Biopolymer Nanocomposite Based Food Packaging

Sherif M. A. S. Keshk and Ameni Brahmia

1 Introduction

Regular fibers are considered as an environmentally friendly material that exhibits good physical properties comparing with petroleum-based plastics. In 2015, the global natural fiber reinforced polymer composites industry sector was about U$ 5.1 billion. The employment of natural fiber reinforced polymer composites has recently expanded in the shopper goods as developing packing sectors. As showed by evaluations over 2012–2017, the biodegradable fiber reinforced polymer composites industry is expected to grow 15% worldwide (Layth et al. 2015). Packaging is a significant subject in developed civilizations; especially, food packaging has experienced a great growth because most commercialized foodstuffs are marketed in packages (Lopez-Rubio et al. 2004). One of the most important roles of packaging technology is to avoid deterioration of food, thus, to extend shelf-life and maintain quality and safety of the packaged food. Starch is one of the most considered biopolymers owing to its wide availability, biodegradability, non-toxicity, and low cost. Despite advantages, starch films are moisture sensitive and very fragile in comparison to the conventional packaging materials (Flores et al. 2007). In order to recover their usability, incorporation of plasticizers, blending with other materials, chemical modifications, and the combinations of these treatments have been attempted (Colussi et al. 2017). On the other hand, natural fibers are neither artificial nor man-made; they can be extracted from animals or plants (Ticoalu et al. 2010). The use of natural fibers from resources, renewable and non-renewable including oil palm, flax, and sisal, gained significant attention in the last decades. Plants that can

S. M. A. S. Keshk (✉)
Nanomaterials and Systems for Renewable Energy Laboratory, Research and Technology Center of Energy, Technoparc borje cedria, BP, Hammam Lif, Tunisia

A. Brahmia
Laboratoire des Materiaux et de l'Environnement pour le Developpement Durable, University of Tunis El Manar, Tunis, Tunisia

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produce cellulose fibers are categorized into bast filaments (such as jute, ramie, flax, kenaf, and hemp), seed fibers (such as cotton, kapok, and coir), leaf fibers (such as sisal and abaca), and grass and reed fibers (such as rice, wheat, and corn), and core fibers (hemp, jute, and kenaf) as well as all other kinds as roots and wood (Faruk et al. 2012; Keshk 2014). The fiber-reinforced polymer matrix got extensive consideration in several aspects owing to their good physical properties and superior benefits over artificial fibers in term of its cost, low weight, less damage to handling equipment, good mechanical characterization as tensile and flexural modulus, improved surface finish of composites, being abundant, renewable resources, biodegradability, flexibility during processing, and least health risks (Shalwan and Yousif 2013; Keshk and Yahia 2018; Alghamdi et al. 2019). Natural fiber reinforced composites possess a high specific stiffness and strength that can be realized by adding the tough and light-weight fiber onto the synthetic polymer (thermoplastic and thermoset) (Xie et al. 2010). However, natural fibers are not problems-free, as they have deficits in physical properties. The structure of natural fibers is composed of cellulose, pectin, hemicelluloses, lignin, and waxy substances. They permit moisture absorption from the surroundings that may cause weak bindings between the polymer and fiber. Furthermore, the lacking compatibility between natural polymers and fibers is considered as a challenge since the chemical structures of both polymers and fibers are two different. Modifications of the natural fiber using certain treatments are required in order to compatibilized both polymers. Such modifications are focused on the use of reactive functional groups that have the capacity for reacting with the fiber structures and changing the chemical composition. Thus, fiber modifications may cause reduction of moisture absorption that lead to an excellent improvement of compatibility between the polymer and fiber (Ray and Bousmina 2005). Cellulose has been successfully shaped into nanoforms, namely nano-fibrillated cellulose (NFC) and micro-fibrillated cellulose (MFC) (Nogi et al. 2009). NFC can deliver reactive site and possess excellent mechanical and oxygen barrier properties. Whereas, high loading of MFC is commonly required to enhance the mechanical stability of the composite, because of the MFC is larger, and it decreases intrinsic energy and element ratio. MFC films displayed opportunity for food packing owing to its high rigidity together with the essential barrier properties (Zhang et al. 2011; Aulin et al. 2012). Current developments in packaging material have focused on high barrier performance with a minimal amount of material. Therefore, there is a need for functional coatings of cellulosic materials for special or enhanced properties in the field of food packaging (Gouda and Keshk 2010).

2 Starch

In order to recover starch usability, blending with other materials, chemical modifications, and the combinations of these treatments have been evaluated (Colussi et al. 2017; Keshk et al. 2018a, b). Starch films with clay nanoparticles were prepared and their tensile, barrier properties and transition temperature were

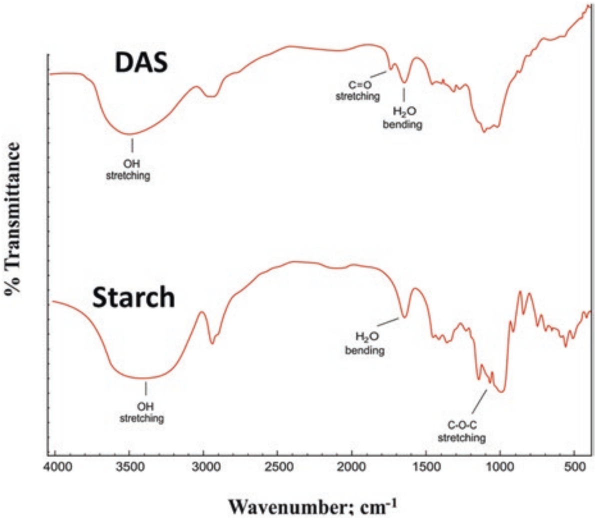

Fig. 1 FT-IR spectra of starch & dialdehyde starch (DAS)

investigated (Souza et al. 2012). The presence of clay affected the tensile and barrier properties; whereas, the glass transition temperature was not affected (Souza et al. 2012). In additional investigation, a biodegradable film obtained from acetylated starch displayed higher moisture content and water solubility in comparison to starch film (Colussi et al. 2017). Among various derivatives of starch, dialdehyde starch (DAS) that produced from the periodate oxidative cleavage of C2–C3 bond of the starch molecule. FT-IR spectroscopy data of starch and DAS are shown in Fig. (1) (Keshk et al. 2016a, b). In the fingerprint region from 800 cm^{-1} to 1500 cm^{-1}, the spectral features of starch and DAS were dissimilar; where the peaks in starch at 1158 cm^{-1} and 930 cm^{-1} that are characteristic to a C–O stretching vibration were missing in DAS (Keshk et al. 2016a, b). Furthermore, a new absorption band at 1735 cm^{-1} appeared in the DAS spectrum, which was assigned to the C=O stretching vibration.

DAS is highly reactive and possesses higher thermal stability (T = 355 °C) than starch (T = 191 °C), hence, it is widely used as a cross-linking agent (Keshk et al. 2016a, b; Wisniewska et al. 2016). The rigidity of cross-linked DAS matrix formed due to hydrogen bonds confers a better thermal stability to DAS (Wisniewska et al. 2016). Nanotechnology can remarkedly recover the quality and safety of food packing. Different food concerns have used nanotechnology to develop safer and more attractive products with longer shelf-life and lower costs. Nanomaterials in food packing technology can alter permeation properties, increase barrier properties, improve mechanical and heat-resistance, confer active antimicrobial and antifungal surfaces, and detect and signal microbiological and biochemical changes (Cichello 2015). Magnetic iron oxide nanoparticles (MNPs) have been used in various arenas owing to their unique properties including large specific surface area and simple

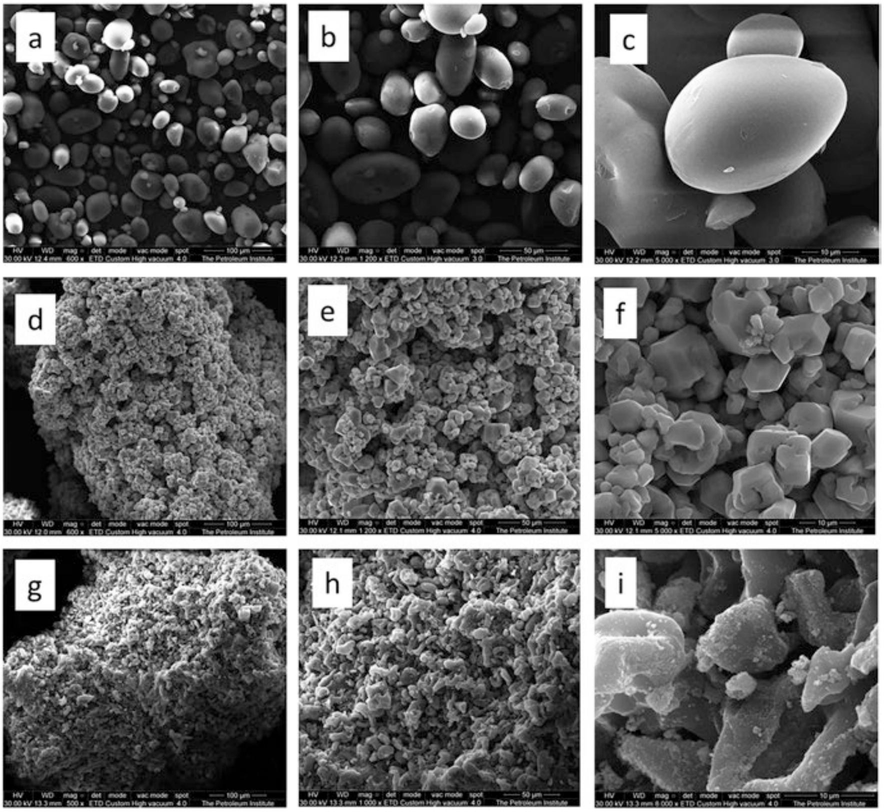

Fig. 2 SEM micrographs at different magnifications for potato starch (**a-c**), DAS, (**d-f**), and MNPs/DAS (**g-i**)

separation with magnetic fields. For food-related applications, they have been used for enzyme immobilization, protein purification, and food analysis (Caoa et al. 2012). The incorporation of MNPs with a polymer packing film will modify barrier properties and prevent the destruction of basic structure of starting materials. Besides this, the addition of MNPs will significantly recover the mechanical (tensile strength, elongation at break) and thermal properties (Reščcek et al. 2016). Furthermore, an MNPs/DAS composite showed good thermal stability, small particle size, low biological toxicity, and slow anticancer drug-releasing capability (Saikia et al. 2015). Recently, MNPs/ DAS composite film was fabricated for use in food packaging (Keshk et al. 2018a, b). Scan electron microscope showed that the starch granules were of ellipsoidal morphologies with smooth surfaces and were larger than those of the DAS and MNPs/DAS granules, as the latter were of irregular polygonal shape (Fig. 2).

A comparison of the DAS and MNPs/DAS granules at high magnifications (Fig. 2f and i) indicated that the DAS granules were smoother, while MNPs/DAS

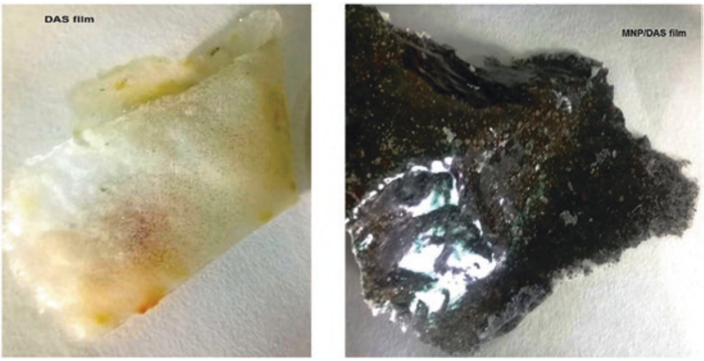

Fig. 3 DAS and MNPs/DAS Films

granules designed agglomerations owing to the magnetic properties of iron. It can also be caused by the crosslinking of DAS and MNPs. The average pore sizes in DAS and MNPs/DAS composite were 4.25 μm and 0.65 μm, respectively. Thus, the MNPs/DAS composite film was more compact with a higher thickness than DAS film (Fig. 3).

Furthermore, thermogravimetric analysis confirmed that the MNPs/DAS film was thermally stable up to 300 °C, and the maximum decomposition happened at 500 °C. Furthermore, SEM micrographs recognized the homogenous distribution of MNPs onto the DAS film. The MNPs/DAS composite film displayed lower water vapor transmission in comparison to DAS film, thus it can be decided that MNPs improved the hydrophobicity and mechanical properties of starch film. Therefore, the prepared MNPs/DAC composite film could be considered for oxygen sensitive foods like Chilled meat, as it contains a highly effective oxygen scavenger (Fe_3O_4) (Keshk et al. 2018a, b).

3 Cellulose

Cellulose fibres offer a large renewable raw material base for various kinds of products, e.g., from paper and board to various composite materials ranging from packaging applications to building materials. The physical modification of cellulose fibres has recently received attention in the field of composite applications (Alghamdi et al. 2019). The physicochemical modification of cellulose is important for making it more compatible with nonpolar polymers by introducing a hydrophobic polymer into its structure (Thielemans et al. 2008). Therefore, there is a need for new derivatives of cellulosic materials for special or enhanced properties in the field of food packaging. Zinc oxide is generally used in several applications, such as in the pharmaceutical, commodity chemical, and glass industries (Arrieta et al. 2010; Jia et al. 2012; Ko et al. 2014; Espitia et al. 2016). ZnO is presently listed as a safe

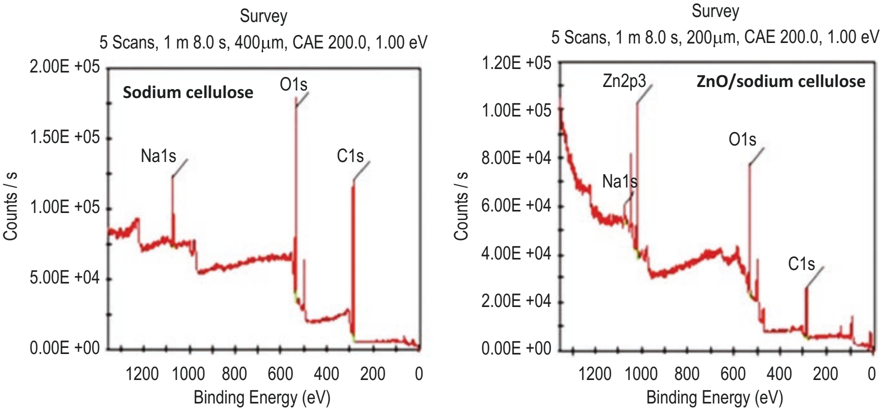

Fig. 4 XPS survey scan spectra recorded with a photon energy of Al Kα (hv = 1486.6 eV)

food additive and preservative by the US Food and Drugs Administration. The reported synthetic methods of metal/cellulose composite preparation have poor metal stability in the composite and heterogeneous distributions of metals (Ma et al. 2013; Al-Sehemi et al. 2014). The preparation of metal/cellulose composites via the reduction of metal salts in aqueous suspensions of cellulose has been investigated (El-Kemary et al. 2013). In this method, a soluble metal salt is used with a suitable reducing agent in the presence of a co-stabilizer to avoid agglomeration and to improve the metal particle distribution on the cellulose (Yue et al. 2013). On the other hand, microwave-assisted synthesis of metal/cellulose composites have been reported, in which ionic liquids were used to obtain cellulose fibres coated with metal particles (Dinand et al. 2002; Keshk et al. 2016a, b). In the fact, the hydrophilicity of cellulose made it difficult to form a good composite with metals owing to hydrogen bonds between cellulose chains that hinder any other metal or metal oxide from forming a good composite. Sodium hydroxide treatment (mercerization) of natural cellulose (cellulose-$(OH)_3$) fibres results in the structural transformation to sodium cellulose (cellulose-$(ONa)_3$) (Keshk 2015; Keshk and Hamdy 2019). During mercerization, cellulose I proceeds through a crystal-to-crystal phase transformation. The intermediate structure between the parallel chains (cellulose I) and anti-parallel chains (cellulose II) is sodium cellulose (Keshk et al. 2018a, b; Keshk and Hamdy 2019). Sodium cellulose increases the interplanar distance between cellulose chains owing to $O^- Na^+$ group formation. The mercerization affects the twisting and swelling of cellulose because of the presence of Na^+ ions, which play a crucial role in widening the accessible regions between the lattice planes to allow diffusion of the Na^+ ions into those planes (Keshk et al. 2018a, b; Keshk and Hamdy 2019). Zinc oxide/sodium cellulose composite with different ZnO loadings was prepared and characterized by FT-IR, XRD, XPS, SEM, and EDX Keshk and Hamdy 2019). ZnO/sodium cellulose showed a similar XRD pattern to that of cellulose II. The XPS spectrum emphasized the presence of Zn^{2+} and Na^+ ions in the prepared composite (Fig. 4) (Keshk and Hamdy 2019).

Table 1 Barrier properties of cellulose, sodium cellulose and its composite

Sample	Air permeability (cm^3/ (m^2/Pa. S))	Water vapour permeability (g/m s Pa)
Cellulose	1.05	4.68 X 10^{-9}
Sodium cellulose	1.15	4.12 X 10^{-9}
ZnO/sodium cellulose	0.137	2.44 X 10^{-9}

Furthermore, the SEM analysis displayed the growth of ZnO crystals on the sodium cellulose surface. UV-Vis spectrometry of the ZnO/sodium cellulose spectrum exhibited a distinguished absorption band at 360 nm that was attributed to the presence of ZnO particles on the cellulosic fibres (Keshk and Hamdy 2019). Therefore, the ZnO/sodium cellulose fibres swelled, and their diameter increased from 15 μm to 30 μm. Furthermore, ZnO/sodium cellulose exhibited lower air and water vapor permeability than cellulose and sodium cellulose and can be perfectly utilized as food packing film to increase the shelf life of preserved foods (Table 1) (Keshk and Hamdy 2019).

4 Chitosan

Chitosan is considered as a safe natural polymer that possesses biocompatible and biodegradable properties. Chitosan is a polysaccharide produced by chemical or enzymatic deacetylation of chitin. There are at least four prepared methods presented: ionotropic gelation (Calvo et al. 1997), microemulsion (Maitra et al.1999), solvent emulsification diffusion (Niwa et al. 1993) and polyelectrolyte complex (Erbacher et al. 1998). The most widely developed methods are ionotropic gelation and self-assemble polyelectrolytes; as there are simple and mild preparation method without the use of organic solvent or high shear force (Tiyaboonchai 2003; Sudarshan et al. 1992). The nanofibers based on chitosan have large surfaces and high porosity therefore potentially working in the fields of enzyme immobilization (such as chitosan/PVA), filtration (chitosan/PEO, Chitosan/nylon-6…) wound dressing (chitosan/PVA, Chitosan/PET), tissue engineering (Chitosan/collagen) drug delivery (PEG-g-CS/ PLGA…) and catalysis (CS-g-AA) (Sun and Li 2011). Depending on the technique of preparation, chitosan-based nanofibers size can vary from 10 nm to 4 nm (Sun and Li 2011; Van et al. 2013). Chitosan-based nanofibers were prepared via acid hydrolysis of chitin whiskers (Lu et al. 2004; Sriupayo et al. 2005). The average dimensions of the whiskers obtained were 500–417 nm (length) and 50–33 nm (diameter) (Lu et al. 2004; Sriupayo et al. 2005). The suspension consisted of individual chitin fragments that having a spindle shape. As shown in the AFM image of a dilute suspension of chitin whiskers (Fig. 5).

These fragments have a broad distribution in length (L) ranging from 100 to 650 nm and diameter (D) ranging from 10 to 80 nm. SEM images of the fractured

Fig. 5 AFM imaging of a dilute suspension of chitin whiskers

surface of the GSPI sheet and nanocomposites of SPI-5, SPI-15, and SPI-30 are shown in Fig. 6.

The GSPI sheet exhibits a relatively uniform surface. The chitin whiskers, as particles, are easily identified. A relatively uniform distribution of the chitin whisker in the SPI matrix can be observed when the chitin content is lower than 15 wt %. However, as the chitin content increases, the resulting nanocomposites show agglomerates of whiskers. The diameter of whiskers determined by SEM is larger than identified by AFM shown in Fig. 2, which resulted from a charge concentration effect due to the emergence of whiskers from the observed surface.

This suggests that the adhesion between SPI and chitin whisker is strong. Chitosan nanoparticles can be obtained by ionic gelation, where the positively charged amino groups of chitosan form electrostatic interactions with polyanions worked as cross-linkers, such as tripolyphosphate (López et al. 2005). Chitosan–tripolyphosphate (CS–TPP) nanoparticles that incorporated with hydroxy propyl methylcellulose (HPMC) films was significantly improved the mechanical and barrier properties (Caner and Cansiz 2007; De Moura et al. 2009). Chitosan-based nanocomposites have several applications like food industry, medicine and paper manufacturing, etc. These nanocomposites, films and coating based on chitosan, offer capable improvement in food packaging industrial because of chitosan's capability to hold up the life of food products (Shahidi et al. 1999). Different types of nanofillers with different nanoscale have been synthesized and investigated till now (Radhakrishnan et al. 2015). Therefore, physicochemical properties along with the types, size, and surface areas of nanofillers could significantly improve the chitosan. Clay-based nanocomposite enhanced oxygen barricade capacity of chitosan film (Radhakrishnan et al. 2015). Therefore, the integration of clay into the chitosan matrix enhances the transport and barrier characteristics. For the substitute of plastic resources to decrease the ecological contamination, chitosan/methyl cellulose nanocomposite can substitute the plastic in packaging foods (Mura et al. 2011).

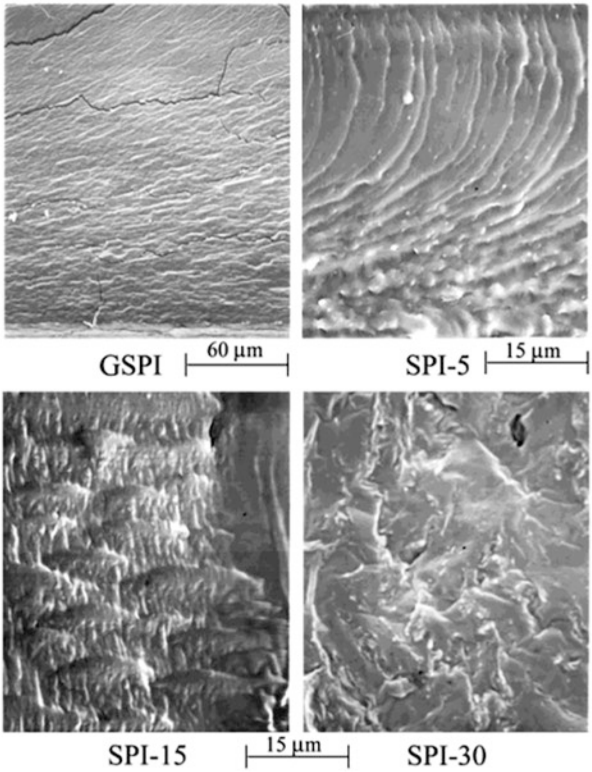

Fig. 6 SEM image of GSPI sheet and SPI/chitin whiskers nanocomposites

5 Conclusion

Nanotechnology has revealed numerous advantages in food packaging industry, including better barriers; mechanical, thermal, and biodegradable properties. However, the use of nanocomposites in food packaging might be challenging owing to the reduced particle size of nanomaterials and the physicochemical characteristics of such nano- materials may be quite different from those of their macro-scale counterparts. Despite several advantages of nanomaterials, their use in food packaging may cause safety problems to human health since they exhibit different physicochemical properties from their macro-scale chemical counterparts. Different research disciplines including identification, characterization, and quantification of the nanoparticles are requested.

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