

Synthesis and Properties of Polyurethane/Clay Nanocomposite by Clay Modified with Polymeric Methane Diisocyanate

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ABSTRACT: A polyurethane (PU)/clay nanocomposite was synthesized from polyol, polymeric 4,4'-diphenyl methane diisocyanate (PMDI), and modified clay with PMDI. To achieve the modified clay with PMDI, the silanol group of the clay and the NCO group of the PMDI were reacted for 24 h at 50°C to form urethane linkage. Fourier transform IR analysis of the clay modified with the PMDI demonstrated that the NCO characteristic peak was observed in the clay after a modification reaction with PMDI. The results of the X-ray pattern suggested that the clay layers were exfoliated from the PU/clay nanocomposite. From the results of the mechanical properties, the maximum values of the flexural

and tensile strength were observed when 3 wt % clay based on PMDI was added into the PU/clay nanocomposites. The glass-transition temperature and change in the heat capacity at glass transition temperature (ΔC_p) of the PU/clay nanocomposite decreased with an increase in the modified clay content. We suggested that the decrease in the ΔC_p with the modified clay content might be due to the increase of steric hindrance by the exfoliated clay layers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2879–2883, 2006

Key words: polyurethanes; clay; nanocomposites; mechanical properties; wide-angle X-ray diffraction

INTRODUCTION

A polymer containing a functional group of urethane (—NHCOO—) or urea (—NHCONH—) is called a polyurethane (PU). PU has unique properties and can form a variety of starting materials. Hence, this class of materials has received wide attention for their synthesis, morphology, and chemical and mechanical properties. With the chemical component and composition, PUs can be manufactured in an extremely wide range of grades and densities from 6 to 1220 kg/m³. They can be used as adhesives, binders, coatings, paints, elastomers, flexible foams, and rigid foams.¹

Nanocomposites are a new class of composite materials with one of their constituents having dimensions in the nanometer range. In the polymer/organic clay nanocomposites the polymer matrix is filled with clay consisting of 1 nm thick silicate layers with aspect ratios in the range of 100–1000. In recent years, these kinds of materials have attracted the attention of many researchers^{2–5} because of their prominent properties.

These nanocomposites exhibit increased mechanical properties, decreased thermal expansion coefficients, reduced gas permeability, and increased solvent resistance when compared with the virgin polymers or conventional composites.

The purpose of this article is to examine the effects of the organoclay concentration and degree of exfoliation of the clay on the mechanical and thermal properties of the PU/clay nanocomposite. The organoclay used in this study was modified with polymeric 4,4'-diphenyl methane diisocyanate (PMDI) to achieve the exfoliated structure of the PU/clay nanocomposite.

EXPERIMENTAL

Materials

The materials used in this study were obtained from commercial sources. PMDI was supplied by BASF Korea Ltd. (Seoul). The average functionality of PMDI was 2.7 and the NCO content was 31.5 wt %. The equivalent weight and viscosity of PMDI were 135.0 g mol⁻¹ and 550 cps, respectively. Pentaerythritol base polyether polyol purchased from KPC Co. (Ulsan, Korea) was used for the preparation of the PU/clay nanocomposite. Amine treated organoclay supplied by Southern Clay Co. was used. Dimethylcyclohexylamine (Air Products and Chemicals, Inc.), was used

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as a catalyst. The polyol and clay were dehydrated at 90°C for 24 h in a vacuum oven before use.

Sample preparations

Clay modification with PMDI

The organoclay and PMDI were mixed at 3000 rpm with a mechanical stirrer in an oil bath for 2 h. The temperature of the oil bath was maintained at 50°C on the hot plate and the relative humidity was kept below 30%. The clay content was fixed at 5 wt % based on PMDI. Because the clay is similar to wheat flour, the mixing could not be started at 3000 rpm. If the mix starts forming at high speed, the clays do not disperse well and are aggregated with each other. Therefore, the mixing was started at a low speed of about 100 rpm and rose to 3000 rpm gradually. After the clay modification reaction, the modified clay was separated from the PMDI with suction equipment. Because the PMDI including the modified clay has high viscosity, dimethylformamide (DMF) was added to dilute the PMDI. DMF (200 g) was added to the PMDI (105 g) and then slightly stirred. It was poured through filter paper into the suction equipment in small amounts and then the separated clay was washed several times with cyclopentane.

PU/clay nanocomposite

The PU/clay nanocomposite was synthesized by the reaction between the polyol and the PMDI that contained the modified clay obtained from the reaction of clay modification with PMDI, varying the contents of the clay. In the clay modification, the amount of the clay was varied from 0 to 5 wt % (based on PMDI). The PMDI containing the modified clay, polyether polyol, and amine catalyst were used for the preparation of the PU/clay nanocomposite. All chemicals were put into the reactor and mixed for 30 s with a brushless-type stirrer.^{6–8} The stirrer speed was set at 3000 rpm. The amounts of the polyether polyol and catalyst were fixed at 100.0 and 1.0 by weight, respectively. The amount of the PMDI containing the modified clay required for the reaction with polyether polyol was calculated from the equivalent weight. For the completion of the reaction, excess PMDI (ca. 5 wt %, NCO/OH = 1.05) was used.

Characterization

Fourier transform ir spectroscopy (FTIR)

The IR spectra of the samples were obtained with a PerkinElmer FTIR apparatus over a frequency range from 600 to 4000 cm^{-1} . By pressing the powdered samples with KBr, the samples that were thin enough for spectroscopic analysis could be obtained. Scans

(32–128) with a resolution of 2 cm^{-1} signals were averaged.

Wide angle X-ray diffraction (WAXD)

The distribution of clay layers in the PU/clay nanocomposites was measured by X-ray diffractometer (model MXP-18, Mac Science). $\text{CuK}\alpha$ ($\lambda = 1.54056 \text{ \AA}$) was used as an X-ray source at a generating voltage of 40 kV and current of 100 mA. WAXD scans were obtained in reflection mode using an incident X-ray wavelength of 1.54 Å at a scan rate of 2.0°/min. The d-spacing was calculated by Bragg's law ($d = n\lambda/2 \sin \theta$) from the position of the (001) or (002) plane peak in the WAXD pattern.

Differential scanning calorimetry (DSC)

The thermal properties of the PU/clay nanocomposite samples were measured with a PerkinElmer DSC 7 differential scanning calorimeter (Cetus Instruments, Norwalk, CT). Temperature calibration was performed with indium (melting temperature = 156.6°C, heat of fusion (ΔH_f) = 28.5 J/g). The PU/clay nanocomposite samples were investigated in a nitrogen atmosphere from 20 to 250°C at a heating rate of 20°C/min. After 40°C/min programmed cooling, the samples were reheated at a heating rate of 20°C/min. The DSC curves taken for the analysis were obtained from the second run.

Mechanical properties

The mechanical properties of the PU/clay nanocomposite samples were measured under ambient conditions with a universal testing machine (model 4467, Instron, Canton, OH). A tensile test was performed according to ASTM D 638. The size of the specimen was 10 × 63 × 3 mm (width × length × thickness). The gauge length was 13 mm, and the crosshead speed was 1.5 mm/min. A flexural test was performed according to ASTM D 790. The size of the specimen was 24.8 × 60 × 3 mm (width × length × thickness). The span distance was 48 mm, and the speed of crosshead movement was 1.2 mm/min. The strengths of 10 specimens per sample were measured and averaged for each mechanical test.

RESULTS AND DISCUSSION

Clay modification with PMDI

FTIR

Figure 1 shows the result of the FTIR analysis of the modified clay obtained by the reaction of clay modified with PMDI. We used amine treated organoclay.

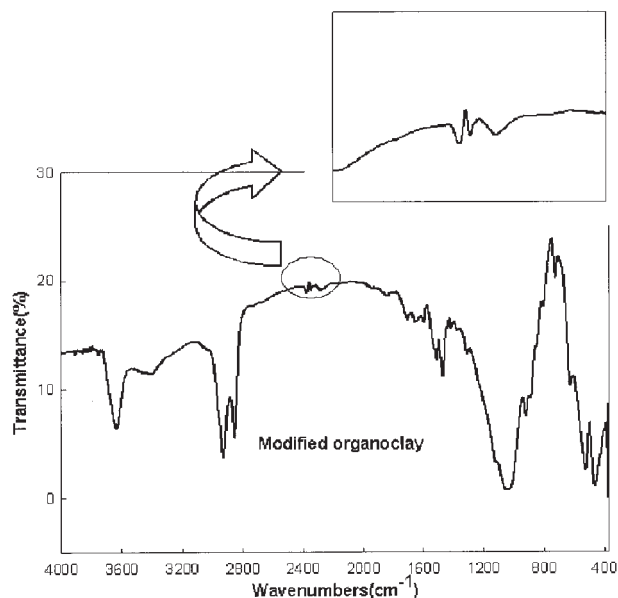


Figure 1 The FTIR peak of the organoclay after modification with PMDI.

PMDI has the NCO characteristic peak at 2266 cm^{-1} as found by FTIR analysis and shown in Figure 1. For the organoclay, it is observed that the NCO characteristic peak exists at 2266 cm^{-1} after the reaction of the clay modified with PMDI.¹ In this study, we used DMF as a solvent to refine the modified clay. DMF is a solvent that can dissolve PMDI. If PMDI is not attached to the clay layers by covalent bonds, it will dissolve in DMF and pull out within the clay layer during the suction process. Therefore, because the NCO characteristic peak is observed in the FTIR analysis of the modified clay after the modification reaction, we suggest that PMDI is bonded to the clay layers by covalent bonds.

WAXD pattern

To investigate the d-spacing of the clay, the WAXD pattern of the modified clay is shown in Figure 2. Generally, as the d-spacing of the clay layers increases, the 2θ of the clay decreases. Figure 2 shows that the d_{002} peak of the modified clay is lower than that of pure organoclay. The 2θ of the clay is obtained from the d_{001} peak. The X-ray diffractometer used in this study could not measure the pattern in front of 2.0° . From the lower d_{002} peak of modified clay than that of pure organoclay, it can be supposed that the 2θ of the modified clay is lower than that of pure organoclay. From this result, it is suggested that after modification, the d-spacing of the modified clay is wider by PMDI intercalated to the clay layers via covalent bonds during the clay modification.

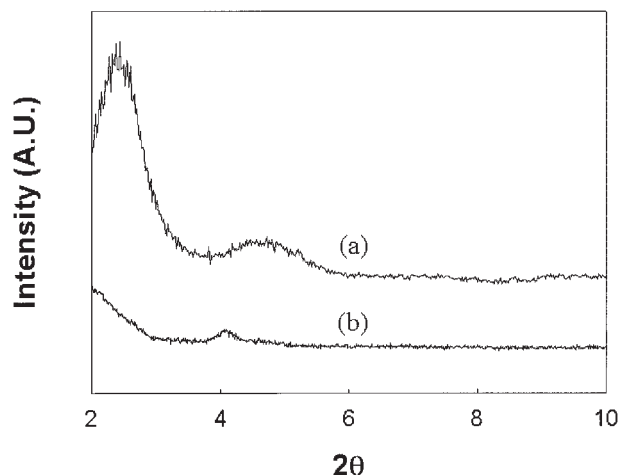


Figure 2 WAXD patterns of the organoclay (a) before and (b) after modification with PMDI.

Clay/PU nanocomposite

WAXD pattern

To investigate the nanometer scale dispersion of the clay, the WAXD pattern of the synthesized PU/clay nanocomposite is shown in Figure 3. Generally, as the d-spacing of clay layers increases, the 2θ of the nanocomposite decreases. If the layers of the clay are exfoliated, the 2θ of the nanocomposite disappears. Figure 3 demonstrates that the 2θ of the nanocomposite synthesized with the modified clay disappears. The PMDI bonded in the clay layer can react with polyol and then the formed urethane linkage can react with the PMDI and polyol, which exist in the space of the clay layers, by the reaction of forming PU. Therefore, the exfoliation of the clay layers is achieved by the PU, which was formed by the reaction between the polyol

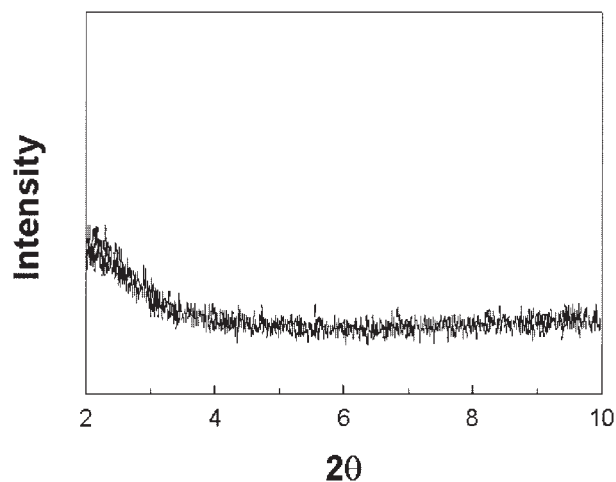


Figure 3 The WAXD pattern of the PU/clay nanocomposite.

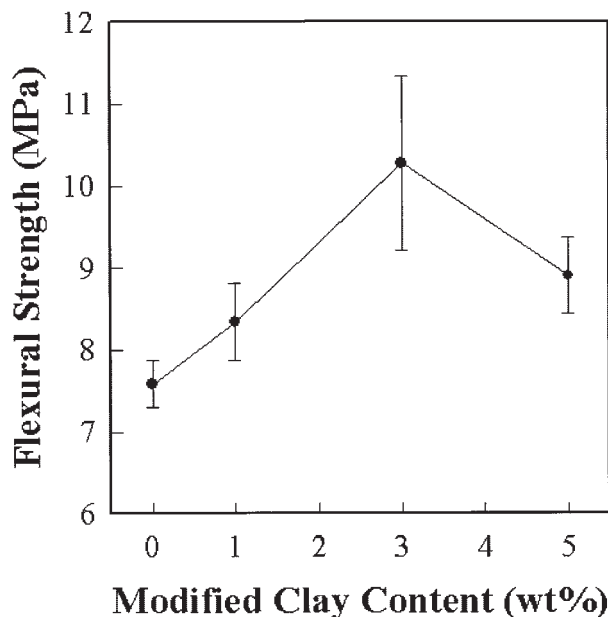


Figure 4 The effect of the modified clay content on the flexural strength of the PU/clay nanocomposite.

and the PMDI attached on the clay layers by covalent bonds.

Mechanical strength

Figures 4 and 5 show the flexural and tensile strength of the PU/clay nanocomposite with the modified clay content. In Figure 4, when the amounts of the modi-

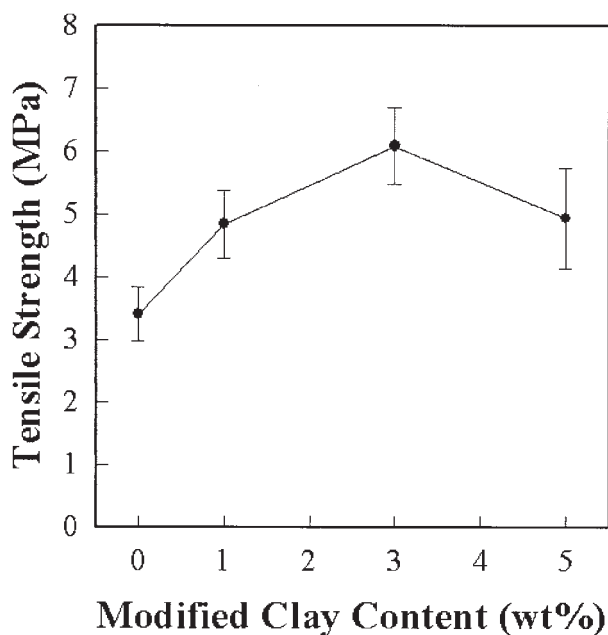


Figure 5 The effect of the modified clay content on the tensile strength of the PU/clay nanocomposite.

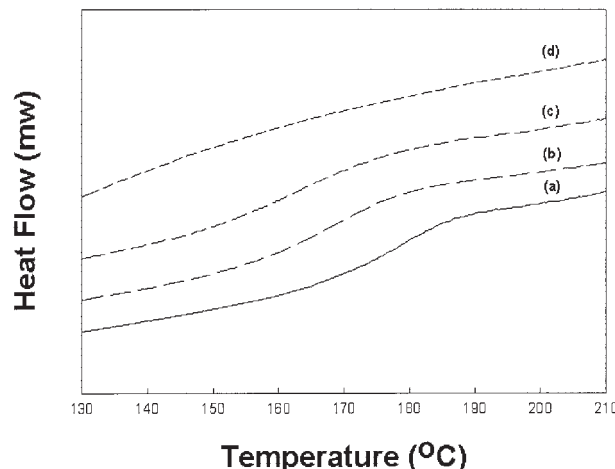


Figure 6 DSC thermograms of the PU/clay nanocomposite with modified clay contents of (a) 0, (b) 1, (c) 3, and (d) 5 wt %.

fied clay are 0, 1, 3, and 5 wt % based on PMDI, the flexural strengths of the PU/clay nanocomposites are 7.59, 8.35, 10.28, and 8.91 MPa, respectively. In addition, from Figure 5, when the amounts of the modified clay are 0, 1, 3, and 5 wt % based on PMDI, the tensile strengths of the PU/clay nanocomposites are 3.40, 4.83, 6.08, and 4.94 MPa, respectively. From these results, the flexural and tensile strengths of the PU/clay nanocomposite show that the maximum strength is with 3 wt % modified clay. We suggest that the decrease in the flexural and tensile strengths of the nanocomposite with more than 3 wt % modified clay may be due to the aggregation of excess clay.

Thermal properties

Figure 6 shows the glass-transition temperature (T_g) of the PU/clay nanocomposite. Previous research reported that, if the content of the clay increases, the T_g of the nanocomposite decreases.^{9,10} For the PU/clay nanocomposite synthesized with the modified clay (see Fig. 6), as the amount of the modified clay increases from 0 to 5 wt % based on PMDI, the T_g of the nanocomposite decreases from 176.3 to 151.1°C, respectively.

The T_g depends primarily on chain flexibility, molecular weight, branching/crosslinking, intermolecular attraction, steric effects, and so forth. As the chain flexibility of a polymer increases, the T_g of the polymer decreases. In the PU/clay nanocomposite, the intermolecular attractions of the PU segments seem to be interrupted by the charged clay layers; subsequently, the PU backbone chains also gain segmental mobility. Thus, the PU backbone chains can move at lower temperature. Therefore, the decrease in the T_g of the PU/clay nanocomposite with the modified clay con-

ment may be due to the decrease in the intermolecular attraction of the PU segments by the charged clay layers.

However, the exfoliated clay layers may provide steric hindrance to the PU chains. As shown in Figure 6, as the amount of the modified clay increases from 0 to 5 wt %, the change in the heat capacity at glass transition temperature (ΔC_p) at the T_g of the nanocomposite is decreased. The ΔC_p , which is the magnitude of the transition at the T_g , is related to the amount of mobility of the polymer chains. The strong steric hindrance can decrease the ΔC_p at the T_g . Therefore, the decrease in the ΔC_p of the PU/clay nanocomposite with the modified clay content may be attributable to the increase of steric hindrance by the exfoliated clay layers. In addition, the DSC trace at the top is continuous and does not show the T_g . This may indicate higher crystallinity caused by the nucleation of the polymer, which is caused by the clay.

CONCLUSIONS

The PU/clay nanocomposite was synthesized by the reaction between the polyol, PMDI, and the modified clay with the PMDI. To achieve the modified clay with the PMDI, the silanol group of the clay and the NCO group of the PMDI were reacted to form a urethane linkage. The FTIR analysis of the modified clay demonstrated that the NCO characteristic peak was observed after the modification reaction with the PMDI. Therefore, we conclude that the PMDI is covalently bonded between the silanol group of the clay and the

isocyanate group of the PMDI. From the results of the WAXD pattern, the 2θ peak of the PU/clay nanocomposite disappeared, which suggested that the exfoliation of the modified clay layers was achieved. The results of the mechanical properties shows that the maximum values of the flexural and tensile strengths were observed when the 3 wt % clay (based on PMDI) was added into the PU/clay nanocomposites. As seen in the DSC results, the T_g and ΔC_p of the PU/clay nanocomposite were decreased with the increase of the modified clay content. We suggest that the decrease in the ΔC_p of the PU/clay nanocomposite with the modified clay content may be due to the increase of steric hindrance by the exfoliated clay layers.

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