

Nanocomposite Alkyd Coatings

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ABSTRACT: Organophilic montmorillonite intercalants were prepared by a cation-exchange process between Na⁺ ions of montmorillonite and ammonium salt of octadecylamine. Fourier transform infrared (FTIR) spectrometry and X-ray diffraction analyses of the compounds were carried out. The layer spacings of both modified and unmodified montmorillonites were calculated with Bragg's law. FTIR and X-ray profiles showed organophilic characteristics for the modified montmorillonite, the layer spacing of which increased by two orders of magnitude with respect to that of the unmodified montmorillonite. The prepared organo-

clay was incorporated into an alkyd-based clear coating, and X-ray profiles showed an exfoliated structure for the organoclay alkyd coating. The application of the prepared organoclay to alkyd-based clear coatings showed a significant enhancement of the hardness and impact strength of the coating film compared with those of unmodified montmorillonite equally incorporated into the coating formulations. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2639–2642, 2006

Key words: coatings; nanocomposites; organoclay

INTRODUCTION

The word *nanocomposite* refers to composites whose reinforcements have at least one dimension on the nanometer scale.^{1,2} To make a successful nanocomposite, it is very important that the inorganic material be dispersed throughout the polymer. If a uniform dispersion is not achieved, agglomerates of inorganic materials are found within the host polymer matrix, thus limiting property improvement.

Recently, silicate-type clays such as montmorillonite, hectonite, and saponite have received a great deal of attention as reinforcing materials for polymers because of their potentially high aspect ratios and unique intercalation/exfoliation characteristics. The montmorillonite clay employed by the coating industry is either hectorite or bentonite.³ Bentonite clays are widely used in paint, particularly in interior water-based paint, because of their high affinity for water and function as a viscosity modifier. However, some types of clay can be used as fillers in paint formulations to adjust the total volume of the pigment in the dry paint film without excessive cost. Because montmorillonites are filled with sodium cations, the hydrophilic properties are enhanced, leading to a high degree of swelling in water. This makes it difficult to achieve a complete intercalation/exfoliation of mont-

morillonites because of the hydrophobic nature of most polymers. To produce an exfoliated nanocomposite, a high degree of wetting of polymer chains onto clay particles is required so that the polymer chains are exfoliated between the clay galleries. To achieve better interaction between clay particles and organic polymers, the sodium cations present on the surface of montmorillonite are exchanged with organic molecules containing cationic groups, such as alkyl ammonium ions, to produce an organoclay.⁴ The obtained organoclay, which is more hydrophobic, is incorporated into a thermoplastic polymer matrix to produce nanocomposite materials. The incorporation of an organoclay into a polymer matrix was first disclosed by Nahin and Backlund of Union Oil Co.⁵ Polymer-clay nanocomposites often exhibit better mechanical and chemical properties, compared with their macrocomposite counterparts,^{6–8} because of the dimensions and microstructure of the dispersed phase of organoclay, which significantly affect the properties of polymer composites.

Alkyd resins, oil-modified polyesters, are among the most widely used resins in exterior solvent-based coatings because of their high gloss and durability.⁹ However, alkyd resins possess flexibility at a certain level because of the long-chain fatty acid of the oil used in the modification. In this study, organophilic montmorillonite intercalants were prepared with the cation-exchange process between Na⁺ ions of montmorillonite and ammonium salt of octadecylamine. The prepared organoclay was characterized and incorporated into alkyd clear-coating formulations, and the mechanical properties were tested.

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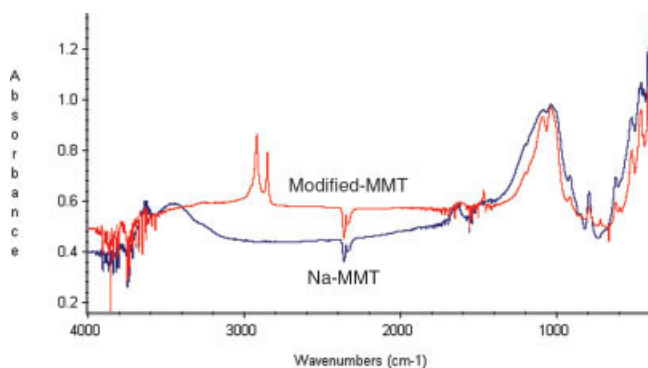


Figure 1 FTIR spectra of pure Na-MMT and octyl dodecyl amine modified MMT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

EXPERIMENTAL

Preparation of modified montmorillonite (Mo-MMT)

Sodium montmorillonite (Na-MMT) was supplied by Siam Nippon Co., Ltd. (Bangkok, Thailand). For the preparation of octadecyl ammonium organophilic compounds, 1.08 g of octadecylamine was mixed with concentrated HCl (1 mL) and 15 mL of water, heated at 80°C for a few minutes, and then mixed with 100 mL of a Na-MMT dispersion (2.5 g of Na-MMT dispersed in 100 mL of water at 80°C). 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 precipitate was subsequently dried in air and then in an oven at about 50°C for 4 h. Mo-MMT was then ground and screened through a 100-mesh sieve before characterization.

Fourier transform infrared (FTIR) and X-ray diffraction (XRD) characterization

The FTIR spectra of the samples were recorded on KBr pellets with a Nicolet Impact 400D infrared spectrometer (Madison, Wisconsin) having a frequency response varying from 200 to 4000 cm^{-1} . The XRD intensities of the clay samples were recorded with a Rigaku Rint 2000 DMAX diffractometer (Tokyo, Japan) with monochromatic $\text{Cu K}\alpha$ radiation. The interlayer spacing (d -spacing) was calculated according to Bragg's law.¹⁰

Organoclay application in coating

Synthetic organoclay was incorporated into alkyd-based clear-coating formulations with a high-speed disperser at a speed of 400 rpm for 30 min. The coatings contained Mo-MMT and Na-MMT, from 0 to 5 wt %, according to the formulations. The coatings, with a film thickness of 60 μm , were coated onto tin plates and allowed to dry for 7 days before testing. The hard-

ness (ASTM D 2240¹¹) and impact strength (ASTM D 5628¹²) of the coating films were tested with respect to those formulated with Na-MMT.

RESULTS AND DISCUSSION

The preparation of the organoclay was based on the ion-exchange reaction. The synthetic organoclays were made through the treatment of Na-MMT with primary ammonium ions. The characterization of Na-MMT and corresponding Mo-MMT by FTIR is shown in Figure 1.

The spectra of Mo-MMT show the presence of two new bands at about 3000 and 2900 cm^{-1} due to NH_3^+ stretching and C—H stretching of the aliphatic hydrocarbon of the octadecyl chain.¹³ This can be explained as follows: the octadecyl chains reside in the d -spacing of Na-MMT. In addition, the d -spacing of Na-MMT and Mo-MMT can be identified from the XRD patterns. The XRD patterns of the samples (Na-MMT and Mo-MMT) were taken with $\text{Cu K}\alpha$ sources with a wavelength of 1.5405 Å. The XRD results are shown in Figure 2.

In the XRD pattern of Na-MMT, there is a peak at a 2θ value of 7.1, whereas that of Mo-MMT shows its highest intensity peak at a 2θ value of 2.84°. This means that after the organophilic modification of the montmorillonites, the diffraction shifted to lower 2θ values. According to Bragg's law, the d -spacing can be calculated if the 2θ value is known. Hence, with 2θ values from XRD patterns corresponding to Na-MMT and Mo-MMT, the d -spacing values were 12.44 Å with $2\theta = 7.1^\circ$ and 31.1 Å with $2\theta = 2.84^\circ$, respectively. This shows that the cation-exchange process of Na-MMT with octadecyl ammonium salt gave intercalated montmorillonites with d -spacing values more than twice those of unmodified montmorillonites (Na-MMT). The increase in the d -spacing came from the exchange of the long-chain alkyl of octadecyl ammonium salts with sodium salts (Na^+) in the clay lattice. Here intercalated montmorillonite is a so-called organoclay.

Prepared organoclay and unmodified clay were incorporated into clear-coating formulations with the

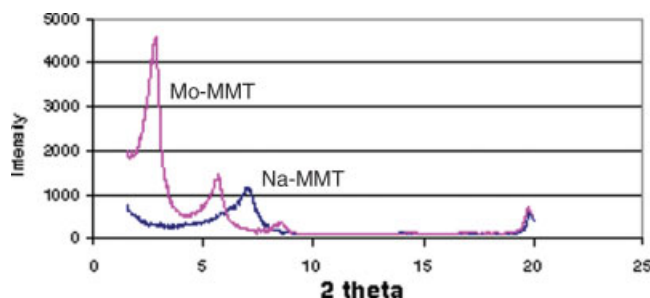


Figure 2 XRD patterns of Na-MMT and Mo-MMT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

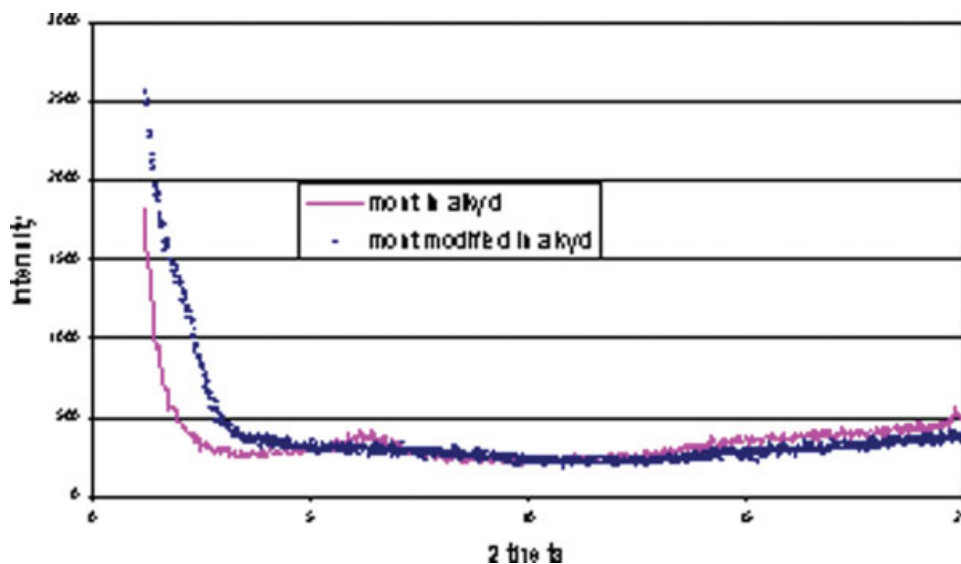


Figure 3 XRD patterns of Na-MMT and Mo-MMT in an alkyd resin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

alkyd resin as a binder. The coatings were then coated onto tin plates and dried for 7 days before investigation. The XRD profiles are shown in Figure 3. The XRD profile of the organoclay incorporated with the alkyd resin did not show the 2θ peak at 7.1° , whereas the unmodified clay still showed a trace of it. This can be explained as follows. The alkyd resin in the organoclay-alkyd coating formulation caused the exfoliation of the structure of the organoclay. Therefore, the organoclay-alkyd coating could be considered a nanocomposite.

Meanwhile, there remained a small peak on the unmodified montmorillonite-alkyd coating profile. The small peak was at the same position as that found in the unmodified montmorillonite XRD profile. This meant that the alkyd resin did not provide complete exfoliation of the clay crystals.

Application of the prepared organoclay in the coating formulation

The prepared organoclay was incorporated into a clear-coating formulation with the alkyd resin as a binder. The coatings were coated onto tin plates with a film applicator with a thickness of $60\ \mu\text{m}$ and dried for 7 days before the testing. The hardness and impact strength of the dried films were measured to evaluate the reinforcing effect of the organoclay. Film hardness measurements indicated the minimum weight in grams required to make a scratch mark on the coating film. Figures 4 and 5 summarize the hardness and impact strength properties of the coating films as a function of the organoclay content, respectively.

The hardness of the dried coating films with unmodified montmorillonite remained at the levels of the film without montmorillonite up to 5 wt % unmodified montmorillonite and then increased slightly when

the concentration of unmodified montmorillonite increased to 10%. On the other hand, the hardness of the coating film with organoclay dramatically increased as the amount of organoclay increased. At the clay concentration of 5 wt %, the hardness of the films with organoclay was greater than that of unmodified montmorillonite by approximately 6 times. Because of the significant improvement in the mechanical properties, it is possible that the incorporation of organoclay into alkyd coatings causes exfoliated structures of the organoclay.⁴ It can be supposed that the long-chain hydrocarbon of octadecyl ammonium salts, used in clay modification and residing in the interlayer of the organoclay, is quite compatible with the long-chain hydrocarbon of the fatty acid in the alkyd resin. Thus, the alkyd resin can diffuse into the interlayer of the organoclay, causing exfoliated structures, which correspond to a dramatic increase in the hardness.

The impact strength of the coating films was measured by forwarding weight drop down (ASTM 5628). The maximum weight required not to damage the coating film was taken. Figure 5 shows that the impact

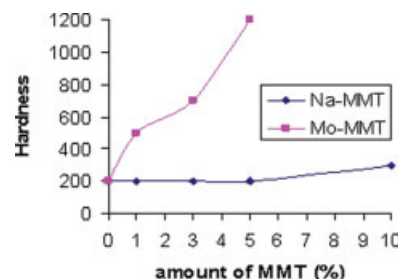


Figure 4 Hardness of the coating film as a function of the organoclay. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

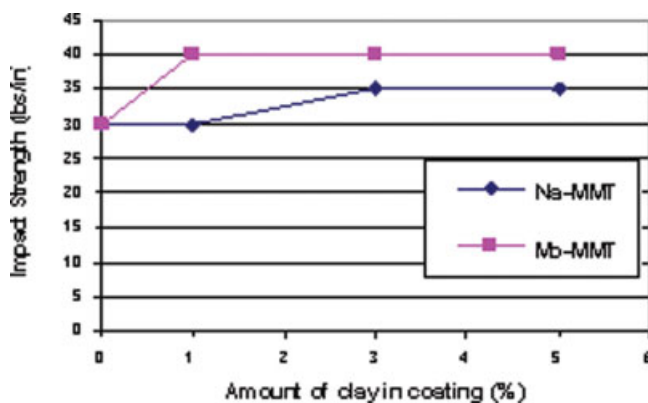


Figure 5 Impact strength of the coating film as a function of the organoclay. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

strengths of the coating films with organoclays incorporated were greater than those of the coating films with neat alkyd resins. In addition, the films with organoclays showed greater impact strength than those with unmodified montmorillonites. This indicates that the organophilic part of organoclays promotes exfoliated structures when the alkyd resin is incorporated, whereas unmodified montmorillonites possess hydrophilic character, causing incompatibility with the hydrophobic alkyd resin. As a result, coating films incorporated with organoclays provide higher impact strength.

CONCLUSIONS

The organoclay prepared by cation exchange between sodium ion montmorillonites and octadecyl ammonium salts exhibited intercalating characteristics with *d*-spacing 2.5 times greater than that of unmodified montmorillonite. The alkyd resin, incorporated into

the organoclay, imparted an exfoliated structure to the organoclay and resulted in an alkyd coating nanocomposite. The coating films formulated with the organoclay showed greater hardness and impact strength than those formulated with unmodified montmorillonite.

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