Influence of Structure of Organic Modifiers and Polyurethane on the Clay Dispersion in Nanocomposites via *In Situ* Polymerization

Mallikarjuna Shroff Rama, Sivaram Swaminathan

Division of Polymer Science and Engineering, National Chemical Laboratory, Pune 411 008, Maharashtra, India

ABSTRACT: Influence of polyurethane (PU) structure on the nature of PU/clay nanocomposite was studied using varying amounts of trimethylol propane (TMP) as branching agent. The effect of hydroxyl groups in the modifier of organoclays on the structure of PU/clay nanocomposites was studied. Nanocomposites were characterized using wide-angle X-ray diffraction measurements (WAXD) and transmission electron microscopy (TEM). The results show that formation of completely exfoliated and well dispersed polyurethane/clay nanocomposites via *in situ* polymerization, is facilitated by the presence of tethering groups on the clay surface and an ability to form branched and cross-linked structures. Incorporation of long alkyl chains in addition to tethering hydroxyl groups in the modifier structure of the clay did not significantly improve the compatibility of linear PU with the clay. Intercalated thermoplastic polyurethane/clay nanocomposites, prepared using poly(caprolactone diol) as soft segment and isophorone diisocyanate and 1,4-butanediol as hard segments show increase in storage tensile moduli at temperatures before glass transition temperature when functional groups capable of chemically reacting with the growing polymer chains are present in the clay modifier. This is indicative of improved interaction of the polymer with the clay surface when the modifier has larger number of hydroxyl groups. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1774–1786, 2010

Key words: polyurethane; nanocomposites; organoclay; intercalation and exfoliation

INTRODUCTION

Polyurethanes (PU) are versatile polymeric materials exhibiting a wide range of physical and chemical properties and finds wide applications in coatings, adhesives, foams, rubbers, thermoplastic elastomers, and composites.[1–3] Nevertheless, PU also suffers from a few weaknesses, such as, low thermal stability and poor mechanical strength. Chemical modifications of PU or use of inorganic filler may in specific instances mitigate these problems. Many properties of PU are reported to be improved by incorporation of fillers. Calcium carbonate, aluminum hydroxide, kaolin, titanium dioxide, zinc oxide, were used to improve mechanical properties.[4–9] However, use of inorganic particulate fillers also has a deleterious effect on the fatigue property of PU and reduces its elongation at break.[10]

Nanostructured PU/clay composites have been extensively studied in recent years.[11] Wang and Pinnavaia[12] reported the preparation of nanocomposites of elastomeric PU based on a polyol, poly(glycerol propoxylate), and Rubinate methylene diphenyl diisocyanate prepolymer (Mn: 1050) with a functionality of two. They found that clays exchanged with long chain onium ions (carbon number ≥ 12) have good compatibility with several polyols commonly used for the synthesis of PU. In general, tensile strength and thermal stability of PU nanocomposites showed improvements without loss of elongation[13–31] except for one study where a decrease of tensile modulus was observed.[13] In the case of *in situ* polymerization studies, clay particles were intercalated either by soft polyols before reaction with diisocyanates, or prepolymer terminated with diisocyanates were mixed with organoclay followed by chain extension with short chain diols.[32–35] Exfoliated PU/clay nanocomposites, based on polyether polyol and hydrogenated MDI, were obtained whenever the functionality of the polyol used was greater than two.[36]

Tien and Wei,[19] showed that PU based on poly (tetramethylene glycol) and 4,4'-methylene diphenyl diisocyanate can be ionically tethered to the surface of the clay by choosing modifiers having reactive hydroxyl groups. They used short chain hydroxyl containing modifiers. The hydroxyl groups in the modifier of the clay were reacted with isocyanate terminated PU-prepolymer. The presence of 3 hydroxyl groups per modifier favored formation of

exfoliated PU nanocomposites. Moon et al.[37] utilized the same organoclay to prepare PU nanocomposites based on poly(butylene succinate) (PBS). Poly(ethylene glycol) was employed as the soft segment and 1,4-butanediol and hydrogenated MDI as hard segments. The nanocomposites obtained exhibited an intercalated structure. Inability to form exfoliated structures was attributed to the poorer swelling of organoclay by PBS over PTMG. Chavarria and Paul[38] studied the effect of organoclay structure on the dispersion of thermoplastic polyurethane nanocomposites prepared by melt mixing. It was shown that the ammonium ion having one alkyl tail rather than two, presence of hydroxyethyl groups rather than methyl groups on the nitrogen and a longer alkyl tail along with hydroxyethyl group rather than shorter alkyl chain along with hydroxyethyl group leads to better clay dispersion. The study also showed that PU with more hard segments, i.e., with more polar functionalities, favors better interaction. Pattanayak and Jana[39–42] utilized a combination of tethering reaction and melt shear force to disperse the clay in PU matrix. The PU was derived from polypropylene glycol, 1,4-butanediol and MDI. They showed that partially exfoliated structures could be obtained by adding the organoclay during bulk polymerization. The extent of dispersion of clay depends on the polarity of polyol used. However, bulk polymerization method has its own limitations such as (i) poor diffusion of reactants that hinder the rate of the reaction (ii) exotherm resulting in steep rise in temperature during polymerization leading to the formation of biurets and allophanates.

In spite of several earlier studies, dependence of the nature of nanocomposites obtained on the structure and composition of the poly(urethane)s are poorly understood. An exfoliated nanocomposite results when a branched polyol is used.[36] Similarly when a modifier containing three methylol groups was ionically anchored to the clay and reacted with an isocyanate terminated prepolymer, (based on PTMG and MDI), an exfoliated structure was obtained.[19]

This study was undertaken to better understand the effect of composition of PU and the nature of modifier functionality on the structure of PU nanocomposites. Objective of the study is portrayed in three parts, discussing the influence of (i) effect of branching agents and presence of hydroxyl functionality, (ii) degree of functionality in the modifier, and (iii) soft segments in the matrix (for obtaining thermoplasticity) on dispersion.

For the first study, PU nanocomposites were prepared via *in situ* solution polymerization using 2-ethyl-1, 3-hexanediol and toluenediisocyanate (TDI) as monomers and trimethylolpropane (TMP) as a branching agent. Organically modified montmorillonite clays Cloisite 30 B, (in which the modifier has

a long alkyl chain and two hydroxy ethyl groups) and Cloisite 25 A (in which the modifier have only long alkyl chain and no hydroxyl groups) were chosen for the study (Table I). For the second study, organoclays were prepared by exchanging the Na^{+} ions in pristine sodium montmorillonite with three different quaternary ammonium bromides namely N-(2-hydroxyethyl)-N,N-dimethylhexadecyl-1-ammonium bromide (**1**), N,N-bis(2-hydroxyethyl)-N-methylhexadecyl-1-ammonium bromide (**2**) and N,N-bis(2-hydroxyethyl)-N-methyl-2-(hydroxymethyl)octadecyl-1-ammonium bromide (**3**), having 1, 2, or 3 hydroxyl functionality respectively and designated as 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT) respectively. The state of dispersion of clays was evaluated for preparation of polyurethane–clay nanocomposites via *in situ* solution polymerization of 2-ethyl-1, 3-hexanediol, and TDI. In addition, a thermoplastic polyurethanes (polycaprolactone diol and isophorone diisocyanate with butanediol as chain extender)/clay nanocomposites was also prepared using modified clays such as 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT).
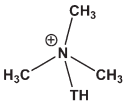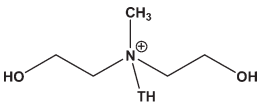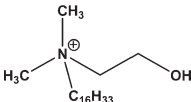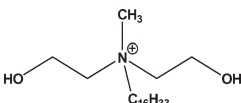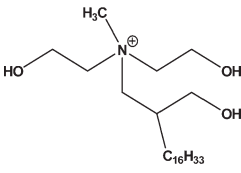
EXPERIMENTAL

Materials

Cloisite 30B and Cloisite 25A which are organomodified Montmorillonites and Na^{+} Montmorillonite were obtained from Southern Clay Products, USA. They were dried by subjecting the sample to azeotropic distillation with toluene and stored in a vacuum desiccator. 2-ethyl-1,3-hexanediol, 1-hexadecyl bromide, N,N-bis(-2-hydroxyethyl)-N-methylamine, N-(2-hydroxyethyl)-N,N-dimethylamine and isophorone diisocyante were obtained from Aldrich Chemical Co., and used without further purification. 2-ethyl-2-(hydroxymethyl)propane-1,3-diol (TMP), 1,4- butanediol, and dimethyl malonate were obtained from Sd fine chemicals, India and used as such. Toluene diisocyanate (mixture of 2,4 and 2,6 isomers in the ratio 20 : 80) were obtained from Narmada Chemicals, India. Polycaprolactone diol (CAPA 2077A, Mn: 750, PDI: 1.2) was kindly supplied by Solvay Chemicals, USA.

Preparation of N-(2-hydroxyethyl)-N,N-dimethyl-N-hexadecylammonium bromide (1)

N-(2-hydroxyethyl)-N,N-dimethyl amine (4.457 g, 50 mmol) was mixed with hexadecyl ammonium bromide (15.268 g, 50 mmol) in the stoichiometric ratio 1 : 1 and heated to 60°C. White solid particles started forming immediately at 60°C. Heating was continued for another 6 h to ensure that the reaction was complete. 2-hydroxyethyl dimethyl hexadecylammonium bromide (1) (19.7 g) was obtained in a pure form and

TABLE I
List of Organoclays Used and the Structure of Their Modifiers

Organoclay	Structure of the modifier	Name of the modifier
Cloisite 25A	 Where TH = hydrogenated tallow	N-(hydrogenated tallow)-N,N,N-trimethyl ammonium cation
Cloisite 30B	 Where TH = hydrogenated tallow	N,N-bis(hydroxyethyl)-N-(hydrogenated tallow)-N-methyl ammonium cation
1-OH(MMT)	 **1**	N-(2-hydroxyethyl)-N,N-dimethyl-N-hexadecylammonium cation
2-OH(MMT)	 **2**	N,N-bis(2-hydroxyethyl)-N-methyl-N-hexadecylammonium cation
3-OH(MMT)	 **3**	N,N-bis(2-hydroxyethyl)-N-methyl-N-(2-(hydroxymethyl) octadecyl)ammonium cation

used without further purification. Yield: 75%. ^{1}H-NMR: δ 0.88 (3H, t); 1.26 (26H, m); 1.76 (2H, m); 3.38 (6H, s); 3.55 (2H, m); 3.77 (2H, b); 4.14 (2H, b); 5.03 (1H, b).

Preparation N,N-bis(2-hydroxyethyl)-N-methyl-N-hexadecylammonium bromide (2)

Bis(hydroxyethyl)methyl amine (5.958 g, 50 mmol) was mixed with hexadecyl ammonium bromide (15.268 g, 50 mmol) in the stoichiometric ratio 1 : 1 and heated to 60°C. White solid particles started forming 15 min after attaining the temperature of 60°C and the heating was continued for another 8 h to ensure completion of reaction. Obtained N,N-bis(2-hydroxyethyl)-N-methyl-N-hexadecylammonium bromide (2) (21.2 g) was used without further purification. ^{1}H-NMR: δ 0.88 (3H, t); 1.26 (26H, m); 1.75 (2H, m); 3.33 (3H, s); 3.54 (2H, m); 3.73 (4H, b); 4.14 (4H, b); 5.03 (2H, b).

Preparation of N,N-bis(2-hydroxyethyl)-N-methyl-N-(2-(hydroxymethyl)octadecyl) ammonium bromide (3)

Hydroxyl alkyl bromide was prepared from dimethyl malonate and hexadecyl bromide in three

steps and was used for the quartenization of bis (hydroxyethyl) methylamine. Reactions are depicted in Scheme 3.

Alkylation of dimethyl malonate with hexadecyl bromide

Clean dry sodium (2.0 g, 85 mmol) was placed in a three-neck round bottom flask fitted with double surface condenser, dropping funnel and septum adapter. Dry methanol (100 mL) was added to sodium slowly under cooling. Sodium methoxide was formed with the evolution of hydrogen gas. Cooling was stopped after the evolution of hydrogen gas ceased. Dimethyl malonate (11.2 g, 85 mmol) was added under stirring and heated to gentle reflux. Hexadecyl bromide (24.4 g, 80 mmol) was taken in dropping funnel and added slowly into the contents of the round bottom flask over a period of 20 min and reflux continued for 12 h. Progress of the reaction was monitored by TLC. The reflux was stopped when all the alkyl bromide was consumed. The crude reaction mixture was concentrated by evaporating methanol, diluted with ethyl acetate and washed with water several times until the washings was neutral to litmus. Pure dimethyl-2-hexadecyl

malonate (18.5 g), was separated from the crude mixture by flash chromatography. Yield: 65%. ^{1}H-NMR: δ 0.88 (3H, t); 1.26- (28H, m); 1.91 (2H, m); 3.36 (1H, t); 3.73 (6H, s).

Reduction of dimethyl-2-hexadecyl malonate to 2-(hydroxymethyl) octadecanol

Lithium aluminum hydride (LAH) (4.9 g, 130 mmol) was dispersed in 80 mL of dry tetrahydrofuran. Dimethyl-2-hexadecyl malonate (17.8 g, 50 mmol) was dissolved in 100 mL of dry THF and added slowly into LAH dispersion at 0°C for 1 h duration. After the addition was completed, temperature of the reaction mixture was brought to room temperature on its own and then heated to mild reflux for 6 h. The reaction was monitored by TLC analysis and stopped when there was no starting material. Excess LAH was quenched by addition of ethyl acetate. The aluminum adduct formed was cleaved by adding the reaction mixture slowly into hydrated sodium sulfate and the slurry was stirred for 1 h and filtered over celite bed. The filtrate was concentrated to get the diol. Pure 2-(hydroxy methyl) octadecanol (9.8 g) was isolated by column chromatographic separation. Yield 65%. ^{1}H-NMR: δ 0.88 (3H, t); 1.26–1.60 (30H, m); 1.75 (1H, m); 3.61 to 3.86 (4H, 2dd).

Monobromination of 2-(hydroxymethyl)octadecanol to 2-(hydroxymethyl) octadecyl bromide

2-(hydroxymethyl)octadecanol (6) (10 g, 33.3 mmol) and CBr_4 (13.28 g, 0.040 mol) was dissolved in dry tetrahydofuran (100 mL) and taken in a three-neck round bottom flask fitted with a dropping funnel, a condenser and a three-way stopcock. Triphenylphosphine (9.16 g, 35 mmol) was dissolved in tetrahydrofuran and added to the reaction mixture at 0°C dropwise over period of 30 min. Stirring was continued for an additional 4 h at 0°C. Progress of the reaction was monitored by TLC. The crude reaction mixture was concentrated by evaporating tetrahydrofuran and the residue dissolved in ethyl acetate

and washed with water. 2-(hydroxymethyl)octadecyl bromide (9.7 g) was isolated in a pure form after column chromatography. Yield: 80%. ^{1}H-NMR: δ 0.88 (3H, t); 1.26 (28H, m); 1.60 (2H, m); 1.83 (1H, m); 3.47 to 3.74 (4H, 4dd).

Preparation of N,N-bis(2-hydroxyethyl)-N-methyl-N-(2-(hydroxymethyl) octadecyl)ammonium bromide (3)

N,N-Bis(2-hydroxyethyl)-N-methyl amine (2.98 g, 25 mmol) was mixed with hexadecyl ammonium bromide (9.1 g, 25 mmol) in the stoichiometric ratio 1 : 1 and heated to 60°C in ethanol (65 mL). Progress of reaction was monitored by TLC anaysis. Even after 3 days the reaction did not go to completion, as evidenced by presence of unreacted alkyl bromide and amine. A white crystalline powder of N,N-bis(2-hydroxyethyl)-N-methyl-N-((2-hydroxymethyl)octadecyl)ammonium bromide (6.1 g) was obtained from the pasty crude reaction mixture by repeated recrystallization from ethyl acetate. Yield: 50%. ^{1}H-NMR: δ 0.88 (3H, t); 1.26 to 1.44 (30H, m); 2.12 (1H, m); 3.07(1H,m); 3.33(1H,m); 3.45(1H, m); 3.28(3H, s); 3.76 (4H, b); 3.83 (1H, m); 4.12 (4H, b); 4.59 (1H, b), 4.89 (2H, b).

Preparation of organomodified clays

Na^+ montmorinollite (10 g) with CEC 92 meq/100 g, d-spacing 12 Å was dispersed in water/methanol (300 mL) by stirring with an over head stirrer at room temperature for 2 h. The modifier (11 meq) dissolved in methanol/water mixture was added slowly to the dispersion of clay and stirred for 24 h at 65°C. The reaction mixture was cooled, centrifuged, and washed several times with distilled water and methanol until free of bromide ions. The organoclay obtained was freeze dried in vacuo and obtained as fine, dry powder. The interlayer d-spacing for the organomodified montmorillonite was measured from WAXD. The content of modifier was measured using thermogravimetric analysis performed at 900°C.

TABLE II
Compositions PU/Organoclay Nanocomposites

Entry no.	Organoclay	Amount of TMP (g)	Amount of EHG (g)	Amount of Cloisite 30B (g)	Amount of prepolymer stock solution (mL)
A	Cloisite 30B	0.1423	0.0	0.130	10
B	Cloisite 30B	0.1067	0.0581	0.130	10
C	Cloisite 30B	0.0711	0.1163	0.130	10
D	Cloisite 30B	0.0356	0.1744	0.130	10
E	Cloisite 25A	0.1500	0.0	0.130	10
F	Cloisite 25A	0.1126	0.0581	0.130	10
G	Cloisite 25A	0.0711	0.1163	0.130	10
H	Cloisite 25A	0.0375	0.1744	0.130	10
I	Cloisite 25A	0	0.2325	0.130	10

TABLE III
Composition of Reactants for Preparation of TPU and Nanocomposites

Entry No.	Organo-clay or modifier	Amount of organoclay or modifier (g)	(mmol)	Poly(caprolactone diol) (g)	(mmol)	IPDI (g)	(mmol)	1,4-Butanediol (g)	(mmol)
1	**1**	0.185	0.469	7.55	10.07	4.85	21.83	0.895	9.94
2	**2**	0.195	0.458	7.58	10.11	4.84	21.77	0.874	9.69
3	**3**	0.230	0.477	7.51	10.02	4.76	21.43	0.826	9.17
4	1-OH (MMT)	0.656	0.469	7.59	10.12	4.84	21.77	0.875	9.71
5	2-OH (MMT)	0.656	0.458	7.56	10.08	4.84	21.77	0.857	9.51
6	3-OH (MMT)	0.7000	0.477	7.52	10.03	4.65	20.90	0.826	9.17

Preparation of prepolymer terminated with isocyanate from 2-ethyl-1,3-hexanediol (EHG) and toluene diisocyanate (TDI)

EHG (17.656 g) was dissolved in 180 mL of dry toluene. Dibutyltin dilaurate (DBTDL) (2.5 mL of 1 wt % solution) was added to the above solution. The mixture was cooled to 0°C. TDI (29.348 g), was added slowly for 40 min. Temperature of the reaction mixture was maintained below 5°C during the addition of TDI. After complete addition, the reaction mixture was allowed to come to room temperature. The reaction mixture was heated at 70°C for 1 h. Prepolymer solution thus obtained was transferred to a 250 mL volumetric flask fitted with a septum adapter through a cannula under a positive pressure of nitrogen. The level was made up to 250 mL by adding dry toluene through the cannula. The prepolymer solution was stored at room temperature under a nitrogen atmosphere. This solution was used for further studies and analysis. Isocyanate content of this prepolymer stock solution was estimated by titration and found to be 9.17 wt %.

Preparation PU/organoclay nanocomposites using trimethylol propane

Various compositions of PU/organoclay nanocomposites prepared are shown in Table II. Four two-neck round bottom flasks fitted with a condenser and septum adapter were taken and to each flask 10 mL of dry toluene was transferred under nitrogen atmosphere through a cannula. To each of them 0.130 g of the organoclay was added and dispersed thoroughly by stirring with magnetic stirring bar. Varying amounts of trimethylolpropane and EHG was added (Table II). The reaction mixture was stirred for 2 h. Thereafter, 10 mL of prepolymer stock solution was added through a cannula to each flask at room temperature. Temperature was increased to 70°C slowly and stirring continued for an additional 4 h. Thereafter, the solvent was evaporated *in vacuo*. A fine powder was obtained, which was subjected to analysis.

Preparation of PU/clay nanocomposites using clays having modifiers with varying hydroxyl functionality

Organoclays (0.130 g each), (1-OH(MMT), 2-OH(MMT), and 3-OH(MMT)), which are modified by ion exchange with various organoammonium cations **1**, **2**, and **3** having hydroxyl functionality of 1, 2, and 3 were dispersed in toluene medium separately in round bottom flasks by stirring at 70°C. The prepolymer stock solution (10 mL) was added to the organoclay dispersion slowly at room temperature and after the addition was over the temperature was slowly raised to 70°C for 2 h. Then EHG (0.230 g) was added to the reaction mixture and continued stirring at 70°C for another 4 h to obtain PU nanocomposites.

### Preparation of thermoplastic polyurethanes (TPU)

In the first step, isocyanate terminated prepolymer was prepared by reacting polycaprolactone diol (Mn: 750) with excess of isophorone diisocyanate (IPDI) in the mole ratio 1: 2.1. Calculated amount of IPDI was added slowly to the solution of polycaprolactone diol at 80°C and stirred for 2 h under nitrogen atmosphere in presence of dibutyltin dilaurate as catalyst. In the second step, the prepolymer was chain extended by addition of 1,4-butanediol and the modifier salt (either **1**, **2**, or **3**) with stirring at 80°C for 4 h. The composition of reactants are shown in Table III

Preparation of TPU/clay nanocomposites

In the first step, isocyanate terminated prepolymer was prepared by reacting polycaprolactone diol
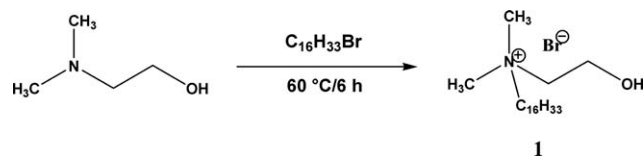
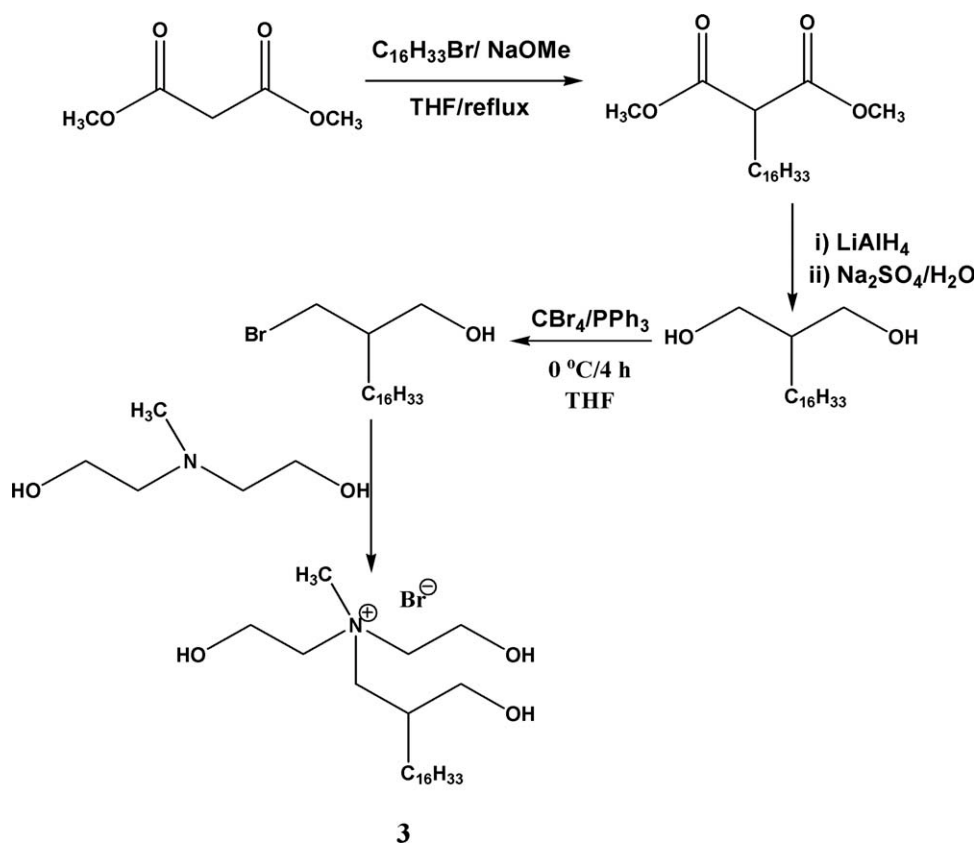
Scheme 1   Preparation of organo-modifier 1.
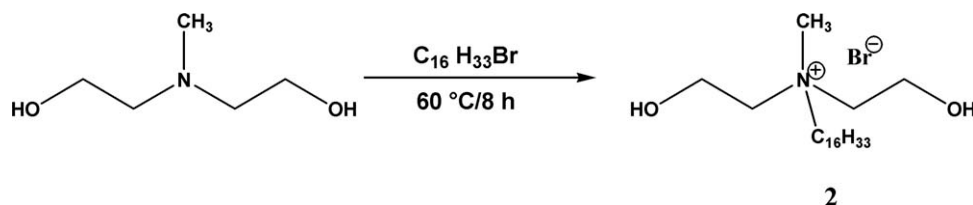
Scheme 2 Preparation of organo-modifier 2.

(Mn: 750) with excess of isophorone diisocyanate (IPDI) in the mole ratio 1 : 2.1. Calculated amount of IPDI was added slowly to the solution of polycaprolactone diol at 80°C and stirred for 2 h under nitrogen atmosphere in presence of dibutyltin dilaurate as catalyst. The reaction mixture containing the prepolymer was cooled to room temperature. Organoclay was added and stirred at room temperature for 30 min to disperse the clay in the reaction mixture. Temperature was raised to 80°C and stirred for an additional period of 1 h. 1,4-butanediol was added as chain extender and continued the polymerization for another 4 h. Thermoplastic polyurethane clay nanocomposites were obtained as films by pouring the reaction mixture onto a glass plate and casting the film by solvent evaporation under nitrogen flow at 55°C. The amounts of reactants taken are shown in Table III.

Analytical methods

^{1}H-NMR spectra were recorded in CDCl$_3$ solution with tetramethylsilane (TMS) as an internal standard using a Bruker DSX300 NMR spectrometer. WAXD measurements were performed using Rigaku Dmax 2500 diffractometer fitted with a diffracted beam graphite monochromator. The system consists of a rotating anode generator and wide-angle power goniometer. Generator was operated at 40 kV and 150 mA. The radiation was Ni-filtered Cu-Kα and samples were scanned between 2θ = 2 to 10° and the scan speed was 2°/min. TGA-7 (PerkinElmer) thermal analysis system was used to determine the onset of degradation and the organic content in the organoclays. Samples were heated under a flow of nitrogen atmosphere from 50 to 900°C at a heating rate of 10°C/min and the weight loss was recorded. Weight

Scheme 3 Preparation of organo-modifier **3.**

loss at 900°C was taken as the % organic content in the organoclay. TEM imaging was done using a FEI-Tecnai G^2 transmission electron microscope operating at an accelerating voltage of 300 kV. Nanocomposite samples were sectioned into ultrathin slices ($<$100 nm) using a Leica Ultracut UCT microtome equipped with a diamond knife and then mounted on 200 mesh copper grids. PU nanocomposites samples based on EHG, TDI, and TMP were sectioned at room temperature after embedding the nanocomposite powder in epoxy matrix. TPU nanocomposite sample films based on poly(caprolactone)diol were directly mounted on the microtome holder and sectioned at −120°C. The Density of clay particles was enough to produce contrast between polymer and clay stacks without any need for staining. Images were captured using charged couple detector (CCD) camera for further analysis using Gatan Digital Micrograph analysis software. Dynamic mechanical properties of the samples were studied using Rheometrics Dyanamic Mechanical Analyzer, model DMTA IIIE. T_g was measured as the temperature at which the maximum in tan δ appeared. DMA scans were performed in a rectangular sample tensile testing mode at a constant heating rate of 5°C/min and a frequency of 1 Hz from −150°C to 80°C. Samples were cut (with span length of 10mm and thickness X width being 0.5 mm × 7 mm) from the sheets obtained by solvent casting at 55°C after *in situ* polymerization.

RESULTS AND DISCUSSION

Preparation of organomodifiers

Organomodifiers **1**, **2**, and **3** were prepared according to Schemes 1, 2, and 3. Structures of the products were confirmed by ^{1}H-NMR.

Preparation of organoclays with modifiers bearing varying hydroxyl functionality

Organoclays were prepared with the modifiers **1**, **2**, and **3** bearing varying hydroxyl functionalities. These organomodified clay samples are designated as 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT). Modified clay samples were characterized by WAXD
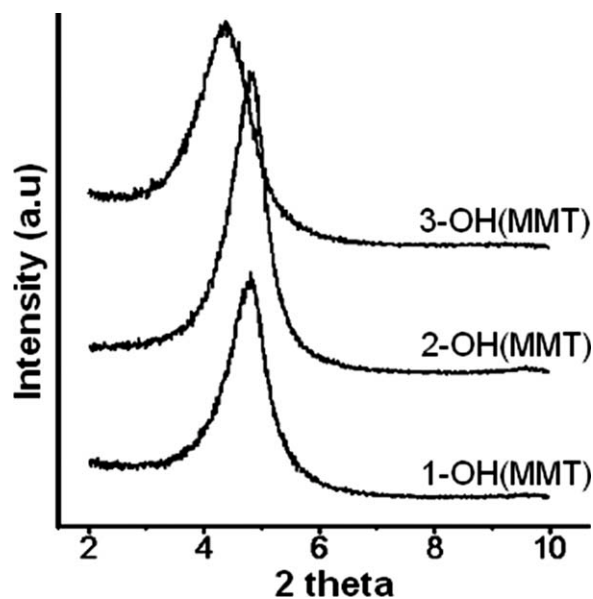
Figure 1 WAXD patterns for organoclays such as 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT).

(Fig. 1). WAXD patterns show 001 peak, which correspond to the interlayer d-spacing of the organoclay. Table IV shows the interlayer distance of the organoclays. The interlayer distance increases due to exchange of the larger organo-cation with Na^+ ion in the interlayer gallery. The larger increase in d-spacing for 3-OH(MMT) when compared to the other two clays, namely 1-OH(MMT) and 2 OH(MMT), can be attributed to the presence of slightly longer alkyl chain (18 C) in case of **3** as compared to **1** and **2** (16 C). Organic content estimated from TGA was in agreement with the theoretically calculated value indicating quantitative exchange of the Na^+ with the quaternary ammonium ion.

Preparation of prepolymer terminated with isocyanate

A urethane prepolymer terminated with isocyanate was prepared by taking toluene diisocyanate with 2-ethyl-1,3-hexanediol (EHG) in a mole ratio 1 : 1.4 in toluene. Prepolymer thus obtained contained 9.2 wt % isocyanate, which is close to the theoretically calculated value.
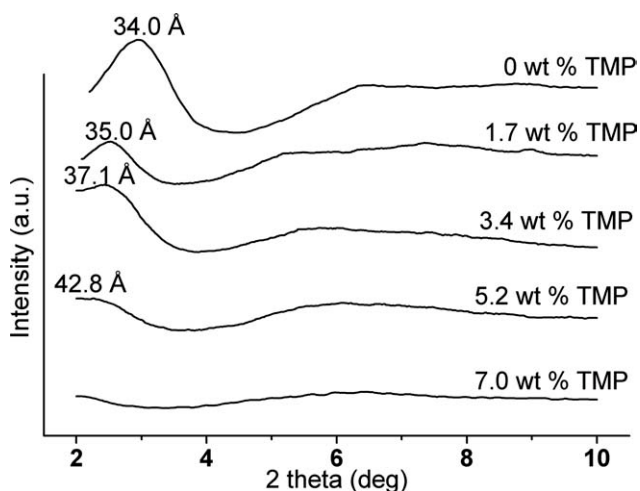
TABLE IV
Organic Content and d-Spacing for Various Organoclays

Organoclay	Modifier	Organic content (%)		d-Spacing[b] for clay, Å
		Theoretical	Experimental[a]	
1-OH(MMT)	**1**	22.7	22.8	18.5
2-OH(MMT)	**2**	24.5	24.6	18.5
3-OH(MMT)	**3**	27.5	27.7	20.2

[a] Obtained from weight loss data upon charring at 900°C using TGA.
[b] Obtained from 001 peak of WAXD patterns.

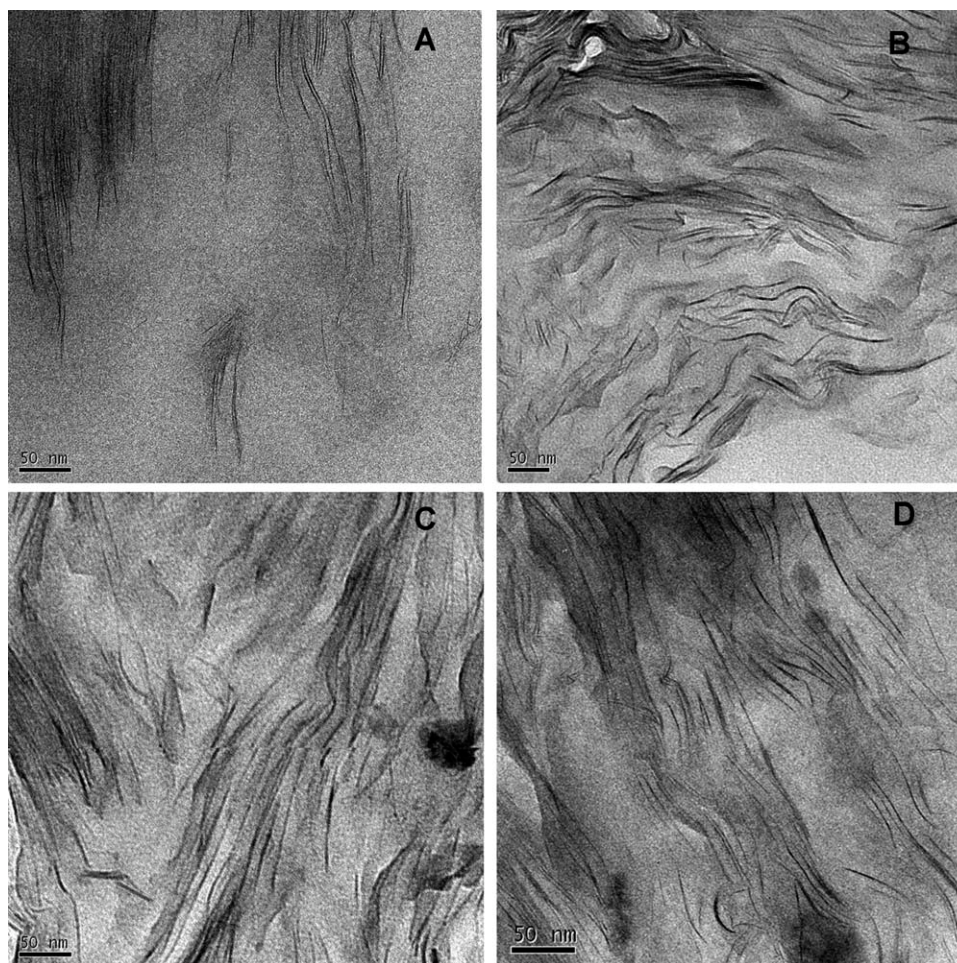**Figure 2** WAXD of PU/Cloisite 30B nanocomposites with varying amount of trimethylol propane.

Effect of trimethylol propane on the dispersion of clay in PU

Prepolymer was reacted with Cloisite 30B and cross-linked using TMP. The effect of amount of branch-ing agent used on the dispersion of clay was studied by scanning the WAXD patterns and TEM images of the obtained nanocomposites keeping the clay content constant by varying the amount of TMP (1.7, 3.4, 5.2, and 7.0 wt %). Figure 2 shows WAXD of the obtained PU nanocomposites.

Interactions between silicate layers and polyurethane chains are demonstrated by a shift in peak assignable for 001 basal plane. For example, d-spacing, corresponding to 001 plane, between the silicate layers was found to be 35.0 Å for nanocomposites with 1.7 wt % of TMP, whereas, it was found to be 37.1 Å and 42.8 Å for nanocomposites with 3.4 and 5.2 wt % of TMP, respectively.

Increase in d-spacing with increasing content of TMP indicates better intercalation. It can also be seen that in case of nanocomposites prepared using 7 wt % TMP, the peak corresponding to 001 basal plane completely disappears. This seems to indicate the formation of exfoliated structures. This is also confirmed by the TEM images (Fig. 3). It is observed that with 1.7 wt % TMP, the obtained nanocomposites show intercalated structures [Fig. 3(a)]. Thus,

Figure 3 TEM images of PU/Cloisite 30B nanocomposite with (a) 1.7 wt % TMP (b) 3.4 wt % TMP (c) 5.2 wt % TMP, and (d) 7.0 wt % TMP.
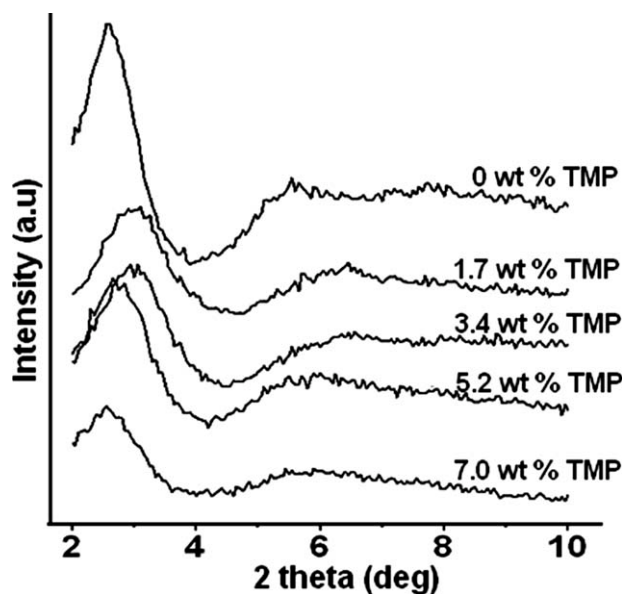
Figure 4 WAXD of PU/Cloisite 25A nanocomposites with varying amount of trimethylol propane (TMP).

the extent of intercalation increases with increasing TMP content. Evidence for some exfoliated structures can also be deduced from TEM. Nanocomposites prepared using 7 wt % TMP show higher degree of exfoliated structures [Fig. 3(d)]. These observations are similar to that reported earlier with nanocomposites of polyurethane prepared using poly(propylene glycol) of functionality 3 as soft segment and 4,4′-methylene bis(cyclohexyl isocyanate) and 1,4-butanediol as hard segments.[36] Thus, formation of tightly crosslinked PU networks in the gallery of clay results in exfoliation of the clay layers.

To understand the role of reactive hydroxyl groups on the clay surface, a similar composition of PU/clay nanocomposites was prepared by cross linking the urethane prepolymer with TMP using

Cloisite 25A. The WAXD of the obtained products are shown in Figure 4.

No significant changes in the diffraction pattern are seen with increasing content of TMP. This observation is different from what was observed with Cloisite 30B, suggesting that the presence of reactive hydroxyl groups on the surface of the clay is critical for a better dispersion of the organoclay. TEM images (Fig. 5) of PU nanocomposites prepared using Cloisite 25A and with (7 wt %) and without branching agent confirm the formation of predominantly intercalated structures.

Thus, introduction of mere branch point in PU structure does not favor delamination of clay layers. Exfoliation is favored by the ability of the growing chain to chemically tether to the surface of the clay in addition to branched structure. Consequently, this study was further extended to include organomodifiers containing a graded number of hydroxyl functionalities.

Effect of degree of functionality of the modifier on clay dispersion in PU nanocomposites

Three organoclays designated as 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT) were prepared and used for the formation of PU/nanocomposites. It should be noted that the organoclays, Cloisite 30B and 2-OH(MMT) have similar structures except that the alkyl group present in the former is a hydrogenated tallow moiety, which is a mixture of C-14, C-16, and C-18 alkyl chains while, the alkyl group present in the latter case is only C-16 chain. Isocyanate terminated prepolymer was reacted with 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT). No crosslinker was added. WAXD of the obtained nanocomposites are shown in Figure 6. It is seen that the d-spacing for the clay increases from 18.5 Å (the organoclay) to 34.0 Å in the nanocomposites
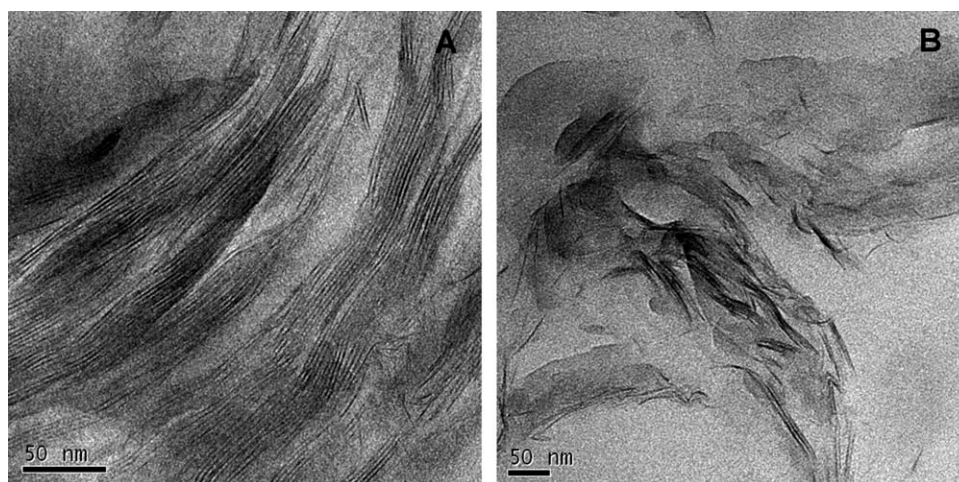
Figure 5 TEM pictures of PU/Cloisite 25A nanocomposites with (a) 0 wt % TMP and (b) 7.0 wt % TMP.
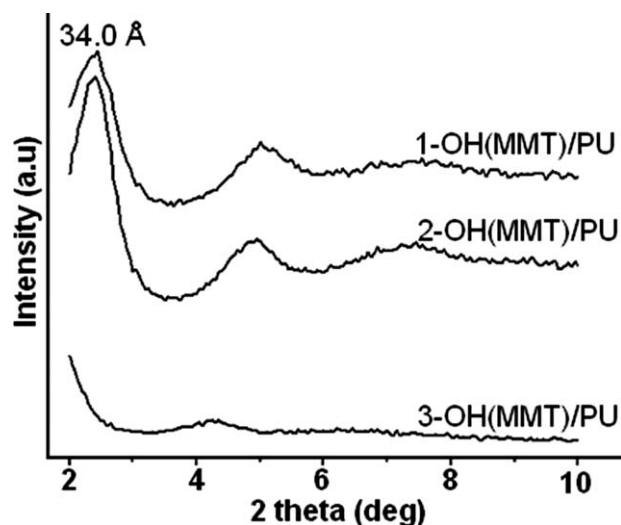
Figure 6 WAXD patterns of PU/clay nanocomposites with 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT).

of 1-OH(MMT) and 2-OH(MMT), indicating the formation of intercalated structures.

When the organoclay used was 3-OH(MMT), no peak corresponding to 001 basal plane was observed in the 2θ range of 2–4°. There can be two reasons for this observation. One, the peak might have shifted to an angle lower than 2° as a result of better/more intercalated nanostructures or, second, complete exfoliation of the clay layers. Further evidence of the structure was sought using TEM. Figures 7(a,b) and (c) show the TEM images of PU/clay nanocomposites based on 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT), respectively. All the three nanocomposites show only an intercalated structure with 3-OH(MMT)/PU nanocomposite showing a marginally higher degree of intercalation.

Effect of degree of functionality of the modifier on the clay dispersion in thermoplastic polyurethane matrix

To further elucidate the role of functional modifiers on the properties of PU/clay nanocomposites a thermoplastic polyurethane derived from poly(caprolactone diol) and isophorone diisocyanate (IPDI) was prepared and chain extended with 1,4-butanediol and reacted with 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT). Figure 8 shows the WAXD of the obtained nanocomposites. Nanocomposites derived
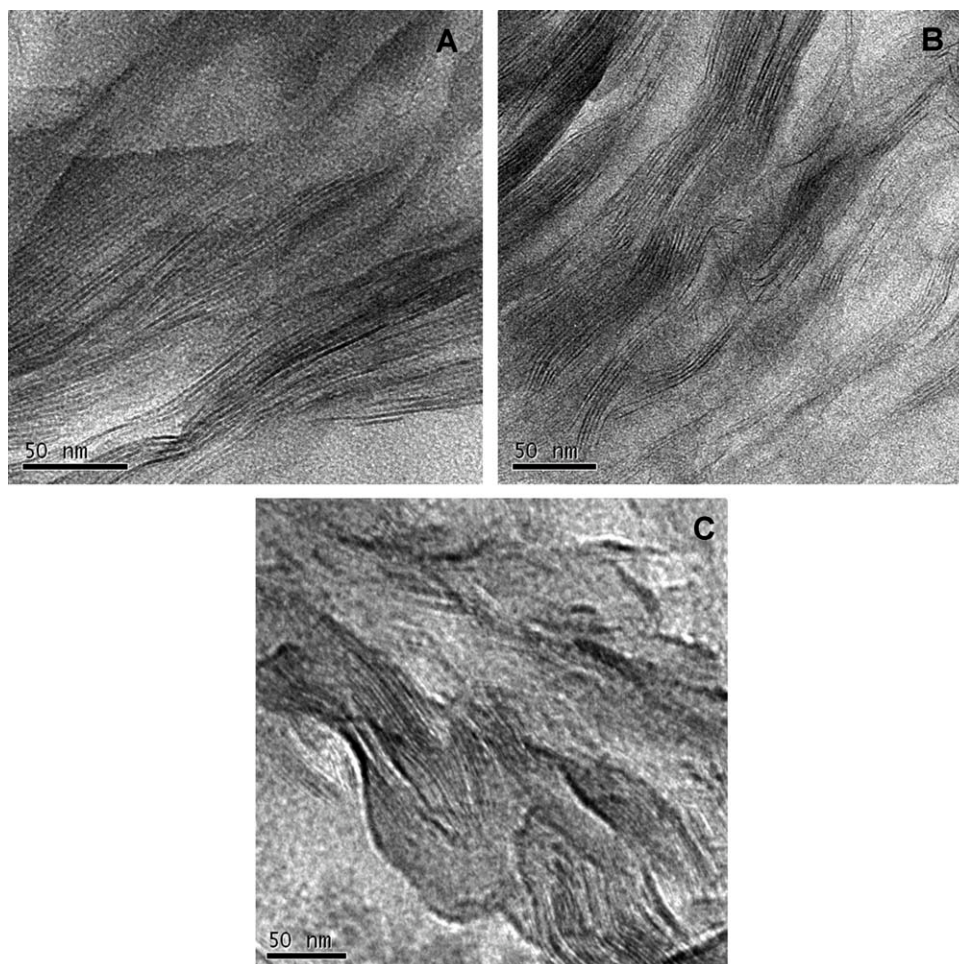
Figure 7 TEM pictures of (a) PU/1-OH(MMT), (b) PU/2-OH(MMT), (c)PU/3-OH(MMT), nanocomposites.
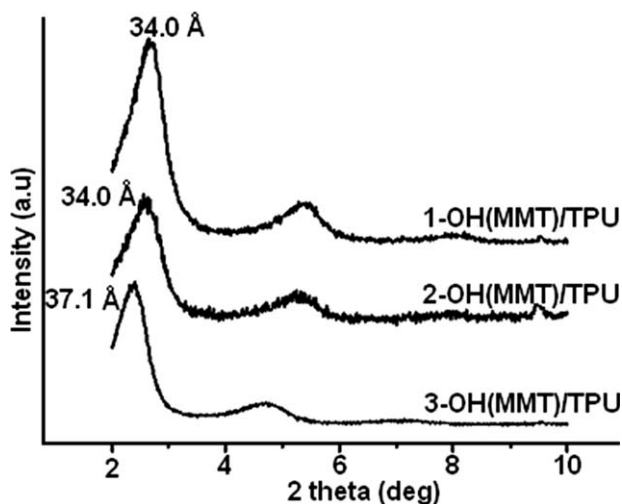
Figure 8 WAXD pattern of TPU/clay nanocomposites with 1-OH(MMT), 2-OH(MMT), and 3-OH(MMT).

from 1-OH (MMT) and 2-OH(MMT) showed an increase in d-spacing from 18.5 to 34.0 Å. In case of nanocomposites derived from 3-OH(MMT), the d-spacing further increased to 37.1 Å.

The dispersion of clay in TPU was further examined by TEM (Fig. 9). All the three composites show highly intercalated nanostructures and the interlayer distance obtained from TEM is comparable to the d-spacing observed by WAXD. When compared to nanocomposites of EHG-TDI based polyurethanes, the extent of intercalation or dispersion of clay is poorer in poly-caprolactone diol based PU system. Better dispersion of silicate layers in polyurethanes containing harder segment can be attributed to the interactions imparted via higher degree of hydrogen bonding between the polar groups of PU chains and the hydroxyl groups on the clay surface. In other words, lower degree of intercalation in the thermoplastic polyurethane system containing poly(caprolactone diol) soft segments can be attributed to the lower polarity and degree of hydrogen bonding. Presence of long alkyl chains (C_{16} or C_{18}) does not appear to significantly enhance the compatibility of the polymer with the clay.
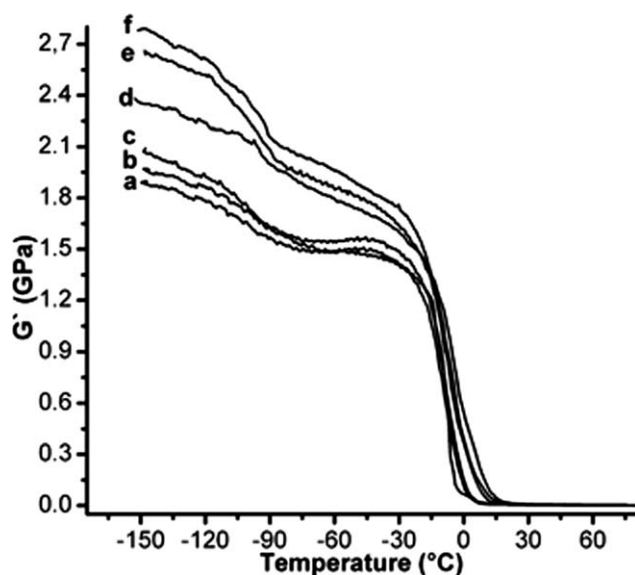
Dynamic mechanical properties

Temperature dependent dynamic mechanical property of the thermoplastic polyurethane nanocomposites
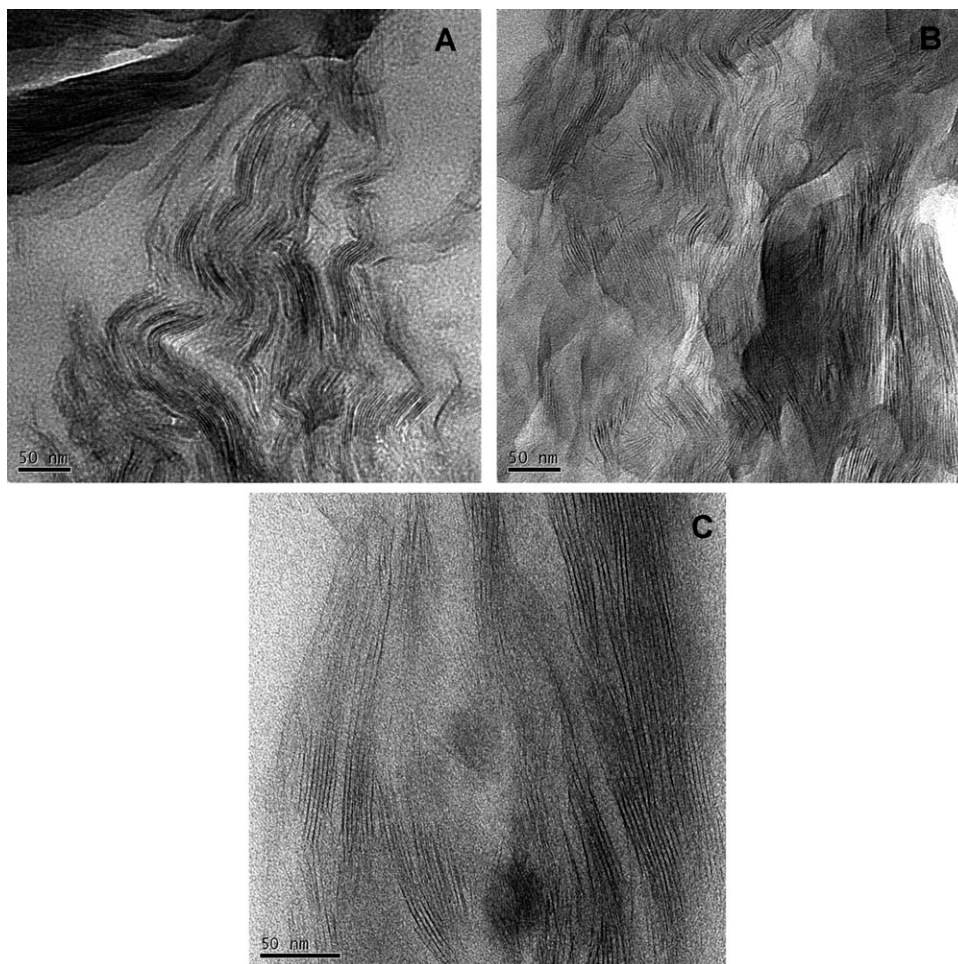
Figure 9 TEM pictures of nanocomposites based on TPU and (a) 1-OH(MMT), (b) 2-OH(MMT), and (c) 3-OH(MMT).

Figure 10 Tensile storage modulus (G') of various samples measured by dyanamic mechanical analysis, (a) pristine TPU-1OH, (b) pristine TPU-2OH, (c) pristine TPU-3OH, (d) 1-OH(MMT)/TPU, (e) 2-OH(MMT)/TPU, and (f) 3-OH(MMT)/TPU.

was measured using DMA and compared with pristine polyurethanes prepared using the same reactive modifiers. Figure 10 shows the storage modulus (G') plotted against temperature. Two transitions are clearly observed. The first transition observed as broad peak at around −100°C in the tan δ plot arises due to the relaxation arising from local mode motions of the methylene sequences in the poly(caprolactone) soft segment. The second transition was observed −10 to 0°C range, which is due to glass transition.

All nanocomposite samples exhibit higher tensile storage moduli (G') at all temperatures below the glass transition temperature. Increase in the number of hydroxyl functionality of the modifier in the clay results in nanocomposites which show higher G' values at all temperatures below glass transition temperature. This can be attributed to the improved interaction of the polymer chain with the clay surface arising as a consequence of the chemical tethering of the polymer chains to the clay surface.

CONCLUSIONS

This study points to the importance of tethering groups on the clay surface and an ability to form branched and crosslinked structure for the preparation of completely exfoliated and well dispersed polyurethane/clay nanocomposites via *in situ* polymerization. Mere presence of either tethering groups in the organoclay or branch points in PU does not result in exfoliated structures. Incorporation of long alkyl chains in addition to tethering hydroxyl groups

in the modifier structure of the clay did not significantly improve the compatibility of linear PU with the clay. Intercalated thermoplastic polyurethane/clay nanocomposites, prepared using poly(caprolactone diol) as soft segment and isophorone diisocyanate and 1,4-butanediol as hard segment show increase in storage tensile moduli at temperatures before glass transition temperature when compared to pristine polymers when functional groups capable of chemically reacting with the growing polymer chains are present in the clay modifier. This is indicative of improved interaction of the polymer with the clay surface.

References

1. Meckel, W.; Goyert, W.; Wieder, W. Thermoplastic Elastomers; Hanser: Munich, 1987.
2. Frisch, K. C. Rubber Chem Technol 1980, 126.
3. Bayer, O.; Muller, E.; Petersen, S.; Piepenbrink, H. F.; Windemuth, E. Angew Chem 1950, 62, 57.
4. Goda, H.; Frank, C. W. Chem Mater 2001, 13, 2783.
5. Furukawa, M.; Yokoyama, T. J Appl Polym Sci 1994, 53, 1723.
6. Dolui, S. K. J Appl Polym Sci 1994, 53, 463.
7. Feldman, D.; Lacasse, M. A. J Appl Polym Sci 1994, 51, 701.
8. Otterstedt, E. A.; Ekdahl, J.; Backman, J. J Appl Polym Sci 1987, 34, 2575.
9. Nunes, R. C. R.; Fonesca, J. L. C.; Pereira, M. R. Polym test 2000, 19, 93.
10. Hepburn, C. Polyurethane Elastomer; Applied Science Publishers: London, 1982.
11. Khudyakov, I. V.; Zopf, D. R.; Turro, N. J. Designed Monomers Polym 2009, 12, 279.
12. Wang, Z.; Pinnavaia, T. J. Chem Mater 1998, 10, 3769.
13. Zilg, C.; Thomann, R.; Muelhaupt, R.; Finter, J. Adv Mater 1999, 11, 49.
14. Petrovic, Z. S.; Javni, I.; Waddon, A.; Banhegyi, G. J Appl Polym Sci 2000, 76, 133.
15. Chen, T. K.; Tien, Y. I.; Wei, K. H. J Polym Sci Part A: Polym Chem 1999, 37, 2225.
16. Chen, T. K.; Tien, Y. I.; Wei, K. H. Polymer 2000, 41, 1345.
17. Xu, R.; Manias, E.; Snyder, A. J.; Runt, J. Macromolecules 2001, 34, 337.
18. Ma, J.; Zhang, S.; Qi, Z. J Appl Polym Sci 2001, 82, 1444.
19. Tien, Y. I.; Wei, K. H. Macromolecules 2001, 34, 9045.
20. Tien, Y. I.; Wei, K. H. Polymer 2001, 42, 3213.
21. Hu, Y.; Song, L.; Xu, J.; Yang, L.; Chen, Z.; Fan, W. Colloid Polym Sci 2001, 279, 819.
22. Yao, K. J.; Song, M.; Hourston, D. J.; Luo, D. Z. Polymer 2002, 43, 1017.
23. Tien, Y. I.; Wei, K. H. J Appl Polym Sci 2002, 86, 1741.
24. Chang, J. H.; An, Y. U. J Polym Sci Part B: Polym Phys 2002, 40, 670.
25. Tortora, M.; Gorrasi, G.; Vittoria, V.; Galli, G.; Ritrovati, S.; Chiellini, E. Polymer 2002, 43, 6147.
26. Zhang, X.; Xu, R.; Wu, Z.; Zhou, C. Polym Int 2003, 5, 790.
27. Song, M.; Hourston, D. J.; Yao, K. J.; Tay, J. K. H.; Ansarifar, M. A. J Appl Polym Sci 2003, 90, 3239.
28. Mishra, J. K.; Kim, I.; Ha, C. S. Macromol Rapid Commun 2003, 24, 671.
29. Chen, X.; Wu, L.; Zhou, S.; You, B. Polym Int 2003, 790.

30. Rhoney, I.; Brown, S.; Hudson, N. E.; Pethrik, R. A. J Appl Polym Sci 2003, 91, 1335.

31. Osman, M. A.; Mittal, V.; Morbidelli, M.; Suter, U. W. Macromolecules 2003, 36, 9851.

32. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T. J Mater Res 1993, 8, 1185.

33. Fukushima, Y.; Okada, A.; Kawasumi, M.; Kurauchi, T.; Kamigaito, O. Clay Miner 1998, 23, 27.

34. Ni, P.; Li, J.; Suo, J. S.; Li, S. B. J Appl Polym Sci 2004, 94, 534.

35. Ni, P.; Wang, Q. L.; Li, J.; Suo, J. S.; Li, S. B. J Appl Polym Sci 2006, 99, 6.

36. Xia, H. S.; Song, M. Polym Int 2006, 55, 229.

37. Moon, S.-Y.; Kim, J.-K.; Nah, C.; Lee, Y.-S. Eur Polym J 2004, 40, 1615.

38. Chavarria, F.; Paul, D. R. Polymer 2006, 47, 7760.

39. Pattanayak, A.; Jana, S. C. Polymer 2005, 46, 3275.

40. Pattanayak, A.; Jana, S. C. Polymer 2005, 46, 3394.

41. Pattanayak, A.; Jana, S. C. Polymer 2005, 46, 5183.

42. Pattanayak, A.; Jana, S. C. Polym Eng Sci 2005, 45, 1532.