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Synthesis of Epoxy and Block Oligomer Modified Clay Nanocomposite

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ABSTRACT

Acrylic triblock ($A_xM_yB_z$) and diblock (M_yB_z) oligomers containing methyl methacrylate (MMA, M), methacrylic acid (MAA, A) and dimethylaminoethyl methacrylate (DMAEMA, B) groups are intercalated into the layers of montmorillonite. The results indicate that the block oligomer lay flatly between the clay layers. ICP analyses of Na^+ content indicate no unexchanged sodium ions are left in the intercalated clay.

Nanocomposites of epoxy and clay modified with block oligomers were synthesized. Glass transition temperature (T_g) of the nanocomposite is 129.6°C ($M_{18}B_{24}^{24+}$ modified clay) compared to 84.1°C for the physical mixture of epoxy and unmodified clay. T_g increases with decreasing amount of modified clay. When modified clay content are below 2 phr, T_g higher than 131.7 °C can be obtained. Water resistance and light transmittance of the nanocomposite is also improved over composite of epoxy and unmodified clay.

INTRODUCTION

Clay or other inorganic materials have been added into polymer as fillers in order to improve the properties of the polymer such as dimensional stability, conductivity, mechanical, thermal and other potential properties.[1,2]. The intercalation of modified ions into the layers affects the exfoliation of the clay layer in the composite. Lan and Pinnavaia reported the enlargement of d-spacing to 18.0 Å by intercalation of onium ions [3,4]. The largest d-spacing of modified montmorillonite reaches 20.27 Å [5]. It is interesting to understand the intercalation of the clay such as montmorillonite. Acrylic block oligomers were synthesized in different chain length, hydrophobicity, sequence and charge density. Onium ions such as $[H_3N(CH_2)_{n-1}COOH]^+$, $[H_3N(CH_2)_{n-1}CH_3]^+$, $[H_3N(CH_2)_nNH_2]^+$ and $[H_3N(CH_2)_nNH_3]^{2+}$ were reported to be intercalated into the clay layers. When $n>17$, the compounds become too hydrophobic to be soluble enough in water. In contrast, the acrylic oligomers are soluble in water even when the atomic weight is about 7,000 Da. With these advantages, we used acrylic block oligomers as the exchanged ions to be intercalate in the layers of montmorillonite and study the effects of electron charge, charge density, hydrophobicity and block sequence on intercalation. Nanocomposites of epoxy and

acrylic block oligomers intercalated montmorillonite were synthesized. The properties of the nanocomposites including T_g , water resistance and light transmittance are also reported.

EXPERIMENTAL

Materials

Na^+ -montmorillonite with an exchange capacity of 145 mequiv/100g (CWC) was obtained from Nanocor Inc. Na^+ -montmorillonite with an exchange capacity of 96 mequiv/100g (CL-42) was donated by Pai Kong Ceramic Materials Co. LTD. All block copolymers were provided by Prof. Hui Chen of Department of Chemical and Material Engineering, National Central University, Taiwan.

Intercalation of clay with oligomers

The protonated forms of block oligomers were formed by dissolving 5 mmole of the block oligomers in 400 ml of 0.01 N aqueous HCl solution at 60 °C. The solution was adjusted to 500 ml and pH 2 with 1N HCl and deionized water. Five grams of clay was thoroughly dispersed in the solution of protonated block oligomer at 60 °C for three hours. Montmorillonite was separated by centrifugation and washed with deionized water.

Synthesis of epoxy-montmorillonite nanocomposite

Intercalated clay was added with stirring to diglycidyl ether of bisphenol A and cured by addition of either nadic methyl anhydride and benzyldimethylamine. The amount of curing agent used for each formulation was as follows: 87.5 phr (per hundred epoxy resin) of NMA and 5phr of BDMA. All samples were cured at 80 °C for 1 hr, 100 °C for 1 hr, 120 °C for 1 hr, 150 °C for 6 hr, and 200 °C for 1 hr.

RESULTS AND DISCUSSION

The effect of block oligomer structure on intercalation of montmorillonite

Charge and charge density

In medium of pH 10, $\text{A}_{12}\text{M}_{12}\text{B}_{12}$ is negatively charged, and in medium of pH 2, $\text{A}_{12}\text{M}_{12}\text{B}_{12}$ is positively charged. Results in table 1 show that only cations can be intercalated into the clay layers. The influence of charge density on intercalation were also shown in table2. D-spacings of montmorillonite intercalated with MB diblock oligomers of different charge densities (M_{18}B_n , $n=3, 18, 24, 36$) are almost the same. The electrostatic interaction between MB oligomers and layer surface are too strong to yield distinct difference in d-spacing.

Table 1. D-spacings of various modified montmorillonites.

Gallery cation	pH	Charge	D-spacing(Å)
A ₁₂ M ₁₂ B ₁₂	10	-12	14.5
A ₁₂ M ₁₂ B ₁₂	2	+12	19.7
H ⁺ (0.01N)	2	+1	15.0
Na ⁺ (CL-42-mont.)	---	+1	12.5

Hydrophobicity

The hydrophobicity of the block oligomers increases in the following order : A₁₂M₁₂B₁₂ > A₁₂M₈B₁₂ > A₁₂M₄B₁₂. These are confirmed by the magnitude of partition coefficient determined. According to the results in table 2, there is no relationship between d-spacing of oligomer intercalated montmorillonite and hydrophobicity of intercalated oligomer. This result further evidence that the electrostatic interaction between the positive charges of oligomers and the negative charges of the clay layers is the most important factor for intercalation.

Table 2. Partition coefficients of block oligomers and d-spacings of block oligomers modified montmorillonites.

Gallery cation	Charge	D-spacing(Å)	Partition coefficient(K)*
M ₁₈ B ₃	+3	19.9	>>1.74
M ₁₈ B ₁₈	+18	19.4	0.69
M ₁₈ B ₂₄	+24	19.9	0.54
M ₁₈ B ₃₆	+36	19.6	0.41
A ₁₂ M ₄ B ₁₂	+12	20.8	0.65
A ₁₂ M ₈ B ₁₂	+12	19.1	0.74
A ₁₂ M ₁₂ B ₁₂	+12	19.7	1.74

*measured in media of pH=2.

Block sequence

Comparison of M₁₈B₁₈ with different block sequence B₉M₁₈B₉ are shown in table 3. The oligomers showed the same molecular weight (chain length) and charges, the change of d-spacing was caused by different block sequence. D-spacing of the B₉M₁₈B₉⁺¹⁸ intercalated montmorillonite is slightly smaller than that of M₁₈B₁₈⁺¹⁸ intercalated montmorillonite. This result was due to the montmorillonite is pinned at B₉M₁₈B₉'s two ends between layer surfaces.

Table 3. D-spacings and displaced percentage of Na⁺ for M₁₈B₁₈ and B₉M₁₈B₉ modified montmorillonites.

Gallery cation	Charge	D-spacing(Å)	Displaced Na ⁺ (%)
M ₁₈ B ₁₈	+18	19.4	99.1±0.04
B ₉ M ₁₈ B ₉	+18	19.2	99.4±0.03

Synthesis and properties of epoxy and block oligomer modified clay nanocomposite

TEM photographs of epoxy and modified nanocomposite are shown in fig. 1. The results indicate that the distance between clay layers in epoxy and $M_{18}B_{24}^{-24}$ modified montmorillonite (CL42) composite are larger than 200\AA . The delamination of $M_{18}B_{24}^{-24}$ —montmorillonite in epoxy matrix was observed.

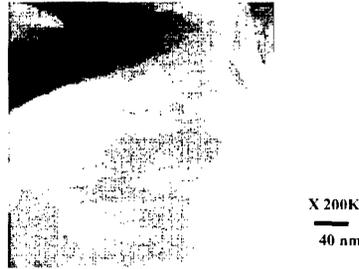


Figure 1. TEM photograph of nanocomposite of epoxy and $M_{18}B_{24}^{-24}$ -montmorillonite(CL42).

Glass transition temperature

DSC results in fig. 2 showed that T_g of nanocomposite formed from epoxy and modified clay ($129.6\text{ }^\circ\text{C}$) is $45.5\text{ }^\circ\text{C}$ higher than that of composite formed from epoxy and unmodified clay ($84.1\text{ }^\circ\text{C}$). The modification of the hydrophilic montmorillonite layer surface to more hydrophobic is the main factor for the higher T_g in epoxy/modified clay system. The interaction of epoxy polymer with more hydrophobic montmorillonite surface is stronger than hydrophilic montmorillonite surface, hence restrict epoxy chain movement.

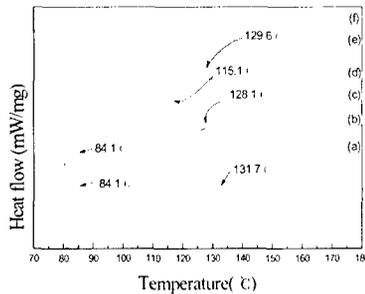


Figure 2. DSC curves for the T_g of composites of epoxy and modified montmorillonites(CL42, Sphr). (a)Without addition of clay, (b) Na^+ -mont(pristine), (c) $A_{12}M_8 B_{12}^{-12}$ -mont, (d) $A_{12}M_{12} B_{12}^{-12}$ -mont, (e) $M_{18}B_{18}^{-18}$ -mont, (f) $M_{18} B_{24}^{-24}$ -mont.

Water resistance

Fig. 3 shows that the water content of $M_{18}B_{24}^{+24}$ -montmorillonite-epoxy nanocomposite is lower than pure epoxy after soaking in water. The results show that $M_{18}B_{24}^{+24}$ -montmorillonite in nanocomposite decrease water permeability. Water resistance was strongly depends on the delamination of clay within an epoxy resin by increasing the permeant trace of water in epoxy resin. The modification by $M_{18}B_{24}^{+24}$ change the clay surface to be more hydrophobic, because the M_{18} blocks of the oligomer are more hydrophobic group.

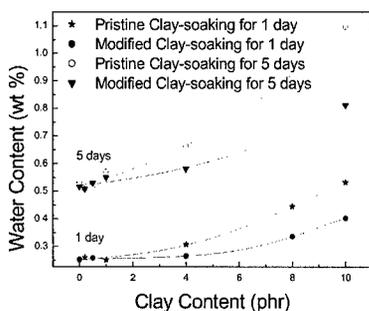


Figure 3. Water content of composite of epoxy and pristine or modified clay with various clay loadings after soaking in deionized water(23 °C) for one day and five days.

Light transmittance

The variation of light transmittance of nanocomposite with modified clay content is shown in fig. 4. The nanocomposites with modified clay show better transmittance than that with unmodified clay.

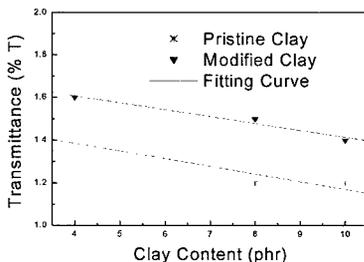


Figure 4. The transmittance of visible light at 550nm for composites of epoxy and modified clay ($M_{18}B_{24}^{+24}$ -montmorillonite) and pristine clay(Na^+ -montmorillonite).

CONCLUSIONS

The d-spacings of block oligomers modified montmorillonites are not affected by chain length of the block, hydrophobicity and charge density of the oligomers. Unlike previous experimental investigations on onium ions, the interlayer spacing depends on the chain length, functional group and charge number of alkylammonium ion. It indicates that all block oligomers lie flat in the interlayer spacing.

TEM photographs show that exfoliation of block oligomer modified clay layers in epoxy resin. The distances between clay layers are larger than 20nm. Nanocomposites of epoxy and modified clay are formed. Improvements for water resistance and transmittance of light are observed for nanocomposites. DSC results showed that the T_g of epoxy composite with modified clay(129.6 °C) is 45.5 °C higher than the epoxy composite with unmodified clay(84.1 °C). When clay content ([B₂₄M₁₈]⁺²⁴—montmorillonite(CL42)) is lower than 2 phr, T_g higher than 131.7 °C is obtained.

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