

Nanoclay Filled Soy-Based Polyurethane Foam

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ABSTRACT: Polyurethane foam was fabricated from polymeric diphenylmethane diisocyanate (pMDI) and soy-based polyol. Nanoclay Cloisite 30B was incorporated into the foam systems to improve their thermal stabilities and mechanical properties. Neat polyurethane was used as a control. Soy-based polyurethane foams with 0.5–3 parts per hundred of polyols by weight (php) of nanoclay were prepared. The distribution of nanoclay in the composites was analyzed by X-ray diffraction (XRD), and the morphology of the composites was analyzed through scanning electron microscopy (SEM). The thermal properties were evaluated through dynamic mechanical thermal analysis (DMTA). Compression and three-point bending tests were conducted on the composites. The densities of nanoclay

soy-based polyurethane foams were higher than that of the neat soy-based polyurethane foam. At a loading of 0.5 php nanoclay, the compressive, flexural strength, and modulus of the soy-based polyurethane foam were increased by 98%, 26%, 22%, and 65%, respectively, as compared to those of the neat soy-based polyurethane foam. The storage modulus of the soy-based polyurethane foam was improved by the incorporation of nanoclay. The glass transition temperature of the foam was increased as the nanoclay loading was increased. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1857–1863, 2011

Key words: polyurethane foam; soy-based; nanoclay; composites

INTRODUCTION

Many engineering materials are heavily relying on petroleum as feedstock. However, the steadily going up price of petroleum oil results in rising feedstock price of these raw materials. In contrast, agricultural products maintained steady low price. The supply of petroleum oil is not stable and most petroleum-based material is not biodegradable and may cause environmental concerns.

Therefore, development of bio-renewable feedstock for material manufacturers becomes very crucial for both economic and environmental reasons. Soybean oil can be an excellent annually renewable natural feedstock for the polyols. For each pound of soybean oil produced, 2.67 pounds of carbon dioxide are removed from the air.¹ It is affordable and available in a large quantity. The chemical structure of soybean oil can be tailored by its functional groups depending on specific application. For example, soy-based polyols (Fig. 1) with various functionalities can be made by introducing hydroxyl group to soybean oil unsaturated sites by hydrogenation,² epoxidation followed by oxirane opening,³ ozonoly-

sis followed by hydrogenation,⁴ and microbial conversion.⁵ Soy-based polyols can be used in varied polyurethane applications by selecting proper functional group and side chain. Polyurethanes produced from soy-based polyols normally exhibit equivalent or improved physical and chemical properties due to the hydrophobic nature of triglycerides.^{6,7}

Some research efforts have been made on substituting part or all of petroleum resource polyols with soy-based polyols. Petrovic et al.^{8,9} studied the effect of isocyanate index (ratio of isocyanate groups to hydroxyl groups) on the properties of soy-based polyurethane networks. The isocyanate index changed the crosslinking density of the polyurethane network and the amount of dangling ends within the network, both of which were found to be responsible for the increased glass transition temperature when the isocyanate index was increased. The structure and property relationships in polyurethanes derived from soybean oil were also investigated.¹⁰

Research result has shown that dramatic improvement in thermal and mechanical properties can be achieved by incorporating nanoparticle into a polymer matrix.^{11–15} Nanoparticle is defined as having at least one dimension in the nanometer range.¹⁶ Nanoclay is one type of platelet particle and modified montmorillonite clay. The single layer thickness of a nanoclay platelet is about 1 nm and the lateral dimensions of the layer may vary from 200 to 2000 nm. Nanoclay is potentially well suited for making hybrid composites because their lamellar elements

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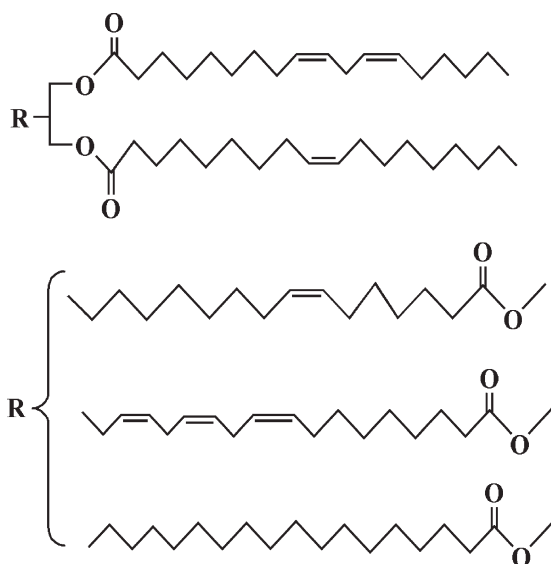


Figure 1 Representative structure of soy-based polyol.

have high in-plane strength and stiffness and a high aspect ratio. The rich intercalation chemistry of nanoclay allows them to be chemically modified to be more compatible with polymers.

Tien and Wei¹⁷ synthesized nanoclay polyurethane nanocomposites with high tensile property by using reactive silicates as pseudo chain extenders. It was found that the hydroxyl groups of the swelling agent help layered silicates to disperse into the polymer matrix. When the number of hydroxyl groups increased, the dispersion of the nanoclay transformed from an intercalated to an exfoliated structure, which resulted in an ultrahigh efficiency in improving the mechanical properties of polyurethane. Lee and coworkers¹⁸ studied the processing, structure, and properties of clay polyurethane nanocomposites. It was found that the functional groups of the clay organic modifiers, synthesis procedure, and molecular weight of polyols greatly influenced the morphology and properties of polyurethane nanocomposites foams. Higher cell density and smaller cell size were obtained for the nanoclay polyurethane foam as compared to the neat polyurethane foam. A nanoclay loading of 5% resulted in a 6°C increase in glass transition temperature (T_g), 650% increase in reduced compressive strength and 780% increase in reduced modulus. Effects of nanoclay on the thermal insulating properties of rigid polyurethane foams have been explored by Kim et al.¹⁹ Rigid polyurethane foams were synthesized with nanoclay with and without the aid of ultrasound. The tensile strength of the clay polyurethane foam nanocomposites was higher than that of the neat polyurethane foams and that of nanocomposites with the use of ultrasound was even higher. The cell

size of nanocomposites was smaller than that of neat foam. The thermal conductivity of the nanocomposites was less than that of neat foam. These results were attributed to the uniform dispersion of clay into polymer matrix. The uniform dispersed clays in the polymer matrix act as heat diffusion barriers.

In this article, nanoclay Cloisite 30B was incorporated into water blown soy-based polyurethane foam. Neat soy-based polyurethane is used as a control. Soy-based polyurethane/clay composites with 0.5, 1, and 3 php were synthesized. The morphology, mechanical, and viscoelastic properties of nanoclay soy-based polyurethane foam were studied.

EXPERIMENTAL

Materials

Polymeric diphenylmethane diisocyanate (pMDI, LuPranate[®]M20S) from BASF Company and soy-based polyol from BioBased Technologies Company were used as reactants to make polyurethane foam. Distilled water was used as a chemical blowing agent. Dibutyl Dilaurate (DBTDL) and *N,N*-dimethylethanolamine (DMEA) were used as catalysts. Tegostab B8404 from Goldschmidt Chemical was used as surfactant. Nanoclay Cloisite 30B (Fig. 2) modified by methyl tallow bis-2-hydroxyethyl ammonium from Southern Clay, was used as nanoparticle incorporated into soy-based polyurethane foam. Table I shows the characteristics of different materials used in the preparation of nanoclay soy-based polyurethane foam.

Foam preparation

Polyurethane foams were prepared by one-pot, free-rising method and their chemical compositions are shown in Table II. The experimental procedures were as followings: weigh the polyol, catalysts, surfactant, and blowing agent (B-side material) using disposable plastic cups; mix them with a mechanical stirrer at 3000 rpm for 10–15 sec; allow the mixture to degas for 2 min; rapidly add pMDI (A-side material) into the mixture and continue to stir for another 10–15 sec at the same speed; allow the foam to rise and set at room temperature for 24 h.

Nanoclay was dehydrated in an oven at $103 \pm 2^\circ\text{C}$ for overnight before use. Sonication and mechanical

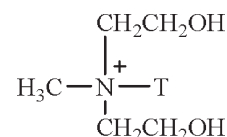


Figure 2 Chemical structure of pillaring agent of Cloisite 30B.

TABLE I
Characteristic of the Raw Materials Used

Materials	Supplier	Comments
pMDI	BASF	NCO% = 31.5
Soy-based polyol	BioBased	167 mg KOH/g ^a
DBTDL	Aldrich	Catalyst
DMEA	Aldrich	Catalyst
Tegostab B8404	Goldschmidt	Surfactant
Distilled water	Laboratory	Blowing agent

^a This is hydroxyl value.

mixing were used to aid a thorough mixing of nanoclays with the B-side material before the addition of pMDI. Ultrasonic processor (Model: CP 750) made by Cole-Parmer Instruments (Vernon Hills, IL) was used to provide ultrasound. The ultrasonic processor was run at 20 kHz. Nanoclays were added to B-side material in disposable plastic cups and mixed thoroughly by using a mechanical stirrer at 3000 rpm for 10–15 sec, then the mixture was ultrasonicated for 10 min.

Property measurements

A Field Emission Scanning Electron Microscopy (JSM-6500F, JEOL, Ltd., Tokyo, Japan) with the accelerating voltages of 0.5–30 kV and the magnification ranging from 10× to 500,000× was used to examine the fracture morphology of the specimen. The specimens were platinum coated before scanning to obtain an electrically conductive surface.

The viscosity of polyol blended with nanoclays was measured with Brookfield viscometer (RVTD model). The temperature was maintained at 25 ± 2°C during the measurements using a thermostatically controlled tank.

The density of the composites was determined by averaging the mass/volume measurements of six specimens in accordance with the procedure described in ASTM D1622-03 standard.

The distribution of nanoclay in the foams was measured by an X-ray diffraction System (SmartLab, Rigaku America Corporation, TX). Cu K α radiation ($\lambda = 1.541867$ Å) was used to generate X-ray at 40 kV and a current of 44 mA. Scans were taken over the 2 θ range of 1.5–8.5° with the scanning speed at 0.9°/min. The d -spacing was calculated according to Bragg's law:

$$n\lambda = 2d \sin \theta$$

where n is an integer representing the order of the diffraction peak, λ is the wavelength of the X-ray, d is the interplanar spacing generating the diffraction, and θ is the diffraction angle.

The compressive properties of the foams were measured using an Instron universal testing machine (model 5500) based on ASTM D1621-00 standard. Samples were cut to a size of 40 mm × 40 mm × 25 mm (width × length × thickness). The orientation was parallel to foam rise direction. The cross-head speed was 2 mm/min with a load cell of 500 kgf. The load was applied until the foam was compressed to ~ 85% of its original thickness. Six replicates per sample were tested and the results were averaged.

Flexural strength and modulus of the panels were tested on six specimens using an Instron universal testing machine (model 5869, Canton, MA) in accordance with the procedure described in ASTM D 790 standard. The specimen dimension was 80 mm × 25 mm × 3.2 mm (length × width × thickness). Three-point bending set-up was used with a span of 50 mm and a crosshead speed of 1.3 mm/min. The flexural strength (FS) and flexural modulus were determined.

Dynamic storage modulus was determined in the bending mode using a TA Q800 Dynamic Mechanical Analyzer (DMTA). The measurements were carried out from 30°C to 120°C. The temperature was raised at a rate of 5°C/min. The composite samples were ~ 2.5 mm thick, 10 mm wide, and 48 mm long.

RESULTS AND DISCUSSION

The viscosity was a very important factor in the polyurethane foaming process. The high viscosity of B-side material would make it difficult to mix with MDI and result in less uniform for foam forming. Figure 3 shows the effect of nanoclay content on the viscosity of nanoclay/soy-based polyol mixture after sonication. The viscosity of the nanoclay/soy-based polyol mixture was increased as the content of nanoclay increased.

Polyurethane foam composites containing nanoclay with 0.5, 1, and 3 php were synthesized at room temperature. The density of the polyurethane foam was dependent on the amount of the blowing

TABLE II
Chemical Compositions of Soy-Based Polyurethane Foam Blown by Water

Ingredients	php ^a
Polyether polyol	100
Tegostab B 8404	2
DBTDL	1
DMEA	1
Distilled water	0.5
Nanoclay	Vary
pMDI	104

^a Parts per hundred of polyols by weigh.

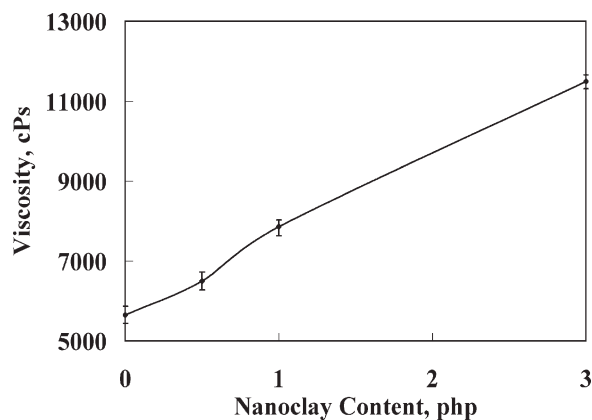


Figure 3 The viscosity of nanoclay/soy-based polyol mixture as a function of nanoclay content after sonication.

agent used and filler materials added. The amount of water (blowing agent) was kept at 0.5 php polyol while the amount of nanoclay was varied from 0.5 to 3 php. Figure 4 shows the foam density as a function of nanoclay content. The densities of the foam were increased when nanoclays were incorporated and the densities were increased as the nanoclay loading was increased. The increase in density was due to the following two reasons. First, the density of nanoclay Cloisite 30B (1.98 g/cm^3) was higher than that of the neat polyurethane foam (0.196 g/cm^3). Second, the viscosity of the nanoclay polyol mixture was higher than that of neat polyol. The viscosity of the nanoclay polyol mixture increased as the nanoclay loading increased. The increase in viscosity would cause the resin mixture difficult to rise during foaming process.

The distribution of nanoclay in the soy-based polyurethane foam was analyzed by X-ray diffraction (XRD). Figure 5 shows the XRD pattern of the nanoclay, neat soy-based polyurethane foams, and soy-based polyurethane foams with 0.5, 1, and 3 php

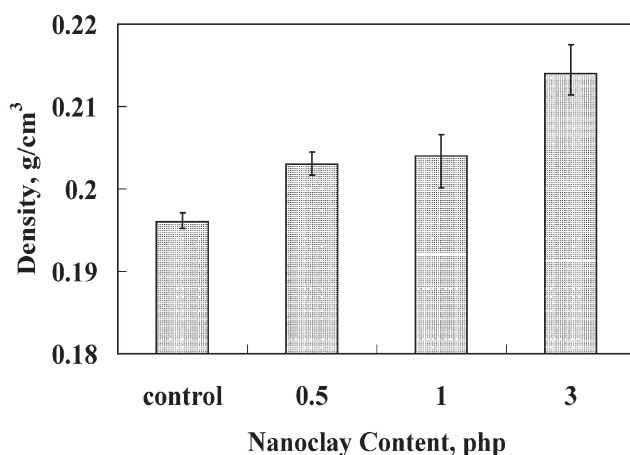


Figure 4 Soy-based polyurethane foam density as a function of nanoclay content.

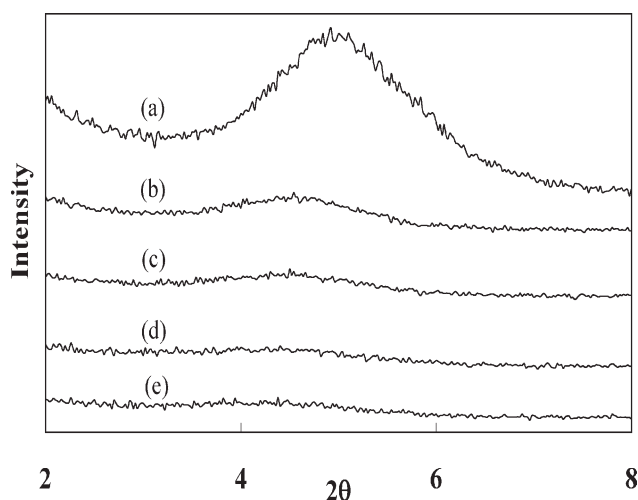


Figure 5 XRD patterns of (a) pure nanoclay, (b) 3 php nanoclay soy-based polyurethane foam, (c) 1 php nanoclay soy-based polyurethane foam, (d) 0.5 php nanoclay soy-based polyurethane foam, and (e) neat soy-based polyurethane foam.

nanoclay. A strong peak at $2\theta = 4.8^\circ$ which was the characteristic of crystallinity in the organoclay and corresponding to a basal spacing $d_{001} = 18.3 \text{ \AA}$ was observed [Fig. 5(a)]. This peak disappeared in soy-based polyurethane foam with 0.5 php nanoclay [Fig. 5(d)]. It indicated that the clay was delaminated or exfoliated in soy-based polyurethane foam with 0.5 php nanoclay. The XRD spectra of soy-based polyurethane foam with 1 and 3 php nanoclay [Fig. 5(b,c)] showed a weak characteristic broad at $2\theta = 4.3^\circ$. A moderate intercalation was achieved: the interlayer distance increased from 18.3 \AA to 20.6 \AA . This indicated that there was a combination of aggregated and intercalated structure occurred at higher loading of clay. The intensity of this peak was stronger at loading of 3 php nanoclay than that of 1 php nanoclay. The clay tended to aggregate or intercalate at higher loading.

The fractural surfaces of neat and 3 php nanoclay soy-based polyurethane foams were observed (Fig. 6). The cell size and shape of soy-based polyurethane/clay composites were less uniform than that of the neat foam. In general, the average cell size of soy-based polyurethane/clay composites was smaller than that of the neat foam. The decrease in the cell size of soy-based polyurethane/clay composites may be due to: (1) the viscosity of the nanoclay polyol mixture increased as the loading of nanoclay increased. The increase in viscosity would cause the resin mixture difficult to rise during foaming process and resulted in smaller cell size (2) Nanoclay could act as nucleation site during foaming process resulting in smaller cell size.²⁰ Some larger cell size in 3 php nanoclay foam might be due to the excessive coalescence of the nucleating sites.²¹ Fractural

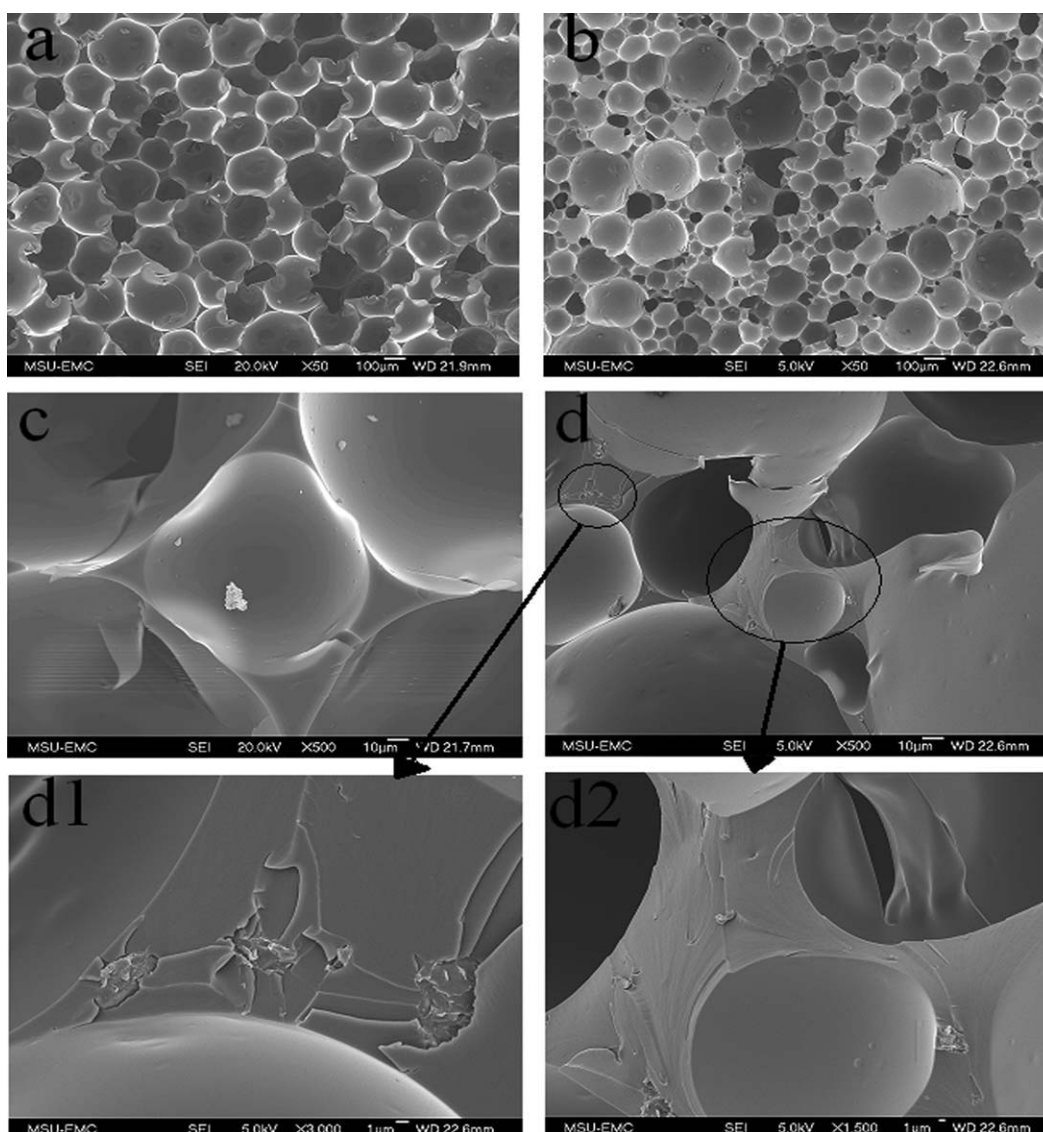


Figure 6 Fractural surface of neat (a and c) and 3 php nanoclay (b, d, d1, and d2) soy-based polyurethane foam.

surface of soy-based polyurethane/clay composites [Fig. 6(d1,d2)] was rougher than that of the neat foam.

Figure 7 shows the compressive strength and modulus as a function of nanoclay content. Incorporating the nanoclay Cloisite 30B into soy-based polyurethane foam improved the compressive strength and modulus of the polyurethane foams. The compressive strength and modulus of nanoclay polyurethane foams were first increased with nanoclay loading at 0.5 php, then decreased as the nanoclay loading increased. At 0.5 php nanoclay loading, the compressive strength and modulus reached the maximum which were 1.86 MPa and 37.93 MPa, respectively. The compressive strength and modulus were increased by 98 and 26%, respectively, as compared to the neat soy-based polyurethane foam. The increase in the compressive strength and modulus of

nanoclay soy-based polyurethane foams was due to the higher density and smaller cell size of foam composites. Nanoclay was much easier to be uniformly dispersed into polyol resin at a low loading, resulting in more uniform and smaller cell size. Thus, the compressive property of the nanoclay polyurethane foam was largely improved at a low nanoclay loading. However, the viscosity of nanoclay polyol mixture was higher at high nanoclay loading which made nanoclay difficult to be uniformly dispersed into the resin mixture. This would cause less uniform and some larger cell size due to the excessive coalescence of the nucleating sites. Thus, the compressive strength and modulus of nanoclay soy-based polyurethane foam decreased when the nanoclay loading increased.

The flexural properties of neat soy-based polyurethane foam nanoclay soy-based polyurethane foams

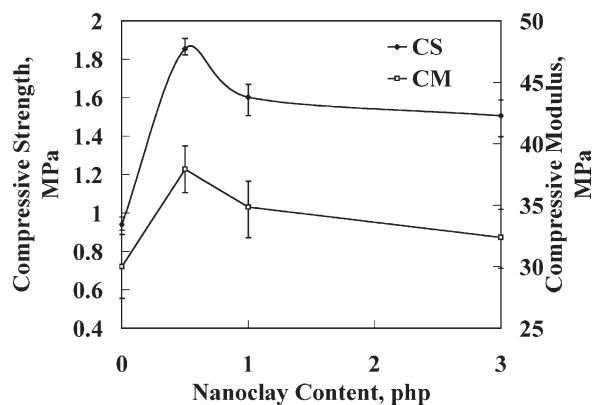


Figure 7 Soy-based polyurethane foam compressive strength and modulus as a function of nanoclay loading.

are shown in Figure 8. The overall flexural strength and modulus of nanoclay soy-based polyurethane foams were higher than those of the neat soy-based polyurethane foam. The enhancements in flexural properties could be attributed to the stress transfer from the resin matrix to nanoclay particles and also the high in-plane strength and stiffness and high aspect ratio of the nanoclay. This was confirmed from SEM (Fig. 6) that the fractural surface of soy-based polyurethane/clay composite was rougher than that of the neat foam. Also, the homogeneously distributed nanoclay throughout the foam matrix enhanced the load transferred from the matrix to nanoclay. Similar to the compressive property, the maximum flexural strength (1.86 MPa) and modulus (37.93 MPa) were achieved at 0.5 php nanoclay loading. The flexural strength and modulus were increased by 22 and 65%, respectively, as compare to neat soy-based polyurethane foam. Nanoclay could act as nucleation sites to promote a more efficient polymer network of soy-based polyurethane foam at a lower loading. However, this process could be hindered when nanoclay loading was increased at a certain level. The aggregation of nanoclay at high loading

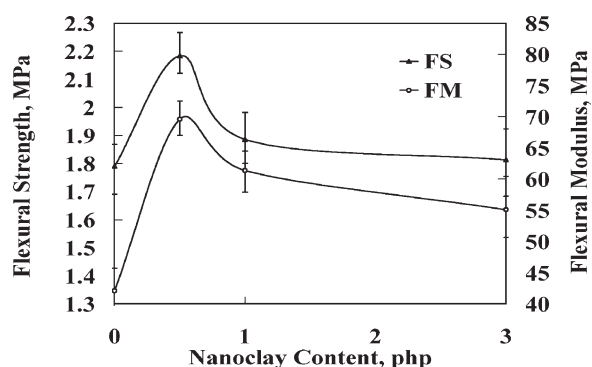


Figure 8 Soy-based polyurethane foam flexural strength and modulus as a function of nanoclay loading.

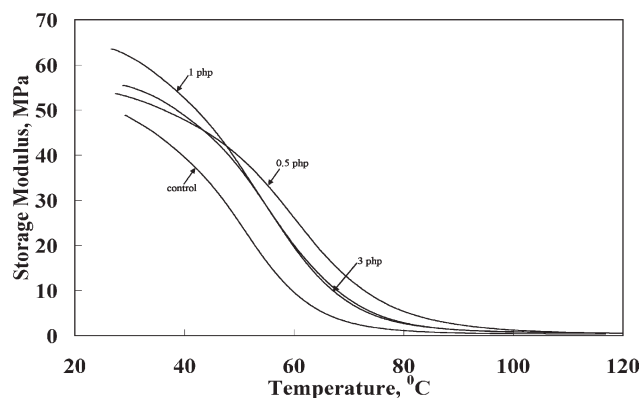


Figure 9 Soy-based polyurethane foam storage modulus as a function of temperature.

also reduced the stress transfer efficiency from the matrix to the nanoclay particles.

The storage modulus and loss modulus ($\tan \delta$) of the neat and nanoclay soybased polyurethane foams were examined from 25°C to 120°C, in this study. Figure 9 shows the neat and nanoclay soybased polyurethane foams storage modulus as a function of temperature. The storage modulus of all samples decreased as the temperature increased due to the increase of the mobility of molecular chain. The storage modulus of the nanoclay soybased polyurethane foams was higher than that of the neat soy-based polyurethane foam during the whole temperature range. The storage modulus of 1 php nanoclay was higher than those of other foams at a temperature below 50°C, while 0.5 php nanoclay foams had the highest storage modulus at a temperature higher than 50°C. The increase in storage modulus of nanoclay soy-based polyurethane foams was due to the fact that nanoclay had higher stiffness than neat soy-based polyurethane foam and could restrict the mobility of soy-based polyurethane foam molecules. However, the aggregation of nanoclay at high loading would cause less uniform cell structure and size,

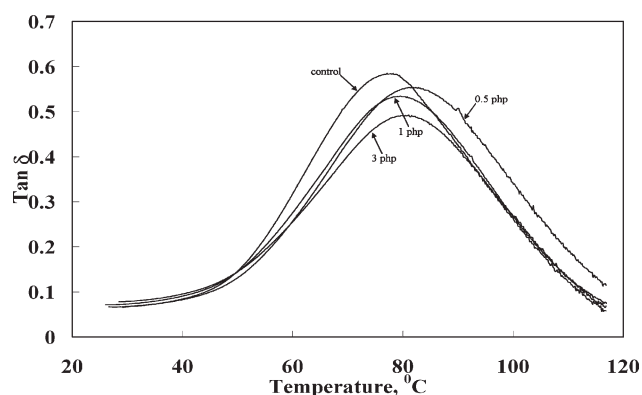


Figure 10 Soy-based polyurethane foam $\tan \delta$ as a function of temperature.

and hence compensated the increase in storage modulus by the incorporation stiffer nanoclay. This was more evident when the temperature was over 50°C. Incorporation nanoclay Cloisite 30B improved the storage modulus of the foam.

The $\tan \delta$ of the soy-based polyurethane foams as a function of temperature is shown in Figure 10. The glass transition temperature was defined, herein, as the $\tan \delta$ peak temperature. The T_g values of the neat foam, and 0.5, 1, and 3 php soy-based polyurethane foam were 78.2, 81.3, 79.6, and 81.0°C, respectively. The T_g of nanoclay foams was higher than that of the neat foam. The increase of T_g was due to the restriction of molecular chain motion by the incorporation of nanoclay.²² The T_g of the 0.5 php nanoclay foams showed the highest among the test samples. This was because that the nanoclay was more easily exfoliated and evenly distributed into polymer matrix system at a low loading. The maximum $\tan \delta$ for neat and nanoclay soy-based polyurethane foam was different. The maximum $\tan \delta$ values of neat foam, and 0.5, 1, and 3 php nanoclay foams were 0.578, 0.554, 0.534, and 0.492, respectively. The decrease in maximum $\tan \delta$ indicated that the elastic nature of the soybased foam was increased by the incorporation of nanoclay into the matrix, which would lead to less friction due to the rigidity of nanoclay.²³

CONCLUSIONS

Nanoclay soy-based polyurethane foams were prepared by one-pot, free-rising method. The densities of nanoclay soy-based polyurethane foams were higher than those of neat soy-based polyurethane foam. The mechanical properties such as compressive and flexural properties were improved by the incorporation of nanoclay into the polymer matrix. The mechanical properties of the nanoclay soy-based polyurethane foams reached a maximum at 0.5 php nanoclay loading. The thermo mechanical properties of the foams were also improved by adding the nanoclay.

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