

Effect of Different Preparation Routes on the Structure and Properties of Rigid Polyurethane-Layered Silicate Nanocomposites

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ABSTRACT: To identify the effect of reactive preparation on the structure and properties of rigid polyurethane (PU)-layered silicate nanocomposite, a range of nanocomposites were prepared by combining the various precursors in different sequences. The morphology of the samples was characterized by XRD and TEM. Tensile properties and dynamic mechanical thermal properties were measured. The reactions between the layered silicates and PU precursors were monitored via FTIR to gain an understanding of the participation

of nanofiller in the polymerization reaction, and the impact of this on system stoichiometry. The XRD and TEM results provided evidence that morphology can differ significantly if different synthesis methods are used. However, the mechanical properties are dominated by the stoichiometry imbalance induced by the addition of the layered silicates. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2894–2903, 2006

Key words: polyurethane; nanocomposite; thermoset

INTRODUCTION

With regards to the preparation and optimization of polyurethane (PU) nanocomposites, it is believed that properties such as stiffness, tensile strength, and heat distortion temperature could be improved without sacrificing the impact strength, ductility, and in some cases, the optical transparency of the composites. A number of studies have been performed on PU nanocomposites, however they are mostly based on elastomeric formulations.^{1–3} To the best of the authors' knowledge, there is very little literature on rigid PU nanocomposites. Yet, rigid PUs are used in many different industrial applications such as rotational molding, structural foams, and vacuum cast prototyping.^{4–6} If the properties of rigid PU can be further enhanced and tailored while retaining processability, it will be of value to some of the existing markets and new applications could be made possible.

Scattered information exists in the area of PU nanocomposites processing in the literature. However, processing is usually not the focal point of these studies^{7–9} and normally not investigated systematically. Furthermore, the processing for elastomeric systems tends to be less complex than the more reactive rigid PU systems. Hence there is a need for systematic investigation in the processing of rigid PU-layered silicate nanocomposites.

For elastomeric PU, it has been discovered that the addition sequence of different molecular weight polyols contribute to different properties for the resulting nanocomposites.⁹ However, the mechanism behind these changes was not investigated. The difference between various dispersion techniques such as high shear homogenizer and sonifier has also been compared.⁷ Sonification can create better dispersion and more stable suspensions but there is evidence that ultrasonic energy can give rise to polymer degradation.¹⁰

The *in situ* polymerization reaction pathways and kinetics have not been well investigated for PU nanocomposite systems. PUs are very sensitive to stoichiometry in that an excess of isocyanate can alter physical properties such as tensile, flexural, and impact properties significantly. How this excess affects the nanocomposites has not been investigated until recently by Rodlert et al.⁸ They demonstrated the changes in tensile properties by varying the excess isocyanate ratio.

It is clear that there is a deficiency in information for rigid PU. This study aims to provide some understanding about the effect of different synthesis routes on the structures and properties of rigid PU-layered silicates nanocomposites.

EXPERIMENTAL

Materials

BF was the name of the PU matrix used in this study. It was made from Isonate 181, Voranol 5471, and Voranol

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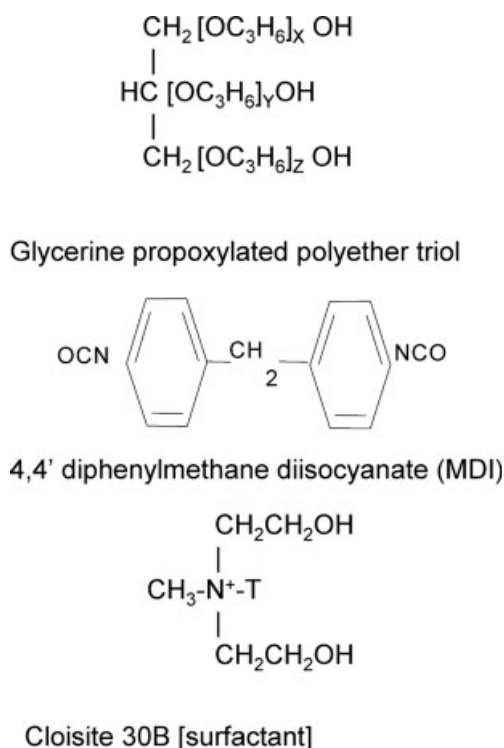


Figure 1 Summary of key chemical structures and information of precursors.

CP 450. The nanocomposites system can be divided into three components. Component A was the isocyanate component, the Isonate 181 was an isocyanate ($-\text{NCO}$) terminated prepolymer made from 4,4' diphenylmethane diisocyanate (MDI) reacted with a small amount of glycol ethers. Component B was a mixture of glycerine propoxylated polyether triol of molecular weight of 4800 and 450 (Voranol 5471 and Voranol CP 450 from Dow Plastics). Component C was Cloisite 30B purchased from Southern Clay Products, which was the organoclay used without further purification. The surfactant used to modify the montmorillonite Cloisite 30B is a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium which contains two hydroxyl groups and is hydrophilic in nature. [Cloisite Na^+ is the unmodified (no surfactant added) montmorillonite clay]. The catalyst used was organomercury-based system [and is denoted by * in the schemes]. A summary of the chemical structures and information about precursors is also provided in Figure 1.

Synthesis methodology

All the various synthesis routes described below are shown in Figure 2.

A approach

In the A approach (A), the organoclay was allowed to react with the isocyanate for 5 min. After that,

remaining polyols were added to complete the reaction. The organoclay used in this experiment (Cloisite 30B) contained surfactant with reactive hydroxyl groups which would be capable to react with the isocyanate. The hydroxyl groups from $\text{Si}-\text{OH}$ bonds of the clay may also participate in the reaction. This could create a chemical bond between the organoclay and the PU matrix.

B approach

B approach (B) was the most commonly used method for layered silicate PU nanocomposites synthesis via *in situ* polymerization. The organoclay was first intercalated with the nonreactive (towards the organoclays) hydrophilic polyols component (B component). The *d*-spacing of the layered silicate increased after intercalation by the polyols, which could promote molecular diffusion into the interlayer during the polymerization reaction. The isocyanate (component A) was then added to complete the reaction.

Masterbatch

The masterbatch (MB) method was a concentrated mixture of Cloisite 30B and a low viscosity polyol. The clay content in the masterbatch was 15% wt of Cloisite 30B. Catalyst could also be added in the masterbatch. The masterbatch was allowed to equilibrate under vacuum at 80°C for at least 1 week

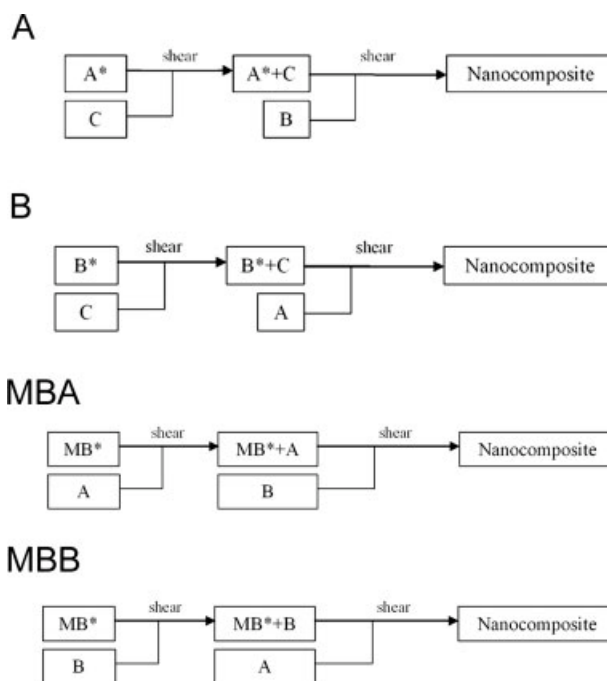


Figure 2 Schematic representation of different synthesis methods used in this study (component A, B, and C are defined in the material section).

before use. There were some experimental evidence that this would improve dispersion and exfoliation in the final nanocomposites. Lepoittevin et al.¹¹ demonstrated in their PCL nanocomposites synthesized via the “two step” masterbatch approach a much higher stiffness than samples produced by direct melt intercalation. From their XRD and TEM data, higher degree of exfoliation and dispersion was also achieved with the masterbatch approach.

Masterbatch A approach

In the masterbatch A approach (MBA), the isocyanate component first reacted with the masterbatch. Because of the high concentration of clay in the masterbatch, a large portion of the polyols would be closely interacted with the clay. By introducing excess isocyanate at this point, this approach encouraged the polymerization reaction in the interlayer of the clay to take place, which in turn could enhance the degree of exfoliation. After this step, more polyols were added to balance the stoichiometry.

Masterbatch B approach

The masterbatch B approach (MBB) involved diluting the masterbatch with polyols first before polymerization with the isocyanate component. This approach focused on enhancing the dispersion and the level of intercalation.

Measurements

Tensile tests were carried out following the ASTM D-638 standard on an Instron model 4505 universal testing machine using at least five replicates of each material. Dumbbells of 3-mm thickness were pressed from an ATSM D-638M-3 die [as mentioned in the standard, care was taken to eliminate edge cracks using this procedure]. A crosshead speed of 5 mm/min was employed. Dynamic viscoelastic properties were measured using a Rheometric Scientific dynamic mechanical thermal analyzer (DMTA-v4). Linear viscoelastic tests were carried out to determine the appropriate linear strain. Samples were tested with a heating rate of 2°C/min at a frequency of 1 Hz. Wide angle X-ray experiments were performed at room temperature on a Bruker AXS-D8 advanced X-ray diffractometer with twin Goble mirrors and horizontal split geometry using CuK α radiation ($\lambda = 1.54$) in powder diffraction mode. Intensity versus scattering angle (2θ) was recorded at room temperature in the range $2\theta = 1^\circ$ – 10° (0.04° step-size at 2.5 s/step). The operating voltage was 40 kV and the filament current was 30 mA. For TEM imaging, the thin sections (20–80 nm) were prepared by microtome and placed on 400 mesh Cu grids for analysis on a JEOL 1010 JEM TEM at 100 keV. The

images were obtained using a SIS megaview slowscan camera and image capture. The magnification of the images was from 3000 up to 600,000 \times on this microscope. Fourier transform infrared (FTIR) spectroscopy measurements were performed with a PerkinElmer infrared spectrometer (Spectrum 2000). The samples were placed between two KBr discs. The peak of particular interest is the NCO peak (2280 cm^{-1}). The conversion used in the analysis is defined as follows:

$$\text{Conversion}_t = (A_{2280,t=5\text{ min}} - A_{2280,t}) * 100 / A_{2280,t=5\text{ min}}$$

where t is the time in minutes; A_{2280} is the absorbance at 2280 cm^{-1} wavelength.

RESULTS AND DISCUSSION

Reaction between layered silicates and PU precursors

Most PU nanocomposites research acknowledges the reactions between the layered silicates and the PU precursors.^{1,8} This problem is overcome by employing a slight excess of the PU precursors containing the isocyanate groups to balance the stoichiometry. Rodlert et al.⁸ looked at how the isocyanate index impacted on the mechanical properties of their elastomeric PU-layered silicate nanocomposites. However, the cause of these changes has not been investigated. In this study, the reactions between layered silicates and the rigid PU precursors have been monitored via FTIR to determine how the layered silicates and the surfactants associate with them affect the stoichiometry.

Figure 3 shows the reactivity of the isocyanate to clays and isocyanate to polyol in the presence of clay, respectively. This data is derived from FTIR measurements. The control was pure isocyanate and it appeared that the reaction between the moisture in the

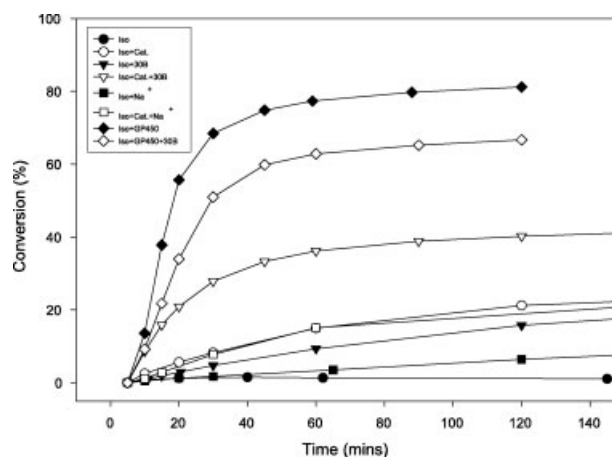


Figure 3 Reactivity of the layered silicates to PU precursors monitored via FTIR.

air and the isocyanate was low. If the catalyst was present, this reaction accelerated. When the unmodified Cloisite Na⁺ was inserted in the system, there was no significant difference when compared to the isocyanate reacting with the moisture in the atmosphere in the presence of catalyst. When no catalyst was present, more isocyanate reacted when Cloisite Na⁺ was present compared to without Cloisite Na⁺. Besides the moisture in the atmosphere, the other available reactant for the isocyanate would only be the adsorbed water associated with the layered silicate.

When the Cloisite 30B was introduced there was a significant increase in conversion in a given time with or without the addition of catalyst. Thus, it was clear that there was more than just water on the layered silicate that reacted with the isocyanate. The obvious cause would be the organic surface modifier of Cloisite 30B which contained two reactive hydroxyl groups. Note that there was an excess of surfactant compared to the CEC of the montmorillonite, which means that there would be a number of "free" surfactants not cationically bound to the layered silicate. From the manufacturer's specification, the modifier content for Cloisite 30B was 30% by weight. After Cloisite 30B was washed to remove the excess surfactants, TGA measurement indicated that the surfactant was only 17% by weight (result not shown here). Hence the excess "free" surfactant would be equivalent in amount to around 70% of the exchanged, properly-bound surfactants. The amount of isocyanate reacted was significantly more than the surfactant present, thus it is likely that there were other side reactions, and quite possibly the large excess of isocyanate could also have reacted with the Si—OH groups on the montmorillonite in the presence of the catalyst.

It was clear that the organoclay and its surfactant would consume extra isocyanate than the amount estimated from a stoichiometric calculation if the organoclay was exposed to large excess of isocyanate precursors in the presence of the catalyst. In the actual synthesis of PU nanocomposites, the ratio of isocyanate and polyols would be roughly one to one, hence the surfactants and the clay would be exposed to much less isocyanate and the importance of these side reactions would be reduced. From the differences between the reaction profile of isocyanate and polyol with or without Cloisite 30B, the consumption of the isocyanate groups was much more rapid than the trails without the polyols. When Cloisite 30B was inserted, the reaction rate decreased. The presence of the layered silicate hindered the diffusion and also interacted with precursors molecules, which caused the reduction in reaction rate.

The data suggested that Cloisite 30B could consume more isocyanate than the amount required to react with all the surfactants when excess isocyanate was presented. This effect was also intensified by

the catalyst. However, in the presence of sufficient polyols, this effect would be reduced significantly. Essentially, the results here suggested that there would be a lot of unwarranted side reactions in the A synthesis approaches and the masterbatch A approaches where the other synthesis method such as the B approach is not as affected. Given that all the samples made from different synthesis routes had the same chemical composition, the role of the organic modified layered silicates in the PU polymerization reaction directly affected the reaction mechanism of the system and altered the stoichiometry to some degree.

Structure of the nanocomposites made via different reaction routes

Figure 4 shows the differences in the structure of the BF/Cloisite 30B nanocomposites determined by XRD. Since all samples had exactly the same chemical composition and amount of organoclay, the changes in their structures were solely caused by the differences in synthesis routes. For the neat PU, there was no peak for 2^θ between 1° and 10° and for Cloisite 30B, one distinct peak located at around 2^θ = 4.8° which corresponded to ~ 1.9 nm was recorded. With the four nanocomposites synthesized, two distinct patterns were observed.

The first groups included samples made with the B and the masterbatch approaches. They showed a well intercalated structure with a distinct peak corresponding to a *d*-spacing of around 4.5 nm. This was more than twice the *d*-spacing of original Cloisite 30B. Such patterns were commonly observed in well intercalated nanocomposites.^{12,13} There was also a small peak at around 2 nm which indicated the possibility of flocculation. TEM would be able to clarify this.

Figure 5 is the TEM images from the B, MBB, and MBA synthesis routes. The structures were very sim-

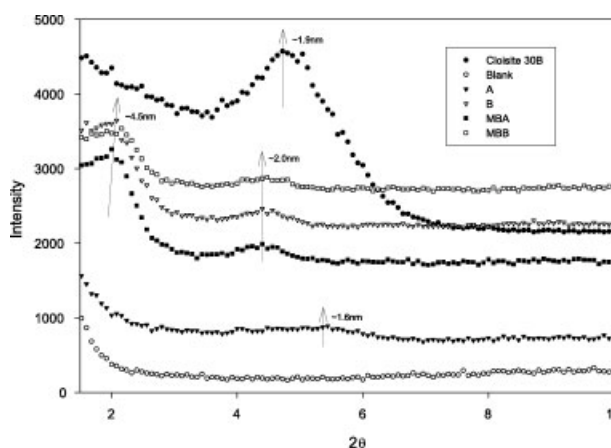


Figure 4 XRD plot of the various nanocomposites, the control (neat PU) and Cloisite 30B.

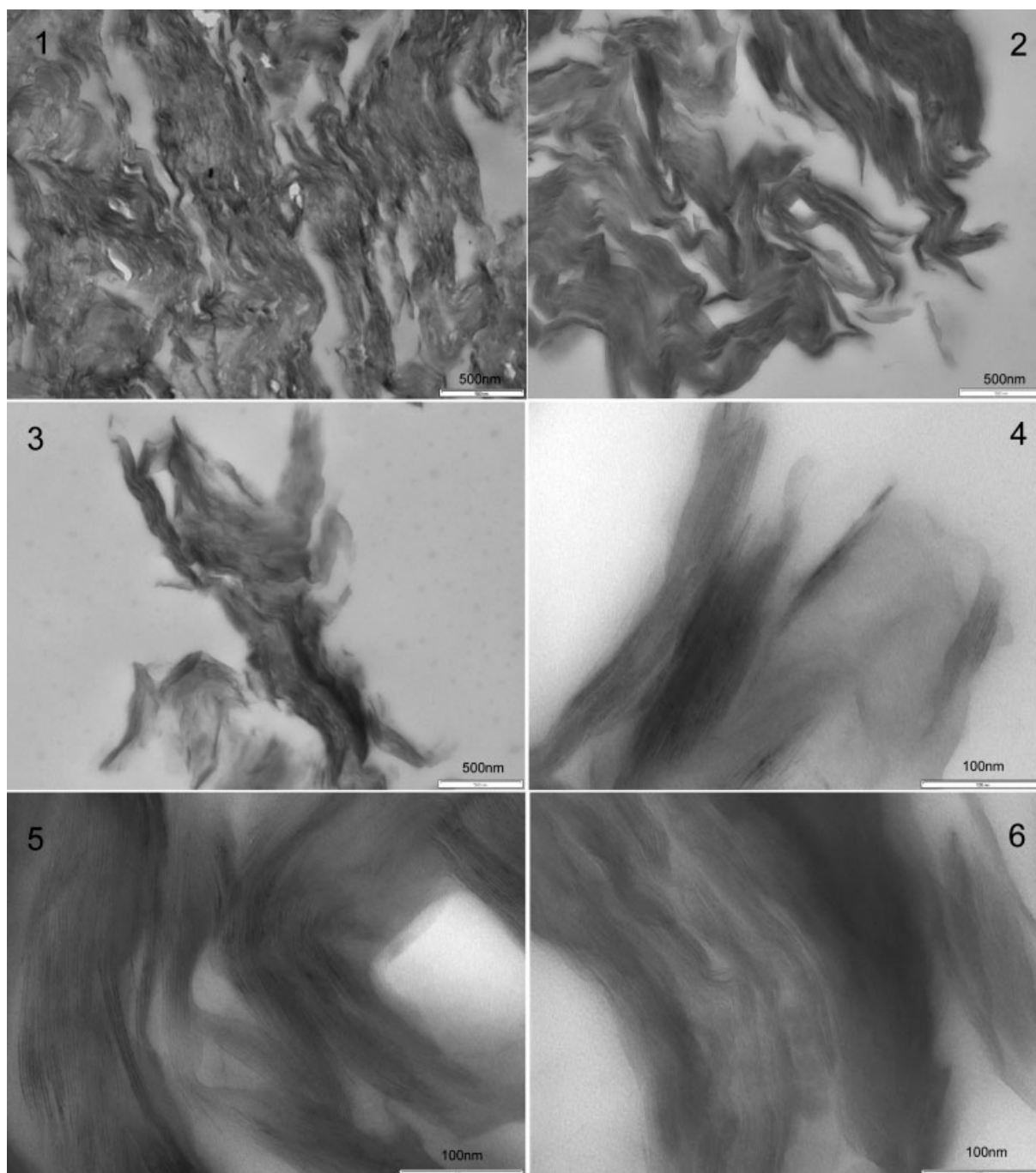


Figure 5 TEM images of the nanocomposites synthesized under different methods. Lower magnification (1) B approach, (2) MBA approach, (3) MBB approach, higher magnification (4) B approach, (5) MBA approach, (6) MBB approach.

ilar, as expected, since the XRD data for the samples based on these synthesis routes have almost identical low angle diffraction patterns (Fig. 3). From the higher magnification images, the level of intercalation could be seen more clearly. The basal spacing between the layers could be measured and the results were consistent with the XRD measurements. Image 5 is a higher magnification of the sample made from the MBA approach. It is taken from a more ordered area, where the basal spacings are

between 3 and 5 nm, indicating a well intercalated structure.

The second group includes the A approach samples, which shows no distinct peaks. There was a very small peak at around 1.6 nm. This was very different to the B and masterbatch approach samples. The absence of peaks could indicate that the layered silicates were exfoliated, or that of an immiscible system.¹⁴ Figure 6 shows the TEM image of the samples made with the A synthesis route. It could be seen

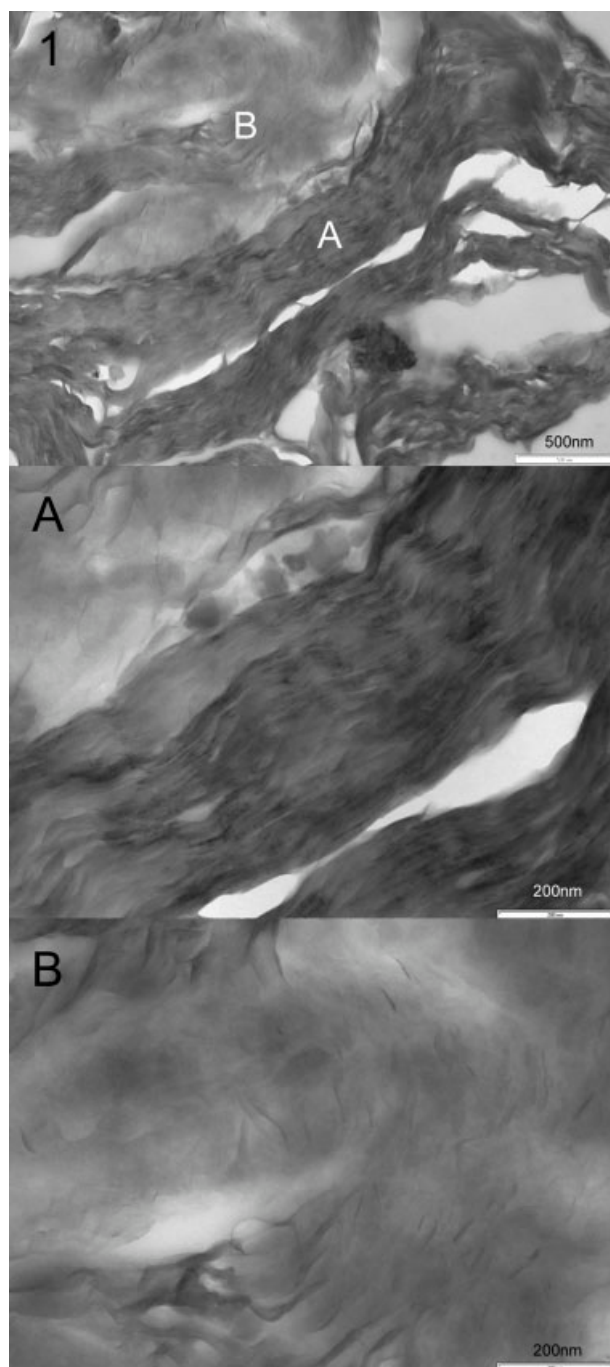


Figure 6 TEM images of samples synthesized via A approach (A) intercalated and flocculated region and (B) exfoliated region.

that the structure of the nanocomposites synthesized from the A approach is composed of two types of structure. An ordered flocculated, intercalated region (A), and an exfoliated/intercalated region (B) were identified.

By using low magnification TEM images, the degree of dispersion/intercalation could be monitored. Figure 7 summarizes the result of the agglomerate sizes of samples made by the various synthesis routes. The tac-

toids' sizes were analyzed with an image analysis program (ImageJ) on TEM images of low magnification. Three images of different sections were analyzed and the averages were used to provide a "more representative" semiquantitative result. From Figure 8, there were clear differences between the two groups of structures discussed earlier. There were many more tactoids observed in the B, MBB, and MBA samples (all of these preparations involved preintercalation of polyol precursors into Cloisite 30B first) compared to the A sample, especially at lower tactoid size fractions. This can be clearly seen in the TEM images (Fig. 8).

This difference was due to the level of polymerization reaction taking place in the interlayer under various synthesis routes. In the B synthesis route, the degree of polymerization was lower than the others because of the encapsulation of the stacks of swollen clay platelets caused primarily by the faster polymerization reaction in the bulk phase (for details, see Chapter 6 in Ref. 15). In contrast, where the isocyanate precursors were introduced to the organoclay first in the A approach, the excess isocyanate could begin reacting with the surfactants of Cloisite 30B. This, in effect, reduced the difference between reaction rates of the interlayer and the bulk phase. Exfoliation was encouraged in the nanocomposites as evidenced in the TEM images, and this, in turn, lowered the degree of tactoid formation. From the morphological view point, the A approach produced samples with the best level of intercalation/exfoliation and the best dispersion (least tactoids).

Mechanical properties of the nanocomposites made via different synthesis routes

Tensile properties

From XRD and TEM characterization, it was clear that the structure of the nanocomposites made via differ-

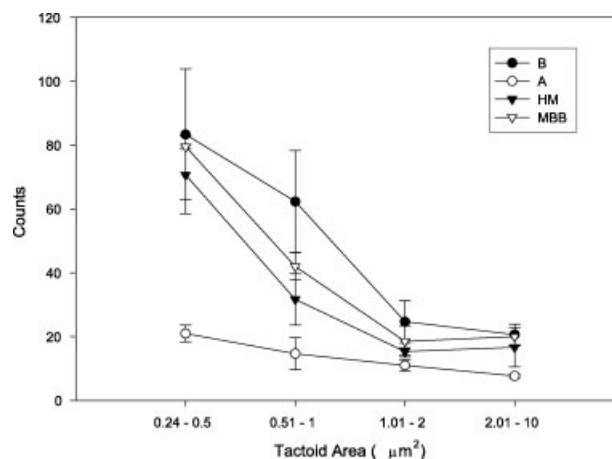


Figure 7 Tactoids size distribution analysis of the nanocomposites made using different methods.

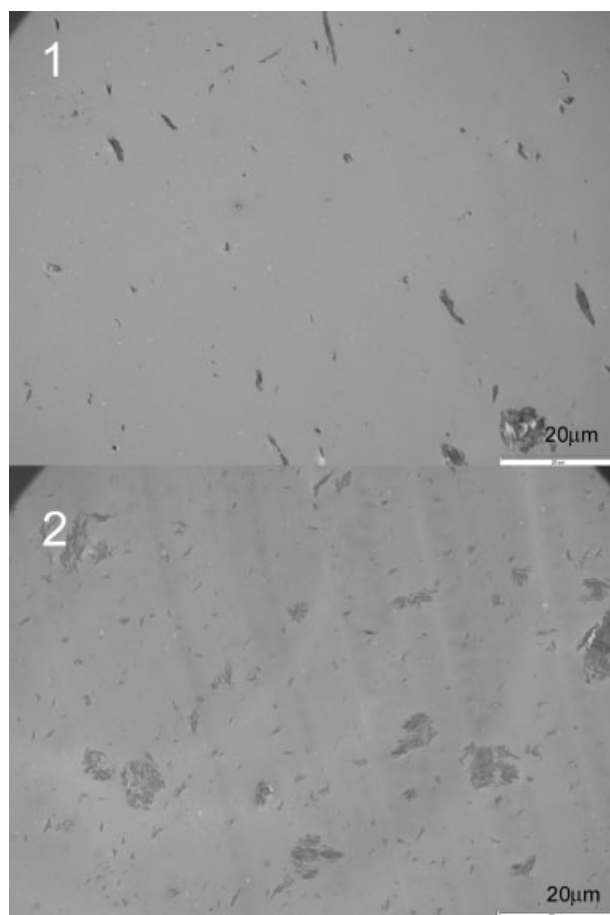


Figure 8 Low magnification TEM images of (1) A approach and (2) B approach.

ent synthesis routes were not the same. Since structure and properties of the nanocomposites were related, the mechanical properties of the nanocomposites synthesized with different approaches were expected to vary.

Table I displays the tensile properties of the samples. The samples contained 2% Cloisite 30B with identical compositions.

In terms of Young's modulus, the masterbatch B approaches demonstrated the best enhancement. The improvements were around 10% which in itself was not very significant compared to the pristine PU given the variance of the result. Other approaches were almost identical as the neat PU, and some were even

weaker. Considering all the nanocomposites had identical formulations, the differences of around 20% between the A and MBB approach were more significant. Looking at the maximum tensile stress, the trend was similar to that of the modulus. PU is very sensitive to stoichiometry, the large variation in the tensile stress suggesting that there could be an imbalance in stoichiometry in some of these materials (detail in later section).

For elongation at break, a marked reduction in rigid PU was always the case in previous studies even at low level of layered silicate addition¹⁵ (this is different in elastomeric PU where many reported increase in elongation at break^{1,16}). In the previous studies,¹⁵ it was demonstrated that the elongation and impact strength followed similar trends with the addition of layered silicate. Both decreased significantly at low loading of Cloisite 30B. That was one of the drawbacks with traditional microfillers, and "true nanocomposites" with exfoliated and distributed structures were supposedly able to minimize this effect.⁴ The source of the reduction in impact strength and elongation for the previous experiments was believed to be caused by defects or large agglomerates of clays in the samples forming "stress raisers." However, for samples in this experiment, they were essentially the same with the control suggesting the level of dispersion was satisfactory.

Thermomechanical properties

Figure 9 shows the changes in stiffness (E') of the nanocomposites between 30 and 100°C that are made via different synthesis routes. At lower temperature (between 30 and 40°C), the pristine PU had the highest stiffness. This was due to the lower crosslink density of the nanocomposites induced by the surfactants of Cloisite 30B. As demonstrated in the earlier section, there were excess dihydroxyl functionalized surfactants on Cloisite 30B and they were capable to react with the isocyanate prepolymer, and various side reactions also occurred. Hence, reducing the isocyanate content leads to the reduction in crosslinking density. The direct experimental evidence showing this stoichiometry imbalance in the nanocomposites indeed occur would be discussed in later part of this

TABLE I
Tensile Properties of BF/Cloisite 30B Nanocomposites via Different Synthesis Routes

Sample	Young's modulus (MPa)		Maximum tensile stress (MPa)		Elongation at break (%)	
		SD		SD		SD
Blank	2110	120	41.4	1.0	144	27
B	2030	70	37.0	0.3	146	8
A	1940	140	33.7	2.6	174	24
MBA	2110	40	40.1	1.2	152	51
MBB	2350	110	44.8	1.0	136	36

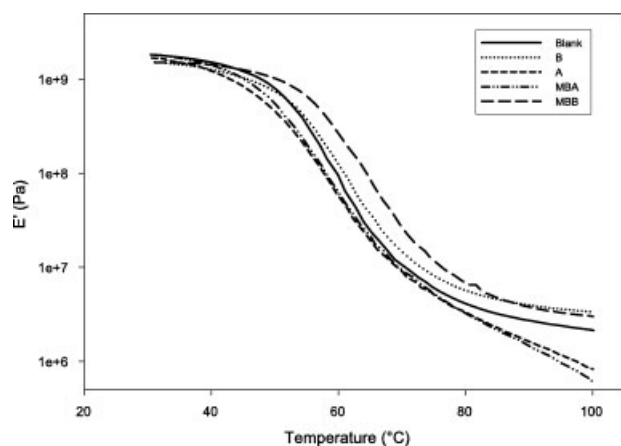


Figure 9 Storage modulus of the nanocomposites synthesized by different methods.

article. There was a clear difference in the higher temperature region (basically from 50°C upwards, and even more pronounced between 80 and 100°C). In this region, the behavior of the nanocomposites appeared to be divided into two groups. The masterbatch B and the B approaches were markedly stiffer than the pristine PU, while the A and the masterbatch A approaches were clearly weaker. This highlighted how a stoichiometry imbalance could weaken the PU and also the ability of Cloisite 30B to improve the reinforcement of the PU at elevated temperature providing a “suitable” synthesis method.

Rhoney et al.⁷ also synthesized layered silicate PU nanocomposites via nonsolvent *in situ* polymerization with Cloisite 30B. They performed DMTA measurement with their 3% samples made using a high shear mixer and sonifier. Rhoney et al.⁷ achieved no enhancement in sample made using the high shear mixer. In their sonicated samples, the improvement was similar to the result in this series of experiments in terms of stiffness. The synthesis route they employed was the B approach and the softening temperature improvement was in line with the B approach experiments in this study as well. So the DMTA results of this series of experiments were consistent with experimental results observed by other researchers and also in agreement with the prediction from the model by Gersappe,¹⁷ which showed better reinforcement capability of the layered silicate at elevated temperature.

Effect of stoichiometric imbalances on PU nanocomposites

According to Hur et al.,¹⁸ the damping behavior of crosslinked PU could be related to network structure which was affected by the stoichiometry and composition. They demonstrated the relationship between $\tan \delta$ (the loss tangent as measured from DMTA), stoichiometric imbalances, and crosslink density.

When there were more unreacted hydroxyl groups in the network, the value of $\tan \delta$ peak decreased. Hence the value of $\tan \delta$ peak could be used as an indicator of the crosslink density and the stoichiometry of the PU network.

Figure 10 is the $\tan \delta$ data for the nanocomposites made under various synthesis routes. The value of the $\tan \delta$ peaks in descending order were A, masterbatch A, blank, masterbatch B, and B approaches. According to the Hur's data,¹⁸ this would mean that the PU matrix using the A approach had the most unreacted hydroxyl groups. This was in agreement with the FTIR data in the previous section showing that if Cloisite 30B was exposed to excess isocyanate, a large number of undesired side reactions occurred which substantially reduced the amount of isocyanate available to react with the polyol components. Since less isocyanate is available for the polyol to react with, this would induce stoichiometry imbalance into the system and the PU network would contain more unreacted hydroxyl groups. The $\tan \delta$ peak value for the masterbatch A approach was lower than the A approach but still higher than the neat PU. This was because in the masterbatch A approach, the Cloisite 30B was initially intercalated with polyols, and the amount of side reactions is reduced (relative to the A approach) resulting in lower stoichiometry imbalance.

For the masterbatch B and B approaches, they had $\tan \delta$ peak values lower than the neat PU. For these three approaches the Cloisite 30B was preintercalated with enough polyols so that Cloisite 30B would not be exposed to excess isocyanate and significant side reactions should not occur. The fact that their peak $\tan \delta$ values were lower than that of the pristine PU indicated that a portion of the polyols might not take place in the polymerization reaction. It has been well demonstrated that organoclay could be dispersed well in the polyol components, and that the polyols

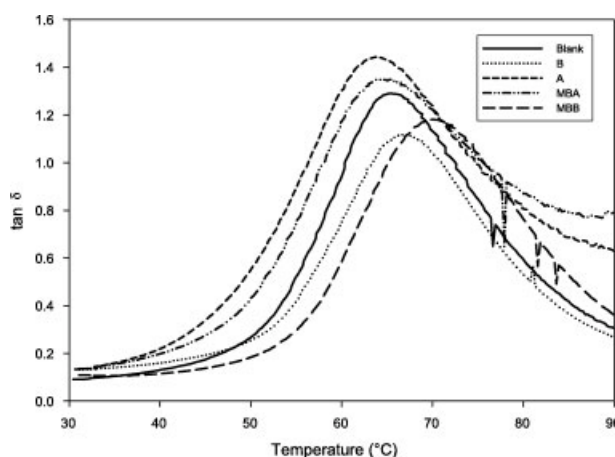


Figure 10 $\tan \delta$ curves measured from DMTA test of the various nanocomposites made using different methods.

TABLE II
Summary of the Properties of Nanocomposites Made via Various Synthesis Routes

Synthesis routes	Degree of exfoliation	Degree of dispersion	Stoichiometry	Properties ^a
A	1	1	-2	Stiffness: 4; modulus: 5; strength: 5
B	5	5	3	Stiffness: 3; modulus: 4; strength: 4
MBA	4	4	-1	Stiffness: 5; modulus: 2; strength: 2
MBB	2	3	1	Stiffness: 1; modulus: 1; strength: 1

^a The numbers represent the level of the properties with 1 being the highest and 5 being the lowest. For stoichiometry, 1 being the closest to the neat polyurethane and the "+" sign represents hydroxyl groups excess and the "-" sign represents hydroxyl groups deficiency. The stiffness is the elastic modulus measured by DMTA, while the modulus and the strength are the tensile modulus and ultimate strength (resp.) measured by the Instron in uniaxial tension.

readily intercalate into the interlayer of the layered silicate.¹⁹ However, how the reactivity of these confined reactive components was affected with respect to the bulk precursors remained unclear.

From this experiment, it would appear that in the B and masterbatch B approaches, the polyol was pre-intercalated into the clay. In the bulk phase, there were both polyol and isocyanate. So the reaction rate in the bulk phase would be faster relative to the interlayer of the clay because the isocyanate component would have to diffuse in to the galleries first for the reaction to occur. As the reaction proceeds, a network structure would be established in the bulk phase while there could still be unreacted precursors in the interlayers. The network structure could encapsulate some stacks of clay platelets and prevent a complete and homogeneous polymerization reaction from occurring. This explanation was supported by the experimental data of the B and masterbatch B approaches. Both samples had exactly the same composition. The difference in the synthesis methods was that the masterbatch B approach used a masterbatch, and hence could be classified as a two-step process, while the B approach was just a one-step process. From the XRD and TEM analysis, there were no marked changes in morphology between the two samples. So this was not the cause for the difference in their level of stoichiometry imbalances. The difference in catalyst distribution between the two methods, which essentially determined the reaction rates, was the main factor. In the B approach, the catalyst was added to the polyol, meaning that the concentration of catalyst would be the same for the polyol in the bulk phase and the polyol intercalated in the layered silicate. However, in the masterbatch B approach the catalyst was added in the masterbatch meaning that the polyol closely associated with the clay would have a higher concentration than the bulk phase. This essentially reduced the difference in the reaction rates between the bulk and the intercalated regions, possibly resulting in a more

homogeneous polymerization throughout the intra and extra-gallery regions of the system.

Table II summarizes the properties of the PU nanocomposites made via various approaches. In terms of dispersion and exfoliation, the A approach showed the highest degree of exfoliation and degree of dispersion, however crosslink density suffered due to stoichiometry imbalance and also the higher level of exfoliation. This was reflected in the mechanical properties. The masterbatch B approach produced the best results in terms of mechanical properties.

CONCLUSIONS

The importance of synthesis methodology was investigated in this study. Various approaches were tested to improve the level of dispersion and degree of exfoliation. It was interesting to discover that even when identical composition was employed, varying the synthesis routes could affect the structure and properties of the nanocomposites greatly. Stoichiometry, dispersion of the layered silicates, and chemical structure were the principle factors inducing these changes. In the various synthesis routes, the extent of reaction between the surfactant on the organoclay and the isocyanate precursors of the PU varied. This led to stoichiometry imbalances in the different samples which directly affected their mechanical properties. The level of exfoliation of the layered silicates also showed strong correlation with the degree of polymerization reaction occurring in the interlayer of the organoclay with the A approach samples showing the highest degree of exfoliation. In the low temperature region, mechanical properties dictated by stoichiometry resulted in different crosslinking densities. At higher temperature, the reinforcement effect of the layered silicates overcomes that resulting in marked improvement in stiffness in some samples. This was consistent with the molecular simulation result by Gersappe.¹⁷ To produce rigid

PU-layered silicates nanocomposites with greatly enhanced properties, the reaction mechanism of the system needs to be investigated in more detail and the stoichiometry has to be optimized.

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