

Overview on in Polymer-Nano Clay Composite Paper Coating for Packaging Application

Gaikwad KK* and Seonghyuk Ko

Department of Packaging, Yonsei University, Wonju, 220-710, South Korea

Abstract

This is a review of the existing studies on the Polymer/ clay nano composite used for improving water and moisture barrier in coating. Clays have been and continue to be one of the more important industrial minerals. Research and development activities by clay scientists in academia, government, and industry are continually resulting in new and innovative clay products many of these new applications are the result of improved processing which provides clays of higher purity, more precise particle size and distribution, whiter and brighter color, modified surface chemistry, and other physical and chemical modifications. Some new and improved clay products include tailored or engineered paper coating kaolins, nanocomposites for plastics etc. The use of mineral pigments in coating to provide improved barrier properties has recently gaining increased attention. I described the use of Polymer nano clay for improving the barrier properties of the coated paper studied by several researchers.

Keywords: Paper coating; Polymer/clay nanocomposite; Moisture barriers

Introduction

The paper packaging industry is one of the growing industries due to an increasing demand for packaging products in the market. In addition, market competition often forces companies, especially in market of consumer products, to enhance the packaging in order to improve the image of their products and by this attract more consumers to buy them. Paper coating, which is one way to enhance the packaging, is a process where a coating film is applied onto paper to impart certain qualities to the paper, including weight, surface gloss, smoothness and protection. The coating materials widely used are thin laminated-plastic films or liquid polymeric coat. Without coatings, paper does not have the strength, gloss, printability or resistance to grease and moisture that is required in most of these growth areas [1].

The term “clay” refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally appropriate water contents and will harden with dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fired [2]. Associated phases in clay may include materials that do not impart plasticity and organic matter. Clays have been and continue to be one of the more important industrial minerals. Clays and clay minerals are widely utilized in many facets of our society. They are important in geology, agriculture, construction, engineering, process industries, and environmental applications. Traditional applications are many. Some of the more important include ceramics, paper, paint, plastics, drilling fluids, foundry bondants, chemical carriers, liquid barriers, decolorization, and catalysis Kaolin is one of the most widely used pigments in paper industry and exploited in a large range of coating applications [3]. Fine secondary kaolin's are used for good gloss because of their smaller particle size. In general, platy kaolin particles carry out good coating opacity and printability [4,5] Kaolin has a layered structure, which is composed so that (0 0 1) crystal plane is parallel to the surface of kaolin particle (Table 1).

Nanocomposite Properties

Polymer composites are mixtures of polymers with inorganic or organic additives having certain geometries (fibers, flakes, spheres,

particulates). The use of nanoscale fillers is leading to the development of polymer nanocomposites and represents a radical alternative to these conventional polymer composites [6-8]. This new generation of composites exhibits significant improvements in modulus, dimensional stability and solvent or gas resistance with respect to the pristine polymer. Nanocomposites also offer extra benefits like low density, good flow, better surface properties and recyclability. It is worth recalling that all these improvements are obtained at very low filler contents (generally lower than 5%) [6].

The enhancement of many properties resides in the fundamental length scales dominating the morphology and properties of these

| Kaolin | Smectite | Palygorskite |
|------------------------------|--|---------------------------------|
| 1:1 layer | 2:1 layer | 2:1 layer invetted |
| White or near white | Tan, olive green, gray, or white | Light tan or gray |
| Little substitution | Octahedral and tetrahedral substitutions | Octahedral substitution |
| Minimal layer charge | High layer charge | Moderate layer charge |
| Low base exchange capacity | High base exchange capacity | Moderate base exchange capacity |
| Pseudo-hexagonal flakes | Thin flakes and laths | Elongate |
| Low surface area | Vety high smface area | High surface area |
| Vety low absorption capacity | High absotption capacity | High absotptiou capacity |
| Low viscosity | Vety high viscosity | High viscosity |

Table 1: Some important properties of clay minerals that relate to their applications.

***Corresponding author:** Gaikwad KK, Department of Packaging, Yonsei University, Wonju, 220-710, South Korea, Tel: 82 1599-1885; E-mail: gaikwadk@yonsei.ac.kr

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materials. The inorganic particles have at least one dimension in the nanometer (from 1 to 100 nm) range. It means that a uniform dispersion of these particles can lead to ultra-large interfacial area between the constituents. The very large organic/inorganic interface alters the molecular mobility, the relaxation behavior and the consequent thermal and mechanical properties of the resulting nanocomposite material.

Various inorganic nano-particles have been recognized as possible additives to enhance the polymer performance. Some examples of these particles are represented by the solid layered, the synthetic polymer nano-fibers, the cellulose nano-whiskers and the carbon nanotube. Among these, up to now only the layered inorganic solids like clay have attracted some attention by the packaging industry. This is not only due to their availability and low cost but also due to their significant enhancements and relative simple process ability. The first successful example of a polymer-clay hybrid, developed at Toyota Central Research Laboratories in 1986 was a nylon-clay hybrid (Figure 1) [9].

Packaging Application

Paper and paperboard are coated in order to improve their optical properties and printability. Paper coating formulations generally consist of inorganic pigments such as kaolin and calcium carbonate, binder, soluble co-binders, dispersants, water as carrier and other additives. Pigment is the abundant component in the coating and is naturally the most important factor affecting the properties of the coating materials [10]. The use of mineral pigments in dispersion coating to provide improved barrier properties has recently gaining increased attention [11-16]. Important physical or chemical properties of the pigments which affect the water vapor permeability are their aspect ratio, particle size distribution and hydrophilic/hydrophobic character found that a narrow particle size distribution and a large aspect ratio both had a positive effect on the barrier properties of talc-filled dispersion-coated paper substrates [11-13]. Talc pigments in the polymer coatings were also shown by to give slightly lower water vapor transmission rates (WVTR) than kaolin clays [17,18].

Improving Water and Moisture Barrier in Coating

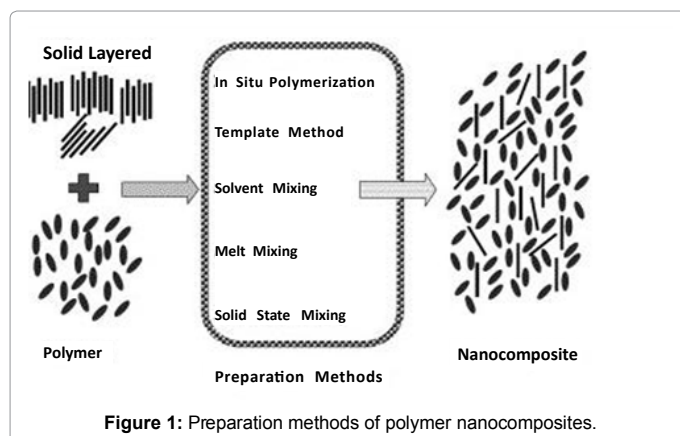
Polymer-clay nanocomposites, with fully-exfoliated platelet structure of nanoclay dispersed within a polymer matrix, provide excellent mechanical and barrier performances due to the high surface-to-volume ratio of the nanofiller and the increased tortuosity of the diffusion path against the permeant [19-23]. The modification of the clay by intercalating cationic surfactants into its interlayer space allows the entry of hydrophobic monomer or polymer into the organophilic

intergalleries. The *in situ* polymerization of monomer within the clay interspacing causes the expansion and exfoliation of the nanoclay platelets [24,25]. Although many polymer-nanoclay composites have been developed, it is generally accepted that a strong mechanical force, such as delamination and extrusion, is needed to help polymer molecules penetrating into the nanoclay basal interspacing.

Barrier coating is one of the most important properties for paper packaging containers. The conventional barrier boards for water vapor, grease and oxygen-proofing applications have been developed based on the extrusion products of a range of polymers, such as polyethylene (PE), poly (ethyl terephthalate) (PET), or natural wax as well Recently, aqueous-based polymers have come into use in many on-machine or off-machine coatings, due to their environmentally friendly process and easy to use, in comparison with the conventional extruding machine coating processes. There are some challenges in improving barrier coating efficiency using water-based nanoclay composite suspensions. For example, the nanoclay particles must be colloidal stable in the suspension and the clay particles must be exfoliated in the final polymer matrix. The former requires a high hydrophilic surface of the clay so the clay can be well dispersed in water phase but the latter requires a high hydrophobicity so the polymer can diffuse into the intergalleries between clay plates. Furthermore, the nanoclay particles must possess strong affinity to polymer to avoid interior defects formation in hindering the diffusion of permeants through the coating layer. In conventional polymer composites, the micron-sized fillers, for example, kaolin with particle size up to a few microns, are immiscible with polymer matrix, leading to a coarsely blended composite with chemically distinct phases. The poor compatibility causes a poor physical attraction between the organic and inorganic components, resulting in agglomeration, and therefore, weaker mechanical properties, and thus low barrier resistance at the same process conditions [26].

Moisture barrier coatings containing clay

Moisture barriers are frequently applied to paper wrappers or paperboard to protect food products and to corrugated paperboard in order to withstand high humidity storage conditions. In the latter case, it is important to prolong the lifetime of the packaging box by resisting creep failure. Barriers can be applied to a substrate such as paperboard by extrusion coating, lamination or dispersion coating techniques. The latter has recently gained much interest as a low cost alternative with many benefits [27-33]. Moisture barrier dispersion coatings have a competitive advantage over wax based coatings, laminates or extruded products in recyclability and higher application speeds as well as fewer processing steps. Barrier dispersion coatings being more readily compostable and repulpable are far more environmentally friendly than extrusion coatings or laminated boards where recovery of the fibres and disposal of polymer film and/or wax represent a significant cost impost. In some food applications, the use of coatings that are free of fluorine containing compounds is also of interest. The two most attractive reasons for using barrier dispersion coatings are lower cost and the ability to use conventional coating techniques. The barrier dispersion coatings studied by C. Kugge based on styrene-butadiene latex and clay, with latex solid ratios of less than one; the coatings are transparent and clay acts as filler in a polymeric matrix. This situation compares with conventional paper coatings where the pigment to latex ratio is greater than one and the latex functions as a binder.



Clay and Polymer Matrix Varieties on the Barrier Properties

The mechanism to increase the barrier properties of materials from nanoclay is based on the increase in the tortuous length of the diffusion path through a polymer matrix. Because nanoclay has much greater specific surface area than micron-sized clay particles, higher barrier resistance will be expected for nanoclay-polymer composite than micron-clay-polymer complex. This also suggests that the barrier properties of the polymer/claynanocomposite will strongly depend on the degree of the dispersion of the nanoclay in the polymer matrix, or obviously on the exfoliation degree of nano-clay layers. Therefore, the change of the barrier properties of the composite reflects indirectly the dispersion state of the nanoclay in polymer matrix, if other conditions are maintained the same.

Filler Reinforcement

Fillers can be added to a barrier polymer to reduce the price of the coating, to enhance the opacity or for mechanical reinforcement. The addition of fillers to polymer matrices can either increase or decrease the permeability, depending on the compatibility and adhesive properties between the polymer and the filler and also on their relative concentrations. Dispersion polymers are readily compatible with conventional coating pigments such as clay. The barrier properties are improved by increasing the diffusion path length of the permeating species (Figure 2).

The critical pigment volume concentration CPVC is an important factor concerning filler addition. The CPVC concept refers to the point where the binder concentration is just large enough to fill in the interstitial voids between pigment particles for conventional paper coating, the addition of fillers is usually done at concentrations considerably higher than the CPVC. In barrier dispersions, on the other hand, pigments are added at a concentration well below the CPVC. The reason is that an increased number of filler particles will lead to an increase in voids, thus leading to an increase in permeability a higher binder concentration gives a more flexible coating, and the optimum pigment volume concentration becomes a compromise between barrier properties and flexibility. The CPVC of dispersions is affected by the immobilization volumes (i.e. the packing volume of the wet coating, which is dependent on particle shape, size, size distribution of pigment and binders, colloidal, chemical and rheological properties), the consolidation power of the binders, the type of substrate and the drying conditions. The most important factors concerning filler addition to barrier dispersions are the adhesion of the binder to the pigment particles, the particle shape and the chemical nature of the pigments. The CPVC value of a polymer/pigment system depends on

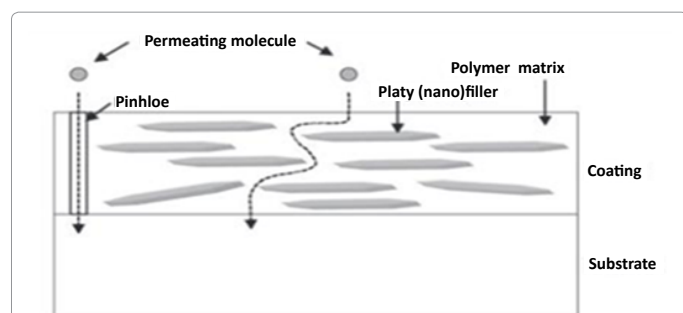


Figure 2: Mechanism of barrier improvement by fillers or nanocomposites.

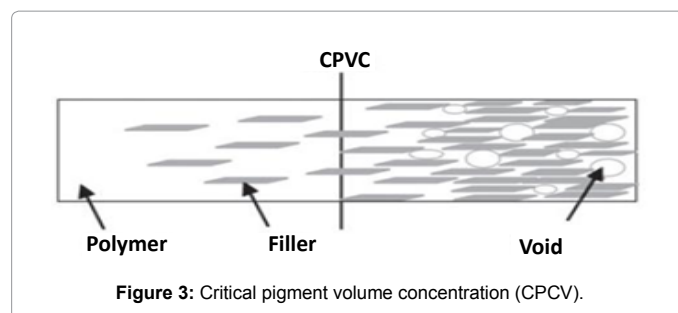


Figure 3: Critical pigment volume concentration (CPVC).

the latex particle size and its size distribution [34]. Increased particle size decreases the CPVC as does an increased value of the glass transition temperature. In contrast, in dispersions where strong deformation of the latex particles occurs, a higher CPVC is obtained due to the more dense packing of polymer (Figure 3).

Nanoparticulate Materials

Montmorillonite is a naturally abundant clay material with a layered aluminosilicate structure that is often used in nanocomposite technology due to its high surface area and large aspect ratio. Dispersion of layered silicates in a polymer matrix can result in a number of different states, leading to micro composites, intercalated or exfoliated nanocomposites. It is believed that complete and homogeneous dispersion in which the clay platelets are arranged in a non-parallel manner (exfoliation) will give the highest performance improvements in coatings. The aluminosilicates can be dispersed into individual layers only 10 Å thick. The distance between the platelets, the basal spacing, is defined as the distance from a certain plane in one layer to the corresponding plane in a parallel layer. Montmorillonite is hydrophilic but can be made organophilic by exchanging the naturally occurring Na^+ ions in the galleries of the clay with organic cations, e.g. alkyl ammonium surfactants, making them more compatible with organic polymers. The relationship between surface diameter and thickness of the nanoclay particles is defined as the aspect ratio. Typically, commercial nanoclays have aspect ratios between 50 and 1000, which is much larger than for typical clay pigments (10–30) used in paperboard coating. The large aspect ratio of nanoclays makes them effective for barrier improvement even at very low ($\leq 5\%$ by weight) concentrations [35–37]. Higher weight additions may be difficult from a processing perspective, because the viscosity of the dispersions increases significantly at increased loads of clay. The use of nanoparticles in paper and board coating is thus advantageous, particularly given that less material is required (thinner coating layers) to reach the desired barrier or mechanical properties. Less material use leads to reduced costs and reduced amounts of waste [38]. Southern Clay Products and Nanocor are among the biggest suppliers of montmorillonite clays for nanocomposite applications. The addition of a nano filler is made to reinforce the polymer, i.e. to increase the strength and toughness of the material [39]. Other issues are to enhance the optical, thermal or barrier properties. The mechanism of barrier improvement relies on increasing the path length that the molecules have to traverse while diffusing through the film, i.e. forcing them to take a tortuous path, which leads to significantly prolonged transmission rates. The barrier properties of a nanocomposite material depend on the relative orientation of the silicate layers and on the state of aggregation and dispersion. The plate-like structure of clay increases the path for diffusing molecules, thus decreasing the permeability of molecules through the material [40]. Porous nanoparticles into which the diffusing molecules can penetrate

are also efficient in this respect [41]. Improvement of barrier properties by up to four orders of magnitude upon incorporation of nanoclays in a polymer coating has been reported. The lack of a completely exfoliated structure has been used to explain why an efficient reduction in WVTR could not be observed when montmorillonite clays were dispersed in a barrier latex [42]. The incorporated clay particles can inhibit crystallization of the polymer matrix by restricted chain mobility through the association with the clay plates. This has led to an increase in the tensile strength of starch/polyester blends with increased montmorillonite content. Fischer et al. reported the blend of a thermoplastic starch with clay particles using a modifier (e.g. cat ionized starch) which is compatible with both the clay and the matrix. The results observed were a homogeneous incorporation of clay particles in the starch matrix, followed by an easier processing and a strong decrease in hydrophobicity. The stiffness, strength and toughness of the film could also be changed by changing the water content. Homogeneous dispersion of nanoparticles in nematic crystal matrices of liquid crystalline polymers has also been observed [40]. Nanoclays have been demonstrated to reduce both the water vapor and the OP of PLA and PLA-PCL films. The use of nanosized materials in food packaging should be approached so as to minimize the potential risks with inhalation or ingestion of small particles that can have unhealthy effects on the human body [41]. However, overall migration tests and analysis of specific metals (Fe, Mg and Si) have shown no change in the quantity of these species in food that has been in contact with a potato starch/clay nanocomposite film (Figure 4).

Characterization and Test Methods

The coated specimens should condition for 24 h at 23°C and 50% relative humidity before any measurements, this is as per ISO standards.

Scanning electron micrographs (SEM) SEM of the surfaces of the samples is obtain with a Digital Scanning Electron Microscope.

X-ray diffraction (XRD) is employ to estimate the degree of orientation of the clay particles in the polymer film. The measurements should perform in the cross-direction of the coating.

Electron spectroscopy for chemical analysis (ESCA) is use to assess the chemical composition of the surface of the coatings on paper.

Water vapor transmission rate, WVTR, is measure using gravimetric cups according to TAPPI method T 448 om-97. Silica gel, 35 ± 0.1 g in each cup, as the desiccant WVTR g/ (m² day⁻¹) is calculate

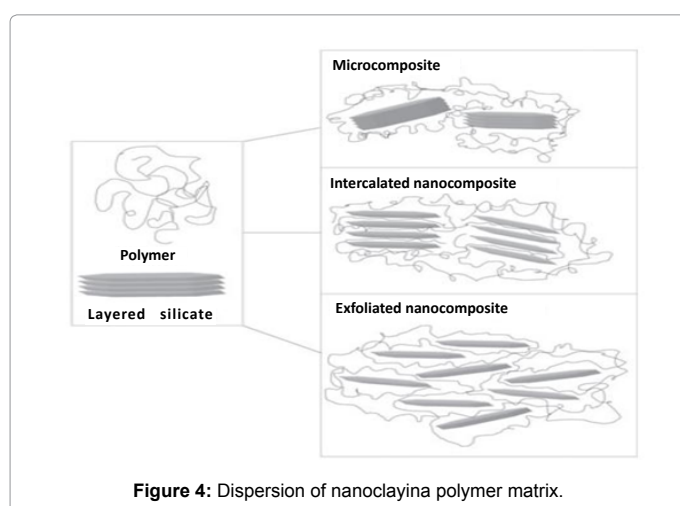


Figure 4: Dispersion of nanoclay in polymer matrix.

by dividing the slope of total weight and number of days by the sample area. All samples need conditioning as per ISO conditions for at least 24 H prior to measurements.

OTR: Oxygen transmission measurements is perform with Oxygen Permeation Analyser The tests were carried out at 23°C and 0, 50, and 80% relative humidity as per ISO standards

Water contact angle: Water contact angles of the coated surface is measure in test conditions of 23°C and 50% relative humidity. Contact angle values is measure as a function of time.

Cobb test: This is important test to determine the water resistant properties of paper. This test can be done by Cobb tester.

Conclusions

Polymer-nano clay is good choice in the development of new functionality of paper by coating. While there is still further research needed to reach the requirements set on all types of functional properties as well as on material availability, process ability, suitability for product contact, etc., the remaining hindrance to be overcome is, in most cases, the cost. Although the price for materials and processing will increase with increased modification of polymers and clay. Reduction of the final price for each package should be achievable by increased volume of production. However, there exists no universal barrier chemical that covers all potential applications and still fulfil is all possible requirements. Future functional surface treatment of Paper will most likely involve multilayer coatings where each single layer makes its own specific, property-based contribution with its specific properties to the overall performance of the coated products. Replacing one or more barrier layers consisting of plastic film in demanding packaging especially with bio-based polymers.

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