



# Bio-nanocomposites for food packaging applications



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## ABSTRACT

There is growing interest in developing bio-based polymers and innovative process technologies that can reduce the dependence on fossil fuel and move to a sustainable materials basis. Bio-nanocomposites open an opportunity for the use of new, high performance, light weight green nanocomposite materials making them to replace conventional non-biodegradable petroleum-based plastic packaging materials.

So far, the most studied bio-nanocomposites suitable for packaging applications are starch and cellulose derivatives, polylactic acid (PLA), polycaprolactone (PCL), poly-(butylene succinate) (PBS) and polyhydroxybutyrate (PHB). The most promising nanoscale fillers are layered silicate nanoclays such as montmorillonite and kaolinite. In food packaging, a major emphasis is on the development of high barrier properties against the diffusion of oxygen, carbon dioxide, flavor compounds, and water vapor.

Moreover, several nanostructures can be useful to provide active and/or smart properties to food packaging systems, as exemplified by antimicrobial properties, oxygen scavenging ability, enzyme immobilization, or indication of the degree of exposure to some detrimental factors such as inadequate temperatures or oxygen levels. Challenges remain in increasing the compatibility between clays and polymers and reaching complete dispersion of nanoparticles.

This review focuses on the enhancement of packaging performance of the green materials as well as their biodegradability, antimicrobial properties, and mechanical and thermal properties for food packaging application. The preparation, characterization and application of biopolymer-based nanocomposites with organic layered silicate and other fillers, and their application in the food packaging sector are also discussed.

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**Abbreviations:**  $\alpha$ , aspect ratio ( $L/D$ ) of a clay; AgNP, silver nanoparticle; AMP clay, aminopropyl functionalized magnesium phyllosilicate clay; BOD, biochemical oxygen demand; CA, cellulose acetate; CAB, cellulose acetate butyrate; CNF, cellulose nanofiber; CNT, carbon nanotube; CVD, chemical vapor deposition;  $D_0$ , zero concentration diffusion coefficient; E, exfoliated PCL nanocomposite; EDTA, ethylenediamine tetraacetic acid; EVOH, ethylene/vinyl alcohol copolymer; I, intercalated PCL nanocomposite;  $L/D$ , length/diameter; LDH, magnesium aluminium hydroxide; LDPE, low density polyethylene; M, PCL microcomposite; MMT, montmorillonite; Mw, molecular weight; ODA-M, octadecylamine-modified MMT; OMC, organically modified clay; OMMT, organically modified MMT; OPP, oriented polypropylene; OREC, organic rectorite modified by cetyltrimethylammonium bromide; PBAT, poly(butylenes adipate-co-butylene terephthalate); PBS, poly(butylene succinate);  $P_c$ , permeability of a nanocomposite; PCL, polycaprolactone or poly( $\epsilon$ -caprolactone); PET, poly(ethylene terephthalate); PGA, poly(glycolic acid); PHA, poly(hydroxyalkanoate); PHB, polyhydroxybutyrate, poly(3-hydroxybutyrate), or poly( $\beta$ -hydroxybutyrate); PHBV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PLA, polylactic acid or poly(L-lactide); PLSNM, PLA/layered silicate nanocomposite membrane;  $P_g$ , permeability of a neat polymer; PVA, poly(vinyl alcohol); REC, unmodified  $\text{Ca}^{2+}$ -rectorite; RFID, radio frequency identification; RH, relative humidity; RIT, relative inhibition time; ROS, reactive oxygen species;  $R_w$ , residual weight; S, sorption; SPI, soy protein isolate; TEC, triethyl citrate; TEM, transmission electron microscopy;  $T_g$ , glass transition temperature;  $T_m$ , melting temperature; TPIP, gutta percha; or 1, 4-trans-polyisoprene; TPS, thermoplastic starch; TTI, time temperature indicator; WPI, whey protein isolate; WVP, water vapor permeability; WVTR, water vapor transmission rate.

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## 1. Introduction

The main function of food packaging is to maintain the quality and safety of food products during storage and transportation, and to extend the shelf-life of food products by preventing unfavorable factors or conditions such as spoilage microorganisms, chemical contaminants, oxygen, moisture, light, external force, etc. In order to perform such functions, packaging materials provide physical protection and create proper physicochemical conditions for products that are essential for obtaining a satisfactory shelf life and maintaining food quality and safety. The food package should hinder gain or loss of moisture, prevent microbial contamination and act as a barrier against permeation of water vapor, oxygen, carbon dioxide and other volatile compounds such as flavors and taints in addition to the basic properties of packaging materials such as mechanical, optical, and thermal properties (Fig. 1) [1–7]. Food packaging is not only used as a container but also acts as a

protective barrier with some innovative functions. In that sense, food packaging is quite different from other durable goods such as electronics, home appliances, and furniture, etc. because of its safety aspects and relatively very short shelf life.

Basic packaging materials, such as paper and paper-board, plastic, glass, metal, and a combination of materials of various chemical natures and physical structures, are used to fulfill the functions and requirements of packaged foods depending on their type. However, there has been ever increasing effort in the development of different kinds of packaging materials in order to enhance their effectiveness in keeping the food quality with improved convenience for processing and final use.

Among the four basic packaging materials, petroleum-based plastic materials have been widely used since the middle of the twenties century. It is mainly because they are cheap and convenient to use with good processing property, good aesthetic quality, and excellent

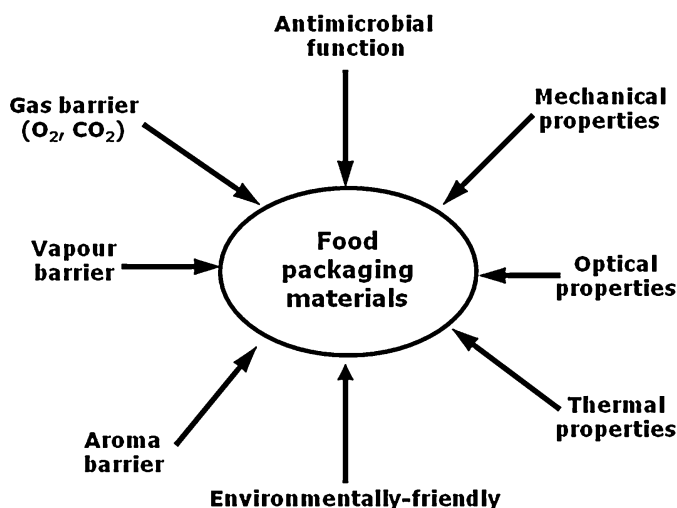


Fig. 1. General properties required for food packaging materials.

physico-chemical properties. More than 40% of the plastics are used for packaging and almost half of them are used for food packaging in the form of films, sheets, bottles, cups, tubs, and trays, etc. After their useful life, it is desirable for the packaging materials to biodegrade in a reasonable time period without causing environmental problems. Though the synthetic plastic packaging materials have been widely used for the packaging of various types of food, they caused a serious environmental problem since they are not easily degraded in the environment after use.

Recently, the environmental impact of persistent plastic packaging wastes is raising general global concern, since disposal methods are limited. Ever increasing concerns have been raised over environmental burdens and exhausting natural resources caused by non-biodegradable plastic packaging materials and over food safety caused on increased demand for biodegradable packaging materials from renewable sources (biopolymers) as an alternative to synthetic plastic packaging materials, especially for use in short-term packaging and disposable applications such as disposable cutlery, disposable plate, cups and utensils, diapers, trash bags, beverage containers, agricultural mulching films, fast food containers, medical devices, etc. [8–12].

The ideal biodegradable packaging materials are obtained from renewable biological resources, usually called biopolymers, with excellent mechanical and barrier properties and biodegradable at the end of their life. Biopolymers have been considered as a potential environmentally-friendly substitute for the use of non-biodegradable and non-renewable plastic packaging materials. Biopolymer packaging materials also may serve as gas and solute barriers and complement other types of packaging by improving the quality and extending the shelf-life of foods. Furthermore, biopolymer packaging materials are excellent vehicles for incorporating a wide variety of additives, such as antioxidants, antifungal agents, antimicrobials, colors, and other nutrients [13–15].

Several concerns must be addressed prior to commercial use of biobased primary packaging materials. These concerns include degradation rates under various conditions, changes in mechanical properties during storage, potential for microbial growth, and release of harmful compounds into packaged food products. In reality, relatively poor mechanical and high hydrophilic properties with poor processibility of those biopolymer-based packaging materials are causing a major limitation for their industrial use [16]. Protein and carbohydrate packaging films are generally good barriers against oxygen at low to intermediate relative humidity and have good mechanical properties; however, their barrier against water vapor is poor due to their hydrophilic nature. Though many research efforts focused on improving the film properties of biopolymer-based packaging films indicated a significant improvement in film properties, their physical, thermal, and mechanical properties are still not satisfactory and find difficulties in industrial applications.

Recently, a new class of materials represented by bio-nanocomposites with enhanced barrier, mechanical and thermal properties has been considered as a promising option in improving the properties of

these biopolymer-based packaging materials [9,12,17–22]. Bio-nanocomposites consist of a biopolymer matrix reinforced with particles (nanoparticles) having at least one dimension in the nanometer range (1–100 nm). Bio-nanocomposites are a new class of materials exhibiting much improved properties as compared to the base biopolymers due to the high aspect ratio and high surface area of nanoparticles. Therefore, efforts have been devoted to develop bio-nanocomposites for food packaging films with improved mechanical, barrier, rheological, and thermal properties [19,23,24].

This review contains an overview of the state-of-the-art of a new class of materials comprised of biopolymer-based nanocomposites with the potential for use in the food packaging sector focused on the aspects of nanotechnology that are related to the extension of shelf life of packaged food with maintaining food safety and quality, and the development of active and smart/intelligent food packaging materials using bio-nanocomposite materials.

## 2. Bio-nanocomposites

### 2.1. Biopolymers

Biopolymer or biodegradable plastics are polymeric materials in which at least one step in the degradation process is through metabolism of naturally occurring organisms [9,25]. Under appropriate conditions of moisture, temperature, and oxygen availability, biodegradation leads to fragmentation or disintegration of the plastics with no toxic or environmentally harmful residue [26].

Biopolymers can be broadly divided into different categories based on the origin of the raw materials and their manufacturing processes as shown in Fig. 2. They include (i) natural biopolymers such as plant carbohydrate like starch, cellulose, chitosan, alginate, agar, carrageenan, etc., and animal or plant origin proteins like soy protein, corn zein, wheat gluten, gelatin, collagen, whey protein, casein, etc.; (ii) synthetic biodegradable polymers such as poly(L-lactide) (PLA), poly(glycolic acid) (PGA), poly( $\epsilon$ -caprolactone) (PCL), poly(butylene succinate) (PBS), poly(vinyl alcohol) (PVA), etc.; (iii) biopolymers produced by microbial fermentation like microbial polyesters, such as poly(hydroxyalkanoates) (PHAs) including poly( $\beta$ -hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), etc., and microbial polysaccharides, such as pullulan and curdlan [12,15].

However, biopolymers present relatively poor mechanical and barrier properties, which currently limit their industrial use. The problems associated with biopolymers are 3-fold: performance, processing, and cost. Although these factors are somewhat interrelated, problems due to “performance and processing” are common to all biodegradable polymers in spite of their origin [17,27,28]. In particular, brittleness, low heat distortion temperature, high gas and vapor permeability, poor resistance to protracted processing operations have strongly limited their applications [29–33].

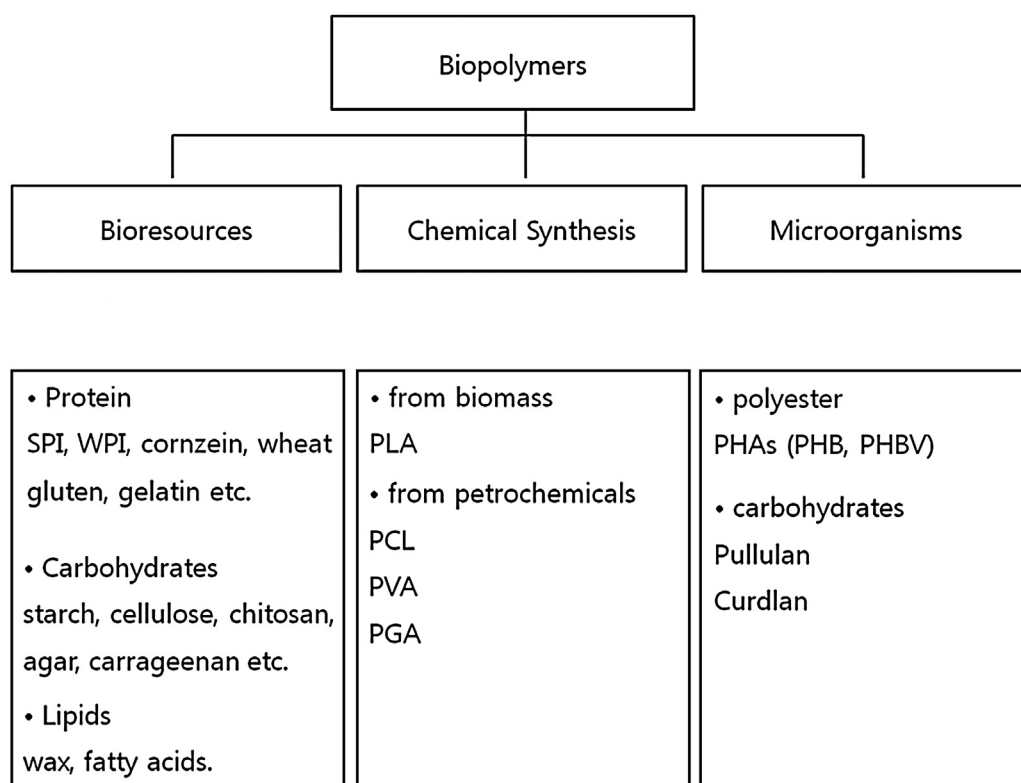


Fig. 2. Classification of biopolymers. The abbreviations of materials mentioned here are listed in the list of abbreviations.

## 2.2. Biopolymer-based nanocomposites

It has been suggested that inherent shortcomings of biopolymer-based packaging materials may be overcome by nanocomposite technology [24]. Nanocomposites exhibit increased barrier properties, increased mechanical strength, and improved heat resistance compared to their neat polymers and conventional composites [9,34–36]. A classical example is the use of nanosized montmorillonite clay to improve mechanical and thermal properties of nylon [37]. When used in food packaging, nanocomposites are expected to withstand the stress of thermal food processing, transportation, and storage [34,38]. Also, because of their improved mechanical properties, nanocomposites may allow down gauging, thus reducing source materials.

Clay nanocomposites gave rise to a remarkable interest since 1950s, when they appeared for the first time [39]. Since the pioneering work by Toyota's research team [40], who prepared polyamide 6/montmorillonite (MMT) nanocomposites by *in situ* polymerization of  $\epsilon$ -caprolactam, extensive research works from both academic and industrial groups have been followed [40–43]. As the material performance turned out to depend on the degree of clay delamination, several strategies have been considered to prepare polymer layered silicate nanocomposites characterized by extensive dispersion of the filler in the polymer matrix [44,45].

Nanoclay relies on the high surface area of clay platelets, in excess of 750 m<sup>2</sup>/g, and high aspect ratio (100–500).

However, montmorillonite clays come in platelet clusters with little surface exposed. Thus, processing at high shear or sonication techniques are necessary to prevent aggregation and exfoliate the clusters and increase the surface area exposed to the polymer [46]. There are 3 types of possible polymer–clay formations, namely (1) tactoid, (2) intercalated, and (3) exfoliated [34,47].

Tactoid structures remain in a polymer when the interlayer space of the clay gallery does not expand, usually due to its poor affinity with the polymer. No true nanocomposites are formed in this way [48]. Intercalated structures are obtained at moderate expansion of the clay interlayer. In this case, interlayer spaces expand slightly as polymer chains penetrate the basal spacing of clay, but the shape of the layered stack remains. This is the result of moderate affinity between polymer and clay. In the case of exfoliated structures, clay clusters lose their layered identity and are well separated into single sheets within the continuous polymer phase. This is due to a high affinity between polymer and clay. It is essential that the clay should be exfoliated into single platelet and distributed homogeneously throughout the polymer matrix to take full advantage of nanoclays high surface area [34,49,50].

Recently, several research groups started the preparation and characterization of various kind of biodegradable polymer nanocomposites i.e., bio-nanocomposites, showing properties suitable for a wide range of applications [18]. Biodegradable natural and synthetic polymers have been filled with layered silicate in order to enhance their desirable properties while retaining their biodegradability

**Table 1**

Typical biodegradable polymers and inorganic or antimicrobial materials investigated for the preparation of bio-nanocomposites.

| Biodegradable polymers  | Antimicrobial materials   |
|---|---|
| Starch or thermoplastic starch (TPS)  | Clay (e.g. Montmorillonite (MMT))   |
| Chemically modified cellulose (e.g., cellulose acetate (CA) and cellulose acetate butyrate (CAB)) | Organically modified nanoclay (quaternary ammonium modified MMT, Ag-zeolite)                                |
| Poly(lactic acid) (PLA)   | Metal ions (e.g. silver, copper, gold, platinum)  |
| Polycaprolactone (PCL)  | Metal oxide (e.g. TiO <sub>2</sub> , ZnO, MgO)  |
| Poly(hydroxyalkanoate) (PHA)  | Natural biopolymers (e.g. chitosan)   |
| Poly(hydroxybutyrate) (PHB)   | Natural antimicrobial agents (e.g. nisin, thymol, carvacrol, isothiocyanate, antibiotics)                   |
|   | Enzymes (peroxidase, lysozyme)  |
| Poly(butylene succinate) (PBS)  | Synthetic antimicrobial agents (quaternary ammonium salts, EDTA, propionic acid, benzoic acid, sorbic acid) |

in a comparatively economic way. In particular, they show great promise in providing excellent barrier properties, due to the presence of the clay layers able to delay the molecule pathway making the diffusive path more tortuous. The extraordinary success of the nanocomposite concept in the area of synthetic polymers has stimulated new research on nanocomposites based on biodegradable polymers as matrix. Table 1 lists typical biodegradable polymers and inorganic or antimicrobial materials investigated for the preparation of bio-nanocomposites.

### 3. Mechanical and barrier properties

Formation of nanocomposite with organoclays has shown pronounced improvement in the mechanical properties of various bio-polymers substantially even with a low level of filler loading (<5 wt%). For instance, Lee et al. [51] reported a pioneering work on the biodegradable polymer/MMT nanocomposites in 2002, where PBS and Cloisite 30B were used as a biodegradable polymer matrix and MMT, respectively, where Cloisite 30B is one of commercially available organically modified clays. The tensile properties of PBS/Cloisite 30B nanocomposites with various contents of the nanoclays are shown in Table 2.

It has been frequently observed that mechanical properties of polymer/clay nanocomposites are strongly dependent on filler content. Herein we can take some examples reported in recent seven years. Huang and Yu [52] determined tensile properties of starch/MMT nanocomposites prepared with various filler concentrations of 0–11 wt% to the starch. Tensile strength and Young's modulus increased monotonously with increase in filler content up to 8%, then leveled off, while tensile strain decreased with increase in filler loading except for 8% loading. Huang

et al. [53] reported an increase in tensile strength and strain of corn starch/MMT nanocomposites by 450% and 20%, respectively, on addition of 5% clay. Chen and Zhang [54] also reported the tensile strength of soy protein/MMT nanocomposite sheets increased from 8.77 to 15.43 MPa as the MMT content increased up to 16%, while percent elongation at break of the bio-nanocomposite sheets decreased with increasing MMT content. Similar results on the tensile testing of bio-nanocomposites based on other biopolymer have been reported [55–62].

The enhancement in mechanical properties of polymer nanocomposites can be attributed to the high rigidity and aspect ratio of nanoclay together with the good affinity through interfacial interaction between polymer matrix and dispersed nanoclay.

Polymer nanocomposites have excellent barrier properties against gases (e.g., O<sub>2</sub> and CO<sub>2</sub>) and water vapor. Studies have shown that such reduction in gas permeability of nanocomposites strongly depends on the type of clay (i.e., compatibility between clay and polymer matrix), aspect ratio of clay platelets, and structure of the nanocomposites. In general, the best gas barrier properties would be obtained in polymer nanocomposites with fully exfoliated clay minerals with large aspect ratio [63].

Yano et al. [64] prepared polyimide/clay nanocomposite films with four different sizes of clay minerals such as hectorite, saponite, MMT, and synthetic mica in order to investigate the effect of the aspect ratio on the barrier properties of the hybrids. They found that, at constant clay content (2 wt%), the relative permeability coefficient decreased with increasing the length of the clay. Rhim et al. [61,62] reported that the water vapor transmission rate (WVTR) of agar/unmodified MMT (Cloisite Na<sup>+</sup>) nanocomposite films was significantly lower than those of agar/organically modified MMT (Cloisite 30B, 20A)

**Table 2**

Tensile properties of PBS/Cloisite 30B hybrid nanocomposites [51].

| Content of Cloisite 30B (Wt%) | Tensile strength (Kgf/cm <sup>2</sup> ) | Elongation at break (%) | Tensile modulus (Kgf/cm <sup>2</sup> ) |
|-------------------------------|---|-------------------------|--|
| 0                             | 131.7                                   | 12.45                   | 106.7                                  |
| 1                             | 139.0                                   | 12.25                   | 112.3                                  |
| 3                             | 144.1                                   | 11.95                   | 114.4                                  |
| 5                             | 149.8                                   | 11.40                   | 118.2                                  |
| 10                            | 157.7                                   | 10.90                   | 129.5                                  |
| 20                            | 190.8                                   | 11.30                   | 144.4                                  |
| 30                            | 213.5                                   | 12.25                   | 173.8                                  |

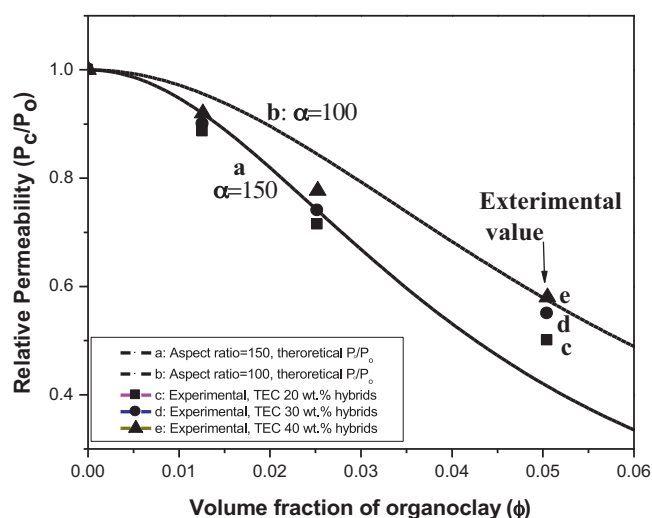
nanocomposite films. On the contrary, Cloisite 30B was more effective in reducing the WVP of chitosan-based nanocomposite film [65] and PLA-based nanocomposite films [66] compared to Cloisite Na<sup>+</sup>. Rhim [61] also showed that the water vapor permeability (WVP) of agar/clay (Cloisite Na<sup>+</sup>) nanocomposite films decreased exponentially with increase in clay content from 0 to 20 wt%. Similar results on the WVP of bio-nanocomposite films based on other biopolymers such as starch [67], whey protein isolate [68,69], soy protein isolate [70,71] wheat gluten [72] and PCL [18] have been reported.

Park et al. [73] tested the WVTR of the thermoplastic starch (TPS)/clay nanocomposite films using the relative WVTR (WVTR of hybrid/WVTR of base polymer;  $P_c/P_o$ ) versus the contents of Cloisite Na<sup>+</sup> or Cloisite 30B in the TPS matrix. For the TPS hybrid nanocomposite films the WVTR decreased remarkably when small amounts of clays of both Cloisite Na<sup>+</sup> and Cloisite 30B were added. It means that the layered structure of clay blocks the transmission of moisture vapor through the film matrix. Note that the relative WVTR of the TPS nanocomposites decreased down to about half of the pristine TPS when only 5 wt% of silicate was added. The dramatic decrease in the WVTR of the nanocomposites is due to the presence of dispersed silicate layers with large aspect ratio in the polymer matrix as seen in other polymer-layered silicate composites [74–76]. The observed dramatic decrease in WVTR is of great importance in evaluating TPS composites for use in food packaging, protective coatings, and other applications where efficient polymeric barriers are needed. Reduced WVTR in biodegradable polymer composite films may have the added benefit for modifying degradation rates, because hydrolysis of the matrix polymer is likely to depend on the transport of water from the surface into the bulk of the material [77].

Park et al. [78] prepared TPS/PBS/clay ternary nanocomposites by melt intercalation method. The WVTR of the TPS/PBS/clay ternary nanocomposite films decreased with increase in PBS contents, though the WVTR of TPS films were much higher than PBS films [51,78]. The permeability of PBS/TPS/Cloisite 30B nanocomposite with only 15 wt% PBS decreased significantly compared with TPS/Cloisite 30B hybrid.

The relative water vapor permeability (WVP) of cellulose acetate (CA)/clay nanocomposites with different triethyl citrate (TEC) plasticizer and organoclay content was examined by Park et al. [79] in a controlled temperature and relative humidity chamber (i.e. 37.8°C, 100% and 0% RH) and the results are shown in Fig. 3 in terms of  $P_c/P_o$ , i.e., the permeability of the nanocomposite ( $P_c$ ) relative to that of the neat plasticized CA matrix ( $P_o$ ). Reduction in the WVP of the nanocomposite films as much as 2-fold compared with the control film was observed at high organoclay content (Fig. 3c–e).

When starch was filled with cellulose whiskers a decrease in water sensitivity and increase in thermo-mechanical properties was observed [80]. The addition of cellulose nanofibers (CNF) was also effective to improve water vapor barrier of the films, in which the WVP decreased from 2.66 to 1.67 g mm/kPa h m<sup>2</sup>. The water vapor permeability was significantly decreased when CNF was incorporated at least 10 wt%. Koh et al. [32] prepared PLA (L/D ratio 98:2 from Cargill Dow Co.)/layered silicate nanocomposite membrane (PLSNM). The authors reported that gas permeabilities of PLSNMs decreased with the increase of organoclay content (Fig. 4). When compared to gas permeabilities of PLSNMs with different types of organoclay, the barrier feature of PLSNMs with Cloisite 30B was extremely outstanding compared with other types of nanoclay [32]. It was expected that the gas permeabilities of



**Fig. 3.** Water vapor relative permeability curve of the CA/TEC hybrid nanocomposites with different TEC plasticizer and organoclay contents: (a)  $\alpha$  (aspect ratio) 150, theoretical relative permeability, (b)  $\alpha$  (aspect ratio) 100, theoretical relative permeability, (c) CA/TEC (80/20 wt%), (d) CA/TEC (70/30 wt%); (c, d, and e) experimental relative permeability value of nanocomposites; clay contents 0–10 wt% [79]. Copyright 2004. Reproduced by permission of American Chemical Society.



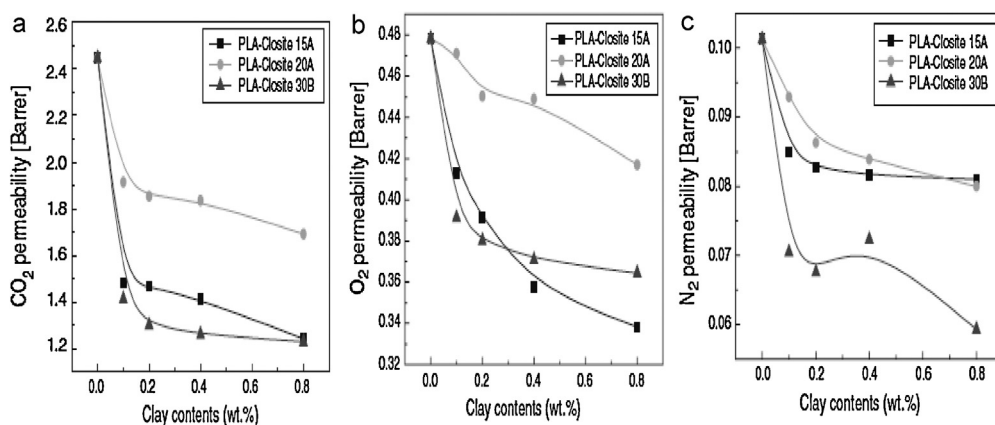


Fig. 4. Gas permeabilities of PLSNMs: (a) CO<sub>2</sub> permeability; (b) O<sub>2</sub> permeability; (c) N<sub>2</sub> permeability [32].

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PLSNMs decreased compared to the neat PLA membranes. The similar barrier feature was observed through the comparison of gas permeabilities in PLSNMs for O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>. The organoclay was found to behave as the barrier against gas molecules to pass through polymer matrix [75].

PLA had been filled with many organic clays such as hexadecyl amine-MMT (C16-MMT), dodecyltrimethyl ammonium bromide-MMT (DTA-MMT), Cloisite 25A [81]. The O<sub>2</sub> permeability values for all the hybrids for clay loadings up to 10 wt% were less than half of the corresponding values of pure PLA, regardless of the type of organoclay [19]. Nanocomposites of amorphous PLA and chemically modified kaolinite were studied by Cabedo et al. [16]. They observed good interaction between polymer and clay, which led to an increase in oxygen barrier properties of about 50%.

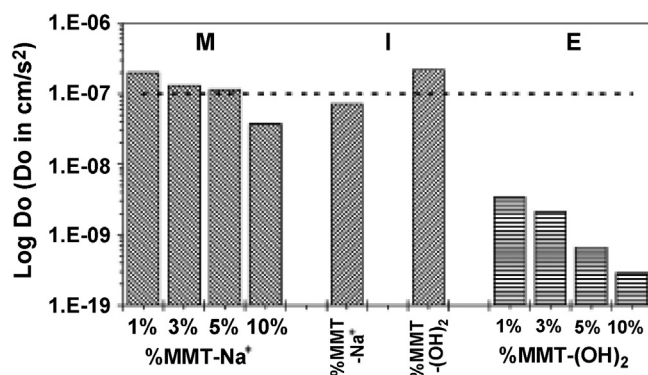
Correlation between morphology and vapor barrier properties of PCL/MMT composites has been studied by Gorrasi et al. [82]. They prepared different compositions of PCL/organically modified clay (OMC) nanocomposites by melt blending or catalyzed ring-opening polymerization of caprolactone. Micro-composites were obtained by direct melt blending of PCL and pristine MMT. Exfoliated nanocomposites were obtained by in situ ring-opening polymerization of CL with an OMC by using dibutyltin dimethoxide as an initiator/catalyst. Intercalated nanocomposites were formed either by melt blending with OMC or in situ polymerization within pristine MMT. The barrier properties were studied for water vapor and dichloromethane as an organic solvent. The sorption (*S*) and the zero concentration diffusion coefficients (*D*<sub>0</sub>) were evaluated for both vapors [45]. The water sorption increased with increase in the MMT content, particularly for the micro-composites containing the unmodified MMT. The thermodynamic diffusion parameters, *D*<sub>0</sub>, were compared to the value of the parent PCL and found that both micro-composites and intercalated nanocomposites showed diffusion parameters very close to PCL. On the contrary, exfoliated nanocomposites showed much lower values, even for small MMT content. In the case of organic vapor, the value of sorption at low relative pressure is

mainly dominated by the amorphous fraction present in the samples, not showing any preferential adsorption on the inorganic component. At high relative pressure the isotherms showed an exponential increase of sorption, due to plasticization the polyester matrix. The *D*<sub>0</sub> parameters were also compared to those of the unfilled PCL; in this case, both exfoliated and intercalated samples showed lower values, due to a more tortuous path for the penetrating molecules (see Fig. 5) [45,83].

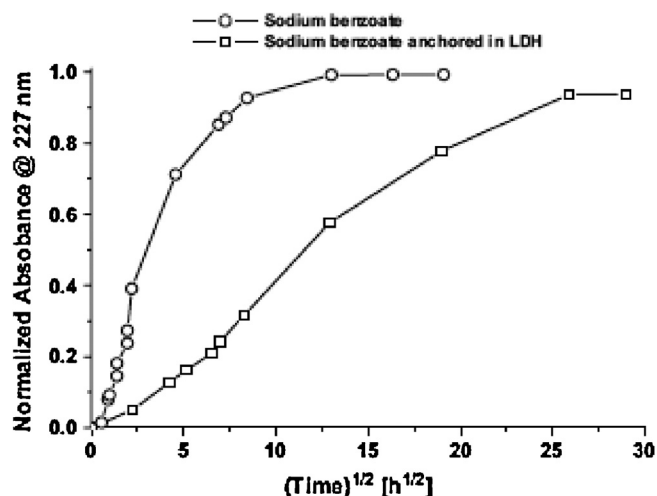
The increase in gas barrier properties of nanocomposite films is believed to be due to the presence of ordered dispersed silicate layers with large aspect ratios in the polymer matrix which are impermeable to water molecules [63,84]. This forces gas travel through the film to follow a tortuous path through the polymer matrix surrounding the silicate particles, thereby increasing the effective path length for diffusion [76]. The enhanced gas barrier properties of nanocomposites make them attractive and useful in food packaging applications.

An innovative procedure was proposed by Sorrentino et al. [85]. In particular, they anchored an antimicrobial molecule, benzoic acid, on an Mg/Al layered double hydroxide, through ionic bonds, followed by incorporation into a PCL matrix. Fig. 6 shows the release kinetics of the sodium benzoate directly incorporated into the PCL by solvent casting method, and the release of the benzoate ionically bonded to magnesium aluminium hydroxide (LDH) and blended with the PCL [45]. In recent years, layered materials have also received considerable attention as drug delivery vehicle [86].

Another systematic study on PCL nanocomposites was performed on the influence of different percentages of MMT, degree of MMT intercalation, and different organic modifiers of MMT on the diffusion coefficient of dichloromethane [86]. For the organic solvent (dichloromethane) diffusion, the intercalated samples showed lower values of the diffusion parameters. This result confirms that it is not only the content of clay but also the type and size of dispersion of the inorganic component in the polymer phase that is important for improving the barrier properties of the samples.



**Fig. 5.** Diffusivity of water vapor, as function of clay content, for the PCL micro-composite (M), the PCL exfoliated nanocomposites (E) and the 3 wt% PCL intercalated nanocomposites (I) [9]. Copyright 2007. Reproduced by permission of Elsevier Science Ltd.



**Fig. 6.** Diffusion profiles for Benzoate into water [9].

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Particularly interesting are the results on the degree of MMT dispersion in the polymeric matrix. For the diffusion of dichloromethane in the PCL composite samples with 3 wt% of MMT, it was shown that the diffusion parameter decreased from micro-composites (values very similar to the pure PCL) to exfoliated nanocomposites, and intermediate values of diffusion were observed in the intercalated nanocomposites (see Fig. 7). In the case of water vapor, both micro-composites and intercalated nanocomposites showed diffusion parameters very close to the PCL. On the contrary, the exfoliated nanocomposites showed much lower values, even for small montmorillonite content [87].

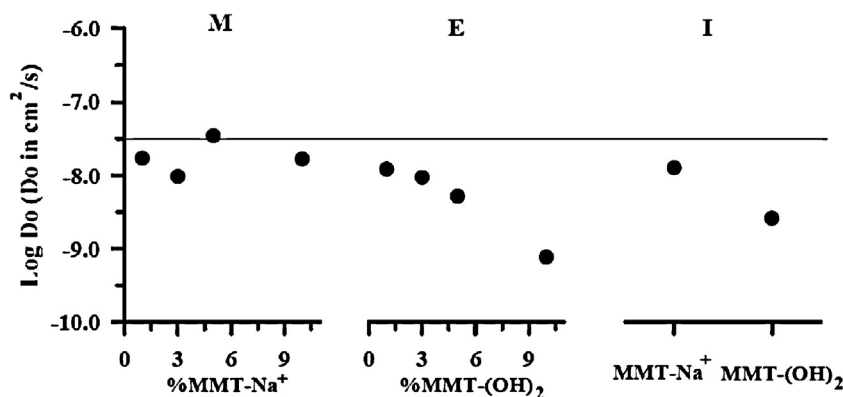
PCL chains grafted onto montmorillonite modified by a mixture of non-functional ammonium salts and ammonium-bearing hydroxyl groups were studied in order to understand the influence of different polymer chain-grafting density on the diffusion coefficient [50]. The clay content was fixed to 3 wt% with varying the hydroxyl functionality of 25%, 50%, 75%, and 100%, resulting in intercalated or exfoliated systems [83].

#### 4. Biodegradation

Biodegradability of bio-nanocomposites is one of the most interesting and controversial issues in the bio-nanocomposite materials. For biodegradable polymers, biodegradation may mean fragmentation, loss of mechanical properties, or sometimes degradation through the action of microorganisms such as bacteria, fungi, and algae. The biodegradation of polymers is a complex process, which can proceed via hydrolysis catalyzed by enzymes and oxidation [88].

Since one of the main reasons for using biopolymers for the preparation of bio-nanocomposite materials is to utilize the biodegradability of the biopolymer matrix, it is expected that the biodegradability of the resulting nanocomposites should not be sacrificed after the formation of nanocomposites. Tetto et al. [89] first tested the biodegradability of nanocomposites based on PCL and reported that the PCL/clay nanocomposites showed improved biodegradability compared to pure PCL. They explained that such an improved biodegradability of PCL in





**Fig. 7.** Log  $D_0$  ( $D_0$  in  $\text{cm}^2/\text{s}$ ) to dichloromethane vapor, as function of clay content for the microcomposite (M), the exfoliated nanocomposites (E) and the 3 wt% intercalated nanocomposites (I) [87]. Copyright 2003. Reproduced by permission of Elsevier Science Ltd.

clay-based nanocomposites may be attributed to catalytic role of the organoclay during the biodegradation process.

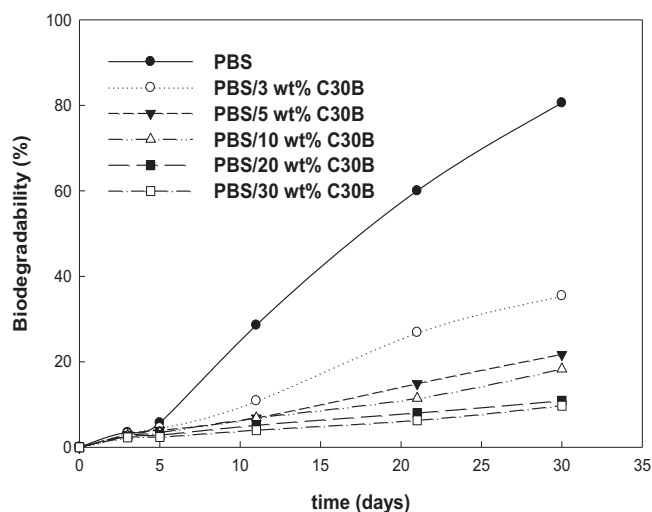
Among the biopolymer-based nanocomposite materials, PLA-based nanocomposites have been deserved a particular attention for the study of its biodegradation in the environment [88,90–93]. Sinha Ray et al. [92–94] performed a series of biodegradation tests with PLA nanocomposite made from PLA and organoclay. First, they compared biodegradability of both PLA and PLA nanocomposite films using soil compost test at 58 °C with both PLA and PLA/organoclay nanocomposite films prepared by melt blending and presented photographs of the recovered film samples with composting time. They found no clear difference in biodegradability between neat PLA and PLA nanocomposite until a month of composting, but distinguishably higher disintegration of the PLA nanocomposite was observed within two months, which was completely degraded by compost. They also measured molecular weight ( $M_w$ ) and residual weight ( $R_w$ ) of both PLA and PLA nanocomposite films with time and observed that both the extent of  $M_w$  and  $R_w$  losses are almost the same for the PLA and PLA composite films for a month. After one month, a sharp decrease in the residual weight loss occurred in the PLA nanocomposite films, which was consistent with the photographically observed result. Later, they confirmed the biodegradability of PLA nanocomposite films using a respirometric test by measuring  $\text{CO}_2$  evolution during biodegradation [93].

Through the series of biodegradation tests they reached to the conclusion that the biodegradability of PLA nanocomposite was significantly enhanced compared to neat PLA. The degradation of polyester materials like PLA is reported to occur by uptake of water followed by hydrolysis of ester bond, fragmentation into oligomer, solubilization of oligomer fragments, diffusion of soluble oligomers, and final mineralization into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [95]. Therefore, any factor that increases the hydrolysis tendency of the PLA polymer matrix would increase degradation of the polymer. Though the hydrolysis tendency of PLA and PLA nanocomposites was almost the same, the degradation of the PLA nanocomposites was greatly enhanced compared to the neat PLA after a month of compost. Sinha Ray et al.

[93] assumed that the enhanced biodegradability of PLA nanocomposite films is attributed to the presence of terminal hydroxylated edge groups in the clay layers. They also confirmed this assumption by conducting the same type of test with PLA nanocomposites prepared by using synthetic mica modified by dimethyl dioctadecylammonium salt which has no terminal hydroxylated edge group, and showed that the degradation tendency was almost the same as that of neat PLA.

Nieddu et al. [96] also reported similar results of enhanced biodegradation of PLA-based nanocomposites prepared with five different types of nanoclays and different level of clay content using a melt intercalation method. They measured the degree of biodegradation of PLA nanocomposite films by measuring both the amount of lactic acid released and weight change of the sample materials during hydrolytic degradation in plasma incubated at 37 °C. They found degradation rate of nanocomposite was more than 10 times (when measured the lactic acid release) or 22 times (when measured weight change) higher than that of neat PLA. The degradation rate was dependent on the clay types and their concentration, i.e., the degree of degradation was higher in the better intercalated nanocomposite which was dependent on the type of clays. They showed fluorohectorite with a dihydroxy organic modifier was more compatible with PLA than MMT clays to develop better intercalated structure with more enhanced biodegradation.

During the hydrolytic degradation of PLA and PLA nanocomposites, the formation of lactic acid oligomers obtained from the chain scission of PLA increases carboxylic acid end groups concentration and these carboxylic groups are known to catalyze the degradation reaction. Since the hydrolytic degradation of PLA is a self-catalyzed and self-maintaining process, the hydrolysis of PLA can be affected by not only such structural factors as stereostructure, molar mass and their distribution, crystallinity, and purity, but also type of fillers. Paul et al. [88] tested the effect of clay type on the hydrolytic degradation using phosphate buffer solution of PLA and PLA/organoclay nanocomposite films prepared by melt blending method using three different types of organoclays, i.e., Cloisite Na<sup>+</sup>, Cloisite 30B, and



**Fig. 8.** Effect of organoclay (Cloisite 30B) content on biodegradability of polybutylene succinate (PBS) and its clay nanocomposites [51]. Copyright 2002. Reproduced by permission of Elsevier Science Ltd.

Cloisite 25A. They found that the biodegradability of PLA nanocomposites was enhanced compared to the neat PLA and also found that among the nanoclays tested, the more hydrophilic the filler, the more pronounced the degradation. Fukushima et al. [91] also observed the enhanced biodegradability of PLA-based nanocomposite and concluded that the higher rates of PLA biodegradation in compost by the addition of nanoclays was attributed to the high relative hydrophilicity of the clays, allowing an easier permeability of water into polymer matrix and activating the hydrolytic degradation process.

Similar results were observed with other bio-nanocomposite films including PHB [97], soy protein-based nanocomposite [98], nano-silica/starch/polyvinyl alcohol films [99].

However, contradictory results on biodegradability of bio-nanocomposite are also found in the literature. Lee et al. [51] prepared melt intercalated aliphatic polyester, polybutylene succinate (PBS)/organoclay (Cloisite 30B) nanocomposites films with different content of nanoclay and performed soil compost test. They found rate of biodegradability of the nanocomposite decreased compared to the pristine polymer (PBS) and the more loading of nanoclay incorporated, the lower the biodegradability of the nanocomposite was observed (Fig. 8). They attributed such seemingly contradictory result to the improved barrier properties of the nanocomposites developed by the intercalated clays with high aspect ratio, which hinder microorganism to diffuse in the bulk of the film through more tortuous paths.

Similarly, Maiti et al. [100] and Wu and Wu [101] also reported on the decrease in biodegradation tendency with PHB nanocomposite and PLA/chitosan-organically modified MMT nanocomposite films, respectively. The results of Lee et al. [51], Maiti et al. [100], and Wu and Wu [101] are not agreed with those of Sinha Ray et al. [102,103], who found no relation between biodegradability and barrier properties in PLA nanocomposite films.

Rhim et al. [65] provided the clue to explain the reason for the reduced biodegradability of nanocomposites of PBS [51] and PHB [100]. During the antimicrobial test of chitosan-based nanocomposite films, Rhim et al. [65] found that a nanocomposite film prepared with an organoclay (Cloisite 30B) has a strong antimicrobial activity against food poisoning bacteria, especially against Gram-positive bacteria, and suggested the antimicrobial action was attributable to the quaternary ammonium group in the modified organoclay. Later, Hong and Rhim [104] proved that the same organoclay (Cloisite 30B) has a strong bactericidal activity against Gram-positive bacteria and bacteriostatic activity against Gram-negative bacteria, which was caused by the quaternary ammonium group in the organoclay. They concluded that the retarded biodegradability of PBS/Cloisite 30B nanocomposite observed by Lee et al. [51] was attributed to the antimicrobial action of the organoclay modified with the quaternary ammonium group. This has been also observed by Someya et al. [105] who tested the effect of biodegradability of poly(butylene adipate-co-butylene terephthalate) (PBAT)-based nanocomposites prepared by melt blending with two different types of layered silicates, i.e., non-modified MMT and octadecylamine-modified MMT (ODA-M). The biodegradability test in the aqueous medium, by determining biochemical oxygen demand (BOD), showed that the addition of MMT to PBAT promoted biodegradation, whereas the addition of ODA-M did not. Biodegradation of the bio-nanocomposites seems to be controlled both by the nature of the layered silicates and by the presence of certain surface modifying chemicals, such as quaternary ammonium cations. The quaternary ammonium compounds, surfactants commonly used as organic modifiers in commercial nanoclays, are suggested to influence the stability of biopolymer films. Results of Hablot et al. [106] suggested that the quaternary ammonium compounds can have a catalytic effect on the thermal degradation of PHB, as reflected by a dramatic decrease in PHB molecular weight.

These results indicate that by a judicious choice of the organoclay fillers, it is possible to tune the biodegradable properties of the bio-nanocomposite materials. However, the thermal stability of the organic part, such as quaternary ammonium salts which is used up to 40% for surface modification of nanoclay, of the organoclay needs to be considered before drawing conclusion. At temperatures of commercial scale processing using extrusion or injection molding required for most polymers, the thermal stability of the ammonium salts is very limited as most of the structures tend to Hofmann elimination resulting in volatile olefins and amines [107]. The thermal degradation of ammonium salts starts as low as 180 °C and is furthermore reduced by catalytically active sites on the aluminosilicate layer [108].

Though the possible enhancement and controlled biodegradation of bio-nanocomposites are yet to be studied [102,109,110], the biodegradability property of bio-nanocomposites can be properly used for the development of biodegradable nanocomposite packaging materials with controlled biodegradation function. However, the proper stability and durability of the bio-nanocomposite packaging materials should be maintained during their useful shelf-life to perform their packaging functions. It is of interest to recognize that the nanoparticles have two opposite effects on polymer nanocomposites, i.e., degradation and stabilization depending on processing and environmental conditions [110]. Hybrid bio-nanocomposites, such as layered silicates embedded in a polymeric matrix, improve stability and their biodegradability can be fine tuned by varying the amount of solvents used or by the incorporation of different types of organocays modified surface with different types of surfactants. Such innovative properties of nanoparticles can be exploited in the packaging industry depending on the final use.

## 5. Antimicrobial properties of bio-nanocomposites

Antimicrobial function of some nanoparticles or nanocomposite materials has long been recognized and exploited in the field of various industries including packaging sector [104,111–119] for their antimicrobial activity as growth inhibitors [115], antimicrobial agents [104], antimicrobial carriers [116] or antimicrobial packaging films [65,117].

Nanocomposite antimicrobial systems are particularly effective, because of the high surface-to-volume ratio and enhanced surface reactivity of the nano-sized antimicrobial agents, making them able to inactivate microorganisms more effectively than their micro- or macro-scale counterparts [118]. Commonly used or tested antimicrobial materials to prepare nanocomposite materials with antimicrobial function include metal ions (silver, copper, gold, platinum), metal oxide (TiO<sub>2</sub>, ZnO, MgO), organically modified nanoclay (quaternary ammonium modified MMT, Ag-zeolite), natural biopolymers (chitosan), natural antimicrobial agents (nisin, thymol, carvacrol, isothiocyanate, antibiotics), enzymes (peroxidase, lysozyme), and synthetic antimicrobial agents (quaternary ammonium salts, EDTA, propionic, benzoic, sorbic acids). Combinations

of more than one antimicrobials incorporated into packaging materials have also been investigated.

### 5.1. Metal and metal oxides

Among the numerous nanoparticles used for functionalizing polymeric materials, silver nanoparticles have been one of the most widely used for the development of innovative packaging materials. This is mainly due to their unique properties such as electric, optical, catalytic, thermal stability, and particularly antimicrobial properties [119,120]. In particular, the benefits of silver materials have been recognized in the many applications including packaging due to the strong antimicrobial activity of silver against a broad spectrum of bacteria, viruses, and fungi [121].

The antimicrobial function of silver is mainly attributed to the action of silver ions and metallic silver nanoparticles. It has been proposed that silver ions interact with negatively charged biomacromolecular components (disulfide or sulfhydryl groups of enzymes) and nucleic acids, causing structural changes and deformation in bacterial cell walls and membranes that lead to disruption of metabolic processes followed by cell death [122,123]. The antimicrobial action of silver nanoparticles is due to the increase surface area and associated increased potential for the release of Ag<sup>+</sup>. The antimicrobial mechanism of silver nanoparticles has also been suggested to be related to membrane damage due to free radicals derived from the surface of the nanoparticles [124]. Silver nanoparticles may accumulate in the bacterial cytoplasmic membrane, causing a significant increase in permeability and cell death [125].

One of the most commonly used type of antimicrobial function of silver nanoparticles is composed of silver ions integrated into inert materials such as zeolite [126], silicate [127], and nanoclay [128]. Silver zeolite (Ag-zeolite), which is produced by substituting the Na<sup>+</sup> ion in the mineral zeolite with Ag<sup>+</sup> ion, is one of the most widely used antimicrobial agents since it has a broad antimicrobial spectrum of microorganisms such as bacteria, yeast, and mycelium fungi. However, Ag-zeolite does not have any antimicrobial activity against spores of heat-resistant bacteria, but rather only against vegetative cells [126]. Ag-zeolite incorporated chitosan film showed strong antimicrobial activity against both Gram-positive and Gram-negative bacteria [65]. Silver-silicate nanocomposite was produced using a flame spray pyrolysis process and incorporated into polystyrene, which showed significant antibacterial activity against both *Escherichia coli* and *Staphylococcus aureus* [127]. Silver-montmorillonite (Ag-MMT) nanoparticles obtained by exchanging the Na<sup>+</sup> of natural MMT with silver ions from silver nitrate solution exhibited profound antimicrobial activity against *Pseudomonas* spp. when they were embedded in agar film [129].

A green synthetic approach for preparing antimicrobial silver nanoparticles have been suggested by using carbohydrates such as sucrose, soluble and waxy corn starch. The carbohydrates act as both reducing and stabilizing agents and also as a template for carrying silver nanoparticles with excellent antibacterial activity. Chitosan nanoparticles loaded with various nanoparticles such as Ag<sup>+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, and Mn<sup>2+</sup> showed a significantly

increased antimicrobial activity against *E. coli*, *Salmonella choleraesuis*, and *S. aureus* [130].

Silver nanoparticles based on silver salts or metallic silver may be readily incorporated into thermoplastic packaging polymeric materials such as polyethylene, propylene, polystyrene, and nylon [131]. Silver nanoparticles have been incorporated into biopolymer films such as chitosan and starch, and they had strong antimicrobial activity against both Gram-positive and Gram-negative bacteria [116,132–134]. Such nanocomposite films with profound antimicrobial function have suggested the potential application in food packaging for the extension of shelf life and enhancement of the safety of packaged food [135–137].

The efficiency of antimicrobial function of these polymeric nanocomposites is greatly influenced by various factors such as particle size, size distribution, degree of particle agglomeration, silver content, interaction of silver surface with the base polymer [124]. In order to fully exploit the properties of silver nanoparticles, they should be well dispersed on the surface of the polymer matrix without the formation of aggregation, which otherwise dramatically reduce the antimicrobial effect of silver.

Copper ions can destroy microorganisms and viruses, and copper is indispensable for life as a constituent of metallic enzymes. Copper is considered as being relatively safe since it is not concentrated by animals and thus has few adverse effects on higher animals. A polymer based nanocomposite loading stabilized copper nanoparticles with antifungal and bacteriostatic properties has been proposed for the food packaging application [26]. However, copper is not generally used in food packaging industry since it is regarded as toxic in contact with food and it would accelerate biochemical deterioration with foods due to its catalytic action of oxidation [126].

Metal oxides such as  $\text{TiO}_2$ ,  $\text{ZnO}$ , and  $\text{MgO}$  have also been exploited for the preparation of antimicrobial packaging films due to their strong antimicrobial activity with high stability compared with organic antimicrobial agents [112]. Essentially, these metallic oxides are used as photocatalysts, which derive catalytic activity by absorbing energy from a light source. When the photocatalyst is irradiated with ultraviolet radiation, highly reactive oxygen species (ROS) are generated, which seems to be one of the mechanism of their antimicrobial activity [138,139].  $\text{ZnO}$  nanoparticles deposited on a glass surface exhibited antibacterial activity against both Gram-positive (*S. aureus*) and Gram-negative (*E. coli*) bacteria [140].

Among the metallic oxides,  $\text{TiO}_2$  has been used most widely in paints, foods, and cosmetics as well as food packaging materials, since  $\text{TiO}_2$  is inert, non-toxic, inexpensive, and environmentally-friendly with antimicrobial activity against a wide variety of microorganisms [141]. However, its practical applications seems limited due to its low photon utilization efficiency and necessity of the ultraviolet (UV) as an excitation source. In order to solve these problems, the modification of  $\text{TiO}_2$  has also been attempted by doping them with metallic ions or oxides such as  $\text{Fe}^{3+}$ , Ag, or  $\text{SnO}_2$  enhances the photocatalytic and antimicrobial activities [142,143]. When  $\text{TiO}_2$  is incorporated into a polymer matrix such as packaging materials, it will provide protection against food-born microorganisms as well as

odor, staining, deterioration, and allergens on the presence of radiation of relatively low wavelength near the ultraviolet region.  $\text{TiO}_2$  thin films can be prepared on several substrates by various techniques such as chemical vapor deposition, evaporation, magnetron sputtering, ion beam technique, chemical spray pyrolysis, electro-deposition, and sol–gel method. The sol–gel process is suitable for producing composite materials of high purity without multiple steps [144]. Thin  $\text{TiO}_2$  films exhibit excellent mechanical and chemical durability in the visible and near-infrared region and incorporation of  $\text{TiO}_2$  into synthetic plastic matrix has shown to increase the biodegradability [145]. Zhou et al. [146] first tried to incorporate  $\text{TiO}_2$  into biopolymer (whey protein isolate) and they tested the effect of content of  $\text{TiO}_2$  on mechanical and water vapor barrier properties without testing antimicrobial effect.

## 5.2. Nanoclays

The use of mineral clays as biocide carriers has been reported previously with the predominant application of inorganic biocides, such as Ag, Cu, Zn, Mg, etc. [147–150]. Biocidal metals can be incorporated into the clay structure as charge compensating ions via ion exchange. Alternatively, nanoparticles of neutral metals can be formed inside the clay gallery by the reduction on metal salts loaded into the clay [65]. Nanoclays also have been functionalized to provide antimicrobial functions [38,39]. Aminopropyl functionalized magnesium phyllosilicates (AMP clay) produced by sol–gel synthesis strongly inhibited the growth of microorganisms such as *E. coli*, *S. aureus* and *Candida albicans* [151]. The inhibition of microbial growth by AMP clay is attributed to the amino propyl groups and their charge interactions, and disrupting membrane integrity to leak the essential components inside the cells. Excellent thermal stability and long-acting antimicrobial activity against *E. coli* and *S. aureus* of quaternary phosphonium salt functionalized few-layered graphite has been suggested for food industry applications [152].

## 5.3. Biopolymer/clay nanocomposites

Interestingly, bio-nanocomposite films prepared with some organically modified nanoclay have been recognized to have antimicrobial activity [65,117]. Rhim et al. [65] prepared chitosan/clay nanocomposite films with two different types of nanoclay (i.e., a natural MMT and an OMMT, Cloisite 30B) and tested for the antimicrobial activity of the films against pathogenic microorganisms. First they tested the antimicrobial activity using an agar diffusion disk method and found that the nanocomposite film prepared with the organically modified MMT (Cloisite 30B) exhibited antimicrobial activity against Gram-positive bacteria (*Listeria monocytogenes* and *Staphylococcus aureus*), while the natural MMT did not show any antimicrobial activity (Table 3). They confirmed the result using a total colony count method (Fig. 9), which showed clear antimicrobial activity of Cloisite 30B incorporated chitosan films against Gram-positive bacteria.

They suggested that the antimicrobial activity of the nanocomposite may be mainly attributed to the quaternary

**Table 3**Antimicrobial activity<sup>a</sup> of the chitosan nanocomposite films as observed by an agar diffusion assay on plate medium<sup>b</sup> [65].

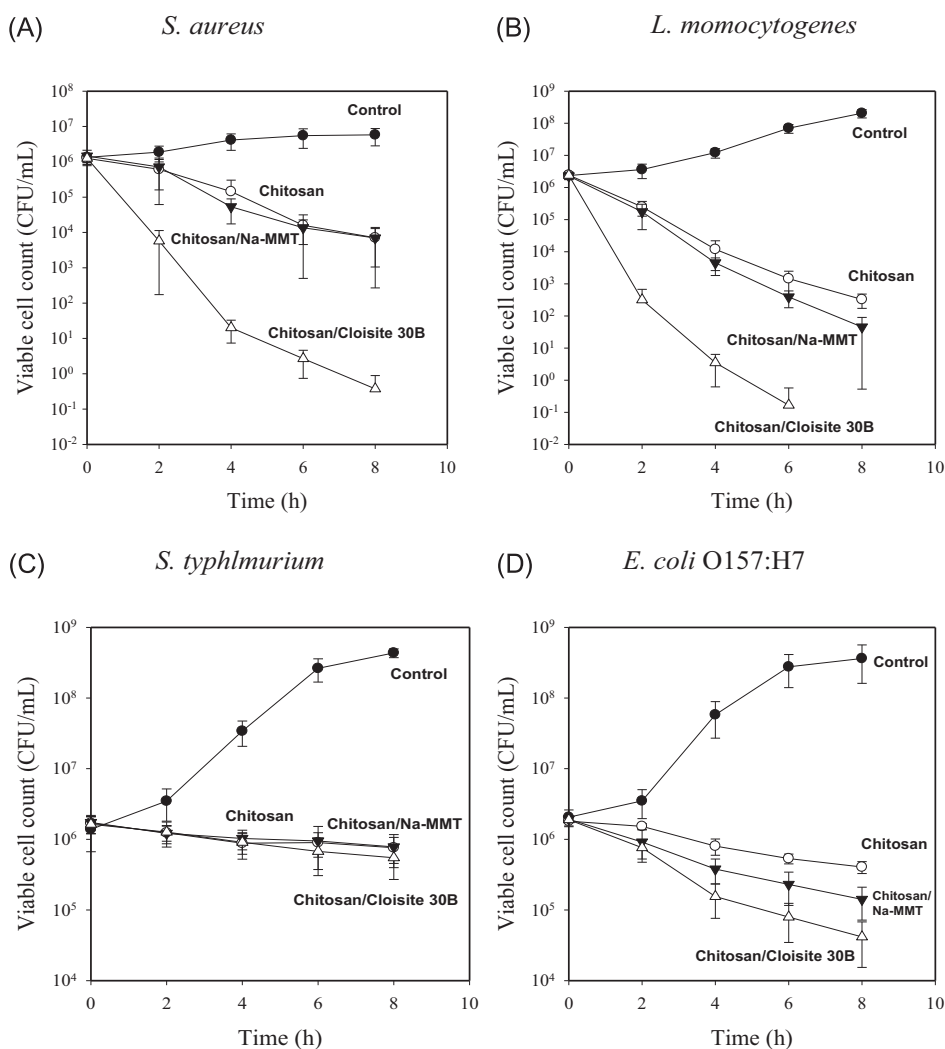
| Microorganisms                     | Film type     |                 |                       |
|------------------------------------|---------------|-----------------|-----------------------|
|                                    | Neat chitosan | Chitosan/Na-MMT | Chitosan/Cloisite 30B |
| <i>S. aureus</i> ATCC-14458        | —             | —               | ++                    |
| <i>L. monocytogenes</i> ATCC-19111 | —             | —               | +                     |
| <i>S. typhimurium</i> ATCC-14028   | —             | —               | —                     |
| <i>E. coli</i> O157:H7 ATCC-11775  | —             | —               | —                     |

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<sup>a</sup> —, no inhibition; +, clear zone of 6–8 mm; ++, clear zone of 8–10 mm.<sup>b</sup> Culture medium: TSA (tryptic soy agar, Difco Lab.), incubation temperature: 37 °C.

ammonium salt of organically modified nanoclay (Cloisite 30B), although it is partly attributed to the chitosan itself, which has long been recognized as an antimicrobial against a wide variety of microorganisms [134,153,154]. Hong and Rhim [104] demonstrated that some organically modified clays, such as Cloisite 30B and 20A, have strong antimicrobial activity against both Gram-positive and Gram-negative

pathogenic bacteria by using agar diffusion method and the total colony count method. They also demonstrated that death of the Gram-positive pathogenic bacteria, *Listeria monocytogenes*, has been attributed to the destruction of cell membrane by organically modified nanoclay with quarternary ammonium salt. They concluded that the antimicrobial activity of the chitosan/clay nanocomposite

**Fig. 9.** Antimicrobial activity of chitosan-based nanocomposite films against various pathogenic bacteria [65].

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is mainly due to the quaternary ammonium salt of organically modified nanoclay (Cloisite 30B). The antimicrobial function of the quaternary ammonium cations in the organoclays could be due to the positively charged ammonium group which could interact with the predominantly anionic molecules at the cell surface. This interaction could change the permeability of the cell membrane of the microorganisms, resulting in a leakage of intercellular components, and then cause death of cell [153].

Wang et al. [117,154,155] performed a series of antimicrobial studies with chitosan/REC (unmodified  $\text{Ca}^{2+}$ -rectorite) and chitosan/OREC (organic rectorite modified by cetyltrimethyl ammonium bromide) nanocomposite films prepared by a solution intercalation method. In their first study [117], they evaluated the antibacterial activity of the nanocomposites by determining the minimum inhibition concentration (MIC) and the relative inhibition time (RIT) and found that although the pristine REC could not inhibit the growth of bacteria, both chitosan-based nanocomposites showed stronger antimicrobial activity than pure chitosan, particularly against Gram-positive bacteria, showing the strongest activity by the chitosan/OREC nanocomposite. They also found that the antibacterial activity of the nanocomposites increased with the increase of the amount of clay and the interlayer distance of the layered silicates in the nanocomposite. Later, they confirmed the result by using the total colony count method for testing the antimicrobial activity [154]. They suggested two stages of antibacterial mechanism of the nanocomposites: (i) adsorption of the bacteria and immobilization on the clay surface, (ii) accumulation of chitosan on the clay surface and inhibiting bacterial growth.

Antimicrobial activity was also observed with different type of bio-nanocomposite films composited with Cloisite 30B [62,66,68,156] though the degree of antimicrobial activity depend on the type of organoclay and polymer matrix used such as agar and PLA.

Bio-nanocomposites with antimicrobial function are highly useful to minimize the growth of post-processing contaminant microorganisms, extending shelf life of food and improving food safety.

#### 5.4. Nanocomposites with combined antimicrobials

Development of antimicrobial biopolymer-based nanocomposite films like chitosan with silver nanoparticles (AgNPs) has long been attempted to exploit the

strong antimicrobial function of silver ions. Silver ions are expected to adhere to the negatively charged bacterial cell wall, changing the cell wall permeability, which is coupled with protein denaturation, induces cell lysis and death. The antimicrobial activity of Ag ion is also related to its ability to modify the DNA replication mechanisms as well as to cause abnormalities in the size, cytoplasm contents, cell membrane, and outer cell layers of sensitive cells [121].

Basically, two different types of method for the preparation of chitosan/AgNP composite films have been used, i.e., direct use of silver nanoparticles [65] and use of reduction of silver ion ( $\text{Ag}^+$ ) from  $\text{AgNO}_3$  [157–160]. Rhim et al. [65] prepared chitosan/AgNP composite films by direct addition of Ag-nanoparticles and chitosan/Ag-adsorbed zeolite (Ag-Ion) into chitosan film forming solution and tested their antimicrobial activity using both an agar diffusion method (Table 4) and total colony count method (Fig. 10). They found that both composite films exhibited strong antibacterial activity against both Gram-positive and Gram-negative bacteria with more effective against Gram-negative bacteria.

Most of chitosan/AgNP composites have been prepared using the method of reduction of silver ion from  $\text{AgNO}_3$ . Silver nanoparticles are conventionally produced by the reduction of silver salt precursors using chemical reducing agents such as  $\text{NaBH}_4$ , formamide, triethanolamine, hydrazine, etc. However, such chemicals cause environmental hazard after processing. On the contrary, physical methods for the reduction of silver salts by UV irradiation,  $\gamma$ -ray irradiation, microwave irradiation, thermal treatment, photochemical process, and sonochemical process have been suggested as green technology without chemical concerns [132].

Yoksan and Chirachanchai [132] prepared silver nanoparticles (AgNPs) by  $\gamma$ -ray irradiation reduction of silver nitrate in a chitosan solution that has been incorporated into chitosan–starch based films. They found the composite films exhibited enhanced antimicrobial activity against *E. coli*, *S. aureus* and *B. cereus* suggesting that the AgNP loaded chitosan–starch based films can be used as antimicrobial food packaging materials. A novel and ‘green’ method of synthesis of a chitosan–AgNP composite has been developed using chitosan as both the reducing and stabilizing agent [161] and the newly synthesized chitosan–AgNP composite had significantly higher antimicrobial activity than its components at their respective

**Table 4**

Antimicrobial activity<sup>a</sup> of the chitosan/AgNP nanocomposite films as observed by an agar diffusion assay on plate medium<sup>b</sup> [65].

| Test organisms                     | Film type     |             |                        |                         |
|------------------------------------|---------------|-------------|------------------------|-------------------------|
|                                    | Neat Chitosan | Nano-silver | Ag-Ion(5) <sup>c</sup> | Ag-Ion(20) <sup>c</sup> |
| <i>S. aureus</i> ATCC-14458        | –             | +           | +/-                    | +                       |
| <i>L. monocytogenes</i> ATCC-19111 | –             | +/-         | +/-                    | ++                      |
| <i>S. typhimurium</i> ATCC-14028   | –             | +           | +                      | ++                      |
| <i>E. coli</i> O157:H7 ATCC-11775  | –             | +           | +                      | ++                      |

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<sup>a</sup> – , no inhibition; +/- , not clear; + , clear zone of 6–8 mm; ++ , clear zone of 8–10 mm.

<sup>b</sup> Culture medium: TSA (tryptic soy agar, Difco Lab.), incubation temperature: 37 °C.

<sup>c</sup> Chitosan/Ag-Ion (5%, 20% Ag-Ion w/w, relative to chitosan) nanocomposite film.



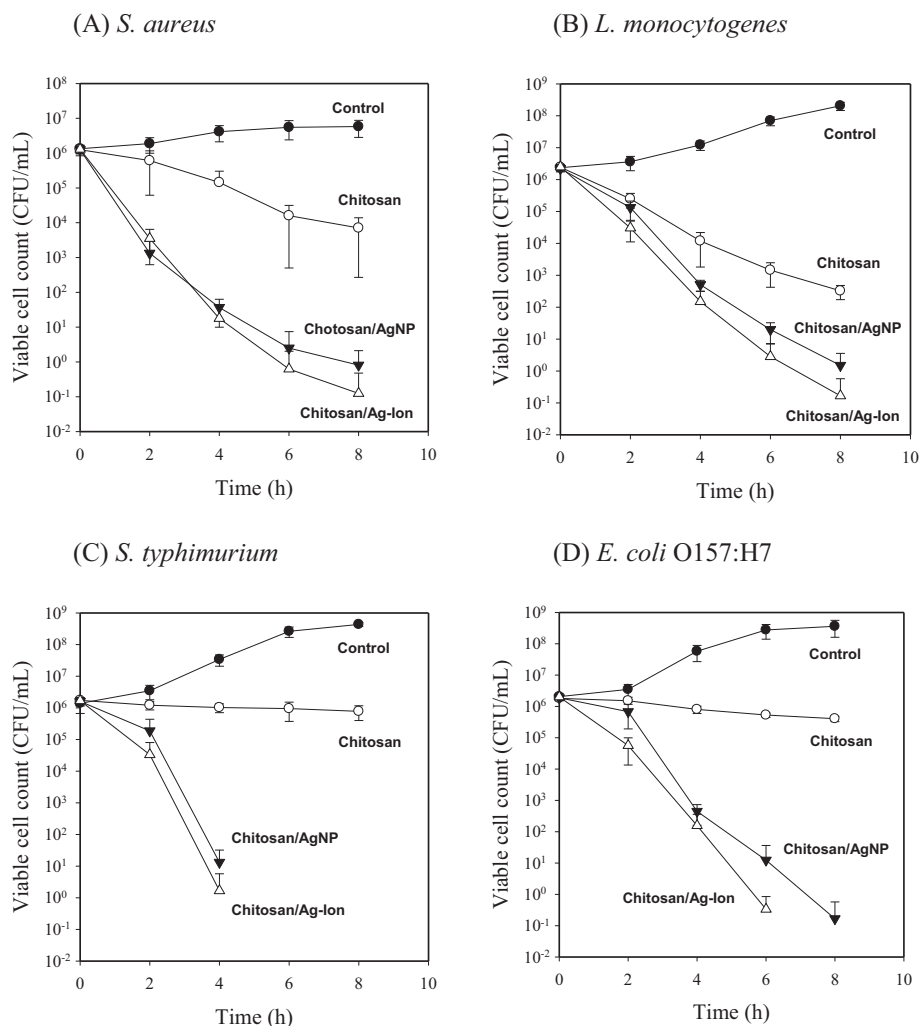


Fig. 10. Antimicrobial activity of chitosan/silver nanoparticle composite films against various pathogenic bacteria [65].

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concentrations [157]. Li et al. [162] prepared three component films, i.e., chitosan/Ag/ZnO (CS/Ag/ZnO) blend films, by a one step sol-cast transformation method, in which AgNPs were generated by using chitosan as the reducing agent under hot alkaline condition and at the same time ZnO NPs formed in the composite. The AgNPs and ZnO were uniformly distributed within chitosan polymer and the CS/Ag/ZnO blend film had excellent antimicrobial activities against wide spectrum of microorganisms such as *B. subtilis*, *E. coli*, *S. aureus*, *Penicillium*, *Aspergillus*, *Rhizopus*, and yeast. And the blend film had higher antimicrobial activities than CS/Ag and CS/ZnO blend films.

Most of the antimicrobial test results showed that silver-nanoparticle loaded chitosan and other biopolymer-based films exhibited excellent antibacterial ability, which have high potential to be used for food packaging materials to extend the shelf life and maintain the food safety.

## 6. Food packaging applications

In the food packaging industry, the use of proper packaging materials and methods to minimize food losses and provide safe and wholesome food products has always been the main interests. Due to the improved performance in the properties of nanocomposite packaging materials such as (i) gas (oxygen, carbon dioxide) and water vapor barrier properties, (ii) high mechanical strength, (iii) thermal stability, (iv) chemical stability, (v) recyclability, (vi) biodegradability, (vii) dimensional stability, (viii) heat resistance, (ix) good optical clarity, as well as (x) developing active antimicrobial and antifungal surfaces, and (xi) sensing and signaling microbiological and biochemical changes, food packaging has been one of the most concentrated nanocomposite technology development. Nanocomposites have already led to several

**Table 5**

Potential applications of nanotechnology in the food packaging sector.

- 
- Improved packaging properties: mechanical, thermal, barrier properties
  - Biodegradability: enhanced biodegradation
  - Active packaging: shelf life extension, oxygen scavenger, antimicrobial
  - Intelligent packaging: interaction with the environment, self-cleaning, self-healing, indication of deterioration
  - Delivery and controlled release: nutraceuticals, bioactive compounds
  - Monitoring product conditions: time temperature indicator (TTI), freshness indicator, leakage indicator, gas detector
  - Nanosensor: indication of food quality, growth of microorganisms
  - Nanocoating
  - Antimicrobial
  - Information on product: RFID, nano-barcode, product authenticity
- 

innovations with potential applications in the food packaging sector (Table 5).

The use of nanocomposite formulations is expected to considerably enhance the shelf-life of many types of food. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-bag foods, also extrusion-coating applications in association with paper-board for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles.

The dominant property improvement is a higher quality shelf life. This improvement can lead to lower weight packages because less material is needed to obtain the same or even better barrier properties. This, in turn, can lead to reduced package cost with less packaging waste. Improved shelf life and lower packaging cost are the reasons why nanotechnology is being pursued in consumer packaging.

Substantial enhancement in packaging performance properties of nanocomposites has been explored to develop the polymer/clay nanocomposites for potential use in a variety of food packaging applications, such as processed meats, cheese, confectionery, cereals, boil-in-bag foods, as well as in extrusion coating applications for fruit juices and dairy products, or co-extrusion processes for the manufacture of bottles for beer and carbonated beverages [163]. The present status and perspectives on application of nanocomposites in the food packaging sector are well documented in several review articles [9,19,23,24,163–167]. However, most applications are mainly focused on nanocomposites made from both thermoset and thermoplastic polymers. Examples of using bio-nanocomposites are very scarce though they are actively under development.

Substantial improvements in gas barrier properties of nanocomposites have been explored in the food packaging industry and some of them are already commercially available. Polymer/clay nanocomposites with improved barrier properties are generally used as a barrier layer in a multilayer packaging material with other structural layers. Multilayer nanocomposites for rigid food packaging applications include beer bottles, carbonated beverages, and thermoformed containers. Typical types of food packaging application of multilayer structures of polymer/clay nanocomposites are shown schematically in Fig. 11. The first type of multilayer is a traditionally used one composed of a barrier layer in the middle and outside structural

layers. The second type is a passive barrier in which the middle layer is reinforced with nanocomposite film with enhanced barrier property. The third one is an active barrier composed of gas ( $O_2$ ) scavenger incorporated film layer. The last one is the combination of passive and active barrier.

Polyamide 6 is one of the most widely used plastic materials used to produce laminated films, sheets, and bottles, since it is inexpensive, clear, thermoformable, strong and tough over a broad range of temperatures with good chemical resistance. However, it is somewhat more permeable to gas and water vapor. Thermoformed nylons are employed in the food packaging industry for packaging meat, cheese and in thermoform/fill/seal packaging. Nylons are often used in coextrusion with other plastic materials, providing both strength and toughness to the structure. Nylon 6 nanocomposites have been developed by a number of companies for the use as a high barrier packaging material.

Nanocomposites would ease the transition between current packaging with metal layers and glass containers to flexible pouches or rigid plastic structures. Many current structures require multiple layers, which render the packaging un-recyclable, but in the facing of global recycling issues, nanocomposite polymers would help to reduce packaging waste and would allow recycling efforts.

On the other hand, the presence of oxygen in the packaged foods causes many deteriorative reactions such as nutrient losses, color changes, off-flavor development, and microbial growth, and it has also a considerable effect on the respiration rate and ethylene production in fruits and vegetables. Although  $O_2$ -sensitive food has been packaged using a passive barrier packaging materials such as high barrier packaging materials such as multilayer structures containing EVOH or aluminum foil [168] as well as a high barrier nanocomposites [169], the passive method cannot completely eliminate the oxygen in the headspace or dissolved  $O_2$  in the food or  $O_2$  permeated into the package wall. More recently, an active packaging method using oxygen scavenger systems has been widely used to eliminate the residual oxygen in the package, although the risk of pathogenic anaerobic bacterial growth must be considered when applying this method.

Antimicrobial packaging is another area with high potential for applying bio-nanocomposite technology to control undesirable microorganisms on foods by means of the incorporation of active molecules such as antimicrobial compounds in or coated onto the packaging materials [3,131,170,171]. Bio-nanocomposites with antimicrobial function are highly useful to minimize the growth of post-processing contaminant microorganisms, extending shelf life of food and maintaining product quality and safety. Nanocomposite antimicrobial systems are particularly effective, because of the high surface-to-volume ratio and enhanced surface reactivity of the nano-sized antimicrobial agents, making them able to control microorganisms more effectively compared to their higher scale counterparts. Nanoparticles or nanocomposite materials have been investigated for antimicrobial activity as growth inhibitors [115], antimicrobial agents [104], antimicrobial carriers [116] or antimicrobial packaging films [65,117]. The major potential food applications for antimicrobial

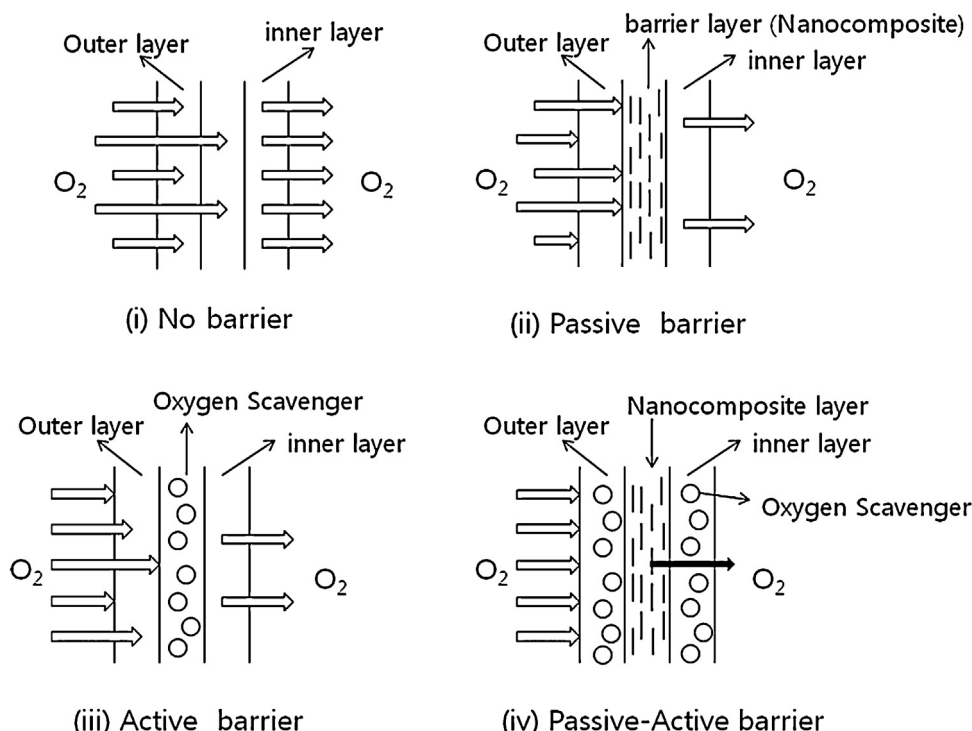


Fig. 11. Schematic representation of typical application structures of multilayer nanocomposite gas barrier packaging materials.

bio-nanocomposite films include meat, fish, poultry, bread, cheese, fruits, and vegetables [172–174].

Other active packaging applications for bio-nanocomposites that are expected to find increased attention in the future include antioxidant releasing films, color containing films, light absorbing/regulation systems, anti-fogging and anti-sticking films, susceptors for microwave heating, gas permeable/breathable films, bio-active agents for controlled release, and insect repellent packages [175].

Intelligent or smart packaging is intended to monitor and provide information about the quality of the packaged food or its surrounded environment to predict or decide the safe shelf life [176,177]. The intelligent/smart packaging may respond to environmental conditions, alert a consumer to contamination of pathogens, detect harmful chemicals or degradation products caused by food deterioration, indicate food quality, and initiate self-healing. The control and manipulation of nano-sized clay platelets made it possible for the creation of smart materials, by combining the wide type of properties provided by the clay with the functionality of organic components. The intelligent packaging application of nanocomposite is mainly based on the function of package to provide information about keeping the product quality such as package integrity (leak indicator), time–temperature history of the product (time–temperature indicators (TTI)), and tracing the origin of the packaged food products (nano barcodes or radio frequency identification (RFID)) [163,178].

High barrier nanocoatings consisting of hybrid organic–inorganic nanocomposite coatings by sol–gel

process [178] are being developed for oxygen-diffusion barriers for plastics such as PET. The coatings are produced through atmospheric plasma technology using dielectric barrier discharges. The coatings have been reported to be very efficient at keeping out oxygen and retaining carbon dioxide, and can rival traditional active packaging technologies such as oxygen scavengers.

Self-cleaning glass is another example for using nanotechnology [179]. In addition, coatings containing nanoparticles are used to create antimicrobial, scratch-resistant, anti-reflective or corrosion-resistant surfaces. Nanoscale silicate and alumina particles have been found to increase the scratch and abrasion resistance of coatings without hindering the transparencies [180]. Applerot et al. [140] prepared ZnO coated glass using ultrasonic irradiation method and they demonstrated a significant antibacterial effect against both Gram-positive and Gram-negative bacteria of the glass slide coated with low level of ZnO coating (as low as 0.13%, mean diameter of ZnO nanocrystals of 300 nm). TiO<sub>2</sub> coated oriented polypropylene (OPP) films showed strong antibacterial activity against *E. coli* and reduced the microbial contamination on the surface of solid food product (cut lettuce) reducing the risk of microbial growth on fresh-cut produce [181]. Bio-hybrid nanocomposite (chitosan and bentonite nanoclay) coated on argon-plasma activated low density polyethylene (LDPE) coated paper had improved barrier properties against oxygen, water vapor, grease, and UV-light transmission [182]. The antimicrobial properties of silver nanoparticles (AgNPs) have been exploited by developing non-cytotoxic coating for methacrylic thermosets by

means of a nanocomposite material based on a lactose-modified chitosan and silver nanoparticles [183]. Such biocompatible antimicrobial polymeric films containing antimicrobial silver nanoparticles may have good potential for using as an antimicrobial active packaging material. Self-cleaning smart nanocoatings that destroy bacteria, isolate pathogens, or fluoresce under certain conditions are under development [184].

## 7. Safety consideration

### 7.1. Migration of nanoparticles

As we have already discussed, nanocomposites have high potential applications in the food packaging sector as an innovative packaging materials with new functional properties that can better protect the quality and safety of food. However, there are important safety concerns about nanocomposite applications to food contact materials. Reijnders [185] claimed that claims that nanocomposites are 'environmentally safe', 'environmentally-friendly' or 'eco-friendly' do not seem to have a firm foundation in empirical data. When nanocomposites are applied into the food packaging materials, direct contact with food is only possible following migration of the nanoparticles. Though there is limited scientific data about migration of nanoparticles from packaging materials into food, it is reasonable to assume that migration may occur because of their tiny dimensions. Especially, nanoparticles may be released when nanocomposites are subjected to wear [186]. Few studies have been conducted to assess the risks associated to the presence of such extremely small particles, some of them biologically active, in the human body or dispersed in the environment. Nano-sized particles frequently exhibit different properties from those found at the macro-scale, because the very small sizes of the former, in principle, would allow them to move through the body more freely than larger particles, while their high surface area increases their reactivity and allows a greater contact with cell membranes, as well as greater capacity for absorption and migration [187]. Hence, their toxicity profiles cannot be extrapolated from those of their non-nanosized counterparts [188]. Moreover, nanostructures can have more free movement through the body when compared to their higher scale counterparts [126].

Accordingly, the major concern on the application of nanocomposite in the food contact packaging materials is regarding the indirect exposure due to potential migration of nanoparticles from packaging. Only a few studies are available in literature on the migration of nanoparticles from the package to the food [189,190].

For the final consumers of food packaged with nanocomposite materials the first concern is to verify the extent of migration of nanoparticles from the package into the food and then if this migration happens, the effect of the ingestion of these nanoparticles inside the body from the mouth to the final gastrointestinal tract [191]. There is a crucial need to understand how these particles will act when they get into the body, how and if the nanoparticles are absorbed by the different organs, how

the body metabolizes them and how and in which way the body eliminate them.

On the contrary, there is a report on the positive influence on the migration from food packaging into food of chemicals that may produce potential adverse health effects. The presence of polymer nanoparticles was found to slow down the rate of migration of some potential hazardous chemicals such as caprolactam and triclosan from the nanocomposite polyamide films into the food up to six times [192]. Avella et al., [189] reported that migration of metals from the biodegradable starch/clay nanocomposite films used for packaging of vegetable samples was minimal, but more studies are needed to reach a conclusive statement.

Although there are limited scientific data available about migration of nanostructures from packaging materials into food, it is prudent to consider that, once present in the food packaging material, nanoparticles might eventually migrate into food. So it is mandatory to verify the extent of migration of nanoparticles from the package into the food and to develop a method to prevent such migration before applying the nanocomposite in the food packaging.

Reijnders [185,186] suggested possible options for hazard reduction caused by migration of nanoparticles from nanocomposite food packaging materials, which include: better fixation of nanoparticles in nanocomposites, including persistent suppression of oxidative damages to polymer by nanoparticles, changes of nanoparticle surface, structure or composition, and design changes leading to the release of relatively large particles.

### 7.2. Impact on human health

Generally, beneficial effects of nanocomposite materials are well recognized, but the potential (eco-)toxicological effects and impacts on human health of nanoparticles have so far received little attention. The high speed of penetration of nanocomposite-based consumer products bring about the need for a better understanding about the potential impacts that nanoparticles may have on biological systems [193]. Some recent studies have shown that there are reasons to suspect that nanoparticles may display toxicological effects on biological systems [194,195]. Concerns on the effects of nano-sized particles on the human body and the environment are increasing recently. The high surface-to-volume ratio of nanomaterials makes them more reactive and potentially more toxic. Because they are more reactive, they may interact with other materials during disposal and recycling of nanoparticle-bearing composite materials. Others fear that nanomaterials may cause new allergens, new toxic strains, and increased rates of nanoparticles absorption by the environment.

Exposure to nanoparticles present in food packaging materials can occur through three different ways i.e., dermal contact, inhalation or ingestion of nanoparticles which have migrated to food [119,187,188,196]. Moreover, nanoparticles may eventually be released into the environment and enter the food chain indirectly [197].

Some nanoparticles such as CNTs may be cytotoxic to human cells, exhibiting epidermal [198,199] or pulmonary toxicity [200–202]. Although bulk ZnO is known to be

non-toxic [203], Sharma et al. [204] demonstrated that ZnO nanoparticles have a genotoxic potential in human epidermal cells. Some nanoparticles cause more inflammation than larger respirable particles elaborated from the same material at the same mass dose [126].

Growing scientific evidences indicated that free nanoparticles can cross cellular barriers and that exposure to some of these nanoparticles may lead to oxidative damage and inflammatory reactions [191]. However, little is known about what happens if these nanomaterials get into the body. The risk assessment of nanomaterials after ingestion has been studied only for few of the nanoparticles used in food packaging. Some results on TiO<sub>2</sub> [205–210], Ag nanoparticles [211] and carbon nanoparticles/nanotubes [212–217] show that nanoparticles can enter blood circulation from the gastro-intestinal tract. These processes are likely to depend on the physico-chemical properties of the nanoparticles, such as size, and on the physiological state of the organs of entry. The translocation fractions seem to be rather low; however, this is subject of current intense research. After the nanoparticles have reached the blood circulation, the liver and the spleen are the two major organs for distribution. Circulation time increases drastically when the nanoparticles are hydrophilic and their surface is positively charged [191].

As the knowledge of the long-term behavior of nanoparticles is very limited, a conservative estimate assumes that insoluble nanoparticles may accumulate in secondary target organs during chronic exposure with consequences not yet studied. There is a specific concern considering the possible migration of nanoparticles into the brain and unborn fetus. Research in both of these areas has to be conducted in order to either confirm or reject the hypothesis of nanoparticles association with various brain diseases. The effect of other particles used in food packaging on the health is under investigation, like ZnO nanoparticles [218] and fullerenes [219].

Few studies have been conducted to assess the risks associated to the presence of such extremely small particles in the human body or in the environment. Hence, significant research is still required to evaluate the potential toxicity of nanocomposite materials, as well as the environmental safety of their use. It is vital to set up clear guidelines and regulations in the applications of nanomaterials, and the validation and monitoring of potential toxicological as well as ecotoxicological impacts of nanoparticles on human and the environment for the continuous development and growth of nanocomposite applications in the food and biomedical sectors [220].

## 8. Summary and outlook

Nanocomposite concept has been considered as a stimulating route for creating new and innovative materials with improved performance properties. Renewable resource-based biopolymers such as starch, cellulosic plastics, corn-derived plastics such as PLA, and polyhydroxyalkanoates (PHAs) are some of the most widely used biopolymers to produce nanocomposites for use of food packaging applications. Enhanced barrier properties of the bio-nanocomposites against O<sub>2</sub>, CO<sub>2</sub>, water vapor, and

flavor compounds would have a major impact on extending the shelf-life of various fresh and processed foods. In addition, biodegradability of the bio-nanocomposites can be fine tuned through proper choice of polymer matrix and nanoparticles, which is also a driver for the use of bio-nanocomposites in food packaging. Such property enhancements are generally attained at low nanoclay content (less than 5%) compared to that of conventional fillers (in the range of 10–50%). For these reasons, nanocomposites are far lighter in weight than conventional composite materials, making them competitive with other materials for specific applications such as in food packaging. It will help to reduce the packaging waste associated with processed food and will support the preservation of packaged foods extending their shelf-life.

Utilization of these unique materials can be expanded by adding extra biofunctional properties like antimicrobial or antioxidative functions through formation of nanocomposites formulated with various types of nanoparticles such as nanoclays, silver nanoparticles, silver-zeolite, metal oxides, and functional biopolymers like chitosan. Bio-nanocomposite materials with such added functional properties have a high potential for the development of various innovative food packaging technologies such as active and intelligent packaging, high barrier packaging, nanosensors, freshness indicator, self-cleaning, and nanocoating.

However, the present level of improvements is not enough to compete with petroleum-based plastics. In particular, water resistance is too poor to utilize the bio-nanocomposites as packaging materials, especially in wet environmental conditions. Therefore, further improvement of the bio-nanocomposites is needed including development of the optimum formulation for the individual polymer and processing method to obtain desired properties to meet a wide range of applications as well as cost reduction of the bio-nanocomposites.

In addition, there are some safety concerns about use of nanocomposites as food contact materials. There is limited scientific data about migration of nanostructures from packaging materials into food. Significant research is still required to evaluate the potential toxicity of nanocomposite materials, as well as the environmental safety of their use.

None the less, bio-nanocomposite packaging materials appear to have a very bright future for a wide range of applications in the food and bio-medical industries as well as innovative active and intelligent food packaging with bio-functional properties.

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