Sustainable Nanocomposites in Food Packaging

**H. Anuar, F. B. Ali, Y. F. Buys, M. A. Siti Nur E'zzati,
A. R. Siti Munirah Salimah, M. S. Mahmud,
N. Mohd Nordin and S. A. Adli**

List of Abbreviations

APs	Alkyl phenols
CNCs	Cellulose nanocrystals
CNT	Carbon nanotube
CNW	Cellulose nanowhisker
CO_2PC	Carbon dioxide permeability coefficient
CO_2TR	Carbon dioxide transmission rate
DSC	Differential scanning calorimetry
DMF	N, N-dimethylformamide
EVOH	Ethylene vinyl alcohol copolymer
HDPE	High-density polyethylene
HPMC	Hydroxyl propyl methyl cellulose
HT	Hydroxytyrosol
HV	Hydroxyl-valerate
LDPE	Low-density polyethylene
MgO	Magnesium oxide
MMT	Montmorillonite
MWNT	Multi-walled carbon nanotube
OPC	Oxygen permeability coefficient
OTR	Oxygen transmission rate
PANI	Polyaniline
PCL	Poly(e-caprolactone)
PEG	Polyethylene glycol
PEGME	Polyethylene glycol methyl ether

H. Anuar (✉) · Y. F. Buys · M. A. Siti Nur E'zzati · A. R. Siti Munirah Salimah ·
M. S. Mahmud · N. Mohd Nordin
Department of Manufacturing and Materials Engineering, Faculty of Engineering,
International Islamic University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia
e-mail: hazleen@iium.edu.my

F. B. Ali · S. A. Adli
Department of Biotechnology Engineering, Faculty of Engineering, International Islamic
University Malaysia, Jalan Gombak, 53100 Kuala Lumpur, Malaysia

Inamuddin et al. (eds.), *Sustainable Polymer Composites and Nanocomposites*,
https://doi.org/10.1007/978-3-030-05399-4_15

PET	Polyethylene terephthalate
PHA	Poly hydroxyalkanoate
PHB	Polyhydroxy butyrate
PHBV	Polyhydroxybutyrate-co-hydroxyvalerate
PLA	Polylactic acid
PP	Polypropylene
PVA	Polyvinyl alcohol
ROP	Ring-opening polymerization
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
WHO	World health organization
WSC	Water-soluble chitosan
WVPC	Water vapour permeability coefficient
WVTR	Water vapour transmission rate

1 Introduction

Human activities have already brought about changes to the ecological system worldwide, thereby giving rise to global warming and pollution. These problems have led to increased environmental degradation, which is destroying many things. Many plastic packaging industries are trying to minimize their reliance on synthetic materials in order to reduce toxicity levels [47]. Therefore, new environmental guidelines are forcing the exploration of novel packaging materials that are compatible with the environment. Such materials are currently being developed from various natural resources, among which biopolymers are the most popular. Biopolymers have many advantages compared to petroleum-based plastics in terms of performance, processability, and biodegradability [82]. There are several types of biopolymer matrices including polylactic acid (PLA), polyvinyl alcohol (PVA), polyhydroxy butyrate (PHB) and starch-based polymers. The poor gas and water barrier properties, unstable mechanical properties and weak resistivity of plastics have limited their use in various applications [55]. Therefore, to improve their mechanical and barrier properties, and to impart novel features to them, biopolymers are reinforced with various nanofillers for the development of nanocomposites.

1.1 Nanocomposites

Various terms have been used for advanced multifunctional packaging such as smart, active, and intelligent packaging. The idea behind using such terms for this technology is to describe the selected reaction of a certain type of packaging when located in different environments. This reaction allows the smart or active packaging to sense changes in certain properties of food products and report them to the customer [40]. Active food packaging materials encompassing nanocomposites play several roles, including those of protecting food products from the outside environment, as well as increasing their shelf life by preserving their value for a longer period of time [79]. Other than that, smart packaging materials prevent oxidation of the food item from taking place, hence delaying its deterioration. They also function as a moisture controller, anti-microbial agent and freshness indicator [40]. Thus, active and intelligent packaging systems also deal with nanocomposite materials when they show ideal properties of smart packaging through their features.

Nanocomposites have been used in recent years in many industries such as in textiles, home decorations, packaging, furnishings, and agriculture. The application of natural fibers in nanocomposite materials is not a serious concern due to new technologies on the fabrication of synthetic fibers [79]. These synthetic fibers are mass produced for application in various industries. However, during the fabrication of these fibers, pollutants are produced that have an effect on the environment. The structure of biopolymer plastics tends to limit their application when there is a lack of reinforcement such as nanofillers or nanofibers [55]. Synthetic fibers are improved by reinforcement with nanofibers to enable them to be used in packaging applications. During this phase, the load is transferred by the matrix to the nanofibers. Apart from the mechanical and thermal properties, permeability is considered to be the most important parameter in the selection of materials for food packaging applications [40]. A high resistance to vapour and moisture is important when choosing a suitable polymer-based plastic. Bio-nanocomposites provide an excellent balance in mechanical, thermal and barrier properties.

The incorporation of nanofillers from inorganic and organic natural fibers can lead to green food packaging [43]. Natural fibers are more compatible with the environment than other fibers because they are biodegradable and renewable. In addition, these materials are cheap and have a low level of toxicity [49]. Nanofibers are measured in nanometres (10^{-9} m), and the term ‘nano’ relates to a range of nanoparticles. The measurement of the diameter of nanoparticles changes to nanometres following the shrinkage of micrometre materials. Deepa et al. [13] mentioned that the nanometre measurement of constituents is equivalent to being 80,000 times thinner than that of the hair of a person. However, this depends on whether the nanocomposite materials originated from material or fiber sources. Sometimes, they may become tiny particles but do not reach the nano-size range. The unique properties of nanocomposite materials are that they enhance the properties of composites, they have more attractive features in terms of their mechanical properties, they have flexible surfaces, and high surface area ratios [75]. Their surface area ratios are 10^3 times more than those of micrometre materials [48].

Nanofillers play a potential role in improving or altering the properties of the material in nanocomposites. Nanocomposite materials have a more acceptable demand due to the specific advantages that they have over non-biodegradable products. Being more environmentally friendly, nanomaterials are used in many applications like the aerospace, automotive, electronics and biotechnology sectors [63]. Nanofibers and their composites offer a highly attractive contemporary to the research line. Nanocomposites show an outstanding improvement due to the nano-reinforcement. Basically, nanofibers are extracted for the stiffness that they provide to the reinforcement in nanocomposite materials [48]. Unlike natural fibers, synthetic fibers are produced from petrochemicals, while natural fibers originate from farm or agricultural crops. Due to environmental processes, biopolymer nanocomposite packaging is subject to degradation when exposed to environmental conditions such as moisture, sunlight, temperature or different pH solutions [77].

In nanoclay composites, the barrier properties depend on the orientation of the nanofiller, and it dispersion condition in the polymer matrix. The clay layers able to create a barrier to delay the diffusion of molecules through the food packaging. According to Majeed et al. [40], nanoclay composites have gained a lot of attention from packaging manufacturers due to their cost-effectiveness, wide availability and simple processability. Nanoclay-based composites are usually reinforced with a polymeric starch-based material. Talegaonkar et al. [79] and his group identified the reason behind the successful use of nanoclay composites as a nanofiller in food packaging materials. According to them, the nanoclay that is used as a nanofiller improves the barrier properties of the biocomposite, possibly by increasing the tortuosity of the diffusive path for permeants, such as gas, moisture, and vapour. Li et al. [36] also added that the addition of 60 wt% of nanoclay in agarose starch increases the elastic modulus by five times than that of neat agarose starch at 2.4 GPa. It has been proven that the mechanical behaviour of bio-nanocomposites can be improved with the presence of nanoclay in it.

Smart or active packaging plays the most important role in the security of food products by preserving their integrity throughout their shelf life. The use of nanocomposite materials in food packaging industries is a new green technology aimed at attaining markedly enhanced packaging properties like improved mechanical properties and water resistance, increased thermal stability and barrier properties, and decreased migration activity. In addition, nanocomposites also offer an environmental approach, where they can be degraded within a few months. There are various types of nanofiller-based natural fibers that are suitable for preparation as nanocomposite materials. Thus, the nanocomposite materials are remarkably incorporated as packaging materials and also provide smart properties to the packaging system, thereby ultimately increasing the shelf life of food products and improving product quality.

2 Nanocomposite Preparation

The properties of nanocomposites heavily depend on the dispersion states of the reinforcement phase in the matrix. In order to optimize the properties of nanocomposites, it is necessary to disperse the particles in homogeneous "nano-level" dispersion. For the cases of clay reinforced nanocomposites, there are three possible polymer/clay nanocomposite structures, i.e. flocculated, intercalated, and exfoliated [71], with exfoliation structure, followed by intercalation are the preferred ones. It also should be noted that in preparing nanocomposites specimens, degradation of the matrices should be avoided.

Various procedures to disperse the nanoparticles inside the polymeric matrices have been reported, and mainly can be classified into three classes, i.e. solution casting, melt mixing and in situ polymerization.

2.1 Polymer Solution Casting

Solvent casting technology, for the production of high-quality flexible films, has attracted widespread interest from plastic manufacturers. Driven by the requirements of the photographic industry well over a century ago, the solvent casting method has gradually declined due to the development of new film extrusion technology. However, due to the existence of certain limitations which constrain the applicability of conventional polymer processing methods, researchers' have adopted several measures to develop and modify polymer processing methods to suit natural polymers [53]. Solution casting is known as solvent casting or the wet processing method and is used for forming polymer thin films. Polymer films have many technological applications and advantages in industries such as packaging, medical devices, and photography tools and are also used in the coating industry. Notably, uniformity is the main characteristic for any of these applications.

Solution casting is a unique process where it is not reliant upon conventional extrusion and injection moulding machines, yet it incorporates well-mixed constituents like those produced by more traditional methods [30]. Solution casting is a manufacturing process that involves mixing of the solubilized polymer matrix and filler under continuous agitation via stirring, which is then followed by casting into a flat mould and solution drying. Moreover, it is often referred to as the evaporation method where the film is left for one day [58]. Salehifar et al. [65] stated in their findings that the solvent casting process is used in industrial food packaging for a broad range of applications. Accordingly, each polymer matrix has its own co-solvent to assist in dissolving the polymer. Notably, alcohol, chemical solvent, water or dissolving solutions are used in this kind of process as co-solvent [38]. Moreover, the dissolved polymer process can be improved using applied heat or via a readjusted PH condition which will enhance the formation of properties of the thin film matrix.

For the raw materials in the solvent casting method, several prerequisites are required. First, the polymer matrix should be soluble in the inorganic solvent or PH water. Also, the solution needs to be stable with suitable minimum solid substance and viscosity to achieve satisfactory performance [57]. The second prerequisite is the opportunity to produce a homogeneous thin film and removing the film after the drying process [66]. Figure 1 illustrates the solvent casting process to produce

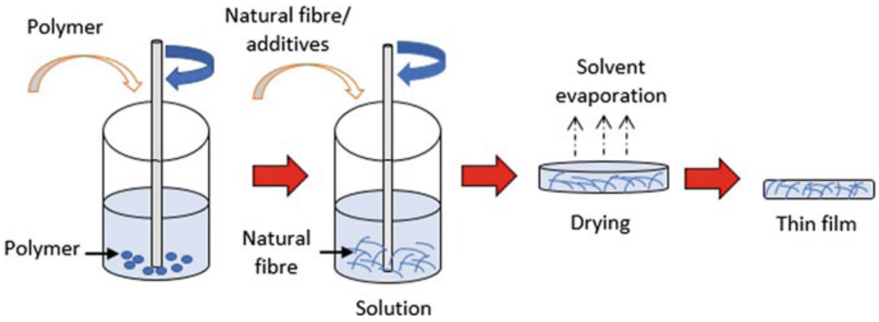

Fig. 1 Process to produce polymer nanocomposites film

biocomposite film. Notably, basic film applications are produced using different polymer and solvent combinations. During the casting process, the solid polymer matrix of various shapes (i.e. granules, powder or pellet size) is gradually dissolved in pure co-solvent. As a precautionary measure, the material type and geometry of the paddle or magnetic stirrer needs to be carefully selected due to the significant difference in viscosity between the polymer and co-solvent which may affect the mixture solvent [69]. Therefore, the temperature and mechanical stirring rate need to be carefully controlled given it affects the quality of solvent evaporation, polymer chain and skin formation of the polymer film. Typically, the induced temperature is varied between room temperature and the boiling point of the solvent [30]. Also, the dissolution time usually takes several iterations which are dependent on the type of solvent and method used.

The advantages of the manufacturing process of polymer solution casting over traditional film extrusion methods are mainly due to the unique approach and without the need to apply thermal or mechanical stress. Therefore, the degradation process or adverse side reaction is considered to be significant. Accordingly, solution casting is becoming an attractive process where the production of film offers uniform thickness distribution, maximum optical purity and extremely low toxicity [69]. Additionally, the process is conducted at a low temperature where it is relevant for thermally activated films although, in some circumstances, it may be temperature sensitive with active constituents. According to Salit et al. [66], due to the process being conducted at low temperature, the thin film shelf life can be extended to incorporate a much longer period. Furthermore, the non-melting process from soluble raw materials will possibility produce high-temperature resistant films. Notably, the main advantages of solvent casting are primarily due to the total cost of manufacturing prototypes and production volumes, which are much less than in extrusion blending. Also, this includes an inexpensive mould with a standard manufacturing/production line [57].

Next, a case study is used to examine nanocellulose reinforced with biodegradable polymer matrix where the focus is on the polymer process and to achieve outcomes. Jiang et al. [27] reported on cellulose nanowhisker

(CNW) reinforced poly(3-hydroxybutyrate) (PHB) by solvent casting and extrusion blending. Polyethylene glycol (PEG) acts as a compatibiliser or dispersion agent, and N, N-dimethylformamide (DMF) is co-solvent for this composite. Firstly, CNW/PEG was dissolved in a DMF stable suspension for 4 h of sonication at 258 °C. PHBV was also dissolved in DMF, and the mixture continued to be sonicated further for 2 h for complete homogeneity, followed by the solvent mixture casted on a glass plate. The film PHBV/CNW composite was formed following the complete evaporation of DMF. Finally, the sample was removed from the glass plate and kept in a desiccator to maintain a constant humidity. The homogeneous dispersion of CNW posed a significant challenge in preparing the nanocomposite, due to the possibility of hydrogen bonding inducing agglomeration on the sample.

The solvent casting technique demonstrated better dispersion of CNW in the nanocomposite compared to the extrusion method in which good dispersion significantly improved the properties of the PHBV nanocomposite [27]. PEG was also added to increase the dispersion in the nanocomposite. The addition of CNW also enhanced the PLA molecular mobility. Whisker content from 0 to 30 wt% also increased the tensile strength and Young's modulus obtained. Therefore, the enhanced tensile properties indicate good dispersion and strong interfacial adhesion between the fiber and the polymer matrix. The water resistance of the composite also increases with whisker content. By comparing the preparation method, the result for the composite prepared via extrusion showed lower tensile properties as compared to solution casting. Agglomeration of cellulose nanowhisker was reported to be observed under the scanning electron microscopy (SEM) micrograph and no intimate contact between cellulose nanowhisker and polymer matrix even though with the presence of a compatibilizer. Notably, the influences of agglomeration decreased the performance of the composite.

In conclusion, solution casting has numerous benefits compared to other fabrication methods due to lower production temperature required and no mechanical stress. Medical manufacturers are producing materials such as silicone urethane, via solution casting to produce breakthrough products subsequently excel in manufacturing performance and shorter lead times in supplying the demands. Solution casting as a manufacturing process depends only on the reaction between the co-solvent and polymer or the natural fiber mixture [53]. One of the primary reasons is due to solvent casting requiring lower energy, thereby reducing costs in recovering the solvent, and only a small investment is necessary for installing the facilities needed in handling the solvents and dope solutions which differs from other manufacturing methods [30]. Therefore, high quality of the thin film can only be achieved using the solvent casting methods and not using other methods.

2.2 Polymerization

Polymers are basically made of a large number of repeating unit of monomers. There are various methods that can be used to produce the polymers; step-growth polymerization method (condensation polymer) and chain growth polymerization method (cationic polymerization and anionic polymerization). Depends on the constituents of the monomer, homopolymer and copolymers can be prepared. For an example, homopolymer polypropylene (PP) has been used extensively in food packaging industry as this polymer is known for its' exceptional properties [8]. PP is polymerized from its monomer which is propylene through Ziegler-Natta polymerization and by metallocene catalysis polymerization. Despite its low impact strength at low temperatures and high gas permeability, PP is reinforced with other components such as fillers, inorganic materials and many more in order to improve its properties. Previous studies show significant improvement in gas barrier properties of PP when blended with montmorillonite (MMT) by a twin-screw extruder [11, 93] and coating with corn zein nanocomposite [34].

Another polymer extensively used as packaging material is polyethylene terephthalate (PET). PET is produced by a step-growth polymerization of ethylene glycol and terephthalic acid or dimethyl terephthalate [20]. PET exhibit exceptional properties such as strength, permeability, chemical resistance and high transparency making it suitable for many applications. PET is also blended with other components such as clay by stretch blow molding machine in order to study the migration of aluminium and silicon from the composite into acidic food simulant bottle [20]. The study shows that the migration of aluminium and silicon is dependent on storage time and temperature. Another study had produced a nanocomposite by blending PET with layered double hydroxide by using high energy ball milling process and the results obtained showed that the oxygen diffusion and permeability are lower than that of neat PET [80].

Both PP and PET are known as non-degradable polymers. Despite its non-degradability, they are extensively used as food packaging material as they possess suitable properties for application in packaging. Nowadays, the biopolymer is emerging to substitute this conventional plastic as they can degrade naturally into the environment [20]. Biopolymers are categorized into their synthesis process namely from biomass product, microorganism, biotechnology and oil-products. Starch can be used to form a biodegradable film and different sources of starch can be obtained from plant biomass such as corn or sugarcane [81]. A study done by Heydari et al. [23] prepared corn starch film with glycerol by casting method where with increasing glycerol content, the tensile strength decreases. Chitosan is another polymer synthesize from chitin which is the most abundant agro-polymer in nature next to cellulose. Chitosan nanocellulose is developed in previous studies in order to improve its anti-microbial properties in food packaging, for extending the shelf life of meat in particular [14].

Poly hydroxyalkanoate (PHA) is a biopolymer synthesize from a microorganism. The homopolymer of PHA, poly(3-hydroxybutyrate) (PHB) and copolymer hydroxyl-valerate (HV) have been extensively studied to improve their properties [81]. From a previous study, PHA is combined with nano keratin by using two methods, direct melt compounding and pre-incorporated into an electrospun masterbatch of PHA and also solution casting [31]. Barrier properties are enhanced by both methods while sample prepared by solvent casting shows good adhesion.

Another study had been done by incorporating polyhydroxybutyrate-co-hydroxyvalerate (PHBV) with cellulose nanowhiskers using electrospinning techniques and showed improve barrier properties despite the extreme brittleness [31]. In another study, PHB had also been fabricated with cellulose nanocrystal by using solution casting technique and the results from the study show enhance gas barrier and migration properties [67]. Previous studies had also blended Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) with other components such as clay [31], zinc oxide [15] and cellulose nanocrystal [92].

PLA is a polymer formed by ring opening polymerization of lactic acid [81]. PLA is considered a renewable material as it is manufactured by fermentation of renewable agriculture resources. Despite the attention towards PLA for its commercialization towards substituting conventional plastic, PLA brittleness and high cost limit its application. Many research had been done to modify PLA in order to widen its applications. PLA/zinc oxide film prepared by twin-screw extruder proven to improve PLA mechanical properties [44]. Other than that, PLA had also been blended with MMT by using a twin-screw extruder to form a nanocomposite. Comparing to neat PLA, the study shows that PLA/MMT exhibit good mechanical and oxygen barrier properties. Another study had been done by Pinto et al. [59] where PLA is incorporated with graphene by using solvent casting method. This study also shows improvement in mechanical and oxygen barrier properties.

Poly(e-caprolactone) (PCL) is a synthetic biopolymer that can be synthesized either by ring opening polymerization from ε-caprolactone (monomer) or by free radical ring opening polymerization of 2-methylene-1-3-dioxepane [6]. Because of its high cost and brittleness, PCL applications is limited to medical purpose. However, many researchers have attempted to modify PCL by blending it with other components in order to widen its applications to other fields such as in food packaging sector. Beltrán et al. [6] had done a study on blending PCL with hydroxytyrosol (HT) and a commercial montmorillonite by melt blending method. The presence of montmorillonite decrease oxygen permeability but enhance the elasticity PCL. Another study had developed an antimicrobial PCL/clay nanocomposite films by melt blending method [90]. Results obtained from the study shows that mechanical water vapour barrier properties and antimicrobial properties improved for the nanocomposite, showing that it is suitable for the application in food packaging.

PVA is another type of synthetic biopolymer. Unlike other polymers, PVA is not synthesized from its monomer, instead, PVA is prepared by partial or complete hydrolysis of polyvinyl acetate to remove acetate groups [10]. According to Butnaru et al. [10], for PVA to be used in applications such as food sector and pharmaceutical, PVA need to be cross-linked first by the freeze-thawing method. Butnaru et al. [10] also had done a study to prepare a nanocomposite by blending PVA with chitosan and clay. The study shows enhanced properties in terms of thermal stability, mechanical and antimicrobial properties. A previous study had also been done where PVA had been blended with cellulose nanocrystal by a solvent casting method and the result proven to improve its mechanical properties [18] (Table 1).

Table 1 Summary of nanocomposites preparation in food packaging industry

No.	Nanocomposite	Processing method	References	Remarks
1	Polypropylene blended with montmorillonite (MMT) (PP/MMT)	Polypropylene (PP): Ziegler-Natta polymerization and by metallocene catalysis polymerization	Zehetmeyer et al. [93]	Improve gas barrier properties
2	Polypropylene/Organoclay Nanocomposites	Polypropylene (PP): in situ polymerization supported Ziegler-Natta catalysts	Almeida et al. [1]	Improve thermal degradation
3	PET blended with clay	Polyethylene terephthalate (PET): step-growth polymerization of ethylene glycol and terephthalic acid or dimethyl terephthalate	Galotto and Ulloa [20]	Migration of aluminium and silicon is dependent on storage time and temperature
4	PET blended with layered double hydroxide (PET/LDH)		Tammaro et al. [80]	Oxygen diffusion and permeability is lower than that of neat PET
5	Corn starch film with glycerol	Casting method	Heydari et al. [23]	With increasing glycerol content, the tensile strength decreases
6	Chitosan nanocellulose	Casting method	Dehnad et al. [14]	Improve its anti-microbial properties in food packaging (extending the shelf life of meat)
7	PHA combined with nano keratin	Poly hydroxyalkanoate (PHA): synthesized from a microorganism (fermentation)	Lagarón et al. [31]	Barrier properties are enhanced by both methods while sample prepared by solvent casting shows good adhesion
8	PHB fabricated with cellulose nanocrystal	Poly(3-hydroxybutyrate) (PHB): synthesize from a microorganism (fermentation)	Sengupta et al. [67]	Enhance gas barrier and migration properties

(continued)

Table 1 (continued)

No.	Nanocomposite	Processing method	References	Remarks
9	Polyhydroxybutyrate-co-hydroxyvalerate (PHBV) with cellulose nanowhiskers	Polyhydroxybutyrate-co-hydroxyvalerate (PHBV): synthesized from mixed microbial cultures	Lagarón et al. [31]	Improve barrier properties despite the extreme brittleness
10	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) blended with clay		Lagarón et al. [31]	Improve thermal stability
11	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) blended with zinc oxide		Diez-Pascual and Diez-Vicente [15]	Improve stiffness, strength, toughness, and glass transition Temperature as well as a reduction in water uptake and oxygen and water vapour permeability
12	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate) blended with cellulose nanocrystal		Yu et al. [92]	Improve mechanical performance, thermal stability, barrier, and migration properties, improve PLA mechanical properties
13	PLA/ZnO film	Polylactic acid (PLA): Ring-opening polymerization (ROP) of lactic acid	Marra et al. [44]	
14	PLA blended with montmorillonite (MMT) (PLA/MMT) PLA blended with graphene		Pinto et al. [59]	PLA/MMT exhibit good mechanical and oxygen barrier properties Improvement in mechanical and oxygen barrier properties
	PCL blended with hydroxytyrosol (HT) and a commercial montmorillonite PCL/clay nanocomposite films	Poly(e-caprolactone) (PCL): ring opening polymerization from ε-caprolactone (monomer) or by free radical ring opening polymerization of 2-methylene-1-3-dioxepane	Beltrán et al. [6]	Presence of montmorillonite decrease oxygen permeability but enhance the elasticity PCL
			Yahiaoui et al. [90]	Mechanical, water vapour barrier properties and antimicrobial properties improved
15	PVA blended with cellulose nanocrystal	Poly(vinyl alcohol) (PVA): partial or complete hydrolysis of polyvinyl acetate to remove acetate groups	Fortunati et al. [18]	Improve its mechanical properties
16	Polyaniline/polyvinyl alcohol/Ag (PANI/PVA/Ag)	Poly(vinyl alcohol) (PVA): in situ chemical oxidation polymerization of aniline monomer	Ghaffari-Moghaddam and Eslah [21]	Improve antibacterial properties

2.3 Melt Mixing

Amongst the three methods, melt mixing is the most economically attractive and scalable method for dispersing nanoparticles into polymers. To some extent, this method is also preferable over other two methods because it aligns well with the currently established industrial processing routes. This method also can be considered as environmentally benign, due to the unnecessity to use organic solvents. Melt mixing process involves melting of the thermoplastic polymer matrix to form viscous liquid followed by incorporation of nanoparticles.

In order to ensure proper dispersion of the nanoparticles during melt processing, two key factors need to be considered, i.e. (i) favourable interaction between the polymer matrix and the nanoparticle, and (ii) suitable processing conditions [50]. The favourable enthalpic interaction between particles and the matrix is necessary, because, in the absence of such favourable interactions, the dispersion of the nanoparticles within the matrix becomes difficult, and may only result in the formation of micro-composites instead of nanocomposites. Meanwhile, the processing conditions are also needed to be controlled carefully. Although high shear mixing in principle can improve the dispersion states of the particles, too high mechanical shearing, combined with high temperature and possible oxidation, may degrade certain types of polymers, especially biopolymers [50].

There are numerous works that reported successful attempts in preparing PLA based nanocomposites by melt mixing method. PLA nanocomposites reinforced with various types of particles such as silica [32, 86, 94], clay [33, 72], carbon nanotube [87], graphene [28, 46], titanium dioxide (TiO_2) [17] and nanocellulose [2, 22] have been successfully prepared by melt mixing process. In most cases, nanoparticles were surface modified to facilitate favourable interaction with the polymer matrix, which leads to better dispersion states. For example, –COOH surface modified multi-walled carbon nanotube (MWNTs) displayed better dispersion in the PLA matrix than the unmodified MWNTs [87], or polyethylene glycol methyl ether (PEGME)-modified nanosilica exhibited better dispersion states in the PLA matrix compared to pristine nanosilica.

Beside surface modification of nanoparticles, processing conditions in melt mixing method also affect the dispersion state of the particles in PLA nanocomposites. Villmow et al. [83] showed that higher rotating speed (500 rpm compared to 100 rpm), more mixing elements in extruder screw configuration, and temperature profile with raising value towards the extruder die contributed to better dispersion of CNT inside PLA matrix. Okubo et al. [52] exhibited that dispersion of cellulosenano- or microfibers was improved with decreased gap distance in roll-milling, while Oksman et al. [51] also pointed out that the type of screw in extruder influence the dispersion states of nanoparticles inside the matrix, i.e. in case of nanocellulose processing, the co-rotating twin-screw extruders are preferred over counter-rotating, because they are better for mixing and dispersing. In principle, higher mechanical shearing may lead to better dispersion of nanoparticles inside the matrix.

Preparation of PHA family based nanocomposites by melt mixing method has also been reported. The examples include PHBV reinforced with carbon nanotube (CNT) [68], PHBV reinforced with hydroxyapatite [54], PHB/clay nanocomposites [9, 39], etc. Similar to PLA based nanocomposites, surface chemistry of nanoparticles play a critical role in helping good dispersion. Organo-modified MMT dispersed better compared pristine MMT inside PHB matrix [9]. In PHBV matrix, hydroxyapatite treated with silane coupling agent exhibited better dispersion states and mechanical properties compared to untreated hydroxyapatite particles [54]. However, since many of PHA are sensitive to thermo-mechanical degradation, the melt-processing of PHA nanocomposites occurred within a short window and caution should be taken be taken to avoid degradation during processing [9, 50].

3 Characterization of Nanocomposites

3.1 Mechanical Property

Mechanical characteristic is one of the crucial factors in nanocomposite especially in designing food packaging. Chemical resistance of the product can be affected by its process-ability and mechanical properties such as tensile strength, tear strength, elongation, toughness, softness and puncture resistance [5]. So, it is mandatory to perform the suitability test for nanocomposite food packaging stored with food as a function of duration. For example, the tensile test is conducted to determine the tensile strength, Young's modulus, yield stress and elongation at break of the nanocomposite. Generally, this testing is carried out according to the ASTM D88 standard testing method for tensile properties of thin plastic sheeting and ASTM D638 for testing materials up to 14 mm of thickness.

Moreover, impact properties test is also conducted to determine the amount of energy needed for the plastic deformation at certain condition according to ASTM D1709 for plastic film. Impact test consists of Charpy and IZOD specimen configuration according to ASTM D256 and ASTM 6110, respectively. The flexural test measures the force required to bend the sample under three-point loading conditions according to ASTM D790. This test is conducted as an indication of a material's stiffness when flexed. The sample lies on a support span and the load is applied to the centre by the loading nose producing three-point bending.

The modification of polymer content leads to increase in tensile performance up to 50% of the original value [5]. Nanocomposite film with the addition of water-soluble chitosan (WSC) increased the tensile strength of the polymer [78]. Relative elongation is also an important mechanical property as it could affect the biodegradable rate during the degradation process. As studied by Mostafa et al. [45], the percentage of elongation values for starch blend film was reduced in inoculated soil faster than in non-inoculated soil. Elongation of starch blend film dropped rapidly by 56% in inoculated soil compared to 12% decrement in elongation within the fixed time basis. Therefore, mechanical stability properties help to improve the new innovations in biobased food packaging for commercial use.

3.2 Thermal Property

Addition of nanoparticles into polymeric materials also may enhance the thermal properties. Higher thermal stability is important in food packaging application to withstand a wide range of temperature exposure during food processing, transportation, and storage [55]. A recent report by De Silva et al. [12] showed that incorporation of magnesium oxide (MgO) into chitosan exhibited higher thermal stability and fire retardancy, due to the high thermal stability of MgO along with the homogeneous distribution of MgO nanoparticles in chitosan films. Kim and Cha [29] also reported that addition of organically modified MMT nanoclays into ethylene vinyl alcohol copolymer (EVOH) resulted in enhancement of thermal stability as indicated by thermogravimetric analysis (TGA), as well as shifting the crystallization temperature of EVOH as displayed by differential scanning calorimetry (DSC) result.

3.3 Degradation Behaviour

Development of new food packaging materials that capable to be degraded in a controlled manner has been a focus of interest of researchers nowadays. Incorporation of nanoparticles into degradable polymeric matrix may affect the degradation behaviour of the composites. Addition of cellulose nanocrystals (CNCs) into PLA helps to enhance the disintegrability rate of PLA since this nanocellulose is equipped with hydrophilic nature [3, 19]. However, different observation has been found when PLA is added with coated CNC with surface surfactant (s-CNC). Even though s-CNC accelerate the disintegration process of PLA, however, water diffusion is slightly restricted due to the improvement in barrier properties and therefore slowdowns the hydrolysis process and delays the degradation process [19]. It can be concluded that the addition of appropriate plasticizers will help to improve the disintegration of PLA in composting conditions [3, 35], which indirectly speed up the disintegration of PLA-plasticizer nanocomposites.

In other literature reported by Pandey et al. [56], the addition of addition of nano-layered silicate into PLA matrix increased the biodegradation rate of the materials. The increment was predicted due to the presence of terminal hydroxylated edge groups in the silicate layers. Addition of 4% of nano-layered silicate lead to the good dispersion of silicate layer in PLA matrix and these hydroxy groups begin the heterogeneous hydrolysis of PLA matrix by absorbing water from compost. Up to one month, the weight loss and hydrolysis of PLA and PLA with 4% filler is about the same, however, after one month, the degradation of nanocomposites increased significantly.

3.4 Migration Testing

Migration is the process where chemicals are transferred from nanocomposites to food as they come in contact with each other. The term “migration”, according to Icoz and Eker [26], is used to define the diffusion of substances from high concentration regions to low concentration regions within the food and the packaging material. The chemical substances that are added to polymeric materials to enhance the characteristics of a composite may interact with the food components and move into the food during the processing, storage, and distribution. The quality, such as taste and odour, as well as safety of the food will be affected and cause significant health problems to the consumer. There are various factors that influence the rate of migration, such as the contact time, temperature, structure of the nanocomposite (thickness for plastics), chemical properties (molecular size, polarity, vapor pressure, etc.) of the migrants, and the types of materials that come in contact with the food [7, 26]. Migration can occur in different ways such as contact migration, gas phase migration, penetration migration, set-off migration, and condensation or distillation migration [26].

Generally, this testing is carried out according to the EN 1186 standard testing method, and several types of food simulants are used to analyze the overall migration testing. These food simulants are chosen as they are less chemically complex than foods [7] according to the regulations by EU 10/2011. The recommended simulants, as stated by Bhunia et al. [7], are: ethanol (10% v/v) (simulant A) to simulate aqueous foods ($pH > 4.5$); acetic acid (3% v/v) (simulant B) to simulate acidic foods; ethanol (20% v/v) (simulant C) to simulate alcoholic products; ethanol (50% v/v) (simulant D1) and vegetable oil (simulant D2) to simulate fatty foods, and lastly, Tenax (PPPO) (simulant E) to simulate dry food. The overall migration is limited to 10 mg/dm^2 on a contact area basis or 60 mg/kg in the stimulant or food (for plastics).

The food contact material or migration testing is important especially in producing food packaging as it affects the quality and shelf life of food and has a bad impact on human health. The substances that migrate into food can transform to become toxic and hazardous to consumers, especially babies and children. The composition of the materials that come in contact with food, such as additives and plasticizers, may affect the safety and quality of food. They affect the human reproductive system and are carcinogenic as both of them are described as endocrine disruptors. Phthalate esters, alkyl phenols (APs) and 2,2-bis (4-hydroxyphenyl) propane, also known as bisphenol A, are examples of hazardous chemicals that have serious toxic effects if exposed to the human body even at low concentrations [85].

Therefore, migration testing is very important in food packaging applications in order to maintain the safety and quality of the food and also consumer health. It is necessary to choose carefully the materials and their properties to protect the quality and safety of food.

3.5 Antimicrobial Testing

Nanomaterial has revealed many benefits in various fields. As the uses of nanomaterials have been increasing, it has been found to be a promising advancement for the food packaging productions in the global market. However, the use of nanomaterials in food packaging could be challenging due to the method in reducing particle size and the fact that characteristic of nanoparticles material is quite different from microparticles [24]. Food packaging offers to maintain the quality of food taste, prolong shell life and protect food from contamination. However, food security is an excessive problem due to increasing disease from contamination adverse from food packaging materials. World Health Organization (WHO) stated the spoilage of food arise at any time during production of food to consume. Pathogens bacterial are to blame in many cases because it easily grows on food surface [84]. This leads to the introduction of nanocomposite as an active antimicrobial packaging and particularly designed to control the bacteria from adversely affect health. By using active packaging, the internal environment is modified via constant interaction with the food over the specified shell life [41].

Nanoscale materials consist of a high surface to volume ratio than micro-size particles which make them easier to attach with a numerous number of the molecule and increased the efficiency [88]. Nanoparticles such as copper, silver and zinc oxide usually used in the retarded growth of microorganism due to strong antibacterial or antifungal activities. The reinforcement of this kind nanoparticles in biocomposite may overcome the problem of food spoilage. So, the main goal of active packaging enhances the packaging products quality by guarantee food security and improve sensory properties of food while sustaining food quality [61]. Active antimicrobial packaging may be described as a structure that alters the environment inside the plastic package by modifying the condition of the packaged food system. Food spoilage can be formed when it is exposed to air via processing, production, and packaging of food [70]. Generally, active food packaging is divided into two categories; biodegradables and non-biodegradable materials. Petroleum-based packaging has particularly benefit of high mechanical strength, low cost of raw material, availability, ease production process, good barrier properties but not biodegradable [84]. They cause environmental pollution as they can take hundreds of years to completely degrade.

Besides, petroleum-based packaging material can also preserve food over the particular period but, currently, consumers do prefer products made of biodegradable resources [76]. Besides, those packaging have chemical additives diffused through the plastic barrier into food products thus provides a negative effect on the health. Biopolymer materials have attracted widespread industries because they can be decomposed easily. Therefore, utilization of antimicrobial material in biopolymer packaging can provide significant enhancement of property which can help to increase health security and shelf life of food. It is one of the methods that effectively kill or inhibit pathogenic microorganism from growth in infected food [62]. Hence, a good food packaging able to reduce contamination over the food [44, 64].

The improvement of biopolymer-based nanocomposites with antibacterial agent presents interesting potentials because the bio-based polymer can be varied according to specific technology requirements and also fulfil the nanostructures with envisaged applications [60]. The antimicrobial elements most commonly introduced into packaging products can be characterized into many types such as plant oil extract, enzymes, bacteriocin, preservation, chemical substance and others [76, 84]. Previous literature have recognized the potential application of antimicrobial nanocomposite for wound dressing [89], bactericides [60] and medical devices [16].

Nanoparticles have different activities depending on pathogenic and spoilage microorganism species [44]. Pinto et al. [60] reported based on their finding in antimicrobial activity test, the presence of nanoparticle copper (0.93–4.95%) can against *K. pneumoniae* (Gram-negative bacteria) in cellulose nanocomposite specimens. The inhibition of bacteria depends on the nanofiller content in the specimens, where increasing copper content gave significant inhibited bacteria growth. This study believed that Gram-negative bacteria can be affected by copper-based material as they have a strong antimicrobial action against peptidoglycan layer. The interaction of nanoparticles could cause in changing its permeability and the structures promote the membrane degradation which ultimately causing the death of bacteria [25]. According to Lai et al. [33], the incorporated nanoclay into PVA film showed strong antimicrobial activity against Gram-positive bacteria (*L. moncytogenes* and *S.aureus*). Nanoclay was known as an active agent due to its highly dispersed in biocomposite and increased their exposure toward microorganism [37]. These may result in deteriorated bacterial cell membranes and cause cell lysis. Current food technology used antimicrobial in covering substances because this method will make sure food product are safe and lead to extend shell life [61]. Therefore, selection of removal of any microorganism should be identified for selection of an appropriate antimicrobial agent.

The main function of nanomaterials to act as an antioxidant agent is, it consists of microbial cidal effects and microbial static effects on the microorganism. Microbial static effects related to the active function of substance to enhance the concentration below minimal inhibitory during preserved or storage process of food product [41]. This state may reduce perishable to occur by contamination. The main concept permitted in this packaging are wrapping system with presence of antimicrobial agent either natural or synthetic agents. The existence of an antimicrobial agent in packaging product is more significant than adding antimicrobial agent directly onto food, the fact of covered product that consists antimicrobial agent could not diffuse into food product as well as can be thrown away after its' usage [25]. The major challenge in food packaging is the design of nanocomposite material with active antimicrobial products. Lately, many customers concern about potential health risks when chemical additives are added to packaging products. The achievement by scientists with the new formulation of reinforced nanoparticles verified the potential of bio-nanocomposites as an active food packaging, can be considered as an alternative to conventional composites used in the packaging material.

3.6 Optical Behaviour

Greater lightness and transparency in food packaging are vital as they are in high demand by consumers. Most non-composite foods packaging are colourless and transparent. These characteristics, however, are slightly affected by the addition of other materials, which in the end influence the aesthetic value of the food packaging. Arrieta et al. [4] revealed that the lightness of PLA is 94.08 ± 0.07, while that of PLA/limonene is 93.86 ± 0.10. Both PLA and PLA/limonene have high brightness characteristics, but their lightness is reduced once additives are added. In other researches, the lightness and transparency of coated films for food packaging were affected in the presence of proteins and plasticizers.

Lee et al. [34] stated that the transparency of protein-coated films was increased from 16.9 to 19.7 for corn zein, 13.3 to 30.3 for soy protein isolate and 17.8 to 28.6 for whey protein isolate. Moreover, the transparency of protein-coated films also increased with the addition of plasticizers. Yoo and Krochta [91] compared the transparencies of biopolymer, biopolymer blended and synthetic polymer films. The results indicated that the percentage of transparency of biopolymers like hydroxyl propyl methyl cellulose (HPMC) films was higher compared to synthetic polymers such as low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP) films.

Generally, the optical properties of nanocomposites are evaluated according to the *CIELAB* colour system. In this system, the colour coordinates L^*, a^* and b^* represent lightness, red-green and yellow-blue, respectively. An increase in the L^* value indicates that the nanocomposite specimen is lightening. The colour is switching to red if the* value is increasing, while it is turning green if the value is decreasing. The increase in the value of b^* shows that the colour is switching towards yellow, and a decreasing value indicates that it is turning to blue. Therefore, the total colour difference (ΔE) can be determined by using Eq. 1.

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2} \tag{1}$$

Transparency and opacity are essential properties in food packaging application as they improve the appearance of a product. Opacity is the degree to which light is not allowed to travel through. Products with high transparency, especially in packaging, have become more popular in the market as consumers prefer see-through rather than opaque packaging. Thus, nanocomposites with high transparency and lightness are important in food packaging applications as there is a high demand for them from consumers.

3.7 Permeability and Barrier Properties

The determination of the barrier properties of the nanocomposite is important as it determines the shelf-life of the product. Various factors may affect the barrier properties to gases and vapours on the nanocomposite such as environmental conditions like temperature and relative humidity. Permeability according to Siracusa [73], stated that the ability of the gas or vapour transmits through a resisting material. Permeates diffusion is influenced by the structure of the nanocomposite, permeability to specific gases or vapour, area, thickness, temperature, the difference in pressure or concentration gradient across the nanocomposite.

Oxygen transmission rate (OTR), water vapour transmission rate (WVTR) and carbon dioxide transmission rate (CO_2TR) are main examples of the barrier properties that used in food packaging application [74]. The oxygen permeability coefficient (OPC) exhibits the amount of oxygen that permeates into packaging materials in term of per unit area and time ($\mathrm{kg\,m/m^2\,s\,Pa}$) [73, 74]. When the nanocomposite film packaging has lower oxygen permeability coefficients, it prolongs the product's lifespan as the pressure of the oxygen inside the packaging decrease to the point where it slows down the oxidation. The OPC is correlated to the OTR by using Eq. (2)

$$OPC = \frac{OTR \cdot l}{\Delta P} \tag{2}$$

For water vapour permeability coefficient (WVPC) and carbon dioxide permeability coefficient (CO_2PC), both indicate the amount of water vapour and carbon dioxide, respectively that permeates per unit area and time as well ($\mathrm{kg\,m/m^2\,s\,Pa}$). The WVPC and CO_2PC are correlated to the WVTR and CO_2TR by using Eqs. (3) and (4), respectively.

$$WVPC = \frac{WVTR \cdot l}{\Delta P} \tag{3}$$

$$CO_2PC = \frac{CO_2TR \cdot l}{\Delta P} \tag{4}$$

where l is the thickness of the nanocomposite film and ΔP is P_1–P_2, P_1 is the gas partial pressure at the temperature test on the test side and P_2 is equal to zero on detector side.

In order to improve barrier properties to gasses, vapour and aromas due to the sensitivity of various food products to oxygen degradation, microbial growth stimulated by moisture and aroma for keeping the food quality, nano or microfilters can be incorporated into biopolymers food packaging. Mali et al. [42] stated that the oxygen permeability was decreased while mechanical and heal seal properties were improved in bio-nanocomposite films from sago starch and bovine gelatin with nanorod-rich zinc oxide as the nanofillers.

Thus, oxygen and water vapour permeabilities in nanocomposite are essential properties as they give a major impact on the shelf-life of fresh and processed foods. It is important to know if there is an interaction between food and packaging and factors that influence the transport mechanism through the material.

Acknowledgements The authors wish to thank Ministry of Education Malaysia for the Fundamental Research Grant Scheme, FRGS14-105-0346, FRGS14-108-0349, FRGS16-003-0502 and RIGS16-085-0249 for the financial support and International Islamic University Malaysia for the facilities and equipment in making these studies a success.

References

1. Almeida LA, Marques MDFV, Dahmouche K (2015) Synthesis of polypropylene/organoclay nanocomposites via in situ polymerization with improved thermal and dynamic-mechanical properties. J Nanosci Nanotechnol 15(3):2514–2522
2. Arias A, Heuzey MC, Huneault MA et al (2015) Enhanced dispersion of cellulose nanocrystals in melt-processed polylactide-based nanocomposites. Cellulose 22(1):483–498
3. Arrieta MP, Fortunati E, Dominici F et al (2014) PLA-PHB/cellulose based films: mechanical, barrier and disintegration properties. Polym Degrad Stab 107:139–149
4. Arrieta MP, Lopez J, Ferrandiz S et al (2013) Characterization of PLA-limonene blends for food packaging applications. Polym Testing 32(4):760–768
5. Badmus AA, Gauri S, Ali NI et al (2015) Mechanical stability of biobased food packaging materials. Food Sci Q Manag 39:41–47
6. Beltrán A, Valente AJM, Jiménez A et al (2014) Characterization of poly(ε-caprolactone)-based nanocomposites containing hydroxytyrosol for active food packaging. J Agric Food Chem 62(10):2244–2252
7. Bhunia K, Sablani S, Tang J et al (2013) Migration of chemical compounds from packaging polymers during microwave, conventional heat treatment and storage. Compr Rev Food Sci Food Saf 12:523–545
8. Boone Lox F, Pottie S (1993) Deficiencies of polypropylene in its use as a food-packaging material—a review. Packag Technol Sci 6(June):277–281
9. Bordes P, Pollet E, Bourbigot S et al (2008) Structure and properties of PHA/clay nano-biocomposites prepared by melt intercalation. Macromol Chem Phys 209(14):1473–1484
10. Butnaru E, Cheaburu CN, Yilmaz O et al (2016) Poly(vinyl alcohol)/chitosan/montmorillonite nanocomposites for food packaging applications: influence of montmorillonite content. High Perform Polym 28(10):1124–1138
11. Choi RN, Cheigh CI, Lee SY et al (2011) Preparation and properties of polypropylene/clay nanocomposites for food packaging. J Food Sci 76(8):62–67
12. De Silva RT, Mantilaka MMMGPG, Ratnayake SP 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
13. Deepa B, Abraham E, Cherian BM et al (2011) Structure, morphology and thermal characteristics of banana nanofibers obtained by steam explosion. Bioresour Technol 102(2): 1988–1997
14. 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

15. Diez-Pascual AM, Diez-Vicente, Angel L (2014) ZnO-reinforced poly (3-hydroxybutyrate-co -3-hydroxyvalerate) bionanocomposites with antimicrobial function for food packaging. Appl Mater Interf 9822–9834
16. Feldman D (2016) Review-polymer nanocomposites in medicine. J Macromol Sci, Part A: Pure and Appl Chem 53(1):55–62
17. Fonseca C, Ochoa A, Ulloa MT et al (2015) Poly (lactic acid)/TiO2 nanocomposites as alternative biocidal and antifungal materials. Mater Sci Eng 57:314–320
18. Fortunati E, Puglia D, Monti M et al (2012) Cellulose nanocrystals extracted from okra fibers in PVA nanocomposites. J Appl Polym Sci 128(5):3220–3230
19. Fortunati E, Rinaldi S, Peltzer M et al (2014) Nano-biocomposite films with modified cellulose nanocrystals and synthesized silver nanoparticles. Carbohydr Polym 101:1122–1133
20. Galotto M, Ulloa P (2010) Effect of high-pressure food processing on the mass transfer properties of selected packaging materials. Packag Technol Sci 23(May):253–266
21. Ghaffari-Moghaddam M, Eslahi H (2014) Synthesis, characterization and antibacterial properties of a novel nanocomposite based on polyaniline/polyvinyl alcohol/Ag. Arab J Chem 7(5):846–855
22. Herrera N, Mathew AP, Oksman K (2015) Plasticized polylactic acid/cellulose nanocomposites prepared using melt-extrusion and liquid feeding: mechanical, thermal and optical properties. Compos Sci Technol 106:149–155
23. Heydari A, Alemzadeh I, Vossoughi M (2013) Functional properties of biodegradable corn starch nanocomposites for food packaging applications. Mater Des 50:954–961
24. Honarvar Z, Hadian Z, Mashayekh M (2016) Nanocomposites in food packaging applications and their risk assessment for health. Electr Phys 8(6):2531–2538
25. Hu W, Chen S, Yang J et al (2014) Functionalized bacterial cellulose derivatives and nanocomposites. Carbohydr Polym 101(1):1043–1060
26. Icoz A, Eker B (2016) Selection of food packaging material, migration and its effects on food quality. In: 1st international conference on quality of life, Center for Quality, Faculty of Engineering, Unviersity of Kragujevac, June 2016
27. Jiang L, Morelius E, Zhang J et al (2008) Study of the Poly(3-hyroxybutyrate-co-3-hydroxyvalerate)/Cellulose Nanowhisker composites prepared by solution casting and melt processing. J Compos Mater 42(24):2629–2645
28. Kim IH, Jeong YG (2010) Polylactide/exfoliated graphite nanocomposites with enhanced thermal stability, mechanical modulus, and electrical conductivity. J Polym Sci, Part B: Polym Phys 48(8):850–858
29. Kim SW, Cha SH (2014) Thermal, mechanical, and gas barrier properties of ethylene–vinyl alcohol copolymer-based nanocomposites for food packaging films: Effects of nanoclay loading. J Appl Polym Sci 131(11):40289
30. Kong I, Tshai KY, Hoque ME (2015) Manufacturing of natural fibre-reinforced polymer composites by solvent casting method. In: Salit MS (ed) Manufacturing of natural fibre reinforced polymer composites. Springer International Publishing, Switzerland, pp 331–349
31. Lagarón JM, López-Rubio A, José Fabra M (2015) Bio-based packaging. J Appl Polym Sci 133(2):42971
32. Lai SM, Hsieh YT (2016) Preparation and properties of polylactic acid (PLA)/silica nanocomposites. J Macromol Sci, Part B 55(3):211–228
33. Lai SM, Wu SH, Lin GG et al (2014) Unusual mechanical properties of melt-blended poly (lactic acid)(PLA)/clay nanocomposites. Eur Polym J 52:193–206
34. Lee JW, Son SM, Hong SI (2008) Characterization of protein-coated polypropylene films as a novel composite structure for active food packaging application. J Food Eng 86(4):484–493
35. Lemmouchi Y, Murariu M, Santos DAM et al (2009) Plasticization of poly(lactide) with blends of tributyl citrate and low molecular weight poly(D, L-lactide)-B-poly(ethylene glycol) copolymers. Eur Polym J 45(10):2839–2848
36. Li X, Gao H, Scrivens WA et al (2005) Structural and mechanical characterization of nanoclay-reinforced agarose nanocomposites. Nanotechnology 16(10):2020–2029

37. Liu G, Song Y, Wang J et al (2014) Effects of nanoclay type on the physical and antimicrobial properties of PVOH-based nanocomposite films. LWT-Food Sci Technol 57(2):562–568
38. Lunineau G, Rahaman A (2012) A review of strategies for improving the degradation properties of laminated continuous-fiber/epoxy composites with carbon-basednanoreinforcements. Carbon 50:2377–2395
39. Maiti P, Batt CA, Giannelis EP (2007) New biodegradable polyhydroxybutyrate/layered silicate nanocomposites. Biomacromol 8(11):3393–3400
40. Majeed K, Jawaid M, Hassan A et al (2013) Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. Mater Des 46:341–410
41. Malhotra B, Anu K, Harsha K (2015) Review-antimicrobial food packaging: potential and pitfalls. Front Microbiol 6(611):1–9
42. Mali S, Victoria EM, Garcia M et al (2004) Barrier, mechanical and optical properties of plasticized Yam starch films. Carbohydr Polym 56:129–135
43. Marina R, Alfonso J, Mercedes P et al (2014) Development of novel nano-biocomposite antioxidant films based on poly (lactic acid) and thymol for active packaging. Food Chem 1–31
44. Marra A, Silvestre C, Duraccio D et al (2016) Polylactic acid/zinc oxide biocomposite films for food packaging application. Int J Biol Macromol 88:254–262
45. Mostafa HM, Sourell H, Bockisch FJ (2010) The mechanical properties of some bioplastics under different soil types for use as a biodegradable drip tubes. CIGR Ejournal 12:1–8
46. Murariu M, Dechief AL, Bonnaud L et al (2010) The production and properties of polylactide composites filled with expanded graphite. Polym Degrad Stab 95(5):889–900
47. Mushi NE, Utsel S, Berglund LA (2014) Nanostructured biocomposite films of high toughness based on native chitin nanofibers and chitosan. Front Chem 2:99
48. Nascimento P, Marim R, Carvalho G et al (2016) Nanocellulose produced from rice hulls and its effect on the properties of biodegradable starch films. Mater Res 19(1):167–174
49. Neelamana IK, Thomas S, Parameswaranpillai J (2013) Characteristics of banana fibers and banana fiber reinforced phenol formaldehyde composites-macroscale to nanoscale. J Appl Polym Sci 130(2):1239–1246
50. Ojijo V, Sinha Ray S (2013) Processing strategies in bionanocomposites. Prog Polym Sci 38 (10–11):1543–1589
51. Oksman K, Aitomäki Y, Mathew AP et al (2016) Review of the recent developments in cellulose nanocomposite processing. Compos Part A: Appl Sci Manuf 83:2–18
52. Okubo K, Fujii T, Thostenson ET (2009) Multi-scale hybrid biocomposite: processing and mechanical characterization of bamboo fiber reinforced PLA with microfibrillated cellulose. Compos Part A: Appl Sci Manuf 40(4):469–475
53. Olatunji O, Richard O (2016) Processing and characterization of natural polymers. In: Olatunji O (ed) Natural polymers. Springer International Publishing, Switzerland, pp 19–34
54. Öner M, İlhan B (2016) Fabrication of poly (3-hydroxybutyrate-co-3-hydroxyvalerate) biocomposites with reinforcement by hydroxyapatite using extrusion processing. Mater Sci Eng, C 65:19–26
55. Othman SH (2014) Bio-nanocomposite materials for food packaging applications: types of biopolymer and nano-sized filler. Agric Agric Sci Proc 2:296–303
56. Pandey JK, Reddy KR, Kumar AP et al (2005) An overview on the degradability of polymer nanocomposites. Polym Degrad Stab 88:234–250
57. Pazourkova L, Martynkova G, Placha D (2015) Preparation and mechanical properties of polymeric nanocomposites with hydroxyapatite and hydroxyapatite/clay mineral fillers—review. J Nanotechnol: Nanomed Nanobiotechnol 2(007):1–8
58. Petersson L, Kvien I, Oksman K (2007) Structure and thermal properties of poly (lactic acid)/ cellulose Whiskers nanocomposites. Compos Sci Technol 67:2535–2544
59. Pinto AM, Cabral J, Tanaka DAP et al (2012) Effect of incorporation of graphene oxide and graphene nanoplatelets on mechanical and gas permeability properties of poly(lactic acid) films. Polym Int 62(1):33–40
60. Pinto RJB, Daina S, Sadocco P et al (2013) Antibacterial activity of nanocomposites of copper and cellulose. BioMed Res Int, 1–6

61. Qin Y, Yang J, Xue J (2015) Characterization of antimicrobial poly(lactic acid)/ poly (trimethylene carbonate) films with cinnamaldehyde. J Mater Sci V50(3):1150–1158
62. Ramos M, Jiménez A, Peltzer M et al (2014) Development of novel nano-composite antioxidants films based on poly (lactic acid) and tymol for active packaging. Food Chem 162:149–155
63. Saba N, Paridah MT, Mohammad J (2014) Potentiality of nano filler/natural fiber filled polymer hybrid composites. A review. Polymers 2014(6): 2247–2273
64. Saeedeh SA, Hosseini H, Mohammadifar MA et al (2014) Characterization of k-carrageenan films incorporated plant essentialoils with improved antimicrobial activity. Carbohydr Polym 101:582–591
65. Salehifar M, Mohammad Hadi BN, Reza A et al (2013) Effect of LDPE/MWCNT films on the shelf life of Iranian Lavash bread. Eur J Exp Biol 3(6):183–188
66. Salit MS, Jawaid M, Yusoff NB, Hoque ME (2015) Manufacturing of natural fibre reinforced polymer composites. Springer, Switzerland
67. Sengupta R, Chakraborty S, Bandyopadhyay S et al (2007) A short review on rubber/ clay nanocomposites with emphasis on mechanical properties. Engineering 47:21–25
68. Shan GF, Gong X, Chen WP et al (2011) Effect of multi-walled carbon nanotubes on crystallization behavior of poly (3-hydroxybutyrate-co-3-hydroxyvalerate). Coll Polym Sci 289(9):1005–1014
69. Siemann U (2005) Solvent cast technology—a versatile tool for thin film production. Prog Coll Polym Sci 130:1–14
70. Singh P, Ali AW, Sven S (2011) Active packaging of food products: recent trends. Nutr Food Sci 41(4):249–260
71. Sinha RS, Bousmina M (2005) Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. Prog Mater Sci 50:962–1079
72. Sinha RS, Maiti P, Okamoto M et al (2002) New polylactide/layered silicate nanocomposites. 1. Preparation, characterization, and properties. Macromolecules 35(8):3104–3110
73. Siracusa V (2012) Food packaging permeability behaviour: a report. Int J Polym Sci 2012:1–11
74. SiracusaV Rocculi P, Romani S et al (2008) Biodegradable polymers for food packaging: a review. Trends Food Sci Technol 19(12):634–643
75. Siti Nur E'zzati MA, Anuar H, Siti Munirah Salimah, AR (2018) Effect of coupling agent on durian skin fibre nanocomposite reinforced polypropylene. In: IOP conference series: materials science and engineering, University Islamic University Malaysia, Malaysia, 8–9 August 2017
76. Souza AC, Souza C, Dias AMA et al (2014) Impregnation of cinnamaldehyde into cassava starch biocomposite films using supercritical fluid technology for the development of food active packaging. Carbohydr Polym 102:830–837
77. Sriupayoa J, Supaphola P, Blackwell J et al (2005) Preparation and characterization of alpha-Chitin Whisker-reinforced poly (vinyl alcohol) nanocomposite films with or without heat treatment. Polymer 46(15):5637–5644
78. Suzuki S, Shimahashi K, Takahara J et al (2005) Effect of addition of water-soluble chitin on amylose film. Biomacromol 6:3238–3242
79. Talegaonkar S, Sharma H, Pandey S et al (2017) Chapter 3: Bionanocomposites: smart biodegradable packaging material for food preservation. In: Grumezescu AM (ed) Food Packaging, Nanotechnology in the Agri-Food Industry 7. Elsevier, United Kingdom, pp 79–110
80. Tammaro L, Vittoria V, Bugatti V (2014) Dispersion of modified layered double hydroxides in poly(ethylene terephthalate) by high energy ball milling for food packaging applications. Eur Polym J 52(1):172–180
81. Tang XZ, Kumar P, Alavi S et al (2012) Recent advances in biopolymers and biopolymer-based nanocomposites for food packaging materials. Cri Rev Food Sci Nut 52(5):426–442
82. Valdés A, Mellinas AC, Ramos M et al (2014) Natural additives and agricultural wastes in biopolymer formulations for food packaging. Front Chem 2(6):10

83. 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 (16):3500–3509
84. Vodnar DV, Oana LP, Francisc VD (2015) Antimicrobial efficiency of edible films in food industry. Notule Botanicae Horti Agrobotamici 3(2):302–312
85. Wagner M, Oehlmann J (2009) Endocrine disruptors in bottled mineral water: total estrogenic burden and migration from plastic bottles. Environ Sci Pollut Res 16(3):278–286
86. Wen X, Lin Y, Han C et al (2009) Thermomechanical and optical properties ofbiodegradable poly($_L$-lactide)/silica nanocomposites by melt compounding. J Appl Polym Sci 114:3379–3388
87. Wu D, Wu L, Zhang M et al (2008) Viscoelasticity and thermal stability of polylactide composites with various functionalized carbon nanotubes. Polym Degrad Stab 93(8):1577–1584
88. Wu J, Yu C, Li Q (2017) Novel regenerable antimicrobial nanocomposite membranes: effect of silver loading and valence state. J Membr Sci 531:68–76
89. Wu J, Zheng Y, Song W et al (2014) In situ synthesis of silver-nanoparticles/bacterial cellulose composites for slow-released antimicrobial wound dressing. Carbohydr Polym 104(1):762–771
90. Yahiaoui F, Benhacine F, Ferfera-Harrar H et al (2014) Development of antimicrobial PCL/nanoclay nanocomposite films with enhanced mechanical and water vapor barrier properties for packaging applications. Polym Bull 72(2): 235–254
91. Yoo S, Krochta JM (2011) Whey protein–polysaccharide blended edible film formation and barrier, tensile, thermal and transparency properties. J Sci Food Agric 91(14):2628–2636
92. Yu H, Yan C, Yao J (2014) Fully biodegradable food packaging materials based on functionalized cellulose nanocrystals/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) nanocomposites. RSC Adv 4(104):59792–59802
93. Zehetmeyer G, Soares RMD, Brandelli A et al (2012) Evaluation of polypropylene/montmorillonite nanocomposites as food packaging material. Polym Bull 68(8):2199–2217
94. Zheng Y, Yan K, Zhao Y et al (2016) Preparation and characterization of poly (L-lactic acid)/hollow silica nanospheres nanocomposites. Fibers Polym 17(12):2020–2026