

Research Article

Preparation and Properties of OMMT/PU Composites

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Prepolymer of polyurethane (PU) was prepared by toluene diisocyanate (TDI) and polyether diol through polymerization, organically modified montmorillonite (OMMT) gained by montmorillonite (MMT) that was modified by octadecyl trimethyl ammonium chloride (OTAC), and the OMMT was used as intercalator; alcohol-based OMMT/PU adhesive was synthesized. The micromorphology of OMMT/PU adhesives was observed by XRD, SEM, and AFM, and the shear strength, elongation at break, peel strength, and water resistance were tested and the relationship between structure and properties of the adhesives was observed and analyzed. XRD suggested that OMMT has been completely peeled in the polyurethane matrix and the spacing of layers has increased. SEM and AFM indicated that the OMMT dispersed evenly in the PU matrix and had a good transition with PU matrix, and the interface effects between two phases were strong. The results of the mechanical properties showed that OMMT could significantly help to improve properties of OMMT/PU adhesive, and the shearing strength, fracture tensile strength, and peel strength of 4 wt% OMMT/PU adhesive were 7.24 MPa, 2.14 MPa, and 451.2 N/m, respectively; the water absorption quantity was 2.82%. Compared with the unmodified PU, the shearing strength, tensile strength, and elongation at break of 4 wt% OMMT/PU adhesive were increased by 36.75%, 134.90%, and 76.80%, respectively. The peel strength decreased by 30.76%, and the water absorption decreased by 17.54%, in the meanwhile.

1. Introduction

Nanoparticles have much large surface area and shorter interparticle distance at the same particle content, exist in superior properties, and may have a significant impact on the electrical properties, heat resistance, and mechanical properties of the composites, and the montmorillonite (MMT) is the one of nanoparticles, which is a kind of natural clay mineral and has a layered structure. It consists of stacked, layered silicate about 1 nm thickness including two silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. There are some hydrophilic cations residing in the gallery, such as Na⁺ or K⁺ ions, which can be exchanged by other cations [1]. MMT and related layered silicates are the materials of choice for polymer/clay nanocomposites with excellent performances.

Polyurethane (PU) is widely used in engineering thermoplastic material with excellent properties such as good mechanical properties and thermal property; more attention has been given to the PU/filler composites [2, 3]. The curing cycle of water-soluble PU adhesive is long and has a low solid content. The infiltration of solvent-free PU adhesive is bad and the production cost is high; alcohol-based PU adhesive is used widely in the field of fabric, plastic flexible packaging and leather finishing [4, 5], because it has no NCO groups, it is nontoxic, it does not pollute the environment, and it saves energy, and it has excellent flexibility and oil resistance, abrasion resistance [6, 7]. But the drawback of alcohol-based PU adhesive is low bond strength and permeability is not ideal, in some special cases. MMT is lamellar material, having large length thick ratio, but it is difficult to form intercalated or exfoliated structure while MMT is used to modify polymer matrix directly. Polymer chain is difficult to insert between

the MMT layers because the polarity of MMT is strong and the layer thickness is very small, so the MMT should be organically modified (OMMT). On one hand, OMMT has a good compatibility with the PU matrix; on the other hand, due to the presence of nanomaterial, the composite material exhibits high mechanical strength, high modulus, and high thermal stability properties, and nanocomposite modified by OMMT shows excellent performance in these areas [8, 9]. OMMT can improve the mechanical properties of PU adhesive and reduce the permeability effectively [10, 11].

Toluene diisocyanate (TDI) and polyether diol were used to prepare PU and OMMT was used as modifier in this paper, the microstructure and mechanism were studied by XRD, SEM, and AFM, the shear strength, peel strength, and water absorption of OMMT/PU film are tested, and the relationship of structure and properties has been researched and provided experimental data and theoretical basis for the development and application of PU.

2. Experimental

2.1. Materials. MMT (200 mesh, 90~110 mmol/100 g) was obtained from Henan Yongshun Water Treatment Materials Co., Ltd. (CHN). Polyether diol ($M_n = 1000$) was obtained from Jiangsu Hai'an Petroleum Chemical Plant. Toluene diisocyanate (TDI) was from Shanghai Shengan Chemical Industry Co. (CHN), industrial products. Diethylenetriamine was from Newtop Chemical Material (CHN) Co., Ltd., AR grade. Epoxy resin (E-51) was from Wuxi Guangming Chemical Factory. Octadecyl trimethyl ammonium chloride (OTAC) was from Boxing County Runda chemical Co., Ltd. (CHN).

2.2. Modification of Na-MMT. MMT (20 g) was placed in a 500 mL flask, and then distilled water (380 g) and OTAC (7.66 g) were added, where the quality of OTAC could be calculated according to the following formula. The reaction temperature was controlled at 353 K and rapidly stirred for 4 h and filtered. Modified MMT was rinsed with distilled water for 3~5 times and placed in an oven, dried for 6 h at 373 K, grinded and collected OMMT (organically modified montmorillonite) sieved by 200 mesh:

$$m_{\text{OTAC}} = \frac{\text{CEC} \times 10^{-3}}{100} \times m_{\text{Na-MMT}} \times M_{\text{OTAC}}, \quad (1)$$

where m_{OTAC} was the mass of OTAC, CEC was the maximum capacity when Na^+ in Na-MMT would exchange with the outside cations, $m_{\text{Na-MMT}}$ was the mass of Na-MMT, and M_{OTAC} was the molar mass of OTAC.

2.3. Preparation of Prepolymer. Polyether diol ($M_n = 1000$) was added into the flask and vacuum dried at 373 K and 2 mmHg for 0.5 h and cooled to 353 K, and TDI, isopropyl alcohol, acetone, and diethylenetriamine were added into above solution, stirred for 1.5 h, heated continuously to 373 K, and kept for 2 h. The mixture was allowed to cool to 318 K and stirred for 3 h before being used.

2.4. Preparation of A and B Component

A Component. Chain growth agent diethylenetriamine was quickly added into the prepolymer and stirred for 1 h at 313 K~328 K. The temperature was raised to 343 K, and solvent was volatilized for 0.5 h, when the distillate reduced significantly, continued to heat up to 393 K~398 K, and started vacuum, kept for 0.5 h. Lower the temperature to 343 K and added anhydrous ethanol and stirred 0.5 h, got OMMT/PU, finally.

B Component. Curing agent was prepared by the epoxy resin E-51 and acetic ether. The B component was mixed with A component in a certain proportion before being used.

2.5. Preparation of OMMT/PU Adhesive. B component mixed with A component according to the mass ratio of 1:10, was cured for 24 h at 60°C (333 K), and got OMMT/PU adhesive.

2.6. Methods of Testing

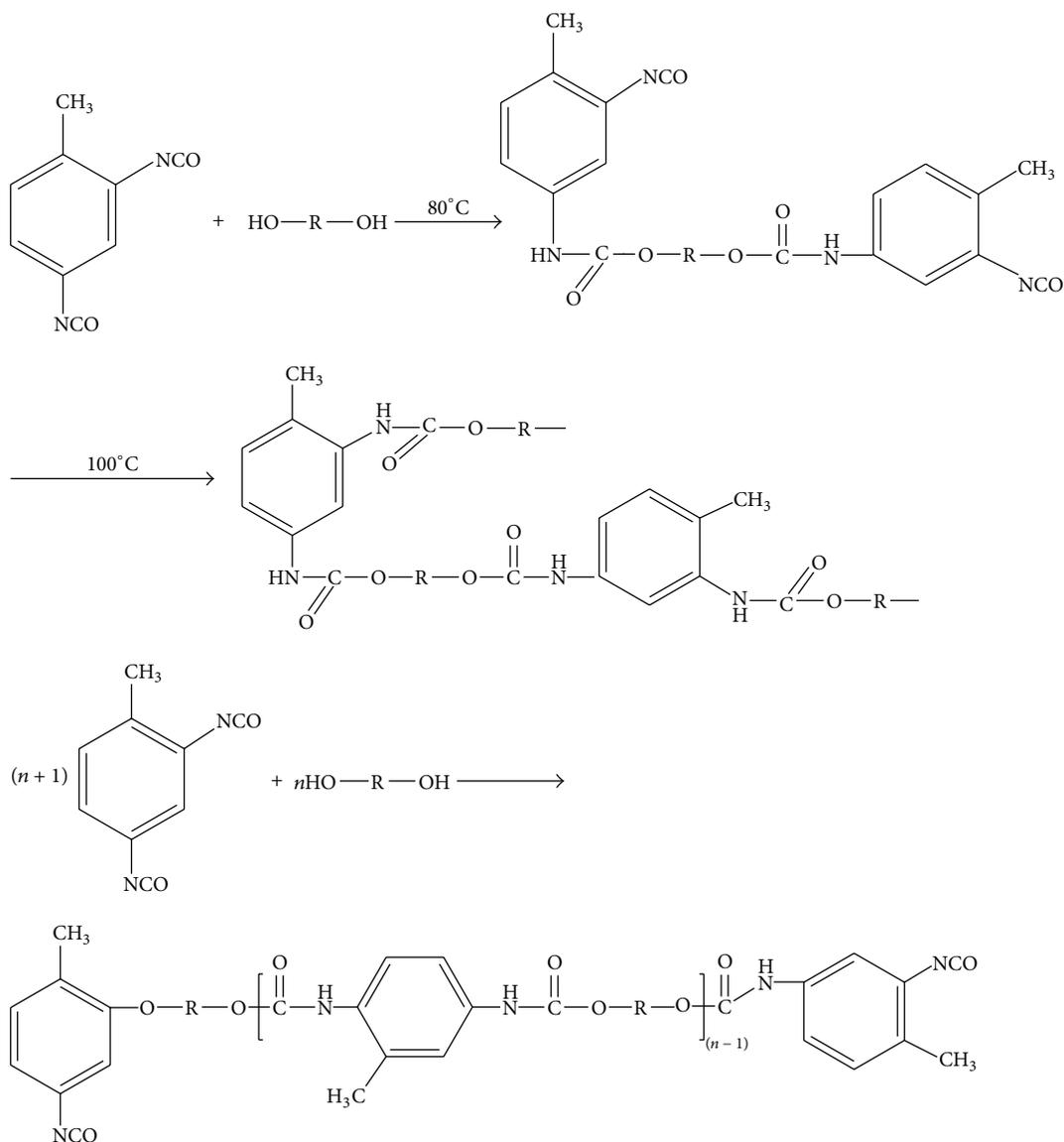
FT-IR. The FT-IR spectra, which are used to characterize the chemical structure of the polymer matrix, are performed with EQUINOX-55 Fourier transform spectrometer (GER), in the 400~4000 cm^{-1} range; 5 scans are averaged for each spectrum. And it could be seen that there exist the characteristic absorption peaks of material.

XRD. X-ray diffraction (XRD) patterns are obtained using a Philips (Holland) Y500 diffractometer with a back monochromator and Cu anticathode (scanning rate 1.5°/min, scanning range 2~14°, and step 0.15406 nm). Special attention is paid to the 2θ region for accurate determination of d_{001} (i.e., the MMT and OMMT d -spacing). Spacing of MMT and OMMT are analyzed, and the dispersion effect of OMMT in PU matrix is identified.

SEM. The fracture structures of samples were examined on the HITACHI S-4300 scanning electron microscope (SEM, JAPA). Samples were deposited on a sample holder with adhesive carbon foil and were sputtered with gold. The dispersion effect of MMT and the interfacial morphology of OMMT in PU matrix are also observed and analyzed.

AFM. Atomic force microscope (Veeco Instruments, USA) is used to observe decentralized state and roughness of OMMT in PU matrix.

2.6.1. Mechanical Measurements. Tensile strength, elongation (%), and peel strength are measured using a universal testing machine (model 3000, Shoreatzo Co., Japan) at $23 \pm 2^\circ$ (276 ± 278 K), with a tensile speed of 5 ± 1 mm/min, according to GB/T7124-1986. The dimensions of the sample are 2 mm in width, 12.5 mm in thickness, and 35 mm in length. The mean value of five measurements for each sample is taken.



SCHEME 1: The reaction equation of performed polymer in the system.

3. Results and Discussions

3.1. FT-IR Spectral Analysis. FT-IR spectra of composite materials were presented in Figure 1. The curves of (a), (b), and (c) were PU adhesive solution, EP resin, and the film after curing in the FT-IR spectra, respectively. The reaction equation was listed in Schemes 1 and 2. As seen in Figure 1(a) few absorption peaks can be found at 3297 cm^{-1} , 2970 cm^{-1} , and 1725 cm^{-1} which can be attributed to $-\text{OH}$ and $-\text{NH}$ stretching vibration [12, 13], stretching vibration absorption peak of $-\text{CH}$, and $-\text{C}=\text{O}$ stretching vibration, respectively, indicating that the organic modifier has been exchanged into the galleries of the silicate layers. This showed that the urethane groups were generated by the reaction of $-\text{NCO}$ and $-\text{OH}$ in the system. The absence of the characteristic absorption spectral bands of the $-\text{NCO}$ at $2280\sim 2270\text{ cm}^{-1}$

confirmed that the $-\text{NCO}$ groups were completely consumed. According to the curve (a), the carbamate was formed due to the reaction between $-\text{NCO}$ group of TDI and $-\text{OH}$ of polyether.

Curve (b) was the FT-IR spectrum of curing agent (epoxy resin E-51); 909 cm^{-1} and 840 cm^{-1} were the vibration absorption peak of the epoxy ring. The absorption peak at 1508 cm^{-1} belonged to the *p*-substituted benzene absorption, and a strong absorption peak at 1242 cm^{-1} was due to the aliphatic aromatic ether bond antisymmetric stretching vibration.

The small peak at 1100 cm^{-1} in curve (c) was due to $-\text{O}-$ stretching vibration, which was wider than the curve (a), because of the overlap of the $-\text{O}-$ in the EP and PU stretching vibration [14, 15]. The absence of the peak of the epoxy groups at 915 cm^{-1} confirmed the epoxy groups were completely

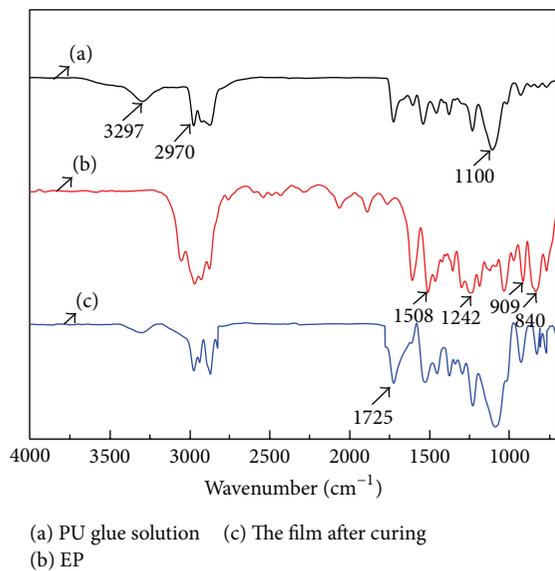
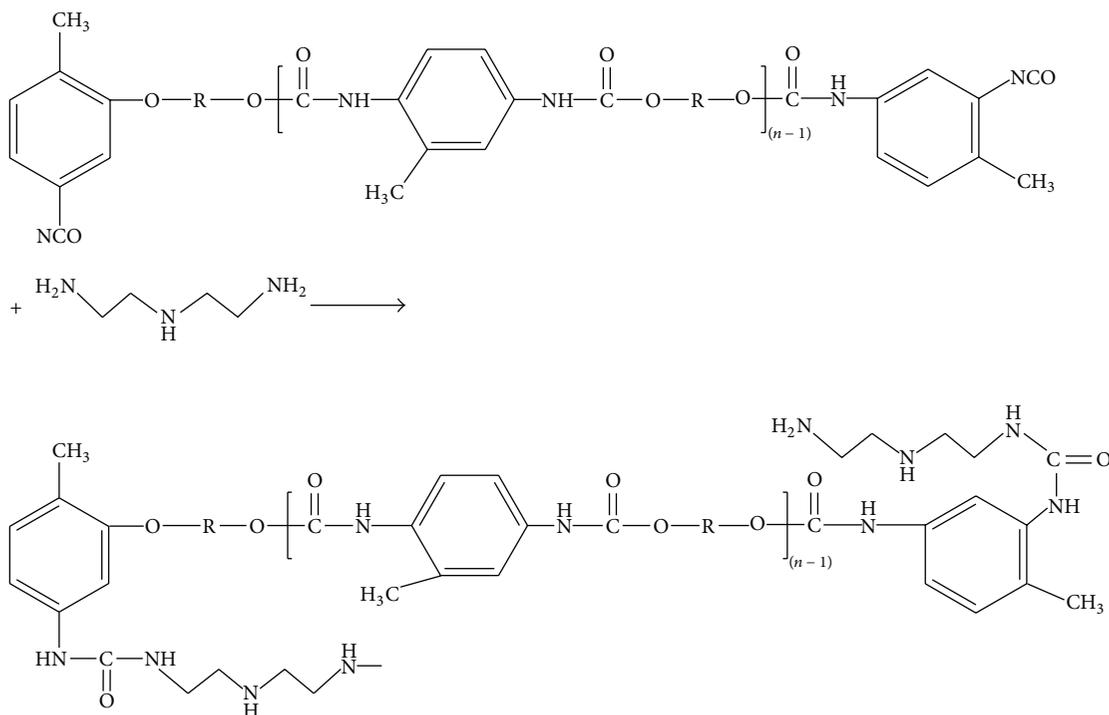


FIGURE 1: FT-IR spectra of the alcohol-based polyurethane adhesives.

consumed. According to the curve of (a), (b), and (c) the target product of alcohol soluble polyurethane adhesive was gained by the reaction between TDI and polyether polyol. The reaction between PU and EP was complete, formed network structure, and achieved the purpose of curing. The reaction mechanism is indicated in Schemes 1 and 2.

3.2. SEM and AFM Analysis. The SEM images of MMT and OMMT were shown in Figure 2. Figure 2(a) was SEM of MMT; it indicated that lamellar spacing was fuzzy, layer spacing was not clear, and there were a lot of granular impurities on the surface of layer, and this would influence the performance of MMT as filler material [16, 17]. Figure 2(b) was the SEM image of OMMT (organically modified by OTAC), which showed that the surface of the lamella was with no impurities, clean and clear, and the lamellar spacing was increased. Meanwhile, it was noted that the ratio of length to thickness of OMMT was large, and the thickness was about 1 nm; while the length was about 100 nm, the layer was peeled in the PU matrix and could be further confirmed from the result of XRD.

Figure 3 was the AFM images of OMMT/PU adhesive [18], and Figure 3(a) was the appearance diagram, and Figure 3(b) was three-dimensional phase diagram. The bright part was the higher area, OMMT component, while the dark part was the lower area, PU matrix, in Figures 3(a) and 3(b). OMMT component of the phase diagram was nanoscale dispersion and was uniformly dispersed in PU matrix. The interface between PU matrix and OMMT was fuzzy, which could indicate that the modifier OTAC could play a role of bridge between OMMT and PU matrix, and showed that the surface of OMMT/PU film was jagged, and this could prove the layer of OMMT was peeled completely in matrix, and spatial distribution of layer was random occurrence. The reason was that crossing reaction between PU and OTAC would lead the layer of OMMT to peel completely. On the other hand, there existed electrostatic force between OTAC

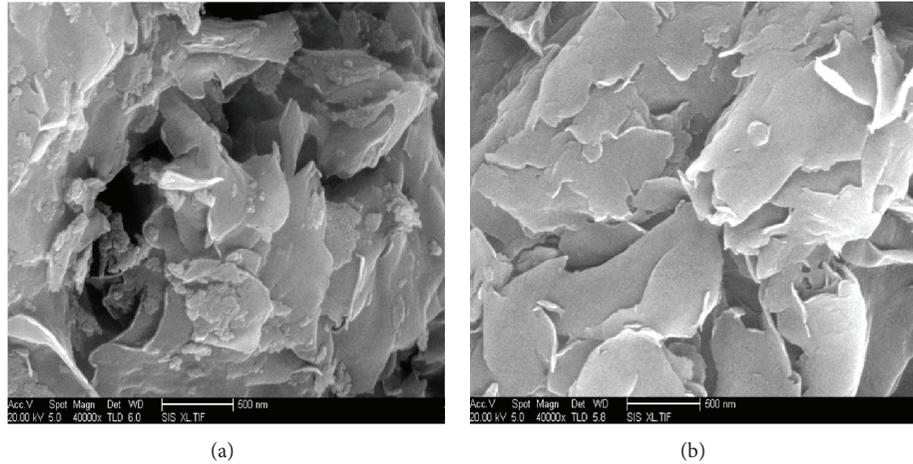


FIGURE 2: The SEM photographs of OMMT.

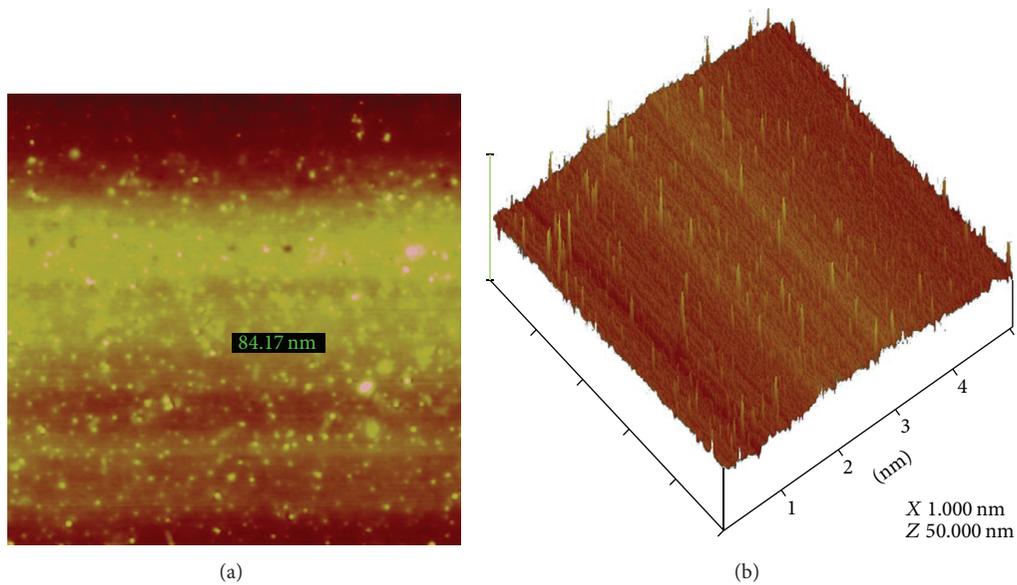


FIGURE 3: The AFM images of OMMT/PU.

and the layer of MMT, so it could play a very good transition connecting role between matrix and inorganic components.

3.3. XRD Analysis of OMMT/PU. Figures 4(a) and 4(b) were the XRD [19] patterns of MMT and OMMT; 2θ angle of them were 6.4° and 4.3° , respectively. According to Bragg's law, $2d \sin \theta = n\lambda$, X-ray was a copper target, and the wavelength was 0.15406 nm , $n = 1$, and then spacing of MMT and OMMT was 1.38 nm and 2.05 nm , respectively. The interlayer spacing was increased 48.6%, which suggested that the interlayer spacing of OMMT was improved.

Figure 5 was XRD patterns of OMMT/PU; it showed that 2θ angle at the range of $3^\circ \sim 4^\circ$ gradually appeared as peak with the increase of OMMT content; the peeling effect was fine when the content of OMMT was in the range of 1~4 wt%, and it dispersed disorderly, so no obvious peak appeared. When

the content of OMMT was 5 wt%, weak peak appeared in the range of 3.8° nearby, and it may influence OMMT dispersion in the matrix and there was locally orderly arrangement that was intercalated structure.

3.4. Mechanical Properties Analysis of OMMT/PU Films

3.4.1. Shear Strength Analysis. Shear strength was tested according to GB/T 7124-1986; the sample was made with 45 carbons steel, and the size of length was $100 \pm 0.2 \text{ mm}$, width was $25 \pm 0.2 \text{ mm}$, and thickness was $2 \pm 0.1 \text{ mm}$. The length of the bonding part was $12.5 \pm 0.5 \text{ mm}$, and stretching rate was $5 \pm 1 \text{ mm/min}$.

Figure 6 noted the change of shear strength of PU adhesive with the increase of content OMMT from 1 wt% to 5 wt%. The shear strength increased with the content of

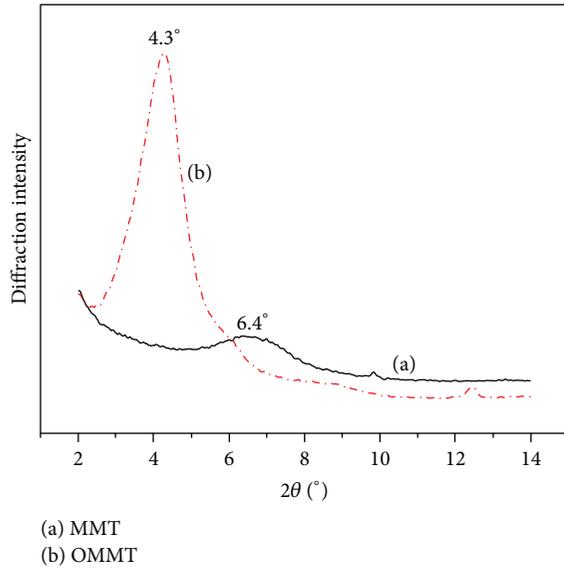


FIGURE 4: XRD patterns of MMT.

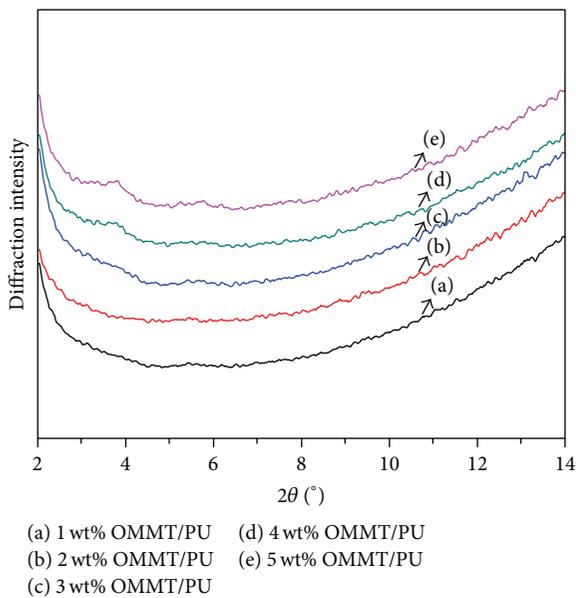


FIGURE 5: XRD patterns of OMMT/PU.

OMMT 1 wt%~4 wt%. The maximum shear strength was 7.24 MPa when the content of OMMT was 4 wt%, which increased by 36.75% than that of pure PU material. But shear strength decreased when the content of OMMT exceeded 5 wt%. The reason was that too many OMMT would result in appearing of the phenomenon of agglomeration. It would help to enhance the interactions of OMMT and weaken the interactions between OMMT and PU. So, it rapidly decreased the shear strength.

3.4.2. Peel Strength Analysis. Peel strength [20] was tested according to GB/T 2791-1995, 200 mm in length, 25 ± 0.5 mm

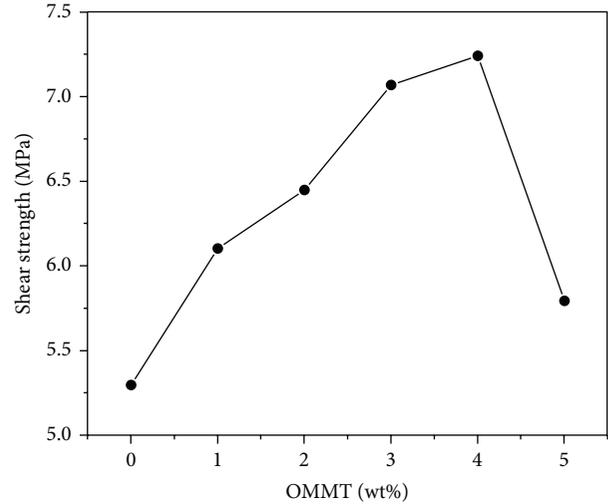


FIGURE 6: The shear strength curve of OMMT/PU.

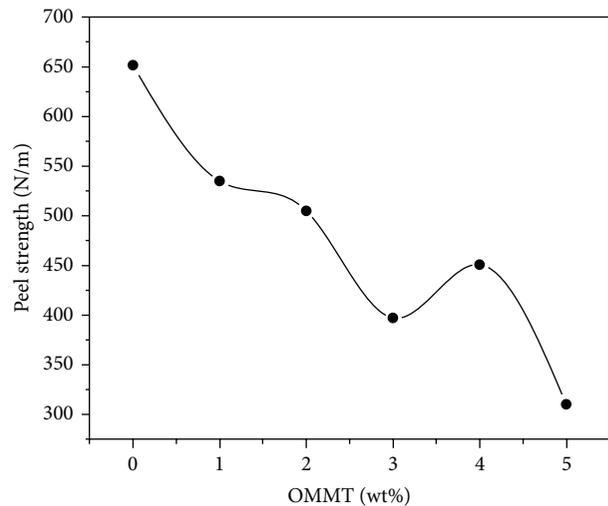


FIGURE 7: The peel strength curve of OMMT/PU.

in width, and 3 mm in thickness. Speed of peeling was 100 ± 10 mm/min, and the length of peeling part was more than 125 mm. The peeling strength was decreased when the content of OMMT was 0%~5 wt% in Figure 7. When the content of OMMT was 4 wt%, there was an inflection point, and it was because the amount of urethane and carbamido which played the role of connection increased, instead of inorganic component OMMT, so the peeling strength of OMMT/PU decreased. The inflection point might be because the dispersion of OMMT in 4 wt% OMMT/PU was better than that of 3 wt% OMMT/PU, OMMT on the surface of 3 wt% OMMT/PU was little, and its peeling strength was lower than that of 4 wt% OMMT/PU, but the overall trend was reduced.

TABLE I: Tensile strength and elongation at failure of OMMT/PU.

Index sample	Thickness (mm)	Width (mm)	Gauge length (mm)	Tensile force (MPa)	Elongation at break (%)	Tensile strength at break (MPa)
Pure	1.883	6.103	30.10	13.89	20.4	1.21
I	1.786	6.385	32.94	15.87	31.76	1.391
II	1.863	6.075	33.61	16.64	34.44	1.471
III	2.012	6.207	37.45	22.02	49.80	1.761
IV	2.113	6.015	36.98	27.16	47.92	2.14
V	1.996	6.154	36.27	18.44	45.08	1.50

3.4.3. Tensile Strength Analysis. The tensile strength of the film was tested according to GB/T 528-1998, the sample size was 25.0 ± 0.5 mm in length, 2.0 ± 0.2 mm in thickness, and 6.0~6.4 mm in width, and stress rate was 500 mm/min ± 50 mm/min. Table 1 showed that the tensile strength and elongation at break of the film mixed with OMMT increased in some degree, and the mechanical properties of film decreased while the content of OMMT was larger than 4 wt%. The reason was that the intercalation agent molecules reacted with isocyanate groups and then formed a part of PU, and electrostatic interactions existed between the intercalation agent and MMT, so the intercalation agent between MMT and PU matrix sheet played a role as a bridge. The effect of stress concentration would produce around ions and the matrix resin would produce many microcracks, absorbed more fracture energy, and then blocked or inactivated the further expansion of microcracks, while the matrix resin was subjected to external force. So the tensile strength of the composite increased. OMMT could not disperse in the matrix uniformly while the content of OMMT was more than a certain amount. Then made the microcrack develop into macroscopic fracture easily, and then the tensile strength of the composite decreased. The tensile strength at break of 4 wt% OMMT/PU achieves was 2.14 MPa that improved 76.8% than that of unmodified adhesive [21]; elongation at break rose to 47.92% from 20.4% and improved by 134.9%, and it accorded with the front analyzing result.

3.5. Water Absorption Analysis of OMMT/PU Film. The size of PU film was 3 cm \times 3 cm, and PU film was immersed in the water (1–5 days) at room temperature and took it out; it absorbed the water on the surface of film by filter paper. We weighed the quality of wet film and dry film, from the formula $(W_2 - W_1)/W_1$, (W_1 , the quality of dry film, W_2 , the quality of wet film) and calculated the water absorption quantity of the film. Figure 8 was the trend of the film water absorption. It reduced the water absorption effectively; with the increase of OMMT content, inflection point appeared when the content of OMMT was 4 wt% and continued to increase OMMT that would increase water absorption quantity. It was because the high content of OMMT could cause local reunion, the resistance of water molecules entering into PU matrix was small, and water absorption quantity was bigger, which was

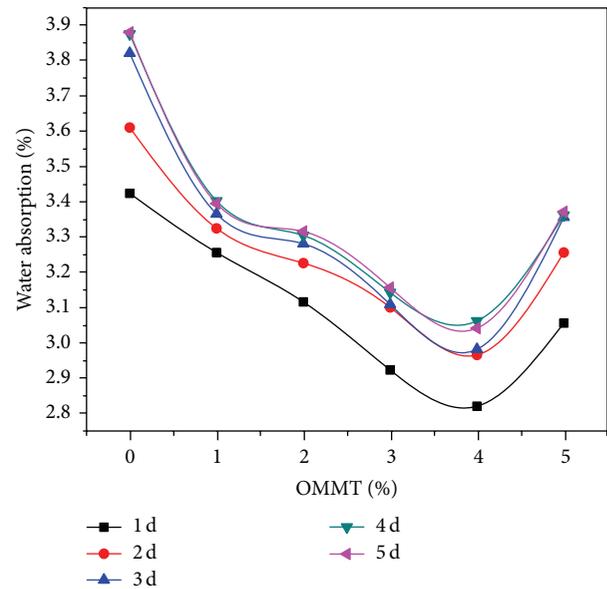


FIGURE 8: Water absorption curves of OMMT/PU.

consistent with the result of XRD. On the other hand, water absorption quantity was increased with the extension of soaking time, achieved a certain values, and tends to be stable. The value of water absorption quantity tended to a certain number when the soaking time was 2 d to 5 d, the reason was that water molecule was quickly infiltrated in shallow film at the beginning and made the water absorption increase. It was difficult to infiltrate deeply; as the lamella of MMT enlarged the path of a water molecule, the water would slowly permeate into the structure of OMMT/PU over time. On the other hand, as the density of OMMT was larger than that of PU matrix, the quality would increase at the same volume; even if it absorbed the same quality of moisture, the water absorption quantity would reduce, too. Soaking time was 1d, water absorption of pure film was 3.42%, and the film of 4 wt% OMMT/PU was lowest, which was 2.82%. Water absorption quantity was reduced by 17.54% after adding OMMT filler and improved the performance of water resistance, effectively.

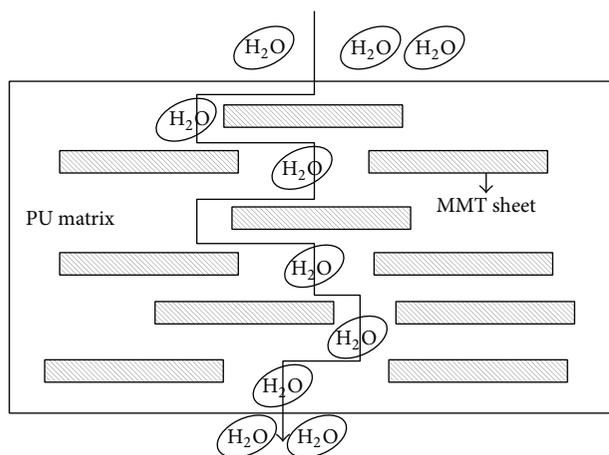


FIGURE 9: The ideal path of water molecules through OMMT/PU film.

Figure 9 showed the process of water molecules through film that mixed with OMMT. The water absorption increased rapidly at the beginning, because the water molecules could rapidly infiltrate into the shallow surface film. But the OMMT formed a barrier; then the path of water molecules crossed PU matrix to increase, so it is difficult to penetrate deeply into the film in limited time. The water absorption quantity rate increased slowly with the increasing of time. On the other hand, because the density of OMMT was much larger than that of the adhesive film, the quality would increase in the same volume. Although it absorbed the same quality of moisture, water absorption rate still decreased.

4. Conclusions

OMMT/PU nanocomposites have synthesized, and the morphologies, mechanical properties, and water absorption property of OMMT/PU nanocomposites have been investigated in this study. The research results lead to the following conclusion. According to the results of FT-IR could determine the reaction product was the target product. SEM and AFM images noted that the morphology of OMMT filler was clear and OMMT dispersed uniformly in OMMT/PU adhesive, and the size of OMMT was nanoscale. Angle 2θ and spacing of OMMT were 6.4° and 2.05 nm, which improved by 48.8% and 48.6% than that of MMT in XRD patterns, respectively. When the content of OMMT was 4 wt%, the shear strength was 7.24 MPa, tensile strength was 2.14 MPa, elongation at break was 47.92%, peeling strength was 451.2 N/m, and water absorption decreased by 17.54%. The uniform mixing of OMMT layer and PU matrix could achieve on nanoscale, so mechanical properties of OMMT/PU were improved, and water absorption quantity decreased.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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