

Nanocomposites of Urethane and Montmorillonite Clay in Emulsion: *In Situ* Preparation and Characterization

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Received 9 July 2008; accepted 26 April 2009

DOI 10.1002/app.30760

Published online 30 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Nanocomposites of polyurethane-montmorillonite (PU-MMT) were successfully prepared by *in situ* emulsion polymerization. The PU-MMT particles size in emulsion was controlled in nanolevel, which was confirmed by laser scattering size distribution analyzer. The morphology of MMT in PU-MMT composites was observed by transmission electron microscopy (TEM). Wide angle x-ray diffraction (WAXD) was also used to detect the dispersion of MMT in composites. The thermal property was evaluated by dynamic mechanical analysis. Mechanical and fracture properties were also been tested. Gas barrier property was discussed on the basis of testing oxygen perme-

ability of PU-MMT films. The permeability coefficient of the films is found to reduce after composing with MMT, which indicates that the potential application of PU-MMT could be realized as coating materials to prevent metal rusting. It is also found that dimethyl distearylbenzyl ammonium chloride (DMDSBA) is a better modifier for MMT in PU than dimethyldistearyl ammonium chloride (DMDSA). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1964–1969, 2009

Key words: polyurethane; clay; emulsion; nanocomposite; anti-corrosion

INTRODUCTION

In past decades, sodium montmorillonite (Na-MMT) has been widely studied and applied in industry for preparing clay-polymer nanocomposites due to its abundance in nature and its special properties.^{1–3} Besides of its interesting nanosize, the thickness of each MMT sheet could be effectively controlled in 1 nm. The latitudinal dimensions of MMT sheets may considerably vary from 80 to 300 nm, with ca. 200 nm on average. Interestingly, MMT strongly affects the properties of the polymers when it is composed with polymers to form nanocomposites. Some desired properties are usually reached at a low-filler volume fraction of MMT in polymers.^{4–7} Among many types of polymers-clay nanocomposites, polyurethane-clay nanocomposite has drawn considerable attention because they have shown increased thermal stability, transition temperature, and gas permeability.^{8,9} Differently from other nanofillers, gas barrier enhancement depends strongly on aspect ratio of MMT sheet.¹⁰

Polyurethane (PU) has been developed into many types of products with widely varied properties

resulting from its special structure. Besides used in foam, polyurethane is also extensively used in lacquers, varnishes, coatings synthetic leather, adhesives and fibers, etc.^{11–14} Recently, one significant study is that enhance of gas barrier of PU-clay improved its application in the field of coating.¹⁰ However, almost all of PU-MMT nanocomposites reported were prepared in organic system. Few studies have been focused on preparing such a nanocomposite in PU emulsion or dispersion, that is, nanocomposite was prepared in aqueous system.¹⁵ So, it is a challenge to prepare it in PU emulsion. At the same time, it is an interesting work to study its properties comparing with that prepared in organic system. Our works will provide a proof to prepare nanohybrid of polymers and inorganic materials in aqueous solution rather than organic solvents commonly used.

EXPERIMENTAL

Chemicals

Industrial grade Montmorillonite clays (MMT) with a cation ion exchange capacity of 90 meq/100 g, modified by dimethyldistearylbenzyl ammonium chloride (DMDSBA) and dimethyldistearyl ammonium chloride (DMDSA), respectively, were purchased from TOUMEN, Japan. Hydrated methyl diphenyl isocyanate (H-MDI) was purchased from Japanese Urethane Industry (phenyl groups are hydrated into cyclohexyl groups). The other agents were the products of Wako (Japan).

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Contract grant sponsors: Scientific Research Foundation for the Returned Overseas Chinese (SRF), State Education Ministry (SEM), and The Research Fund.

Preparation of PU-MMT in emulsion

Typically, 0.3 mol H-MDI, 0.2 mol polyols (Mw 400 containing carbonyl groups) were dissolved in 103 g acetone. Then 6.2 g MTT was added and vigorously stirred. The whole solution was heated to 90°C for 5 h to form a preurethane-MMT solution. A pale transparent solution was obtained.

After preurethane-MMT solution was cooled to room temperature, the carbonyl groups were neutralized by triethyl amine, then 10 g of that was taken and added into 15 g de-ion water with vigorously stirring for 1 min. The left concentration of isocyan groups was checked. After that, equal molar 1,2-diamino ethane was added to increase the molecular weight. After a few minutes stirring, a white PU-MMT hybrid emulsion was obtained. Solvents (mixture of acetone and water) were distilled under vacuum till under one percent for acetone in water. The molecular weight of PU was measured by GPC after PU-MMT composites were dissolved in DMF (Mn, 30,000–50,000). The solid weight percent was measured after drying.

Preparation of PU-MMT film

PU-MMT emulsion was cast in PET film by bar coating, which was dried at room temperature for 10 h then at 80°C under vacuum for 2 h. The thickness of films was controlled ranging from 1 μm to 30 μm , respectively. For thicker film preparation, emulsion was put into a plate and dried.

Characterization

WAXD was prepared at room temperature with a Gigaku D-Max/400 X-ray diffractometer (Japan). The X-ray beam was nicle-filtered Cu $k\alpha$ ($\lambda = 0.154$ nm) radiation operated at 75 kV and 150 mA. X-ray diffraction data were obtained from 1 to 10° (2 θ) at a rate of 2°/min. The particles size of PU-MMT particles in emulsion was measured by laser scattering size distribution analyzer HORIBA LA-750. The samples for TEM were prepared in advance by microtoming the PU-MMT nanocomposites into 80- to 100-nm thick silices at -40°C. The graphs were obtained with a Hitachi H-800 instrument using an acceleration of 100 kV. GPC (Gel permeation chromatography) analyses of polymers were carried out using DMF as solution and eluent with a Japan Analytical Co. LC908. Tensile and fracture tests were performed on an MTS universal testing machine (Alliance RT/5). The film for measurement was 60 mm in length and 50 mm in width. Dynamic mechanical analysis (DMA) was performed with a TA Instrument DMA 983 in a resonance mode with a displacement amplitude of 0.2 mm and a frequency

of 1 Hz. The temperature varied from -80 to 150°C to the soft point at a rate of 2°C/min. Tensile and fracture tests were performed on an MTS universal testing machine (Alliance RT/5) at 25°C. Oxygen permeability was measured with GTR-30XAD and G6800T-F(S) instruments.

RESULTS AND DISCUSSION

The size of polyurethane-MMT particles in aqueous dispersion

As shown in Figure 1, the diameter of the particles is almost distributed between 100 to 200 nm while the amount of carbonyl group was 0.18 mL/g in PU. Of course, the size of the particles was influenced by the amount of carbonyl group in PU and this result is shown Table I. While the amount of carbonyl group decreased to 0.10 mL/g in PU, the average diameter is over 1 μm . That is, the amount of carbonyl groups has to be more than 0.1 mL/g in PU to make sure of controlling the particles size in nanolevel. Some attempts have been tried to obtain smaller than 100-nm PU-MMT particles by increasing the amount of carbonyl groups in PU, but the result indicates its difficulty. The reason maybe attribute to the size of MMT or the aggregation of PU, which limited finer particles formation of PU-MMT in emulsion.

The morphology of MMT in PU-MMT composites

The films of PU-MTTs were prepared by coating bar No. 9 (20.6 μm in wet) after the emulsion of

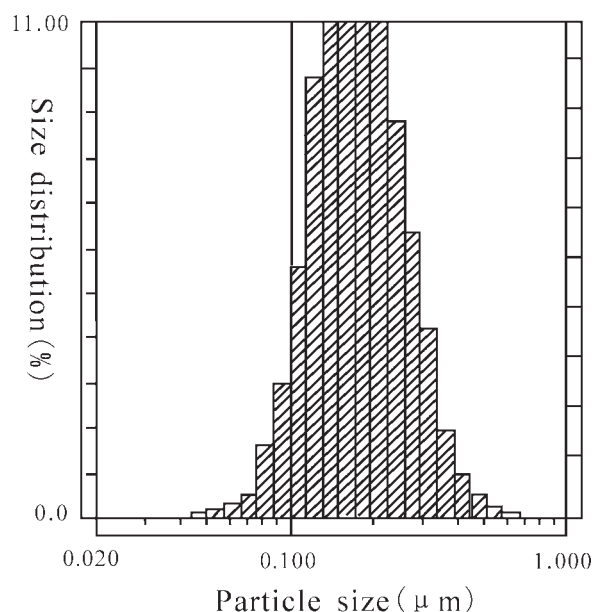


Figure 1 Particle size distribution for PU-MMT (modified with DMDBSA) in emulsion.

TABLE I
PU-MMT^a Particles' Size in Emulsion

Weight ratio of carbonyl groups in PU-MMT (%)	0.4	0.6	0.8	1.0	1.2
Particle size ^b of PU-MMT (μm)	0.36	0.25	0.17	0.13	0.12

^a MMT modified by DMDBSA, 8% to PU.

^b Median diameter of the particles.

PU-MMT was precipitated by adding 1% potassium chloride into solution. The dried films were used for TEM measurement.

As shown in Figure 2, DMDSBA-modified MMT is well dispersed in PU, and the observed size is about 100 nm. However, DMDSA modified MMT shows different results (Fig. 3), which show about 500 nm aggregation in PU. Although all images are not shown here, DMDSA modified MMT always shows larger size in PU than that of DMDSBA although they were synthesized in the same conditions. This result indicates that the DMDSBA modified MMT is more easily dispersed in PU to form nanocomposite than that of DMDSA. The other reason may be that DMDSBA is more compatible to PU, so that it could keep MMT-DMDSBA well dispersed in PU rather than disturbed by PU in composites. Although further works are needed for such modifier to MMT, our result confirms that DMDSBA-modified MMT is better dispersed in PU than that of DMDSA.

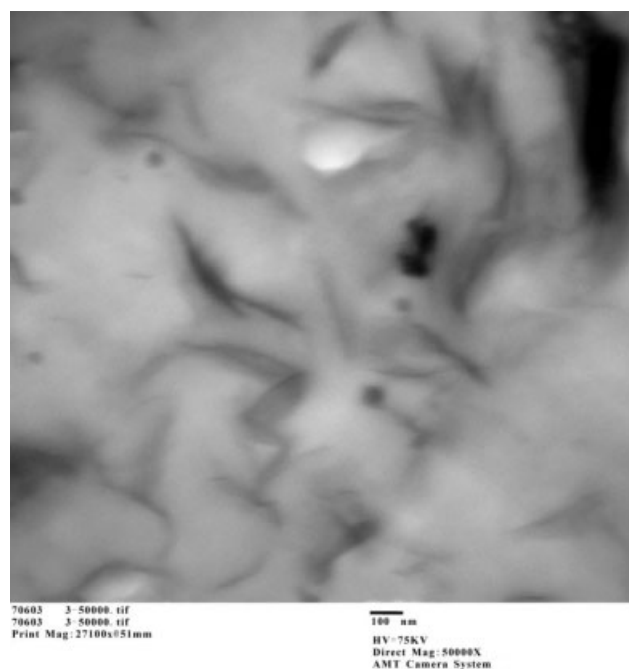


Figure 2 The TEM image of PU composed with MMT modified by DMDSBA.

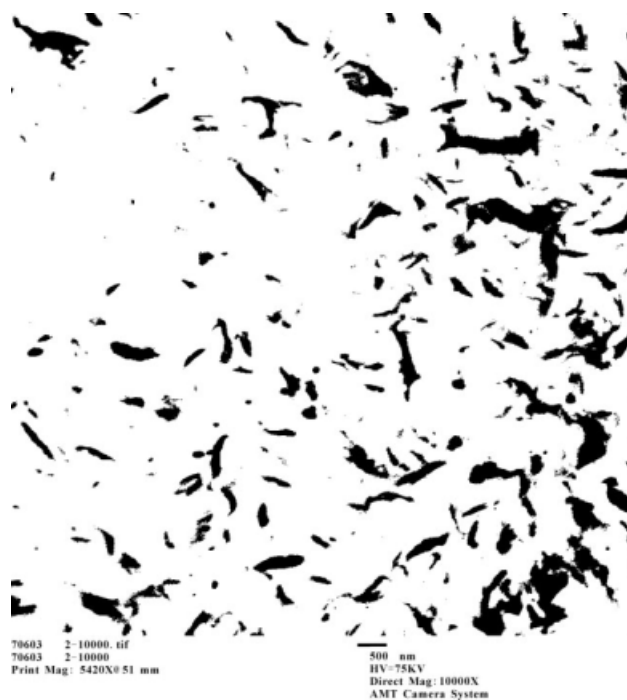


Figure 3 The TEM image of PU composed with MMT modified by DMDSA.

WAXD

The WAXD patterns of DMDSBA-modified MMT and PU-MMT composite (with 8% of DMDSBA modified MMT in PU) are shown in Figure 4. The WAXD of modified MMT shows the same character peaks as that

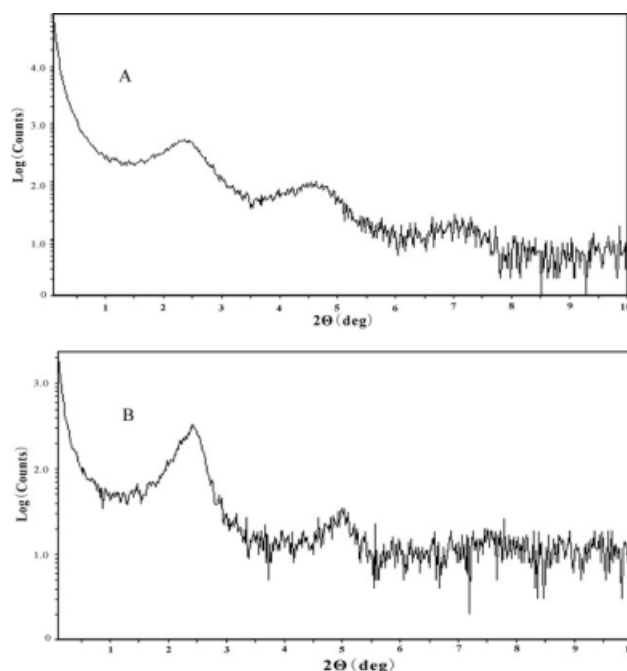


Figure 4 The WAXD patterns of MMT (A) and PU-MMT (B) modified by DMDSBA.

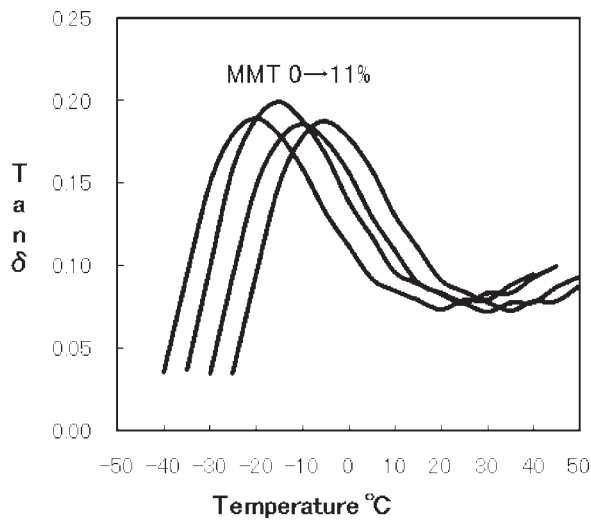


Figure 5 Dynamic mechanical properties of PU-MMT composed with various weight ratio of MMT (modified by DMDSBA) (0, 4, 8, 11%).

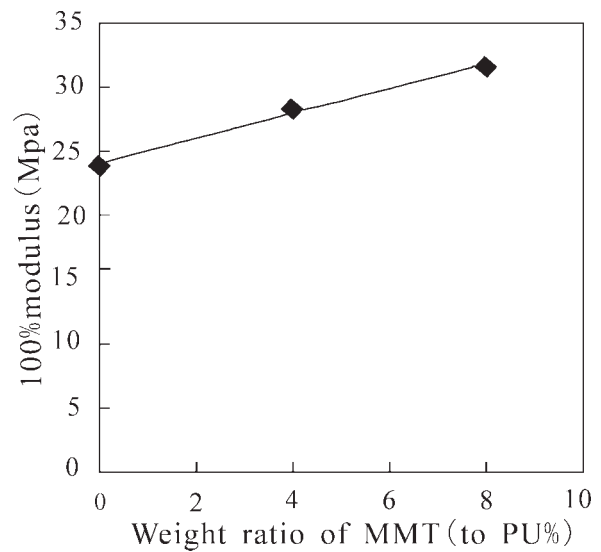


Figure 6 The mechanical properties (100% modulus) of PU-MMT composites.

in composite. The characteristic peak is at $2\theta = 4.5^\circ$, which is assigned to the 001 basal reflection. Another peak is observed at $2\theta = 2.5^\circ$ resulted from the expansion of basal spacing of silicate layers by interaction of DMDSBA. The result is similar to others reports.^{4,8} The WAXD data indicate that MMT was well dispersed in PU after its emulsion and film forming, which has been confirmed by TEM images in above discussion.

DMA characterization

Figure 5 shows the dynamic mechanical properties of PU and PU-MMT at different weight ratio of MMT (DMDSBA modified MMT). One damping peak for each curve was observed, which shift to a higher temperature with increasing MMT content in composite. Such a characterization indicates that the synthesized PU-MMTs have a homogeneous morphology without significant phase separation. That

is, MMT was homogeneously hybrid with PU. In addition, it could be observed that T_g (loss tangent in Fig. 5) of PU-MMTs increases gradually whereas the ratio of MMT in composites increased, which is commonly observed in organic-inorganic hybrids and the inorganic fillers improve the thermal properties of polymers.^{9,10} Also, it is well known that the polymer's T_g or thermal properties affects greatly their others properties and characteristics.

Mechanical and fracture properties

PU is widely used as coating material. Recently, lots of studies have been focused on gas barrier property of PU-MMT due to its high application potential in coating filed. So, it is important to keep the mechanical and fracture properties of PU-MMT act as that of PU films. To check it, these properties of PU and

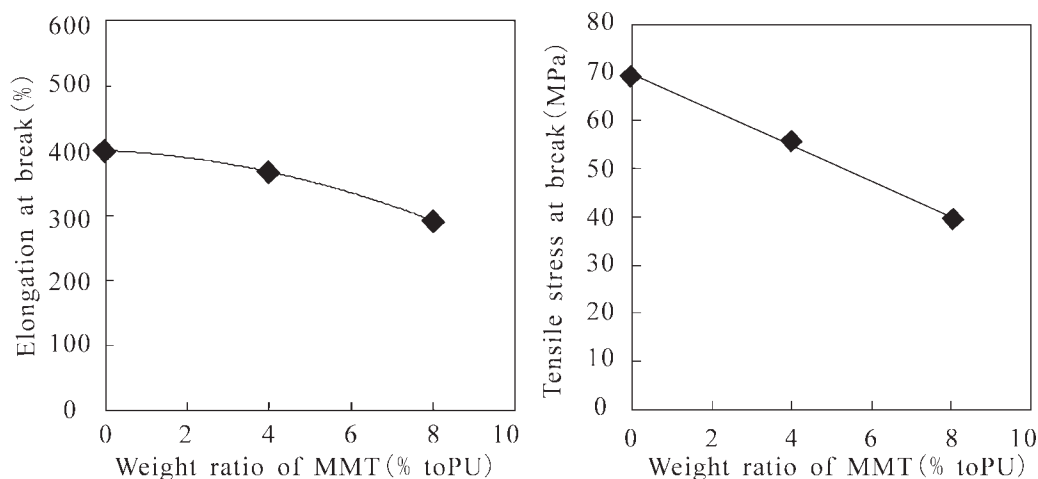


Figure 7 The mechanical properties at break of PU-MMT composites.

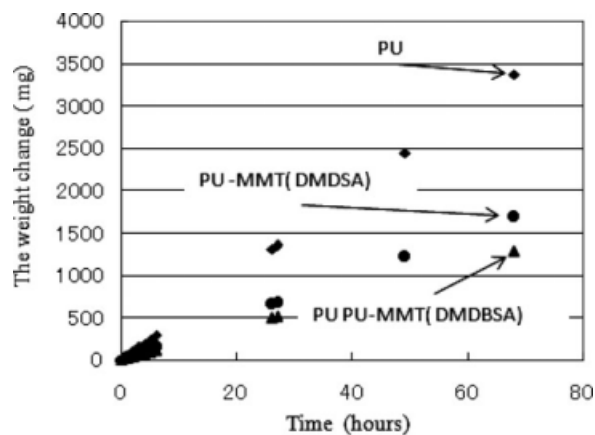


Figure 8 The relationship between time and amount of aqueous penetrating throughout films (25 μm in thickness).

PU-MMT films were tested. Because the mechanical properties are greatly influenced by polymer's T_g , the testing temperature was set at 25°C, which is over all samples' T_g to make sure a correct comparison.

Three parameters were selected to observe the mechanical properties of PU-MMT composites with 0, 4, 8% MMT to PU in composites. Although the weight percent of MMT was increased to 11%, the film was too fragile to operate. The one is tensile stress in 100% elongation of the films (Fig. 6). The others are tensile strength and elongation at break (Fig. 7). The effect of the films' thickness was modified by calculating soft ware.

As shown in Figure 6, the tensile stress increases with increase of the amount of MMT in PU-MMT composites, which indicates that the strength of the PU-MMT is improved through the nanohybrid. Such result could be understood from the T_g temperature shifting from lower to higher (Fig. 5) as MMT addition. Two types of PU-MMT has been measured for the these properties, DMDSBA and DMDSA modified MMT. Generally, the films of PU-MMT modified by DMDSBA have shown better mechanical properties than these of PU-MMT modified by DMDSA. Such results can well understand from the difference of PU-MMT dispersion states discussed earlier.

However, the tensile strength and elongation at break (Fig. 7) decrease as the addition of MMT in PU. Such result has also been reported in other cases. Although further works are needed in this work, it is commonly considered that the best tensile strength and elongation could be found by modifying the ratio of the amount nanofiller in polymers. The reason may be understood as that, the surface between the MMT and PU weakens the stress of PU during straining the PU-MMT films. Although no SEM or TEM images to confirm the supposition, it is easily understood that the gap on the surface between MMT and PU increased with the strain increasing, which destroyed the continuing phase of PU films and weakened the stain elongation.

Gas barrier properties

The most potential application of PU-MMT is used as coating material due to its gas barriers properties, such as preventing metal rusting. Oxygen is commonly considered to affect the rusting of metals in nature.¹⁰ So, the permeability oxygen gas throughout PU-MMT films were tested to check it.

Oxygen permeability was measured with GTR-30XAD and G6800T-F(S) instruments. The detection of oxygen was performed with gas chromatogram (temperature conduct sensor TCD) under 1 atm at 23°C. The area of penetration film for oxygen is $1.52 \times 10^{-3} \text{ m}^2$ ($\phi 4.4 \times 10^{-2} \text{ m}$). Testing data are shown in Table II. Although 8% in weigh of DMDSBA modified MMT was composed with PU, the permeability coefficient of composites is ca. 1/4 of PU. DMDSA modified MMT shows different results, and the coefficient of PU-MMT just decreased to 1/2 of PU. That is, the coefficient of PU-MMT modified with DMDSBA is two times to that of PU-MMT modified with DMDSA. Based on this result, it is confirmed that PUs oxygen barrier are improved by composing MMT into PU and DMDSBA modifier is better than DMSA for MMT in PU. The difference between the modifiers could be understood from the dispersion of MMT in PU, which has been confirmed by TEM images. The better dispersion could provide the

TABLE II
Oxygen (dry) Penetration Test Results Under 1 atm at 23°C

Samples	Films' thickness, μm	Permeability $\text{mol}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$, $\text{cm}^3/\text{m}^2\cdot 24 \text{ h}\cdot\text{atm}$	Coefficient of permeability $\text{mol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$, $\text{cm}^3\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$
PU	56	3.84×10^{-12} , 753	2.15×10^{-16} , 6.42×10^{-11}
PU-MMT ^a modified by DMDSBA	57	8.47×10^{-13} , 166	4.83×10^{-17} , 1.44×10^{-11}
PU-MMT ^a modified by DMDSA	53	1.76×10^{-12} , 346	9.36×10^{-17} , 2.79×10^{-11}

^a 8% weigh ratio of MMT to PU.

better oxygen barrier. Although the images are not shown here, the dispersion in one direction is very important to shut down oxygen penetrating. Gas barriers theory has been detail studied in other reports.¹⁰ As shown in Figure 8, aqueous gas are also shut down by PU-MMT films.

Based on the above results, it is indicated that gas barrier property of PU can be improved by hybrid of it with MMT.^{11,16} DMDSBA is more suitable to be used as modifier than DMDSA for MMT in PU. So the application of PU-MMT composite could be expected to be used as coating material to prevent rusting of metals. Further works are continued in our group applying PU-MMT as coating materials for steel-rust preventing.

CONCLUSIONS

We successfully prepared nanocomposites of PU-MMT in aqueous emulsion rather than in organic solvents reported. The particles' size of PU-MMT was controlled in ca. 200 nm, and MMT was well dispersed in PU matrix, which was confirmed by TEM images and WAXD. After composed with MMT, PU-MMT shows higher thermal property than PU. Although the mechanical properties were weakened after composed with MMT, the results indicated no influence on its application. Gas barrier property was studied by the test of oxygen permeability through PU-MMT films. The result shows that, DMDSBA is more suitable to be used as modifier than DMDSA for MMT in PU. The conclusion is clear that perme-

ability coefficients reduced to 1/4 times for oxygen while 8% MMT modified with DMDSBA was added in PU. So, the application of such emulsion could be expected, such as applying as coating material to prevent metal-rusting. Another significance of our work is providing a proof to prepare PU-MMT nanocomposite in emulsion, which has been reported scarcely.

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