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Bio-nanocomposite Materials for Food Packaging Applications: Types of Biopolymer and Nano-sized Filler

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Abstract

Majority of materials employed for food packaging are non-biodegradable materials which do not meet increasing demands in society for sustainability and environmental safety. Thus, numerous biopolymers have been exploited to develop biodegradable food packaging materials. Nonetheless, the usage of biopolymers has been limited due to the poor mechanical and barrier properties. These properties can be enhanced by adding reinforcing nano-sized compounds or fillers to form composites. This article reviews variety types of biopolymer and nano-sized filler used to form bio-nanocomposite materials.

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Keywords: Nanocomposite; biopolymer; nanofiller; food packaging

1. Introduction

To date, the production and use of non-biodegradable materials or plastics as food packaging materials have significantly increased. These types of materials are usually derived from petroleum products and cause the problem in waste disposal (Avella et al., 2005). To meet the increasing demand for sustainability and environmental safety, a growing number of investigations have been directed towards development of food packaging materials that could rapidly degrade and completely mineralize in environment (Jayaramudu et al., 2013; Majeed et al., 2013). Biopolymers have been one of the favorable alternatives to be exploited and developed into eco-friendly food packaging materials due to its biodegradability (Tang et al., 2012). Used food packaging materials produced from

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biopolymers can be disposed into bio-waste collection for further compose, leaving behind organic by-product such as carbon dioxide (CO_2) and water (H_2O).

Unfortunately, the use of biopolymers as food packaging materials has drawbacks such as poorer mechanical, thermal, and barrier properties as compared to the conventional non-biodegradable materials made from petroleum. Due to this, many research efforts were made to improve the properties of the biopolymers. This include the use of the nanocomposite concept (Abdollahi et al., 2012; Arfat et al., 2014; Di Maio et al., 2013; Kanmani and Rhim, 2014; Nafchi et al., 2013; Reddy and Rhim, 2014; Sadeqh-Hassani and Mohammadi Nafchi, 2014; Sanuja et al., 2014; Trovatti et al., 2012). From the researches done, nanocomposite was established as a promising route to enhance mechanical and barrier properties of biopolymers. Bio-nanocomposite is a multiphase material comprising of two or more constituents which are continuous phase or matrix particularly biopolymer and discontinuous nanodimensional phase or nanofiller (<100 nm). The nano-sized fillers play a structural role in which they act as reinforcement to improve the mechanical and barrier properties of the matrix. The matrix tension is transferred to the nanofillers through the boundary between them (Arfat et al., 2014; Azeredo et al., 2011; Kanmani and Rhim, 2014; Trovatti et al., 2012).

The incorporation of nanofillers such as silicate, clay, and titanium dioxide (TiO_2) to biopolymers may improve not only the biopolymers' mechanical and barrier properties but also offer other functions and applications in food packaging such as antimicrobial agent, biosensor, and oxygen scavenger (Azeredo, 2009; Azeredo et al., 2011, Rhim et al., 2013). The bio-nanocomposite can be an active food packaging whereby the food packaging can interact with food in some ways by releasing beneficial compounds such as antimicrobial agent, antioxidant agent, or by eliminating some unfavorable elements such as oxygen or water vapor. The bio-nanocomposite can also be a smart food packaging whereby it can perceive property of the packaged food such as microbial contamination or expiry date and uses some mechanism to register and convey information about the quality or safety of the food (Azeredo et al., 2011).

The development of bio-nanocomposite materials for food packaging is important not only to reduce environmental problem but also to improve the functions of the food packaging materials. This review highlights several types of biopolymers and nano-sized fillers used to form bio-nanocomposite materials. Some recent results on the properties and characteristics of the bio-nancomposite materials are also discussed.

2. Biopolymers

Biopolymers are polymers which consist of monomeric units that are covalently bonded, forming chain like molecules. The prefix bio denotes that biopolymers are biodegradable. Thus, biopolymers have the capability to be degraded or broken down through the action of naturally occurring organisms leaving behind organic by-product such as CO_2 and H_2O which are safe towards environment. Biopolymers have been regarded as alternative materials to plastic made from petroleum because they are biodegradable, renewable and abundant (Liu, et al., 2005; Muratore et al., 2005).

Previously, the most common type of biopolymers for food packaging applications is natural biopolymers for instance starch, cellulose, chitosan, and agar which are derived from carbohydrate as well as gelatin, gluten, alginate, whey protein, and collagen which are derived from protein. Nowadays, the advent of technology has led to the formation of synthetic biopoloymers which include polylactic acid (PLA), polycaprolactone (PCL), polyglycolic acid (PGA), polyvinyl alcohol (PVA), and polybutylene succinate PBS (Rhim et al., 2013). The advantages of synthetic biopolymers include the potential to create a sustainable industry as well as enhancement in various properties such as durability, flexibility, high gloss, clarity, and tensile strength.

Biopolymers can be categorized into four groups depending on the origin of the biopolymers, which includes = natural biopolymers extracted from biomass (e.g. agro resources), synthetic biopolymers from microbial production or fermentation (e.g. polyhydroxy-alkanoates (PHA)), synthetic biopolymers conventionally and chemically synthesized from biomass (e.g. PLA) and synthetic biopolymers conventionally and chemically synthesized from petroleum product (e.g. PCL). The first three groups are derived from renewable resources while the last group is derived from petroleum. Fig. 1 represents the categories of the biopolymers used for food packaging applications.

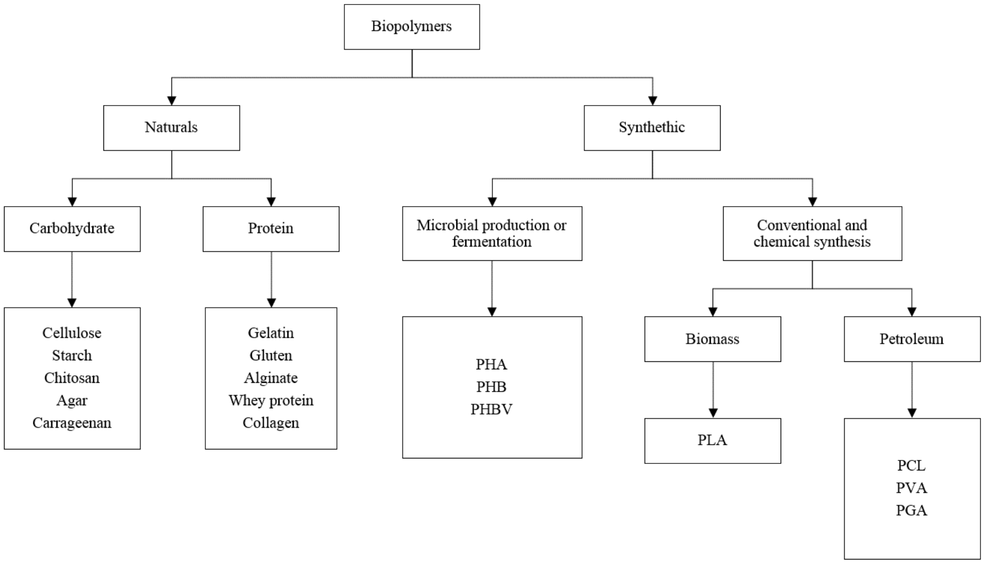

Fig. 1. Categories of the biopolymers (Adapted from Kfoury et al., 2013; Rhim et al., 2013).

Among the biopolymers, the most common type that has been studied to produce bio-nanocomposite materials for food packaging applications are starch and derivates (Heydari et al., 2013; Nafchi et al., 2013; Pan et al., 2014; Tang et al. 2008). Starch and derivates are commonly edible, thus they are safe as food packaging materials. Studies have shown that starch is completely degradable and could stimulate biodegradability of non-biodegrable materials when mixed. However, starch has low mechanical properties which can be improved with additives such as plasticizer and nanofillers (Sorrentino et al., 2007).

Other biopolymers studied include cellulose such as cellulose acetate, carboxylmethyl cellulose (CMC), and hydroxypropylmethylcellulose (HPMC) (Bruna et al., 2014; George et al., 2014; Mondal et al., 2013), chitosan (Pereda et al., 2014; Tripathi et al., 2014), agar (Kanmani and Rhim, 2014; Rhim, 2011, Rhim et al. 2011, Rhim et al., 2013;), gelatin (Kanmani and Rhim, 2014; Nafchi et al., 2013; Rouhi, 2013), gluten (Rafieian et al. 2014), alginate (Abdollahi et al., 2013), and synthetic biopolymers such as PLA (Conte et al., 2013; Di Maio et al., 2013; Jorda-Beneyto et al., 2014), PHA (Bordes et al., 2009), and PCL (Gorrasi et al., 2004).

The most common synthetic biopolymers that has been studied till today is PLA. PLA is produced from lactic acid which may simply be generated through fermentation of carbohydrate from plant resources such as sugar beet and corn (Sorrentino et al., 2007). Among the advantages of PLA include biodegradability (Letian et al., 2013) and the lifespan of PLA can be tailored accordingly.

However, some of the drawbacks of using biopolymers as food packaging materials compared to the conventional non-biodegradable materials especially those made from petroleum include poor mechanical (e.g. low tensile strength) and barrier properties (e.g. high water permeability). Biopolymers are generally brittle, low in heat distortion temperature, and low resistance to prolonged process operations. For instance, the used of most favorable synthetic biopolymers, PLA, as food packaging material exhibits low performance (Sorrentino et al., 2007) due to low heat distortion temperature, low resistance to extreme heat and humidity, and low flexibility.

Nevertheless, weighing the advantages of using biopolymers as packaging materials, especially to cater for demands in society for sustainability and environmental safety, many studies have been directed towards improvement of biopolymers for food packaging applications. Bio-nanocomposite has been established to be a promising route to enhance mechanical and barrier properties of biopolymers.

3. Nanofillers

At nano-scale level, the size of the nano phase or filler is significantly reduced, leading to the dramatic increment in the surface area of the fillers. This is desired because bio-nanocomposites rely on the high surface area of the nanosized fillers which results to a large interfacial or boundary area between the matrix or biopolymer and nanofiller. The large interface enabled the modification of molecular mobility, the relaxation behaviour besides mechanical, thermal, and barrier properties of the bio-nanocomposites (Azeredo et al., 2011). Especially for food packaging applications, bio-nanocomposite materials are usually designed to have the ability to endure the mechanical and thermal stress during food processing, transportation, and storage (Rhim et al., 2013).

Many types of nanosized fillers (less than 100 nm) have been used to enhance the performance of the biopolymers. The nanofillers that are commonly studied for food packaging applications can be classified into few types which include nanoparticles, nanofibrils, nanorods, and nanotubes. To the best of our knowledge, no study has been done to compare the properties of the bio-nanocomposite materials prepared from different classification of nanofillers. Researchers used different types of filler and biopolymer to produce bio-nanocomposite materials and they studied different properties of the produced bio-nanocomposite materials, making the comparison based on literature difficult. For example, Kanmani et al. (2014) studied the physiochemical properties of antimicrobial composite films made from gelatin and silver nanoparticles, Rafieian et al. (2014) studied the thermomechanical and morphological properties of bio-nanocomposite films made from wheat gluten matrix and cellulose nanofibrils while Rouhi et al. (2013) studied the physical properties of bio-nanocomposite films made from fish gelatin incorporated with zinc oxide (ZnO) nanorods.

The nanosized fillers can be either organic or inorganic such as clay (e.g. Montmorillonite (MMT)), natural biopolymers (e.g. chitosan), natural antimicrobial agents (e.g. nisin), metal (e.g. silver), and metal oxides (e.g. TiO_2). Table 1 represents some of the nanofillers that have been studied for food packaging applications.

Table 1. Some of the nanofillers that have been studied for food packaging applications.

Classification	Type of nanofiller	Example
Organic	Clay	MMT (e.g. Pinto et al., 2014)
		Cloisite Na+ (e.g. Lee et al., 2014; Rhim et al., 2011; Shin et al., 2014)
		Cloisite 30B (e.g. Kanmani and Rhim, 2014; Rhim et al., 2011; Shin et al., 2014)
		Cloisite 20A (e.g. Rhim et al., 2011; Shin et al., 2014)
		Cloisite 10A (e.g. Lee et al., 2014)
	Natural biopolymers	Chitosan (e.g. Martelli et al., 2013)
		Cellulose (e.g. Shakeri and Radmanesh, 2014)
	Natural antimicrobial agents	Nisin (e.g. Imran et al., 2012)
Inorganic	Metal	Silver (e.g. Youssef et al., 2014)
		Copper (e.g. Conte et al., 2013)
		Gold (e.g. Youssef et al., 2014)
	Metal oxide	ZnO (e.g. Kanmani and Rhim, 2014)
		TiO_2 (e.g. Zhu et al., 2012)
		MgO (e.g. Sanuja et al., 2014)
		Ag_2O (e.g. Tripathi et al., 2011)

Among the numerous nanofillers, the most common type that has been modified as bio-nanocomposite materials for food packaging applications was clay (Abdollahi et al., 2012; Di Maio et al., 2013; Kanmani and Rhim, 2014; Kim and Cha, 2014; Lee et al., 2014; Mondal et al., 2013; Pinto et al., 2014; Shin et al., 2014). This is because it occurs *naturally,* abundant in which it originates from the earth's crust, cost effective, proven to result in significant reinforcement and relative processability of bio-nanocomposite materials. The most extensively studied clay was

MMT (Bruna et al., 2014; Heydari et al., 2013; Park et al., 2013; Pinto et al., 2014) due to the high surface area and aspect ratio.

Different types of clay exhibit different surface areas and aspect ratios. A few studies have been done to compare the effects of clay type on the produced bio-nanocomposite materials. For instance, Lee et al. (2014) studied the effect of Cloisite Na^+ and Cloisite 10A on the physical properties of sesame seed meal protein bio-nanocomposite films. Rhim et al. (2011) studied the effect of clay type that includes Cloisite Na+, Cloisite 30B, and Cloisite 20A on the characteristics of agar and clay bio-nanocomposite films. The effects on the properties of the bio-nanocomposite films were different due to the differences in properties of the clay.

The most common type of metal studied to produce bio-nanocomposite materials was found to be silver (De Moura et al., 2012; Incoronata et al., 2011; Kanmani and Rhim, 2014; Rhim et al., 2013; Youssef et al., 2014) due to the antimicrobial properties as well as stable and low volatile at high temperature whilst the most common type of metal oxide is ZnO (Kanmani and Rhim, 2014; Nafchi et al., 2013; Rouhi et al., 2013) due to the deodorizing and antibacterial properties.

Usually, low amount of fillers (<5%) is adequate to results in an improvement in the biopolymer properties (Rhim et al., 2013). Generally, mechanical properties of the bio-nanocomposites are significantly dependent on the amount of nanofillers. Many studies have demonstrated that the tensile strength and modulus of bio-nanocomposite materials increase while elongation at break decrease with an increase in the amount of nanofillers (Rhim, 2011; Rhim et al., 2011; Tang et al., 2012). The increase in mechanical properties of the bio-nanocomposite materials is attributed to the high rigidity of the nanofillers as well as excellent affinity between biopolymer and nanofiller at the interface (Rhim et al., 2013). The interfacial interaction would lead to rigid bio-nanocomposite materials due to the incorporation of rigid nanofillers, thus enhancing the thermal properties of bio-nanocomposite materials.

Apart from that, bio-nanocomposites materials also exhibit improved barrier properties towards gases and water vapour. Previous studies shown that improvement in barrier properties was dependent on the types and amount of nanofillers used as well as aspect ratio of the nanofillers (Rhim et al., 2013). Between those two, aspect ratio was found to have major effect on the barrier properties of bio-nanocompsite materials. High ratios nanofillers exhibit high tendencies towards filler incorporation thus dramatically improved the barrier properties (Choudalakis and Gotsis, 2009). Due to the excellent barrier properties, bio-nanocomposite materials have received considerable attention for food packaging applications because this could lead to considerable shelf life enhancement of food product.

The incorporation of nanofillers may not only enhance the mechanical, thermal, and barrier properties of the biopolymers but also offer other desired functions and applications in food packaging such as antimicrobial agent, biosensor, and oxygen scavenger. The incorporation of nanofillers that exhibit antimicrobial properties could enhance food safety by controlling the growth and invasion as well as killing bacteria and pathogenic microorganisms in the food (Azeredo et al., 2009; Sorrentino et al., 2007). The large surface area of nanofillers permits more microorganisms to attach to the nanofillers thus increase the antimicrobial efficiency of bio-nanocomposite materials (Azeredo et al., 2009).

Some of the nanofillers tabulated in Table 1 (e.g. MMT, chitosan, silver, ZnO) exhibit antimicrobial properties which are favourable for food packaging applications. Occasionally, other antimicrobial agents such as enzymes (e.g. peroxidase, lysozyme) and synthetic antimicrobial agents (e.g. benzoic acid, propionic acid, sorbic acid) are also incorporated in the bio-nanocomposite materials (Rhim et al., 2013). The most widely used nanofillers as antimicrobial agent is silver due to the strong toxicity properties towards variety of microorganisms (Azeredo et al., 2009). For example, Kanmani et. al (2014) have studied the antimicrobial properties of gelatin based active bio-nanocomposite films containing silver nanoparticles and nanoclay. Rhim et al (2013) studied agar based bio-nanocomposite with silver nanoparticles filler while De Moura et al. (2012) developed cellulose-base antimicrobial nanocomposites containing silver nanoparticles. All of the studies showed promising antimicrobial activity of the bio-nanocomposite films.

Reactive nanofillers incorporated in biopolymers can act as sensor. Bio-nanocompsite materials as biosensor exhibit the ability to respond to changes in the environment such as temperature, humidity, and levels of oxygen as well as to degradation and contamination of food products (Azeredo et al., 2009; Bouwmeester et al., 2009). These responds are important to be monitored especially during storage of food in order to ensure the freshness of the food. Sealing defects in food packaging are sometimes left undetected, thus, the sensor is important to indicate undesirable changes in the food product and to alert consumers if the food has gone unpleasant or bad. Carbon nanotube (CNT) is among the nanofillers that exhibit sensor properties. According to Han et al. (2011), Georgia Technology is one of the institutions that has utilize nanofillers as nanosensor in packaging development. Georgia Technology Institution develops polyamide and multiwall carbon nanotube (MWNT) based biosensor to detect microorganisms, toxic proteins, and spoilage of foods and beverage.

Some of the nanofillers exhibit oxygen scavenger properties. The incorporation of oxygen scavenger nanofillers into food packaging can help to reduce and maintain oxygen level. This is important because high concentration of oxygen can lead to deterioration of some food (Azeredo et al., 2009). For example, direct oxidation of fruits and vegetables can result to browning while oxidation of fats results in rancid odors, flavors, and stale of food that contains the fat. Oxidation of food pigments results in color changes which will affect the looks of the product thus makes the product less appealing. Packaging the food products using materials with oxygen scavenger properties can limit oxidation and help to keep the freshness of food. TiO_2 is one of the nanofillers that exhibit oxygen scavenger properties under ultraviolet (UV) light radiation. Xiao-e et al. (2004) have successfully developed films with oxygen scavenger properties with the incorporation of TiO_2.

Based from the literatures, it was found that researchers tend to study the effect of nanofillers addition on the properties of the bio-nanocomposite materials in which most research studied the effect of the amount of nanofillers addition on the properties of the materials. The literature is clearly lacking study on the effect of types of biopolymer and nanofiller on the properties of the bio-nanocomposite materials. Kanmani et al. (2014) characterized the properties of bio-nanocomposite films produced from different types of biopolymers that were agar, carrageenan and CMC of which all were from carbohydrate group with the addition of various amount of ZnO nanoparticles as the nanofiller. They highlighted that for all types of biopolymer, addition of ZnO nanofiller was found to increase the color, UV barrier, moisture content, hydrophobicity, elongation and thermal stability of the bio-nanocomposite films and decrease the water vapor permeability, tensile strength, and elastic modulus. Nafchi et al. (2013) has characterized bio-nanocomposite films made from sago starch and bovine gelatin with nanorod-rich zinc oxide as the nanofillers. They found a decrease in oxygen permeability and an increase in mechanical and heal seal properties of the films. The increase in ZnO nanorod contents lead to a decrease in moisture content and water absorption capacity of the bio-nanocomposite films. The films also exhibited UV absorption.

4. Conclusions

The addition of nanofillers such as MMT, silver, and ZnO to the biopolymers such as starch and PLA open up new potential to create new and innovative bio-nanocomposite materials with improved properties and performance. Nanofillers have the ability to improve the mechanical, thermal, and barrier properties as well as exhibit other desired functions and applications in food packaging such as antimicrobial agent, biosensor, and oxygen scavengers. Bio-nanocompsite materials have been a promising alternative to be used for food packaging applications instead of the conventional plastics especially those made from petroleum. It offers possibilities to create eco-friendly and sustainable food packaging materials to replace those non-biodegradable materials. Although many important fundamental results concerning the effect of addition of nanofillers to the properties of bio-nanocomposite materials have been clarified by previous work, the effect of types of biopolymer and nanofiller on the properties of bio-nanocomposite materials have not been studied extensively. Further studies are crucial to investigate the maximum potential of bio-nanocomposite materials performance for food packaging applications.

Regardless the many benefits of bio-nanocomposite materials, the use of nanofillers to produce the materials need proper considerations in terms of safety for end use because there are limited studies done on the toxicological effects and migration of nanofillers into food from the packaging films.

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