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Effect of layered nano-organosilicate on the gel point rheology of bismaleimide/diallylbisphenol A resin

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Abstract

The effect of organically modified clay (organoclay) on the cross-linking of a high performance thermoset resin—diallylbisphenol A (DBA) modified bismaleimide (DBA/BMI), is studied using rheometry and FTIR spectroscopy. The validity of the Winter–Chambon criterion was examined for the cross-linking of these filled polymers. Physical gels have been formed prior to the chemical cross-linking with 3.0 and 5.0% organoclay I.30TC. The physical properties of the gel, including the loss tangent, critical relaxation exponent and the gel strength in the absence and presence of organoclay, were investigated and the results indicated that organoclay showed a great effect on the physical properties of the gel. Organoclay reduced the gel time but decreased the degree of the cross-linking slightly at the gel point, as revealed by the FTIR spectroscopy. The dispersion of organoclay also affected the gel characteristics. More elastic and stronger gel can be obtained when organoclay was better exfoliated. When another type of organoclay Cloisite 30B was used, results indicated that the nature of organoclay had a considerable effect on the cross-linking in the polymer system.

Keywords: Organoclay; Bismaleimide; Gelation

1. Introduction

Organosilicate clays have been considered as potential candidates for filler materials to polymers due to their ready availability, well-studied intercalation chemistry, and the superior physical and mechanical properties, including improved heat resistance, decreased permeability and flammability, increased moduli and optical properties [1]. During the last decade, a large number of researchers have reported on the preparation, characterization, rheological and mechanical properties of clay nanocomposites based on thermoplastic polymers. In recent years, thermosetting polymer-based clay nanocomposites have attracted more and more attentions. Epoxy [2–7], polyurethane [8], and unsaturated polyesters [9] are the common matrices studied so far [1]. A few examples of the nanocomposites based on high performance thermoset resins such as PMR-15 [10], cyanate esters [11,12] can be found. Recently, diallyl compound modified bismaleimide (BMI) resin system, diallylbisphenol A (DBA)/BMI based clay nanocomposites have also been synthesized in our laboratory.

One important aspect of thermosetting polymers is their gelation behavior, especially, the kinetics of gelation as well as gel time. Gelation of thermoset resins such as epoxy, polyester and polyurethane have been studied extensively. Gelation of BMI/DBA and BMI/DBA-cyanate ester (CE) IPN was also reported by our group [13]. The rheological properties such as elastic (G') and viscous (G'') moduli of BMI systems have been studied. Several theories have been employed to determine the gel point including the determination of divergence point of the steady state shear viscosity (η) or normal strain (N1), the cross-over point of G' (dynamic elastic modulus) and G'' (dynamic viscous modulus) [13]. However, Winter–Chambon criterion is commonly used in polymer gels recently. In accordance with Winter–Chambon criterion, loss tangent ($\tan\delta$) is

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independent of the frequencies at the gel point for most of the polymers. The frequency-independence of the loss tangent in the vicinity of the gel point has been widely used to examine the chemical and physical gels and has also been employed to determine the gel point [13,14]. It was demonstrated that Winter–Chambon criterion is valid for the studied BMI systems [13] for accurate determination of the gel point from the rheological data.

The question is whether or not the Winter–Chambon criterion would be applicable for the cross-linking thermosetting polymers such as BMI resins in the presence of fillers. With the introduction of fillers, the situation becomes complicated due to the various existing states of fillers in polymer matrix. The effect of colloidal silica fillers on the cross-linking behaviour of a model UV cured polymer system (thiol–ene) has been studied [14]. The validity of the Winter–Chambon criterion is examined for the cross-linking of these filled polymers with two types of colloidal silica particles. It was found that the Winter–Chambon criterion were not valid for both types of silica particles filled systems. Different fillers have a wide range of effects on the reactions. They may have increasing, decreasing or no effect on the reaction rates. As a result, gelation properties can be very different. Therefore, it is impossible to predict how certain filler may affect the kinetics and the gelation rheological properties based on the results obtained from different fillers.

Our previous studies on the effect of organoclays on the reactions in diallylbispehnol A (DBA) modified BMI indicated that the reactions in DBA/BMI system were affected considerably and the effect was also found to be related to the state of the dispersion of organoclay [15]. In this study, we utilize the dynamic rheometry and FTIR spectroscopy to investigate the effects of organoclays on the gelation behavior and gel physical properties of DBA/BMI resin system.

2. Experimental section

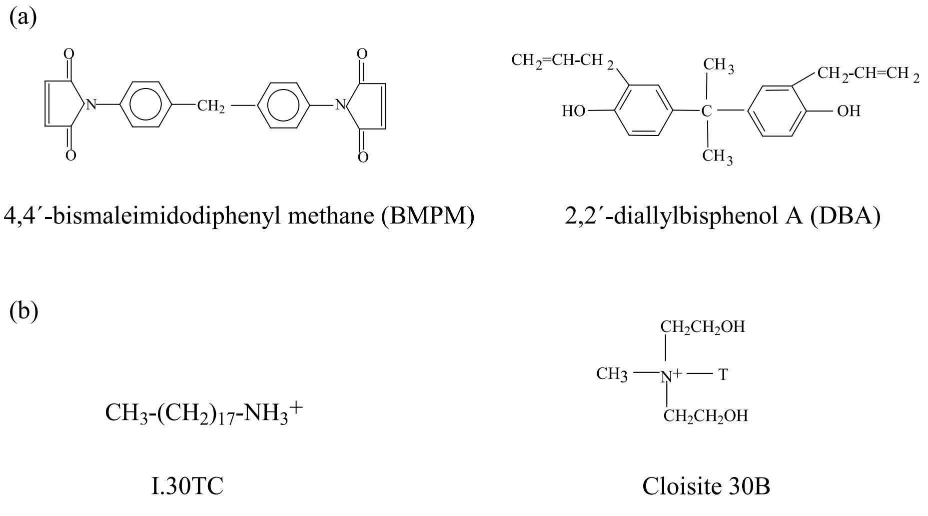
2.1. Materials and preparation of nanocomposites

BMI system used in this study consisted of 4,4′-bismaleimidodiphenyl methane (BMPM) and 2,2′-diallylbisphenol A (DBA) resins. The chemical structures of these resins are shown in Fig. 1(a). Both monomers were supplied by Aldrich Chemicals and were used as received. A fixed molar ratio of BMPM and DBA (1:0.78) was used in the study.

In the present study, organoclay I.30TC (Nanocor Incorporation) treated with a surfactant octadecylammonium chloride was employed. In addition, Cloisite 30B (Southern Clay Products) treated with a surfactant (MT2EtOH) methyl, tallow, bis(2-hydroxyethyl) quaternary ammonium chloride as shown in Fig. 1(b) was also used in order to study the effect of the surface modifiers on the gelation rheology of BMPM/DBA system.

BMPM was added to DBA in an oil bath at 140 °C with mechanical stirring until a homogeneous solution is obtained. The neat pre-polymers were prepared by pre-polymerization of BMPM and DBA at 130 °C for 10 min.

The concentrations of each of the organoclays used in this study ranged from 1.0 to 5.0 wt% of the total monomers. The organoclay was added to DBA in oil bath at 140 °C. Mechanical stirring (2.0 h) followed by high-speed homogenizer (1.0 h) and ultrasonication (1.0 h) was utilized to mix the organoclay with DBA completely. After that BMPM was added into the mixture and pre-polymerized for 10 min at 130 °C as in the case of the neat pre-polymers. By using this method, better-exfoliated structure was obtained. In addition, intercalated system with 3.0 wt% I.30TC was also prepared in order to study the effect of degree of the exfoliation of organoclay on the gelation properties. The intercalated structure was achieved when



4,4′-bismaleimidodiphenyl methane (BMPM) 2,2′-diallylbisphenol A (DBA)

$CH_3\text{-}(CH_2)_{17}\text{-}NH_3^+$

I.30TC Cloisite 30B

Fig. 1. Schematic representation of (a) chemical structures of the monomers comprising BMI system and (b) surface modifiers of organoclays used in this study.

organoclay and DBA was mixed only using mechanical stirring for 2.0 h, followed by adding BMPM and the pre-polymerization for 10 min at 130 °C. The systems studied in the report are listed in Table 1.

2.2. Morphological characterization

2.2.1. XRD

XRD patterns were obtained using a Rigaku X-ray generator operated at 40 kV and 30 mA to determine the mean interlayer spacing of the (001) plane (d_{001}) for organoclays used and the nanocomposites. The X-ray beam was monochromatized to Cu Kα with a graphite crystal. The scanning angle (2θ) was 2.0–10°, and the scanning speed was 1°/min.

2.2.2. TEM

TEM specimens were cut from cured nanocomposite blocks using a Leica Ultracut UCT Ultramicrotome equipped with a diamond knife. Thin specimens, 80–100 nm, were cut from a mesa of about 0.5×0.5 mm^2. They were collected in a water-filled trough and placed on 200 mesh copper grids. Transmission electron micrographs were taken with a Jeol JEM 2010 microscope at an acceleration voltage of 200 kV.

2.3. Fourier transform infrared (FTIR) spectroscopy

Infrared spectra of neat BMPM/DBA system and the nanocomposites with organoclay were obtained using a Perkin–Elmer FT-2000 Fourier Transform Spectrometer in the range of 4000–600 cm^{-1} with a resolution of 2 cm^{-1}. For the nanocomposites with organoclay, FTIR samples were prepared by first mixing them with anhydrous potassium bromide (KBr) powder and subsequently pressing into pellets. For neat BMPM/DBA system, the samples for FTIR were prepared by casting the solution of BMPM/DBA in the acetone on NaCl disk. Samples were treated at 140 °C to simulate the conditions of the rheological analysis. The absorption bands associated with C–N–C maleimide (1149 cm^{-1}) and C–N–C succinimide (1185 cm^{-1}) were closely monitored. In addition, the absorption band due to aromatic C=C at 1512 cm^{-1} was used as an internal reference band since this peak should remain unchanged during the curing process. The degree of cross-linking in BMPM/DBA system can be determined by using the normalized peak intensity of succinimide against internal reference peak.

Table 1
Summary of sample codes of the nanocomposites investigated in this study

Sample code	Description
BD	Pure BMPM/DBA pre-polymer
BDTC1.0	1.0 wt% I.30TC
BDTC1.5	1.5 wt% I.30TC
BDTC3.0	3.0 wt% I.30TC
BDTC3.0Int	3.0 wt% I.30TC with intercalated structure[a]
BDTC5.0	5.0 wt% I.30TC
BD30B1.0	1.0 wt% B30
BD30B1.5	1.5 wt% B30
BD30B3.0	3.0 wt% B30
BD30B5.0	5.0 wt% B30

[a] Based on XRD results.

2.4. Dynamic rheometry

A Rheometric Scientific ARES rheometer was used to determine the gel point of the pre-polymers in the absence and presence of I.30TC and Cloisite 30 B organoclays. The rheometer was used in parallel-plate configuration (diameter $D=25$ mm, gap $H=0.5$ mm). First, the dynamic frequency sweep method was used to obtain G' and G'' at various frequencies at 100 °C in order to study the rheological behavior of the systems before cross-linking. The temperature selection criterion is to ensue that no significant reaction occurred during the test. The temperature dependence of the rheological properties was measured at a heating rate of 10 °C/min to investigate the gelation process of the systems in the absence and presence of organoclay. The rheological properties of the systems were then measured at the temperatures of 130, 140 and 150 °C. Superimposed signals of 25, 50 and 100 rad/s with a strain γ of 2% were used at each frequency in multiwave test. Tan δ (loss tangent) as a function of curing time was plotted simultaneously from the multiwave dynamic rheological tests. All tests were conducted in air.

3. Results and discussion

3.1. Gelation rheology theory

The widely accepted experimental and theoretical methods for the description of the gelation are based on the scaling law. A scaling law of $G'(\omega)=G''(\omega)\sim\omega^{1/2}$ was first experimentally found at the gel point. Later it was generalized to be

$$G'(\omega) = \Gamma(1-n)\cos(n\pi/2)S_g\omega^n \quad (1)$$

$$G''(\omega) = \Gamma(1-n)\sin(n\pi/2)S_g\omega^n \quad (2)$$

or

$$G''(\omega)/G'(\omega) = \tan\delta = \tan(n\pi/2) \quad (3)$$

The shear relaxation modulus $G(t)$ is expected to obey a power law relaxation at the gel point:

$$G(t) = S_g t^{-n} \quad (4)$$

ω is the testing frequency, n is the critical relaxation exponent because n determines the stress relaxation rate at the gel point. $\Gamma(1-n)$ is Γ function. S_g is the gel strength and has an unusual unit of Pa s^n. However, the physical meaning of S_g is abstract due to its unusual dimensions. It can be simply considered as the relaxation modulus at the gel point when the relaxation time is 1 s. Its physical meaning can be understood from the Eq. (4) when n approaches the extreme values. S_g represents the elastic modulus (G_0) or the rigidity of the system when $n=0$, while it represents the viscosity when $n=1$.

In practice, Eq. (1) or Eq. (2) is applied to calculate dynamic moduli G' and G'' at the gel point. S_g can be calculated from $G'(\omega)$ or $G''(\omega)$ at the gel point, if n is known.

3.2. Rheology of neat pre-polymer during cross-linking

The essential features of the rheology of the neat resin BMPM/DBA pre-polymer are shown in Fig. 2. It shows the plots of tan δ at various frequencies as a function of curing time. We can see that the neat BMPM/DBA pre-polymer obeys the Winter–Chambon criterion, as shown in Fig. 2, where all the tan δ curves intersect at a single point, which corresponds to the gel point. The gel time t_{gel} for neat pre-polymer BD from this plot is approximately 3000 s at 140 °C.

3.3. Rheology of the nanocomposites before cross-linking

Before curing the dynamic rheological behavior of nanocomposites of I.30TC at 100 °C is shown in Fig. 3. G' and G'' for each system show a monotonous increase with the concentration of clay at all frequencies. G' and G'' show strong frequency dependence, with G'' higher than G' at all frequencies when 1.0 and 1.5 wt% I.30TC was used (Fig. 3(a)). However, with the increase of clay loads to 3.0 and 5.0%, G' and G'' are much less frequency dependent and G' is higher than G'' in the frequency range analyzed as seen in Fig. 3(b). This means that these samples behave like gels. The increase of the elastic modulus of the system with increasing clay concentration maybe due to the interaction between the organoclay with the pre-polymer, such as hydrophobic interaction, hydrogen bonding and the entanglement of the polymer chains. When the clay concentration is increased to a critical value, a physical gel would be formed. This phenomenon can be further illustrated by using the corresponding plots of G' and G'' versus clay concentration as shown in Fig. 3(c). It can be seen that G'

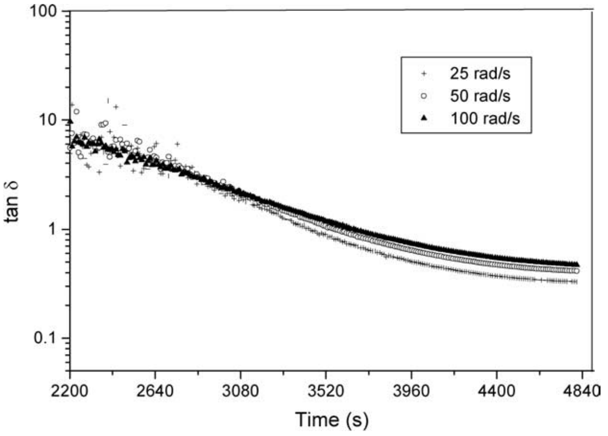


Fig. 2. Loss tangent at various frequencies as a function of time for BD system at 140 °C.

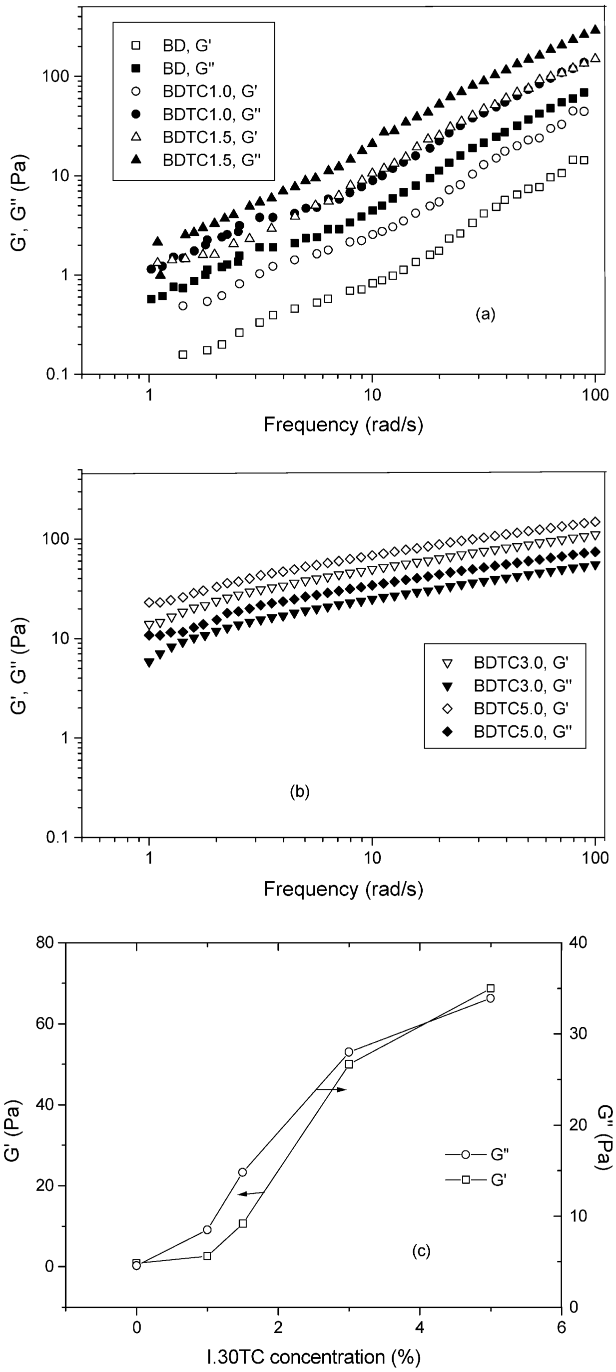


Fig. 3. Frequency spectra of the elastic moduli G' and viscous moduli G'' for BMPM/DBA samples containing I.30TC (a) 0, 1.0 and 1.5 wt% and (b) 3.0 and 5.0 wt% and (c) corresponding plots of G' and G'' versus I.30TC concentration.

and G'' increase gradually with increasing clay concentration to 1.5 wt%. However, when the clay concentration increases further, G' and G'' increase more significantly. In order to confirm whether a physical or chemical gel is formed, acetone was used to dissolve the nanocomposites after the frequency scan at 100 °C. It was found that the gels could be dissolved completely in the solvent. Therefore, they can be considered as physical gels formed during the pre-polymerization at higher concentrations of clay. This conclusion is supported by FTIR results.

3.4. Rheology of the nanocomposites during cross-linking

The rheological behavior of the BMPM/DBA system with the introduction of I.30TC is investigated. Fig. 4 shows the temperature dependence of rheological properties of the systems. It can be seen that the onset temperature of gelation, defined as the onset of rapid increase in G', decreases with increasing clay concentration. This result indicated that the cross-linking of the system was accelerated in the presence of I.30TC. In order to further understand the evolving gelation in the presence of I.30TC, the time dependence of the rheological properties of the systems at various frequencies was investigated at 140 °C. Figs. 5–8 show tan δ as a function of curing time for the samples containing I.30TC. When the loading of I.30TC is less than 5.0%, the tan δ curves at each frequency converge and intersect at a single point. This suggests that the Winter–Chambon criterion is valid even for these clay-filled systems and the intersection point corresponds to the gel time. This indicates that no micro-structural evolution occurred during rheological experiment. Violation of the Winter–Chambon criterion has been reported [14] in a silica filler filled UV-curable polymer system. This phenomenon was attributed to possible phase separation before the gel point, which interfered with the formation of self-similar structures.

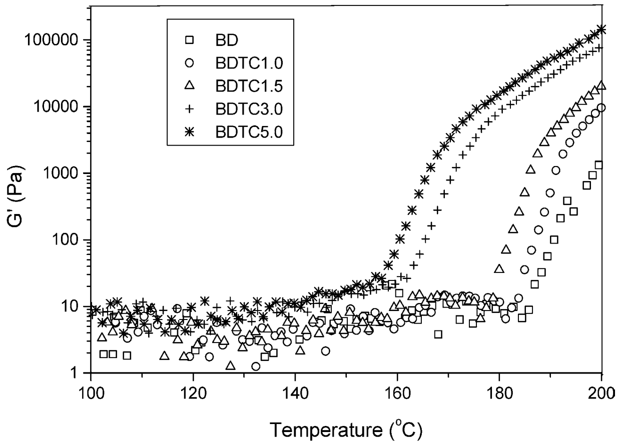


Fig. 4. Elastic modulus (G') as a function of temperature for the systems with various I.30TC concentrations.

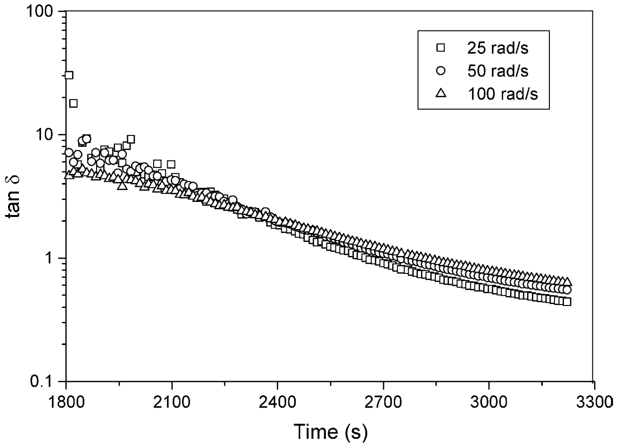


Fig. 5. Loss tangent at various frequencies as a function of time for BDTC1.0 at 140 °C.

From Figs. 5–8, it can be seen that the presence of I.30TC accelerates the chemical cross-linking of the polymer. The gel time reduced from 3000 s for the pure pre-polymer BD to 2370, 1290 and 680 s for 1.0, 1.5 and 3.0 wt% I.30TC systems, respectively. There is no intersection of the loss tangent curves when I.30TC clay load increased to 5.0% indicating that gelation may have occurred during the pre-heating stage of rheological measurement.

In order to understand the chemical cross-linking, FTIR spectra were collected for samples treated at 140 °C as a function of time in the absence and presence of I.30TC as shown in Figs. 9–13. The degree of chemical cross-linking at the gel point has been calculated based on FTIR analysis from the normalized intensity of the absorption band 1185 cm^{-1} to that of 1512 cm^{-1}. 1185 cm^{-1} absorption band appears as a result of the cross-linking reactions, which is related to but different from the curing conversion in the system. The degree of cross-linking as a function of curing time for the systems in the absence and presence of I.30TC is shown in Fig. 14.

From the FTIR spectra of neat pre-polymer (bottom spectrum in Fig. 9), we can see that the linear extension

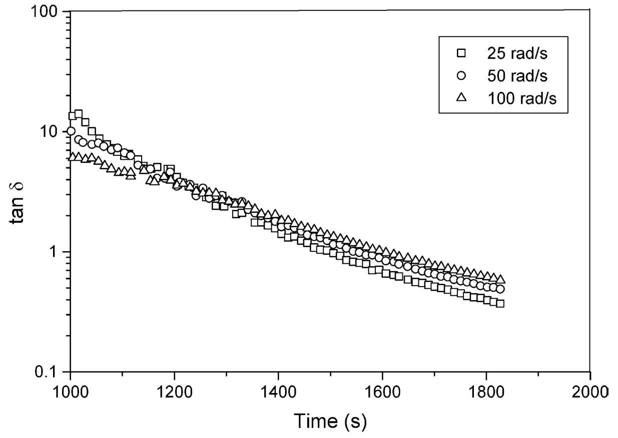


Fig. 6. Loss tangent at various frequencies as a function of time for BDTC1.5 at 140 °C.

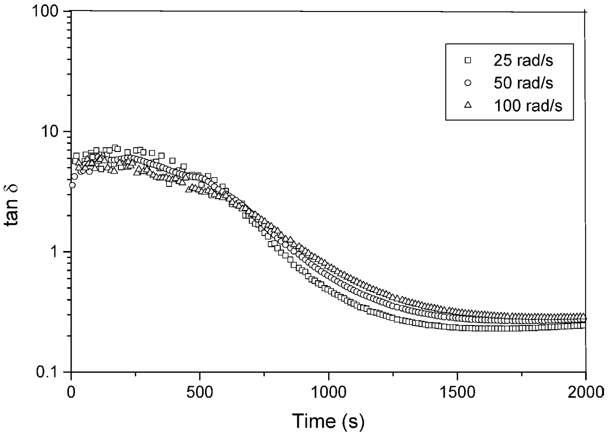


Fig. 7. Loss tangent at various frequencies as a function of time for BDTC3.0 at 140 °C.

reactions are dominant during the pre-polymerization process at 130 °C. In the subsequent isothermal curing at 140 °C, the cross-linking reactions occurred gradually as shown in Fig. 14. Fig. 14 indicates that with lower concentrations of I.30TC such as 1.0 and 1.5 wt%, the cross-linking reactions occurred much faster than those of the neat pre-polymer at 140 °C. However, with further increasing I.30TC concentration to 3.0 wt%, the cross-linking reactions occurred slightly faster. In the presence of 5.0 wt% I.30TC, the cross-linking reactions occurred even more rapidly as seen from the rapid emergence of 1185 cm^{-1} band in Fig. 13. However, it seems that the FTIR spectrum of the clay containing pre-polymer is similar to that of the neat pre-polymer. This suggests that the chemical cross-linking did not occur significantly during the pre-polymerization even for the system with high clay load of 5.0 wt%. Nevertheless, rheological properties of the system showed a higher G' value than G'' before the curing process at 140 °C as seen in Fig. 3. FTIR study concurs with the earlier conclusion that the pre-polymer with 5.0 wt% I.30TC is not a chemical gel before the curing process at 140 °C. On the other hand, there is no intersection of tan δ in mulitwave test as seen in Fig. 8. This indicates that there is no obvious transition of the system from the physical gel to chemical gel during the test process. It maybe due to the fact that at high clay concentration the physical gel can only exist for a short time and rapidly becomes a chemical gel due to the relatively fast cross-linking reactions. Indeed, Fig. 15 also shows these features in the plots of G' and G'' versus time for BDTC5.0 system (containing 5.0 wt% of I.30TC). For a typical transition from physical gel to chemical gel, the tan δ curves should first increase, reach a maximum, and then decrease [14]. This transition is clearly seen in Fig. 7 for BDTC3.0 system (containing 3.0 wt% of I.30TC). The initial increase in tan δ with time implies that during the initial period, the viscous modulus increases more rapidly than the elastic modulus, as confirmed in Fig. 16. Initially, G' is larger than G'' since BDTC3.0 is a physical gel made up of I.30TC interacted through weak, physical bonds. As chemical cross-linking increases, small covalently linked polymer clusters are initially formed. Their main contribution is to increase the viscosity and the viscous modulus G''. Consequently, G'' rises more rapidly

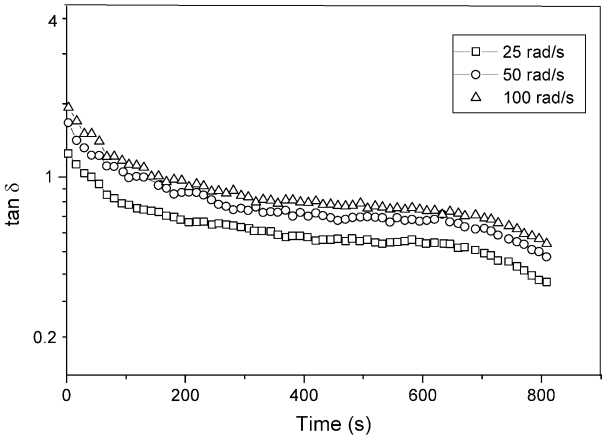


Fig. 8. Loss tangent at various frequencies as a function of time for BDTC5.0 at 140 °C.

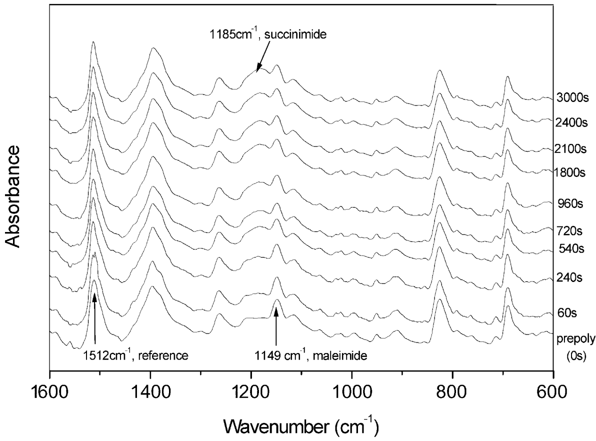


Fig. 9. FTIR spectra of BD as a function of curing time at isothermal temperature of 140 °C.

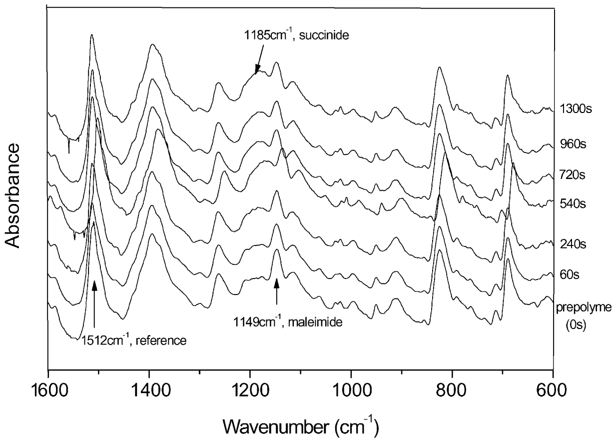


Fig. 10. FTIR spectra of BDTC1.0 as a function of curing time at isothermal temperature of 140 °C.

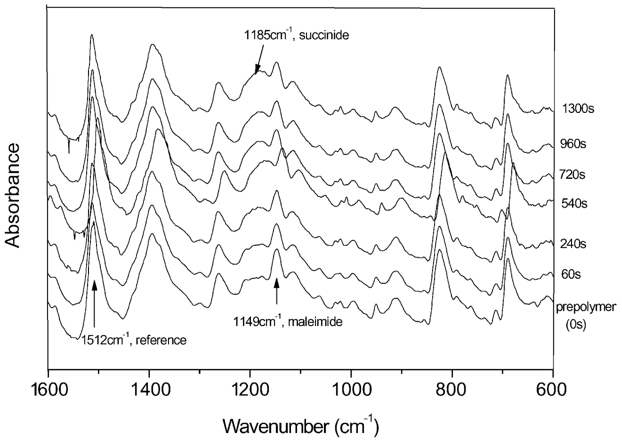


Fig. 11. FTIR spectra of BDTC1.5 as a function of curing time at isothermal temperature of 140 °C.

than G' and tan δ exceeds unity. As the viscosity of the fluid phase surrounding the organoclay becomes so large that it disrupts the particulate or physical gel network. Beyond this point, chemical cross-linking dominates, and the growing polymer clusters eventually connect to form a sample-spanning cluster at the gel point. Thus, the gel point corresponds to network formation via chemical cross-links. The fact that the Winter–Chambon criterion is obeyed also suggests that there is a self-similar structure at the gel point called the critical gel. Beyond the gel point, elastic effects dominate, since the network is capable of store more energy. This is why G' increases at a more rapid rate than G'' at longer curing time (Fig. 16).

In addition, From Fig. 14 and Table 2, we can see that with the introduction of I.30TC, although the degree of cross-linking increased faster than the unfilled pre-polymer system as discussed above, the degree of cross-linking at the gel point is slightly decreased. For BDTC1.0, the degree of cross-linking of 0.16 is practically identical to that of the neat resin system. With increasing I.30TC concentration to 3.0%, the degree of the cross-linking is about 0.145 as shown in Table 2. This seems to suggest that the gel formed in the presence of I.30TC is not only attributed to the chemical cross-linking reactions but also, to certain extent, the physical network due to the interactions between the organoclay and the polymer.

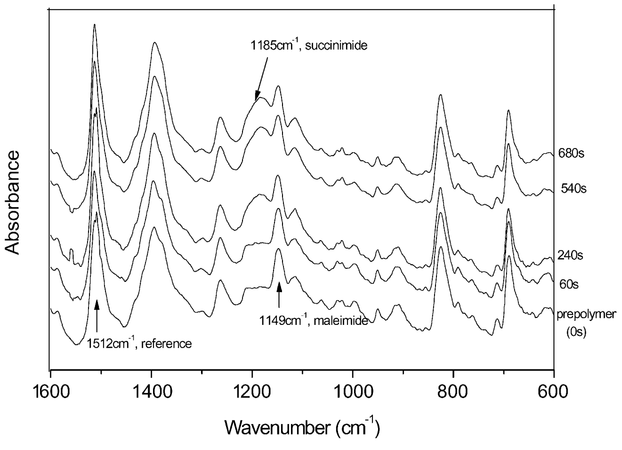


Fig. 12. FTIR spectra of BDTC3.0 as a function of curing time at isothermal temperature of 140 °C.

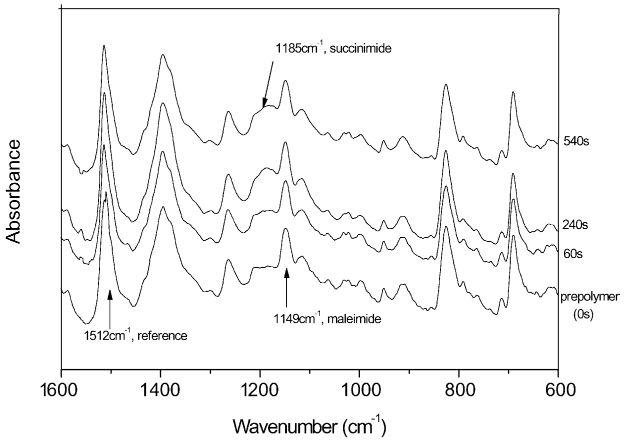


Fig. 13. FTIR spectra of BDTC5.0 as a function of curing time at isothermal temperature of 140 °C.

3.5. Activation energy of gelation

The gel times at different temperatures (130, 140 and 150 °C) were determined based on the Winter–Chambon criterion and are shown in Table 3. Increasing the temperature reduced the gel time. Furthermore, the activation energies can be determined and calculated based on the gel times at different isothermal temperatures by plotting the curves of ln(t_{gel}) versus 1/T, as shown in Fig. 17. The relationship between the activation energy and I.30TC concentration is shown in Fig. 18. It indicates that the activation energy was drastically reduced with the introduction of organoclay, which is consistent with the DSC results obtained in our previous studies [15].

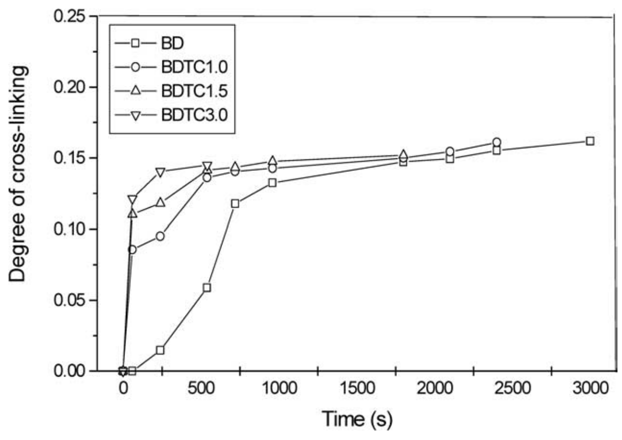


Fig. 14. The degree of cross-linking as a function of curing time for BMPM/DBA systems in the absence and presence of I.30TC before the gel point.

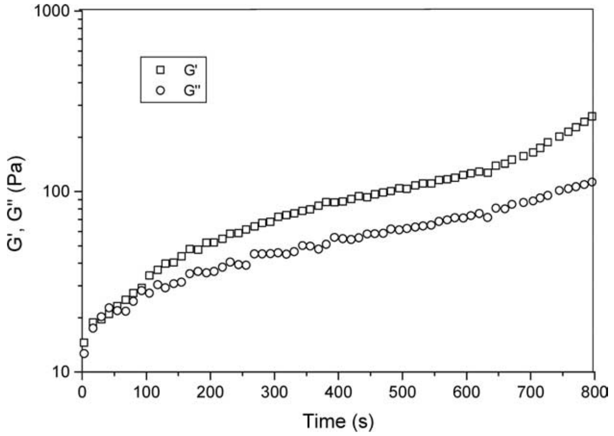


Fig. 15. Elastic (G') and viscous (G'') moduli as a function of curing time for BDTC5.0 system at 140 °C.

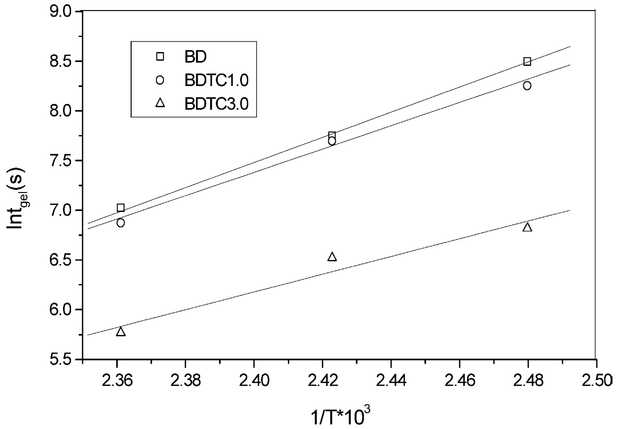


Fig. 17. Plots of gel times as a function of $1/T$ based on rheology data.

Table 2
Effect of I.30TC nano-clay on the degree of chemical cross-linking of BMPM/DBA system at the gel point

System	BD	BDTC1.0	BDTC1.5	BDTC3.0
I.30TC concentration (wt%)	0	1.0	1.5	3.0
Normalized intensity (I_{1185}/I_{1149})	0.162	0.161	0.152	0.145

3.6. Effect of organoclay on the gel properties

In addition to the gel time, tan δ, n and S_g at the gel point are three important parameters to evaluate the gel properties. The values of these parameters are listed in Table 4. It was also found that tan δ and n showed similar trend when plotting tan δ and n curves as a function of I.30TC concentration. Fig. 19 shows the curves of n and S_g versus clay concentration. It can be seen that the critical relaxation exponent n decreases with increasing I.30TC concentration. This means a more highly elastic gel was formed when more clay is present. The decreasing tan δ and n values indicate that the cluster size increases at the gel point and hence lower viscous component in the viscoleastic gel. It may be due to the increased constraining effect of clay on the polymer chains and networks with increasing clay concentration. Correspondingly, the gel strength increases with clay concentration due to less polymer chain mobility. From another point of view, organoclay is rigid reinforcement, therefore, a stronger gel is formed with increasing clay concentration.

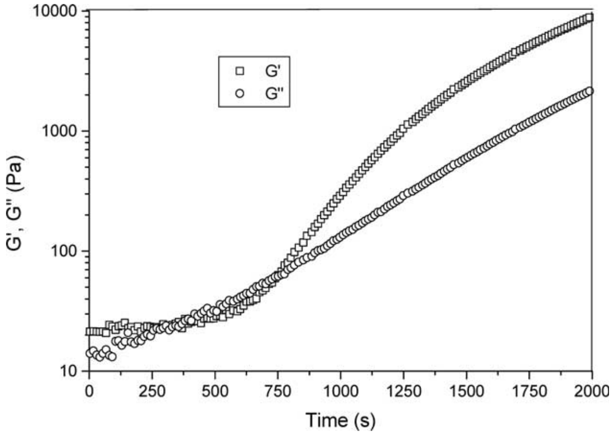


Fig. 16. Elastic (G') and viscous (G'') moduli as a function of curing time for BDTC3.0 system at 140 °C.

3.7. Effect of dispersion of nano-clay on gel characteristics

The dispersion of nano-clays in the polymeric matrix will affect the rheological properties of the system. Table 5 lists the gel characteristics of BMPM/DBA/3.0% I.30TC with different degrees of exfoliation (exfoliated and intercalated) based on XRD data. The d_{001}-reflections of I.30TC, BDTC3.0, BDTC3.0Int, were found at 2θ values of 3.6°, less than 2 and 2.8°, respectively, as shown in Fig. 20. TEM micrographs of BDTC3.0Int and BDTC3.0 are also given in Fig. 20, showing an intercalated and an exfoliated structure.

Data in Table 5 indicate that the intercalated structure exhibits a shorter gel time compared with the exfoliated clay. This may be due to the fact that during the pre-polymerization, BMPM was added after the dispersion of organoclay in DBA, and would need longer time to diffuse into the clay galleries. This creates more excess of BMPM

Table 3
Gel times (s) of BMPM/DBA/I.30TC systems at different temperatures

	130 °C	140 °C	150 °C
BD	4306	3000	972
BDTC1.0	3840	2370	967
BDTC1.5	2950	1290	780
BDTC3.0	915	680	320

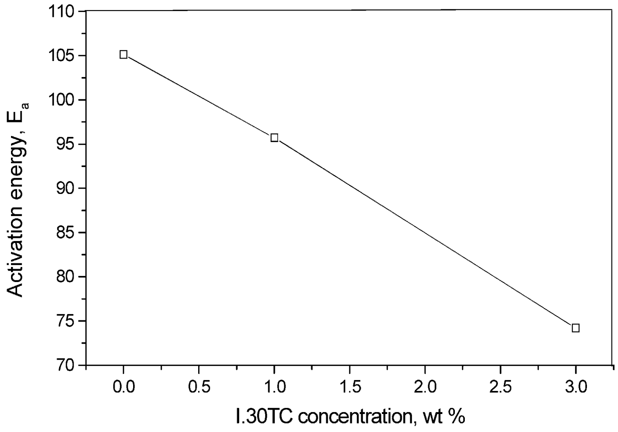


Fig. 18. Activation energy of gelation as a function of I.30TC concentration.

compared to DBA in extragallery during the pre-polymerization and results in higher possibility of extragallery homo-polymerization of BMPM. This phenomenon and the related homo-polymerization of BMPM in extragallery have been discussed in detail elsewhere [15].

Furthermore, the critical gel characteristics are also listed in Table 5. With increasing degree of exfoliation, tan δ and n decrease, suggesting the formation of less viscous or more elastic gel. The gel strength increases with degree of exfoliation. This is due to more constraining effect of organoclay on the polymer chains with increasing exfoliation degree, where more effective interface is formed and more interactions between the clay surface and the polymer networks can occur.

3.8. The nature of organoclay on gel characteristics

In order to understand the nature of organoclay on the gel characteristics, we compared Cloisite 30B with I.30TC. Based on our previous studies [15], Cloisite 30B showed only a very weak acceleration effect on reactions in BMPM/DBA system. Table 6 lists the gel characteristics in the presence and absence of Cloisite 30B. It can be seen that the gel time reduced with increasing clay load but the extent is less than that of I.30TC. This means that the nanocomposites based on Cloisite 30B possess better processing properties than that of I.30TC due to its longer gel time (pot life). When used for processing techniques such as RTM (Resin Transfer Molding), a longer pot life of the resins is preferred. However, tan δ, and n of the critical gels based on Cloisite 30B are similar to or very slightly higher than that based on I.30-TC. However, the gel strength in the presence of Cloisite 30B was higher than that of the systems with I.30TC. This is due to the reduced chain mobility with the introduction of Cloisite 30B. The compatibility of Cloisite 30B with the matrix is better than that of I.30TC due to the hydroxyl group in the surface modifier, which allows better exfoliation to occur at the same amount of clay concentration as evidenced in Fig. 20. More systematic and detailed study on clay exfoliation in the bismaleimide system is reported elsewhere [16]. Better exfoliation would result in closer interaction, even entanglement between the organoclay and the polymer matrix. All these contribute to the increase of S_g. Results also indicate that the gel strength S_g does not always have a monotonous correlation with n.

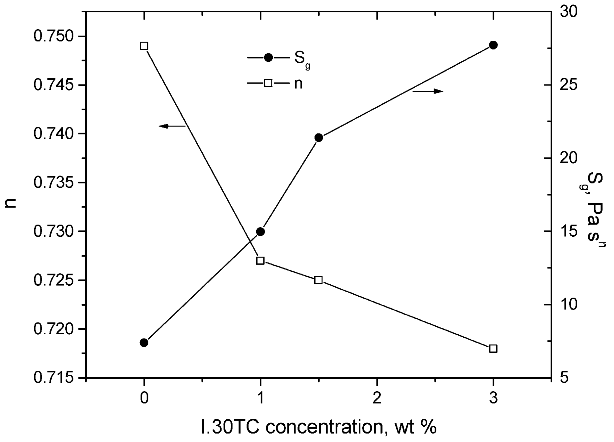


Fig. 19. Critical relaxation exponent (n), and gel strength (S_g) as a function of I.30TC concentration.

Table 5
Effect of dispersion of the organoclay on the gel characteristics

	BDTC3.0	BDTC3.0Int
Gel time (s)	680	370
tan δ	2.10	2.35
n	0.718	0.744
S_g (Pa s^n)	27.71	23.52

4. Conclusions

In this study, the effect of organoclay on the cross-linking in BMPM/DBA system was examined by focusing on the rheology at the gel point. With the introduction of

Table 4
Effect of I.30TC on the gel properties

	I.30TC concentration (wt%)				
	0	1.0	1.5	3.0	5.0
tan δ	2.41	2.19	2.17	2.10	–
n	0.749	0.727	0.725	0.718	–
S_g (Pa s^n)	7.40	14.97	21.38	27.71	–

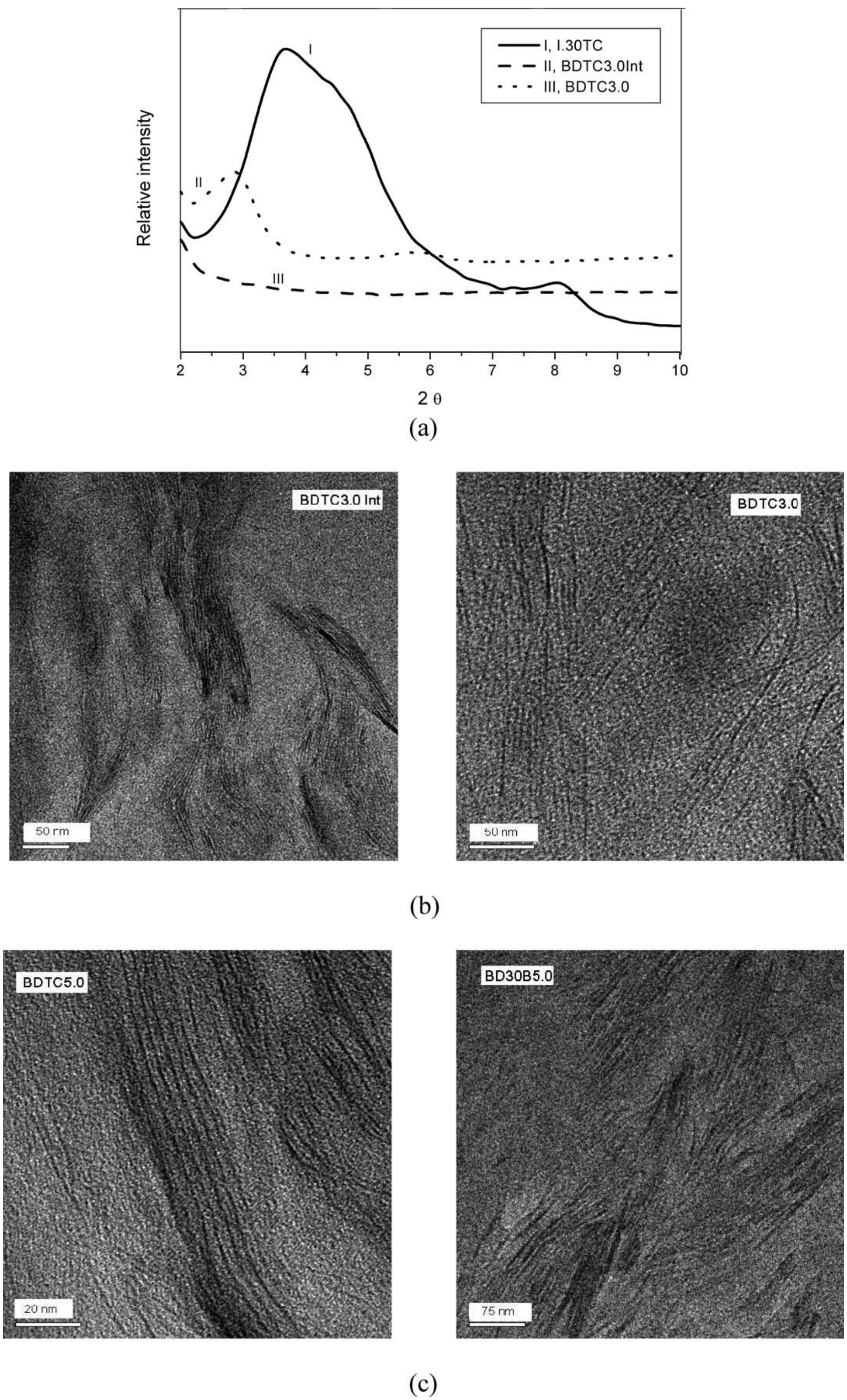


Fig. 20. (a) XRD patterns and (b) TEM micrographs of BDTC3.0Int and BDTC3.0 systems and (c) TEM micrographs of BDTC5.0 and BD30B5.0.

Table 6
Effect of Cloisite 30B on the gel characteristics

	Cloisite 30B load (wt%)				
	0	1.0	1.5	3.0	5.0
Gel time (s)	3000	2800	2560	1900	1320
tan δ	2.41	2.32	2.18	2.10	2.06
n	0.749	0.741	0.727	0.718	0.713
S_g (Pa s^n)	7.40	18.22	25.58	30.71	31.82

organoclay, the pre-polymers exhibited gelation and rheological behavior distinctly different from that of the neat pre-polymer when the clay concentration increased to 3.0 and 5.0%. The pre-polymer containing 3.0 and 5.0% nanoclay effectively form physical gels during the pre-polymerization. During isothermal curing, the chemical cross-linking occurs, which eventually transformed the samples into dense polymer networks. For the pre-polymer containing 3.0% nanoclay, there is a typical transition from physical gel to chemical gel during the rheological experiment. However, the transition occurred during the pre-heating stage of rheological measurement when 5.0% nanoclay is introduced. All systems studied in this work obeyed the Winter–Chambon criterion at the gel point since the loss tangents intersected at a single point in multiwave scan. The degree of cross-linking was determined from FTIR spectra by the normalized value between the succinimide absorption peak and the internal reference absorption peak. Results indicate that the degree of chemical cross-linking is slightly lower with the introduction of organoclay at the gel point although the chemical cross-linking occurred faster than that in the neat pre-polymer during the isothermal curing. Furthermore, the activation energy of the gelation was determined based on the gel times at different isothermal temperatures. It showed that organoclay reduced the activation energy of the cross-linking reactions.

Physical properties of the gel indicate that more elastic gel is formed with higher gel strength in the presence of organoclay. Gel properties are also found to depend on the degree of exfoliation of the nanoclay. With the exfoliated structure, more elastic gel can be obtained with higher gel strength and longer gel time. Lastly, the type of organoclay also has a large effect on the cross-linking and gelation of the system. This will be investigated systematically in future work.

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