The Potential Use of Polymer-Clay Nanocomposites in Food Packaging

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Abstract

With today’s advancement in nanotechnology, Polymer-Clay Nanocomposite has emerged as a novel food packaging material due to its several benefits such as enhanced mechanical, thermal and barrier properties. This article discusses the potential use of these polymer composites as novel food packaging materials with emphasis on preparation, characterization, properties, recent developments and future prospects.

KEYWORDS: nanocomposites, food packaging, barrier, mechanical and thermal properties
1. **INTRODUCTION**

To meet the increasing expectations of consumers, food must be safe, of consistently good quality and sensory attributes, healthy and inexpensive and should have a good shelf life (Kilcast and Subramaniam, 2000). These considerations have led to ongoing extensive investigation of suitable packaging materials for food products. In a recent era, a new and an emerging class of clay filled polymers, called Polymer-Clay Nanocomposites (PCN) has been developed. Properties such as superior mechanical strength, reduction in weight, increased heat-resistance and flame retardancy, improved barrier properties against oxygen, carbon dioxide, ultraviolet, moisture and volatiles, as well as conservation of flavour in drinks and beverages are achievable with these novel composites (Moore, 1999, Quarmley and Rossi, 2001, Moraru, *et al.*, 2003, Lange and Wyser, 2003, Ranade *et al.*, 2003).

The concept of PCN was developed in the late 1980s. Toyota was the first company to commercialise these nanocomposites and to use nanocomposite parts in one of its popular models for several years (Collister, 2002). PCN are a class of hybrid materials made from nanoscale particles such as layered silicates, for example montmorillonite (MMT), with layer thickness in nanometer dimension. Several potential applications have been identified so far in various industrial sectors, for example automobiles (gasoline tanks, bumpers, interior and exterior panels etc.), construction (building sections, structural panels), aerospace (flame retardant panels, high performance components), electronics and electrical (printed circuit boards, electric components), food packaging (containers, wrapping films), and coatings and pigments. The present review will be restricted to food packaging applications only, including a brief outline of preparation, characterisation, properties, recent developments and future prospects.

2. **PREPARATION AND CHARACTERISATION OF NANOCOMPOSITE**

Researches on the preparation and characterisation of PCN intended for food packaging have been published only since the late 1990s. Most of the research that has been published so far involved the use of montmorillonite (MMT) clay as the nano-component. A wide range of synthetic polymers such as polyethylene (PE), nylon and PVC, and biopolymers such as starch, have been investigated. Varying amounts of nanoclay (usually 1 to 5 weight %) (Lange and Wyser, 2003) were used in most of the published studies on PCN. Silicates used in the synthesis of PCN are layered with a layer thickness of around 1 nm. The lateral dimensions of these layers can vary up to several micrometres; consequently the aspect ratio of these fillers (ratio of length to thickness) is particularly high with values greater than 1000. These layers form stacks with a gap between them called the ‘interlayer’ or the ‘gallery’. The inorganic cations within the interlayers can be substituted by other cations such as lithium and sodium. A schematic presentation of the atom arrangements in a unit cell for a three-layer clay such as MMT is shown in Figure 1.
There are usually three possible arrangements of these layered silicate clays, which can be obtained when they are dispersed in a polymer matrix:

i) Non-intercalated: if the polymer cannot intercalate between the silicate sheets, a non-intercalated microcomposite is obtained. Beyond this traditional class of polymer-filler composites, two other types of composites can be obtained.

ii) Intercalated structure: the separation of clay layers by increasing the interlayer spacing.

iii) Exfoliated or delaminated structure: the complete separation of clay platelets into random arrangements. This is the ideal nanocomposite arrangement but is harder to achieve during synthesis and/or processing.

Figure 1. Structure of a layered silicate
These structures are presented schematically in Figure 2.

![Figure 2. Schematic representation of intercalated and exfoliated nanocomposite from layered silicate clay filler and polymer](image)

Usually, the structure of nanocomposites can be characterised by two complementary analytical techniques, namely, X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD is used to identify intercalated structures by determination of the interlayer spacing. Intercalation of the polymer chains increases the interlayer spacing and according to Bragg’s law, it should cause a shift of the diffraction peak towards lower angle. However, if the spacing between the layers becomes too large, those diffraction peaks will disappear in the X-ray diffractograms, which implies complete exfoliation of the layered silicates in the polymer matrix. In this case, TEM is used to identify the exfoliated silicate layers.

The nanocomposites are generally prepared by i) solution method, ii) *in-situ* /interlamellar polymerisation technique and iii) melt processing.

i) In the solution method, the organoclay is swollen in a solvent. The polymer, separately dissolved in that solvent is added to it so that the polymer molecules can crawl between the silicate layers of the filler. The solvent is then evaporated to obtain intercalated/exfoliated nanocomposite forms.

ii) The *in-situ* method, also known as interlamellar polymerisation, involves swelling of the layered silicates by absorption of a liquid monomer, or a monomer solution. The monomer migrates into the galleries of the layered silicate, so that polymerisation can occur within the intercalated sheets. Polymerisation can be initiated either by heat or radiation, by diffusion of a suitable initiator, or by an organic initiator.
iii) The melt intercalation method involves incorporation of clay filler in the molten state of the polymer to form the nanocomposite material. The last method is widely accepted in nanocomposite research due to its solvent-free process.

3. PROPERTIES OF NANOCOMPOSITES

Several properties e.g., mechanical strength, thermal properties, flammability and barrier properties of PCN materials are claimed to be improved when compared to neat polymer counterparts. The extent of the enhancement is dependent on the type of polymer and nanoclay used as well as the extent of dispersion of the nano-particle in the polymer matrix (Gopakumar et al., 2002; Hotta and Paul, 2004; Morawiec et al., 2005).

3.1 Mechanical Properties

The modified organoclays have the potential to improve the mechanical properties of the matrix polymer substantially even with a low level of filler loading, usually 1-5 wt%. At such a low filler loading, polymers such as Nylon-6 show significant improvement in mechanical properties e.g., an increase in Young’s modulus of 103%, and in tensile strength of 49% (Kojima et al. 1993). A recent research programme focus on the Meal, Ready-To-Eat (MRE) packaging to reduce solid waste conducted at the US Defence Department and the Natick Soldier Centre found that 100% increase in Young’s Modulus of low-density polyethylene (LDPE) could be achieved using chemically treated nanoclay fillers (Nanotechnology applied to ration packaging, 2004).

3.2 Barrier properties

Barrier properties against oxygen, carbon dioxide, ultraviolet, moisture and volatiles are perhaps the most important properties that a nanocomposite food packaging can offer. Recently, Akkapeddi et al. (2003) observed significant improvement in the gas barrier properties of Nylon-6 in which ultra-thin, nanoscale silicate platelets of high aspect ratio were incorporated via an *in-situ* polymerisation process. The oxygen barrier properties of nylons were further enhanced by a novel active barrier approach where proprietary polymeric oxygen scavengers were melt blended into nanoscale dispersions of high oxygen scavenging efficiency.

By combining the nanocomposite and oxygen scavenger technologies, a new family of barrier Nylons (Aegis) were developed for use in multilayer packaging structures, particularly in multilayer, co-injection stretch blow moulded polyethylene terephthalate (PET) bottles for extended shelf-life packaging of oxygen sensitive foods and beverages. In the environmental research programme carried out in NASA, ethylene-vinyl alcohol copolymer (EVOH) nanocomposite has achieved the oxygen barrier requirement for the MRE. However, these properties are dependent on temperature and humidity. These EVOH nanocomposite layers are being sandwiched between LDPE using a new in-house co-extrusion line to make multilayer films (Nanotechnology applied to ration packaging, 2004). Eastman Chemical and Nanocor jointly carried out
investigation to develop nanocomposites of PET and other packaging materials (e.g. polyethylene). Eastman is developing its first PET nanocomposites via the in-reactor approach with the initial focus on rigid containers.

These applications are likely to utilize a co-injected multi-layer preform with the nanocomposite barrier layer on the inside. Nanocor claimed significant progress in joint development of EVOH nanocomposites for multi-layer packaging. Nanocor introduced a new nanoclay, Nanomer I.35L, designed for compounding with EVOH. Within the range of 50-80% relative humidity, it reduces oxygen permeability of EVOH by 66-80%. Nanocor has introduced another new nanoclay, Nanomer I.28MC, for compounding with MXD6 aromatic Nylon (from Mitsubishi Chemical), which could be useful for producing packaging films for moisture- and oxygen-sensitive foods (Sherman, 1999).

The improvement in the barrier properties by incorporation of nanoclay fillers in the polymer matrix can be explained by considering the layered clay sheets as impermeable obstacles in the path of the diffusion process. In a well exfoliated and dispersed state, individual clay platelets are believed to increase the barrier properties by creating a maze or ‘tortuous path’ (Figure 3) that retards the progress of gas and vapour molecules through the polymer matrix. Very recently, Sorrentino et al. (2006) reviewed and proposed a geometric model for predicting the effective diffusivity through PCN as a function of clay sheet orientation, volume fraction, polymer-clay interaction and aspect ratio.

It has been found that moisture absorption and diffusion is dependent on the type of organoclay. Kim et al. (2005) have found that the moisture permeability of octadecylamine-modified MMT (I30P) was lower than that of quaternary alkylamine-modified MMT (KH-MT), due to the larger interlayer distance in I30P that extends the water molecules’ diffusion path in the nanocomposites. Kim et al. measured the interlayer distances of I30P and KH-MT by XRD and TEM, as 2.38 and 1.96 nm, respectively. Mixing with an epoxy resin followed by curing resulted in intercalation of KH-MT clay with an interlayer distance of 3.3 nm, whereas a mixture of exfoliation and intercalation was manifested by the I30P system with an interlayer distance larger than about 8 nm, as measured from the TEM micrograph.

![Figure 3 Schematic presentation of the formation of ‘tortuous path’ in PCN](image)
The enhanced gas/vapour barrier properties of nanocomposites make them attractive and useful in food packaging applications, both flexible and rigid. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, also extrusion-coating applications in association with paperboard for fruit juice and dairy products, together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles. The use of nanocomposite formulations is expected to considerably enhance the shelf life of many types of food. It provides gas barriers to carbon dioxide and oxygen resulting in a shelf life up to 3-6 months for beers and fruit juices and up to one year for carbonated soft drinks (Polymer nanocomposite technology brief, 2003).

3.3 Thermal stability

The thermoplastic poly(vinyl chloride) (PVC) together with polyethylenes, is nowadays used in a wide range of food packaging (Brandsch and Piringer, 2000). Although PVC provides excellent mechanical properties, high compatibility with additives, processability and low cost, the evolution of hydrogen chloride gas, extensive discoloration and lowering of physical and mechanical properties are still serious thermal degradation problems (Brandsch and Piringer, 2000). Yoo et al. (2004) observed that the thermal decomposition behaviour and linear dimensional changes of recycled PVC (RPVC) could be improved by the incorporation of organically modified clays. In the case of RPVC/clay nanocomposites the degree of improvement of the above properties was proportional to the clay content. Yoo et al. found that the coefficients of thermal expansion (CTE) of RPVC/clay nanocomposites decreased with increasing clay content. For example, CTE of RPVC was decreased by about 3.5 times by incorporating only 5% of organically modified clay (Closite® 30B).

3.4 Flammability reduction

It has been reported that this novel class of clay fillers can also be useful to reduce flammability. Under fire-like conditions nanocomposites form char with a multilayered carbonaceous silicate structure which helps in improving flammability properties regardless of exfoliation or intercalation of clay lamellae. This multilayered carbonaceous silicate char formed on the surface during burning insulates the underlying material and reduces volatile products’ escape rate during decomposition (Gilman et al., 2000, Morgan et al., 2005). This property can be estimated by measuring the heat release rate (HRR) of the nanocomposites. Improved flammability reduction of polystyrene, Nylon 6 and maleic anhydride grafted polypropylene nanocomposites are evident from 50 to 75% lower HRR during combustion (Gilman et al., 2000).

4. BIODEGRADABLE POLYMER CLAY NANOCOMPOSITES

In recent years, much research has been carried out on biodegradable polymers as potential packaging materials in order to reduce the environmental pollution caused by
plastic wastes. This special class of polymer follows microbially induced chain scission (i.e. the enzymatic action of living organisms such as bacteria, yeasts and fungi) leading to mineralisation, often called biodegradation, under a few specific conditions such as pH, humidity, oxygenation and the presence of some metals. Biodegradable polymers such as starch, polyactic acid (PLA) and polycaprolactone (PCL) have attracted considerable attention in the packaging industry. Sinha Ray and Bousmina (2005) have recently reviewed the use of biodegradable polymers in PCN. Owing to its biodegradability, wide availability and low cost, starch-based material has received enormous interest for food packaging applications. Starch is commonly pretreated with a plasticiser to make it thermoplastic thus enabling melt-processing as thermoplastic starch (TPS) (Chen and Evans, 2005). However, there are a few drawbacks associated with the use of starch films such as high water, gas and solute permeability and uptake. These problems of starch and starch products can be decreased by homogeneous incorporation of sheet-like non-permeable barrier elements such as clay minerals by mix-melting. The nanoclays are the potential ingredient in this application as they are environmentally acceptable, naturally abundant minerals that are toxin-free and can be used as one of the components for food packaging.

Park et al. (2003) reported that the tensile strength of TPS was increased from 2.6 to 3.3 MPa with the presence of 5 wt% sodium montmorillonite (Closite Na+), while the elongation at break was increased from 47 to 57%. It was also found that the relative water vapour diffusion coefficient of TPS was decreased to about 65% of the value without montmorillonite and the temperature at which the composite lost 50% weight was increased from 305 to 336°C. Chang et al. (2003) observed noticeable improvement in the O₂ gas permeability of PLA clay nanocomposites made using a melt intercalation technique. They found systematic improvement in the above property with increasing clay content. Even at 4% clay loading, the permeability of the nanocomposite was reduced by about 40%, which further reduced to about half of the PLA permeability value at 6% clay loading. This phenomenon might be explained by the increase in the lengths of the tortuous paths in nanocomposites in the presence of high clay content. Gorrasi et al. (2003) supported the morphology-dependent vapour barrier properties of PCL/MMT nanocomposites. They prepared different compositions of PCL/OMLS nanocomposites by melt blending or catalysed ring opening polymerisation of caprolactone.

Interestingly, a critical literature survey indicates that most effort has been devoted to preparation and characterisation, and relatively little attention has been paid to final applications such as food packaging. Very recently, Avella et al. (2005) have verified the possibility of using starch for this development. It has been found that nanocomposite materials from starch and clay (PS/C) have higher Young’s modulus and stress at peak values indicating the highest tensile strength at all relative humidity storage conditions, compared with the material without nanoclay. It is suggested that the clay reinforces the starch blend when it is dispersed and exfoliated/intercalated in the matrix. Adjustable stiffness, strength and toughness can be achieved by varying the water content in the starch/clay nanocomposite materials. In addition, the very high moisture permeability of starch based material is largely decreased after mixing with clay regardless of the clay content in the matrix. This effect is due to the formation of
tortuous paths by clay which make the diffusion of moisture more difficult. However, when polyester is added to the mixture (PS/PE/C), Young’s modulus is decreased and strain at break is increased.

5. FUTURE PROSPECTS

Due to the excellent barrier properties, PCN has major applications in food packaging industries for processed meats, cheese, confectionary and cereals as it enhances the shelf life of food materials. Active projects are under way both in industries as well as in academic research laboratories. Alcoa CSI has already applied multilayer PCN as barrier liner materials for enclosure applications. Honeywell has developed commercial Nylon-6/clay nanocomposite products, Aegis™ NC resin, for drink packaging applications (Auto applications drive commercialization of nanocomposites, 2002). Mitsubishi Gas Chemical and Nanocor have jointly developed Nylon-MXD6 nanocomposites for multilayered PET bottle applications. By 2009, it is estimated that the flexible and rigid packaging industry will use 5 million pounds of nanocomposites materials in the beverage and food industry. By 2011, consumption is estimated to be 100 million pounds. Beer bottles are expected to be the biggest consumer by 2006 with 3 million pounds of nanocomposites, until carbonated soft drinks bottles are projected to surpass that with use of 50 million pounds of nanocomposites by 2011 (Butschli, 2004).

Nanocomposites can also be designed to incorporate and deliver active substances into biological systems, at low cost and with limited environmental impact. For example, creating “bacteria-repellent” surface in packaging film which changes colour in the presence of harmful microorganism or toxins (Moraru et al., 2003). Nanocomposites with these types of unique characteristics could be used for a wide range of minimally processed and processed food products such as meat and fish products, dairy foods, cereals, confectionery, boil-in-bag food, fruit juices, beer and carbonated drinks.

Polymer nanocomposites are the future for the global packaging industry. Once production and material costs are reduced, companies will be using this technology to increase their product’s stability and shelf life so that higher quality products can be delivered to their customers while saving money. It seems that the advantages that nanocomposites offer far outweigh the costs and concerns, and with time the technology will be further refined and processes more highly developed. Research continues into other types of nanofillers (i.e. carbon nanotubes), allowing new nanocomposite structures with different improved properties that will further advance the use of nanocomposite in many diverse packaging applications. On the other hand, the safety and regulatory aspects toward the use of nanocomposites as food packaging materials will be another topic of concern in near future (IFST, 2006).

6. CONCLUDING REMARKS

It appears that the momentum of PCN utilisation is building slowly in the world possibly due to the cost and variability in the quality of some of the products as well as popular
resistance to accepting new technology. The potential of nanocomposites as food packaging materials is largely due to the enhanced gas and moisture barrier properties, increased stiffness with lighter weight, strength and thermal stability. Novel biodegradable biopolymer/clay nanocomposite films are also developed as environmentally friendly material to reduce plastic waste. They too provide improved strength and barrier properties that are desirable for food packaging. More understanding of the clay modification, dispersion and polymer-filler interaction are needed to fill the gaps.

REFERENCES


http://www.bepress.com/ijfe/vol2/iss4/art5
DOI: 10.2202/1556-3758.1149


Published by The Berkeley Electronic Press, 2006