

## Review Article

# Nanoclays in Food and Beverage Packaging

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In this study, we present and discuss the technical benefits of using nanoclays as a promising property enhancer in organic polymers for food and beverage packaging. The incorporation of nanoclays can improve the thermal, mechanical, and barrier properties of a host polymer. Both natural hydrophilic and modified organophilic nanoclays provide unique characteristics to the host polymer depending on the selected applications. Besides the advantage of polymer reinforcement, various novel applications of nanoclays in food packaging have been suggested recently, such as control and release for active ingredients, antimicrobial agent, and carrier for the colorimetric indicator system. The existing migration studies discussing the transition from plastic to nanoclay packaging revealed that the diffused level of aluminum and silicon in the nanoclay packaging are within the limitation proposed in Council Directive 90/128/EEC (1990). Therefore, until now, there is no safety restriction in the use of clay nanocomposite films in food packaging applications.

## 1. Introduction

Over the last few decades, food and beverage packaging has progressed enormously because of the diverse consumer demands. The passive role of packaging for logistic and marketing functions has evolved into a smart role for protection, detection, and communication. This paradigm shift in the packaging technology has led to a greater role of packaging in improving the consumers' health and safety. An active function of packaging has been developed to extend a product's shelf life by diminishing the incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food. Furthermore, an intelligent function has been designed for recording, tracing, and providing information relevant to the changes in quality or conditions of the packed food to the consumers [1, 2]. Recently, an emerging nanotechnology has had a monumental influence on the development of both active and intelligent packaging materials.

The research and development of novel hybrid materials with extraordinary properties for food and beverage packaging is one of the most expanding fields in nanoclay

application according to a report from Grand View Research Inc. The global nanoclay market for food packaging was the largest segment in 2014, accounting for USD 343.0 million, and is expected to grow significantly through 2022 [3]. Comparing with other nanofillers such as nanosilica [4], calcium carbonate [5], and crystalline cellulose [6], nanoclay shows an equivalent or better performance. Study from Voon et al. [4] showed that halloysite nanoclay provides better mechanical property over nanosilica when blending with bovine gelatin polymer, while barrier properties and water solubility were equally improved. Zare et al. [5] reported that the addition of either nanoclay or calcium carbonate enhance the mechanical strength of the polypropylene film but the required minimum content of each compound is quite different, 2 wt% for nanoclay and 8 wt% for calcium carbonate. Resano-Goizueta et al. [6] reported that the aspect ratio and particle shape of the nanofiller affected the mechanical improvement. The platy morphology of nanoclay confers better mechanical properties to the bio-based polymer than the spherical, cubical, or acicular morphology of the nanocellulose. Moreover, nanoclays are relatively inexpensive and are, in cost-effective terms, reasonable to be employed as a

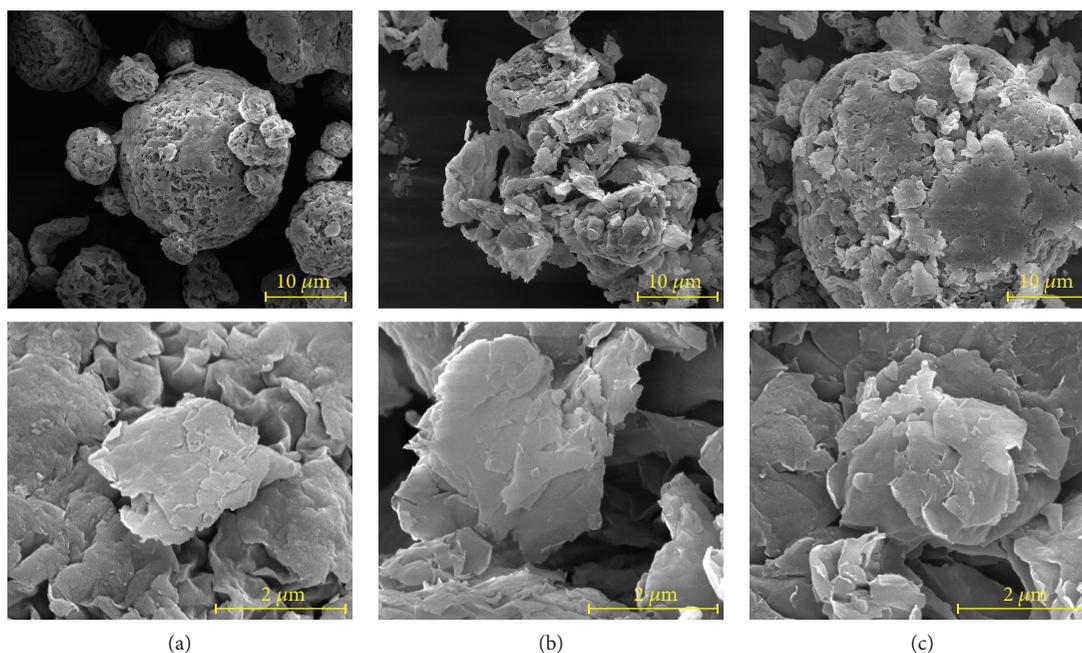


FIGURE 1: SEM micrographs of different types of nanoclays with 3000x and 25000x magnification. (a) Bentonite, (b) Cloisite® 30B, and (c) Nanocor® I.44P.

functional material for packaging/container of fast-moving consumer goods, such as food and beverage. The addition of a small amount of nanoclay (<10 wt%) can enhance a host polymer's barrier, mechanical, thermal, and degradation properties substantially [7, 8].

This review presents a brief overview of nanoclay applications in food and beverage packaging by delving into the unique characteristics of each polymer. Different chemical surface modifications of a nanoclay offer divergent desirable properties, which make it an excellent candidate for use in numerous applications. Further, a recent progress and research on the advanced functions of nanoclays have been introduced in this study to extend the idea of novel applications in the active and intelligent packaging areas. In addition, the possibility of these ultrafine particles migrating from food packaging into food stuff and the perceived potential toxicity induced in humans are also discussed.

## 2. Nanoclays in Food Packaging Materials

Nanoclays possess a characteristic platelet form, flaky soft structure, low specific gravity, and high aspect ratio with nanoscale thickness [9]. Different types of nanoclays are incorporated into the polymers to improve their characteristics. Among these nanoclays, montmorillonite (MMT, MMT- $\text{Na}^+$ ) and organophilic MMT (organic modified MMT, OMMT) have gained most attention in the packaging area, from both academic and industrial researchers, because they possess a high surface area with a fairly large aspect ratio (50–1000) and good compatibility with most of the organic thermoplastics [10, 11]. Figure 1 illustrates the flake-like particles of different types of nanoclays. The agglomerated form is observed in a powder format before being processed with a polymer.

In nature, MMT is the determinative component in bentonites, which has a hydrophilic surface. It is miscible with only hydrophilic polymers, i.e., poly vinyl alcohol and polylactic acid. However, most of the food packaging materials are from petroleum-based polymers, such as polyethylene and polypropylene that are hydrophobic in nature. To improve compatibility with an organophilic host matrix, the hydrophilic silicate surface (typically  $\text{Na}^+$ ,  $\text{K}^+$ , or  $\text{Ca}^+$ ) of a nanoclay must be chemically modified with organic cations (i.e., ammonium salt) through ion-exchange reactions to yield an organophilic surface, which exhibits lower surface energy and higher affinity with the polymer [12]. Moreover, the basal spacing of an organically modified clay is expanded because of the bulkiness of alkyl ammonium, thereby improving the penetration level of the polymer chain [13]. Table 1 summarizes various types of commercially available MMTs and OMMTs frequently used for the preparation of food packaging materials.

In the 1990s, nanoclays were first used for food packaging to improve the mechanical and barrier properties of the packaging [14]. The incorporation of an inorganic nanoclay into an organic polymer matrix yields a hybrid material called polymer nanocomposite. By using a lower content of nanoclay, a nanocomposite exhibits lower weight and superior properties than conventional microcomposites. The well-dispersed layered silicates of nanoclays and the confinement of the polymeric matrix at a nanometer level lead to a new class of structural materials [15]. In principle, a nanocomposite can be prepared via four different techniques: solution intercalation, in situ intercalative polymerization, in situ direct synthesis, and melt intercalation. However, the latter technique has gained relatively more interest from industrial and academic researchers because of its cost effectiveness, simplicity, feasibility, and environmentally benign

TABLE 1: Commercially available organically modified clay minerals used in food packaging application [21, 22].

Commercial name	Clay	Chemical structure of organic modifier	Modifier concentration
Southern Clay Products Inc. (USA)	Cloisite® Na <sup>+</sup>	MMT	Unmodified clay CEC = 92.6
	Cloisite® 10A	MMT	Dimethyl benzyl hydrogenated tallow quaternary ammonium 125 meq/100 g of clay
	Cloisite® 15A	MMT	Dimethyl dihydrogenated tallow quaternary ammonium 125 meq/100 g of clay
	Cloisite® 20A	MMT	Dimethyl dihydrogenated tallow quaternary ammonium 95 meq/100 g of clay
	Cloisite® 30B	MMT	Methyl tallow bis-2-hydroxyethyl quaternary ammonium 90 meq/100 g of clay
	Cloisite® 93A	MMT	Methyl dehydrogenated tallow ammonium 90 meq/100 g of clay
Nanocor Inc. (USA)	Nanocor® I.24TL	MMT	12-Aminododecanoic acid N/A
	Nanocor® I.30P	MMT	Octadecyl ammonium 28-32 wt%
	Nanocor® I.34TCN	MMT	Methyl octadecyl di-2-hydroxyethyl quaternary ammonium N/A
	Nanocor® I.44P	MMT	Dimethyl dialkyl tallow amine 25-30 wt%
Zhejiang Fenghong Clay Chemicals Co. Ltd. (China)	Nanolin® DK1	MMT	Octadecyltrimethyl ammonium 110-120 meq/100 g of clay
	Nanolin® DK2	MMT	Methyl tallow bis-2-hydroxyethyl alkyl quaternary ammonium 110-120 meq/100 g of clay
	Nanolin® DK4	MMT	Octadecyl trimethyl ammonium bromide 90 meq/100 g of clay
Laviosa Chimica Mineraria SpA (Italy)	Dellite® LVF	MMT	Unmodified clay Lowest CEC
	Dellite® HPS	MMT	Unmodified clay Highest CEC
	Dellite® 43B	MMT	Dimethyl-benzyl-hydrogenated tallow ammonium N/A
	Dellite® 67G	MMT	Dimethyl dehydrogenated tallow ammonium High modifier content
	Dellite® 72 T	MMT	Dimethyl dehydrogenated tallow ammonium Low modifier content
Nanoshel LLC (USA)	Shelsite Na <sup>+</sup>	MMT	Unmodified clay N/A
	Shelsite 15A	MMT	Dimethyl benzyl hydrogenated tallow quaternary ammonium 125 meq/100 g of clay
	Shelsite 20B	MMT	Dimethyl benzyl hydrogenated tallow quaternary ammonium 95 meq/100 g of clay
	Shelsite 30B	MMT	Methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride 90 meq/100 g of clay
	Shelsite 93A	MMT	Methyl dehydrogenated tallow ammonium N/A

CEC: cation-exchange capacity; tallow: a mixture of octadecyl, hexadecyl, and tetradecyl.

process [16, 17]. In this process, a nanoclay is blended with a polymer by shear force, at a temperature above the softening point of the polymer. The shear force from the blending process, produced by using either the twin screw of an extruder machine or the mixing blades of a Brabender mixer, alters the orientation and dispersion of the nanoclay in the host polymer [18, 19]. The organization of the nanoclay platelets in the polymer matrix is considered to be most crucial for reinforcement. As displayed in Figure 2(a), a delaminated or intercalated nanocomposite is obtained when the polymer is located between the interlayers of the stacked nanoclay platelets, while an exfoliated nanocomposite is obtained when the individual nanoclay platelets are well separated and randomly dispersed throughout the host matrix [20]. Figure 2(b) illustrates the images obtained from a scanning

electron microscope. The formation of sheet-like layered structures of nanoclay platelets from the cross-section of an LDPE nanocomposite film with 10 wt% Nanocor® I.44P loading was observed. The parallel orientation of the nanoclay to the film surface was initiated by the shear force produced during the extrusion and film-forming processes.

Nowadays, nanocomposites can be produced on an industrial scale by using nanoclay masterbatches (pellet form) that are commercially available with various trademarked products, such as Nanocor™, Aegis™, Durethan®, NanoTuff™, Imperm®, ColorMatrix Corp., and NanoSeal™ [23]. Nanocomposites are manufactured either in the form of a rigid bottle/container for beverages or a flexible film for fresh and dried food, for example, Debbie Meyer BreadBags™ for bread storage, Aisaika Everfresh Bag for fruits and

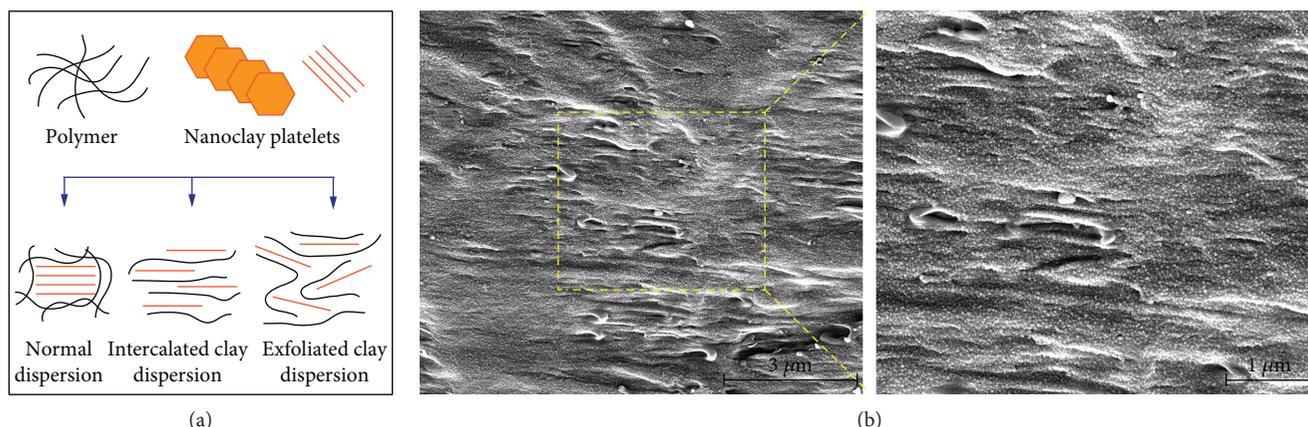


FIGURE 2: (a) Scheme showing states of dispersion of nanoclay platelets in a polymer matrix (reprinted from [20], copyright 2011, with permission from the Hindawi Publishing Corporation). (b) Cross-sectional scanning electron microscopy (SEM) images of an LDPE nanocomposite film with 10 wt% Nanocor® I.44P produced by melt intercalation.

vegetables, Plantic® Plastic Tray for Cadbury® Dairy Milk™ and Mark & Spencer Swiss Chocolate, beer bottles from Miller Brewing and Hite Brewery Co., and packaging for ready-to-eat meals for soldiers and astronauts from the US military and NASA [23–26].

The incorporation of nanoclays into organic polymers is controlled by several factors, for example, the type of polymer and nanoclay, loading content, processing technique, desired properties and applications, and aftereffects (i.e., color alteration, change in elongation, or surface roughness). Different types of surface modifiers provide different characteristics to OMMTs. Cloisite® 10A exhibits a relatively low range of hydrophobicity with benzene ring structures, while Cloisite® 30B exhibits lower hydrophobicity with hydroxyl groups and Cloisite® 15A exhibits higher hydrophobicity with larger basal spacing between each layer [13]. Therefore, exhaustive investigations are required to avoid any significant reduction or effect in other relevant properties. Kim and Cha [27] reported that an addition of over 3 wt% OMMT substantially improved the oxygen and moisture barrier performances of ethylene-vinyl alcohol (EVOH) copolymer films; however, it caused reduction in the optical transparency and mechanical properties (tensile strength, modulus, and elongation) because of the formation of agglomerates. A study from Arora et al. [28] revealed that the inclusion of Nanolin® DK4 caused remarkable enhancement in the barrier properties of polystyrene (PS). The maximum oxygen barrier of the nanocomposite was observed at 4 wt% loading content with 51% improvement. However, 2 wt% loading was optimum for tensile modulus improvement (40% higher than pristine PS) before incessant decrease with higher nanoclay content. Kumar et al. [29] investigated the effects of nanoclay loading on the gas permeability property of a poly (ethylene-co-vinyl acetate) (EVA) nanocomposite film. The result showed that gas permeability was significantly reduced by the incorporation of Cloisite® Na<sup>+</sup> at 3 wt% loading content. However, above 3 wt%, gas permeability adversely increased due to aggregation and poor filler interaction. Parvinezadeh et al. [17] studied the effects of different types of MMTs (Cloisite® Na<sup>+</sup>, Cloisite® 15A, and Cloisite® 30B) on

the surface properties of polyethylene terephthalate (PET). The nanocomposite films were prepared by casting them with 5 wt% MMT. The SEM images revealed the notable surface roughness of the nanocomposites using Cloisite® 30B and Cloisite® Na<sup>+</sup>, while the result obtained using Cloisite® 15A showed a smoother surface because of its low hydrophobicity. Fractured and nonuniform nanocomposites from poor interfacial interaction were also observed in Cloisite® Na<sup>+</sup> nanocomposites because of the poor affinity of unmodified MMT to the host polymer.

### 3. Polymers for Nanoclay Composites in Food Packaging

The use of petroleum-based polymers is ubiquitous in food packaging. They are superior materials in terms of their costs, chemical inertness, mechanical strength, weight, and processability. Various polymers are used for different types of food and beverages. The market is dominated by PET and PS for glossy, rigid, and transparent containers; high-density polyethylene (HDPE) for milk bottles and bags; linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), and polypropylene (PP) for translucent bottles and flexible bags; expanded PS foam for trays; and polyvinyl chloride for overwrapping [30].

Packaging materials for fast-moving consumer goods, especially food and beverages, have been a major concern for the global environment because of the waste disposal problem [31]. A replacement for conventional plastics from petroleum-based polymers is in high demand because they are produced from nonrenewable resources and are unassimilated by the ecosystems upon disposal. The search for bio-based and biodegradable polymers from renewable carbon resources is being vigorously conducted since the 1970s. The term “bio-based polymers” are either naturally synthesized polymeric materials from plants and animals or entirely polymerized materials with high molecular weight produced by chemical and/or biological methods from renewable resources [32]. However, not all bio-based polymers are biodegradable and vice versa. In general,

bio-based polymers are preferred as raw materials over petroleum-based ones, such as polylactide (PLA), polyhydroxyalkanoates (PHA), and starch thermoplastics. Whereas, biodegradable polymers such as polycaprolactone (PCL) and poly (butylene adipate-co-terephthalate) (PBAT) are synthesized from either petrochemical feedstocks or bio-based resources and are biodegradable at the end of their lifecycle [33]. Starch, sugar, cellulose, protein, vegetable oil, lignin, and chitosan are considered as the main renewable resources for bio-based and biodegradable polymers.

**3.1. Polyethylene Terephthalate (PET).** PET is a semicrystalline thermoplastic polyester found in numerous packaging applications in the form of transparent bottles and jars or clear films and sheets with a varying thickness. It shows a greater tendency to replace the traditional aluminum cans or glass bottles in beverage packaging because of its lighter weight and lower energy consumption during production [34]. PET exhibits high clarity, permeability, resistance to chemicals, and impact strength. Therefore, they are widely used for water, juices, carbonated soft drinks, beer, tea, and edible oils. The typical manufacturing processes for PET are injection blow molding (IBM), injection stretch blow molding (ISBM), and thermoforming, in which a variety thermo-mechanical stress is imparted on the polymer by heating, shearing forces, and drawing [35]. Several studies have been conducted to improve the original properties of PET by introducing nanoclays as reinforcement to reduce the stress cracking caused during processing, thereby conserving the flavor of beverages and enhancing the barrier properties against oxygen, carbon dioxide, ultraviolet, moisture, and volatiles [36–39]. Litchfield et al. [40] studied the improvement in toughness and strength (tenacity) of different PET filaments with nanoclay (Cloisite® 20A, Cloisite® 30B, and Cloisite® Na<sup>+</sup>). The composite fibers were obtained by two processes: unoriented melt-spinning and oriented drawing processes in nearly 95% of their maximum extent. For the unoriented fiber, the toughness and elongation at the break values of the OMMT nanocomposite fiber were increased rendering to the greater drawability than the pristine PET. Moreover, the oriented nanocomposite fiber showed significant improvement in tensile stiffness, maximum strength, and Young's modulus. Vidotti et al. [41] investigated the effect of addition of polyester ionomer (PETi) as a compatibilizer to PET/Cloisite® 20A. The study showed that the compatibilizer can promote the intercalation and exfoliation of nanoclay in a polymer matrix resulting in the reduction of carbon dioxide and moisture permeability of up to 50% and 30%, respectively, from pristine PET [41, 42].

Although melt intercalation is the most common technique to prepare polymer nanocomposites, the exfoliated structure is quite difficult to be achieved; moreover, the high temperature during the process causes degradation of the polymer. Dini et al. [43] proposed a novel technique for producing PET/Cloisite® 30B nanocomposites by the hydrolyzed low-molecular weight PET from water-assisted melt blending and subsequent solid-state polymerization. The mechanical and gas barrier properties of the nanocomposite prepared by the new technique are better than those of the

one prepared by conventional melt mixing. This was explained by the higher degree of intercalation and delamination of OMMT from the greater mobility of lower-molecular weight PET.

**3.2. Ethylene-Vinyl Alcohol (EVOH).** EVOH is a family of semicrystalline random copolymers possessing an outstanding gas barrier property, high transparency, and chemical resistance. Owing to the ultimate barrier in oxygen and organic compounds (solvents and food aromas), it is widely used in food packaging, accounting for about 70–75% of barrier resin for retortable rigid containers [44]. However, one of the main drawbacks of EVOH is their moisture sensitivity that causes a significant decrease in their gas barrier value when encountering the high relative humidity (RH) conditions because of the presence of hydroxyl groups from vinyl alcohol. This drawback limits EVOH to be only applicable to multilayer structures, in which the EVOH layer is sandwiched between highly hydrophobic materials, such as LDPE or PP, via coextrusion or lamination process [45]. Nevertheless, this multilayer composite has a number of restrictions including a lack of transparency, high production cost, and difficulties in recycling [46]. Nanotechnology has been proposed to overcome this drawback by incorporation of nanoclay to EVOH. A tortuosity from well-dispersed nanoclay decreases the molecular diffusion of gases and moisture as well as increases the thermal resistance. Kim and Cha [27] reported that the addition of OMMT was thought to result in ultrahigh barrier properties of the EVOH film. The oxygen and moisture barriers were dramatically improved by 59.4 and 90.1%, respectively, because of the good dispersion of intercalated OMMT in the EVOH matrix. Their further study revealed that the oxygen barrier properties of the nanocomposite films in high humid condition (100% RH) were prominently improved. The tortuosity not only retarded the diffusion rate of water molecules but also diminished the moisture-derived deterioration in the oxygen barrier performance of EVOH.

In addition, EVOH copolymers compose with ethylene and vinyl alcohol groups distributed along the chains. The high amount of hydroxyl groups in the backbone renders a high density of hydrogen bonds between the macromolecules which is advantageous for gas barriers. However, this causes an increment of stiffness and decrement in stretchability that adds some obstacle to the deep thermoforming process or preparation of oriented films. The use of a flexible grade with high amounts of ethylene in the backbone can mitigate this issue, but the barrier performance is also reduced [47]. Chang [48] proposed an alternative solution by blending 3 wt% of Cloisite® 10A to EVOH (73 mol% vinyl alcohol) processed with equibiaxial stretching. The whitening spots from the failure of the film during stretching were not observed even when the stretching ratio was up to 100–200% range. Moreover, the high stretching ratio promotes the exfoliated orientation and alignment of nanoclay platelets in the EVOH matrix which is positive for overall properties. The oxygen permeability of the biaxial stretched nanocomposite film substantially improved from 12.11 and 1.58 to <0.01 cc/m<sup>2</sup>/day compared to pristine EVOH and unstretched EVOH,

respectively. This study revealed that the well dispersion of exfoliated nanoclay from equibiaxial stretching improved the flexibility of the high-vinyl-alcohol-content EVOH film, simultaneously enhancing the oxygen barrier.

**3.3. Polyolefin.** As inexpensive, nonpolar, and hydrophobic polymers, HDPE, LLDPE, LDPE, and PP are the very common polyolefins which are used in bottles, flexible film format for pouches, sachets, bags, shrink wraps, and labels. Although, they have good mechanical and barrier properties towards moisture, it has poor grease resistance and gas barrier properties [49]. Several studies reported that the incorporation of a small amount of OMMT in polyolefin efficiently improved the barrier properties and concurrently enhanced the mechanical and thermal properties due to the impermeable lamellar of nanoclay [50–57]. The finding from Xie et al. [58] revealed that although the moisture barrier of the LDPE-OMMT nanocomposite was enhanced by the tortuous path of nanoclay, it also can be reduced when the content of OMMT exceeds a critical value due to the greater capacity of moisture absorption from the remaining hydrophilic part of OMMT.

**3.4. Polylactide (PLA).** PLA is a linear aliphatic thermoplastic polyester produced by the polymerization of lactic acid obtained from the fermentation of renewable starch and sugar feedstock. It is one of the most promising thermoplastics, which can be processed in traditional machines used for conventional plastic. However, the application of pristine PLA in food packaging is limited to only fresh products, short-shelf life bottles, and one-time-use food ware because of its brittleness, moderate barrier properties to oxygen and moisture, and low thermal stability [59, 60]. Over the years, many studies have been conducted using nanoclays as potential reinforcements to improve the properties of PLA and extend their application in the food and beverage packaging area [60–64]. Şengül and Dilsiz [65] investigated the effect of different nanoclay types on the oxygen barrier properties of PLA. The nanocomposite film with bentonite and four different surface-modified OMMTs improved the oxygen barrier property of pristine PLA. However, the performance was different and depended on the exfoliated and intercalated level controlled by the surface modifier. The OMMT with dimethyl-dialkyl-tallow-amine performed the highest improvement at 34% reduction in oxygen permeability, while the unmodified bentonite showed the lowest improvement at 13% reduction. The other three OMMTs with distearyl dimethyl ammonium chloride, methyl dihydroxyethyl hydrogenated tallow ammonium, and aminopropyl triethoxysilane showed the moderate improvement by 29, 28, and 25%, respectively. Di Maio et al. [66] revealed that the incorporation of Cloisite® 30B significantly enhanced the elongation at break and thermal stability of PLA. Approximately 130% improvement in elongation at break was observed with 3 wt% of addition. This was due to the energy absorbability of intercalated clay platelets in a brittle PLA matrix. In addition, study from Vilarinho et al. [67] demonstrated that the PLA film-incorporated MMT- $\text{Na}^+$  can

reduce the lipid oxidation of processed meat products and extend the shelf life by enhancing the water barrier property.

The SusFoFlex, an EU project, is aimed at developing active and intelligent packaging to improve the quality of food products by the addition of specific additives/filler (nanoclays, nanocellulose, and silver nanoparticles (AgNPs)) into PLA packaging, demonstrating the use of PLA/nanoclay/AgNP plastic for new packaging designed for fruit salads. The nanoclay strengthens the PLA and retards the diffusion of oxygen into the package. A final recommended protocol for the manufacturing was combined with a smart design. The package has a reservoir to collect liquid exuded by the fruit, thereby increasing shelf life and maintaining quality [63, 68].

**3.5. Starch.** Starch is becoming more prevalent in bio-based material for food packaging due to its low cost, transparency, tasteless, flavorless, environmental compatibility, and wide availability features [69]. The thermoplastic starch film provides stronger and better mechanical properties than other polysaccharide and protein films [70]. Given the hydrophilic nature of polysaccharides, a starch film has high water vapor permeability and poor mechanical properties when compared to commodity plastics. Blends of starch with nanoclays have been proposed to overcome their weaknesses. Unlike other synthetic polymer, incorporation of OMMT tends to agglomerate in the native starch matrix and forms conventional microcomposites with poor properties due to the immiscible phase and low dispersibility [71]. Significant improvements in barrier and mechanical properties were reported with the addition of unmodified hydrophilic nanoclay [6, 72–74]. Due to the plenty of free hydroxyl groups in the starch, the dispersion of clay platelets throughout the starch matrix can be promoted by the hydrogen bonding interaction of hydrated sodium cation in MMT- $\text{Na}^+$  [73, 75]. However, the difficulty involved in dispersing MMT- $\text{Na}^+$  in the starch matrix still exists. Several attempts have been made to improve the interface interactions of MMT- $\text{Na}^+$  and starch by many strategies such as addition of various plasticizers or hydrophilic premodification of MMT- $\text{Na}^+$  with cationic exchange [74]. Zhou and Xu [76] reported that surface modification of MMT- $\text{Na}^+$  with polydopamine (PDA) can improve the interface interactions between starch and nanoclay, resulting in an exfoliated structure and greater tensile strength and Young's modulus. While the unmodified MMT nanocomposite showed only the intercalated structure, it was believed that the catechol groups from PDA was prone to form hydrogen bonding with hydroxyl groups residing in the starch polymer chain.

## 4. Advanced Functional Nanoclays for Food Packaging

Besides the basic functions as reinforcement and barrier modifier for either petroleum-based or bio-based polymer, nanoclay offers many extra features which are applicable for active and intelligent packaging. The advanced functions of nanoclay such as antimicrobial agents, control and release substance, colorimetric indicator template, and

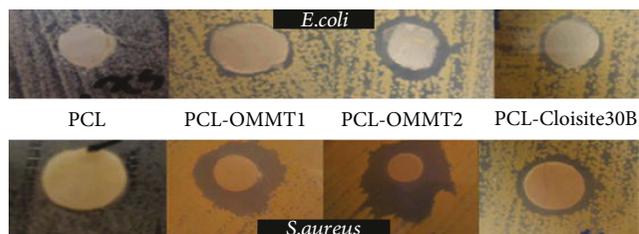


FIGURE 3: Extended inhibition zones of PCL and its PCL nanoclay composite film against *E. coli* and *S. aureus* bacteria. OMMT1: cation exchange method with trimethyl hexadecyl ammonium chloride; OMMT2: pyridinium hexadecyl chloride monohydrate and Cloisite® 30B (reprinted from [80], copyright 2017, with permission from the Springer-Verlag Berlin Heidelberg).

biodegradability stimulator are discussed to bring out the idea for extending the application of nanoclay in food packaging research and industry.

**4.1. Antimicrobial Agents.** Interestingly, there are several reports revealing that nanocomposite films prepared with a certain OMMT showed a strong antimicrobial function against both Gram-positive and Gram-negative bacteria [77, 78]. This could be attributed to the quaternary ammonium groups from surface modifiers [79]. Hadj-Hamou et al. [80] and Yahiaoui et al. [81] reported the antimicrobial activity of a poly ( $\epsilon$ -caprolactone) (PCL) film embedded with different kinds of nanoclay against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*). As illustrated in Figure 3, a significant antibacterial activity was noticed by the clear zone in all nanocomposite films and observed greater performance in *S. aureus*. Since the structure of the cell wall of the Gram-negative strain (*E. coli*) is more complex than the Gram-positive strain (*S. aureus*), the ammonium or pyridinium group from nanoclay was harder to bind than the anionic groups on the surface of the bacteria cell. Liu et al. [82] compared the antimicrobial performance of MMT- $\text{Na}^+$  and OMMT from three surface modifiers. The result revealed that PVOH nanocomposite films with MMT- $\text{Na}^+$ , Nanocor® I.24TL, and Nanocor® I.44PSS lacked antimicrobial activity, similar to a pristine PVOH film, while the nanocomposite film with Nanocor® I.34TCN exhibited substantial bactericidal effect against Gram-positive bacteria, *Listeria monocytogenes*, and *S. aureus* due to the presence of the quaternary ammonium group. Similar result was found by Rhim et al. [61] on the PLA nanocomposite films. Cloisite® 30B was the most effective against *L. monocytogenes* over MMT- $\text{Na}^+$  and Cloisite® 20A. However, Gram-negative bacteria showed resistance to the quaternary ammonium compound. Darie et al. [83] proposed another aspect for antibacterial activity of nanoclay which can be originated from the hydrophilicity. Their study revealed that the inhibitory effect of PLA was higher with the increase in the hydrophilicity of the nanoclay, mainly in the case of *Salmonella typhimurium* and *E. coli*. Unmodified nanoclay as Dellite® HPS and strong hydrophilic modified nanoclay as Cloisite® 93A showed better antimicrobial performance than Cloisite® 30B. A recent study from Cesur et al. [84] revealed that the small amount of OMMT would be

sufficient to inhibit the growth of an opportunistic pathogenic yeast (*Candida albicans*, ATCC 10239).

**4.2. Additive Partitioning.** While the advantages of the nanoclay on the gas and moisture barrier properties of the nanocomposites are already well-evidenced from many studies, the obtained torturous pattern in the polymer matrix has also been investigated in other benefits. A recent study from Nasiri et al. [85, 86] demonstrated that this lamella structure of nanoclay did not induce any detrimental effect on the migration phenomena of immanent additives in food packages to food stuff; moreover, it can reduce the diffusion rate and migration behavior of the additives in nonfat food simulants. The migration models of low-molecular weight chemical compounds such as plasticizers, antioxidants, light stabilizers, and antistatic agents were studied with the 3 types of food simulants. The result showed that the decrease in the degree of crystallinity of both pristine LLDPE and LLDPE/Cloisite® 20A nanocomposites was obtained after immersion in the simulants which theoretically promotes the migration of small molecules. However, the presence of the exfoliated nanoclays leads to a moderate but significant reduction in the diffusivity of additives when the samples were in contact with ethanol 10% and acetic acid 3 w/v% but showed less effect on isoctane. Dardmeh et al. [87] reported that incorporation of 3% Cloisite® 15A into a PET film improved the mechanical properties and decreased the migration amount of terephthalic acid (TPA) even at the low pH condition as 3% acetic acid represents to yoghurt drink.

**4.3. Colorimetric Indicator System for Intelligent Packaging.** Recently, Gutierrez et al. [88] presented a novel and promising application of nanoclay as a colorimetric indicator for intelligent packaging. The indicator system was developed by impregnating a blueberry extract in between the interlayer of nanoclay platelets. The anthocyanins containing MMT and OMMT powder showed good response to the change in pH, for both acid and alkaline mediums. The larger basal spacing of OMMT allowed more blueberry extract to be entrapped and showed the stronger color intensity. This study highlighted that this composite powder could be incorporated in a polymer film for a potential colorimetric indicator system for fresh food of fishery products and meat. Pirsá et al. [89] developed a biodegradable colorimetric indicator film for monitoring milk spoilage. The starch-clay nanocomposite film was fabricated with a pH dye and attached into the milk bottle. The addition of nanoclays significantly reduced the water solubility of the starch-based film and restrained a dye release phenomenon into the milk.

**4.4. Control and Release for Active Ingredients.** Apart from using nanoclay as reinforcement, a substantial amount of the current research activity is devoted to the encapsulation application. Shemesh et al. [90] developed a control and release system using OMMT as an active carrier for the antibacterial packaging. The carvacrol OMMT was dispersed in the LDPE film by melt intercalation. The antibacterial efficacy against *Escherichia coli* and *Listeria monocytogenes* was

investigated along the storage time, 500 days. LDPE/carvacrol films completely lose their efficacy within the first month from production date, while LDPE/carvacrol OMMT films preserve their efficacy up to a year. In addition, halloysite nanoclays from the kaolin group have been proposed as a control and release of active ingredients. It has a tubular structure varying from 500 to 1000 nm in length and 15 to 100 nm in inner diameter [91]. Biddeci et al. [92] demonstrated the use of active halloysite nanoclay for active packaging. The surface of halloysite was functionalized with cucurbit [6] uril molecules with the aim of improving the affinity of the nanoclay towards peppermint essential oil before dispersing in pectin solution. The functionalized pectin bionanocomposite film exhibited good response in the antimicrobial and antioxidant efficiencies with a food simulant (50 v/v% ethanol). A study from Tornuk et al. [93] indicated that the addition of a surfactant in grafting the volatile essential oil with nanoclay can minimize the loss of active compounds against degradation and evaporation during the film production via extrusion. As a result, the LLDPE nanocomposite films showed remarkable antioxidation and antimicrobial activity against foodborne pathogenic bacteria.

**4.5. Biodegradability Enhancement.** Food is the only product class typically consumed three times per day by every person. Consequently, food packaging accounts for almost two-thirds of total packaging waste by volume [94]. The discarded packaging is usually handled through municipal waste management methods such as composting, degradation, landfill, combustion, and recycling. The degradation in the biosphere is highly preferred because of the shorter degradation time and less energy requirement [95]. However, thermoplastic, particularly polyolefin, is inert to the natural environment which becomes disadvantages when it goes to disposal areas rendering nondegradability issues.

Recently, many studies demonstrated that the addition of OMMTs strongly accelerates the biodegradability of both petroleum- and bio-based polymers via different degradation mechanisms [96, 97]. For petroleum-based polymers, an abiotic degradation can be initiated by photoirradiation or thermal energy followed by the changes in properties and chemical structure. It was reported that nanoclays improve the abiotic/oxidation degradation of polyolefin by enhancing the UV absorption capability of polymer nanocomposites [98, 99]. Kumanayaka et al. [100] found that the photooxidation of LDPE/OMMT was greater than the pristine polyethylene determined by the formation of carbonyl and hydroxyl species from oxidation. This reaction was accelerated by the tertiary amine, olefin, and acidic sites which were formed on the clay layers from the decomposition of alkyl ammonium ions in the OMMT. These olefin and acidic sites promote the generation of free radicals, which stimulates photodegradation. Moreover, in bio-based and biodegradable polymers, such as PLA or PBAT, biodegradability is governed by moisture and microorganisms. Mohanty and Nayak [101] reported that the degradation rate of the PBAT/MMT- $\text{Na}^+$  nanocomposites was greater than that of the pristine PBAT and PBAT/OMMT because of the higher hydrophilicity of MMT- $\text{Na}^+$ . Moreover, the high

hydrophobic nature of OMMT and the high intercalated structure of PBAT/OMMT retarded the diffusion of water and enzymes through more tortuous paths. This study showed that the incorporation of OMMT insignificantly hindered the inherent biodegradation tendency of PBAT.

## 5. Potential Migration Associated with Clay Nanocomposites

Nanoclays are already commercially successful in food and beverage packaging materials. They are globally supplied in the form of bottles for beer and flavored alcoholic beverages and plastic bags for fresh and dried food that are in direct contact with the foodstuff. Recently, some studies indicated that nanoclays can adversely affect human health, especially the organically modified form with quaternary ammonium [102–104]. There are only two possible routes for a nanoparticle to be exposed to a human. During polymer processing, it can escape from air filters and contaminate the ambient air and subsequently have toxic effects on humans via inhalation or dermal contact. However, a nanoclay is difficult to be separated to individual airborne nanosheets in the bulk dry powder form. Thus, the related environmental releases and occupational exposures during processing will mainly involve the larger particles of a micrometer size range [105]. By use, the main risk of nanoclay is via swallowing of contaminated food from food packaging, which is likely to be through potential migration of both nanoparticles and the dissolved form (i.e., aluminum and silicon) [106, 107]. Given such potential exposure, the understanding of the migration behavior and ascertaining the level of migration become important requisites.

Up till now, several studies have been conducted on the migration rate and behavior of nanoclays for food packaging. Echegoyen et al. [25] observed the migration of nanoclays from commercially available plastic bags from Debbie Meyer BreadBags and Aisaika Everfresh Bag. The result showed that the migration of aluminum was in the form of both single-particle and dissolved ions. The migration rate was highest when conducted under low-pH condition with 3% acetic acid. Interestingly, they observed that the migration rate of nanoclays was lower than that of the AgNPs from their previous study at the same conditions. It was presumed to be a difference in morphology between platelet-like nanoclay and spherical AgNPs embedded on the surface of the polymer. The larger surface contact area of the nanoclays with the polymer may require a longer etching time for the food simulants to erode the polymer and be able to detach a nanoplatelet than a spherical NP. A study from Huang et al. [108] revealed that the diffusion of dissolved ions into food simulants can be observed even with a multilayered film. The biaxial-oriented PP film containing 4 wt% MMT was laminated with a pristine PP film followed by immersing into food simulants. Among the aqueous food simulants (water, 3 w/v% acetic acid, and 15 v/v% ethanol), the highest migration of silicon ions was observed in acetic acid at 70°C. Farhoodi et al. [106] determined the release of nanoclay from a PET bottle prepared by blow molding. The storage condition was simulated as carbonated beverage containers

by using 3% acetic acid at 24 and 45°C for 7–90 days. It was observed that the migration behavior of aluminum and silicon was significantly dependent on the storage time and temperature.

To date, it is remarkable that there is no framework or specific migration limit on nanoclay or silicon concerning food regulations. However, Council Directive 90/128/EEC (1990) set an overall migration limit, i.e., the sum of constituents that migrated into a foodstuff, of 10 mg/dm<sup>2</sup> for the chemical migration of plastics for food contact applications. With the available migration studies, much of the results show that the migration from polymer/nanoclay composites is low and on a safe level to be applied for food packaging materials. However, a more comprehensive study, which specifically targets each real food simulatant, can facilitate a more effective evaluation and regulation establishment.

## 6. Conclusions

The application of nanoclays in polymer-based packaging materials is being more prevalent because of its certified functional property reinforcement and barrier enhancement. Although the unmodified nanoclays improve the mechanical and barrier properties of thermoplastic starch and enhance the biodegradability of synthetic polymers, their innate hydrophilicity is still, in part, a hindrance to their blending with organic polymers. To improve the compatibility of nanoclays, a chemical surface modification with ammonium salt has been widely developed and several commercialized grades of modified nanoclays are currently available in the market for convenient usage. The organophilic nanoclays not only provide better dispersion in polymers but also offer additional advanced features for packaging materials. Several studies proposed various promising novel functions of nanoclays in food packaging as an antimicrobial agent, control and release for active ingredients, colorimetric indicator template, and additive partitioning, which expand the application area of nanoclays. The lack of legislation for nanomaterials with respect to consumer and environmental safety appears as a restriction in the use of clay nanocomposite films in food packaging. However, the available migration studies revealed that the diffused levels of aluminum and silicon in such packaging are within the limitations of the current regulations.

## Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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