## Montmorillonite Clay/Poly(methyl methacrylate) Hybrid Resin and Its Barrier Property to the Plasticizer Within Poly(vinyl chloride) Composite

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ABSTRACT: A poly(methyl methacrylate) (PMMA)-clay hybrid resin was prepared *via* bulk polymerization methyl methacrylate monomer in the presence of montmorillonite intercalated with an ammonium salt of dctadecylamine. The products were characterized by infrared spectroscopy, X-ray diffraction, pyrolysis gas chromatography, and transmission electron microscopy. Results confirm that the resin is intercalated with PMMA molecules. The layer spacing of montmorillonite are enlarged, whereas the silicate layers are homogeneously dispersed individually. When the PMMA-clay hybrid was blended with plasticized poly(vinyl chloride), the resulting composite exhibited excellent barrier property in preventing the plastizer's migration from the inner matrix to the surface of the product. This is presumably caused by barrier property of the silicate layers dispersed in the composite. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 425–430, 1999

Key words: clay; PMMA; barrier property; plasticizer migration

### **INTRODUCTION**

In recent years, the high technical usages of clays are expanding. Montmorillonite (MMT) is a clay mineral consisting of stacked silicate sheets whose thicknesses are 10 Å. It undergoes intercalation with various organic molecules. Through intercalation, a large number of polymer-clay nanocomposites have been prepared like nylonclay hybrid,<sup>1,2</sup> PS-clay hybrid,<sup>3,4</sup> poly(methyl methacrylate) (PMMA)-clay hybrid,<sup>5</sup> epoxy-clay hybrid,<sup>6</sup> etc. These types of organic-inorganic nanocomposites can potentially show hybrid properties synergistically derived from both the host (clay) and guest (polymer).<sup>7</sup>

A MMT is composed of stacked silicate sheets that provide high molecular barrier properties, as do the polymeric hybrid material. For the plasticized poly(vinyl chloride) (PVC) materials, the migration of plasticizer has become quite a big problem. To prevent the plasticizer migrating from the inner PVC matrix to the surface of the product or the space has great value.<sup>8,9</sup>

In this article, the synthesis and properties of PMMA-clay hybrid and its migration resistance to the plasticizer in PVC/PMMA-clay composite were studied. Results show that, when a specific

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ammonium ion is chosen as the intercalating reagent, MMT dispersed homogeneously in methyl methacrylate (MMA) monomer that allows MMT dispersing in PMMA matrix in the monolayer form. By blending PMMA-clay hybrid resin with PVC, the PVC composites were obtained. The composite shows much better migration resistance to plasticizer (di-*n*-butyl phthalate) than that of the composite made by common blending.

### **EXPERIMENTAL**

#### **Materials**

The clay is a Na<sup>+</sup>-type MMT clay, with a cation exchange capacity of 115 mEq/100 g. MMA was purified through vacuum distillation. Benzoyl peroxide (BPO) was purified through recrystallization with CHCl<sub>3</sub> and the precipitant of CH<sub>3</sub>OH. Other inorganic and organic reagents are commercially available.

### **Preparation of Organophilic Clay**

In 400 mL of water, 50 g of Na<sup>+</sup>-type MMT was added to the solution of dctadecylbenzyltrimethyl ammonium chloride (30%) ( $18Me^+Cl^-$ ) and the mixture was stirred vigorously at 70°C for 1 h. A white precipitate was isolated by filtration, placed into a 1000 mL beaker containing 500 mL of hot water, and agitated for 1 h. This process was repeated twice to remove the residue of  $18Me^+Cl^-$ . The organophilic MMT (18Me-MONT) was then filtrated and dried. In the same preparations, instead of dctadecylbenzyltrimethyl ammonium chloride, dodecyl benzyltrimethyl ammonium chloride ( $12Me^+Cl^-$ ) was used as the intercalating reagent. Thus, 12Me-MONT was obtained.

### Preparation of PMMA-Clay Hybrid Resin

In a 250-mL three-neck flask were placed 8.0 g of 18Me-MONT, 100 mL of purified MMA, 0.5 g of BPO, and 5.0 mL of toluene. The mixture was stirred vigorously to disperse the organophilic clay homogeneously. The mixture was then heated to 85°C and stirred for  $\sim$  5 h. Afterwards, the system was kept at 85°C for 24 h. A transparent resin was obtained.

# Manufacture of the Composite of PVC/PMMA-Clay Hybrid Resin

The ingredients in Table I were mixed intensely

| Table I | <b>Ingredients for the Preparation of</b> |
|---------|---|
| PVC/PM  | MA-Clay Hybrid Composite                  |

| Ingredients                                      | Amount (g)                |
|--|---------------------------|
| PMMA-clay hybrid<br>PVC<br>DBP<br>Tin mercaptide | $100 \\ 100 \\ 30 \\ 0.2$ |

(for the convenience of extruding, 30% of dibutyl phthalate (DBP) was added into the composite) and rolled on a twin-roller at 140°C for 10 min. The blend was extruded on a 400XZ extruder at 180°C to get composite samples with 10 mm in length and 2.5 mm in diameter. The PVC/PMMA-clay hybrid specimens alike were maintained in a dry state.

Other blends for comparison were made in the same procedures, except that the PMMA-clay hybrid resin was replaced by PMMA, organophilic clay, Na<sup>+</sup>-type MMT clay, or other PMMA-clays, respectively.

### **Characterization and Measurements**

X-ray measurement used  $\text{CuK}_{\alpha}$  or  $\text{Co-K}_{\alpha}$  radiation, operated at 40 KV and 40 MA. All the samples for X-ray diffraction measurement were processed to powder form. Transmission electron microscopy (TEM) was obtained with a JEM-100CX II TEM using an acceleration voltage of 100 KV. Samples for the TEM test were slice to thin sections, with the thickness of no more than 500~800 Å. The infrared (IR) spectra for the composite extracted were recorded on a PE-983 spectrophotometer in the range of 4000 cm<sup>-1</sup>–400 cm<sup>-1</sup>. The KBr pellet method was used. Pyrolysis gas chromatography (PGC) testing was on the 102G gas chromatograph with the following condition:

Column temperature: 100°C;

pyrolysis temperature: 660°C; N<sub>2</sub>: 25 mL min<sup>-1</sup>;

 $H_2$ : 40 mL min<sup>-1</sup>;  $O_2$ : 700 mL min<sup>-1</sup>.

The barrier property of the hybrid was estimated by the following experiment: immerse the extruded composite samples (exactly weigh their weights;  $W_0$ ) into CH<sub>3</sub>CH<sub>2</sub>OH/DBP solution (w/w 70/30) for hours, take them out, and carefully weigh their weights ( $W_1$ ) after quickly wiping up



Organo-MMT PMMA/clay hybrid

**Figure 1** Dispersive behavior of MMT in water, organic solvent (MMA), and polymer (PMMA).

their surface. Weigh the samples in each time interval. The same procedures were taken during the experiment when the samples were dried at 60°C for days.  $CH_3CH_2OH$  was just a medium for DBP; it diluted the solution so that the samples may not be dissolved by DBP. The uptake of  $CH_3CH_2OH$  by the samples was nearly zero; thus the weight changes of the samples could be thought to be the contribution of the uptake or the loss of the DBP. The weight change rate was calculated by the following formula:

$$|W_1 - W_0| / W_0 \times 100\%$$

### **RESULTS AND DISCUSSION**

### Synthesis and Characterization

Hydrophilic Na<sup>+</sup>-type MMT is composed of sodium ions and negatively charged MMT. For providing MMT with organophilicity, one can make good use of its excess negative charges to combine with organic cation results in organophilic MMT intercalated with organic cation. When specific ammonium ions are chosen as intercalating reagents, organophilic MMT disperses homogeneously in MMA. It gives the possibility of the preparation of PMMA-clay nanodispersion composite (Figure 1). By appearance, 18Me-MONT was more dispersible in MMA than 12Me-MONT. It indicated a longer carbon chain makes MMT more organophilic.

Figure 2 shows the X-ray diffraction curves of Na<sup>+</sup>-type MMT, 12Me-MONT, and 18Me-MONT in the region from  $2\theta = 3-10^{\circ}$ . Each curve has one peak, at  $2\theta = 5.89^{\circ}$ , 5.80°, and 5.02°, respectively.

These peaks are assigned to the 001 lattice spacing of MMT. The lattice spacing corresponds to an interlayer spacing of organophilic MMT. Therefore, the interlayer spacing of Na<sup>+</sup>-type MMT, 12Me-MONT, and Me-MONT are 14.0, 14.8, and 16.3 Å, respectively.

Data indicate that longer carbon chains lead to the bigger interlayer spacing MMT, and it is helpful for MMA monomer to intercalate into the interlayer and polymerizes in-between silicate layers.

Figure 3 displays the X-ray diffraction curves of PMMA-clay hybrids. The curve of the resin using 18Me-MONT as organophilic MMT shows no peak in the region from  $2\theta = 2^{\circ}-10^{\circ}$  (i.e., the peak of 18Me-MONT in the PMMA matrix has no specific interlayer spacing). The result implies that 18Me-MONT disperses homogeneously in the form of an individual layer within the PMMA matrix.

The curve of the hybrid resin with 12Me-MONT exhibits a peak at  $2\theta = 5.52^{\circ}$ ; the corresponding interlayer spacing of MMT is 16.8 Å. It reveals that a part of MMT was not dispersed homogeneously into the PMMA matrix when 12Me-MONT was used as an organophilic MMT. These results indicate that the organophilicity of MMT in the MMA monomer is important for the synthesis of the PMMA-clay hybrid, where MMT is dispersed in the individual layer.



**Figure 2** X-ray diffraction curves of (a) Na<sup>+</sup>-type MMT, (b) 12Me-MONT, (c) 18Me-MONT.



**Figure 3** X-ray diffraction curves of PMMA-clay hybrids with (a) 12Me-MONT and (b) 18Me-MONT. (The content of clay in the hybrids is 6%.)

A transmission electron micrograph of the hybrid discloses quite clearly the existence of welldispersed individual silicate layers (dark lines in Figure 4), with a 1 nm span embedded in the PMMA matrix. Some areas of the PMMA matrix appear to contain oriented aggregates of 5–10 parallel silicate layers. These domains of parallel layers are presumably remnants of organophilic clay lactoids, but with substantial expansion of the gallery beyond that corresponding to an intercalated silicate phase. It is particularly interesting to note that the samples are mostly homoge-



Figure 4 TEM of the PMMA-clay hybrid.



Figure 5 IR spectra of (a) organo-MMT and (b) extracted hybrid products.

neous, with phase separation between the silicate layers and the PMMA matrix.

The interaction between PMMA and silicate layer has been studied by IR. A part of the product was extracted with hot  $CHCl_3$  for 5 days to remove those nonbonded PMMAs. The unextractable PMMA, which can be regarded as the bonded one (to silicate layer), was verified by IR spectra (Figure 5). The IR spectrum gives an instinct absorption at 1735 cm<sup>-1</sup> (C=O stretching) that is the consequence due to the characteristic frequencies of PMMA. Many other articles<sup>10,11</sup> indicated that there are thoroughly physical interactions between the polymer and silicate layers. Our result coincides with work by Lee and colleagues<sup>5</sup>; there may be some supramolecular interaction between PMMA and the silicate layer.

Figure 6, the PGC, shows an instinct peak at 3.50 min, which has been proven to correspond to the characteristic peak of the monomer of MMA, by comparing it with the PGC of the PMMA standard sample.

### **Barrier Properties**

Silicate layers have excellent barrier property to almost all molecules. We aim to use this perfor-



**Figure 6** PGC of (a) PMMA and (b) extracted hybrid

products.

mance to prevent the migration of some small molecules from the inner composite matrix to the surface. This may have practical application for the plasticized PVC materials. Deducing the migration of plasticizer, such as DBP and diisooctyl phthalate, from inner materials to the surface of the product has a significant meaning. The barrier property of the composite was estimated by calculating the weight change of the samples, after being immersed in some solution. The results are shown in Figure 7. Figure 7 indicates that the weight of samples increase with the immersed time, and the graph of the PVC/PMMAclay hybrid shows the gentlest increase in its weight among the samples. It is evident that PMMA-clay hybrid has much better barrier property in preventing small molecules like DBP in  $CH_3CH_2OH$  from penetrating into the matrix, as does the composite of the PVC/PMMA-clay hybrid. Other samples, like PMMA/PVC/clay or PMMA/PVC/organoclay, or PVC/PMMA are poor in barrier property.

These are presumably explained as follows: disperse behaviors of MMT in each matrix are very different. In the PMMA-clay hybrid or PVC/PMMAclay hybrid system, silicate layers are homogeneously dispersed in almost individual layers. Each layer acts as a barrier to prevent moving small molecules in the matrix. In other systems, the silicate layers exist in aggregate, so they are poor in barrier property. Figure 8 gives the scheme of the small molecules moving within each blend. It is clear that, in the PMMA-clay hybrid and PVC/ PMMA-clay hybrid systems, the nanodispersion system, the small molecules meet more barriers and cause further travel from A to B, compared with the PVC or PVC/PMMA-clay systems.

When the immersed samples were dried at 60°C, we found that the weight decrease rate of



**Figure 7** Weight change of each sample with immersed time and drying time samples: (a) PMMA/PVC, (b) PMMA/PVC/Na<sup>+</sup>-MMT, (c) PMMA/PVC/organo-MMT, and (d) PVC/PMMA-clay hybrid.



**Figure 8** Models for the path of a migrating molecule in each composite of (a) pure polymer, (b) polymer-clay, and (c) polymer-clay hybrid.

the nanodispersion sample was the slowest. This can also be explained by the previously described reason. In the nanodispersion system, the small molecules have to travel a longer distance to get from the inner matrix to the surface of the product.

### **CONCLUSIONS**

A PMMA-clay hybrid, where MMT is dispersed at the molecular level, has been synthesized by using MMT intercalated with an ammonium salt of octadecylamine. The PMMA-clay hybrid shows excellent barrier property in preventing the plasticizer's (DBP) migration within the PVC composite. The financial support of this research by the Natural Science Foundation of Fujian Province and the Natural Science Foundation of China is gratefully acknowledged.

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