

Preparation of Organophilic Montmorillonite and its Application in Alkyd Coatings

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ABSTRACT

Organophilic montmorillonite intercalates were prepared by a cationic exchange process by interaction between the Na⁺ ions of montmorillonite and ammonium salt of octadecylamine. Fourier-transform infrared spectrometry (FT-IR) and X-ray diffraction analyses of the compounds were carried out. Layer spacing of modified montmorillonite and unmodified montmorillonite were calculated using Bragg's Law. FT-IR and X-ray profiles showed organophilic characteristic in modified montmorillonite with layer spacing increased by twice of magnitude relative to unmodified montmorillonite. Application of prepared organoclay in alkyd-based clear coatings showed significant enhancement in hardness of coating film relative to the equal amounts of unmodified montmorillonite incorporated in coating formulations.

Keywords: Montmorillonite, organoclay, alkyd coatings

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INTRODUCTION

A variety of inorganic materials, such as glass fibers, talc, calcium carbonate, and clay minerals, have been successfully used as additives or reinforcement to improve the stiffness and strength of polymers. The degree of enhancement depends on many factors degree of dispersion and orientation in the matrix, and the adhesion at the filler-matrix interface. In General, inorganic materials neither have good interaction with organic polymers to achieve good dispersion nor adequate adhesion. As a result, surface treatments are common.

Recently, silicate type clays such as montmorillonite, hectonite, and saponite have received a great deal of attention as reinforcing materials for polymers due to their potentially high aspect ratio and unique intercalation/exfoliation characteristics. Montmorillonite clay employed by the coatings industry is either hectorite or bentonite clays (Hare, 1994). Bentonite clays are widely used in paint particularly in interior water-based paint due to high affinity for water and function as viscosity modifier to the paint. However, some type of clays can be used as fillers in paint formulation to adjust the total volume of pigment in dry paint film without excessive cost. Since montmorillonites are filled with sodium cations, the hydrophilic properties are enhanced and lead to a high degree of swelling in water. This causes difficulty to achieve completely intercalation/exfoliation of montmorillonites in polymer matrix. To achieve a better interaction with organic polymers, the sodium cations present on the surface of montmorillonite are exchanged with organic molecules with a cation group, e.g. alkylammonium ions to produce organoclay (Chen, *et al.* 2003). The incorporation of organoclay into thermoplastic polymer matrix was disclosed by Nahin and Backlund of Union Oil Co. (Nahin and Backlund, 1963).

Recently, preparation of polymer nanocomposites using organophilic clay has

drawn the attention of many researchers, because the dimension and microstructure of the dispersed phase significantly affect the properties of polymer composites. Polymer-clay nanocomposites often exhibit better mechanical and chemical properties, compared with their macrocomposite counterparts (Fu, *et al.* 2000; Yeh, *et al.* 2002; Brus, *et al.* 1989).

Alkyd resin, an oil modified polyester, is one of the most widely used in exterior solvent-based coatings due to its high gloss and durability (Lambourne, 1993). However, alkyd resins possess flexibility at a certain level due to long chain fatty acid of oil using in modification. In this study, organophilic montmorillonite intercalates were prepared using a cationic exchange process by interaction between the Na⁺ ions of montmorillonite and ammonium salt of octadecylamine, and characterize these intercalates. Prepared organoclay was then incorporated in alkyd clear coating formulation by varying the amount of organoclays and mechanical properties were tested.

EXPERIMENTAL

Preparation of modified montmorillonite

Na-montmorillonite (Na-MMT) was supplied by Siam Nippon Co., Ltd. For preparation of octadecyl ammonium organophilic compounds, 1.08g octadecyl amines was mixed with concentrated 1mL HCl and 15 ml water and heated at 80°C for a few minutes, and then mixed with 2.5g Na-montmorillonite dispersed at 80C with 100ml water. The mixture was stirred vigorously for half an hour. The white precipitate thus formed was filtered and washed repeatedly to make it free from chloride ions. The sample was subsequently dried in air, and then dried in the oven about 50°C for 4 hours. The modified montmorillionite (Mo-MMT) was then ground and sieved with particle size of 100 mesh before characterization.

IR and X-ray diffraction characterization

The IR spectra of the samples were recorded on KBr pellets using a Nicolet Impact 400D infrared spectrometer having a frequency response varying from 200 to 4000 cm^{-1} . The X-ray diffraction (XRD) intensities of clay samples were recorded with Rigaku Rint 2000 DMAX diffractometer using monochromatic $\text{Cu K}\alpha$ radiation. Interlayer spacing (d-spacing) was calculated according to Bragg's law (Cullity, 1978).

Organoclay application in coating

Synthetic organoclay was incorporated in clear alkyd-based coating formulations using high-speed disperser with speed 400 rpm for 30 min. The coatings were varied in the amount of Mo-MMT and Na-MMT incorporated from 0-5% by weight to the

formulations. The coating with film thickness of 60 micron were coated on tin plates and let dry for 7 days before testing. Hardness ASTM D 2240, (2002) and impact strength ASTM D 5628, (2002) of coating films were tested relative to coatings formulated with Na-MMT.

RESULTS AND DISCUSSION

The preparation of the organoclay was based on the ion-exchanged reaction. The synthetic organoclays were made by the treatment of sodium monmorillonite (Na-MMT) with primary ammonium ions. The characterization of Na-MMT and corresponding Mo-MMT by Fourier Transform Infrared Spectrometer (FT-IR) is shown in Figure 1.

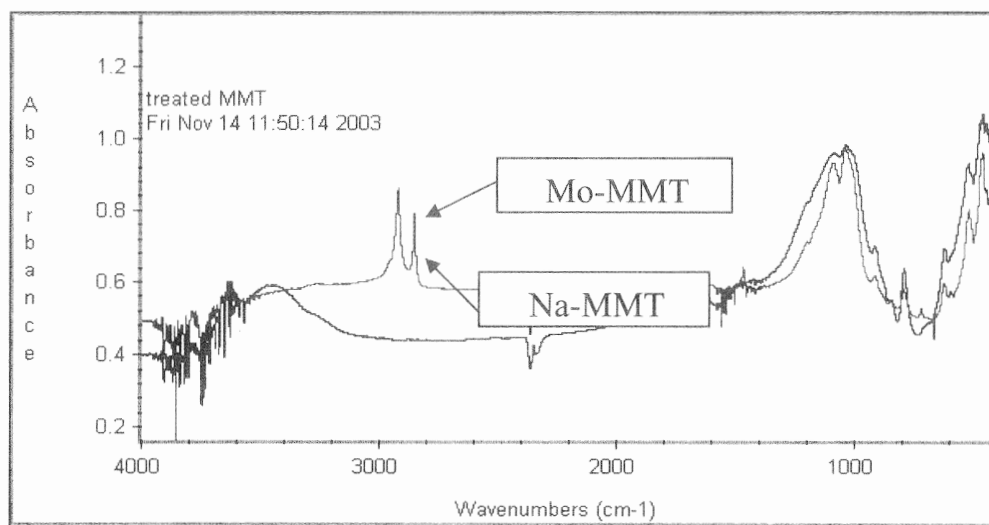


Figure 1 IR spectra of pure Na-MMT and octyldodecyl amine modified MMT.

The spectra of the Mo-MMT shows the presence of two new bands at about 3000 and 2900 cm^{-1} , which are due to NH_3^+ stretching and C-H stretching of aliphatic hydrocarbon of octyldodecyl chain (Socrates, 1980). This confirms the octadecylammonium intercalation in the interlayer spaces of Na-MMT. In addition, the interlayer spacing

of Na-MMT and Mo-MMT can be identified from X-ray diffraction patterns. X-ray diffraction patterns of compound samples; Na-MMT and Mo-MMT, were taken using $\text{Cu K}\alpha$ sources with wavelength of 1.5405\AA . X-ray diffraction results are shown in Figure 2.

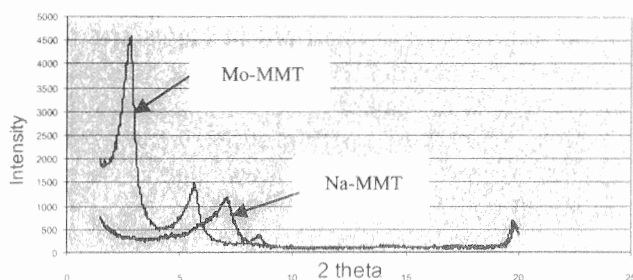


Figure 2 X-ray diffraction patterns of Na-MMT and Mo-MMT.

From x-ray diffraction pattern of Na-MMT, there is a peak at 2-theta value of 7.1, whereas the Mo-MMT x-ray pattern shows the highest intensity peak at 2-theta value of 2.84. This means after organophilic modification of montmorillonites, the diffraction was shifted to lower 2-theta. According to Bragg's law, interlayer spacing (d-spacing) can be calculated if the 2-theta value is known. Hence, by using 2-theta values from X-ray diffraction patterns corresponding to Na-MMT and Mo-MMT, the interlayer spacing were 12.44 \AA with $2\theta = 7.1$ and 31.1 \AA with $2\theta = 2.84$, respectively. This shows that cation exchange process of Na-MMT using octadecyl ammonium salt gave intercalated montmorillonites with interlayer spacing increased more than twice of unmodified montmorillonites (Na-MMT). The increment of interlayer came from long chain alkyl of octadecyl ammonium salts underwent cation exchange with sodium salts (Na^+) in clay lattice.

Application of prepared organoclay in coatings formulation

Prepared organoclay was incorporated into clear coating formulation using alkyd resin as a binder. The coatings were coated onto tin plates using a film applicator with thickness of 60 micron and dried for 7 days before tested. Hardness and impact strength of dried films were measured to evaluate the reinforcing effect of the organoclay. Film hardness measurement indicates the minimum weight in

grams required to make a scratch mark on the coating film. Figure 3 and 4 summarized hardness and impact strength properties of the coating film as a function of the organoclay content, respectively.

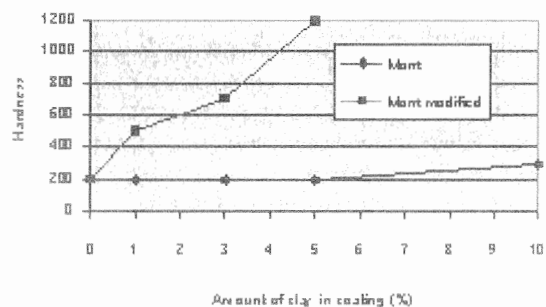


Figure 3 Hardness of coating film as a function of organoclay.

Hardness of dried coating films with unmodified montmorillonite remains at the levels of the film without montmorillonite up to 5% by weight of unmodified montmorillonite, and then increases slightly when the amount of unmodified montmorillonite increased to 10% by total weight formulation. On the other hand, hardness of the coating film with organoclay drastically increases as the amount of organoclay increased. By comparison at the same clay content at 5% by weight, hardness of films with organoclay is greater than that with unmodified montmorillonite by approximately 6 times. This indicates that incorporation of organoclay in alkyd coatings possibly causes exfoliated structures due to significant improvement in mechanical properties (Chen, *et al.* 2003). This can be supposed that long chain hydrocarbon of octadecyl ammonium salts, used in clay modification and resided in interlayer of organoclay, provide well-compatible with long chain hydrocarbon of fatty acid in alkyd resin. Thus, alkyd resins can diffuse in interlayer of organoclay causing exfoliate structures which corresponds to drastically increment of hardness.

Impact strength of coating films was measured by means of forwarding weight drop down (ASTM 5628, 2002). The maximum weight required not to damage the coating films were taken. From figure 4, the impact strength of coating films with organoclays incorporated is greater than that of coating films from neat alkyd resins. In addition, the films with organoclays showed greater impact strength than those with unmodified montmorillonites. This indicates that organophilic part of organoclays promotes exfoliate structures when alkyd resin is incorporated, whereas unmodified montmorillonites possess hydrophilic characters causing them incompatible with the hydrophobic alkyd resin. As a result, coating films incorporated with organoclays provided higher impact strength.

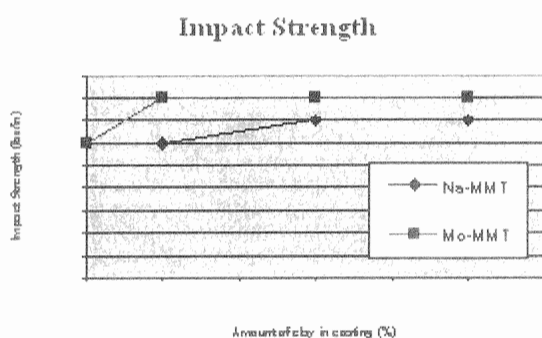


Figure 4 Impact strength of coating film as a function of organoclay.

CONCLUSIONS

Organoclay was prepared by cationic exchanged between sodium ions montmorillonites and octadecyl ammonium salts. Organoclay exhibit intercalate characteristic with interlayer spacing of twice in magnitude compared to unmodified montmorillonite. Coating films formulated with organoclay impart greater hardness and impact strength than those without organoclay.

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