Mohammad Jawaid
Sarat Kumar Swain *Editors*

Bionanocomposites for Packaging Applications

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Mohammad Jawaid · Sarat Kumar Swain
Editors

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Editors are honoured to dedicate this book to the

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

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

Preface

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

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

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

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

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

Serdang, Malaysia Mohammad Jawaid
Burla, India Sarat Kumar Swain

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Chapter 1
Perspectives of Bio-nanocomposites for Food Packaging Applications

Deniz Turan, Gurbuz Gunes and Ali Kilic

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

Keywords Biopolymers · Biodegradable · Bio-nanocomposites · Food packaging

1.1 Introduction

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

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

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

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

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

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

1.2 Biopolymers

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

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

1.2.1 Bio-nanocomposites

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

1.2.1.1 Natural Bioresources (Edible Packaging Materials)

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

Proteins

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

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

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

Carbohydrates

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

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

Lipids

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

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

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

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

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

1.2.1.2 Chemical Synthesis

Biomass

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

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

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

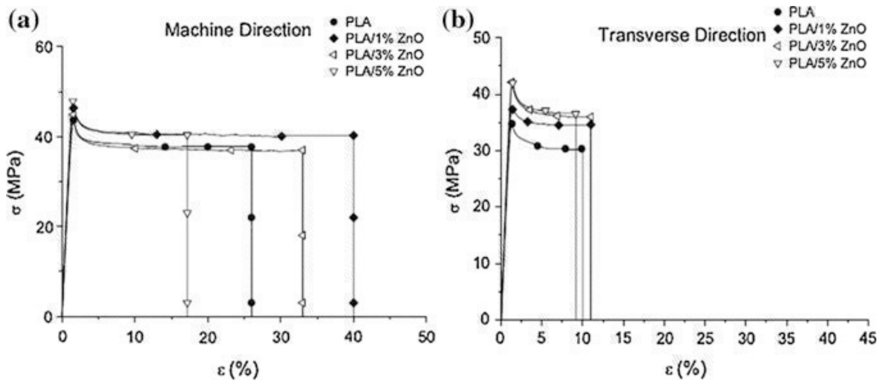

Fig. 1.1 Stress–strain curves of PLA and PLA/ZnO biocomposite films in machine direction (**a**) and in transverse direction (**b**) (Marra et al. 2016)

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

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

Petrochemicals

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

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

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

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

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

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

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