A Novel Synthesis of Reactive Nano-Clay Polyurethane and Its Physical and Dyeing Properties

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ABSTRACT: This study is about polyurea prepolymer, which was synthesized from the extender (*N*-(2-hydroxyethyl) ethylene diamine, HEDA or ethylene diamine, EDA) with 4,4′-diphenylmethane diisocyanate (MDI), as an intercalative agent to intercalate the organic modified montmorillonite clay. Then, it is further reacted with the polyurethane prepolymer, which is polymerized from the polytetramethylene glycol (PTMG) and MDI, to proceed the intercalative polymerization to form a polyurethane/clay nanocomposite polymer. The experimental parameters contain the use of polyurea intercalative prepolymer extender and also the contents of organo-clay in the prepolymer etc. We expect to get better mechanical property and also to improve the dyeing properties of nano-clay polyurethane. The polyurethane/clay polymer is synthesized using two-step method: synthesizing the polyurethane prepolymer from PTMG and MDI and then extended with the polyurea prepolymer modified with the organo-clay. Because the extender HEDA contains side chain of hydroxyl groups, the modified PU can further react with the reactive dye. From the experimental results of the fine structure (X-ray and FT-IR) and mechanical analysis, it is found that the intercalation is successfully achieved. The distance of interlayer spacing is manifestly enlarged. The mechanical properties are significantly improved as the content of organo-clay is increased. Besides, although the dye up-take is decreased with the increasing content of organo-clay, but the water-resistant fastness is improved. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1581–1590, 2007

Key words: clay; polyurethane; polyurea; chain extender

INTRODUCTION

Polyurethane (PU) is a thermoplastic rubber comprised of repeating hard and soft segments and possessing good mechanical properties such as medium tensile strength and high elongation. It is widely used in the synthetic leather, fiber, and adhesive.[1–8] For a colored PU leather, it is mostly made by nonwoven fabrics coated with a mixture of pigment and PU resin. The color is dull, with a lack of brightness and also has poor rubbing resistance. In addition, the elastic PU fiber is usually dyed with an acid dye or a disperse dye at a high temperature of 90–100°C and a long time of 50–60 min.[9–12] It wastes energy and time. Moreover, a silicate organo-clay nanocomposites are intensively investigated after the successful development of nylon/clay[13,14] nanocomposites by Toyota R and D Labs., in 1990, in Japan.[15–18] In this study, we try to synthesize organo-clay modified polyurethanes (PUs) to improve their physical properties and also the dye ability properties of the polyurethane copolymer with reactive dye. The structure, mechanical, and dyeing properties of the nanocomposite dyed PU are studied.

EXPERIMENTAL

Materials

Polytertramethylene glycol (PTMG) with molecular weight of 1000 from the Hodotani Co., Tokyo, Japan, and 4,4′-diphenylmethane diisocyanate (MDI) and *N*-methyl-2-pyrrolidone (NMP) (from Merck Co., Darmstadt, Germany) were used without further purification. The reactive clay of B-30 from Southern Clay Products (Gonzales, TX) and the reactive dye of C.I. Reactive Red 195 (Bayer Co. Ludwigshafen, Germany) were used for modifying the PU and dyeing the modified polyurethane resin, which were also used without further purification.

The chemical structure of the reactive clay and reactive red dye are shown as follows, respectively.
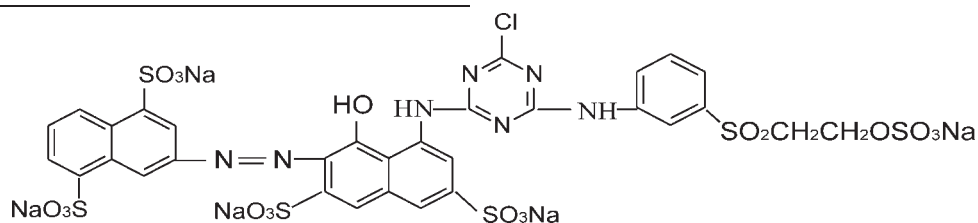
Reactive clay of B-30

$$CH_3 \overset{\displaystyle CH_2CH_2OH}{\underset{\displaystyle CH_2CH_2OH}{\overset{|}{\underset{|}{- N^+ -}}}} T$$
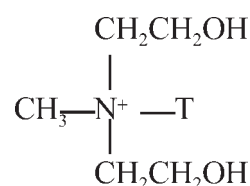
where T is tallow (~65% C18; ~30% C16; ~5% C14); Anion: Chloride.

C.I. Reactive Red 195

## Synthesis of chain extender prepolymer and clay intercalation

Before clay intercalation, the commercial chemically modified clay was added to 50 g of NMP and stirred for 6 h and then homogenized with homogenizer for 0.5 h to ensure a good dispersion of clay in solvent. Then, a different weight ratio of clay dispersion was added to MDI in solvent to react the hydroxy end group of reactive clay with isocyanate group of MDI to form a polyurethane linkage at 100°C for 5 h. The

clay was expected to be intercalated by MDI. Furthermore, a HEDA was added to react with the remainder of isocyanate group in MDI, a further enlargement of clay intercalation was proceeded. The final chain extender of intercalated clay polyurethane prepolymer was synthesized. The reaction scheme is depicted as follows.

1. Hydroxy terminated end group of organoclay to react with MDI (temperature: 75°C, time: 60 min)
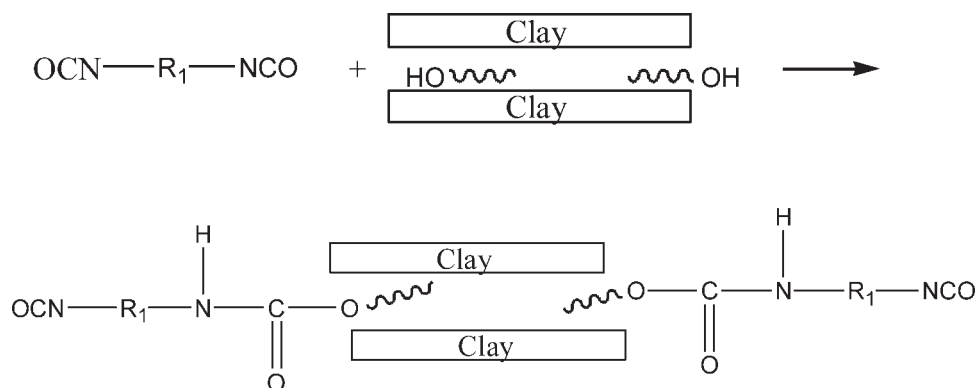


2. The addition of HEDA to react further with MDI (temperature: 5°C, time: 30 min):
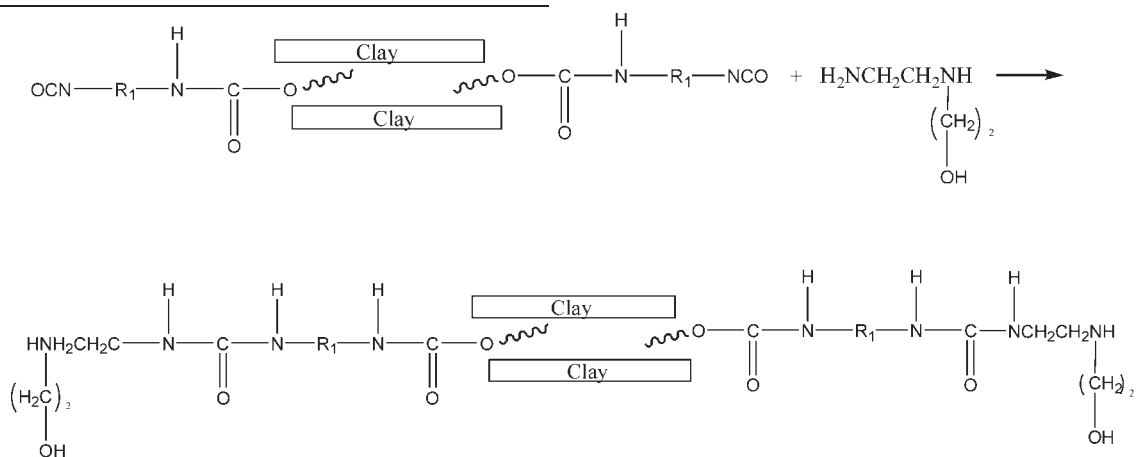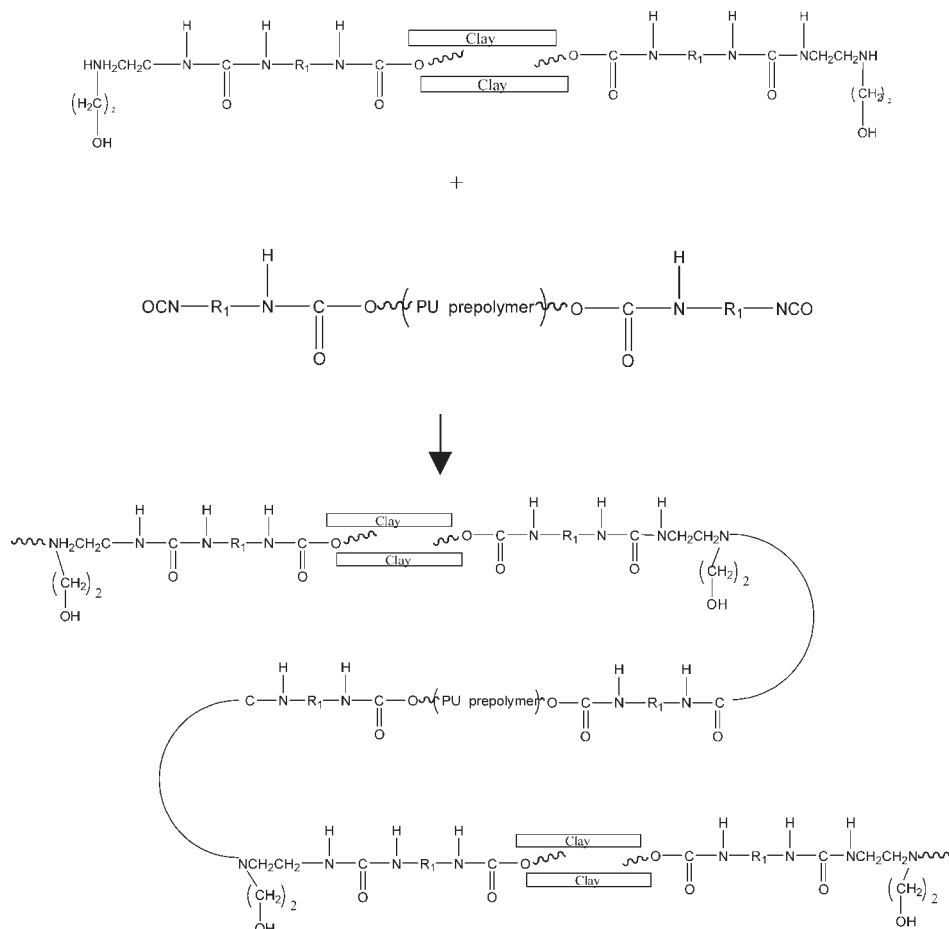
Synthesis of polyurethane prepolymer and its final extension into polyurethane/clay composite

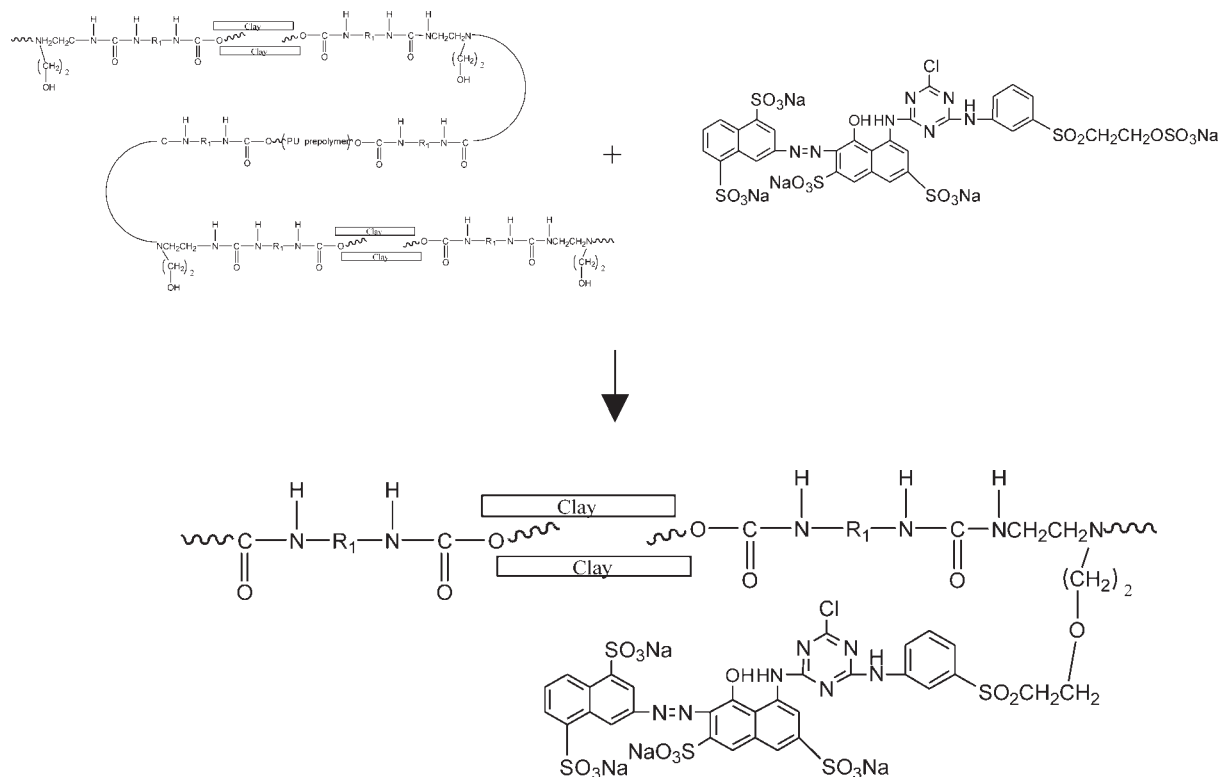The prepolymer was synthesized by the reaction of PTMG with MDI (temperature: 70°C, time: 120 min) and finally extended with clay intercalated polyurea diamine prepolymer (temperature: 30°C, time: 60 min).
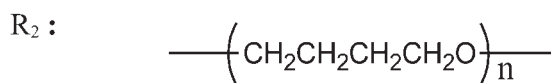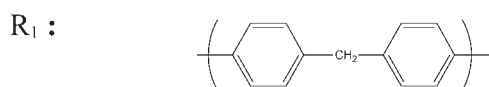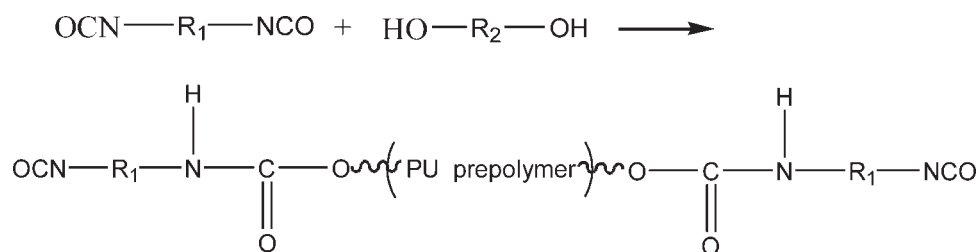
Then

The dyeing of polyurethane (temperature: 80°C, time: 60 min)
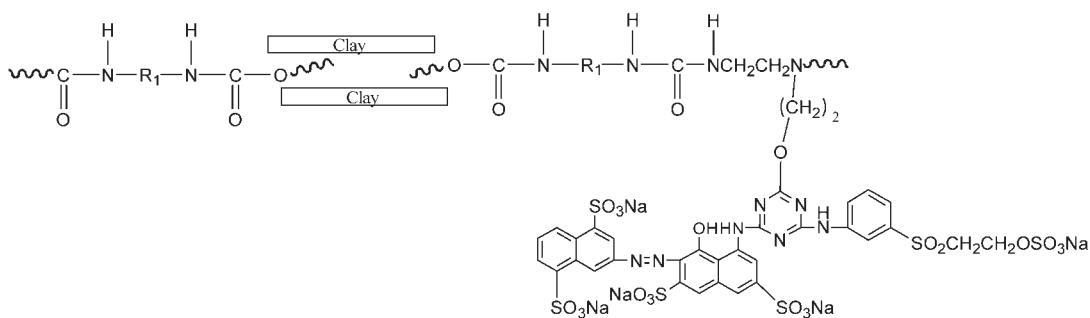
Experimental composition and ratios

The PU/clay experimental composition and ratios are summarized in Table I; the MC and MCH series in Table II are the intermediate product of intercalation of clay with MDI and MDI further with HEDA, respectively.

Measurements

Infrared spectra of PU and PU/clay with different chain extenders were obtained by Hitachi Model 260-50 Type (Hitachi, Tokyo, Japan) over a range of 700–3500 cm^{-1}. Wide-angle X-ray photographs were taken with Ni-filter Cu Kα radiation using a Rigaku D/max-II Type X-ray diffractometer. Mechanical properties were measured using an Instron Mode 1122 testing instrument (Instron, Canton, MA) at a cramp rate of 20 mm/min; a paper extension rate of 10 mm/min with the specimen of 50 mm length, 10 mm width, and 0.1–0.2 mm thickness; and a full load of 20 kg.

To evaluate the dye up-take of the dyed PU, the 0.05 g of dyed PU was dissolved in 100 mL of DMF, dilute to 2×10^{-5} g/mL of concentration, measured

TABLE I
The PU/Clay Experimental Composition

PU/clay series	PU prepolymer		Chain extender prepolymer			Clay	Dye	Hard
Code	MDI (mol)	PTMG (mol)	MDI (mol)	HEDA (mol)	EDA (mol)	(%)	(g)	segment (%)
PU	4.31	2.77	1.23	2.77	–	–	–	37.68
PUC03	4.31	2.77	1.23	2.66	–	3	–	37.52
PUC05	4.31	2.77	1.23	2.59	–	5	–	37.41
PUC07	4.31	2.77	1.23	2.52	–	7	–	37.31
PUC09	4.31	2.77	1.23	2.44	–	9	–	37.20
PUC11	4.31	2.77	1.23	2.37	–	11	–	36.88
PU-E	4.31	2.77	1.23	–	2.77	–	–	35.92
PU-D	4.31	2.77	1.23	2.77	–	–	0.63	37.68
PUC03-D	4.31	2.77	1.23	2.66	–	3	0.60	37.52
PUC05-D	4.31	2.77	1.23	2.59	–	5	0.59	37.41
PUC07-D	4.31	2.77	1.23	2.52	–	7	0.57	37.31
PUC09-D	4.31	2.77	1.23	2.44	–	9	0.56	37.20
PUC11-D	4.31	2.77	1.23	2.37	–	11	0.54	36.88
PU-E-D	4.31	2.77	1.23	–	2.77	–	0.63	35.92

PU is the PU polymer with chain extender molecular weight of 460; PUC03 ~ PUC11, the PU/clay nanocomposite with clay content of 3%–11%; PUC03-D~PUC11-D, the dyed PU/clay nanocomposite with clay content of 3%–11%; PU-E, PU-E-D, the PU polymer with ethylene diamine as chain extender.

by the photometer and compared with the absorption value of the standard dye solution. For the dye-fastness of dyed PU, the AATCC test method of 61-1985 was used.

RESULTS AND DISCUSSION

Characteristics of polyurethane with intercalation

MDI and two kinds of chain extenders (HEDA and EDA) were used to prepare two series of polyurethanes (PU and PU-E series). Seven copolymers were synthesized from one kind of MDI, one kind of PTMG, and two kinds of chain extenders with different weight percentages of reactive clay. As shown in Figures 1 and 2, the absorption peak of clay is characterized at 1046–1040 cm^{-1} for SiO, 523 cm^{-1} for AlO, and 464 cm^{-1} for MgO, respectively. The absorption of pure polyurethane is characterized at 3400–3200 cm^{-1} for >NH stretching vibration. The characteristic absorption of >C=O is observed at 1735 cm^{-1};

>C=O of the urea group is observed at 1640 cm^{-1}; C—O is observed at 1230 cm^{-1}; C—O—C of PTMG is observed at 1110 cm^{-1}. Moreover, the —N=C=O peak at 2275–2240 disappeared after the reaction. With the existence of the above-mentioned absorption peaks, it is suggested that the synthesis of polyurethane/clay nanocomposite is successful.

For the absorption peak of intermediate product of MCH (MDI + clay + HEDA) as shown in Figure 2, it demonstrates that a small characteristic peak of 1735–1700 of urethane is observed. It is the reaction of hydroxyl end group of clay with —NCO of MDI. From that, it could conclude that the clay did react chemically with the MDI to form the urethane linkage.

Wide-angle X-ray diffraction of nanocomposites

The X-ray pattern of MC series (intermediate product of MDI and clay) is shown in Figure 3. It reveals an

TABLE II
The Intermediate Product of Clay with MDI and MDI Further with HEDA

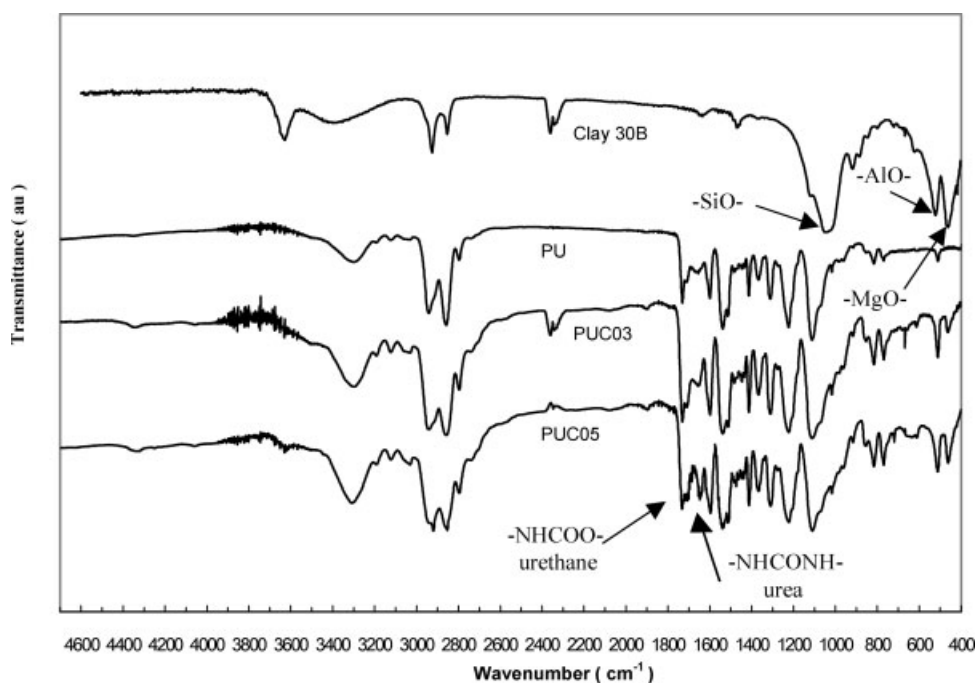| Intermediate product	PU prepolymer		Chain extender prepolymer			Clay
Code	MDI (mol)	PTMG (mol)	MDI (mol)	HEDA (mol)	EDA (mol)	(%)
MC 03	–	–	1.23	–	–	3
MC 05	–	–	1.23	–	–	5
MC 07	–	–	1.23	–	–	7
MC 09	–	–	1.23	–	–	9
MC 11	–	–	1.23	–	–	11
MH	–	–	1.23	2.77	–	0
MCH 03	–	–	1.23	2.66	–	3
MCH 05	–	–	1.23	2.59	–	5
MCH 07	–	–	1.23	2.52	–	7
MCH 09	–	–	1.23	2.44	–	9
MCH 11	–	–	1.23	2.37	–	11

Figure 1 The FTIR of Clay 30B and PU series.

angle of 3.05–3.15° for 2θpeak. Based on Bragg scattering equation, $2d \sin \theta = n\lambda$, the peak shifts from 1.71 nm ($2\theta = 5.15°$) of clay 30B to 2.89–2.80 nm ($2\theta = 3.05$–3.15°). This demonstrates that the intercalation does happen in the reaction of —OH of clay with NCO of MDI. It increases the interlayer distance of 1.09–1.18 nm. In addition to that, there is a smaller peak happened at $2\theta = 5.95$–6.15°. The d value is 1.44–1.48 nm, nearly half size of first peak. It is believed to be the second-order diffraction peak of primary peak. Moreover, for MC09 sample (9% of clay), it exhibits a

unclear peak at $2\theta = 8.92°$ or $d = 0.990$ nm, which is one-third of primary peak 2.89 nm. This is believed to be the tertiary order of the peak. From that, the increase of interlayer distance and appearance of second- and third-order peak can demonstrate that the addition of MDI does exhibit an intercalative effect to clay, but it still remain a multiple layer and orderly structure.

The X-ray pattern of MCH series (intermediate product of MDI, HEDA, and clay) is shown in Figure 4. A peak of $2\theta = 2.50$–2.75° is shown in the figure, i.e.,
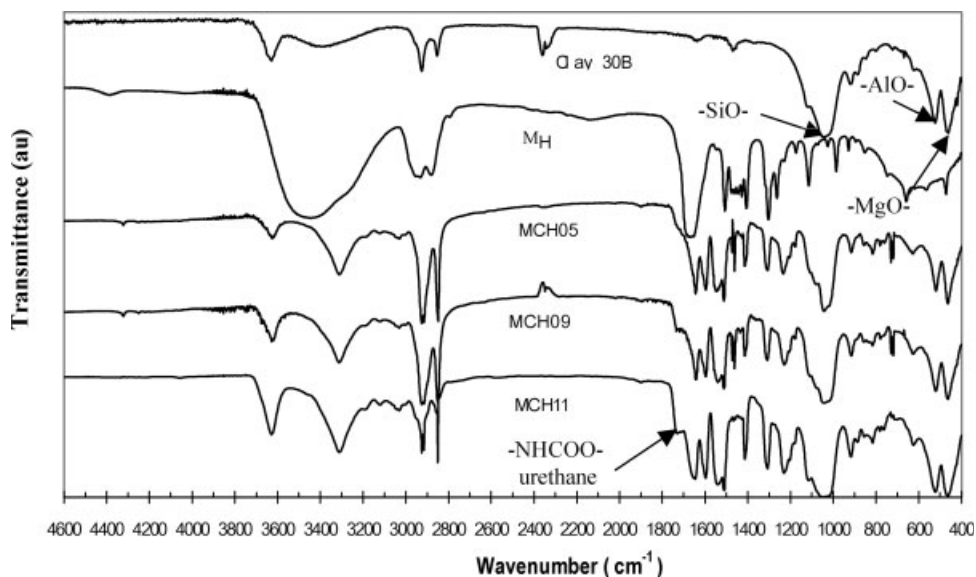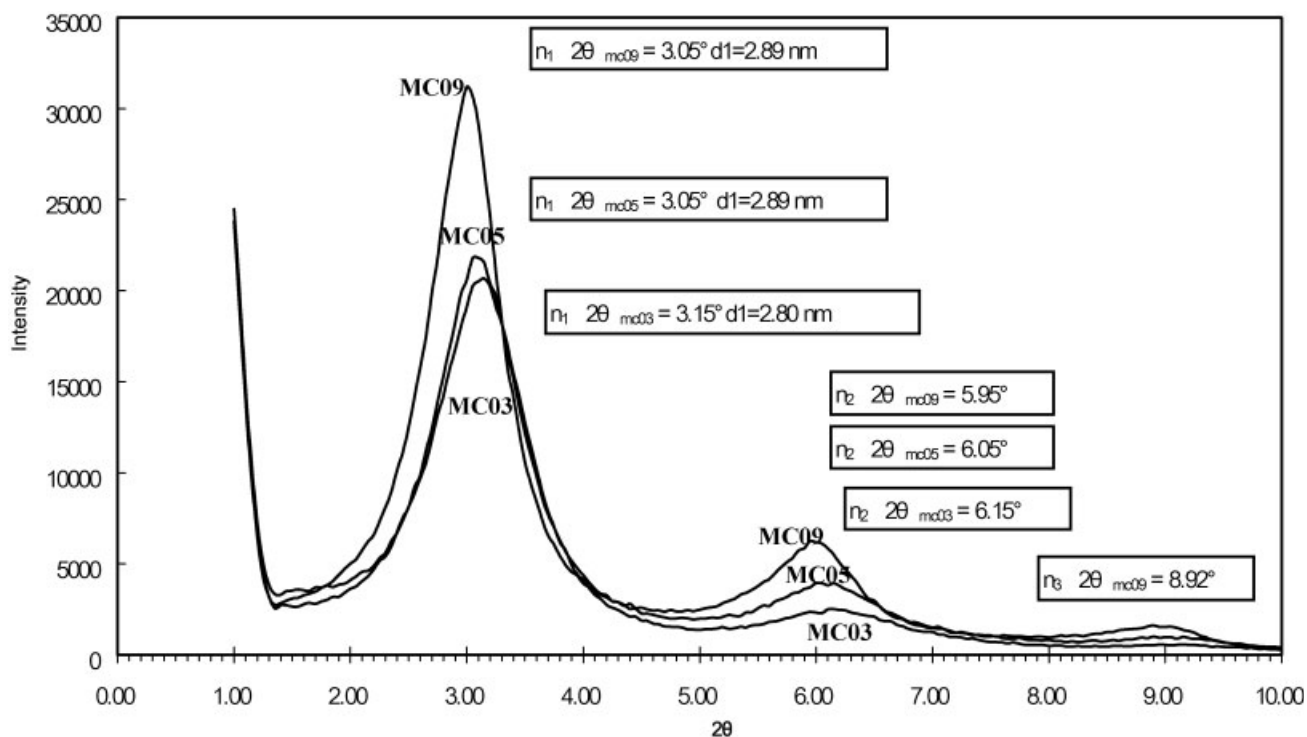

Figure 2 The FTIR of clay 30B, MH and MCH series.

Figure 3 The X-ray diffraction curve of MC series (clay + MDI).

the interlayer distance d shifts from MC series of 2.80–2.95 nm ($2\theta = 3.15$–$3.05°$) to 3.53–3.21 nm ($2\theta = 2.50$–$2.75°$). It increases the interlayer distance of 0.44–0.64 nm. In addition to that, there is a small peak at $2\theta =$ 5.25–6.10° or $d = 1.67$–1.59 nm, which is nearly 1/2 of d value of first peak and the intensity is lowered. It is believed to be the second order of diffraction peak. Based on above observation, the addition of HEDA
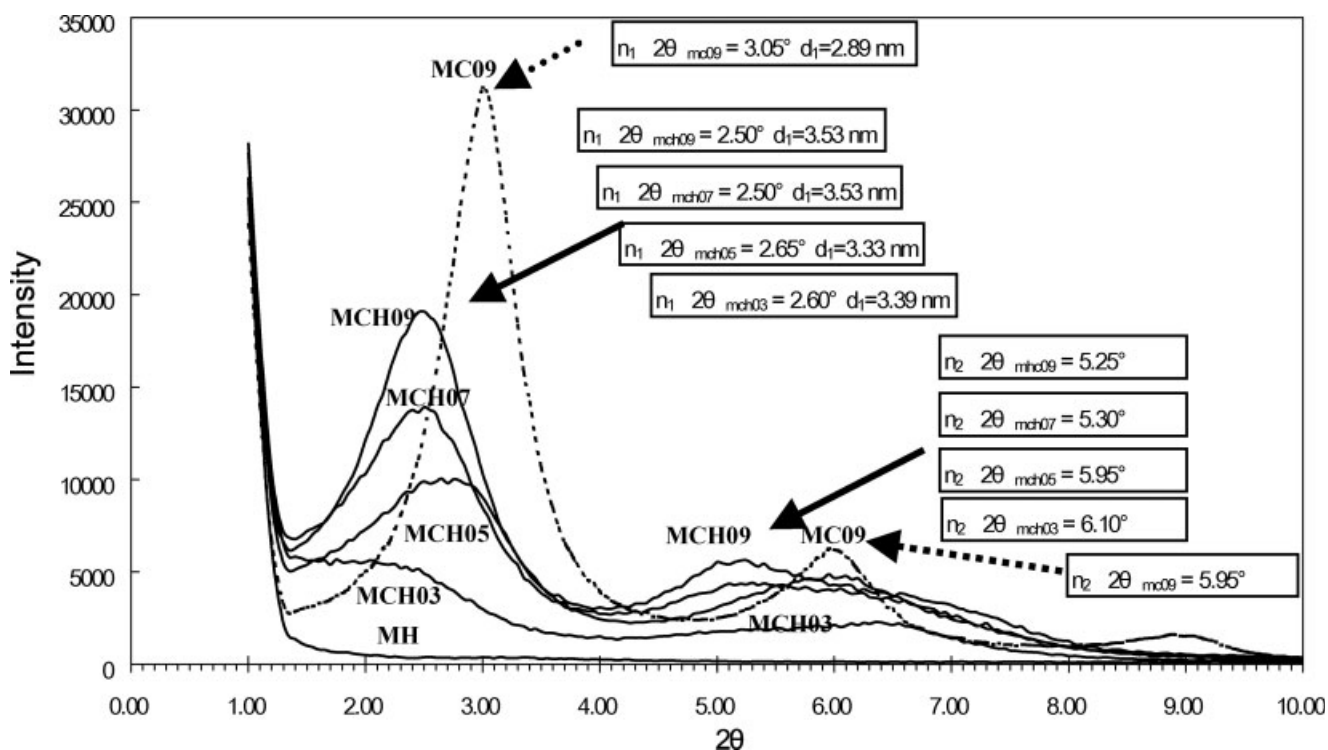

Figure 4 The X-ray diffraction curve of MCH series (clay + MDI + HEDA).
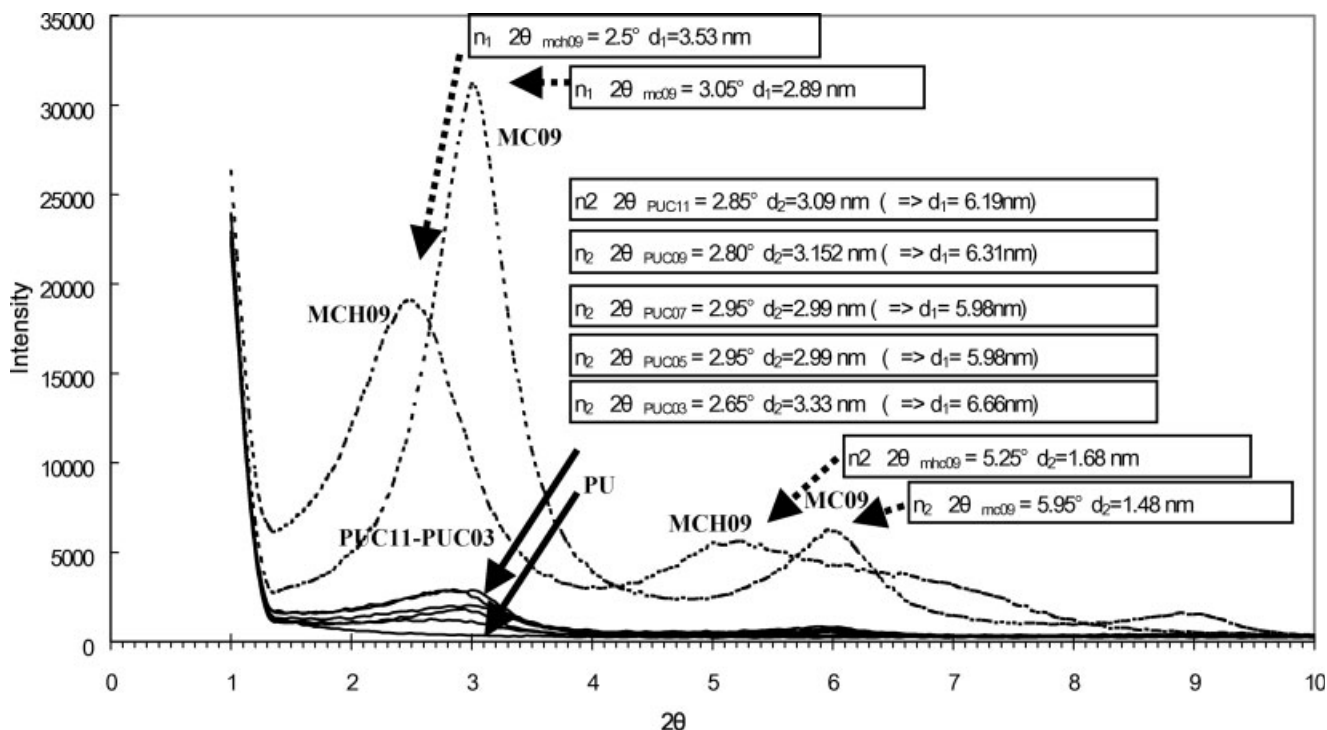
Figure 5 The X-ray diffraction curve of PUC series (clay + PU).

did increase the intercalative effect of MC series, but the MCH series are still a multiple layer and orderly structure.

The X-ray pattern of the final product of PU/clay nanocomposite is shown in Figure 5, which shows a peak at $2.65–2.95°$ ($d = 2.99–3.33$ nm) for PUC03-PUC11. It decreases to 0.06–0.54 nm when compared with the peak of MCH. Nevertheless, the interlayer distance of clay which reacted with MDI (MC series) is found to increase 1.09–1.18 nm and further increase to 0.44–0.64 nm as HEDA was added (MCH series). The interlayer distance of PU/clay is expected to be more intercalated after chain extending. Thus, the diffraction peak of $2.65–2.95°$ is believed to be the second-order diffraction of PU/clay nanocomposite based on a reasonable judgement. From that, the first-order diffraction peak should be at $1.32–1.48°$ ($d = 6.66–5.98$ nm). How-

ever, as shown in the figure, it does not find the peak. It is believed that as the diffraction angle close to $1.45°$, the background effect will be pronounced and the peak can not be seen in the pattern. In all, the interlayer distance of clay is from 1.71 nm of clay 30B to 2.80–2.89 nm of MC series, then to 3.21–3.53 nm of MCH series, and finally to 5.98–6.66 nm of PU/clay nanocomposite. From that, it is concluded that the final PU/clay composite behaves an orderly structure and at least of 2–3 layer of diffraction existed.

Physical properties

The tensile strength and elongation are shown in Table III and Figures 6. As shown in Figure 6, the ten-

TABLE III
The Physical Properties of PU/Clay Nanocomposite

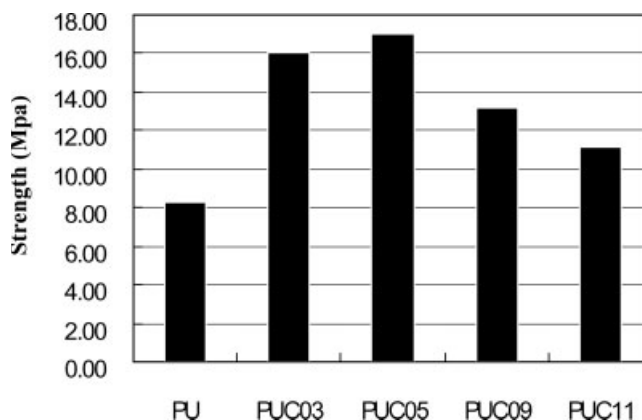| Code	Clay content (%)	Tensile strength (Mpa)	Tensile elongation (%)
PU	0	8.33	1258
PUC03	3	16.05	892.0
PUC05	5	17.03	813.8
PUC07	7	14.36	896.0
PUC09	9	13.17	882.1
PUC11	11	11.16	853.4
PUC03-D	3	8.54	857.3
PUC07-D	7	8.79	737.1
PUC011-D	11	9.06	494.8

Figure 6 The physical property of PU and PUC series (clay + PU).

TABLE IV
Efficiency of Dye-Uptake of PU and PU/Clay Composites

Code	Experimental dye-uptake (mg/g)	Theoretical dye-uptake (mg/g)	Efficiency of dye-uptake (%)
PU-D	12.22	13.96	87.56
PUC03-D	10.59	13.07	81.05
PUC05-D	9.51	12.50	76.08
PUC07-D	9.08	11.95	75.96
PUC09-D	7.67	11.42	67.19
PUC11-D	6.49	10.91	59.47
PU-E-D	5.31	14.35	36.98

sile strength is increased initially and dropped down as the content of clay increased from 0 to 11%. The maximum value appears at 5% of clay concentration.

For the tensile elongation, as in Table III, the elongation seems going down and up. The minimum elongation occurs at 5% of clay concentration. The clay reinforces the PU in nanoscale does improve their tensile strength. It increases nearly 2.05–1.34 times as the concentration varied from 3% to 11%, especially a small concentration of clay added (3%–5%). The reason for improving its tensile strength is believed that the clay will restrict the motion of PU. It is like a physical crosslinking and the tensile strength increased. However, if more clay added, the silicate layer and PU can form a weak point, i.e., the force in the composite will distribute unevenly, and the strength falls.

For tensile elongation, it is alike most of composite, it falls with the addition of filler, but not much change (about 3%). It is believed that most of clay is contained in the hard segment region of PU, a less effect on the elongation property of soft segment region. For the dyed PU composite, the strength is lowered because of the side chain of PU containing the dye molecule. It enlarges the separation distance of PU molecule, leading to a lowering of the strength.

Dye-uptake and dye-fastness analysis

The dye uptake of the dyed PU film was measured by the photometer and is summarized in Table IV.

TABLE V
The Grade of Water-Fastness of
PU and PU/Clay Composites

Code	Grade of water fastness
PU-E-D	2–3
PU-D	3–4
PUC03-D	3–4
PUC05-D	3–4
PUC07-D	4
PUC09-D	5
PUC11-D	5

As shown in the table, the efficiency of dye-uptake (the ratio of experimental dye uptake to theoretical dye uptake) is decreasing with the more content of clay in PU. The reason for its inability to reach 100% efficiency is due to the steric hindrance of the —OH group in the side chain of the PU polymer and also its less content of the —OH group with more amount of clay in PU. The dye-uptake falls from PUC03-D 81.1% to PUC11-D 59.5%. Moreover, the PU-D series show a higher dye-uptake than that of PU-E-D series. This is due to the PU-D series having a side chain of OH groups which can reacts with the reactive dye. The results of water fastness in all dyed PU are also shown in Table V, It is found that the water fastness is promoted from grade of 2–3 to grade of 4–5 as clay is contained in the PU. The improvement of water resistance of PU/clay composite is believed that the clay can contribute more coalescence between PU and dye molecule, thus a better dye fastness resulted. Moreover, the dye fastness in PU-D series is much better than that in PU-E-D series. It demonstrates that the dye fastness of PU with HEDA as chain extender exhibits better dye fastness than that with EDA. This is due to that the PU with covalent bond of dye molecule could contribute better grade of dye fastness.

CONCLUSIONS

In this study, we successfully synthesized the PU/clay nanocomposite with better physical properties. Because the extender HEDA contains side chain of hydroxyl groups, the modified PU can further react with the reactive dye.

From the experimental results of the fine structure (X-ray and FTIR) and mechanical analysis, it is found that the intercalation is successfully achieved. The distance of interlayer spacing was manifestly enlarged. The mechanical properties are significantly improved as the content of organo-clay is increased. Besides, although the dye-up-take is decreased with the increasing content of organo-clay, but the water-resistant fastness is improved.

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