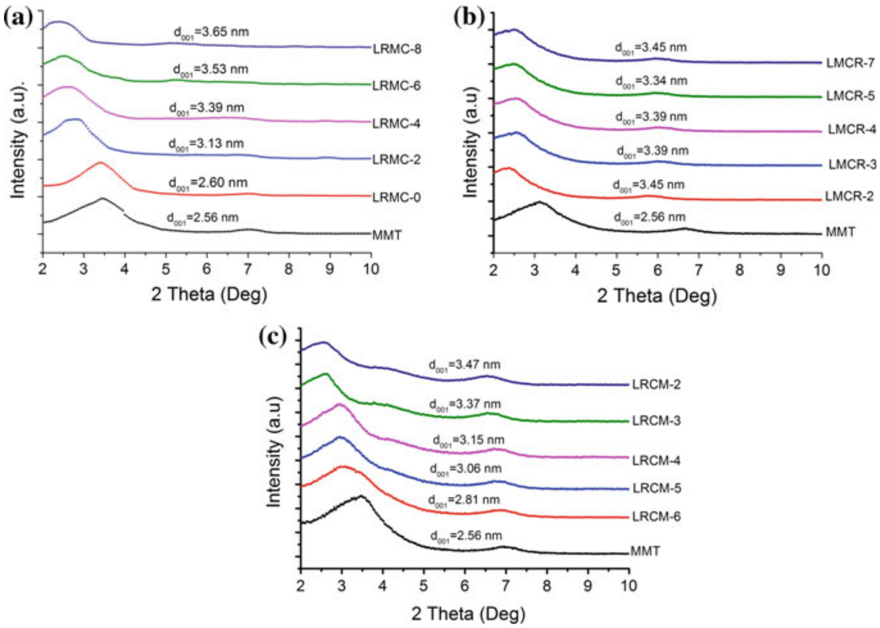


Fig. 11.1 XRD diffractograms of MAPE compatibilized and RH/MMT-filled LDPE composite films with varying contents of **a** MAPE compatibilizer, **b** RH and **c** MMT (Majeed et al. 2014, 2015a, b, 2016)

increase of 33 and 40% with the addition of 4 and 8% MAPE. These findings revealed that dispersion/intercalation of the MMT platelets could be delaminated with the addition of MAPE, and the delamination level increases by adding MAPE. However, this increase in the interlayer spacing is a non-linear function of the compatibilizer concentration. These results are in agreement with previous-reported results (Ali Dadfar et al. 2011). Moreover, delamination of MMT platelets in a composite system increases by increasing the amount of polar groups (Martín et al. 2009).

Delamination level of MMT platelets due to different contents RH in RH/MMT-filled LDPE system is shown in Fig. 11.1b. The MMT diffraction peak shifted towards lower 2θ in comparison with virgin MMT. Movement of diffraction peak towards lower 2θ reveals that the interlayer distances are increased resulting an intercalated structure of the nanocomposites. Shifting of the characteristic peak towards lower 2θ was also reported by Kord (2011) for RH/MMT/HDPE nanocomposites. In addition, results are also consistent with other researchers (Zhong et al. 2007a, b; Najafi et al. 2012).

Figure 11.1c depicts influence of different concentrations of MMT in RH/MMT/LDPE nanocomposite films on the interlayer spacing. As shown, the characteristic peak shifted towards lower angle (interlayer spacing of 3.47 nm) for LRCM-2, and this delamination of MMT could be due to intercalation of polymer chains in the MMT galleries. However, with increasing MMT concentrations, the MMT particles started agglomeration. This aggregation of MMT particles could be due to decrease in MAPE contents (MAPE/MMT ratio) in LDPE. It is worth noting that neat MMT has lesser interlayer spacing than the prepared nanocomposites. Similar results are also reported by Khalili et al. (2013) for LDPE/LLDPE/MMT system.

11.4.2 Mechanical Properties

Mechanical properties of composites are important parameter to judge their suitability for both the indoor and the outdoor applications. In this particular study, tensile and tear tests were performed to study the effect of varying amounts of MAPE compatibilizer, RH loading and MMT concentration in the LDPE-based films. Detailed results of the samples with standard deviation in parenthesis are tabulated in Table 11.4. To compare neat LDPE with the prepared nanocomposite films, tests were also performed on the neat samples, and tensile strength, elongation at break, tensile modulus and tear resistance of 14.6 MPa, 220%, 163.4 MPa and 138.4 g, respectively, were observed for the neat LDPE.

In general, the immiscible composites possess poor mechanical properties. Poor interfacial adhesion between filler(s) and matrix material is the major cause for poor

Table 11.4 Mechanical and oxygen barrier properties of the prepared nanocomposite films (Majeed et al. 2014, 2015a, b, 2016)

Sample Designation	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)	Tear strength (g)	Oxygen Permeability (mL-mm/m^2-d-atm)
LRMC-0	7.1 ± 0.8	59 ± 7	237 ± 10	117.1 ± 3.4	1472 ± 67
LRMC-2	8.7 ± 0.6	67 ± 6	242 ± 7	130.3 ± 1.8	1155 ± 51
LRMC-4	9.9 ± 0.7	72 ± 9	242 ± 9	133.4 ± 2.6	744 ± 47
LRMC-6	10.5 ± 0.4	76 ± 8	246 ± 6	140.8 ± 2.5	421 ± 17
LRMC-8	10.2 ± 0.7	83 ± 7	248 ± 8	138.7 ± 3.5	374 ± 15
LMCR-2	11.9 ± 0.6	111 ± 13	236 ± 7	137.2 ± 3.7	211 ± 7
LMCR-3	11.4 ± 0.6	95 ± 12	240 ± 11	136.5 ± 4.6	277 ± 8
LMCR-4	11.0 ± 0.8	82 ± 8	242 ± 10	133.1 ± 4.5	365 ± 15
LMCR-5	10.7 ± 0.6	75 ± 12	249 ± 14	127.9 ± 2.9	509 ± 17
LMCR-7	8.9 ± 0.4	34 ± 8	267 ± 19	117.2 ± 4.3	1691 ± 61
LRCM-2	11.1 ± 0.4	96 ± 8	234 ± 12	138.5 ± 2.5	281 ± 15
LRCM-3	11.4 ± 0.8	91 ± 11	243 ± 9	139.3 ± 4.3	245 ± 13
LRCM-4	11.9 ± 0.5	84 ± 8	257 ± 8	140.4 ± 3.1	209 ± 16
LRCM-5	11.6 ± 0.8	76 ± 9	266 ± 11	140.1 ± 3.8	221 ± 12
LRCM-6	11.5 ± 0.4	71 ± 8	277 ± 12	139.0 ± 2.8	339 ± 14

mechanical properties. Similar to this general behaviour, strength and elongation decreased drastically with the addition of RH/MMT into the LDPE matrix, when compared with neat LDPE (Nandi et al. 2012). This could be due to less intercalated MMT platelets (as confirmed by XRD diffractograms) and rice husk agglomeration (confirmed by SEM micrographs). This decrease may be attributed to poor compatibility between filler and matrix, poor interfacial adhesion and brittle behaviour of the cellulosic filler (George et al. 2006; Habibi et al. 2008). In order to enhance the interfacial adhesion, MAPE compatibilizing agent was used, and the properties significantly increased as a result of addition of 2 phc MAPE to the composite system. Tensile strength and elongation at break increased to 8.7 MPa and 61% with the addition of 2 phc MAPE (LRMC-2). In addition, properties continued to increase with increasing MAPE content, and the strength reached maximum at 6 phc MAPE and beyond this limit, MAPE affected negatively. This behaviour indicates that MAPE acts as compatibilizer only up to a certain limit, and the excessive loading of MAPE leads it to act as plasticizer. These results are also supported by other researchers (Hemmasi et al. 2010). Concerning modulus, incorporation of RH/MMT filler resulted in significant improvement in modulus. 44% improvement in the modulus of LDPE was observed with the addition of RH/MMT filler. This improvement could be due to rigid nature of the filler. Rigid filler hinders matrix chains mobility. With the incorporation of MAPE, the modulus increased further and this increase in modulus could be attributed to improved interfacial adhesion between filler and the matrix. Tear resistance is the resistance to the growth of a cut or nick in a specimen when tension is applied; Tear resistance is another significant property for high capacity pouches, bags and other industrial applications. Tear resistance decreased with the addition of filler only. However, the resistance improved with the addition of MAPE and recovered to the neat LDPE value at 6 phc MAPE. It is observed that, resistance to the growth of cut varies with varying MAPE contents, as does the tensile strength. Increased compatibility and improved interfacial adhesion could be the reasons for this enhanced resistance to the growth of cut.

Increasing the RH concentration into RH/MMT/LDPE system negatively affected tensile strength and elongation at break. Tensile strength and elongation at break for LMCR-2 are 11.9 MPa and 111%, respectively, that decreased to 8.9 MPa and 34% for LMCR-7. Decrease in the strength and elongation could be due to poor dispersion of RH and its compatibility with LDPE (George et al. 2006). On the other hand, tensile modulus increased with increasing RH concentration in RH/MMT/LDPE films. Tensile modulus of the composite films having 7 phc RH (LMCR-7) is 267 MPA which is about 14% higher than that of LMCR-2. The increment of modulus depends on the morphology of composites (Kord and Kiakojouri 2011) and interfacial adhesion (Demir et al. 2006). Similar results have also been reported by other researchers (Faruk and Matuana 2008; Esnaashari et al. 2013), (Kengkhetkit and Amornsakchai 2012) and (Taşdemır et al. 2009). Concerning tear strength, tear resistance started decreasing with adding RH and continued to decrease further with increasing RH loadings in RH/MMT/LDPE films, as do the tensile strength. This decreased resistance to the growth of cut increasing RH in RH/MMT/LDPE could be due to poor dispersion of the filler and lower compatibility between the RH and LDPE.

Increase in tensile strength was observed with the incorporation of MMT, and a maximum value of 11.9 MPa was observed with the addition of 4 phc MMT (LRCM-4). Further increase in MMT content resulted in decrease in the strength which could originate from two causes: (1) migration of MMT into the RH/LDPE interface and (2) poor dispersion of MMT/RH LDPE. Decrease in tensile strength could also be due to poor interfacial adhesion between filler and matrix material (Taha and Abdin 2011; Bagheri-Kazemabad et al. 2012). Contrary to tensile strength, with varying MMT contents from 0 to 6 phc, elongation at break decreased from 105% for LRCM-0 to 96, 91, 84, 76 and 71% for 2, 3, 4, 5 and 6 phc MMT in RH/MMT/LDPE, respectively. Weak interfacial adhesion and fragile behaviour of filler could be the reasons for this decrease in elongation at break (Arrakhiz et al. 2013). Concerning tensile modulus, progressive increase in modulus continued with increasing MMT concentration. Tear resistance followed a pattern similar to tensile strength and continued to increase by incorporating MMT, with a maximum improvement at 4 phc MMT concentration. Reaching to 140.4 gm with the addition of 4 phc MMT in RH/MMT/LDPE system, which is also a maximum value for the resistance, the tear resistance begins to decrease with further increase in MMT concentration and may be attributed to agglomeration of MMT particles. Formation of MMT aggregates beyond this loading was confirmed by XRD.

11.4.3 Barrier Properties

Oxygen (O_2) deteriorates food products in a variety of ways and its unenviable effects on a variety of foodstuff have been reported in many studies (Ayranci and Tunc 2003; Bonilla et al. 2012). Oxygen spoils food both by direct and by indirect ways. Oxygen permeability (OP) of the prepared nanocomposite films was studied to evaluate their potential for food packaging. Neat LDPE is 224 mL-mm/m^2-d-atm permeable to oxygen and OP values for the prepared nanocomposite films are tabulated in Table 11.4.

Incorporation of RH/MMT filler into LDPE matrix without any MAPE deteriorates oxygen barrier and OP of the composite film increased sharply, 1472 mL-mm/m^2-d-atm for LRMC-0. For MAPE compatibilized and RH/MMT filled-LDPE matrix, OP decreased significantly and can be attributed to delamination and uniform distribution of MMT platelets. Oxygen barrier increased to about 100% with the addition of 4 phc MAPE. Delaminated and uniformly distributed impermeable clay platelets act as obstacles. These obstacles force the diffusing molecules to follow a tortuous path. Thus the gas molecules will have to follow a long and tortuous path (Khalili et al. 2013). Reduced OP with the incorporation of MMT in polyethylene and their compatibilization with grafted copolymer have also been reported by Fendler et al. (2007) and Hemmati et al. (2011).

OP of the nanocomposite films having 2 phc of RH and 2wt% MMT (LMCR-2) decreased slightly, when compared with neat LDPE films. However, higher loadings of RH resulted in significant increase in OP. Thus, improvement in oxygen barrier in the case of LMCR-2 is due to delamination of MMT platelets and their dispersion in the matrix (Duncan 2011). Increase in OP with increasing RH loadings is also reported in literature (George et al. 2006).

OP value started decreasing with the incorporation of MMT and reached minimum (209 mL-mm/m^2-d-atm) with the addition of 4 phc MMT (LRCM-4). This is worth noting that this observed value of OP is even less than that of neat LDPE, and twofold better than the composite film without any MMT. Improvement in the barrier might be due to delamination and dispersion of MMT platelets in the composite film. MMT platelets retard the diffusion of permeating molecules and force them to follow a tortuous path (Ali Dadfar et al. 2011; Khalili et al. 2013). It is worth noting that improvement in O_2 barrier was observed with the addition of only up to 4 phc MMT. Beyond this limit, the permeability started increasing, indicating optimum concentration of MMT for least permeability. This limit in the loadings of MMT could be because of the tendency of MMT particles to agglomerate. XRD results also suggest the agglomeration of MMT particles beyond 4 phc MMT loadings.

11.4.4 Morphological Analysis

Dispersion of natural filler and its interfacial adhesion with matrix material is important in determining mechanical properties of the resulting composites. Dispersion of RH in the LDPE matrix and morphological changes due to varying contents of MAPE compatibilizer, RH and MMT in the LDPE matrix was studied using SEM.

Figures 11.2 and 11.3 depict the influence of varying contents of MAPE compatibilizer on the dispersion of RH and its compatibility with the matrix material. For uncompatibilized composite film sample (LRCM-0), RH agglomerates are quite visible due to the hygroscopic nature of the RH and its poor compatibility with LDPE. Three hydroxyl (OH) groups are present in anhydro-D-glucose which is the main structural element of any cellulosic materials. These hydroxyl groups tend to form hydrogen bonds inside the macromolecule itself and between other cellulose macromolecules (Habibi et al. 2008). Film homogeneity and thus the tensile strength decreases due to the presence of these agglomerates (George et al. 2006). Therefore, different compatibilizers are used to improve filler dispersion. As expected, compatibilized composite films indicate that RH particles are well dispersed and adhered with the LDPE matrix. In addition, composite films with higher compatibilizer loadings have better dispersion and filler-matrix adhesion as compared to the films with lower loadings. Similar observation has also been reported by Gwon et al. (2012), Najafi et al. (2012) and Habibi et al. (2008). As observed, MAPE higher loadings lead to uniform dispersion and better adhering of RH which in turn improves film homogeneity and mechanical properties. Enhanced

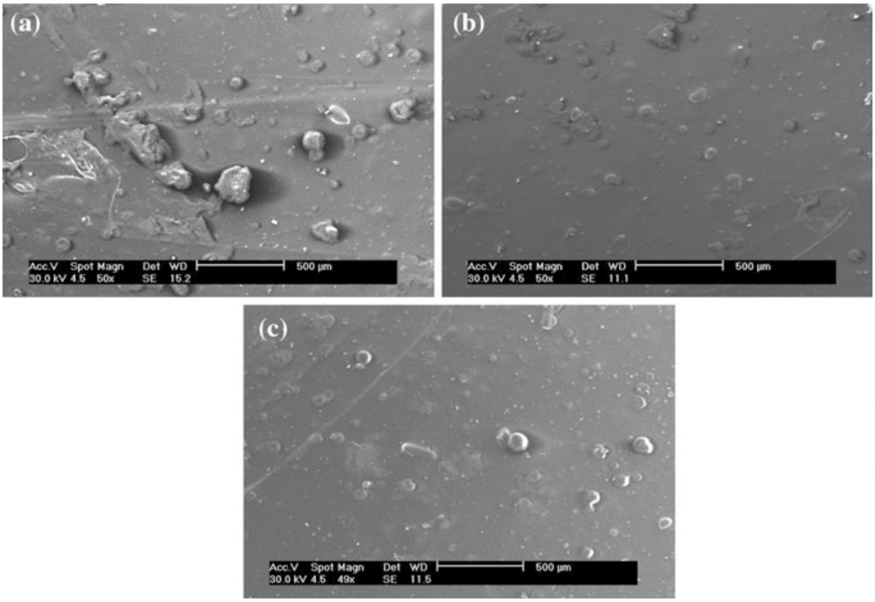


Fig. 11.2 SEM micrographs of the surface of composite films with varying MAPE compatibilizer contents **a** LRMC-0, **b** LRMC-4 and **c** LRMC-6 (Majeed et al. 2014)

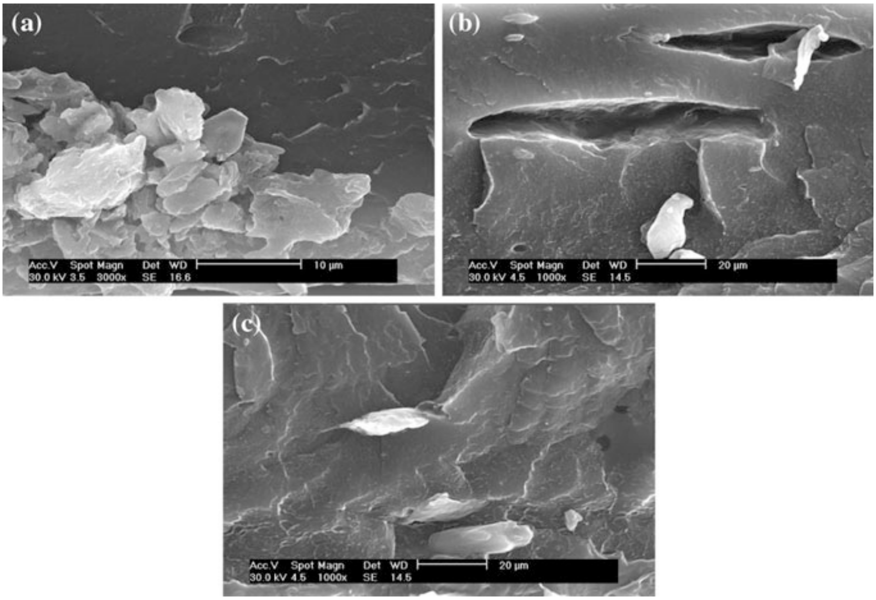


Fig. 11.3 SEM micrographs of the fractured surface of composite films with varying MAPE compatibilizer contents **a** LRMC-0, **b** LRMC-2 and **c** LRMC-6 (Majeed et al. 2014)

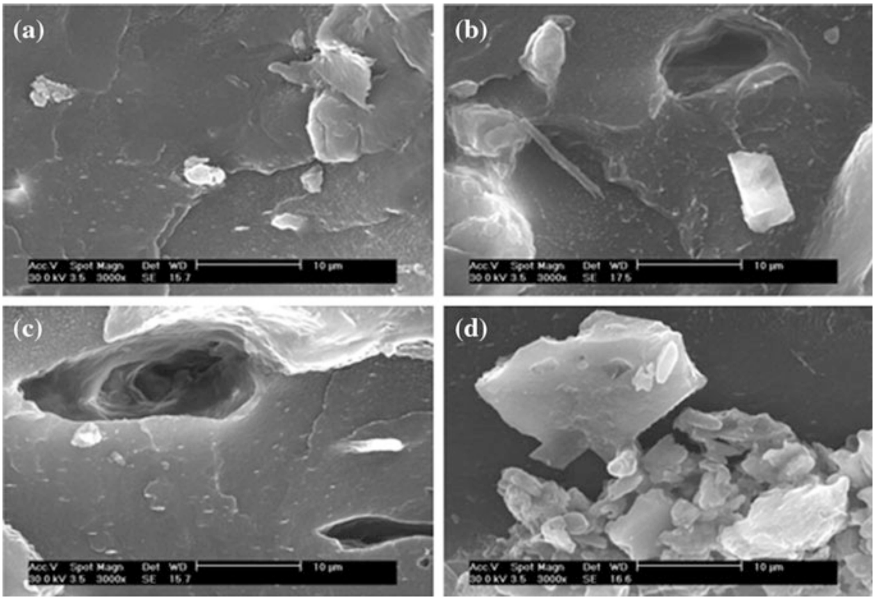


Fig. 11.4 SEM micrographs of the cryo-fractured cross sections of RH/MMT hybrid filler-filled LDPE nanocomposite films **a** and **b** LMCR-2 and **c** and **d** LMCR-7 (Majeed et al. 2015a, b)

mechanical properties of compatibilized composite films are the result of this dispersion and bonding. Contrary, agglomeration deteriorates the performance properties due to poor homogeneity.

Micrographs of representative cryo-fractured film having varying loadings of RH in RH/MMT/LDPE system are shown in Fig. 11.4. Examination of the micrographs revealed that film samples fabricated by using lower loadings of RH have uniform dispersion and better filler-matrix adhesion than the composites containing higher concentration. In other words, RH particles are adhered well to the polymer matrix at lower concentrations and undergo breaking during failure instead of being pulled out from the matrix (shown by arrow in Fig. 11.4a). Filler breakage results in matrix fibrillation which is a good indication of better interfacial adhesion between filler and matrix (Demir et al. 2006). On the other side, if filler/matrix interaction is poor, filler pull-out is more prominent.

SEM micrographs of the films having different amounts of MMT in RH/MMT filler-filled LDPE films are shown in Figs. 11.5 and 11.6. Figure 11.5 shows well-dispersed particles of RH in LDPE regardless of the amount of MMT. In addition, increasing amounts of MMT in RH/MMT filler did not adversely affect the interfacial gaps between RH and LDPE. On the other hand, increase in interfacial gaps is reported with increase in natural filler content (Haq et al. 2008). It is worth noting that the composite films having higher contents of MMT show less pull-out of RH fillers than the films without or lesser MMT (shown by boxed regions in Fig. 11.6). Increased interfacial adhesion could be attributed to bridging

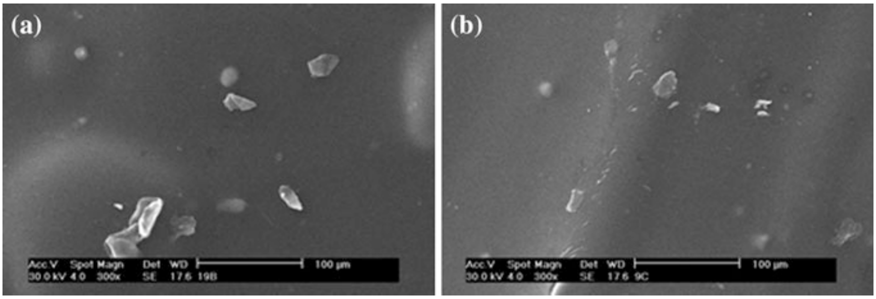


Fig. 11.5 SEM micrographs of the surface of RH/MMT-filled composite films with varying contents of MMT **a** LRCM-0 and **b** LRCM-4 (Majeed et al. 2016)

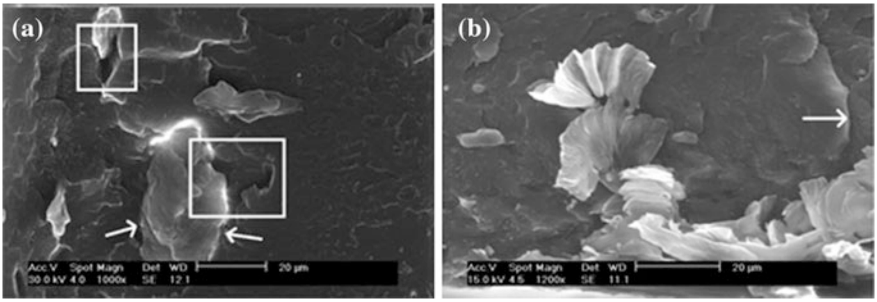


Fig. 11.6 SEM micrographs of the fractured surface of RH/MMT-filled composite films with varying contents of MMT **a** LRCM-0 and **b** LRCM-6 (Majeed et al. 2016)

effect of MMT for natural filler and matrix material. Improved interfacial adhesion due to the addition of MMT in walnut shell/polypropylene composite system has also been reported by Zahedi et al. (2013). It is expected that incorporating MMT to LDPE/RH composites would lead to stronger interface owing to its potential to fill the gaps and increased interaction with LDPE matrix and RH. Enhanced mechanical properties with the addition of MMT in RH/LDPE composite system are consistent with these observations.

11.5 Conclusions

RH/MMT filler-filled and MAPE compatibilized LDPE-based nanocomposite film were successfully blown, and the effect of varying amounts of MAPE compatibilizer, RH loading and MMT concentration mechanical, oxygen barrier and morphological properties were studied. Results revealed that incorporation of MAPE compatibilizer in RH/MMT-filled LDPE composite films is important to delaminate

MMT platelets and uniformly distribute RH/MMT into the matrix. In addition, mechanical and oxygen barrier properties were also improved with the addition of MAPE compatibilizer. Tensile strength and the oxygen barrier improved by about 22 and 49%, respectively, with the incorporation of only 2 and 4 phc MAPE into uncompatibilized system. It was also observed that the addition of 6 phc MAPE is optimum based on the mechanical and barrier properties. Increasing RH content in the hybrid filler did not adversely affect delamination of MMT platelets. However, decreased the tensile strength, tear resistance, elongation at break and oxygen barrier. Tensile modulus increased notably with increasing RH content in RH/MMT filler. Tensile and barrier properties increased with increasing MMT content in RH/MMT filler and LRCM-4 is the optimum formulation as evidenced by mechanical and barrier results. The nanocomposite films showed lower oxygen permeability with higher tear resistance and tensile modulus than neat LDPE.

Acknowledgements The authors wish to acknowledge the Universiti Teknologi Malaysia (UTM) and Fundamental Research Grant Scheme 78354, sub-code: 3F302 and Ministry of Higher Education (MOHE) for financial support.

References

Ali Dadfar SM, Alemzadeh I, Reza Dadfar SM, Vosoughi M (2011) Studies on the oxygen barrier and mechanical properties of low density polyethylene/organoclay nanocomposite films in the presence of ethylene vinyl acetate copolymer as a new type of compatibilizer. Mater Des 32:1806–1813

Arrakhiz FZ, El Achaby M, Malha M, Bensalah MO, Fassi-Fehri O, Bouhfid R, Benmoussa K, Qaiss A (2013) Mechanical and thermal properties of natural fibers reinforced polymer composites: Doum/low density polyethylene. Mater Des 43:200–205

Ayranci E, Tunc S (2003) A method for the measurement of the oxygen permeability and the development of edible films to reduce the rate of oxidative reactions in fresh foods. Food Chem 80:423–431

Azizi S, Yunus WMZW, Ahmad M (2011) Effect of polyethylene-grafted maleic anhydride on properties of high-density polyethylene and polystyrene blend/layered silicate nanocomposites. J Reinf Plast Compos 30:1649–1654

Bagheri-Kazemabad S, Fox D, Chen Y, Geever LM, Khavandi A, Bagheri R, Higginbotham CL, Zhang H, Chen B (2012) Morphology, rheology and mechanical properties of polypropylene/ethylene–octene copolymer/clay nanocomposites: effects of the compatibilizer. Compos Sci Technol 72:1697–1704

Bonilla J, Atarés L, Vargas M, Chiralt A (2012) Edible films and coatings to prevent the detrimental effect of oxygen on food quality: possibilities and limitations. J Food Eng 110:208–213

Dadfar SA, Alemzadeh I, Dadfar SR, Vosoughi M (2011) Studies on the oxygen barrier and mechanical properties of low density polyethylene/organoclay nanocomposite films in the presence of ethylene vinyl acetate copolymer as a new type of compatibilizer. Mater Des 32:1806–1813

Demir H, Atikler U, Balköse D, Tıhmınlıoğlu F (2006) The effect of fiber surface treatments on the tensile and water sorption properties of polypropylene–luffa fiber composites. Compos A Appl Sci Manuf 37:447–456

Duncan TV (2011) Applications of nanotechnology in food packaging and food safety: barrier materials, antimicrobials and sensors. J Colloid Interf Sci 363:1–24

Esnaashari C, Khorasani SN, Entezam M, Khalili S (2013) Mechanical and water absorption properties of sawdust—low density polyethylene nanocomposite. J Appl Polym Sci 127:1295–1300

Faruk O, Matuana LM (2008) Nanoclay reinforced HDPE as a matrix for wood-plastic composites. Compos Sci Technol 68:2073–2077

Fendler A, Villanueva MP, Gimenez E, Lagarón JM (2007) Characterization of the barrier properties of composites of HDPE and purified cellulose fibers. Cellulose 14:427–438

Feng Y, Hu Y, Zhao G, Yin J, Jiang W (2011) Preparation and mechanical properties of high-performance short ramie fiber-reinforced polypropylene composites. J Appl Polym Sci 122:1564–1571

George J, Kumar R, Jayaprahash C, Ramakrishna A, Sabapathy SN, Bawa AS (2006) Rice bran-filled biodegradable low-density polyethylene films: development and characterization for packaging applications. J Appl Polym Sci 102:4514–4522

Gwon JG, Lee SY, Chun SJ, Doh GH, Kim JH (2010) Effects of chemical treatments of hybrid fillers on the physical and thermal properties of wood plastic composites. Compos A Appl Sci Manuf 41:1491–1497

Gwon JG, Lee SY, Chun SJ, Doh GH, Kim JH (2012) Physical and mechanical properties of wood–plastic composites hybridized with inorganic fillers. J Compos Mater 46:301–309

Habibi Y, El-Zawawy WK, Ibrahim MM, Dufresne A (2008) Processing and characterization of reinforced polyethylene composites made with lignocellulosic fibers from Egyptian agro-industrial residues. Compos Sci Technol 68:1877–1885

Haq M, Burgueño R, Mohanty AK, Misra M (2008) Hybrid bio-based composites from blends of unsaturated polyester and soybean oil reinforced with nanoclay and natural fibers. Compos Sci Technol 68:3344–3351

Hemmasi AH, Khademi-Eslam H, Talaiepoor M, Kord B, Ghasemi I (2010) Effect of nanoclay on the mechanical and morphological properties of wood polymer nanocomposite. J Reinf Plast Compos 29:964–971

Hemmati M, Shariatpanahi H, Fereidoon A, Aalaie J, Ahangari MG (2011) Study of a polymer blend/nanoclay nanocomposite of polyethylene and polyamide 6 prepared by mechanical blending. Polym Plast Technol Eng 51:80–85

Horst MF, Quinzani LM, Failla MD (2014) Rheological and barrier properties of nanocomposites of HDPE and exfoliated montmorillonite. J Thermoplast Compos Mater 27:106–125

Kayaisang S, Saikrasun S, Amornsakchai T (2013) Potential use of recycled PET in comparison with liquid crystalline polyester as a dual functional additive for enhancing heat stability and reinforcement for high density polyethylene composite fibers. J Polym Environ 21:191–206

Kengkhetkit N, Amornsakchai T (2012) Utilisation of pineapple leaf waste for plastic reinforcement: 1. A novel extraction method for short pineapple leaf fiber. Ind Crops Prod 40:55–61

Khalili S, Masoomi M, Bagheri R (2013) The effect of organo-modified montmorillonite on mechanical and barrier properties of linear low-density polyethylene/low-density polyethylene blend films. J Plast Film Sheeting 29:39–55

Kord B (2011) Nanofiller reinforcement effects on the thermal, dynamic mechanical and morphological bahavior of HDPE/rice husk flour composites. BioResources 6:1351–1358

Kord B, Kiakojouri SMH (2011) Effect of nanoclay dispersion on physical and mechanical properties of wood flour/polypropylene/glass fiber hybrid composites. BioResources 6:1741–1751

Kumagai S, Matsuo Y (2013) Composite produced from rice husk and chopped carbon fiber without using any binders. Ind Crops Prod 43:640–647

Majeed K, Hassan A, Bakar AA (2014) Influence of maleic anhydride-grafted polyethylene compatibiliser on the tensile, oxygen barrier and thermal properties of rice husk and nanoclay-filled low-density polyethylene composite films. J Plast Film Sheeting 30:120–140

Majeed K, Hassan A, Abu Bakar A (2015a) Barrier, biodegradation, and mechanical properties of (Rice husk)/(Montmorillonite) hybrid filler-filled low-density polyethylene nanocomposite films. J Vinyl Add Technol

Majeed K, Hassan A, Bakar A (2015b) In: Hakeem KR, Jawaid M, Alothman OY (eds) Tensile, oxygen barrier and biodegradation properties of rice husk-reinforced polyethylene blown films. Agricultural biomass based potential materials. Springer

Majeed K, Hassan A, Bakar AA, Jawaid M (2016) Effect of montmorillonite (MMT) content on the mechanical, oxygen barrier, and thermal properties of rice husk/MMT hybrid filler-filled low-density polyethylene nanocomposite blown films. J Thermoplast Compos Mater 29:1003–1019

Martín Z, Jiménez I, Gómez MA, Ade HW, Kilcoyne DA, Hernádez-Cruz D (2009) Spectromicroscopy study of intercalation and exfoliation in polypropylene/montmorillonite nanocomposites. J Phys Chem B 113:11160–11165

Merinska D, Kubisova H, Kalendová A, Svoboda P, Hromádková J (2012) Processing and properties of polyethylene/montmorillonite nanocomposites. J Thermoplast Compos Mater 25:115–131

Mittal V (2013) Polypropylene nanocomposites with thermally stable phosphonium-and pyridinium-modified layered silicates: thermal, mechanical and gas barrier properties. J Thermoplast Compos Mater 26:1082–1099

Najafi A, Kord B, Abdi A, Ranaee S (2012) The impact of the nature of nanoclay on physical and mechanical properties of polypropylene/reed flour nanocomposites. J Thermoplast Compos Mater 25:717–727

Nandi S, Bose S, Mitra S, Ghosh AK (2012) Effect of maleic anhydride grafted polyethylene on engineering properties and morphology of fumed silica filled polyethylene blown films. J Plast Film Sheeting 28:207–227

Silvestre C, Duraccio D, Cimmino S (2011) Food packaging based on polymer nanomaterials. Prog Polym Sci 36:1766–1782

Siracusa V, Blanco I, Romani S, Tylewicz U, Dalla Rosa M (2012) Gas permeability and thermal behavior of polypropylene films used for packaging minimally processed fresh-cut potatoes: a case study. J Food Sci 77:E264–E272

Sliwa F, Charrier F, Marin G, Malet F (2012) Mechanical and interfacial properties of wood and bio-based thermoplastic composite. Compos Sci Technol 72:1733–1740

Taha I, Abdin YF (2011) Modeling of strength and stiffness of short randomly oriented glass fiber-polypropylene composites. J Compos Mater 45:1805–1821

Taşdemır M, Biltekin H, Caneba GT (2009) Preparation and characterization of LDPE and PP—wood fiber composites. J Appl Polym Sci 112:3095–3102

Youssef AM (2013) Polymer nanocomposites as a new trend for packaging applications. Polym Plast Technol Eng 52:635–660

Zahedi M, Pirayesh H, Khanjanzadeh H, Tabar MM (2013) Organo-modified montmorillonite reinforced walnut shell/polypropylene composites. Mater Des 51:803–809

Zhong Y, Janes D, Zheng Y, Hetzer M, De Kee D (2007a) Mechanical and oxygen barrier properties of organoclay-polyethylene nanocomposite films. Polym Eng Sci 47:1101–1107

Zhong Y, Poloso T, Hetzer M, De Kee D (2007b) Enhancement of wood/polyethylene composites via compatibilization and incorporation of organoclay particles. Polym Eng Sci 47:797–803

Chapter 12
Rubber-Based Nanocomposites and Significance of Ionic Liquids in Packaging Applications

Umaima Gazal, Imran Khan, Mohd Amil Usmani, Aamir H. Bhat and M.K. Haafiz Mohamad

Abstract Rubber nanocomposites have currently fascinated vast attention owing to their flexibility and modulus, superior chemical and thermal stabilities. These enhanced properties compose rubber nanocomposites striking in different applications such as space industry, agriculture, medical, and packaging. This chapter focuses on diverse aspects of rubber nanocomposites with their filler properties. Nanofillers are introduced into rubber in accumulation to conventional fillers to increase the presentation plus different efficient properties of the rubber matrix depending on the applications. In the recent year, Ionic liquids (ILs) have gained much interest in research and development because of various dominating physical properties and that may be useful solvent for processing rubber for packaging.

Keywords Rubber nanocomposite · Fillers · Ionic liquids · Packaging

---

U. Gazal
School of Computational and Integrative Sciences, Jawaharlal Nehru University,
110067 Munirka, New Delhi, India

I. Khan
Department of Chemistry, College of Science, Sultan Qaboos University, PC 123,
Muscat PO Box 36 Oman

I. Khan (✉)
CICECO-Aveiro Institute of Materials, Department of Chemistry,
University of Aveiro, 3810-193 Aveiro, Portugal
e-mail: imran.pchr@gmail.com; imrank@squ.edu.om

M.A. Usmani
Department of Chemistry, Gandhi Faiz-E-Aam College, 242001 Shahjahanpur,
Uttar Pradesh, India

A.H. Bhat
Department of Fundamental and Applied Sciences, Universiti Teknologi Petronas Malaysia,
Bandar Seri Iskandar, 31750 Tronoh, Perak Darul Ridzuan, Malaysia

M.K.H. Mohamad
Bioresource, Paper and Coatings Technology Department, School of Industrial Technology,
Universiti Sains Malaysia, 11800 Penang, Malaysia

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_12

12.1 Introduction

Nanocomposites attributed to all kind of composite material having fillers in the nanometer size variety, as a minimum one dimension. Rubber nanocomposites have become a pursuit area of research globally, due to its unique properties and applications in various fields. Rubber is considered as one of the most promising polymeric material which consists of good elasticity, flexibility, and low hardness. It is also acknowledged as an absolute matrix for nanocomposites. Due to its high molecular weight, it is favorable with respect to shearing which promotes the flaking separately of the clay layers. Several scientists later imply this theory for nanocomposite based on epoxidized natural rubber, styrene-butadiene rubber, isobutylene-isopropene rubber, polybutadiene rubber, and natural rubber. In all the applications of rubbers, these are strengthened and filled with high concentrations of hard and tiny particles so as to recover the mechanical properties for example abrasion resistance, functional properties such as electrical/thermal conductivity and gas barrier, elastic modulus, and hardness (Wolff 1996; Dannenberg 1975). Rubbers containing fillers have been broadly useful in different engineering fields because of their excellent mechanical properties, oil resistance, and thermal stability. In latest progress, rubber nanocomposites prepared out of nanofillers were set up to display notable property enrichment compared to conventional micro composites (Novak 1993; Vollath and Szabó 2004) which are completed with conventional fillers. The most common used fillers in rubber industry are silica and carbon black. It has been reported from previous studies that incorporation of very small quantity of particulate fillers such as carbon black can initiate outstanding changes in the physical and mechanical properties of rubber (An et al. 2010; Li et al. 2012). Energizing with diverse types of fillers is necessary for rubbers, as unfilled rubbers have extremely limited applications owing to their deprived physical and mechanical properties. The inclusion of fillers capable of modifying the mechanical properties of rubber such as hardness, tensile strength, stiffness, modulus, stress-softening effect, tearing, wearing resistance, etc. Many polymeric materials exhibit rubbery behavior. In these materials, natural rubber was the first material which was used in industries. It possesses numerous alluring properties which include its good dynamic property, high flexibility, low hysteresis, cheap cost, etc. (Teh et al. 2004). Today, it is integrated by a variety of synthetic materials which have establish position in souk due to such uniqueness as low air permeability, resistance to burning, heat resistance, oil resistance, and resistance to burning. Rubbery material is not restricted up to scholarly awareness. It played a vital role in everyday life, specifically in engineering applications, of which the pneumatic tire is the finest recognized exemplar. The present chapter represents the significance and exclusive position of rubber nanocomposites in various research fields as well as its variety of applications in the packaging industry.

12.2 Natural Rubber Nanocomposites

It is always the first choice of elastomers for numerous factors that involve low heat make up such as vibration dampers, bearings, springs, engine mountings, carcasses of passenger car tires and in large tires. Natural rubber is harvested as latex, which is a colloidal diffusion in an aqueous medium also emanate from the *Hevea Brasiliensis* trees (Khan and Poh 2011). The chemical name of natural rubber is cis-1, 4 polyisoprene. The size of the rubber particles is 3 µm. The molecular weight is in the series of 10^4–10^7 g/mol, depending on the period of the rubber tree, the process of rubber separation, weather conditions, and different extra factors (Roberts et al. 1988; Khan and Poh 2010a, b). Natural rubber has wonderful properties which are displayed in Fig. 12.1.

Rubbers are frequently resistant among mineral fillers to facilitate with extensive improvement in potency and rigidity (Khan and Poh 2010a, b, 2012a, b; Poh and Khan 2012; Khan et al. 2013, 2017; Khan and Bhat 2014). Lacking the filler, rubber formulations would capitulate flexible goods having expandable properties although extremely small force (Khan and Poh 2011). The degree of property development depends on a number of parameters as well as the range of particles, their level of diffusion, their feature proportion, and direction in the medium, and the extent of bond with the rubber chains (Bokobza 2004). Currently, nanometer-scale reinforcing particles have engrossed substantial consideration from rubber scientists due to their tiny range and the matching enhance in the surface area achieving the requisite usual properties at low filler loadings. From some previous time, rubber nanocomposites based on natural rubber have known rising consideration and have been broadly discussed with researchers in view of the

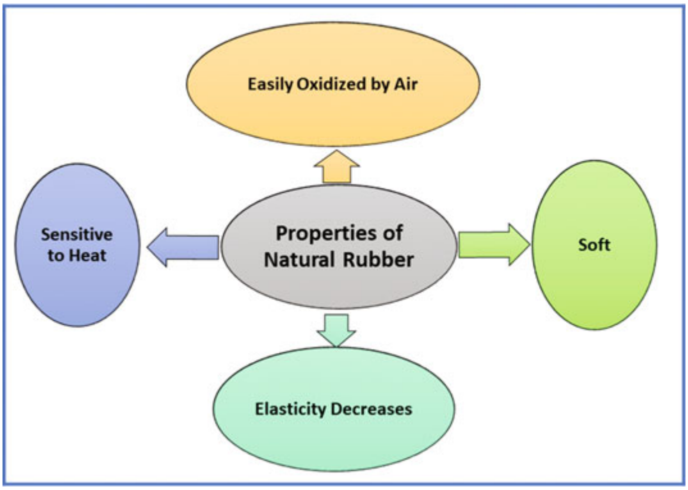


Fig. 12.1 Properties of natural rubber

number of possible nanofillers such as talc, silica, carbon-based fillers, and layered silicates. Rubber nanocomposites based on natural rubber with layered silicates have been a center of interest for scientists in current years. Nanocomposites have received considerable attention in recent years because of their diverse nanometer-sized filler particles and a series of special performance. Scientist had prepared and studied nanocomposites of montmorillonite clay/natural rubber with intercalation of fatty acids (Rooj et al. 2012). The intercalation of fatty acids was completed in an inner mixture, yield extended organo-montmorillonite. Integration of natural rubber with diverse quantity of extended organo-montmorillonite clay was finished in an unlock two-roll mixing mill at 90 °C. The biggest interlayer gap in the company of fatty acid promoted the exfoliation of clay reserves in natural rubber matrix. One more example of natural rubber nanocomposites has been prepared is the palygorskite-cerium oxide filled rubber nanocomposites (Zhao et al. 2012). Palygorskite cerioum oxide was customized with cetyl-trimethylammonium bromide to be used as filler for good presentation natural rubber/styrene butadiene rubber nanocomposites. The organic variation of palygorskite cerium oxide leads to high-quality compatibility with natural rubber/styrene butadiene rubber matrix. The mechanical properties of nanocomposites were extensively enhanced.

12.3 Fillers in Rubber Nanocomposites

Fillers are moderately economical, solid substances that are extra in comparatively big volumes to polymers to regulate mechanical strength, color, surface, cost, weight, volume, processing behavior, and other properties. The choice of filler used in rubber formulation completely depends on the property necessity of the end-product. These are used to increase the presentation-associated properties of rubbers. The fillers used in rubber compounding are symbolized through their stiffening property, which limits from partially dynamic, inactive to extremely active fillers. Generally, fillers are classified as active fillers and non-active fillers. This type of arrangement usually reveals the control of the filler on the composite thickness and on the mechanical properties of the finishing artifact, such as elongation at break, tear resistance, abrasion, tensile strength, and hardness. The enhanced mechanical properties of the rubber nanocomposites not only depend on the inclusion of solid fillers but also depend on the connections refined among the matrix and the filler. These connections can fluctuate from tough (chemical bond) to transitional (dipole interactions and hydrogen bonding) to weak Van der Waals. Recognized active fillers, for example silica and carbon black, have a better control on the substantial properties of a rubber matter than inactive fillers, similar to calcium carbonate and clay (Jincheng et al. 2005). The one of the major industry, the tire built-up units, uses fillers resembling nano-zinc oxide, nano-black nano-silica, etc., for presentation progress. The structure, surface, and particle-size characteristics were the three factors that manipulate and assist to choose the stiffening capability of the stiffening matter. From the above three

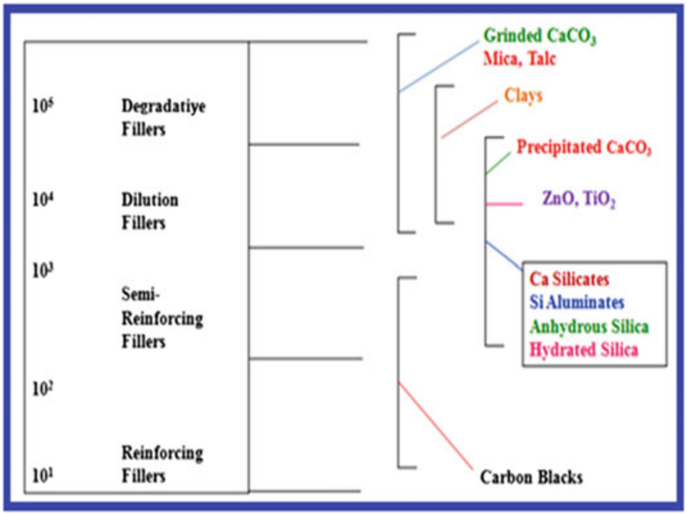


Fig. 12.2 Arrangement of fillers based on particle size (Leblanc 2002)

characteristics, the particle size of filler has the most significant influence (Franta 2012). The normal particle size is naturally the first feature of a filler to be measured (Móczó and Pukánszky 2008).

The fillers are classified by their particle sizes as shown in Fig. 12.2. The latest production of nanosized fillers has appeared in reaction to the significance of small-sized particles in the research of efficient, good act composites with refined architectures. In accumulation to normal particle size, the particle-size division too has a major result on support. Particulate fillers with a wide particle-size sharing have superior packing in the rubber matrix, which outcome in a lesser viscosity than that implemented by an equivalent volume of filler with a contracted particle-size division.

12.4 Carbon Black/Silica as Fillers

Carbon black aggregated molecules of basic carbon which are partially graphitic in composition. It is mainly used as filler to develop the act of rubber composites. It is a colloidal structure of constituent carbon. It is a filler to simply integrate into rubber, generate bound rubber also companionable among hydrocarbon rubber with polybutadiene rubber (BR), natural rubber (NR), isobutylene isoprene rubber (IIR), and styrene butadiene rubber (SBR). The adsorption of rubber on carbon black form bound rubber willingly occur throughout incorporation and as well behind incorporation (Wolff 1996). The most significant factor of carbon black is its outer definite surface area. Its shell consists of simply a small amount of functional

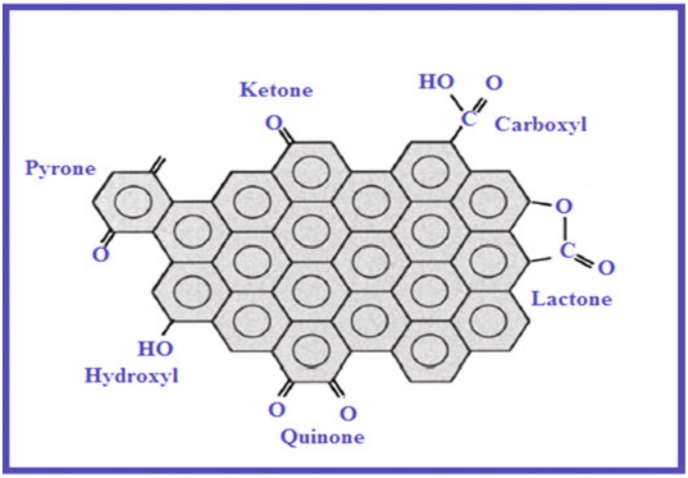
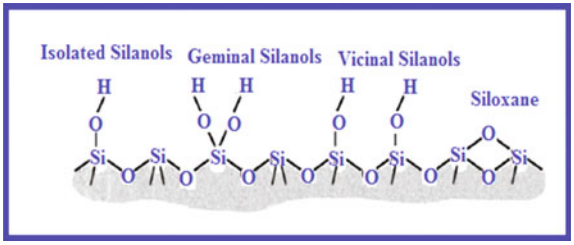


Fig. 12.3 Functional groups on the surface of carbon black (Leblanc 2002)

Fig. 12.4 Three types of silanol groups on silica surface (Leblanc 2002)



groups as revealed in Fig. 12.3 (Leblanc 2002). The particles of carbon black are not distinct but are merged clusters of character particles. It is formed by converting any liquid or gaseous hydrocarbon to carbon and hydrogen through thermal decomposition or combustion (Kraus 1976).

It has reactive organic groups on the shell that source resemblance to rubber. Inclusion of carbon black into rubber gives improved modulus, abrasion resistance, enhanced fatigue, and superior common technical properties. It is broadly used as black pigments for toners, as filler to facilitate electric conductivity, and about 70% of the total quantity of carbon black is used in the tire production.

The first siliceous filler was recognized in 1939 (Kraus 1976). It is an unstructured matter, containing oxygen and silicon atoms linked in an unusual 3D network of Si–O–Si with silanol groups (Si–OH) there within and on the shell in Fig. 12.4. The polar silanol groups guide to a hydrophilic surface.

Above Figure shows typical three kinds of surface hydroxyl groups i.e., isolated silanols, germinal silanols, and vicinal silanols (Wagner 1976). This is the reason it is not companionable with hydrophobic rubbers. Its particles shape tough filler–filler relations with further particles to create agglomerates and aggregates. Besides this, it is also used in shoe soles for civilizing the confrontation to tearing and to wearing. It is also useful in improving the heat aging resistance and tear strength in a broad range of artificial rubber goods, include motor and dock mounts, bumper pads, rubber rolls, hoses, and power transmission belts. These days, the use of rubber depends on discovery of the optimal stability among quantity and kind of filler required for achieving greatest development in mechanical properties (Bokobza and Rapoport 2002). The latest group of fillers in tire applications has been introduced which are known as the nano structures carbon black and nano silica. Nano composition black is a family of fresh carbon black characterized by an irregular surface and improved filler–polymer interactions. This kind of black carbon perfectly meets truck tire necessities, because it provides trample bear in accumulation to small hysteresis. Production of nano silica has gained a lot of interest because of its advanced properties with a large amount of broadly used like filler in rubber. This silica nano-particle shows better mechanical-physico applications as well as development in the dispensation performance.

12.5 Carbon Nanotubes/Graphene Fillers in Rubber Nanocomposites

Carbon nanotubes have a noticeable appearance among the nanofillers everyday as a result of their exceptional structures. Carbon nanotube is a cylinder-designed solid, prepared of carbon, having a width evaluating on the nanometer scale. It has also been reflected as one of the best striking applicants for instructing numerous properties to rubber. It consists of various structures, different in thickness, length as well as in number of layers and in form of helicity. It is created by following methods such as chemical vapor deposition, laser ablation, and arc discharge. The excellence and profit of carbon nanotube powerfully be contingent on the purification and synthesis techniques and on the specific growth conditions recycled (Shaffer and Sandler 2007). Mainly used nanotubes are multi-walled nanotubes (MWCNTs) and single-walled nanotubes (SWCNTs). Carbon nanotube comprises of inimitable mechanical and electrical properties. Carbon nanotube develops the thermal and electrical conductivity of rubbers. Its electrical properties are imperative and reflected to be exactly important in the tire industry as a cause for disintegrating inert charge. Interchanging the carbon black by carbon nanotubes better slide conflict and condensed abrasion of the tire. Carbon nanotube might deliver a faster, harmless, and ultimately inexpensive transport in the future. Scientists have studied the influence of alternate concentration of MWCNTs on the phase transition temperatures, mechanical properties, and thermal transport of polyisoprene rubber (Sagar et al. 2014). The impact of MWCNTs fillings on mechanical and electrical properties of MWCNTs-strengthened natural rubber composites has been reported (Bokobza 2012).

Graphene as well as its derivatives has been extensively investigated and considered as nanofiller of rubber nanocomposites (Sadasivuni et al. 2014). It is the two-dimensional allotrope of carbon and is measured as the structural component of carbon allotropes through diverse dimensionality. Amongst numerous nanocomposite methods, those of graphitic built fillers are significant because of their multi-functional performance. They can develop thermal and electrical conductivities, thermal stability, microwave absorption, tribiological and mechanical properties, gas barrier properties, and dielectric enactments of all rubber matrices (Sadasivuni et al. 2014). Rubber nanocomposites attain new specific belongings because of the existence of graphene-layered filler.

Rise in electrical conductivity as well as power of rubber nanocomposites is expressively better by adding of graphene filler, once equated to a normal nanofillers such as carbon, silicate, or other fillers. Though the strength of carbon nanotubes is alike to that of graphene; however, they are poorer in terms of conductive and thermal properties (Tung et al. 2009) and in terms of production cost. Moreover, it was perceived that this kind of filler can also show the character of an anti-aging agent (Yavari et al. 2010). Strengthening result of graphene oxide has been previously perceived in several types of rubbers as revealed in Table 12.1. It was established that the existence of graphene recovers the gas barrier properties and enriches the influence resistance, mechanical strength, resistance to cracking (Yavari et al. 2010) or might stimulus the vulcanization kinetic of rubbers. The effect of dispersion, the influence of the MLG-concentration on physical and flame retardant properties of multilayer graphene/chlorine–isobutene-isoprene rubber nanocomposites has been reported (Frasca et al. 2016).

12.6 Ionic Liquids in Rubber Nanocomposites

Ionic Liquids (ILs) are the organic salts, with unique properties, as for instance, good solvation capacity to dissolve a broad variety of compounds, a wide liquidus range, and extremely low vapor pressures (Rogers and Seddon 2003; Khan et al. 2015, 2016; Passos et al. 2014; Taha et al. 2016). These have been particularly investigated in organic synthesis and in further practice, for example, as bio-processing operations, gas separation, liquid–liquid extraction, as catalysts, and as a heat transfer fluid (Khan et al. 2014a, b, 2015; Govinda et al. 2015; Bhat et al. 2017). ILs are non-combustible, chemically and thermally constant and establish to be a talented substitute for conventional organic solvents. Ionic liquids can also provide numerous functions in the research of rubber nanocomposites. Homogenous division of fillers and improved ionic conductivity are two main reasons for the inclusion of ionic liquids in rubber composites, though the occurrence of ionic liquids might persuade several additional properties of rubber compounds. Scientists have studied that the doping rubbers with ionic liquids is a simple method to transform their decisive properties include antimicrobial, thermal, and mechanical as well as to organize composites through fine elasticity and high ionic conductivity. The possible applications of ionic liquids in rubber composites comprises to utilize as dispensation aids for the liquefy dispensation of filler/rubber composites (Weyershausen and Lehmann 2005), cure accelerators (Pernak et al. 2010; Przybyszewska and Zaborski 2010; Maciejewska et al. 2013; Khan et al. 2017), antistatic additives (Iwata et al. 2014; Roessler and Schottenberger 2014) and plasticizers that decrease the glass transition temperature of rubber matrix (Bermúdez et al. 2009). Only some applications of ionic liquids in the rubber

Table 12.1 Examples of graphene/rubber composites and their effects

Kind of rubber	Kind of fillers	Composite grounding techniques	Composite effects	References
Natural Rubber (NR)	Graphene Oxide (GO)	Latex compounding	GO take part in vulcanization method as well as improved cross-linking thickness of NR	Wu et al. (2013)
Ethylene propylene diene rubber (EPDM)	Graphene Oxide (GO)	Amalgamation of solution mixing and two-roll mill mixing	Improved the tensile strength, tensile modulus, elongation at break, and decreased thermal strength by GO loading	Chen et al. (2012)
Acrylonitrile butadiene rubber (NBR)	Unfunctionalized few layer Graphene (FLG) nanoplatelets.	Melt mixing	Improved the cure characteristics of NBR and improved tensile properties and gas barrier	Varghese et al. (2013)
Hydrogenated carboxylated acrylonitrile butadiene rubber (HXNBR)	Graphene Oxide (GO)	Amalgamation of solution mixing and two-roll mill mixing	Improved the tensile strength, modulus at 200% elongation and increased glass transition temperature (Tg) of HXNBR	Bai et al. (2011)
Carboxylated acrylonitrile butadiene rubber (XNBR)	Graphene Oxide (GO)	Mixing exfoliated GO aqueous diffusion with XNBR latex	Improved thermal diffusivity, thermal conductivity, and thermal stability	Wang et al. (2013)

composites as well as their authority on the feature properties are specified in Table 12.2.

It has been reported that the action of various ionic liquids (alkylimidazolium (allyl-, ethyl-, butyl-, hexyl-, and octyl-) salts containing chloride, tetraflouroborate, bromide, and hexa flourophosphate ions) that were used to advance the diffusion of coagent particles in peroxide-crosslinked hydrogenated acrylonitrile-butadiene rubber (HNBR). It was initiated that alkylimidazolium salts display a positive contact on the coagent diffusion in the rubber matrix. The outcome obtained for a sequence of tetraflouroborates representing that tensile strength and crosslink density of vulcanizates decrease with increase alkyl chain lengths (Maciejewska and Zaborski 2013). Currently, various studies were in print examined acrylonitrile butadiene rubber (NBR)/ionic liquid composites, due to the detail that NBR is usually defiant to fuel, oil as well as added chemicals. Its elasticity makes NBR a valuable material for numerous operations. Furthermore, NBR's capability to resist a

Table 12.2 Consequences of ionic liquids on the properties of rubber composites

Ionic liquids	Types of rubber and fillers	Properties of composite	References
1-methylimidazolium methacrylate (MimMa)	Styrene-butadiene rubber and precipitated silica	The addition of MimMa effectively improved silica dispersion and mechanical properties of rubber composites	Lei et al. (2010)
1-methyl-3-octylimidazolium chloride, 1-allyl-3 methyl imidazolium chloride, trihexyl tetradecyl phosphonium decanoate, 1-ethyl- 3 methyl imidazolium thiocyanate	Polybutadiene rubber, Solution-styrene butadiene rubber (SSBR), and MWCNTS	MWCNTS with ionic liquid 1-allyl-3methyl imidazolium chloride present a tough stage of support to an S-SBR/BR rubber matrix	Das et al. (2009)
1-butyl 3-methyl imidazolium bis (triflouromethyl sulphonyl) imide (BMIM TFSI)	Solution-styrene butadiene rubber (S-SBR) and MWCNTS	The stiffen cause of MWCNTS was not intense in the composites because of the plasticizing character of ionic liquids in nonpolar SSBR	Subramaniam et al. (2013)
1-methyl-3-butyl Imidazolium (BMIM TFSI)	Silicone rubber and Single walled carbon nanotubes (SWCNTS)	Ionic liquid gives the better dispersibility of the SWCNTS and advanced conductivity in the polymer matrix	Kim et al. (2012)
1-methylimidazolium mercaptopropionate, thiol ionic liquids, bis (1-methylimidazolium mercaptosuccinate)	Styrene butadiene rubber, and Halloysite nanotubes (HNTS)	Major development in mechanical properties and HNTS dispersion	Lei et al. (2011)

broad variety of temperatures makes it a perfect material particularly for acute functions. Researchers exposed better ionic conductivity of NBR/ionic liquid composites (Maciejewska and Zaborski 2013). Ionic liquids were used to develop the diffusion of silica in styrene-butadiene (SBR) composites. 1-methylimidazolidine methacrylate salt was initiated to polymerize by a radical-initiated mechanism and was effortlessly grafted on SBR chains through vulcanization (Lei et al. 2010). It has been reported that imidazolium ionic liquids can be used to diffuse single-walled carbon nanotubes in elastic composite materials (Fukushima and Aida 2007). The capability of ionic liquids to functionalize as well as to enhance the diffusion of carbon nanotubes has been effectively considered (Ma et al. 2010) and in diene elastomers (Das et al. 2009). Ionic liquids resulted in the improvement of a conductive polychloroprene rubber incorporating a low concentration of multi-walled carbon nanotubes (Subramaniam et al. 2011; Steinhauser et al. 2012).

12.7 Packaging Applications of Rubber Nanocomposites

The use of rubber for manufacturing nanocomposites has been rising due to its reversible irregularity. Packaging materials offer a way to save, defend, products, promote, and issue foods and former materials. They play an important function in how this merchandise arrives at the customers in a secure and nutritious variety with no compromise value. Normally, the packaging material might either be inflexible or elastic. Stiffed containers consist of plastic and glass bottles and wood boxes, tins, plastic pots, cans, jars, pottery, and tubes. They provide physical safety to the food within to facilitate is not providing by elastic packaging. Elastic packaging is the most important collection of resources that include plastic films, foils, and papers, and several types of vegetable fibers and cloths to be used to create packaging, sack unseal, or preserved bags. Packaging provisions were urbanized more than the existence to avoid the corrosion of foods through microbes ensuing from contact to humidity, air or pH changes related to the foods or its neighboring environment. Nearly, all aspect of everyday life involves rubber or plastics in various forms or the other. These comprise numerous free fitness reimbursements. They make easy fresh drinking water supply and permit medical policy range during surgical equipment, aseptic medical packaging, drips, and blister packs for pills. They supply packaging that reduces food wastage, for example in the use of adapted environment packaging that prolongs the existence of vegetables and meats (Mullan 2002). For packaging, mold deodorant compress bottles were introduced in 1947; in 1958, warm shrinkable films were urbanized from amalgamation styrene with synthetic rubber. Natural biopolymers can be used for the growth of ecological plus biomedical applications, in food packaging, in agriculture areas, drug delivery systems and pharmaceutical technologies (Valdés et al. 2014).

Ethylene propylene diene rubber (EPDM) is a very multipurpose rubber due to its feature of high resistant to heat, ozone, and weather and also to polar substances and steam. It is an extremely attractive product and used commercially, because it displays oxygen, heat, and ozone resistance in a good amount because of the low level of unsaturation. EPDM is highly used for roof membrane linings, extruded windows gaskets, and the sealing systems which are automotive. Present day, thermoplastic rubbers are one of the most versatile plastics used in the market. It is a substantial mixture of polymers like rubber and plastic. They consist of the features and properties of both rubber and plastic. The thermoplastic rubbers have become a vital part of the polymer industry. Also widely used in packaging applications area from plastic wrap to bottles. They have numerous applications such as food packaging, cling films, water sealing rubbers, ring gaskets, flexible tubing for various applications, nebulizers, footwear, automobile parts, household goods, etc. Polyolefins, Polystyrenes, are recognized as thermoplastic rubber materials.

Table 12.3 Brief description of rubber nanocomposites and their marketable products

Applications	Uniqueness	Nanocomposites	Marketable product
Packaging	Improved: Barrier properties strength modulus	Polyolefin Nylon	Containers, packaging, and multi layer films
Electronics/energy	Environmental stability and conductivity	Silicone Polyurethane	Dielectric elastomer actuators and thin films capacitors in integrated circuits
Automotive	More simply recycled, Excellent impact properties, Stiffer, lighter, stronger, and less brittle	Rubber, Polyolefin, Nylon	Full line, tire side wall, cover engine, timing belt, and cover barrier

Polystyrene is the generally inexpensive and extensively used thermoplastic rubber for manufacturing diverse type of foam and packaging materials. Polyolefins are enormously flexible, chemically inert, especially light weight, and non-toxic. Polyolefins block copolymers are mainly injection molded and can be formed in several shapes similar to wire, cast, or film. The films are most frequently used in food packaging and medicine packaging. Various foods and beverages, for instance isotonic sport drinks, beer, dairy products, and juices require packaging in resources, provide a high wall to oxygen. In medical applications, thermoplastic rubber materials are occasionally purposely engineered for high-barrier applications. These materials are generally used as medical tool mechanism, and for a variety of packages such as blown containers, tubes, sheet materials, and molded closures (Kutz 2003). While the prospective for the industrial application of nanocomposites is massive, the genuine application has been taking place at a very slow rate. But, it is obvious that industrial applications of nanocomposites are still in their immaturity, but if the sell forecasts are exact, nanocomposites could revolve out to be an important impact. Diffusion of nano-scale strengthening in polymers is previously ingoing the market in automotive and packaging applications though in a short report approach and slower than had been expected. However, that rate is likely to expedite radically (Table 12.3).

12.8 Conclusion

Rubber nanocomposites symbolize a good number of talented classes of materials of the history and established a lot of awareness because of an important enhancement in the mechanical and barrier properties in accumulation to the easiness of research during the effortless process for packaging applications. The latent advantage of natural biopolymer-blended nanocomposites is the optimistic ecological contact with esteem to eventual disposability. The use of thermoplastic rubber material is constantly rising for vast applications in everyday life. Painless recycle and repair is the feature that prominence the use of thermoplastic rubber regularly. Fillers played very imperative function in rubber nanocomposites as they improved the presentation. Reinforcement by nanoparticles has fascinated a large amount of concentration in the industrialization of rubber nanocomposites because of the enviable nanofiller properties. The making of rubber materials with enhanced thermal, mechanical properties, and low gas permeability using ecologically satisfying process is extremely smart in diverse branches of production. Ionic liquids are regarded as environmentally responsive solvents as they are ecological, non-volatile, and predictable to be substitute solvents that are striking and vigorous than conservative organic solvents that are unstable and contaminated. Ionic liquids have engrossed growing consideration because of their tempting chemical and physical properties and are measured practical dispensation aid in the functional rubber composites by prohibited morphological, mechanical, and ionic conductivity parameter. Ecofriendly rubber nanocomposites are required for different packaging applications to evade harmful impact on human healthiness.

References

An X, Simmons T, Shah R, Wolfe C, Lewis KM, Washington M, Nayak SK, Talapatra S, Kar S (2010) Stable aqueous dispersions of noncovalently functionalized graphene from graphite and their multifunctional high-performance applications. Nano Lett 10(11):4295–4301

Bai X, Wan C, Zhang Y, Zhai Y (2011) Reinforcement of hydrogenated carboxylated nitrile–butadiene rubber with exfoliated graphene oxide. Carbon 49(5):1608–1613

Bermúdez M-D, Jiménez A-E, Sanes J, Carrión F-J (2009) Ionic liquids as advanced lubricant fluids. Molecules 14(8):2888–2908

Bhat AH, Khan I, Bhat IUH, Soleimani H, Usmani MA (2017). Mechanism of heat transfer with nanofluids for the application in oil wells. pp 175–192

Bokobza L (2004) The reinforcement of elastomeric networks by fillers. Macromol Mater Eng 289 (7):607–621

Bokobza L (2012) Multiwall carbon nanotube-filled natural rubber: electrical and mechanical properties. System 1:2

Bokobza L, Rapoport O (2002) Reinforcement of natural rubber. J Appl Polym Sci 85(11):2301–2316

Chen B, Ma N, Bai X, Zhang H, Zhang Y (2012) Effects of graphene oxide on surface energy, mechanical, damping and thermal properties of ethylene-propylene-diene rubber/petroleum resin blends. Rsc Advances 2(11):4683–4689

Dannenberg E (1975) The effects of surface chemical interactions on the properties of filler-reinforced rubbers. Rubber Chem Technol 48(3):410–444

Das A, Stöckelhuber K, Jurk R, Fritzsche J, Klüppel M, Heinrich G (2009) Coupling activity of ionic liquids between diene elastomers and multi-walled carbon nanotubes. Carbon 47 (14):3313–3321

Franta I (2012) Elastomers and rubber compounding materials, vol 1. Elsevier, Amsterdam

Frasca D, Schulze D, Wachtendorf V, Morys M, Schartel B (2016). Multilayer graphene/chlorine-isobutene-isoprene rubber nanocomposites: the effect of dispersion. Polym Advan Technol

Fukushima T, Aida T (2007) Ionic liquids for soft functional materials with carbon nanotubes. Chemistry—European J 13(18):5048–5058

Govinda V, Vasantha T, Khan I, Venkatesu P (2015) Effect of the alkyl chain length of the cation on the interactions between water and ammonium-based ionic liquids: experimental and COSMO-RS studies. Ind Eng Chem Res 54(36):9013–9026

Iwata T, Tsurumaki A, Tajima S, Ohno H (2014) Bis (trifluoromethanesulfonyl) imide-type Ionic Liquids as excellent antistatic agents for polyurethanes. Macromol Mater Eng 299(7):794–798

Jincheng W, Yuehui C, Jihu W (2005) Novel reinforcing filler: application to natural rubber (NR) system. J Elastomers Plast 37(2):169–180

Khan I, Bhat AH (2014) Micro and nano calcium carbonate filled natural rubber composites and nanocomposites. In: Natural rubber materials, vol 2. Composites and nanocomposites. The Royal Society of Chemistry, London, pp 467–487

Khan I, Poh BT (2010a) The effect of silica on the peel adhesion of epoxidized natural rubber-based adhesive containing coumarone-indene resin. Polym-Plast Technol Eng 49 (13):1356–1360

Khan I, Poh BT (2010b) Effect of silica on viscosity, tack, and shear strength of epoxidized natural rubber-based pressure-sensitive adhesives in the presence of coumarone-indene resin. J Appl Polym Sci 118(6):3439–3444

Khan I, Poh B (2011) Natural rubber-based pressure-sensitive adhesives: a review. J Polym Environ 19(3):793–811

Khan I, Poh B (2012a) Material properties and influence of molecular weight and testing rate on adhesion properties of epoxidized natural rubber-based adhesives. J Polym Environ 20(1):132–141

Khan I, Poh B (2012b) Statistical analysis on the effect of the molecular weight and testing rate on peel strength of epoxidized natural rubber (ENR 25)-based adhesives. J Elastomers Plast 44 (5):453–475

Khan I, Poh BT, Lee K (2013) Material properties and statistical analysis of natural rubber-based adhesives. J Polym Environ 21(3):833–849

Khan I, Kurnia KA, Mutelet F, Pinho SP, Coutinho JA (2014a) Probing the interactions between ionic liquids and water: experimental and quantum chemical approach. J Phys Chem B 118 (7):1848–1860

Khan I, Kurnia KA, Sintra TE, Saraiva JA, Pinho SP, Coutinho JAP (2014b) Assessing the activity coefficients of water in cholinium-based ionic liquids: experimental measurements and COSMO-RS modeling. Fluid Ph Equilib 361:16–22

Khan I, Batista ML, Carvalho PJ, Santos LM, Gomes JR, Coutinho JA (2015) Vapor-liquid equilibria of imidazolium ionic liquids with cyano containing anions with water and ethanol. J. Phys. Chem. B 119(32):10287–10303

Khan I, Taha M, Pinho SP, Coutinho JAP (2016a) Interactions of pyridinium, pyrrolidinium or piperidinium based ionic liquids with water: measurements and COSMO-RS modelling. Fluid Ph Equilib 414:93–100

Khan I, Umapathi R, Neves MC, Coutinho JA, Venkatesu P (2016b) Structural insights into the effect of cholinium-based ionic liquids on the critical micellization temperature of aqueous triblock copolymers. Phys. Chem. Chem, Phys

Khan I, Usmani MA, Bhat AH, Rather JA, Hassan SI, Mumam A (2017) Recent progress on rubber based biocomposites: from carbon nanotubes to ionic liquids. In: Jawaid M, Sapuan SM, Alothman OY (eds) Green biocomposites: manufacturing and properties, Springer International Publishing, Cham pp 91–123

Kim TA, Kim HS, Lee SS, Park M (2012) Single-walled carbon nanotube/silicone rubber composites for compliant electrodes. Carbon 50(2):444–449

Kraus G (1976) Science and technology of rubber. In FR Eirich (Ed) Marcel Dekker, NY

Kutz M, (2003) Standard handbook of biomedical engineering and design. McGraw-Hill, New York

Leblanc JL (2002) Rubber–filler interactions and rheological properties in filled compounds. Prog Polym Sci 27(4):627–687

Lei Y, Tang Z, Guo B, Zhu L, Jia D (2010) Synthesis of novel functional liquid and its application as a modifier in SBR/silica composites. Express Polym Lett 4:692–703

Lei Y, Tang Z, Zhu L, Guo B, Jia D (2011) Functional thiol ionic liquids as novel interfacial modifiers in SBR/HNTs composites. Polymer 52(5):1337–1344

Li X, Xia Y, Li Z, Xia Y (2012) Three-dimensional numerical simulations on the hyperelastic behavior of carbon-black particle filled rubbers under moderate finite deformation. Comput Mater Sci 55:157–165

Ma P-C, Siddiqui NA, Marom G, Kim J-K (2010) Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review. Compos A Appl Sci Manuf 41 (10):1345–1367

Maciejewska M, Zaborski M (2013) Ionic liquids applied to improve the dispersion of coagent particles in an elastomer. J Compos

Maciejewska M, Walkiewicz F, Zaborski M (2013) Novel ionic liquids as accelerators for the sulfur vulcanization of butadiene–styrene elastomer composites. Ind Eng Chem Res 52 (25):8410–8415

Móczó J, Pukánszky B (2008) Polymer micro and nanocomposites: structure, interactions, properties. J Ind Eng Chem 14(5):535–563

Mullan W (2002). Science and technology of modified atmosphere packaging. See http://www.dairyscience.info/map-science.asp

Novak BM (1993) Hybrid nanocomposite materials—between inorganic glasses and organic polymers. Adv Mater 5(6):422–433

Passos H, Khan I, Mutelet F, Oliveira MB, Carvalho PJ, Santos LMNBF, Held C, Sadowski G, Freire MG, Coutinho JAP (2014) Vapor-liquid equilibria of water plus alkylimidazolium-based ionic liquids: measurements and perturbed-chain statistical associating fluid theory modeling. Ind Eng Chem Res 53(9):3737–3748

Pernak J, Walkiewicz F, Maciejewska M, Zaborski M (2010) Ionic liquids as vulcanization accelerators. Ind Eng Chem Res 49(10):5012–5017

Poh BT, Khan I (2012) Effect of test rate on adhesion properties of smr l, enr-25 and enr-50-based pressure-sensitive adhesives. J Adhes Sci Technol 26(6):873–881

Przybyszewska M, Zaborski M (2010) Effect of ionic liquids and surfactants on zinc oxide nanoparticle activity in crosslinking of acrylonitrile butadiene elastomer. J Appl Polym Sci 116 (1):155–164

Roberts AD (1988) Natural rubber science and technology, Oxford University Press, Oxford

Roessler A, Schottenberger H (2014) Antistatic coatings for wood-floorings by imidazolium salt-based ionic liquids. Prog Org Coat 77(3):579–582

Rogers RD, Seddon KR (2003) Ionic liquids–solvents of the future? Science 302(5646):792–793

Rooj S, Das A, Stöckelhuber KW, Mukhopadhyay N, Bhattacharyya AR, Jehnichen D, Heinrich G (2012) Pre-intercalation of long chain fatty acid in the interlayer space of layered silicates and preparation of montmorillonite/natural rubber nanocomposites. Appl Clay Sci 67:50–56

Sadasivuni KK, Ponnamma D, Thomas S, Grohens Y (2014) Evolution from graphite to graphene elastomer composites. Prog Polym Sci 39(4):749–780

Sagar S, Iqbal N, Maqsood A, Bassyouni M (2014) MWCNTS incorporated natural rubber composites: thermal insulation, phase transition and mechanical properties. Intern J Eng Technol 6(3):168

Shaffer MS, Sandler JK (2007) Carbon nanotube/nanofibre polymer composites. In: Processing and properties of nanocomposites, World Scientific, Singapore, pp 1–59

Steinhauser D, Subramaniam K, Das A, Heinrich G, Klüppel M (2012) Influence of ionic liquids on the dielectric relaxation behavior of CNT based elastomer nanocomposites. Express Polym Lett 11:927

Subramaniam K, Das A, Heinrich G (2011) Development of conducting polychloroprene rubber using imidazolium based ionic liquid modified multi-walled carbon nanotubes. Composites Science and Technology 71(11):1441–1449

Subramaniam K, Das A, Simon F, Heinrich G (2013) Networking of ionic liquid modified CNTs in SSBR. Eur Polymer J 49(2):345–352

Taha M, Khan I, Coutinho JA (2016a) Complexation and molecular modeling studies of europium (III)—gallic acid-amino acid complexes. J Inorg Biochem 157:25–33

Taha M, Khan I, Coutinho JAP (2016b) Coordination abilities of good's buffer ionic liquids toward europium(iii) ion in aqueous solution. J Chem Thermodyn 94:152–159

Teh P, Ishak ZM, Hashim A, Karger-Kocsis J, Ishiaku U (2004) Effects of epoxidized natural rubber as a compatibilizer in melt compounded natural rubber–organoclay nanocomposites. Eur Polymer J 40(11):2513–2521

Tung VC, Allen MJ, Yang Y, Kaner RB (2009) High-throughput solution processing of large-scale graphene. Nat Nanotechnol 4(1):25–29

Valdés A, Mellinas AC, Ramos M, Garrigós MC, Jiménez A (2014) Natural additives and agricultural wastes in biopolymer formulations for food packaging. Front Chem 2

Varghese TV, Kumar HA, Anitha S, Ratheesh S, Rajeev R, Rao VL (2013) Reinforcement of acrylonitrile butadiene rubber using pristine few layer graphene and its hybrid fillers. Carbon 61:476–486

Vollath D, Szabó DV (2004) Synthesis and properties of nanocomposites. Adv Eng Mater 6 (3):117–127

Wagner M (1976) Reinforcing silicas and silicates. Rubber Chem Technol 49(3):703–774

Wang J, Jia H, Tang Y, Ji D, Sun Y, Gong X, Ding L (2013) Enhancements of the mechanical properties and thermal conductivity of carboxylated acrylonitrile butadiene rubber with the addition of graphene oxide. J Mater Sci 48(4):1571–1577

Weyershausen B, Lehmann K (2005) Industrial application of ionic liquids as performance additives. Green Chem 7(1):15–19

Wolff S (1996) Chemical aspects of rubber reinforcement by fillers. Rubber Chem Technol 69 (3):325–346

Wu J, Xing W, Huang G, Li H, Tang M, Wu S, Liu Y (2013) Vulcanization kinetics of graphene/natural rubber nanocomposites. Polymer 54(13):3314–3323

Yavari F, Rafiee M, Rafiee J, Yu Z-Z, Koratkar N (2010) Dramatic increase in fatigue life in hierarchical graphene composites. ACS Appl Mater Interfaces 2(10):2738–2743

Zhao G, Shi L, Feng X, Yu W, Zhang D, Fu J (2012) Palygorskite-cerium oxide filled rubber nanocomposites. Appl Clay Sci 67:44–49

Chapter 13
Proteins as Agricultural Polymers for Packaging Production

Showkat Ahmad Bhawani, Hasnain Hussain, Othman Bojo and Sim Siong Fong

Abstract Proteins are natural heteropolymers and are most vital nutrients essential for human survival and life. Proteins generally exist in nature either in the form of fibrous proteins (water insoluble) or in the form of globular proteins (water soluble). Proteins are also available abundant in nature and are biodegradable. Proteins provide a broad spectrum of functional and structural properties because of the presence of polar and nonpolar amino acids and are therefore ideal raw materials for the production of bioplastics used for packaging materials. At present, a number of protein-based films are produced for the purpose of packaging of food. The protein based films possess some unique characteristics such as; excellent optical properties (gloss and transparency), are good fat barriers, at low and intermediate humidity possess an excellent oxygen and organic vapor barrier and have moderate mechanical properties. The contents of this chapter are as follows: introduction, proteins for packaging materials, processing methods, shaping agents, and properties.

Keywords Proteins · Packaging materials · Dry process · Wet process

---

S.A. Bhawani (✉) · S.S. Fong
Department of Chemistry, Faculty of Resource Science and Technology, UNIMAS,
94300 Kota Samarahan, Sarawak, Malaysia
e-mail: sabhawani@gmail.com

H. Hussain
Department of Molecular Biology, Faculty of Resource Science and Technology, UNIMAS,
94300 Kota Samarahan, Sarawak, Malaysia

O. Bojo
Department of Aquatic Science, Faculty of Resource Science and Technology, UNIMAS,
94300 Kota Samarahan, Sarawak, Malaysia

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_13

13.1 Introduction

Proteins are natural heteropolymers composed of more than 100 amino acid residues (Nur Hanani et al. 2014) arranged in different combinations to produce thousands of different proteins (Guilbert and Cuq 2005). Proteins possess a broad spectrum of functional and structural properties due to the presence of many polar and nonpolar amino acids (Gulbert and Cuq 2005). Proteins can be considered as essential and ideal raw materials for bioplastic production. Initially in 1930s, proteins were utilized for production of plastic materials and remained active until 1940. Mainly, milk casein, soy, and corn zein were the raw materials for the production of plastic during this era (Verbeek and Burg 2009). Proteins are therefore considered as ideal biomaterials for the production of different kinds of polymer networks (Guilbert and Cuq 2005). Plant-derived proteins are viable sources of raw materials for bioplastic industry (Irrisin-Mangata et al. 2001) because of low cost, abundant in nature, renewable, and biodegradable.

A great variety of different agricultural and medicinal films have been produced from plant-derived (gluten, zein) and animal-derived (collagen, gelatin, etc.) proteins. The corn zein proteins have been utilized in the form of a film to preserve dry and fresh food, vitamins, and in various medicinal applications. A simple example of film derived from corn zein is forsame optaglaze band produced by opta food integrity Inc. (Cuq et al. 1998a, b). Proteins can be modified into different structures such as in the form of a film (Bourtorm 2008) by denaturation process under heat, acid, alkali, and other solvents. The protein-based films are poor water resistant and possess lower mechanical strength as compared to synthetic films but are superior than polysaccharides with the ability to form films and exhibit greater mechanical and barrier properties (Cuq et al. 1998a, b). The properties (physical and chemical) of protein-based films are greatly influenced by the composition of amino acids, amphiphilic properties, electrostatic charge as well as change in the secondary, tertiary, and quaternary structures due to heat, pressure, irradiation, acid, alkali, mechanical change, etc. (Krochta et al. 1994). Therefore, proteins are considered as good film-forming structures with excellent gas and lipid barrier properties (Popović et al. 2012).

Protein-based packaging materials possess a variety of properties that have attracted a great attention in packaging of food. They have excellent optical properties (gloss and transparency), with selective permeability to gasses, good fat barriers and with moderate mechanical properties. The main drawback of protein-based packaging materials is their high sensitivity toward the water. This compromised their mechanical properties such as oxygen barrier and their integrity (Hernandez-Munoz et al. 2005). The hydrophilic nature of protein-based materials is the main reason for the production of active packaging materials for delivering the functional compounds into the materials (Lopez-Rubio et al. 2004). This is because the mass transfer properties were also affected by water. In this way, the protein-based films are able to release active compound into the hydrophobic foods (Hu et al. 2012) as compared to other materials such as polypropylene (Wessling et al. 1999). This chapter contributes toward the production of packaging materials from various sources of proteins and discussed different processing methods for the production and also the properties of packaging materials.

13.2 Proteins for Packaging Materials

The following proteins are used as agricultural polymers for packaging materials.

13.2.1 Corn Zein

The chemistry, properties, and uses of corn have been reviewed by Shukla and Cheryan (2001). The zein basically consists of two units viz. α-zein and β-zein, both are soluble in ethanol at different concentrations; α-zein is soluble in 95% ethanol, while β-zein is soluble in 60% ethanol. The α-zein is made of two bands with molecular weight of 24 kDa and 22 kDa, respectively, while the β-zein is made of cluster of α-zein connected by disulfide bonds. The β-zein is not often present in commercial zein preparations because of its relatively unstable tendency to coagulate and precipitate (Shukla and Cheryan 2001). The low water solubility of zein is due to the presence of hydrophobic acids such as leucine, alanine, and proline. The corn zein proteins have been used as packaging materials in the form of a film. The properties related to the film-forming potential of zein have been studied extensively (Takenaka et al. 1967; Tryhnew et al. 1973; Guilbert 1988; Park and Chinnan 1990; Aydt et al. 1991; Herald et al. 1996). The films produced from zein by drying of alcoholic aqueous dispersion are insoluble in water but are resistant to grease. The zein-based films and coatings are widely used for the fresh food preservation, for the retention of enriching vitamins, and for controlled drug delivery. The other uses of zein-based films are to safeguard dry or dried and frozen or intermediate moisture foods. The aqueous dispersions of zein are commercially available as optaglaze produced by Opta Food Ingredients, Inc. It has been also investigated that biodegradable plastics can be manufactured from the mixture of starch and zein (Jane et al. 1994).

13.2.2 Wheat Gluten

Gluten consists of two protein fractions differing in structure and solubility in aqueous alcohols as soluble gliadins and insoluble glutenins (Wieser 2007). The glutenins form high molecular weight polymers (300 kDa), and their subunits are connected by intermolecular disulfide bonds. The elastic component of wheat gluten is because of glutenins, while the gliadins are low molecular weight proteins (30–50 kDa) containing a single polypeptide chain and have intramolecular disulfide in their structure (Hernandez-Munoz et al. 2004a, b, c). The viscous component of gluten is because of gliadins. The glutenins are rich in amino acids like glutamine, proline, and cysteine and are poor in amino acids with ionizable side chains. A large number of studies have been done on the film-forming attributes of wheat gluten proteins (Krull and Inglett 1971; Anker et al. 1972; Gennadios and Weller 1990; Park and Chinnan 1990; Aydt et al. 1991; Gontard et al. 1992, 1993, 1994, 1995, 1996). The films based on gluten are synthesized by casting in a thin layer and then drying of aqueous alcoholic proteic solution under acidic or basic conditions in the presence of disruptive agents (e.g., sulfite). The other methods for the formation of films include collecting the skin formed after boiling proteic solution (Watanabe and Okamoto 1973) or by extrusion of wheat gluten in the presence of disruptive agents (Guilbert and Gontard 1995). The properties and applications of wheat gluten-based films are similar to those of zein-based films. The gluten films have been used to encapsulate additives, retain antimicrobial and anti oxidant additives on food surfaces, and are also used to improve the quality of cereal products (Redl et al. 1996). The selective gas permeability of gelatin-based films has potential application for controlling respiratory exchange and could help in preserving fresh and minimally processed fruits and vegetables (Tanada-Palmu and Grosso 2005). The nonfood items can also be produced from the gluten proteins due to their thermoplastic behavior and have potential applications such as production of surface coatings on paper, windows in envelopes, water-soluble bags with fertilizers (Guilbert and Gontard 1995; Bietz and Lookhart 1996). The pressure treatment can be used to alter the rheological properties (smooth to rubber like) of gluten (Koehler et al. 2010, p. 4).

13.2.3 Soy Proteins

The soy proteins are basically classified on the basis of their ultracentrifugation rate (Hernandez-Izquierdo and Krochta 2008). The obtained protein fractions vary from lower to highest molecular weights such as 2S, 7S (conglycinin), 11S (glycinin), and 15S. The total of 70% of proteins is from 7S and 11S. Conglycinin is rich in asparagine, glutamine, and leucine and has a molecular weight of 180 kDa without disulfide bonds in structure, while glycine has a total of 20 disulfide bonds with a molecular weight of 320–350 kDa. They have potential film-forming properties and are widely used in Asia to obtain edible films by boiling the soya milk and collecting the lipoproteic skin (Fukushima and Van Buren 1970; Smith and Circle 1972; Wu and Bates 1972a, b; Bates and Wu 1975; Guo 1983; Snyder and Kwon 1987). These films are mainly composed of proteins, but also polysaccharides and lipids are present in significant quantities. The soy-based films can also be synthesized by casting in a thin film and then drying of aqueous alcoholic proteic solutions (Jaynes and Chou 1975; Guilbert 1988; Brandenburg et al. 1993; Gennadios et al. 1993b; Stuchell and Krochta 1994). The soy-based films possess good mechanical properties and are slightly resistant to water. The soy films are commonly used in coating materials for preserving numerous foods (Cole 1969; Baker et al. 1972).

13.2.4 Peanuts and Cotton Seed Proteins

The peanut proteins can be modified and fabricated into films and water-soluble bags by collecting the lipoproteic skin generated after boiling the peanut milk (Wu and Bates 1973; Okamoto 1978; Aboagye and Stanley 1985). The cotton seed proteins can be fabricated into biodegradable films by adding cross-linking agents into the film-forming solution (Marquié et al. 1995, 1997).

13.2.5 Milk Proteins

Caseins and whey proteins are the major fractions of proteins in milk. Caseins are poor in cysteine, have a molecular weight of 300–350 kDa, and form a major portion of milk proteins, while whey proteins are rich in cysteine and are globular mainly composed of β-lactoglobulin (18 kDa), α-lactalbumin (14 kDa), and bovine serum albumin (16 kDa). Both the casein and whey proteins have film-forming properties. These can be fabricated into transparent, flexible, and tasteless films. The casein-based films have been obtained on processing equipment surfaces and at air–water interfaces on heating of nonfat milk (Wu and Bates 1973; Mabesa et al. 1979). The casein-based films are able to enhance the appearance of foods, to generate water-soluble bags, to retain additives on intermediate moisture foods, and are used to encapsulate polysaturated lipids for animal feeds (Noznick and Bundus 1967; Cole 1969; Tryhnew et al. 1973; Ashes et al. 1984; Guilbert 1988; Avena-Bustillos and Krochta 1993). On the other hand, whey-based films are produced from whey proteins by boiling the whey dispersions and collecting the lipoproteic skin (Wu and Bates 1973; McHugh and Krochta 1994). The whey-based films can also be produced through enzymatic polymerization of whey proteins using transglutaminases (Mahmoud and Savello 1992, 1993). The whey-based films are insoluble in water because of the reason that their network is stabilized by disulfide covalent bonds.

13.2.6 Collagen and Gelatin

Both collagen and gelatin are animal-derived proteins. Collagen is found to be most abundant animal protein in the nature and composed of three cross-linked α-chains, while gelatin is denatured derivative of collagen and is composed by a pool of proteins and polypeptides. The collagen is rich in amino acids like glycine, proline/hydroxyproline and poor in methionine. The collagen-based edible coatings can be produced by extrusion process and have diverse applications in meat (Courts 1977; Hood 1987) and in pharmaceutical industry (Cavallaro et al. 1994), while the films based on gelatin have been produced by cooling and drying an aqueous film-forming solution. Gelatin-based films are transparent, flexible, resistant to water, and impermeable to oxygen (Grouber 1983; Guilbert 1988; Hebert and Holloway 1992). Gelatin-based films have diverse applications and are used to fabricate tablets and capsule, as a raw material for photographic films, and to encapsulate vitamins, aroma, and sweeteners (Balassa and Fanger 1971).

13.2.7 Keratin

Keratins contain about 20 proteins with molecular weight of approximately 10 kDa. They are rich in hydrophobic amino acids and cysteine residues (Gomez-Guillen et al. 2009) and are therefore insoluble in water. The stiffness of keratin is due to the presence of cysteine bonds. Before the formation of film, the chemical modification is required to solubilize them (Schrooyen et al. 2000; Tanabe et al. 2004). The keratin-based water-insoluble films were prepared by casting and drying alkaline dispersions (Anker et al. 1972). The edible coatings based on keratin are not used in food industry because of their unpleasant mouth feel (Daniels 1973).

13.2.8 Egg Albumin Protein

The films obtained from egg albumin were prepared in the same way as obtained from soya milk. The film formation takes place at air–water interface during heating of albumin. The produced films were found to be more transparent as compared to films based on wheat, soy, and corn proteins. Many patents have reported the potential use of egg albumin for the encapsulation of organic hydrophobic compounds in cosmetics and food (Noznick and Bundus 1967; Kosar and Atkins 1968; Baker et al. 1972).

13.2.9 Myofibrillar Proteins

The main myofibrillar proteins are myosin (500 kDa) and actin (42 kDa). Myosin (fibrous protein)-based films possess good mechanical properties as compared to actin (globular protein)-based films, because they need to be denatured first (Hernandez-Izquierdo and Krochta 2008). The main source of myofibrillar proteins are fishes and have been reported to have potential film-forming properties (Cuq et al. 1995, 1996a, b, c, 1997a, b). The main features of films produced from aqueous solutions are transparent, insoluble in water, and possess good mechanical and gas barrier properties (Gontard et al. 1996).

13.3 Methods for the Formation of Packaging Materials from Proteins

The formation of new framework (film/edible coating) from proteins takes place in a stepwise manner such as breaking of low-energy intermolecular bonds, shaping of polymer chains (arrangement and orientation), and formation of new three-dimensional network stabilized by new bonds and interactions (Cuq et al. 1998). The formation of new intermolecular bonds depends on the shape of proteins (chain length/diameter ratio), on the biochemical properties, and also on the fabrication conditions. The new framework (film) of protein is mainly stabilized by hydrophobic, electrostatic, hydrogen, and covalent bonds. The two methods viz. wet and dry processing have been reported to be mainly useful for the production of materials based on proteins. The wet process is based on the dispersion or solubilization of proteins and also the type of solvent and dissolution pH can affect the conformation of proteins (zein, myofibrillar proteins) (Gomez-Estaca et al. 2009; Li et al. 2012; Blanco-Pascual et al. 2013), while the dry process is based on the thermoplastic properties of proteins (keratin, wheat, or whey) in which the thermal and mechanical treatment induces changes through the induction of disulfide/sulfhydryl interchange reactions (Balaguer et al. 2014; Lagrain et al. 2010).

13.3.1 Wet Processing

The wet processing has been widely used for the production of materials from proteins such as zein (Ghanbarzodeh et al. 2007), wheat proteins (Hernández-Muñoz and Hernández 2001; Balaguer et al. 2011; Guilbert and Gontard 2005), soy proteins (Kim et al. 2002; Rhim et al. 2000), sunflower(Ayhllon-Meixueiro et al. 2000), milk proteins (Sothornvit et al. 2010; Pereda et al. 2011), myofibrillar protein (Cuq et al. 1995), keratin (Maria Martelli et al. 2006; Song et al. 2014). This method is also referred as casting or continuous spreading method (Fig. 13.1). This method is based on the solubilization of proteins in a suitable solvent to produce a film-forming solution. The resulting solution is added with desired additives, functional compounds, and fillers such as plasticizers, cross-linkers, antimicrobial compounds, micro-/nanoparticles. This process is followed by the spreading of film and evaporating the solvent. The addition of plasticizers is useful for lowering protein–protein interactions, decreasing stiffness, enhancing flexibility, and facilitating handling.

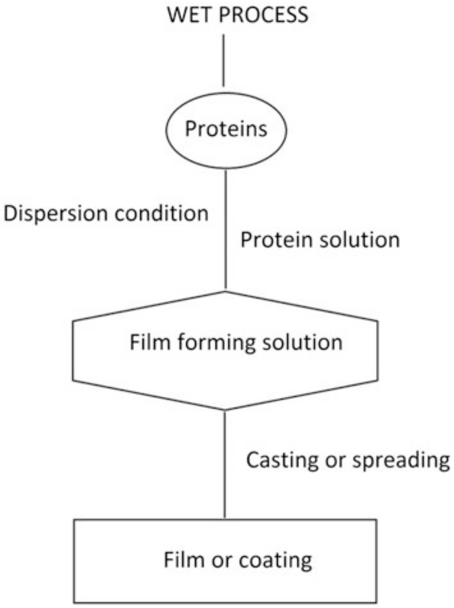


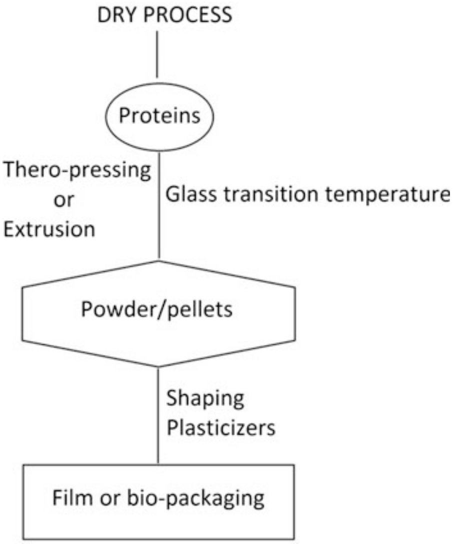
Fig. 13.1 Wet process

The casting method is also used for the production of coatings for conventional packaging materials (Farris et al. 2009; Gastaldi et al. 2007), and this will improve the permeability and maintain the mechanical properties.

13.3.2 Dry Process

The thermoplastic properties of proteins play an important role in the production of agro-packaging materials by dry process. This behavior is well described in relation to the glass transition theory (Van Krevelan 1976), wherein a metastable glassy state is changed into an unsteady rubbery state at a specific temperature called glass transition temperature. The glass transition state induces changes in physical, chemical, and mechanical properties of materials such as increase in disorderness, free volume, and mobility of macromolecules (Ferry 1980; Cherian and Chinachoti 1996). The glass transition behavior of proteins depends on the nature and strength of intermolecular interactions. Thus, proteins could be transformed from rigid to a soft state by increasing the temperature or by the addition of plasticizer (Oudet 1994). In general, proteins can be shaped into the packaging materials in the presence of plasticizers, at high temperature, under low moisture conditions and with force or shear forces. During heating, proteins are denatured that resulted into change in conformation and exposing hidden functional groups. This will allow them to establish new interactions and links that lead to changes in the properties of materials (Hernandez-Izquierdo and Krochta 2008).

Fig. 13.2 Dry process



The packaging materials based on proteins by dry processing method can be produced by different ways such as thermo-pressing/thermoforming and extrusion (Fig. 13.2). The products can be obtained from proteins by employing both the technologies independently. But sometimes both the techniques can be employed together in which extrusion can be used for mixing and partial modifications of the raw materials and thermo-pressing/thermoforming is used to produce final product.

13.3.2.1 Thermo-Pressing/Thermoforming

This technology has been used for the production of materials from proteins such as soy (Paetau et al. 1994a, b; Ciannamea et al. 2014; Pol et al. 2002), zein (di Gioia and Guilbert 1999; Santosa and Padua 1999), myofibrillar proteins (Cuq et al. 1995), whey proteins (Sothornvit et al. 2003; Sothornvit and Krochta 2005), wheat proteins (Sun et al. 2008a, b; Micard et al. 2001; Song and Zheng 2008), sunflower proteins (Orliac et al. 2003), gelatin (Martucci and Rusecaite 2009), keratin (Barone et al. 2005; Katoh et al. 2004), and cotton seed proteins (Grevellec et al. 2001). The thermo-pressing is equipped with a pair of thermostatted plates. The protein mixture is placed in between the plates for processing. The viscoelastic behavior of a mixture of plasticized proteins can be achieved by the application of high temperature and pressure. The film obtained after the cooling down of reaction mixture is stabilized by different interactions and bonds. The physical and chemical modifications can be regulated by altering the parameters such as temperature, pressure, plasticizer, moisture level, time during processing.

13.3.2.2 Extrusion

The extrusion technology has been widely used for the processing of proteins such as zein (Wang and padua 2003), sunflower proteins (Rouilly et al. 2006), whey proteins (Hernandez-Izquierdo et al. 2008), sodium caseinate (Belyamani et al. 2014), wheat proteins (Ullsten et al. 2006, 2009; Türe et al. 2011), feather keratin (Barone et al. 2005), soy protein (Zhang et al. 2001), gelatin (Krishna et al. 2012) into the packaging materials. This equipment is assembled with an endless screw inside a barrel with a double casing that allows to control the temperature. The extrusion process involved the feeding of a polymer from hopper and pushing toward die by the screw. The viscoelastic mass is obtained during this process by subjecting the polymer to shear forces and high-temperature compression. The change in conformation, aggregation, and cross-linking of proteins largely depends on the parameters such as screw speed, feed rate, temperature, plasticizer (quantity), other additives, moisture level, and shape and size of die. The high degree of denaturation and aggregation can be achieved at a sufficiently high extrusion temperature and eventually produces a homogeneous film (Ullsten et al. 2009).

13.4 Shaping Agents

13.4.1 Plasticizers

Plasticizers are small molecules with low volatility, modify the three-dimensional framework of polymeric materials, reduce attractive intermolecular forces, and enhance free volume and chain mobility (Banker 1966; Bakker 1986). Therefore, the addition of plasticizer modifies the functional properties by decreasing cohesion and rigidity and increasing extensibility, distensibility, and flexibility of films (Lieberman and Gilbert 1973; Donhowe and Fennema 1993; Gennadios et al. 1993c; Gontard et al. 1993; McHugh and Krochta 1994; Park et al. 1994; Cuq et al. 1997b). It has been reported that the addition of plasticizer will decrease the glass transition temperature of amorphous materials often important for thermomolding process (Donhowe and Fennema 1993; Slade and Levine 1993a, b; Cherian et al. 1995; Gontard and Ring 1996). Water is regarded as the most effective plasticizer, enabling the biopolymer materials to undergo glass transition, facilitating deformation and processability. It has been reported that the thermal degradation could be reached easily before the formation of films (Tolstoguzov 1993). In addition to water, the other commonly used plasticizers for edible films are as follows: polyols, lipids, monosaccharides, oligosaccharides, and other derivatives (Sothornvit and Krochta 2005). Glycerol has been widely used in the thermoplastic processing of proteins (Redl et al. 1999; Cunningham et al. 2000; Zhang et al. 2001; Pommet et al. 2003, 2005; Sothornvit et al. 2003, 2007; Hernandez-Izquierdo 2007). Because of its high polarizing effect, it can insert and position within the three-dimensional biopolymer network (di Gioia and Guilbert 1999). The sucrose and sorbitol have been used for plasticizing fish myofibrillar proteins by thermal compression molding to produce packaging materials (Cuq et al. 1997c). The plasticizers and processing methods for different proteins are summarized in Table 13.1.

13.4.2 Cross-Linking Agents

The commonly applied cross-linking agents are aldehydes, glyoxal, genipin, gossypol, lactic acid, cysteine, phenolic compounds, tannic acid, epichlorohydrin, and carbodiimides (Tanabe et al. 2004; Balaguer et al. 2011; Zhang et al. 2001, 2010; Paetau et al. 1994a, b; de Carvalho and Grosso 2004; Tropini et al. 2004; Hernandez-Munoz et al. 2004a, b, c; Butler et al. 2003; Cao et al. 2007; Marquie 2001; Sommer and Kunz 2012; Carvalho et al. 2008). These are generally used to improve the barrier properties, mechanical strength, water resistance, cohesion, and rigidity properties of matrix such as keratin (Tanabe et al. 2004; Martucci and Ruseckaite 2009), wheat proteins (Hernandez-Munoz et al. 2004a, b, c; Balaguer et al. 2011; Tropini et al. 2004; Rhim et al. 1999; Martucci and Ruseckaite 2009), gelatin (Cao et al. 2007; Zhang et al. 2010; de Carvalho and Grosso 2004), cotton seed proteins (Marquie 2001, 144), soy proteins (Zhang et al. 2010; Martucci and Ruseckaite 2009; Paetau et al. 1994a, b), corn zein (Rhim et al. 1999; Martucci and Ruseckaite 2009), egg albumin (Rhim et al. 1999), whey proteins (Vachon et al. 2000; Banerjee et al. 1996). The addition of calcium to the casein-based films has improved the functional properties (Guilbert 1986). The enzymatic cross-linking agents such as transglutaminases or peroxidases are also able to stabilize protein-based films (Motoki et al. 1987), but the use of such kind of films in food industry is highly questionable.

13.5 Properties

The interaction between polymers plays important role in defining the macroscopic properties of protein-based agro-packaging materials and their three-dimensional network. The ratio distribution of nonpolar to polar amino acids, network type, and density indicate the barrier properties of packaging materials. In general, proteins containing hydrophilic amino acids limit their moisture barrier properties, but the proteins made of hydrophobic amino acids possess excellent moisture barrier properties and are poor oxygen barriers. It has been observed that proteins with free hydrophilic groups favor sorption and transfer of water vapor rather than

Table 13.1 Plasticizers used in processing of proteins

Plasticizer	Protein studied	Processing method	References
7–17% water	Soy protein	Thermo-pressing	Paetau et al. (1994a, b)
10% water	Wool keratin	Thermo-pressing	Katoh et al. (2004)
10–40% glycerol	Wheat gliadin	Thermo-pressing	Sun et al. (2008a, b)
35% glycerol	Wheat gluten	Thermo-pressing	Sun et al. (2008a, b)
40% glycerol	Wheat glutenin	Thermo-pressing	Song and Zheng (2008)
15–80% glycerol	Feather keratin	Thermo-pressing	Katoh et al. (2004)
30% glycerol	Bovine hide gelatin	Thermo-pressing	Martucci and Ruseckaite (2009)
30% glycerol	Wheat gluten	Extrusion	Ullsten et al. (2006, 2009)
30–70% glycerol and 0–30% water	Sunflower protein	Extrusion	Rouilly et al. (2006)
Glycerol and water	Whey protein	Extrusion	Hernandez-Izquierdo et al. (2008)
17–33% glycerol and 40–80% water	Sodium caseinate	Extrusion	Belyamani et al. (2014)
30% glycerol and 6% water	Wheat gluten	Extrusion	Türe et al. (2011)
Glycerol and water	Feather keratin	Extrusion	Barone et al. (2005)
20–25% glycerol and water	Fish-skin gelatin	Extrusion	Krishna et al. (2012)
Glycerol, water, and methyl glucoside	Soy protein	Extrusion	Zhang et al. (2001)
Sucrose and sorbitol	Fish myofibrillar proteins	Thermo-pressing	Cuq et al. (1995)
50–100% oleic acid or 60–80% linoleic acid	Zein	Thermo-pressing	Santosa and Padua (1999)
1,4-Butanediol	Wheat gluten	Compression molding	Pommet et al. (2005)
Diacetyl tartaric acid ester of monoglycerides	Zein	Compression molding	di Gioia and Guilbert (1999)
Dibutyl tartrate	Zein	Compression molding	di Gioia and Guilbert (1999)
Dibutyl phthalate	Zein	Compression molding	di Gioia and Guilbert (1999)
Lactic acid	Wheat gluten	Compression molding	Pommet et al. (2005)
Octanoic acid	Zein	Compression molding	di Gioia and Guilbert (1999)
Palmitic acid	Zein	Compression molding	di Gioia and Guilbert (1999)

Table 13.2 Mechanical properties of protein-based films and some synthetic films

Film formulation	Processing method	Tensile strength (Mpa)	Elastic modulus (Mpa)	Elongation (%)	References
7–17% water Soy protein	Thermo-pressing	10–40	800–1600	1.3–4.8	Paetau et al. (1994a, b)
10% water Wool keratin	Thermo-pressing	7.9–27.8	697–1218	1.1–4.7	Katoh et al. (2004)
10–40% glycerol Wheat gliadin	Thermo-pressing	0.8–22.2	0.04–4.6	8.5–301	Sun et al. (2008a, b)
35% glycerol Wheat gluten	Thermo-pressing	0.52–6.69	1.2–36	174–288	Sun et al. (2008a, b)
40% glycerol Wheat glutenin	Thermo-pressing	1.7–1.8	–	88–133	Song and Zheng (2008)
15–80% glycerol Feather keratin	Thermo-pressing	6–30	30–650	0.0065–0.65	Barone et al. (2005)
30% glycerol Bovine hide gelatin	Thermo-pressing	1.1–3.9	–	55.3–158.2	Martucci and Ruseckaite (2009)
30% glycerol Wheat gluten	Extrusion	1.8–3	27–36.7	47.3–53.9	Ullsten et al. (2006)
30–70% glycerol and 0–30% water Sunflower protein	Extrusion	0.6–6.7	14–95	9.3–43	Rouilly et al. (2006)
Glycerol and water Whey protein	Extrusion	3.1–4.1	30.6–46.5	121–132	Hernandez-Izquierdo et al. (2008)
17–33% glycerol and 40–80% water Sodium caseinate	Extrusion	~1–18	<10–400	~50–140	Belyamani et al. (2014)
30% glycerol and 6% water Wheat gluten	Extrusion	3.6–2.2	7–3	70–87	Türe et al. (2011)
Glycerol and water Feather keratin	Extrusion	350–500	350	0.25–0.67	Barone et al. (2005)
20–25% glycerol and water Fish-skin gelatin	Extrusion	1.51–2.41	84–132	256–293	88 Krishna et al. (2012)
Glycerol, water, and methyl glucoside Soy protein	Extrusion	7.1–40.6	17–1220	3–185	Zhang et al. (2001)
50–100% oleic acid or 60–80% linoleic acid Zein	Thermo-pressing	1.6–9.4	49–270	5.9–165	Santosa and Padua (1999)
Low-density polyethylene	Extrusion	13	–	500	Lacroix and Cooksey (2005)

(continued)

Table 13.2 (continued)

Film formulation	Processing method	Tensile strength (Mpa)	Elastic modulus (Mpa)	Elongation (%)	References
High-density polyethylene	Extrusion	26	–	300	Lacroix and Cooksey (2005)
Polyester	–	178	–	85	Lacroix and Cooksey (2005)
Polyvinyl chloride	–	93	–	30	Lacroix and Cooksey (2005)

hydrophobic gas (N_2 and O_2) transfer. The excellent moisture and gas barrier properties are necessary for various applications such as controlling transfer of gases for fresh or oxidized foods and decreasing exchange of moisture with external atmosphere (Cuq et al. 1995b). The water vapor permeability of some protein-based films is summarized in Table 13.2. The protein-based films have relatively low water barrier properties and due to that they are used for short-term applications only as protective barrier layers to limit moisture exchange. On the other hand, they have impressive gas (O_2 and CO_2) barrier properties as compared to the synthetic membranes. The gas barrier properties of polymer-based films are given in Table 13.3. This has been observed that the gas barrier properties of proteins are very impressive when they are not moist especially against O_2. While in the presence of moisture, the macromolecular chains are more mobile that leads to increase in permeability of gases (O_2 and CO_2). In this regard, the edible films with selective permeability could be used in food industry for controlling the respiratory exchange.

The mechanical properties mainly depend on the nature and density of interactions that may stabilize the framework in the form of a film or a coating material. In general, when the obtained materials are stabilized by the covalent bonds or bond energy is very high, the resulting materials will be very resistant and relatively elastic, while the interactions with low-energy bonds will produce easily distended films. The mechanical properties of various synthetic and protein-based films are given in Table 13.4. The overall mechanical strength of protein-based films is lower as compared to other synthetic films. This is the main reason that application of protein-based films is limited to food industry only.

Table 13.3 Water vapor permeability of various films

Film	Water vapor permeability ($\times 10^{12}$ mol m $m^{-2}s^{-1}Pa^{-1}$)	Thickness ($\times 10^{3}$ m)	References
Starch, cellulose acetate	142	1.190	Allen et al. (1963)
Sodium caseinate	24.7	–	Avena-Bustillos and Krochta (1993)
Corn zein	6.45	0.200	Park and Chinnan (1990)
Methyl cellulose	5.23	0.075	Landman et al. (1960)
Wheat gluten and glycerol	5.08	0.050	Gontard et al. (1993)
Wheat gluten and oleic acid	4.15	0.050	Gontard et al. (1994)
Wheat gluten and carnauba wax	3.91	0.050	Gontard et al. (1994)
Wheat gluten	3.11	0.127	Gennadios et al. (1993a)
Wheat gluten and soy protein	2.84	0.075	Gennadios et al. (1990)
Wheat gluten and mineral oil	2.28	0.125	Gennadios et al. (1993a)
Corn zein and oleic acid	1.48	0.040	Guilbert and Biquet (1989)
Low-density polyethylene	0.0482	0.025	Myers et al. (1961)
High-density polyethylene	0.0122	0.025	Guilbert and Biquet (1989)
Bees wax	0.0122	0.120	Landman et al. (1960)
Aluminum foil	0.000289	0.025	Myers et al. (1961)

13.6 Application of Proteins-Based Films and Edible Coatings

The protein-based films are widely used in food industry, because they are eco-friendly (Han 2005) in terms of cost and biodegradability. The edible films based on proteins are considered as versatile packaging materials because of several properties such as provides physical protection to the food items, decreases loss of moisture, controls respiratory exchange, decreases lipid migration and improves mechanical handling. The protein-based films have better gas barrier and mechanical properties than polysaccharides and lipids. The application of protein-based films has been reviewed excellently by Gennadios et al. (1994). The edible films have potential uses as wraps, bags, pouches, sachets in the food

Table 13.4 Oxygen (O_2) and carbon dioxide (CO_2) permeability of various films

Film	Oxygen permeability ($\times 10^{-18}$mol m m^{-2} $s^{-1}Pa^{-1}$)	Carbon dioxide permeability ($\times 10^{-18}$mol m m^{-2} $s^{-1}Pa^{-1}$)	a_w	References
Low-density polyethylene	1003	4220	0.0	Baker (1986)
High-density polyethylene	285	972	0.0	Baker (1986)
Polyvinyl alcohol	50.8	–	1.00	Ashley (1985)
Beeswax	480	–	0.00	Donhowe and Fennema (1993b)
Carnauba wax	81.1	–	0.00	Donhowe and Fennema (1993b)
Starch	1085	–	1.00	Allen et al. (1963)
Corn zein	35.8	216	0.00	Ayedt et al. (1991)
Wheat gluten	1	7	0.00	Gontard el al. (1995)
Wheat gluten	1290	36700	0.95	Gontard el al. (1995)
Soy protein	2.30	–	0.00	Gennadios et al. (1990)
Wheat gluten and glycerin	19.6	–	0.00	Gennadios et al. (1990)
Wheat gluten and mineral oil	1.70	–	0.00	Gennadios et al. (1993a)
Wheat gluten and soy protein	1.19	–	0.00	Brandeburg et al. (1993)
Wheat gluten and beeswax	687	6614	0.91	Gontard el al. (1994)
Fish myofibrillar proteins	873	11100	0.93	Gontard el al. (1995)

industry in order to reduce the waste and improve the recyclability. Zein-based films are traditionally used as coating materials in confectionary industry (Arcan and Yemeni-cioglu 2011) and provide improved water barrier properties because it is rich in nonpolar amino acids (Dangaran et al. 2009). The possible applications of soy proteins are the production of water-soluble bags (Krochta 1997). The whey protein-based films could be used for the production of edible wraps for food products (Sothornvit et al. 2007). Sodium caseinate-based films are used for wrapping of breads (Schou et al. 2005) in order to prevent hardening of breads. The broad spectrum applications of protein-based films or coating are to preserve fresh and minimally processed fruits and vegetable, for increasing the shelf life of various meat, poultry, and fish products, for coatings of various cereals, bakery, and dairy products to improve quality and prevent hydration.

13.7 Future Prospects

The bio-based films or coatings must fulfill some requirements necessary for food industry such as edible and biodegradable, provide physical and mechanical protection, possess excellent migration, permeation, and barrier properties, preserve quality of foods, enhance safety and shelf life, and act as active substance carriers and provide controlled release. The future of protein-based materials is bound to improve various properties in comparison with synthetic plastics. This could be tremendous achievement in the food industry to reduce the waste and increase the recyclability. The mechanical and barrier properties can be improved by using various plasticizers and cross-linking agents. The protein-based films or coatings can be transformed into active/functional films or coatings by incorporating antimicrobial and antioxidant agents. The search for new physicochemical treatments and incorporation of new materials is also important for the improvement of various properties such as biodegradability, mechanical properties, barrier properties, enhance shelf life of food items etc. The search for new sources of agricultural proteins is also important.

References

Aboagye Y, Stanley DW (1985) Texturization of peanut proteins by surface film formation. 1. Influence of process parameters on film forming properties. Can Inst Food Sci Technol J 18:12–20

Allen L, Nelson AI, Steinberg MP, McGill JN (1963) Edible corn-carbohydrate food coatings. 1. Development and physical testing of a starch-algin coating. Food Technol 17:1437–1441

Anker CA, Foster GA, Loader MA (1972) Wheat gluten films. U.S. patent 3,653,925

Arcan I, Yemenicioglu A (2011) Incor-porating phenolic compounds opens a new per-spective to use zein as flexible bioactive packaging materials. Food Res Int 44(2):550–556

Ashes JR, Cook LJ, Sidhu GS (1984) Effect of dietary cholesterol protected against ruminal hydrogenation on the plasma cholesterol and liver of sheep. Lipids 19:159–163

Ashley RJ (1985) Permeability and plastic packagings. In: Comyn J (ed) Polymer permeability. Elsevier Applied Science, London, pp 269–308

Avena-Bustillos RJ, Krochta JM (1993) Water vapor permeability of caseinate-based films as affected by pH, calcium cross-linking and lipid content. J Food Sci 58:904–907

Aydt TP, Weller CL, Testin RF (1991) Mechanical and barrier properties of edible corn and wheat protein films. Trans ASAE 34:207–211

Ayhllon-Meixueiro F, Vaca-Garcia C, Silvestre F (2000) Biodegradable films from isolate of sunflower (Helianthus annuus) proteins. J Agric Food Chem 48:3032–3036

Bakker M (1986) Wiley encyclopedia of packaging technology. Wiley, New York

Baker RC, Darfler JM, Vadehra DV (1972) Prebrowned fried chicken. 2. Evaluation of predust materials. Poult Sci 51:1220–1222

Balaguer MP, Gómez-Estaca J, Gavara R, Hernández-Muñoz P (2011) Functional properties of bioplastics made from wheat gliadins modified with cinnamaldehyde. J Agric Food Chem 59:6689–6695. doi:10.1021/jf200477a

Balaguer MP, Gomez-Estaca J, Cerisuelo JP, Gavara R, Hernandez-Munoz P (2014) Effect of thermo-pressing temperature on the functional properties of bioplastics made from a renewable wheat gliadin resin. LWT–Food Science and Technology 56:161–167

Balassa LL, Fanger GO (1971) Microencapsulation in the food industry. CRC Crit Rev Food Technol 2:245–265

Banerjee R, Chen H, Wu J (1996) Milk protein-based edible film mechanical strength changes due to ultrasound process. J Food Sci 61:824–828

Banker GS (1966) Film coating theory and practice. J Pharm Sci 55:81–89

Barone JR, Schmidt WF, Liebner CFE (2005) Thermally processed keratin films. J Appl Polym Sci 97:1644–1651. doi:10.1002/app.21901

Bates RP, Wu LC (1975) Protein quality of soy protein-lipid films (yuba) and derived fractions. J. Food Sci. 40:425–426

Belyamani I, Prochazka F, Assezat G (2014) Production and characterization of sodium caseinate edible films made by blownfilm extrusion. J Food Eng 121:39–47

Bietz JA, Lookhart GL (1996) Properties and non-food potential of gluten. Cereal Foods World 41:376–382

Blanco-Pascual N, Fernández-Martín F, Montero MP (2013) Effect of different protein extracts from Dosidicus gigas muscle coproducts on edible films development. Food Hydrocolloids 33:118–131

Bourtoom T (2008) Edible films and coatings: characteristics and properties. Int Food Res J 15 (3):237–248

Brandenburg AH, Weller CL, Testin RF (1993) Edible films and coatings from soy protein. J Food Sci 58:1086–1089

Butler MF, Ng YF, Pudney PDA (2003) Mechanism and kinetics of the crosslinking reaction between biopolymers containing primary amine groups and genipin. J Polym Sci, Part A: Polym Chem 41:3941–3953. doi:10.1002/pola.10960

Cao N, Fu YH, He JH (2007) Mechanical properties of gelatin films cross-linked, respectively, by ferulic acid and tannin acid. Food Hydrocolloids 21:575–584. doi:10.1016/j.foodhyd.2006.07.001

Carvalho RA, Grosso CRF, Sobral PJA (2008) Effect of chemical treatment on the mechanical properties, water vapour permeability and sorption isotherms of gelatin-based films. Packag Technol Sci 21:165–169. doi:10.1002/pts.792

Cavallaro JF, Kemp PD, Kraus KH (1994) Collagen fabrics as biomaterials. Biotechnol Bioeng 43:781–791

Cherian G, Chinachoti P (1996) 2H and 17O nuclear magnetic resonance study of water in gluten in the glassy and rubbery state. Cereal Chem 73:618–624

Cherian G, Gennadios A, Weller C, Chinachoti P (1995) Thermomechanical behavior of wheat gluten films: effect of sucrose, glycerin, and sorbitol. Cereal Chem 72:1–6

Ciannamea EM, Stefani PM, Ruseckaite RA (2014) Physical and mechanical properties of compression molded and solution casting soybean protein concentrate based films. Food Hydrocoll 38:193–204. doi:10.1016/j.foodhyd.2013.12.013

Cole MS (1969) Method for coating dehydrated food. U.S. patent 3,479,191

Courts A (1977) Uses of collagen in edible products. In: Ward AG, Courts A (eds) The science and technology of gelatin. Academic Press, New York, pp 395–412

Cunningham P, Ogale A, Dawson P, Acton J (2000) Tensile properties of soy protein isolate films produced by a thermal compaction technique. J Food Sci 65:668–671. doi:10.1111/j.1365-2621.2000.tb16070.x

Cuq B, Aymard C, Cuq JL, Guilbert S (1995) Edible packaging films based on fish myofibrillar proteins: formulation and functional properties. J Food Sci 60:1369–1374. doi:10.1111/j.1365-2621.1995.tb04593.x

Cuq B, Gontard N, Cuq JL, Guilbert S (1996a) Stability of myofibrillar protein-based biopackagings during storage. Lebensm Wiss Technol 29:344–348

Cuq B, Gontard N, Cuq JL, Guilbert S (1996b) Functional properties of myofibrillar protein-based biopackagings as affected by film thickness. J Food Sci 61:580–584

Cuq B, Gontard N, Cuq JL, Guilbert S (1996c) A rheological model for the mechanical properties of myofibrillar protein-based films. J Agric Food Chem 44:1116–1122

Cuq B, Gontard N, Aymard C, Guilbert S (1997a) Effect of moisture content and temperature on the main functional properties of myofibrillar protein-based films. Polym Gels Networks 5:1–15

Cuq B, Gontard N, Cuq JL, Guilbert S (1997b) Selected functional properties of myofibrillar protein-based films as affected by hydrophilic plasticizers. J Agric Food Chem 45:622–626

Cuq B, Gontard N, Guilbert S (1997c) Thermoplastic properties of fish myofibrillar proteins: application to biopackaging fabrication. Polymer 38(16):4071–4078

Cuq B, Gontard N, Guilbert S (1998a) Proteins as agricultural polymers for packaging production. Cereal Chem 75:1–9. doi:10.1094/cchem.1998.75.1.1

Cuq B, Gontard N, Guilbert S (1998b) Proteins as agricultural polymers for packaging production. Cereal Chem 74:1–9

Dangaran K, Tomasula PM, Qi P (2009) Structure and function of protein-based edible films and coatings. In: Embuscado ME, Huber HC (eds) Edible films and coatings for food application. Springer, New York, pp 25–56

Daniels R (1973) Edible coatings and soluble packaging. Noyes Data Corporation, Park Ridge

de Carvalho RA, Grosso CRF (2004) Characterization of gelatin based films modified with transglutaminase, glyoxal and formaldehyde. Food Hydrocolloids 18:717–726. doi:10.1016/j.foodhyd.2003.10.005

di Gioia L, Guilbert S (1999) Corn protein-based thermoplastic resins: effect of some polar and amphiphilic plasticizers. J Agric Food Chem 47:1254–1261

Donhowe IG, Fennema O (1993) The effects of solution composition and drying temperature on crystallinity, permeability and mechanical properties of methylcellulose films. J Food Process Preserv 17:231–246

edible films. Food Hydrocolloids 41:86–94

Farris S, Introzzi L, Piergiovanni L (2009) Evaluation of a bio-coating as a solution to improve barrier, friction and optical properties of plastic films. Packag Technol Sci 22:69–83. doi:10.1002/pts.826

Ferry JD (1980) Viscoelastic properties of polymers. Wiley, New York

Fukushima D, Van Buren J (1970) Mechanisms of protein insolubilization during the drying of soy milk. Role of disulfide and hydrophobic bonds. Cereal Chem 47:687–696

Gennadios A, Weller CL (1990) Edible films and coatings from wheat and corn proteins. Food Technol 44:63–69

Gastaldi E, Chalier P, Guillemin A, Gontard N (2007) Microstructure of protein-coated paper as affected by physico-chemical properties of coating solutions. Colloids Surf A: Physicochem Eng Asp 301:301–310. doi:10.1016/j.colsurfa.2006.12.079

Gennadios A, Weller CL, Testin, RF (1990) Modification of properties of edible wheat gluten films. ASAE Paper 90-6504

Gennadios A, Brandenburg AH, Weller CL, Testin RF (1993a) Effect of pH on properties of wheat gluten and soy protein isolate films. J Agric Food Chem 41:1835–1839

Gennadios A, Park HJ, Weller CL (1993b) Relative humidity and temperature effects on tensile strength of edible protein and cellulose andher films. Trans ASAE 36:1867–1872

Gennadios A, Weller CL, Testin RF (1993c) Property modification of edible wheat gluten-based films. Trans ASAE 36:465–470

Gennadios A, Mc Hugh TH, Weller CL, Krochta JM (1994) Edible coating and films based on protein. In: Krochta JM, Balwin EA, Niperos Carriedo MO (ed) Edible coatings and films to improve food quality, 201277, Technomic Publishing, 978-1-42003-198-0 Basel

Ghanbarzodeh B, Oromiehie AR, Musavi M et al (2007) Study of mechanical properties, oxygen permeability and AFM topography of zein films plasticized by polyols. Packag Technol Sci 20:155–163. doi:10.1002/pts.750

Gomez-Estaca J, Montero P, Fernandez-Martin F, Gomez-Guillen MC (2009) Physico-chemical and film-forming properties of bovine-hide and tuna-skin gelatin: a comparative study. J Food Eng 90:480–486

Gómez-Estaca J, Montero P, Gómez-Guillén MC (2014) Shrimp (Litopenaeus vannamei) muscle proteins as source to develop edible films. Food Hydrocolloids 41:86–94

Gomez-Guillen MC, Perez-Mateos M, Gomez-Estaca J et al (2009) Fish gelatin: a renewable material for developing active biodegradable films. Trends Food Sci Technol 20:3–16. doi:10.1016/j.tifs.2008.10.002

Gontard N, Guilbert S, Cuq JL (1992) Edible wheat gluten films: Influence of the main process variables on film properties using response surface methodology. J Food Sci 57(190–195):199

Gontard N, Guilbert S, Cuq JL (1993) Water and glycerol as plasticizers affect mechanical and water vapor barrier properties of an edible wheat gluten film. J Food Sci 58:206–211

Gontard N, Duchez C, Cuq JL, Guilbert S (1994) Edible composite films of wheat gluten and lipids: water vapour permeability and other physical properties. Int J Food Sci Technol 29:39–50

Gontard N, Marchesseau S, Cuq JL, Guilbert S (1995) Water vapour permeability of edible bilayer films of wheat gluten and lipids. Int J Food Sci Technol 30:49–56

Gontard N, Ring S (1996) Edible wheat gluten film: Influence of water content on glass transition temperature. J Agric Food Chem 44:3474–3478

Gontard N, Thibault R, Cuq B, Guilbert S (1996) Influence of relative humidity and film composition on oxygen and carbon dioxide permeabilities of edible films. J Agric Food Chem 44:1064–1069

Grevellec J, Marquié C, Ferry L, Crespy A, Vialettes V (2001) Processability of cottonseed proteins into biodegradable materials. Biomacromol 2:1104–1109. doi:10.1021/bm015525d

Grouber B (1983) Les gélatines: propriétés, contrôles et principales applications. Labo-Pharm. Problèm Techn 337:909–916

Guilbert S (1986) Technology and application of edible protective films. In: Mathlouthi M (ed) Food packaging and preservation. Elsevier Applied Science, New York, pp 371–394

Guilbert S (1988) Use of superficial edible layer to protect intermediate moisture foods: Application to the protection of tropical fruit dehydrated by osmosis. In: Seow CC, Teng TT, Quah CH (eds) Food preservation by moisture control. Elsevier Applied Science, London, pp 199–219

Guilbert S, Biquet B (1989) Les films et enrobages comestibles. In: Bureau G, Multon JJ (eds) L'emballage des Denrées Alimentaires de Grande Consommation. Technique et Documentation, Lavoisier, Apria, Paris, pp 320–359

Guilbert S, Gontard N (1995) Edible and biodegradable food packaging. In: Ackermann P, Jägerstad M, Ohlsson T (eds) Foods and packaging materials—chemical interactions. Royal Society of Chemistry, Cambridge, pp 159–168

Guilbert S, Cuq B (2005) Material formed from proteins. In: Bastioli C (ed) Handbook of biodegradable polymers. Rapra Technology Limited, United Kingdom

Guilbert S, Gontard N (2005) Agro-polymers for edible and biodegradable films: review of agricultural polymeric materials, physical and mechanical. In: Innovative in Food Packaging, Han JH (ed) Food Science and Technology, International Series, Elsevier Academic Press: New York

Guo XA (1983) Research on heat denaturation of soy protein after solvent extraction and traditional Chinese soy foods. In: Irwin BJ, Sinclair JB, and Wang JL (eds) Soybean Research in China and the United States. University of Illinois, Urbana-Champaign, p 64–66

Han JH (2005) New technologies in food packaging: overview. In: Han JH (ed) Innovations in food packaging. Elsevier Academic Press, San Diego, pp 3–11

Hebert GD, Holloway OE (1992) Product and process of coating nuts with edible protein. U.S. patent 5,149,562

Herald TJ, Hachmeister KA, Huang S, Bowers JR (1996) Corn zein packaging materials for cooked turkey. J Food Sci 61:415–421

Hernandez-Izquierdo VM (2007) Thermal transitions, extrusion, and heat-sealing of whey protein edible films [dissertation]. Univ. of California, Davis, Calif. 110 p

Hernandez-Izquierdo VM, Krochta JM (2008) Thermoplastic processing of proteins for film formation—a review. J Food Sci 73:R30–R39. doi:10.1111/j.1750-3841.2007.00636.x

Hernandez-Izquierdo VM, Reid DS, McHugh TH, Berrios JDJ, Krochta JM (2008) Thermal transitions and extrusion of glycerolplasticized whey protein mixtures. J Food Sci 73:E169–E175

Hernández-Muñoz P, Hernández RJ (2001) Glutenin and gliadin films from wheat gluten: preparation and properties. In IFT Annual Meeting. Volume Session 73D, poster 36: New Orleans, Louisiana

Hernandez-Munoz P, Lagaron JM, Lopez-Rubio A, Gavara R (2004a) Gliadins polymerized with cysteine: effects on the physical and water barrier properties of derived films. Biomacromol 5:1503–1510. doi:10.1021/bm0499381

Hernandez-Munoz P, Villalobos R, Chiralt A (2004b) Effect of cross-linking using aldehydes on properties of glutenin-rich films. Food Hydrocolloids 18:403–411. doi:10.1016/s0268-005x(03)00128-0

Hernandez-Munoz P, Villalobos R, Chiralt A (2004c) Effect of thermal treatments on functional properties of edible films made from wheat gluten fractions. Food Hydrocoll 18:647–654

Hernandez-Munoz P, Kanavouras A, Lagaron JM, Gavara R (2005) Development and characterization of films based on chemically cross-linked gliadins. J Agric Food Chem 53:8216–8223. doi:10.1021/jf050952u

Hood LL (1987) Collagen in sausage casings. Adv Meat Res 4:109–129

Hu CY, Chen M, Wang ZW (2012) Release of thymol, cinnamaldehyde and vanillin from soy protein isolate films into olive oil. Packag Technol Sci 25:97–106. doi:10.1002/pts.964

Irissin-Mangata J, Bauduin G, Boutevin B, Gontard N (2001) New plasticizers for wheat gluten films. Eur Polymer J 37:1533–1541. doi:10.1016/s0014-3057(01)00039-8

Jane J, Lim S, Paetau I, Spence K, Wang S (1994) Biodegradable plastics made from agricultural biopolymers. In: Fishman ML, Friedman RB, Huang SJ (eds) Polymers from Agricultural Coproducts. ACS Symposium Series 575: Chicago, pp 92–100

Jaynes HO, Chou WN (1975) New method to produce soy protein-lipid films. Food Prod Dev 9:86–90

Katoh K, Shibayama M, Tanabe T, Yamauchi K (2004) Preparation and physicochemical properties of compression-molded keratin films. Biomaterials 25:2265–2272. doi:10.1016/j.biomaterials.2003.09.021

Kim KM, Weller CL, Hanna MA, Gennadios A (2002) Heat curing of soy protein films at selected temperatures and pressures. Lebensm Wiss Technol Food Sci Technol 35:140–145. doi:10.1006/fstl.2001.0825

Koehler P, Kieffer R, Wieser H (2010) Effect of hydrostatic pressure and temperature on the chemical and functional properties of wheat gluten III. Studies on gluten films. J Cereal Sci 51(1):140–145

Kosar J, Atkins GM (1968) Encapsulation. U.S. patent 3,406,119

Krishna M, Nindo CI, Min SC (2012) Development of fish gelatin edible films using extrusion and compression molding. J Food Eng 108:337–344. doi:10.1016/j.jfoodeng.2011.08.002

Krochta JM (1997) Edible protein films and coatings. In: Damodaran S, Paraf A (eds) Food proteins and their applications. Marcel Dekker Inc, New York, pp 529–550

Krochta JM, Baldwin EA, Nysperos-Car-riedo M (1994) Edible coatings and films to improve food quality. CRC Press, Boca Raton, pp 1–7, 25–101, 189–330

Krull LH, Inglett GE (1971) Industrial uses of gluten. Cereal Sci Today 16(232–236):261

Lacroix M, Cooksey K (2005) Edible films and coatings from animal-origin proteins. In: Han JH (ed) Innovations in food packaging. Elsevier Academic Press, San Diego, pp 301–317

Lagrain B, Goderis B, Brijs K, Delcour JA (2010) Molecular basis of processing wheat gluten toward biobased materials. Biomacromol 11:533–541. doi:10.1021/bm100008p

Landman W, Lovegren NV, Feuge RO (1960) Permeability of some fat products to moisture. J Am Oil Chem Soc 37:1–4

Li Y, Li J, Xia Q et al (2012) Understanding the dissolution of α-zein in aqueous ethanol and acetic acid solutions. J Phys Chem B 116:12057–12064. doi:10.1021/jp305709y

Lieberman ER, Gilbert SG (1973) Gas permeation of collagen films as affected by cross-linkage, moisture, and plasticizer content. J Polym Sci 41:33–43

Lopez-Rubio A, Almenar E, Hernandez-Munoz P et al (2004) Overview of active polymer-based packaging technologies for food applications. Food Rev Int 20:357–387. doi:10.1081/lfri-200033462

Mabesa RC, Marshall RT, Anderson ME (1979) Factors influencing the tenacity of dried milk films exposed to high humidity. J Food Protect 42:631–637

Mahmoud R, Savello PA (1992) Mechanical properties of and water vapor transferability through whey protein films. J Dairy Sci 75:942–946

Mahmoud R, Savello PA (1993) Solubility and hydrolyzibility of films produced by transglutaminase catalytic cross-linking of whey protein. J Dairy Sci 76:29–35

Maria Martelli S, Moore G, Silva Paes S, Gandolfo C, Laurindo JB (2006) Influence of plasticizers on the water sorption isotherms and water vapor permeability of chicken feather keratin films. LWT–Food Sci Technol 39:292–301. doi:10.1016/j.lwt.2004.12.014

Marquie C (2001) Chemical reactions in cottonseed protein cross-linking by formaldehyde, glutaraldehyde, and glyoxal for the formation of protein films with enhanced mechanical properties. J Agric Food Chem 49:4676–4681

Marquié C, Aymard C, Cuq JL, Guilbert S (1995) Biodegradable packaging made from cottonseed flour: formation and improvement by chemical treatment with gossypol, formaldehyde and glutaraldehyde. J Agric Food Chem 43:2762–2766

Marquié C, Tessier AM, Aymard C, Guilbert S (1997) HPLC determination of the reactive lysine content of cottonseed protein films to monitor the extend of cross-linking by formaldehyde, glutaraldehyde, and *N*-glyoxal. J Agric Food Chem 45:922–926

Martucci JF, Ruseckaite RA (2009) Tensile properties, barrier properties, and biodegradation in soil of compressionmolded gelatin-dialdehyde starch films. J Appl Polym Sci 112: 2166–2178. doi:10.1002/ app.29695

McHugh TH, Krochta JM (1994) Sorbitol- vs glycerol-plasticized whey protein edible films: integrated oxygen permeability and tensile property evaluation. J Agric Food Chem 42:841–845

Micard V, Morel MH, Bonicel J, Guilbert S (2001) Thermal properties of raw and processed wheat gluten in relation with protein aggregation. Polymer 42:477–485

Motoki M, Aso H, Seguro K, Nio N (1987) aS1-Casein film prepared using transglutaminase. Agric Biol Chem 51:993–996

Myers AW, Meyer JA, Rogers CE, Stannett V, Szwarc M (1961) Studies in the gas and vapor permeability of plastic films and coated papers. The permeation of water vapor. Tappi J 45:58–67

Noznick P P, Bundus R H 1967 Coating for dry roasted nuts. U.S. patent 3,314,800

Nur Hanani ZA, Roos YH, Kerry JP (2014) Use and application of gelatin as po-tential biodegradable packaging materials for food products. Int J Biol Macromol 10.1016//j.ijbiomac.2014.04.027

Okamoto S (1978) Factors affecting protein film formation. Cereal Foods World 23:256–262

Orliac O, Rouilly A, Silvestre F, Rigal L (2003) Effects of various plasticizers on the mechanical properties, water resistance and aging of thermo-moulded films made from sunflower proteins. Ind Crops Prod 18:91–100. doi:10.1016/s0926-6690(03)00015-3

Oudet C (1994) Polymères. Structure et Propriétés. Paris, Masson

Paetau I, Chen CZ, Jane JL (1994a) Biodegradable plastic made from soybean products. 1. Effect of preparation and processing on mechanical properties and water absorption. Ind Eng Chem Res 33:1821–1827

Paetau I, Chen CZ, Jane JL (1994b) Biodegradable plastic made from soybean products. II. Effects of cross-linking and cellulose incorporation on mechanical properties and water absorption. J Environ Polym Degrad 2:211–217

Park HJ, Chinnan MS (1990) Properties of edible coatings for fruits and vegetables. ASAE Paper 90-6510

Park HJ, Bunn JM, Weller CL, Vergano PJ, Testin RF (1994) Water vapor permeability and mechanical properties of grain protein-based films as affected by mixtures of polyethylene glycol and glycerin plasticizers. Trans ASAE 37:1281–1285

Pereda M, Arnica G, Racz I, Marcovich NE (2011) Structure and properties of nanocomposite films based on sodium caseinate and nanocellulose fibers. J Food Eng 103:76–83. doi:10.1016/j.jfoodeng.2010.10.001

Pol H, Dawson P, Acton J, Ogale A (2002) Soy protein isolate/corn-zein laminated films: transport and mechanical properties. J Food Sci 67:212–217

Pommet M, Redl A, Morel MH, Domenek S, Guilbert S (2003) Thermoplastic processing of protein-based bioplastics: chemical engineering aspects of mixing, extrusion and hot molding. Macromol Symp 197:207–17

Pommet M, Redl A, Guilbert S, Morel MH (2005) Intrinsic influence of various plasticizers on functional properties and reactivity of wheat gluten thermoplastic materials. J Cereal Sci 42:81–91

Popović S, Pericin D, Vastag Z, Lazić V, Lj Popović (2012) Pumpkin oil cake protein isolate films as potential gas barrier coating. J Food Eng 110(3):374–379

Redl A, Gontard N, Guilbert S (1996) Determination of sorbic acid diffusivity in edible wheat gluten and lipid based films. J Food Sci 61:116–120

Redl A, Morel MH, Bonicel J, Vergnes B, Guilbert S (1999) Extrusion of wheat gluten plasticized with glycerol: influence of process conditions on flow behavior, rheological properties, and molecular size distribution. Cereal Chem 76(3):361–370

Rhim JW, Gennadios A, Fu DJ, Weller CL, Hanna MA (1999) Properties of ultraviolet irradiated protein films. Food Sci Technol Lebensm Wiss Technol 32: 129–133

Rhim JW, Gennadios A, Handa A, Weller CL, Hanna MA (2000) Solubility, tensile, and color properties of modified soy protein isolate films. J Agric Food Chem 48:4937–4941

Rouilly A, Meriaux A, Geneau C et al (2006) Film extrusion of sunflower protein isolate. Polym Eng Sci 46:1635–1640. doi:10.1002/pen.20634

Santosa FXB, Padua GW (1999) Tensile properties and water absorption of zein sheets plasticized with oleic and linoleic acids. J Agric Food Chem 47:2070–2074

Schou M, Longares A, Montesinos-Herrero CF, Monahan DJ, O'Riordan M, O'Sullivan (2005) Properties of edible sodiumcaseinatefilms and their application as food wrapping. Lebensm Wiss Technol 38:605–610. ISSN: 0023-6438

Schrooyen PMM, Dijkstra PJ, Oberthü RG, Bantjes A, Feijen J (2000) Partially carboxymethylated feather keratins. 1. Properties in aqueous systems. J Agric Food Chem 48:4326–4334. doi:10.1021/jf9913155

Shukla R, Cheryan M (2001) Zein: the industrial protein from corn. Ind Crops Prod 13:171–192

Slade L, Levine H (1993a) The glassy state phenomenon in food molecules. In: Blanshard JM, Lillford PJ (eds) The glassy state in foods. Nottingham University Press, Loughborough, England, pp 35–102

Slade L, Levine H (1993b) Water relationships in starch transitions. Carbohydr Polym 21:105–131

Smith AK, Circle TW (1972) Protein products as food ingredients. In: Smith AK, Circle SJ (eds) Soybeans: chemistry and technology, vol 1. AVI, Westport, pp 339–388

Snyder HE, Kwon TW (1987) Soybean utilization. Van Nostrand Reinhold, New York

Sommer I, Kunz PM (2012) Improving the water resistance of biodegradable collagen films. J Appl Polym Sci 125:E27–E41. doi:10.1002/app.36461

Song YH, Zheng QA (2008) Preparation and properties of thermo-molded bioplastics of glutenin-rich fraction. J Cereal Sci 48:77–82. doi:10.1016/j.jcs.2007.08.007

Song NB, Lee JH, Al Mijan M, Song KB (2014) Development of a chicken feather protein film containing clove oil and its application in smoked salmon packaging. LWT–Food Sci and Technol 57:453–460. doi:10.1016/j.lwt.2014.02.009

Sothornvit R, Krochta JM (2005) Plasticizers in edible films and coatings. In: Han JH (ed) Innovations in food packaging. Elsevier Academic Press, San Diego, pp 403–433

Sothornvit R, Olsen CW, McHugh TH, Krochta JM (2003) Formation conditions, watervapor permeability, and solubility of compression-molded whey protein films. J Food Sci 68 (6):1985–1989

Sothornvit R, Olsen CW, McHugh TH, Krochta JM (2007) Tensile properties of compression-molded whey protein sheets: determination of molding condition and glycerol-content effects and comparison with solution-cast films. J Food Eng 78:855–860. doi:10.1016/j.jfoodeng.2005.12.002

Sothornvit R, Hong SI, An DJ, Rhim JW (2010) Effect of clay content on the physical and antimicrobial properties of whey protein isolate/organo-clay composite films. LWT–Food. Sci Technol 43:279–284. doi:10.1016/j.lwt.2009.08.010

Stuchell YM, Krochta JM (1994) Enzymatic treatments and thermal effects on edible soy protein films. J Food Sci 59:1332–1337

Sun SM, Song YH, Zheng Q (2008a) Morphology and mechanical properties of thermo-molded bioplastics based on glycerolplasticized wheat gliadins. J Cereal Sci 48:613–618. doi:10.1016/j.jcs.2008.01.005

Sun SM, Song YH, Zheng Q (2008b) Thermo-molded wheat gluten plastics plasticized with glycerol: effect of molding temperature. Food Hydrocoll 22:1006–1013. doi:10.1016/j.foodhyd.2007.05.012

Takenaka H, Ito H, Asano H, Hattori H (1967) On some physical properties of film forming materials. Gifu Yakka Daigaku 17:142–146

Tanabe T, Okitsu N, Yamauchi K (2004) Fabrication and characterization of chemically crosslinked keratin films. Mater Sci Eng C 24:441–446

Tanada-Palmu PS, Grosso CRF (2005) Effect of edible wheat gluten-based films and coatings on refrigerated strawberry (Fragaria ananassa) quality. Postharvest Biol Technol 36(2):199–208

Tolstoguzov VB (1993) Thermoplastic extrusion—the mechanism of the formation of extrudate structure and properties. J Am Oil Chem Soc 70(4):417–424

Tropini V, Lens JP, Mulder W, Silvestre F (2004) Wheat gluten films cross-linked with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide and N-hydroxysuccinimide. Ind Crops Prod 20:281–289. doi:10.1016/j. indcrop.2003.10.012

Tryhnew LJ, Gunaratne KW, Spencer JV (1973) Effect of selected coating materials on the bacterial penetration of the avian egg shell. J Milk Food Technol 36:272–275

Türe H, Gällstedt M, Kuktaite R, Johansson E, Hedenqvist MS (2011) Protein network structure and properties of wheat gluten extrudates using a novel solvent-free approach with urea as a combined denaturant and plasticiser. Soft Matter 7:9416–9423. doi:10.1039/c1sm05830d

Ullsten NH, Gallstedt M, Johansson E, Graslund A, Hedenqvist MS (2006) Enlarged processing window of plasticized wheat gluten using salicylic acid. Biomacromol 7:771–776. doi:10.1021/bm050822u

Ullsten NH, Cho SW, Spencer G et al (2009) Properties of extruded vital wheat gluten sheets with sodium hydroxide and salicylic acid. Biomacromol 10:479–488. doi:10.1021/bm800691h

Vachon C, Yu HL, Yefsah R et al (2000) Mechanical and structural properties of milk protein edible films cross-linked by heating and gamma-irradiation. J Agric Food Chem 48:3202–3209

Van Krevelan DW (1976) Properties of polymers, their estimation and correlation with chemical structure. Elsevier Applied Science, Amsterdam

Verbeek CJR, Berg LEV (2009) Recent developments in thermo-mechanical processing of proteinous bioplastics. Recent Pat Mater Sci 2:171–189. doi:10.2174/1874464810902030171

Wang Y, Padua GW (2003) Tensile properties of extruded Zein sheets and extrusion blown films. Macromol Mater Eng 288:886–893. doi:10.1002/mame.200300069

Watanabe K, Okamoto S (1973) Formation of *yuba*-like film from wheat gluten. Nippon Shokuhin Kogyo Gakkai-Shi 20:66–72

Wessling C, Nielsen T, Leufvén A, Jägerstad M (1999) Retention of α-tocopherol in low-density polyethylene (LDPE) and polypropylene (PP) in contact with foodstuffs and food-simulating liquids. J Sci Food Agric 79:1635–1641. doi:10.1002/(sici)1097-0010(199909)79:12<1635:aid-jsfa413>3.0.co;2-#

Wieser H (2007) Chemistry of gluten proteins. Food Microbiol, 24(2):115–119

Wu LC, Bates RP (1972a) Soy protein-lipid films. 1. Studies on the film formation phenomenon. J Food Sci 37:36–39

Wu LC, Bates RP (1972b) Soy protein-lipid films. 2. Optimization of film formation. J Food Sci 37:40–44

Wu LC, Bates RP (1973) Influence of ingredients upon edible protein-lipid characteristics. J Food Sci 38:783–787

Zhang J, Mungara P, Jane J (2001) Mechanical and thermal properties of extruded soy protein sheets. Polymer 42:2569–2578. doi:10.1016/s0032-3861(00)00624-8

Zhang XQ, Do MD, Casey P et al (2010) Chemical cross-linking gelatin with natural phenolic compounds as studied by highresolution NMR spectroscopy. Biomacromol 11:1125–1132. doi:10.1021/bm1001284

Chapter 14
Layer Double Hydroxide Reinforced Polymer Bionanocomposites for Packaging Applications

Sunita Barik and Sushanta Kumar Badamali

Abstract Layered double hydroxides (LDH's) are a group of inorganic solid possessing structural similarity to that of brucite $Mg(OH)_2$. They are extensively used in the field of catalysis, biomedical applications, nuclear waste storage/ treatment, water treatment, composites etc. LDH offer high surface area and a huge boundary with the polymer, which direct the material properties. For this reason, nowadays, LDHs are drawing much more attention as a filler material for the synthesis of polymer matrix composites. Presently, research on biopolymer based nanocomposite is on the increase because of their relative profusion, low cost and environmental friendly nature. Present chapter focuses on different synthesis route followed for development of LDH based bionanocomposites along with their characterisation. Further, various properties of the synthesised composite are assessed to find out the suitability of the material for different purposes.

Keywords Layered double hydroxide · Bionanocomposites · Exfoliation
Tortuous path · Barrier properties

14.1 Introduction

In our everyday life, packaging plays a vital role starting from the packaging of food, gift or any other objects. Packaging of any product not only offers it an aesthetic look but also protects it from damage. It also helps transportation and prevents impairment while the product is on shelves (Johansson et al. 2012). Wide varieties of packaging materials are available in market. A material suitable for one purpose may not be suitable for the other. One has to choose a suitable packaging material depending on his/her requirements. Some of the general requirements of a packaging material are summarised in Fig. 14.1 (Rhim et al. 2013).

S. Barik (✉) · S. K. Badamali
Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751 004, Odisha, India
e-mail: sunitabarik2010@gmail.com

M. Jawaid and S.K. Swain (eds.), *Bionanocomposites for Packaging Applications*,
https://doi.org/10.1007/978-3-319-67319-6_14

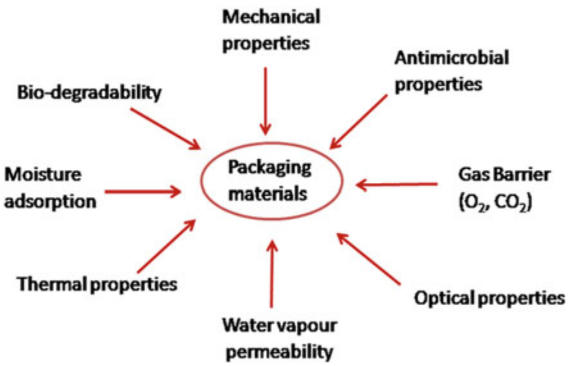


Fig. 14.1 General properties required for packaging materials. Reproduced with permission from Elsevier science, Ltd. (Rhim et al. 2013)

Mainly, we are dependent on petroleum-based products as the packaging materials. Over time to time, the consumer use of these materials is constantly increasing. The rigorous use of petroleum-based plastic material is leading to decrease in its availability and at the same time, it is also creating disposal problem because of its non-biodegradability nature (Othman 2014). For the maintainable expansion of the packaging industry, the development of bio-based eco-friendly material is very much essential. For this reason, now research institutes are focussing on the development of bio-based packaging materials using natural biopolymers as the raw material, which will degrade automatically in a natural way into organic by-products without persisting in the surroundings. Unfortunately, the inborn shortcomings of the use of biopolymer such as their water sensitivity, brittleness, poor gas barrier properties and low thermal and mechanical properties in comparison to petroleum-based material limits its use (de Azeredo 2009). However, these limitations can be improved by implementing nanocomposite technology.

14.1.1 Bionanocomposites

Composite is a heterogeneous system consisting of two or more constituents that are insoluble in one another and differ from each other in respect to their material composition. One of the constituents is the matrix and the other reinforcement or filler. When the dimension of at least one of the constituent phase is in the nano range (<100 nm), it is called as nanocomposite. Nanocomposites are materials with considerably enhanced properties due to the inclusion of little amounts of nanosized fillers into the matrix. Nanocomposites derived from polymer matrix and inorganic filler material not only create immense attention among researchers for their distinctive mode of preparation and properties, but also promise expansion of novel hybrid materials for precise applications in polymer composites field (Nshuti et al. 2008). There is ample variety of both natural and synthetic crystalline fillers that are able under precise conditions to intercalate a polymer. Some of the layered crystals prone to intercalation by a polymer are metal phosphates, metal chalcogenides, clays, layered silicates, layered double hydroxides etc. (Alexandre and Dubois 2000; Tronto et al. 2013).

14.1.2 Layered Double Hydroxide

Layered double hydroxides (LDHs) are a class of inorganic layered materials with structural similarity to that of brucite ($Mg(OH)_2$) where partial substitution of divalent cations by trivalent cations has occurred. This replacement offers a surplus positive charge which is counter balanced by interlayer anionic species. Along with the anions, some water molecules are also necessary for the stabilisation of the crystal structure (Basu et al. 2014). The general chemical formula of LDH is expressed as $[M^{2+}_{1-x}M^{3+}_{x}\ (OH)_2]^{x+}\ (A^{n-})_{x/n}{\cdot}mH_2O]$, where M^{2+} and M^{3+} represents divalent (Ca^{2+}, Mg^{2+}, Zn^{2+} etc.), trivalent (Cr^{3+}, Co^{3+}, Fe^{3+}, Al^{3+} etc.) metal ions, respectively, and A^{n-} represents interlayered anion (Cl^{-}, ${CO_3}^{2-}$, ${NO_3}^{-}$ etc.). A common structure of LDH is shown in Fig. 14.2 (Barik et al. 2017a). Over the last era, substantial advancement has been made in the production of LDHs with new morphologies and compositions. Compositional variety in the interlayer anions, in the hydroxide layers along with controllable morphology leads to functional multiplicity for which LDHs are used for variety of applications such as pharmaceuticals, gene therapy, drug storage–delivery agents, acid residue scavengers, catalyst supports, catalysts, absorbers, sorbents, functional materials, ion-exchange materials and nano fillers (Karan and Ay 2012).

14.1.3 Polymer/LDH Bionanocomposites

Inclusion of polymer into the LDH galleries proceeds via diverse path ways such as co precipitation, surfactant-mediated incorporation, hydrothermal treatment, reconstruction, solution intercalation and in situ polymerisation. However, the

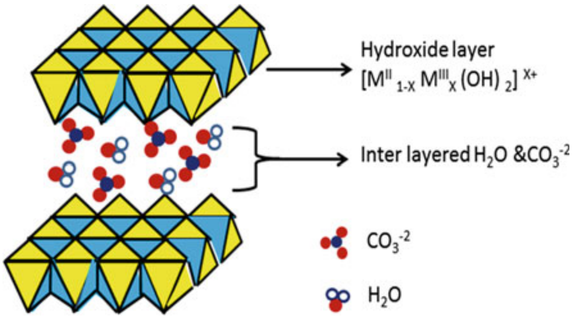


Fig. 14.2 Structure of Layered double hydroxide. Reproduced with permission from Springer science, Ltd. (Barik et al. 2017a)

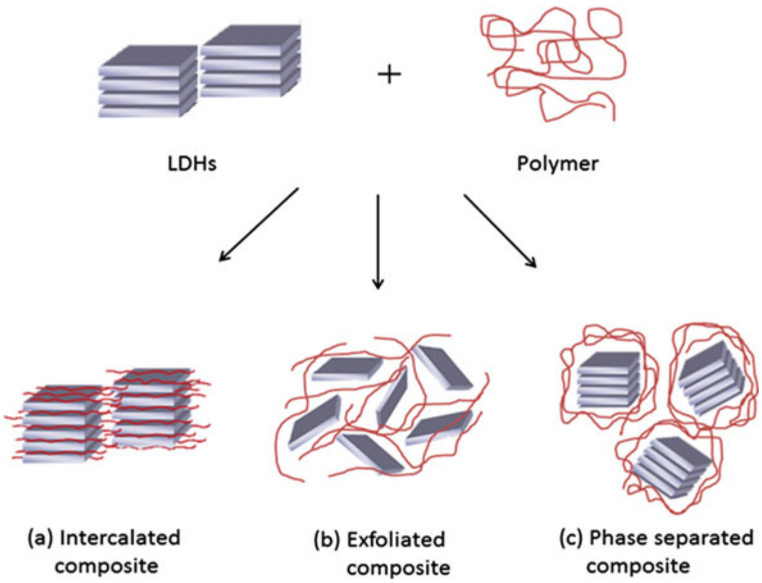


Fig. 14.3 Schematic representation of the different types of composites formed basing on the nature of interactions of polymer with the LDH: **a** Intercalated composite **b** exfoliated composite and **c** Phase separated composite. Reproduced with permission from Intech science, Ltd. (Tronto et al. 2013)

biocomposite materials are almost exclusively obtained by the intercalation of the biopolymer inside the galleries of layered structure. Basing on the chemical nature of the individual components and the synthesis technique followed the following three types of composites can be attained from the interaction of polymer with LDH as shown in Fig. 14.3 (Mittal 2009).

LDH offer a huge interface and large surface area with the biopolymer, which directs the properties of the composite material. The final behaviour of the composite can be significantly enhanced by the wide-ranging strong polymer-nano filler interactions as well as good quality particle distribution. For this reason, sometimes organic modification of the LDH is carried out to achieve better dispersion and compatibility with the polymer matrix. LDH present in these systems not only improve the chemical, thermal and mechanical firmness of the biopolymer but also enhances fire retardancy, protects it from oxidation and thus offers unbelievable enhancement in the performance properties of the biopolymer which makes them more suitable in market (Hussain et al. 2006). Wide varieties of biopolymers are available. Depending upon their origin, they can be outlined as shown in Fig. 14.4 (Othman 2014). Out of them few of the extremely studied biopolymers which might have importance in the upcoming packaging fields are starch, cellulose, chitosan, soya protein, albumin etc.

Some of the nanocomposites comprising LDH/biopolymers are summarised in Table 14.1.

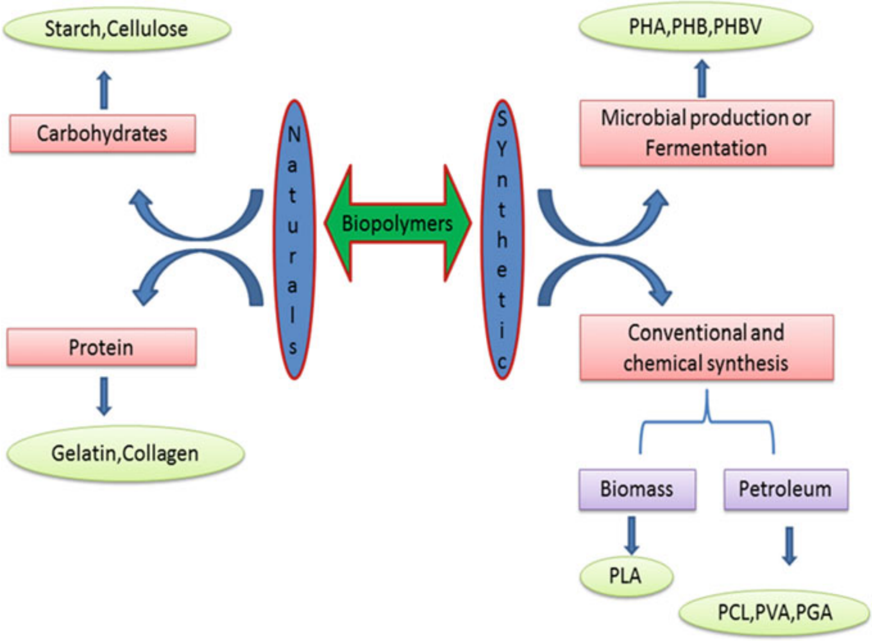


Fig. 14.4 An overview of biopolymers. Reproduced with permission from Elsevier science, Ltd. (Othman 2014)

14.1.4 Importance of Layered Filler Polymer Nanocomposite

In comparison to the conventional fillers, the layered nanofillers offer better hindrance delaying the passage of the gas. At the same time, the ordered nanostructure of the composite (in case of exfoliated composite) produces an increase tortuous path for the permeants compelling them to cover a long distance in order to get diffuse through the material (Niellen theory 1967). This provides additional barrier for air penetration to that of conventional composite as shown in Fig. 14.5, which makes the composite more suitable for packaging application (Azeredo et al. 2011; Swain et al. 2012). At the same time, when the thermal study of the LDH based composites is analysed, it is found that the degradation temperature for the composite is higher than that of the pure polymer which is attributed to the hindrance offered by the LDH layers for the transmission of volatile products and oxygen throughout the composite materials.

In this chapter, the brief description of synthesis and characterisation of LDH-based nanocomposites is given. Further, various properties of nanocomposites are discussed in order to assess the suitability of the material for packaging industry.

Table 14.1 Reviews of literature works comprising of LDH/Biopolymers

Bionanocomposites	Authors and year of publication	Property/Studied carried out
Starch/LDH	Wilhelm et al. (2003)	DMA and Thermal analysis
Chitosan/LDH	Han et al. (2007)	Development of biosensors
Polyvinyl alcohol/LDH	Ramaraj and Jaisankar (2008)	Thermal and morphological properties
Polylactic acid/LDH	Wang et al. (2010)	Burning behaviour
Starch/LDH	Chung and Lai (2010)	Mechanical properties, Moisture adsorption
Glycerol plasticized Starch/LDH-CMC	Wu et al. (2011)	Mechanical properties, Water vapour permeability and Thermal stability
Polylactic acid/LDH	Eili et al. (2012)	Biodegradability
Carboxymethyl cellulose (CMC)/LDH	Yadollahi and Namazi (2013)	Swelling behaviour and Thermal analysis
Polyhydroxybutyrate/LDH	Liau et al. (2014)	Mechanical and Thermal Analysis
Chitosan/LDH	Wei et al. (2015)	Photodynamic Effect
Cotton/LDH	Barik et al. (2017a)	Mechanical, UV protection and flame retardancy and cytotoxicity
Chitosan/LDH	Elanchezhiyan and Meenakshi (2017)	Oil separation

CMC carboxymethyl cellulose

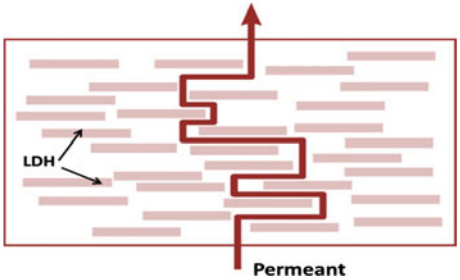


Fig. 14.5 Schematic representation of a tortuous path through an exfoliated polymer-LDH nanocomposite. Reproduced with permission from Taylor & Francis (Swain et al. 2012)

14.2 Synthesis of Polymer-LDH Bionanocomposite

Presently numerous schemes have been adopted by researchers for the synthesis of composites comprising biopolymer as the matrix and LDH as the filler materials (Sorrentino et al. 2007). Some of them are outlined in Fig. 14.6 and are discussed as follows.

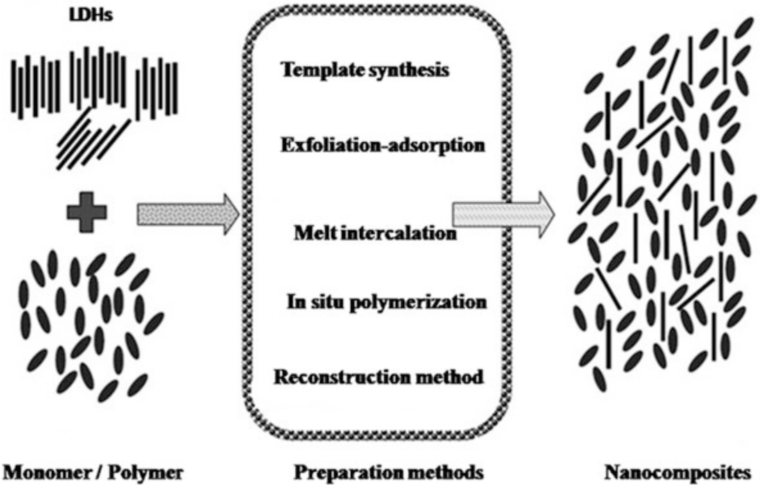


Fig. 14.6 Some preparation routes of polymer-LDH nanocomposites. Reproduced with permission from Elsevier science, Ltd. (Sorrentino et al. 2007)

14.2.1 Template Synthesis

For only water-soluble polymers, this method is suitable. The formation of the layered double hydroxide is carried out in situ in the aqueous solution comprising the polymer. The polymer facilitates the nucleation and growth of the LDH. During the progress, the polymer gets confined in between the layer structure. Although exfoliated composites are more likely to be formed by this method, still it is not extensively used due to the following inadequacies.

- The process requires high temperature.
- At the same time, there is inclination of the filler material to get aggregate.

14.2.2 Exfoliation-Adsorption

This technique involves the initial dispersion of the LDH in a suitable solvent wherein the polymer is also soluble. By mechanical action of stirring, the layered structure easily gets exfoliated in the solvent. The polymer chains then get adsorbed onto the exfoliated layer. Evaporation of the solvent results restacking of the layered double hydroxide with simultaneous entrapping of the polymer chains into it resulting in a well-ordered multilayer arrangement. This method is commonly preferred for polymers those are soluble in water. A schematic illustration of Exfoliation-adsorption process is given in Fig. 14.7.

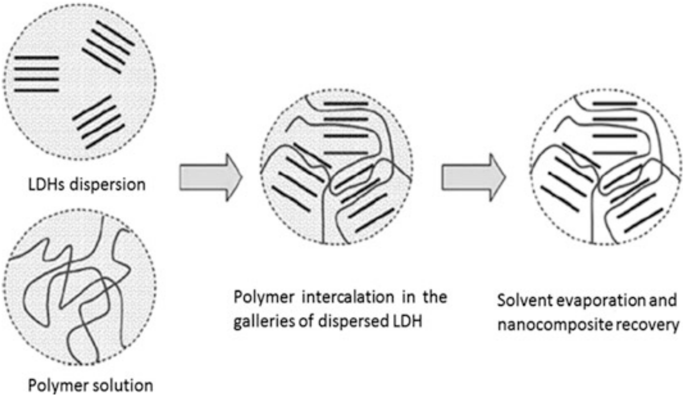


Fig. 14.7 Schematic depiction of Exfoliation-adsorption process. Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA science, Ltd. (Fawaz and Mittal 2015)

14.2.3 Melt Intercalation

In this method, the polymer is first melted and in the molten state the layered filler is blended with it. Under these conditions, if both the components are compatible with one another than the polymer gets penetrated into the interlayer space, resulting in the progress of composites. This method of composite preparation does not require any solvent or chemical which is more environmental benign. Generally for high molecular weight polymer, this method is preferred. Sometimes addition of low molecular weight compatibilizers is required to compatilize both the components in order to enhance polymer intercalation. Since this method is carried out at high temperature, one has to optimise the processing temperature so that neither of the components gets degraded at that working temperature as degradation affects both the micro structure and the filler-matrix interaction. However, by carrying out thermally stable alteration and working at low-temperature degradation can be avoided (Fawaz and Mittal 2015). This technique is industrially encouraging in comparison with other methods. Figure 14.8 illustrates the synthesis of polymer-LDH nanocomposite via melt intercalation process.

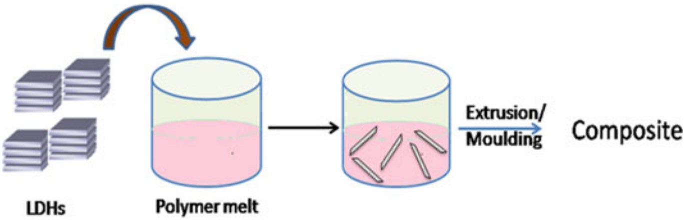


Fig. 14.8 Schematic representation of Melt intercalation process

14.2.4 In Situ Polymerization

In this method, initially the LDH is dispersed in a solvent containing the monomer or within the liquid monomer. The reaction mixture is stirred and sonicated for well dispersion. The formation of polymer takes place in the interlayer region. In order to start the polymerisation process, sometimes an initiator or a catalyst is added to the above reaction mixture at desired reaction condition. In some cases, it is also performed by radiation or heat. This method results in the formation of exfoliated or intercalated nanocomposites. In comparison to exfoliation-adsorption and melt intercalation process, by following In situ polymerization better exfoliation is attained. A schematic representation of this process is given in Fig. 14.9.

14.2.5 Reconstruction Method

In this method, intercalation of the polymer in between the inorganic layers of the LDH is achieved by reconstruction of the layered structure by ***Memory effect*** (Theiss et al. 2012).

Initially, synthesis of the LDH from its precursors is carried out followed by thermal activation/calcinations in the temperature region 300–500 °C. During calcination removal of interlayer anions, water and hydroxyl group takes place resulting in the formation of mixed oxides. The calcined LDH material when placed in an aqueous solution of the polymer results in the reconstruction of the original LDH structure with simultaneous intercalation of the polymer into the LDH gallery. However, if the calcination is carried out at too high temperature then it leads to permanent decomposition of the LDH into mixed metal oxide and memory effect is not exhibited.

Although several methods are employed for composite preparation, the best product is resulted when good affinity exists in between the layered host and the polymer.

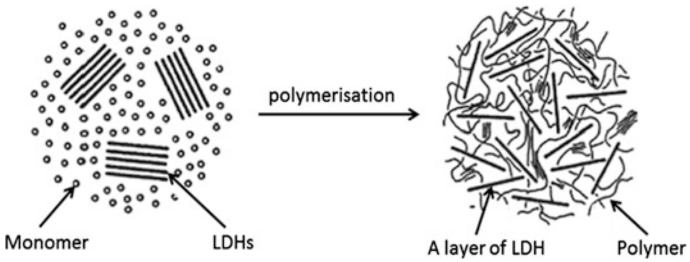


Fig. 14.9 Schematic depiction of In situ polymerisation method. Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA science, Ltd. (Fawaz and Mittal 2015)

14.3 Characterisation of Polymer-LDH Bionanocomposite

Some of the frequently used techniques for the characterisation of LDH and polymer/LDH nanocomposites are X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction studies (SAED), elemental detection studies (EDS) etc.

14.3.1 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier transform infrared spectroscopy (FT IR) is recorded to characterise the molecular interaction of the sample. FT IR spectra is recorded in form of KBr pellets in the wavelength range of 4000–400 cm^{-1}. FTIR data help in understanding the functional groups present in the neat polymer and the LDH. For the nanocomposites, it provides the possible interactions between inorganic and the organic parts. FTIR spectra of Mg–Al-LDH, sodium-carboxymethyl cellulose (Na–CMC) and Na–CMC-LDH nanocomposite are given away in Fig. 14.10. FTIR spectra of Na–CMC show a broad strong band centred at 3420 cm^{-1}, is assigned to the hydroxyl stretching with intramolecular and intermolecular hydrogen bonds. The C–H stretching attached with the ring methane hydrogen atoms appeared at

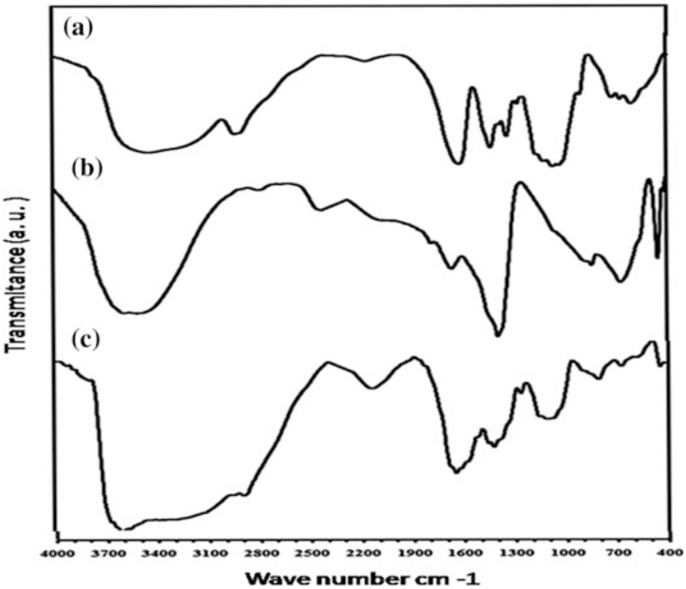


Fig. 14.10 FT IR spectrum of **a** Na-CMC, **b** Mg–Al-LDH and **c** Na–CMC-LDH nanocomposite. Reproduced with permission from Springer science, Ltd. (Yadollahi and Namazi 2013)

2913 cm^{-1}. The symmetric and asymmetric stretching vibration of the carboxylate groups leads to band at 1422 and 1607 cm^{-1}. Further, the bands in the region 1000–1200 cm^{-1} are assigned to the –C–O– stretching of the polysaccharide skeleton (Luna-Martinez et al. 2011). In the LDH, the broad band at around 3600 cm^{-1} is assigned to the –OH stretching of the hydroxide layer. Further, bands at 690 and 870 cm^{-1} are assigned to the Mg–O and Al–O vibrations. respectively (Barik et al. 2015). In the nanocomposites, the features of CMC are clearly observed. However, shifting of the peaks associated with the asymmetric stretching vibrations of the carboxylate group towards higher wave number may be due to the strong interaction with the LDH metal ions (Yadollahi and Namazi 2013).

14.3.2 X-Ray Diffraction

X-ray diffraction is a very use full technique which gives structural information regarding the polymer, filler and the nanocomposites. The sample to be analysed (may be in the form of powder/film) is kept in the sample holder, and a fine X-rays beam is allowed to pass through it. The intensity corresponding to diffraction angel 2θ data is recorded which gives rise to the XRD pattern. From the XRD data, d-spacing can be calculated by using the Bragg's equation, **$n\lambda = 2d\sin\theta$.**

Where d is the inter layer distance between two consecutive layers.

n = diffraction order, θ = Bragg's angle. λ is the wavelength.

A typical XRD outline of Zn–Al-LDH (Zn–Al molar ratio 3:1) is shown in Fig. 14.11 (Barik et al. 2017b).

Also from the XRD data, one can calculate the crystallite size. The crystallite size is measured by using the Scherer's formulae, **$\tau = K\lambda/(\beta \cos\theta)$**

Where τ crystallite size, k is the dimensional space factor and its value is 0.89, β is the full width half of the maximum intensity (FWHM) and λ is the wavelength.

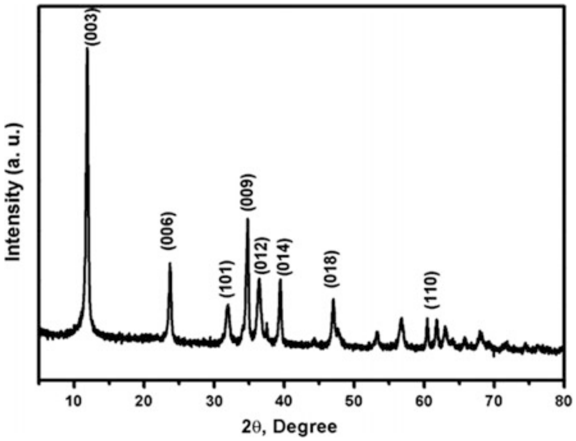


Fig. 14.11 Power XRD study of synthetic Hydrotalcite (Zn–Al-LDH). Reproduced with permission from Taylor & Francis Group Ltd. (Barik et al. 2017b)

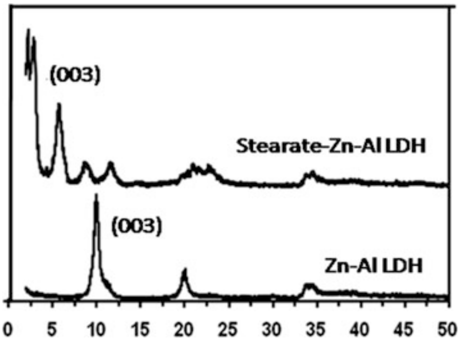


Fig. 14.12 XRD spectra of pristine Zn–Al-LDH and Stearate modified Zn–Al-LDH. Reproduced with permission from MDPI science Ltd. (Eili et al. 2012)

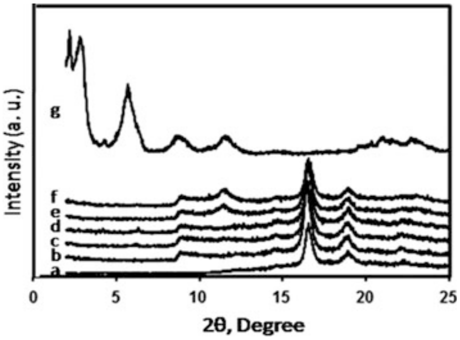


Fig. 14.13 XRD spectra of **a** PLA, PLA/stearate-LDH nanocomposites of LDH concentrations **b** 1%, **c** 3%, **d** 5%, **e** 7%, **f** 10% and **g** stearate/Zn–Al-LDH. Reproduced with permission from MDPI science (Eili et al. 2012)

In an another case in Fig. 14.12, XRD pattern of unmodified Zn–Al-LDH and modified Zn–Al-LDH by stearate ion is compared. Shifting of the (003) plane to lower 2θ value clearly indicates enlarge in interlayer distance from 8.83 Å in Zn–Al-LDH to 40.1 Å in stearate-Zn–Al-LDH.

The XRD patterns of pure PLA, stearate modified Zn–Al-LDH and PLA/stearate-LDH nanocomposites synthesised using different concentration of the filler material are shown in Fig. 14.13. Disappearance of the diffraction peaks in the composites indicating entire exfoliation of the LDH layers in the PLA polymer.

Analysis of the core structure of composites by using XRD technique alone can a lot be deceptive, as this technique cannot identify layers which are relatively present in disorderly manner in exfoliated nanocomposites (Mai and Yu 2006). Hence, it is further to be supported by electron microscopic study like SEM, TEM.

14.3.3 Scanning Electron Microscopy (SEM) Study

In SEM study, a beam of energetic electrons is focussed on the specimen. The signals derived from the interaction of the electrons, and sample reveals varieties information about the material like external morphology (size and shape),

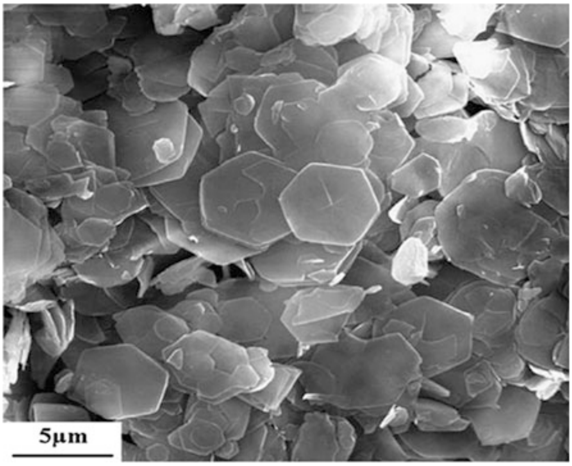


Fig. 14.14 SEM image of Organo-modified Co–Al-LDH. Reproduced with permission from Elsevier science, Ltd. (Peng et al. 2009)

crystalline structure and the orientation of materials. EDS detector attached with SEM helps in determining the chemical composition of the sample. A SEM image of Organo-modified Co–Al-LDH (OCo–Al-LDH) is revealed in Fig. 14.14 (Peng et al. 2009) which undoubtedly indicates hexagonal morphology of the LDH particles with a lateral dimension of about 4 μm.

Even a particular LDH may possess different shapes depending upon the synthesis condition. In Fig. 14.15, a series of Ni–Al–CO_3 LDHs with different morphologies synthesised by following glycine-assisted hydrothermal method is presented. Glycine acts as a complexing reagent and favours the crystal growth. Keeping metal salt concentration of 0.2 M and varying the glycine/Ni ratio, LDH with different morphologies are obtained. When glycine/Ni ratio less than five, thick disk shaped particles are obtained (Fig. 14.15a). On the other hand, when glycine/Ni ratio is 5:1, the presence of both large platelets and small disks is observed (Fig. 14.15b). Further increase in glycine amount (glycine/Ni ratio is 8:1) induces formation of 3D hierarchical nanostructures which shows peony-like particles with an average diameter of 10 μm (Fig. 14.15c). Interestingly, keeping glycine/Ni ratio as 40:1 and decreasing the metal salt concentration to 0.04 M, spherical nanostructures alike to wool balls with an average diameter of 2 μm are resulted (Fig. 14.15d). The above discussion clearly indicates that by controlling the reaction parameters one can change the shape, size and crystallinity of LDH particles (Faour et al. 2012).

14.3.4 Transmission Electron Microscopy (TEM) Study

TEM is another microscopic technique which provides detail about the internal composition. It also provides additional information like crystallinity, arrangement of the atoms (Fringe Width), stress or even magnetic domains. In contrast to SEM,

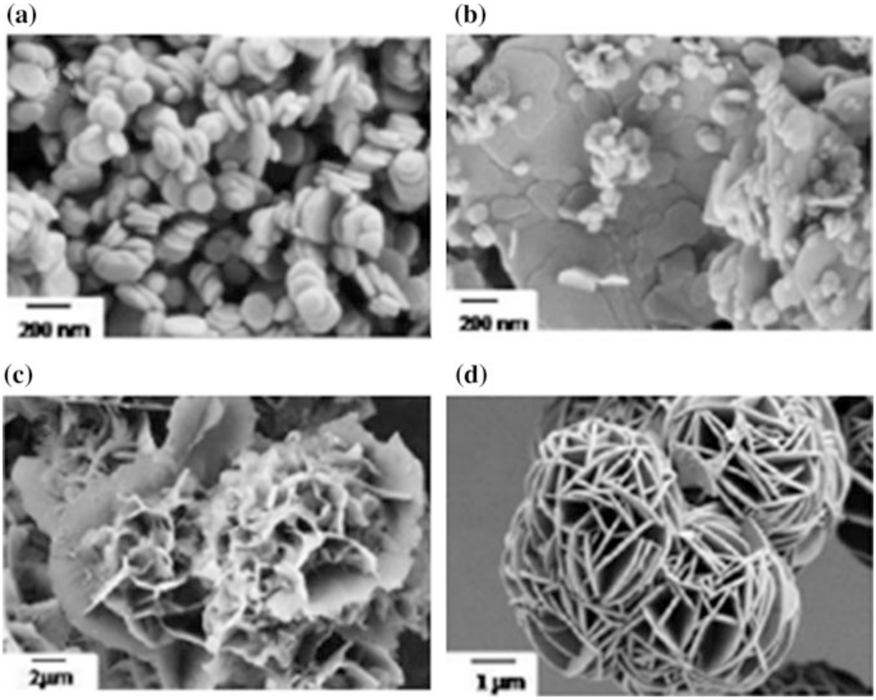


Fig. 14.15 FE-SEM images of Ni–Al-LDH: **a** glycine/Ni ratio 2:1, metal salt 0.2 M, **b** glycine/Ni ratio 5:1, metal salt 0.2 M, **c** glycine/Ni ratio 8:1, metal salt 0.2 M, and **d** glycine/Ni ratio 40:1, metal salt 0.04 M. Reproduced with permission from American Chemical Society science, Ltd. (Faour et al. 2012)

it is based on transmitted electrons. It can work at higher resolution, and atomic scale imaging is possible by this study. For determination of size of nano particles, TEM characterisation is more reliable. For polymeric nanocomposites containing layered filler material, TEM analysis helps to visualise intercalation or exfoliation nature of the layered filler. In Fig. 14.16, TEM images of Poly lactic acid/stearate-Zn–Al-LDH nanocomposites containing different amount of LDH (3.0, 5.0, 7.0 and 10.0 wt%) are shown. In the TEM micrograph, the presence of LDH nano layers is clearly observed as dark lines and is marked as arrows and the grey areas correspond to the PLA matrix. Loss of stacking order and random dispersion of the LDH layers is also clearly visible. Further, in the micrograph absence of aggregation suggests the exfoliated type of nanocomposites which is in agreement with the XRD results (Eili et al. 2012).

Another case of TEM image comprising CMC/LDH composite at lower and higher magnification is represented in Fig. 14.17. This system shows an extremely complex morphology for the dispersed LDH particles. Intercalation along with some exfoliation of LDH layers is clearly visible and is indicated by arrow mark. At the same time at few places, agglomeration of the LDH layers (black spot) is also

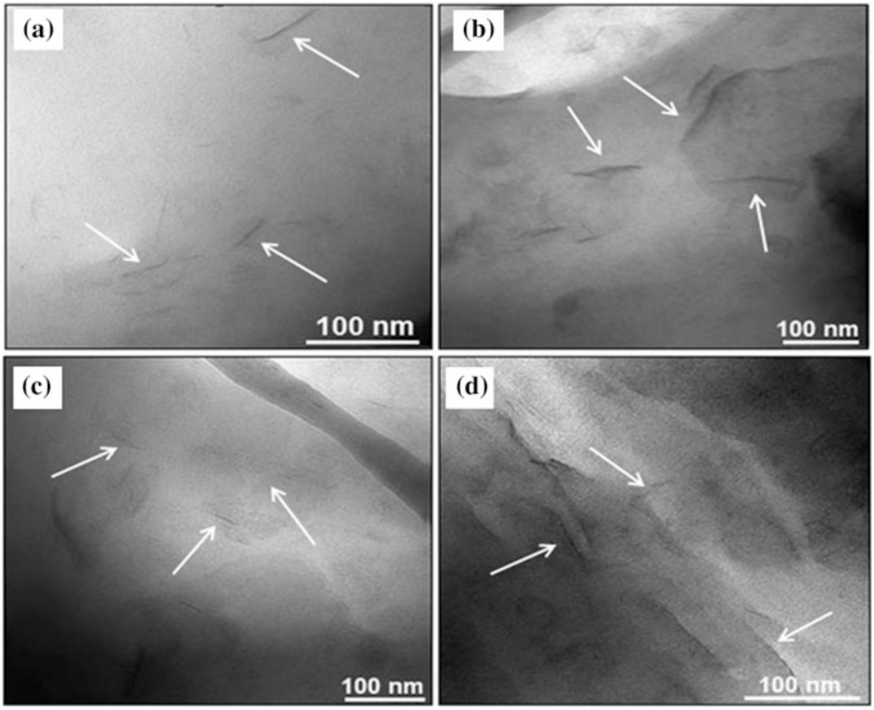


Fig. 14.16 TEM images of Poly Lactic Acid /stearate modified Zn–Al-LDH nanocomposites with different wt% of filler **a** 3.0, **b** 5.0, **c** 7.0, and **d** 10.0 respectivelly. Reproduced with permission from MDPI science (Eili et al. 2012)

seen. That means the given system is composed of intercalated region, exfoliated layers of LDH along with some agglomeration.

14.4 Properties of LDH Based Bionanocomposites

In order to know applicability of a material, the study of its different properties is very much essential. Knowledge of the various properties helps in assessing the suitability of the material for different purposes. Some of the properties of LDH based bionanocomposites are discussed as follows.

14.4.1 Thermogravimetric Analysis (TGA)

The thermal behaviour of LDH, polymer and the composites is determined by following thermo gravimetric analysis, and the experimental results are plotted by taking mass% versus temperature.

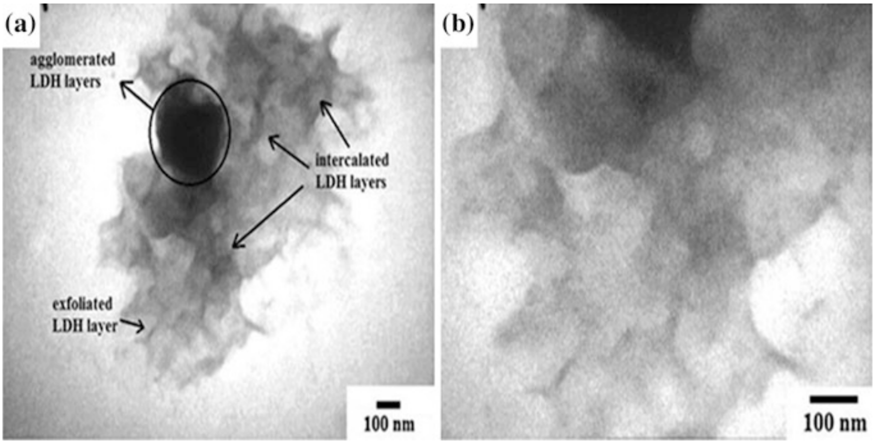


Fig. 14.17 TEM descriptions of the CMC–Mg–Al-LDH composites: **a** at low and **b** at high magnification. Reproduced with permission from Springer science, Ltd. (Yadollahi and Namazi 2013)

In Fig. 14.18, the influence of two different Al containing LDHs (Ni–Al-LDH and Mg–Al-LDH) on the thermal property of Na–CMC (sodium-carboxymethyl cellulose) is represented. Thermo gravimetric profile of Na–CMC shows four-step degradation behaviour for Na-CMC where as three-step decay behaviour is shown for the CMC–LDH nanocomposites. It is clearly noticed that the thermal behaviour of the Na–CMC significantly changes upon composite formation. The % mass loss of the Na–CMC and that of the composites is tabulated in Table 14.2.

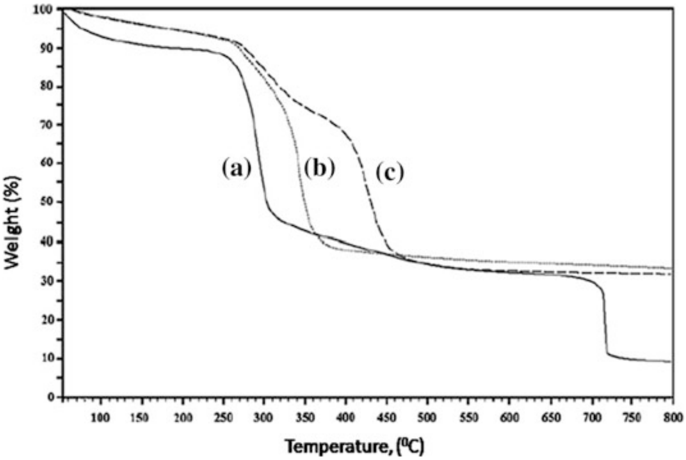


Fig. 14.18 Thermo gravimetric Analysis of **a** Sodium-CMC, **b** Ni–Al–CMC-LDH and **c** Mg–Al–CMC-LDH. Reproduced with permission from Springer science, Ltd. (Yadollahi and Namazi 2013)

Table 14.2 Mass loss determined by TGA curves for Na–CMC, CMC–Ni–Al-LDH, and CMC–Mg–Al-LDH nanocomposites

Degradation step	Na–CMC	CMC–Ni–Al-LDH composite	CMC-Mg–Al-LDH composite
First	About 10% (below 200 °C)	About 5% (below 200 °C)	About 5% (below 200 °C)
Second	About 44% (range 200–600 °C) With max. degradation peak at 292 °C	About 13% (range 200–300 °C)	About 21% (range 200–360 °C)
Third	About 11%	About 46%, Up to 600 °C With max. degradation peak at 342 °C	About 36%, Up to 600 °C With max. degradation peak at 425 °C
Fourth	About 23%		

On comparing the maximum degradation temperature of Na–CMC with its composites, it is observed that the CMC–LDH nanocomposite samples possess enhanced thermal stabilities compared to Na–CMC (about 50 °C for CMC–Ni–Al-LDH composite and 133 °C for CMC–Mg–Al-LDH composite). Such enhancement in stability of CMC upon composite formation could be ascribed to the insulator and obstruct effect of LDH layers. Further, it is noticed that CMC–Mg–Al-LDH nanocomposites possess superior thermal stability in comparison with CMC–Ni–Al-LDH nanocomposites.

In Fig. 14.19, another case of thermo gravimetric analysis comprising PVA and its composites with Mg–Al-LDH is represented which shows a contrast result. Here, despite the barrier effect of layered nanocomposites, the thermo gravimetric analysis shows a decrease in thermal stability in the range 300–400 °C for the PVA-LDH nanocomposites. This may be due to the aggregation of filler leading to definite phase separation into a filler rich phase and a polymer-rich phase. Also the decrease in the crystallinity by the insertion of the overload filler in the crystalline regions of the polymer may be another reason for such type of observation is noticed. Since the product is to be used for packaging purposes, this reduction in thermal stability will not limit the application of the material.

14.4.2 Gas and Moisture Obstruction Properties

Polymer nanocomposites possess tremendous obstruction against water vapour and gases (e.g. O_2 and CO_2). It has been found that layered fillers (like clays and LDH) serve this purpose best. The reduction in gas permeability depends on the compatibility between the LDH and the polymer, structure of the nanocomposites,

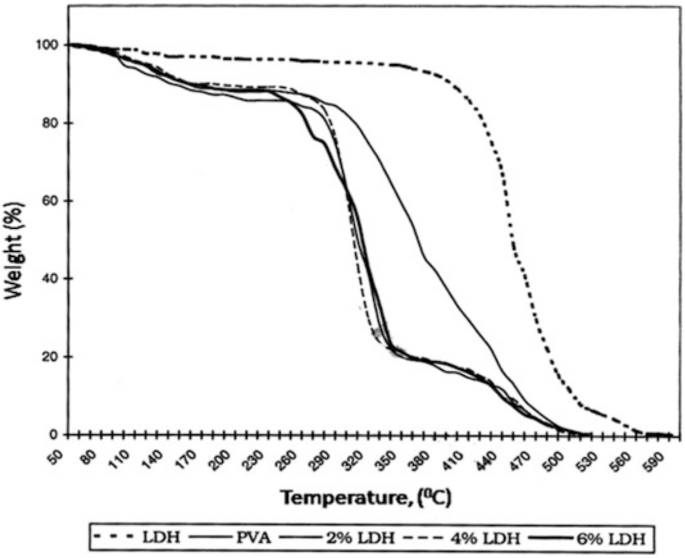
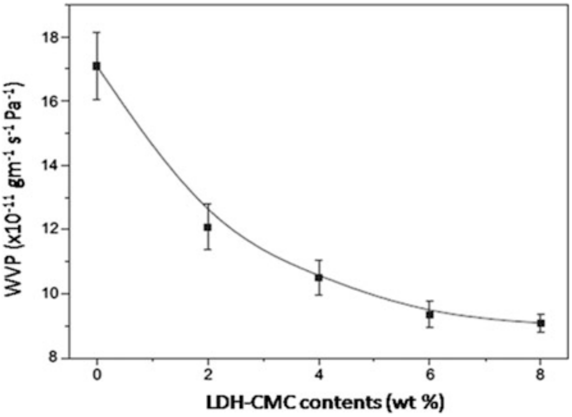


Fig. 14.19 TGA thermo grams of PVA-LDH nanocomposite films. Reproduced with permission from Taylor & Francis Group Ltd. (Ramaraj and Jaisankar 2008)

aspect ratio of the LDH platelets etc. Generally, polymer nanocomposites with totally exfoliated LDH layers having large aspect ratio value show very good gas barrier properties (Choudalakis and Gotsis 2009). The occurrence of ordered dispersed LDH layers with high aspect ratios in the composite is impermeable to water molecules, and it compels the gas travelled through it to follow a tortuous path which results in enhanced gas obstruction properties of the nanocomposites.

In Fig. 14.20, the moisture transport through the LDH-CMC/glycerol plasticized starch nanocomposites containing different LDH-CMC contents is represented. It is

Fig. 14.20 Effect of LDH-Carboxy methyl cellulose contents on water vapour permeability of glycerol plasticized starch nanocomposites from Elsevier science, Ltd. (Wu et al. 2011)



clearly noticed that water vapour permeability (WVP) goes on decreasing with the increase of the filler content. With filler content above 6 wt%, WVP values decreased a little which may be due to the aggregation of LDH-CMC at higher percentage (Wu et al. 2011).

14.4.3 Biodegradable Properties

Biodegradation of a material may mean fragmentation or sometimes it is degradation by the microorganisms. One of the vital reasons of using biopolymers for the preparation of nanocomposite is to make use of the biodegradability property of the polymer. For this reason, it is desirable that this property is retained after nanocomposite formation. In Fig. 14.21, biodegradability of PLA and its composite (PLA/stearate-Zn–Al-LDH) is compared. Soil burial test method is followed over a period of seven months to study the disintegration rate. Thin-plate test specimens of a particular dimension (30 × 30 × 1 mm) were taken, weighed and buried in soil. At an interval of one month the buried thin-plate samples were taken out, washed, dried and weight was recorded. From the difference in weight before and after degradation, the average weight loss percentage for each test specimen was calculated. Weight loss of the samples with variation in time indicates the degradation rate. It is clearly observed that disintegration rate of the PLA and its nanocomposites with stearate-Zn–Al-LDH are nearly same at the beginning (up to about four months), after that the rate of disintegration of the nanocomposites is higher in comparison to the neat polymer, and the weight loss percentage goes on increasing as the LDH loading percentage is increased. This may be due to absorption of water from the soil by the hydroxyl groups of the LDH leading to hydrolysis of the PLA polymer faster in the composite.

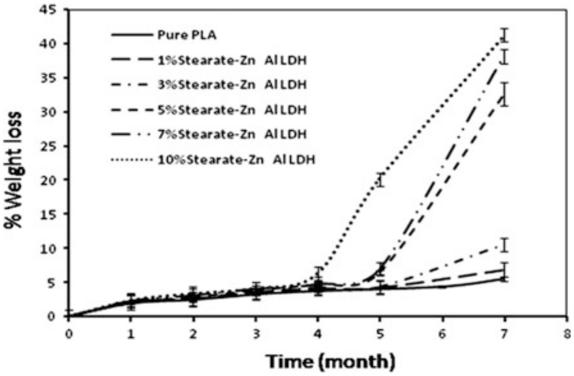


Fig. 14.21 Weight loss of PLA and PLA-Zn–Al-LDH nanocomposites in soil (up to seven months). Reproduced with permission from MDPI science (Eili et al. 2012)

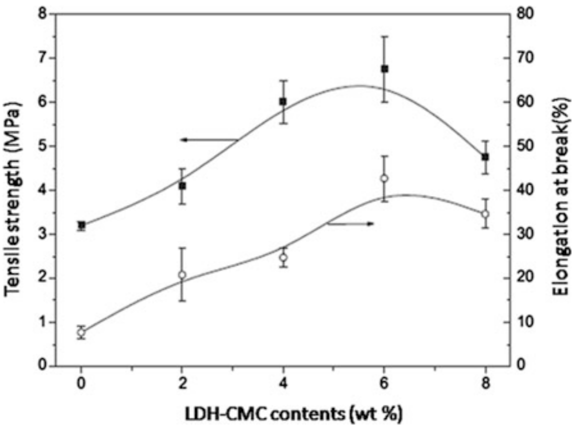


Fig. 14.22 Effect of LDH-CMC contents on tensile yield strength and elongation at break of the composites. Reproduced with permission from Elsevier science, Ltd. (Wu et al. 2011)

14.4.4 *Mechanical Properties*

When a force is applied to a material, the characteristics displayed by it are known as mechanical properties of that material. For example, tensile properties, hardness, toughness, ductility are some of the mechanical properties. These properties usually relate to the elastic or plastic behaviour and indicate the suitability of the material in mechanical application. Generally, destructive tests are followed for the assessment of mechanical property and after the test the material gets destructed. Figure 14.22 represents the result of LDH-CMC percentage on the elongation at break and the tensile strength of LDH-CMC/glycerol plasticized starch nanocomposites. It is clearly observed that with increasing the filler contents from zero to six wt%, tensile strength goes on increasing from 3.2 to 6.75 MPa. This enhancement of tensile strength is interrelated to the superior interfacial interaction between the GPS matrix and the LDH-CMC filler as both the matrix and filler possessed alike polysaccharide structures. On further increasing the filler content to 8%, decrease in the tensile strength value to 4.75 MPa is observed. At higher loading, % agglomeration of the filler occurs which reduces the effective filler loading. Hence the reduction in tensile strength value. For the LDH-CMC/GPS composites, the experimental results for elongation at break also followed a similar type of trend by the increase of LDH-CMC contents.

14.5 Conclusion and Future Prospective

The present chapter includes synthesis and characterisation of LDH-based bionanocomposites. Further descriptions about various analytical techniques are included in order to find out the suitable application of the material. It is found out that LDH based binanocomposites possess enhanced mechanical property. Also they exhibit good gas and moisture barrier properties which make these materials suitable for packaging industry. Further, their disintegration rate in soil is higher which is making them more environmentally friendly.

Acknowledgements Author expresses her thanks to UGC, New Delhi, for providing financial assistance under UGC BSR Fellowship scheme.

References

Alexandre M, Dubois P (2000) Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater Sci Eng 28:1–63

Azeredo HMC, Mattoso LHC, Hugh THM (2011) Nanocomposites in food packaging—a review. Advances in diverse industrial applications of nanocomposites, pp 57–78

Basu D, Das A, Stockelhuber KW, Wagenknecht U, Heinrich G (2014) Advances in layered double hydroxide (LDH)-based elastomer composites. Prog Polym Sci 39:594–626

Barik S, Kisku SK, Behera L, Swain SK (2015) Enhancement of thermal properties of polyacrylonitrile by reinforcement of Mg–Al layered double hydroxide. Polym Compos 36 (11):2140–2144

Barik S, Khandual A, Behera L, Badamali SK, Luximon A (2017a) Nano-Mg–Al-layered double hydroxide application to cotton for enhancing mechanical, UV protection and flame retardancy at low cytotoxicity level. Cellulose 24:1107–1120

Barik S, Behera L and Badamali SK (2017b) Assessment of thermal and antimicrobial properties of PAN/Zn-Al layered double hydroxide nanocomposites. Compos Interfaces 24:579–591

Choudalakis G, Gotsis AD (2009) Permeability of polymer/clay nanocomposites: a review. Eur Polym J 45:967–984

Chung Y-L, Lai H-M (2010) Preparation and properties of biodegradable starch-layered double hydroxide nanocomposites. Carbohyd Polym 80:525–532

Eili M, Shameli K, Ibrahim NA, Yunus WMZW (2012) Degradability Enhancement of Poly (Lactic Acid) by Stearate-Zn_3Al LDH Nanolayers. Int J Mol Sci 13:7938–7951

Elanchezhiyan SSD, Meenakshi S (2017) Synthesis and characterization of chitosan/Mg-Al layered double hydroxide composites for the removal of oil particles from oil in water emulsion. Int J Biol Macromol. doi:10.1016/j.ijbiomac.2017.01.095

Faour A, Mousty C, Prevot V, Devouard B, Roy AD, Bordet P, Elkaim E, Gueho CT (2012) Correlation among Structure, Microstructure, and Electrochemical Properties of NiAl−CO3 Layered Double Hydroxide Thin Films. J. Phys. Chem. C 116: 15646–15659

Fawaz J, Mittal V (2015) Synthesis of polymer nanocomposites: review of various techniques. pp 1–30

Hussain F, Hojjati M, Okamoto M, Gorga RE (2006) Review article: polymer-matrix nanocomposites, processing, manufacturing, and application: an overview. J Compos Mater 40:1511–1575

Han E, Shan D, Xue H, Cosnier S (2007) Hybrid material based on chitosan and layered double hydroxides: characterization and application to the design of amperometric phenol biosensor. Biomacromolecules 8:971–975

de Azeredo HMC (2009) Nanocomposites for food packaging applications. Food Res Int 42: 1240–1253

Johansson C, Bras J, Mondragon I, Nechita P, Plackett D, Simon P, Svetec DG, Virtanen S, Baschetti MG, Breen C, Clegg F, Aucejo S (2012) Renewable fibers and bio-based materials for packaging applications-A review of recent developments. Bio resources 7:2506–2552

Karan BZ, Ay AN (2012) Layered double hydroxides—multifunctional nanomaterials. Chem Pap 66: 1–10

Luna-Martinez JF, Hernandez-Uresti DB, Reyes-Melo ME, Guerrero-Salazar CA, Gonzalez-Gonzalez VA, Sepulveda-Guzman S (2011) Synthesis and optical characterization of ZnS–sodium carboxymethyl cellulose nanocomposite films. Carbohyd Polym 84:566–570

Liau CP, Ahmad MB, Shameli K, Yunus WMZW, Ibrahim NA, Zainuddin N, Then YY (2014) Preparation and characterization of polyhydroxybutyrate/polycaprolactone/Mg-Al layered double hydroxide nanocomposites. Digest J Nanomaterials Biostructures 9:71–82

Mai YW, Yu ZZ (2006) Polymer nanocomposites. Woodhead Publishing Ltd, Cambridge, UK

Mittal V (2009) Polymer layered silicate nanocomposites. Rev Mater 2:992–1057

Nshuti CM, Wang D, Hossenlopp JM, Wilkie CA (2008) Aluminum-containing layered double hydroxides: the thermal, mechanical, and fire properties of (nano)composites of poly(methyl methacrylate). J Mater Chem 18:3091–3102

Othman SH (2014) Bio-nanocomposite materials for food packaging applications: Types of biopolymer and nano-sized filler. Agric Agric Sci Procedia 2:296–303

Peng H, Tjiu WC, Shen L, Huang S, He C, Liu T (2009) Preparation and mechanical properties of exfoliated CoAl layered double hydroxide (LDH)/polyamide 6 nanocomposites by in situ polymerization. Compos Sci Technol 69:991–996

Ramaraj B, Jaisankar SN (2008) Thermal and Morphological Properties of Poly(vinyl alcohol) and Layered Double Hydroxide (LDH) Nanocomposites. Polym Plast Technol Eng 47:733–738

Rhim JW, Park HM, Ha CS (2013) Bio-nanocomposites for food packaging applications. Prog Polym Sci 38:1629–1652

Sorrentino A, Gorrasi G, Vittoria V (2007) Potential perspectives of bio-nanocomposites for food packaging applications. Trends Food Sci Technol 18:84–95

Swain SK, Priyadarshini PP, Patra SK (2012) Soy Protein/Clay Bionanocomposites as Ideal Packaging Materials. Polym Plast Technol Eng 51:1282–1287

Theiss FL, Sear-Hall MJ, Palmer SJ, Frost RL (2012) Zinc aluminium layered double hydroxides for the removal of iodine and iodide from aqueous solutions. Desalination Water Treat 39(1–3):166–175

Tronto J, Bordonal AC, Naal Z, Valim JB (2013) Conducting polymers/layered double hydroxides intercalated nanocomposites. pp 3–31

Wilhelm H-M, Sierakowski M-R, Souza GP, Wypych F (2003) The influence of layered compounds on the properties of starch/layered compound composites. Polym Int 52: 1035–1044

Wang D-Y, Leuteritz A, Wang Y-Z, Wagenknecht U, Heinrich G (2010) Preparation and burning behaviors of flame retarding biodegradable poly (lactic acid) nanocomposite based on zinc aluminum layered double hydroxide. Polym Degrad Stab 95:2474–2480

Wu D, Chang PR, Ma X (2011) Preparation and properties of layered double hydroxide–carboxymethylcellulose sodium/glycerol plasticized starch nanocomposites. Carbohyd Polym 86:877–882

Wei PR, Kuthati Y, Kankala RK, Lee CH (2015) Synthesis and characterization of chitosan-coated near-infrared (nir) layered double hydroxide-indocyanine green nanocomposites for potential applications in photodynamic therapy. Int J Mol Sci 16:20943–20968

Yadollahi M, Namazi H (2013) Synthesis and characterization of carboxymethyl cellulose/ layered double hydroxide nanocomposites. J Nanopart Res 15:1563