THE Society for Food Science & Technology
Journal of Food Science
A Publication of the Institute of Food Technologists

Review: Nanocomposites in Food Packaging

AMIT ARORA AND G.W. PADUA

Editor's note: We are pleased to present in this issue 3 of 6 papers presented in symposia at the IFT09 annual meeting in Anaheim, Calif. that were organized by Jochen Weiss, Univ. of Hohenheim, and Kumar Mallikarjunan, Virginia Polytechnic & State Univ., with coordination by Professor M.A. Rao, Scientific Editor of the Nanoscale Food Science, Engineering, and Technology section of the Journal of Food Science. The Concise Reviews and Hypotheses section of JFS continues to serve as a mechanism to publish several peer-reviewed papers as a group. We look forward to receiving other opportunities to bundle papers together to serve the scientific community.

–Daryl Lund, Editor in Chief

ABSTRACT: The development of nanocomposites is a new strategy to improve physical properties of polymers, including mechanical strength, thermal stability, and gas barrier properties. The most promising nanoscale size fillers are montmorillonite and kaolinite clays. Graphite nanoplates are currently under study. In food packaging, a major emphasis is on the development of high barrier properties against the migration of oxygen, carbon dioxide, flavor compounds, and water vapor. Decreasing water vapor permeability is a critical issue in the development of biopolymers as sustainable packaging materials. The nanoscale plate morphology of clays and other fillers promotes the development of gas barrier properties. Several examples are cited. Challenges remain in increasing the compatibility between clays and polymers and reaching complete dispersion of nanoplates. Nanocomposites may advance the utilization of biopolymers in food packaging.

Keywords: biodegradable, food, nanocomposite, packaging

Introduction

Over the past decades, polymers have replaced conventional materials (metals, ceramics, paper) in packaging applications due to their functionality, lightweight, ease of processing, and low cost. The use of synthetic polymers is ubiquitous in food packaging where they provide mechanical, chemical, and microbial protection from the environment and allow product display. Polymers most frequently used in food packaging are polyethylene, polypropylene, polystyrene, polyvinyl chloride (PVC), and polyethylene terephthalate (PET) (Bureau and Multon 1996; Marsh and Bugusu 2007). High-density polyethylene is used in applications such as milk bottles and bags. Low-density polyethylene is used for trays and general-purpose containers. Polypropylene has excellent chemical resistance, it is strong, and has the lowest density of the plastics used in packaging. It has a high melting point, making it ideal for hot-fill liquids. It is employed in film and microwavable containers (Adapted from Michaels 1995). PET is clear, tough, and has good gas and moisture barrier properties. Soft drink bottles are generally made of PET. It has good resistance to heat, mineral oils, solvents, and acids. Hence, it is becoming the packaging material of choice for many food products, especially beverages and mineral waters. The use of PET to make plastic bottles for carbonated drinks is increasing (van Willige and others 2002). However, despite their enormous versatility, a limiting property of polymeric materials in food packaging is their inherent permeability to gases and vapors, including oxygen, carbon dioxide, and organic vapors. Biopolymers are notorious for their high water vapor permeability. This has boosted interest in developing new strategies to enhance barrier properties and to carry out research aimed at the understanding of structure–barrier properties relationship. This review emphasizes the impact of nanostructures on barrier properties of polymers.

The most frequently used strategies to enhance barrier properties are the use of polymer blends, coating articles with high barrier materials, and the use of multilayered films containing a high barrier film. An effective high barrier material is aluminum foil. Thin coatings of aluminum can be applied to films and containers by several vapor deposition technologies. Multilayers are formed by embedding a thin layer of a high barrier material within layers of structural polymers. Coatings and multilayers are effective but their application is limited by the level of adherence between the materials involved. Polymers can also be added with suitable fillers to form composites of enhanced barrier properties.

Composites typically consist of a polymer matrix or continuous phase and a discontinuous phase or filler (Matthews and Rawlings 1994). Fibers, platelets, and particles, have been used for decades to form polymer composites with enhanced mechanical and thermal properties. A recent breakthrough in composite materials is the advancement of nanotechnology. Nanocomposites are materials in which the filler has at least one dimension smaller than 100 nm. Mechanical, thermal, and properties of nanocomposites often differ markedly from those of their component materials. Polymer nanocomposites promise a new crop of stronger, more heat resistant, and high barrier materials.

Polymer Nanocomposites

Nanocomposites represent a new alternative to conventional technologies for improving polymer properties. Nanocomposites exhibit increased barrier properties, increased mechanical strength, and improved heat resistance compared to their neat polymers and conventional composites (Sinha Ray and Okamoto

---

MS 20090865 Submitted 9/4/2009, Accepted 10/28/2009. *Authors are with Food Science and Human Nutrition, Univ. of Illinois at Urbana-Champaign, Urbana, IL 61801, U.S.A. Direct inquiries to author Padua (E-mail: gwpadua@illinois.edu).*

doi: 10.1111/j.1750-3841.2009.01456.x

2003; Sinha Ray and others 2006; Sorrentino and others 2007). A classical example is the use of nanosized montmorillonite clay to improve mechanical and thermal properties of nylon (Cho and Paul 2001). When used in food packaging, nanocomposites are better able to withstand the stress of thermal food processing, transportation, and storage (Sinha Ray and Okamoto 2003; Thostenson and others 2005). Also, because of their improved mechanical properties, nanocomposites may allow downgauging, thus reducing materials usage. Particle fillers used and proposed in the literature include the nanoclays montmorillonite (MMT) and kaolinite, carbon nanotubes, and graphene nanosheets.

MMT clays consist of nanometer scale platelets of magnesium aluminum silicate (Figure 1). Their dimensions, 1 nm thick and 100 to 500 nm in dia, result in platelets of high aspect ratio (Uyama and others 2003). Clay structure is formed by hundreds of layered platelets stacked into particles or tactoids 8 to 10 μm in dia. The effect of nanoclays on polymer properties stems mainly from their high surface to volume ratio, since polymer–filler interactions are governed by interfacial forces. Clay particles should be exfoliated as individual platelets and uniformly dispersed within the polymer matrix in order to take full advantage of the potential high surface area (Sinha Ray and Okamoto 2003). Exfoliated nanoclays are effective at improving gas barrier properties of polymeric materials. When dispersed into polymers, they create a maze structure that presents a tortuous path to moving gases, greatly slowing their permeation rate (Demetrakakes 2002). Traditional composite structures contain large quantities of filler (approximately 60% vol), but in nanocomposites dramatic changes in properties are possible at very low loads (<2% vol).

The carbon-based graphene nanoplates (GNPs) can form heat resistant, high barrier nanocomposites that are promising in food packaging applications. GNPs, 20 to 60 nm in thickness and 0.5 to 25 μm in dia, dispersed in poly(methyl methacrylate) (PMMA) were recently reported to increase the glass transition temperature for PMMA by 30 °C at 1 to 5 wt% loading (Ramanathan and others 2008). GNPs were dispersed by high-speed shearing methods. Carbon nanotubes (CNTs), another carbon-based nanofiller, have attracted considerable attention due to their intrinsic mechanical and electrical properties. Improvements in modulus and strength of 30% and 15%, respectively, have been reported for 1 wt% loading of functionalized single-walled carbon nanotubes in epoxy. However, the use of CNTs in nanocomposites to date has been limited by challenges in processing and dispersion, and their prohibitively high cost.

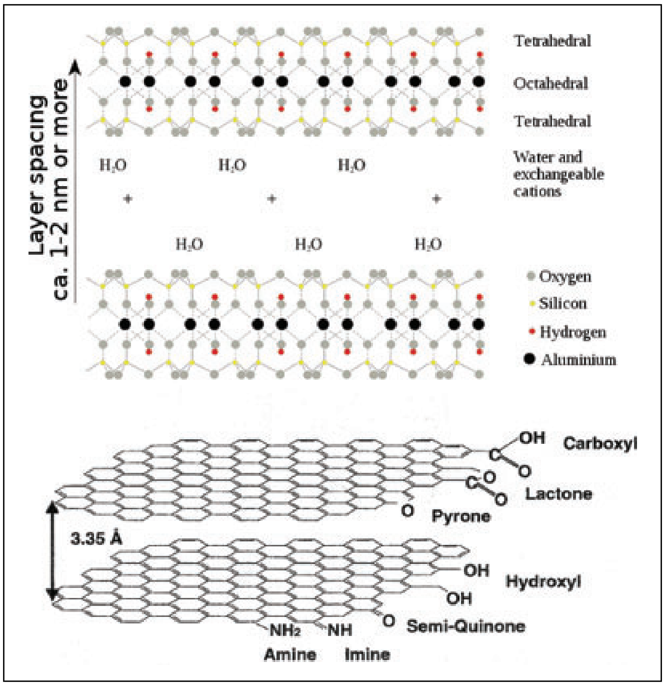

Figure 1 — Structure of Montmorrilonite clay (top) and graphite (bottom).

Nanocomposites Formation

Nanoclay technology relies on the high surface area of clay platelets, in excess of 750 m^2/g, and high aspect ratio (100 to 500). However, montmorillonite clays come in platelet clusters with little surface exposed. Thus, processing at high shear or sonication techniques are necessary to deaggregate or exfoliate the clusters and increase the surface area exposed to the polymer (McAdam and others 2008).

There are 3 types of polymer–clay formations, namely (1) tactoid, (2) intercalated, and (3) exfoliated (Carrado 2003; Sinha Ray and Okamoto 2003) (Figure 2). 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 this way (Alexandre and Dubois 2000). 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 (Figure 2). Clay aggregates must be exfoliated into single platelets and distributed homogeneously throughout the polymer phase to take full advantage of nanoclays high surface area (Sinha Ray and Okamoto 2003; Sinha Ray and Bousima 2005). Dispersion of clay layers into the polymer is affected by mismatches between the hydrophobic/hydrophilic character of polymers and clays. Polymers are typically hydrophobic while clays are hydrophilic. Nanoclays are often chemically modified to render their surface more hydrophobic and improve their compatibility with polymers. Fatty acids are commonly used for this purpose.

Several authors have described the mechanism for silicate clay nanocomposites formation. Vaia and Giannelis (1997) have used

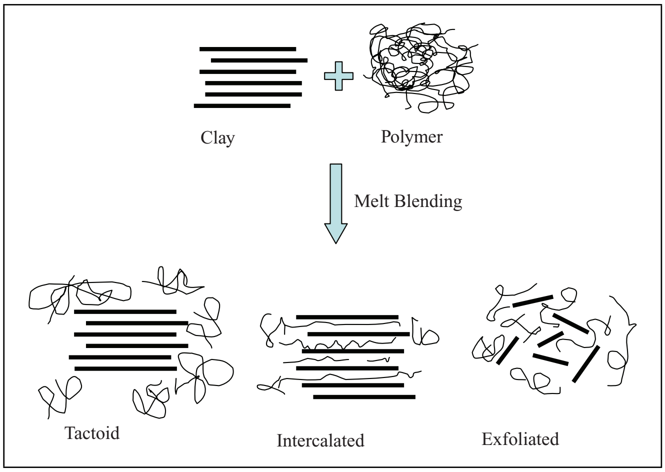

Figure 2 — Polymer clay morphologies.

a simple lattice-based thermodynamic model that examines the entropic and enthalpic contributions during the formation of a polymer layered-silicate nanocomposite to understand the driving forces for intercalation and exfoliation of organically modified layered silicates in long-chain polymer matrices. In their estimation, despite the expected loss of conformational entropy of the confined polymers, the gain in conformational entropy of the surfactant tails compensated. This consideration led to the conclusion that the enthalpy of mixing dominated all free energy considerations. A study by Mackay and others (2006) suggested that the dispersion of nanoparticles in a polymer was a result of a favorable enthalpy of mixing due to increased molecular contacts between the polymer and the dispersed nanoparticles. This was attributed to the increased accessible area of the nanoparticle caused by dispersion. Their results indicated that nanoparticles were capable of being dispersed in polymers if the size of the nanoparticles was smaller than the radius of gyration of the polymers.

Structure Characterization

Characterization is an essential part of materials research. Important aspects of nanocomposite structure characterization include particle dispersion, changes in the bulk matrix, and the nature of the particle–polymer interface. Recent advances in characterization techniques, especially for structure elucidation, have allowed the advancement of nanotechnology. The most common techniques used to probe nanocomposite structures are X-ray diffraction (XRD), both wide angle (WAXS) and small angle (SAXS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy (IR), and atomic force microscopy (AFM) (Karger-Kocsis and Zhang 2005). Sinha Ray and Okamoto (2003) gave a detailed description of nanocomposites characterization techniques in their review paper.

TEM is the preferred method to examine nanoparticle dispersions. Analytical methods to probe the morphology of polypropylene–clay nanocomposites were discussed by Morgan and Gilman (2003). They recommended TEM as the means to qualitatively assess the degree of dispersion of clay in polymer matrices and observe the structure of silicates. The types of structures that can be determined by TEM are polymer structure, void size and shape, filler size, shape, and distribution, local crystallinity, and crystal size. Changes in the polymer matrix may be assessed by polarized light microscopy with assistance from TEM and/or AFM. SEM fracture analysis continues to be the best method for assessing structure-property relations, especially for toughness (Karger-Kocsis and Zhang 2005). The degree of intercalation, exfoliation, and dispersion has been traditionally characterized by XRD (Alexandre and Dubois 2000). Three types of nanostructures can be identified by XRD. When the basal spacing of a mixture is the same as that of the clay cluster, the structure is considered a tactoid with no polymer chains inside the clay gallery (interlayer space). In intercalated structures the *d*-space is increased as the interlayer space is expanded, thus the 2θ position in the X-ray spectra is decreased (smaller value). Exfoliated structures show no peaks in XRD, indicating polymer chains have penetrated the gallery and widened the interlayer space until the regular stacks of clay layers become disordered so that X-ray cannot detect any regular structure. Exfoliation is achieved when clay stacks no longer show an XRD peak. Protein–clay nanocomposite research by Chen and Zhang (2006) demonstrated that MMT tactoids were delaminated into thin lamellas in soy protein. The *d*-spacing values increased from 1.4 nm for the MMT tactoid to a value ranging from 2 to 3 nm.

Biobased Nanocomposites

Biopolymers have attracted considerable attention as potential replacements for conventional plastic packaging materials due to an increased interest in sustainable development. Biopolymers include plant-derived materials (starch, cellulose, other polysaccharides, proteins), animal products (proteins, polysaccharides), microbial products (polyhydroxybutyrate), and polymers synthesized chemically from naturally derived monomers (polylactic acid). Most reports on the formation and properties of biopolymer films are focused on their application as edible films. Pertinent reviews include Daniels 1973; Kester and Fennema 1986; Gontard and Guilbert 1994; Cuq and others 1995; Guilbert and Gontard 1995; Guilbert and others 1996; Anonymous 1997; Debeaufort and others 1998; Guilbert and Cuq 1998; Nussinovitch 1998; Wu and others 2002. For packaging applications, biopolymers present relatively poor mechanical and barrier properties, which currently limit their industrial use. Especially challenging are the development of moisture barrier properties due to the hydrophilic nature of biopolymers. However, it has been suggested that inherent shortcomings of biopolymer-based packaging materials may be overcome by nanocomposite technology.

The forming of nanocomposites to improve mechanical, thermal, and barrier properties of polymers has proven to be a promising option. Researches may be inspired by the various nanocomposites seen in nature. Seashells are natural nanocomposites of a carbonate mineral, aragonite, at 95% and only 1% of organic biopolymer by volume. Seashells have superior mechanical strength and toughness. Bone tissue is another example of nanocomposites in nature. Its structure may serve as a model for the development of biomimetic materials. Its building block is the mineralized collagen fibril. Bone consists of nanosize hydroxyapatite ($Ca_5(PO_4)_3OH$) plates dispersed in a collagen matrix forming an orderly layered array (Fratzl and others 2004). The mineral layers impart harness and the protein matrix lends toughness. Bone provides mechanical support to skeletal tissues and serves as a reservoir of minerals, especially calcium and phosphates (Boyle and others 2003).

Engineered biopolymer-layered silicate nanocomposites are reported to have markedly improved physical properties including higher gas barrier properties, tensile strength, and thermal stability (Alexandre and Dubois 2000; Sinha Ray and Okamoto 2003; Sinha Ray and Bousima 2005; Rhim and others 2007; Zhao and others 2008). Chemically treated nanoscale silicate plates incorporated with appropriate polymers can provide effective barrier performance against water, gases, and grease (Cabedo and others 2004). These hyper-platy, nanodimensional thickness crystals create a tortuous path structure that inherently resists penetration. Detailed reports on biopolymer nanocomposites have been published by several researchers (Avella and others 2005; Rhim and others 2007; Sorrentino and others 2007; Rhim and others 2009).

Starch Nanocomposites

Starch has been extensively investigated as a choice material for food packaging applications due to its environmental compatibility, wide availability, and low cost (Charles and others 2003; Singh and others 2003). The addition of inorganic materials and synthetic polymers (Sinha Ray and Okamoto 2003; Avella and others 2005; Huang and others 2005; Cyras and others 2008) has been proposed to improve water resistance of starch. More recently, blends of starch with nanoclays have been investigated.

Starch-clay are the most often cited biodegradable nanocomposites investigated for various applications including food packaging (Park and others 2002; Huang and others 2003, 2005; Avella and others 2005; Chen and Evans 2005; Yoon and Deng 2006; Cyras and others 2008). Significant improvements in mechanical properties were reported, both Young modulus and tensile strength increased with the addition of MMT clay. Barrier properties are of prime importance in bottling and food packaging. Cyras and others (2008) reported that effective diffusion coefficients for nanocomposites were lower than for starch alone. This suggested that addition of MMT reduced water uptake of starch films, possibly due to the tortuous structure formed by the exfoliated clay. Recently, a starch/ZnO–carboxymethylcellulose sodium nanocomposite was prepared using ZnO nanoparticles stabilized by carboxymethylcellulose sodium (CMC) as the filler in glycerol plasticized-pea starch (Yu and others 2009). When the ZnO–CMC content varied from 0 to 5 wt%, tensile strength increased from 3.9 to 9.8 MPa, although elongation at break was reduced from 42.2% to 25.8%. Water vapor permeability was reported to decrease significantly. Zhao and others (2008) give an overview of the current status of starch based nanocomposites properties, processing, and applications.

Cellulose Nanocomposites

Biopolymer nanocomposites from fruit and vegetable purees and cellulose nanofibers (CNF) have been recently studied as film-forming edible materials. Cellulose nanofibers were added to improve tensile properties, water vapor permeability, and glass transition temperature of mango puree films (Azeredo and others 2009). Tensile strength increased (4.09 to 8.76 MPa) with increase in CNF concentration from 0% to 36%. It was proposed that due to the formation of fibril network within the matrix, there was effective increment in tensile strength, and Young's modulus, especially at higher concentrations of CNF. The addition of CNF was also effective to improve water vapor barrier of the films (2.66 to 1.67 g.mm/kPa.h.m^2). The water vapor permeability was significantly decreased when CNF was incorporated at loadings of at least 10% (10 g/100 g).

Cellulose films in themselves are poor water vapor barriers because of the inherent hydrophilic nature of polysaccharides. Burdock (2007) found cellulose derivative, hydroxypropyl methylcellulose (HPMC) to be a promising material for edible coatings or films for packaging. De Moura and others (2008) proposed nanocomposites using chitosan (CS) as nanofiller in HPMC to improve mechanical and film barrier properties. Different concentrations of CS nanoparticles were incorporated in HPMC to evaluate changes in mechanical properties, water vapor permeability (WVP), and oxygen permeability. Incorporation of chitosan nanoparticles in the films improved tensile strength (30.7 to 66.9 MPa) and film barrier properties. SEM analysis revealed that chitosan nanoparticles tended to fill porous spaces in the HPMC matrix improving film tensile properties and water vapor permeability. Oxygen permeability was reduced significantly by incorporating CS-PMAA in HPMC matrix (182 to 142 cm^3 μ/mm^2 d^{-2} kPa^{-1}). Further reduction in permeability was observed with smaller nanoparticles sizes (142.3 cm^3 μmm^{-2} d^{-2} kPa^{-1} at 110 nm and 110 cm^3 μmm^{-2} d^{-2} kPa^{-1} at 59 nm). Thus, HPMC-CS nanocomposite could be a potential material for food packaging applications to extent the shelf life of foods.

PLA Nanocomposites

Polylactic acid (PLA) has received attention as a sustainable, biocompatible, biodegradable material with good mechanical and optical properties. Lactic acid, the monomer of PLA, may easily be produced by fermentation of carbohydrate feedstock. Thus, PLA offers more disposal options and its manufacture is less environmentally burdensome than traditional petroleum-based plastics (Lunt 1998; Steinbuchel and Doi 2002). However, the large-scale use of PLA as packaging material is still hampered by its high cost and low performance compared to commodity polymers. The most important limitation for the application of PLA in food packaging is its low gas barrier properties. Nanocomposites technology has the potential to improve polymer properties and expand the applications of PLA (Sinclair 1996; Lunt 1998; Thellen and others 2005; Rhim and others 2007).

Nanocomposites of amorphous PLA and chemically modified kaolinite were studied by (Cabedo and others 2006). They observed good interaction between polymer and clay, which led to an increase in oxygen barrier properties of about 50%. The study also included the addition of plasticizers to overcome the inherent brittleness of PLA. In general, plasticizers lower the gas barrier properties of polymers. In that study, the effect of plasticizers on oxygen permeability of PLA was offset by the formation of the kaolinite nanocomposite. The combination of PLA and montmorillonite layered silicate may result in a nanocomposite with barrier properties suitable for food packaging applications (Sinclair 1996; Thellen and others 2005).

Protein Nanocomposites

The film-forming ability of various proteins has been utilized in industrial applications for a long time (Cuq and others 1998). Animal derived proteins used in commercial applications are mainly casein, whey protein, collagen, egg white, and fish myofibrillar protein (Zhao and others 2008). Plant-based proteins under consideration include soybean protein, zein (corn protein), and wheat gluten (Brandenburg and others 1993; Hernandez-Munoz and others 2003; Lee and others 2005). Compared with nonionic polysaccharide films, protein films have better oxygen barrier properties and lower water vapor permeability due to their more polar nature and more linear (nonring) structure, and lower free volume (Miller and Krochta 1997). However, serious concerns remain regarding their performance in food packaging, including their high modulus, high water adsorption, and high gas permeability. Significant efforts have been made to improve the properties of various proteins applying nanocomposites technology, mainly using nanoclays.

Whey protein has received significant attention as edible film and coating material. Sothornvit and Krochta (2005) reported the formation of whey protein transparent films which also acted as oxygen barrier. TiO$_2$ was added to form a nanocomposite with improved antimicrobial properties. Zhou and others (2009) indicated the potential of whey TiO$_2$ nanocomposites to be used as food-grade, biodegradable packaging materials. Addition of small amounts ($<$1 wt%) of TiO$_2$ nanoparticles significantly increased the tensile properties of WPI film (1.69 to 2.38 Mpa). Similar studies regarding interactions on ZnO–whey protein nanocomposite have been reported (Shi and others 2008).

Soy protein has been of great interest to researchers for its thermoplastic properties and its potential as a biodegradable plastic. However, because of its poor response against moisture and high rigidity, its biodegradability has not been exploited effectively (Zheng and others 2009). Similarly to starch, soy protein is also blended with plasticizers to overcome brittleness. However, the use of plasticizers further decreases barrier properties. Soy protein nanocomposite films showed reduced water vapor permeability, improve elastic modulous and tensile strength compared to counterparts without fillers (Dean and Yu 2005; Rhim and others 2005; Chen and Zhang 2006; Yu and others 2007). Dean and Yu found increase in tensile strength, by 23% and 47%, respectively without and with ultrasonic treatment in soy protein

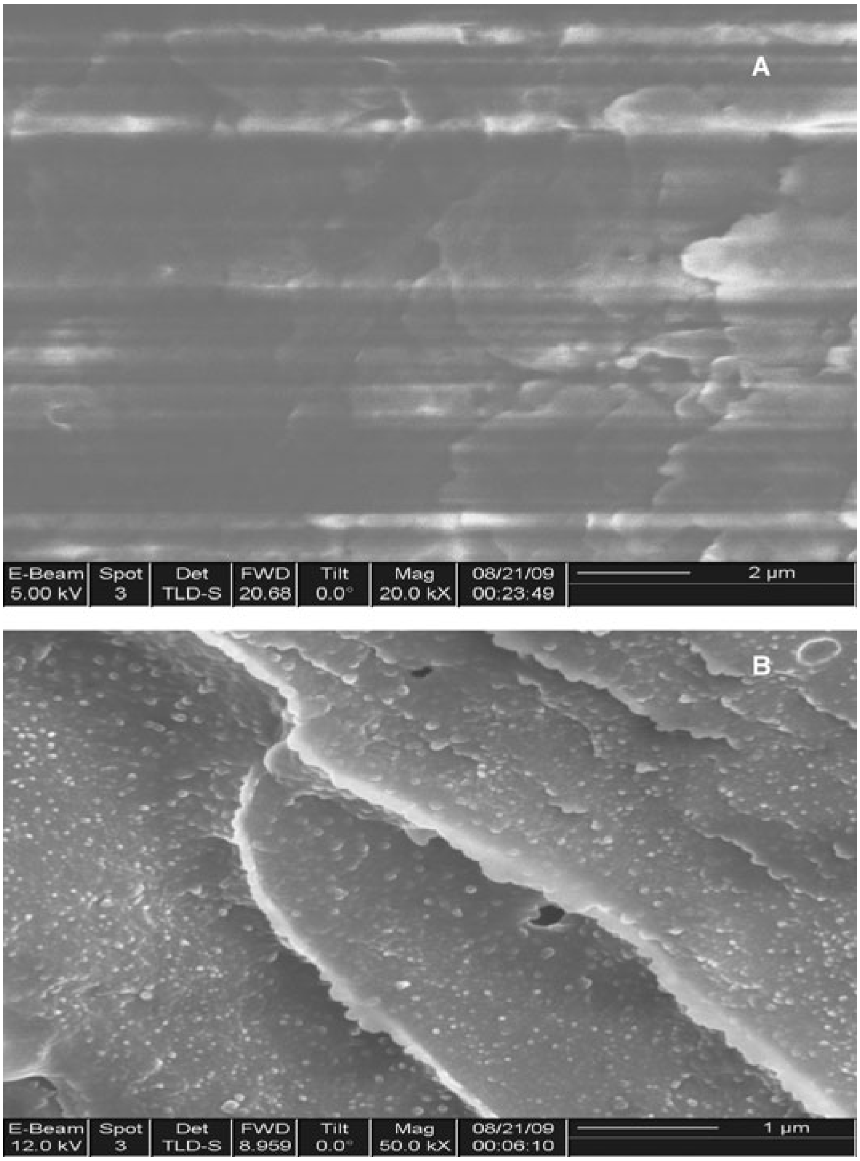

Figure 3—SEM images of untreated (A) Kaolin clay and (B) zein-Kaolin nanocomposites containing 2.5% Kaolin.

nanocomposite. Chen and others investigated the mechanism of interaction between soy protein and MMT clay by correlating structure and properties. The surface electrostatic interaction between the soy protein (+ charged) and the MMT layers (− charge) as well as the hydrogen bonding between the -NH and Si-O groups was understood to be the interacting mechanism for protein/MMT system. Such mechanism resulted into improved mechanical strength of nanocomposite. Young's modulus (*E*) increased from 180.2 to 587.6 MPa with an increase of the MMT content from 0 to 20 wt%. The tensile strength (ób) of the sheets improves from 8.77 to 15.43 MPa when MMT content increased from 0% to 16%.

Zein, a relatively hydrophobic protein found in corn kernels, is known to form films easily (Winters and Deardorff 1958; Shukla and Cheryan 2001; Lawton 2002). Zein is used in the food industry as a coating agent and has shown potential as biodegradable polymer (Shukla and Cheryan 2001; Liu and others 2005). However, zein products although less water sensitive than other biopolymers still shows high water vapor permeability and low tensile strength when compared with commodity polymers. As it was the case for other biopolymers, its inherent brittleness may be ameliorated by the use of plasticizers which, on the other hand, further decrease water vapor and gas barrier properties.

Research in our laboratory (unpublished) is concerned with the formation of zein nanocomposites using kaolin nanoclays. Kaolin-based barrier coatings give useful properties when applied to paper and paperboard. They are expected to replace fluorocarbons in extruded polymer barrier coatings (Rissa and others 2006). The objective of the study was to evaluate changes in water resistance of zein coated paper as a result of added kaolinite. Preliminary results indicated that water vapor permeation decreased by 50%. A reduction in water absorption and oil permeation rate was also observed. Lower permeability was possibly due to the formation of a tiled nanoplate structure kept in place by a film of zein on the paper substrate (Figure 3). Nanoplate layering may have contributed to overcome water sensitivity of both, paper substrate and protein film. Further research is needed to investigate the properties of zein-nanoclay films.

Conclusion

This review illustrated the potential of nanocomposites in food packaging. The main driver is the need for better barrier properties from polymeric materials. Better barriers against the migration of oxygen, CO_2, water vapor, and flavor compounds would have a major impact on the shelf-life of fresh and processed foods. For the case of biopolymers, improving water and gas barrier properties is a critical issue.

Nanocomposites technology is still in its early stages. MMT and kaolinite clays have shown good potential for improving the properties of polymeric materials. Graphene nanoplates are novel highly promising carbon-based nanosized fillers. Best effects are generally observed at low loads (~5 wt%). Good compatibility between filler and polymer is essential, thus the importance of chemically modified clays. With respect to processing, although exfoliation is recognized as a processing goal, an orderly array of platelets in the polymer matrix, which would maximize effectiveness, is still largely unachieved. Improvements in barrier properties are often reported at 50% that of the neat polymer. Thus, polymers of intrinsically better barrier properties will render even better products as nanocomposites. Further improvements could be expected from the development of more compatible filler-polymer systems, better processing technologies, and a systems approach to the design of polymer-plasticizer-filler.

References

Alexandre M, Dubois P. 2000. Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials. Mater Sci Eng 28:1–63.

Anonymous. 1997. Edible films solve problems. Food Technol 51(2):60–60.

Avella M, De Vlieger JJ, Errico ME, Fischer S, Vacca P, Volpe MG. 2005. Biodegradable starch/clay nanocomposite films for food packaging applications. Food Chem 93:467–74.

Azeredo HMC, Mattoso LHC, Wood D, Williams TG, Avena-Bustillos RJ, McHugh TH. 2009. Nanocomposite edible films from mango puree reinforced with cellulose nanofibers. J Food Sci 74(5):N31–N35.

Boyle WJ, Simonet WS, Lacey DL. 2003. Osteoclast differentiation and activation. Nature 423:337–42.

Brandenburg AH, Weller CL, Testin RF. 1993. Edible films and coatings from soy protein. J Food Sci 58(5):1086–89.

Burdock GA. 2007. Safety assessment of hydroxypropyl methylcellulose as a food ingredient. Food Chem Toxicol 45(12):2341–51.

Bureau G, Multon JL. 1996. Food packaging technology. vol 1-2. Weinheim: VCH.

Cabedo L, Gimenez E, Lagaron JM, Gavara R, Saura JJ. 2004. Development of EVOH/kaolinite nanocomposites. Polymer 45:5233–8.

Cabedo L, Feijoo JL, Villanueva MP, Lagaron JM, Gimenez E. 2006. Optimization of Biodegradable nanocomposites based on a PLA/PCL blends for food packaging applications. Macromol Symp 233(1):191–7.

Carrado KA. 2003. Synthetic organo and polymer-clays: preparation, characterization, and materials applications. Appl Clay Sci 17:1–23.

Charles A, Kao H-M, Huang T-Ch. 2003. Physical investigations of surface membrane–water relationship of intact and gelatinized wheat–starch systems. Carbohydr Res 338(22):2403–8.

Chen BQ, Evans JRG. 2005. Thermoplastic starch–clay nanocomposites and their characteristics. Carbohydr Polym 61:455–63.

Chen P, Zhang L. 2006. Interaction and properties of highly exfoliated soy protein/montmorillonite nanocomposites. Biomacromolecules 7(6):1700–6.

Chen C, Lv G, Pan C, Song M, Wu CH, Guo DD, Wang XM, Chen BA, Gu ZZ. 2007. Poly(lactic acid) (PLA) based nanocomposites—a novel way of drug-releasing. Biomed Mater 2:L1–L4.

Cho JW, Paul DR. 2001. Nylon 6 nanocomposites by melt compounding. Polymer 42:1083–94.

Cuq B, Gontard N, Guilbert S. 1995. Edible films and coatings as active layers. In: Rooney M, editor. Active food packaging. London, U.K.: Blackie Academic and Professional. p 111–42.

Cuq B, Gontard N, Guilbert S. 1998. Proteins as agricultural polymers for packaging production: a review. Cereal Chem 75(1):1–9.

Cyras VP, Manfredi LB, Ton-That MT, Vazquez A. 2008. Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films. Carbohyd Polym 73(1):55–63.

Daniels R. 1973. Edible coatings and soluble packaging. Park Ridge, NJ: Noyes Data Corporation.

De Moura MR, Avena-Bustillos RJ, McHugh TH, Krochta JM, Mattoso LHC. 2008. Properties of novel hydroxypropyl methylcellulose films containing chitosan nanoparticles. J Food Sci 73(7):N31–N37.

Dean K, Yu L. 2005. Biodegradable polymers for industrial application. Boca Raton, Fla.: CRC Press. p 289–309.

Debeaufort F, Quezada-Gallo JA, Voilley A. 1998. Edible films and coatings: tomorrow's packagings: a review. Critical Rev Food Sci Nutrition 38(4):299–13.

Demetrakakes P. 2002. Nanocomposites raise barriers, but also face them: Clay-based additives increase the barrier qualities of plastics, but obstacles to commercialization must be overcome. Nanocomposite Materials. Available from: http://www.findarticles.com/p/articles/mi_m0UQX/is_12_66/ai_96123509. Accessed Aug 30, 2009

Fratzl P, Gupta HS, Paschalis EP, Roschger P. 2004. Structure and mechanical quality of the collagen–mineral nano-composite in bone. J Mater Chem 14:2115–23.

Gontard N, Guilbert S. 1994. Bio-packaging: technology and properties of edible-and/or biodegradable material of agricultural origin. In: Mathlouti M, editor. Food packaging and preservation. Glasgow: Blackie-Academic & Professional. p 159–81.

Guilbert S, Gontard N. 1995. Edible and biodegradable food packaging. In: Ackerman P, editor. Cambridge: The Royal Society of Chemistry. p 159–68.

Guilbert S, Cuq B. 1998. Les films et enrobages comestibles In: Bureau G, Multon J, editors. L'emballage des Denrées Alimentaires de Grande Consommation. Paris: Lavoisier TEC & DOC. p 2–66.

Guilbert S, Gontard N, Gorris LGM. 1996. Prolongation of the shelf-life of perishable food products using biodegradable films and coatings. Lebensmittel-Wissenschaft und-Technologie 29:10–17.

Hernandez-Munoz P, Kanavouras A, Ng PKW, Guavara R. 2003. Development and characterization of biodegradable films made from wheat gluten protein fractions. J Agric Food Chem 51:7647–54.

Huang JC, Xiao Y, Mya KY, Liu XM, He CB, Dai J, Siow YP. 2003. Thermomechanical properties of polyimide–epoxy nanocomposites from cubic silsesquioxane epoxides. J Mater Chem 14:2858–63.

Huang JC, He CB, Liu XM, Xu JW, Tay CSS, Chow SY. 2005. Organic-inorganic nanocomposites from cubic silsesquioxane epoxides: direct characterization of interphase, and thermomechanical properties. Polymer 46(18):7018–27.

Karger-Kocsis J, Zhang Z. 2005. In: Balta Calleja JF, Michler G, editors. Mechanical properties of polymers based on nanostructures and morphology. New York: CRC Press. p 547–96.

Kester JJ, Fennema O. 1986. Edible films and coatings: a review. Food Technol 40(12):47–49.

Lawton JW. 2002. Zein: a history of processing and use. Cereal Chem 79:1–18.

Lee C, Scheufele DA, Lewenstein BV. 2005. Public attitudes toward emerging technologies: examining the interactive effects of cognitions and affect on public support for nanotechnology. Science Comm 27(2):240–67.

Liu X, Sun W, Wang H, Zhang L, Wang JY. 2005. Microspheres of corn, zein, for an ivermectin drug delivery system. Biomaterials 26:109–15.

Lunt J. 1998. Large-scale production, properties and commercial applications of polylactic acid polymers. Polym Degrad Stab 59:145–52.

Mackay ME, Tuteja A, Duxbury PM, Hawker CJ, Van Horn B, Guan ZB, Chen GH, Krishnan RS. 2006. General strategies for nanoparticle dispersion. Science 311:1740–3.

McAdam CP, Hudson NE, PethrickRA. 2008. Synthesis and characterization of nylon 6/clay nanocomposites prepared by ultrasonication and in situ polymerization. J Appl Poly Sci 108:2242–51.

Marsh KS, Bugusu B. 2007. Food packaging—roles, materials and environmental issues. J Food Sci 72:R39–55.

Matthews FL, Rawlings RD. 1994. Composite materials: engineering and science. London: Chapman and Hall. 137 p.

Miller KS, Krochta JM. 1997. Oxygen and aroma barrier properties of edible films: a review. Trends Food Sci Tech 8(7):228–37.

Michaels F. 1995. Modern plastic encyclopedia. New York: McGraw-Hill.

Morgan AB, Gilman JW. 2003. Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and Xray diffraction: a comparative study. J Appl Polym Sci 87:1329–38.

Nussinovitch A. 1998. Hydrocolloid coating of food: a review. Leatherhead Food Ind J 1:174–88.

Park HM, Li X, Jin CZ, Park CY, Cho WJ, Ha CS. 2002. Preparation and properties of biodegradable thermoplastic starch/clay hybrids. Macromol Mater Eng 287(8):553–8.

Ramanathan T, Abdala AA, Stankovich S, Dikin DA, Herrera-Alonso M, Piner RD, Adamson DH, Schniep HC, Ruoff RS, Nguyen ST, Aksay IA, Prud'Homme RK, Brinson LC. 2008. Functionalized graphene sheets for polymer nanocomposites. Nature Nanotechnol 3:327–31.

Rhim JW, Lee JH, Kwak HS. 2005. Mechanical and water barrier properties of soy protein and clay mineral composite films. Food Sci Biotechnol 14:112–16.

Rhim JW, Lee JH, Hong SI. 2007. Increase in water of paperboard by coating with poly(lactide). Packag Technol Sci 20:393–02.

Rhim JW, Hong S, Ha C. 2009. Tensile, water vapor barrier and antimicrobial properties of PLA/nanoclay composite films. LWT – Food Sci Technol 42(2):612–7.

Rissa K, Lepistö T, Yrjölä K. 2006. Effect of Kaolin content on structure and functional properties of water-based coatings. J Prog Org Coatings 55(2):137–41.

Shi L, Zhou J, Gunasekaran S. 2008. Low temperature fabrication of ZnO-whey protein isolate nanocomposite. Mater Lett 62(28):4383–85.

Shukla R, Cheryan M. 2001. Zein: the industrial protein from corn. Ind Crops Prod 13:171–92.

Sinclair RG. 1996. The case for polylactic acid as a commodity packaging plastic. J Mass Spec-Pure Appl Chem 33(5):585–97.

Singh RP, Pandey J, Rutot D, Degée Ph, Dubois Ph. 2003. Biodegradation of poly(ε-caprolactone)/starch blends and composites in composting and culture environments: the effect of compatibilization on the inherent biodegradability of the host polymer. Carbohydrate Res 338(17):1759–69.

Sinha Ray S, Okamoto M. 2003. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog Polym Sci 28(11):1539–1641.

Sinha Ray S, Bousima M. 2005. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. Prog Mater Sci 50:962–1079.

Sinha Ray S, Easteal A, Quek SY, Chen XD. 2006. The potential use of polymer-clay nanocomposites in food packaging. Int J Food Eng 2(4):1–11.

Sorrentino A, Gorrasi G, Vittoria V. 2007. Potential perspectives of bionanocomposites for food packaging applications. Trends Food Sci Technol 18:84–95.

Sothornvit R, Krochta JM. 2005. Plasticizers en edible films and coatings. In: Han JH, editor. Innovation in food packaging. New York: Elsevier Publishers.

Steinbuchel A, Doi Y. 2002. Biopolymers volume 4: polyesters III- applications and commercial products. Weinheim, Germany: Wiley-VCH. 398 p.

Thellen C, Orroth C, Froio D, Ziegler D, Lucciarini J, Farrell R, D'Souza NA, Ratto JA. 2005. Influence of montmorillonite layered silicate on plasticized poly(l-lactide) blown films. Polymer 46(25):11716–27.

Thostenson ET, Li CY, Chou TW. 2005. Nanocomposites in context. Compos Sci Technol 65:491–516.

Uyama H, Kuwabara M, Tsujimoto T, Nakano M, Usuki A, Kobayashi S. 2003. Green nanocomposite from renewable resources: plant oil-clay hybrid materials. Chem Mater 15:2492–94.

Vaia RA, Giannelis EP. 1997. Polymer melt intercalation in organically-modified layered silicates: model predictions and experiment. Macromolecules 30:8000–9.

van Willige RWG, Linssen JPH, Meinders MBJ, Van Der Steger HJ, Voragen AGJ. 2002. Influence of flavor absorption on oxygen permeation through LDPE, PP, PC and PET plastics food packaging. Food Addit Contam 19(3):303–13.

Winters EP, Deardorff DL. 1958. Zein as a film-type coating for medicinal tablets. J Am Pharmacol Assoc 47:608–12.

Wu Y, Weller CL, Hamouz F, Cuppett SL, Schnepf M. 2002. Development and application of multicomponent edible coatings and films: a review. Adv Food Nutrition Res 44:347–94.

Yoon S, Deng Y. 2006. Clay–starch composites and their application in papermaking. J Appl Polym Sci 100(2):1032–8.

Yu J, Cui G, Wei M, Huang J. 2007. Facile exfoliation of rectorite nanoplatelets in soy protein matrix and reinforced bionanocomposites thereof. J Appl Polym Sci 104(5):3367–77.

Yu J, Yang J, Liu B, Ma X. 2009. Preparation and characterization of glycerol plasticized-pea starch/ZnO–carboxymethylcellulose sodium nanocomposites. Biores Technol 100:2832–41.

Zhao RX, Torley P, Halley PJ. 2008. Emerging biodegradable materials: starch- and protein-based bionanocomposites. J Mater Sci 43:3058–71.

Zheng H, Ai F, Chang PR, Huang J, Dufresne A. 2009. Structure and properties of starch nanocrystal–reinforced soy protein plastics. Poly Comp 30(4):474–80.

Zhou JJ, Wang SY, Gunasekaran S. 2009. Preparation and characterization of whey protein film incorporated with TiO_2 nanoparticles. J Food Sci 74(7):N50–N56.