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Influence of phenyl-trisilanol polyhedral silsesquioxane on properties of epoxy network glasses

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Abstract

The influence of phenyl-trisilanol polyhedral silsesquioxane (POSS-triol) on the thermo-mechanical properties and curing of epoxy-amine networks were investigated using dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy (FT-IR). Two of the most common epoxy monomers, diglycidyl ether of Bisphenol A (DGEBA), tetraglycidyl diamino diphenyl methane (TGDDM) were used. These epoxies were cured with linear aliphatic diamine: 2-Methyl-1,5-pentadiamine (Dytek® A) or diamine terminated polypropylene oxide (Jeffamine® D230). Using an identical curing schedule, when minor amounts of POSS-triol were added to the epoxy-amine networks, we found a significant improvement on value of T_g. Due to the small quantity of POSS-triol used, this enhancement in T_g is attributed to the catalytic activity of phenyl-trisilanol POSS in promoting a more completely cured epoxy network. This argument is consistent with observed increases in the rubbery plateau modulus due to increases in the crosslink density. But unlike other catalysts such as phenol, we did not observe acceleration of reaction in the pre-gelation stage by this acidic POSS-silanol. Because of its nanoscopic size, this acidic POSS-silanol promotes additional epoxy-amine crosslinking in the post-vitrification stage, which is dominated by diffusion-control mechanisms. We believe this can be utilized in fabrication of fiber-reinforced composites using the resin transfer molding process, where maintaining the low viscosity for a period of time is required to eliminate porosity and to produce higher T_g materials at a lower post-cure temperature.

Keywords: Silsesquioxane; POSS-silanol; Epoxy

1. Introduction

Amine-cured epoxies are one of the most commonly used matrix materials in engineering applications of fiber-reinforced polymeric matrix composites, in part due to their excellent engineering performance and ease of processing prior to cure. The broad interest in epoxy originates from the extremely wide variety of chemical reactions and materials that can be used to form crosslinked networks and the many different properties that result. Depending on the chemical structure of curing agents and curing conditions, it is possible to vary the mechanical properties ranging from extreme flexibility to high strength and hardness, and physical properties such as adhesive strength, chemical resistance, heat resistance and electrical resistance. Different chemical compositions and curing kinetics can permit the user to process over a wide range of temperatures and control the degree of crosslinking.

A significant amount of work has been reported in the literature concerning the nature of reaction between epoxides and amines [1]. The curing kinetics of epoxy can be accelerated by many factors, such as the hydroxyl groups generated during cure [2], the addition of alcohols and Lewis acids. Among them, the catalytic effect of the alcohol has been widely acknowledged. The catalytic efficiency of alcohols can be approximately proportional to its acidity, which explains the high catalytic activity of phenol [3]. This is because acids or electrophilic species accelerate the addition of most nucleophiles considerably by the reversible formation of the more reactive conjugated acid of the epoxide, as in the case of Lewis acids [4,5]. Our particular interest is the influence of silanol groups to the epoxy curing kinetics. It has been studied by some researchers that high concentration of silica fillers, which have silanol groups on the filler surface, could accelerate the reaction of certain epoxy resins [6,7], or at least in the circumstances where aluminum complex was present [8].

In the fabrication of fiber reinforced polymeric matrix

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composites, however, faster cure kinetics may not always be appreciable. For example, in resin transfer molding (RTM) process, it is desirable to have slower initial cure kinetics. This allows for a better mold filling and reduces the voids in the cured laminate. Thus, the abilities to be cured more completely (i.e. higher end-use performance) and more efficiently (i.e. lower temperature cure) become important in the processing of fiber-reinforced composite materials. In this study, we report the use of phenyl-trisilanol polyhedral silsesquioxane (POSS-triol) as promoter in the curing of epoxy-amine networks. The phenyl groups that are attached to the silanol groups increase the acidity of silsesquioxane, and compatibility to aromatic epoxies used. As discussed in the following, this increase in the acidity of silanol attached to nanoscopic size of POSS macromer facilitates it to be used to promote a more complete epoxy-amine reaction, especially in the regime where the glass transition temperature of the epoxy-amine network becomes greater than the curing temperature.

2. Experimental

2.1. Sample preparation

Two conventional epoxy monomers were used in this study, diglycidyl ether of Bisphenol A, DGEBA (D.E.R.® 332, Dow Chemical, equivalent epoxide [E] weight: 173), and tetraglycidyl diamino diphenyl methane, TGDDM (Aldrich Chemicals, equivalent [E] weight: 105.6). The epoxies were cured with either 2-methyl-1,5-pentadiamine (Dytek®A, DuPont Chemicals, equivalent hydrogen [H] weight: 29) and a diamine terminated polypropylene oxide (Jeffamine®D230, Huntsman Chemicals, equivalent [H] weight: 57.5). Stoichiometric, $[E]/[H] = 1$, of epoxy and amine were used for this study. The amounts of phenyl-trisilanol POSS (POSS-triol) used in this study range from 0.2 to 1 weight percentage. A schematic drawing of chemical compounds used in this study is depicted in Fig. 1.

In the curing process, epoxy monomer was first pre-heated at 50 °C for 30 min to melt any crystals present. POSS-triol was added to the epoxy, the mixture was then heated at 50 °C for an additional 30 min. The POSS-triol was completely dissolved in the epoxy. Equivalent molar amount of the curing agent (Dytek®A or Jeffamine®D230) was added to the mixture. The mixture was mechanically mixed then degassed in vacuum for 10 min at room temperature. The mixture was poured in a mold and cured in a mechanical convection air oven set at a specified temperature for 12 h. All samples were cut into rectangular specimens and stored in a desiccator at room temperature until the experiments were performed. The curing parameters of epoxy-amine samples used in this study are shown in Table 1.

2.2. Dynamic mechanical analysis (DMA)

Thermomechanical properties of cured network glasses were analyzed using a Rheometric Scientific Solid Analyzer RSA III operated in a three-point bending mode with a span of 25 mm. Samples used were in a shape of rectangular strips with dimensions of $30 \times 12 \times 2\ \mathrm{mm}^3$. The experiments were performed using an oscillatory frequency of 6.26 rad/s and strain amplitude of 0.02%. All measurements were carried out from room temperature to 150 °C for all DGEBA based epoxy resins and up to 250 °C for the TGDDM based epoxy resins at a heating rate of 1 °C per minute. In this study, the glass transition temperature is referred from the peak temperature of tan δ (E''/E') curve.

2.3. Fourier transform infrared spectroscopy (FT-IR)

In each FT-IR experiment, samples were cast into thin films on FT-IR cards (polyethylene) immediately after the mixing of epoxy monomers and amines. These FT-IR cards were placed in an oven at desired temperatures, and they were subjected to FT-IR scans periodically during the experiments. FT-IR spectra were obtained using a Bio-Rad Excalibur spectrometer equipped with LN_2 cooled MCT detector. Each spectrum was collected by using 64 scans at $2\ \mathrm{cm}^{-1}$ resolution.

3. Results and discussion

3.1. Solubility observations

Phenyl-trisilanol POSS was found to have good solubility in DGEBA and TGDDM up to 5 wt% at 25 °C. However, the solutions became cloudy when the POSS-triol concentration becomes much higher than 5 wt% at 25 °C. Although one can increase the amount of POSS-triol dissolved in epoxy liquids when heated, but it precipitated as the temperature decreased back to room temperature.

In a separate experiment, for POSS-triol with that of isobutyl groups instead of phenyl groups as substituents, we were not able to dissolve even small amount of isobutyl-trisilanol POSS into DGEBA or TGDDM epoxy liquid. Even when heated to 50 °C, the isobutyl-trisilanol POSS was not soluble in the epoxy monomers used for this study [9]. We attribute the better solubility of phenyl-trisilanol POSS to two factors: the organophilic phenyl substitutes which are compatible with the bisphenol A in the epoxy monomers, and more acidic silanol groups that form hydrogen bonds with epoxy monomers [10,11]. Thus, the phenyl-trisilanol POSS was able to dissolve in DGEBA and TGDDM.

It was demonstrated by us [12] and others [13], high weight fraction of POSS can be co-cured with epoxy to form nano-filler reinforced network. However, the work

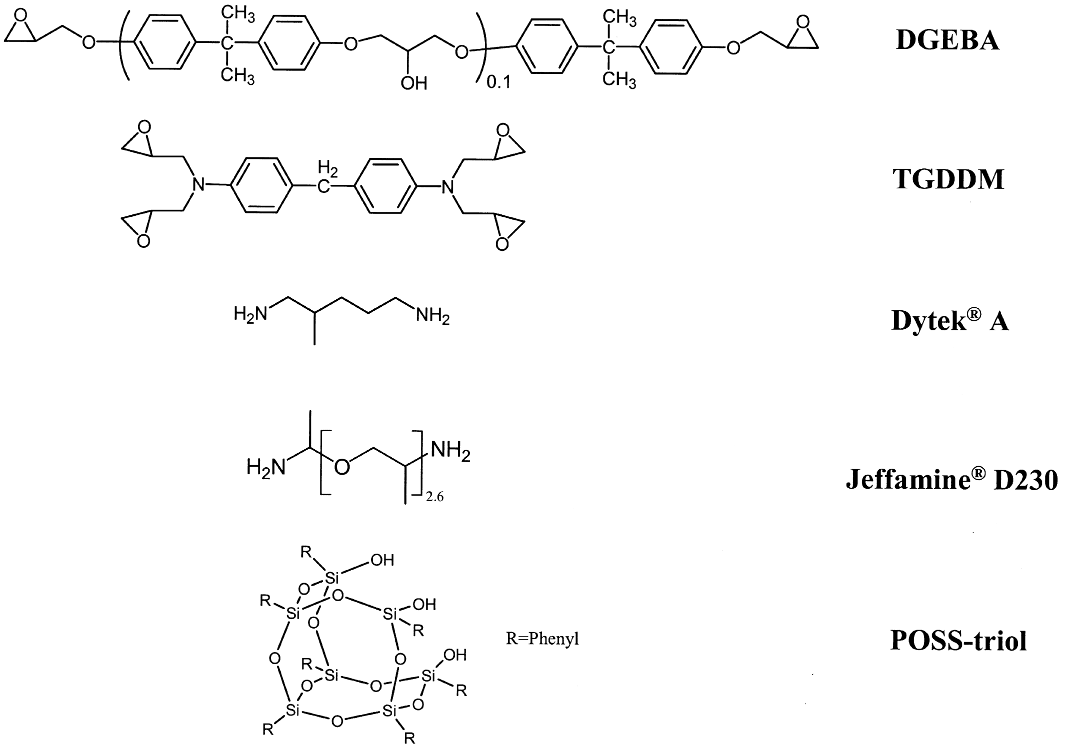

Fig. 1. Schematic diagram of chemical compounds used in this paper.

presented here addresses the influence of acidic silanol group on the thermomechanical properties of cured epoxy glasses and kinetics at the initial pre-gelation stage of epoxy-amine reaction. Therefore, all samples investigated in this study contained less than 1 wt% of phenyl-trisilanol POSS.

3.2. Effects of POSS-triol on the T_g value

Representative DMA results for TGDDM cured with Dytek®A at 150 °C for 12 h are shown in Fig. 2. All samples showed a shoulder in tan δ versus temperature curves before T_g, indicating the complexity of as-cured networks that may

Table 1
Composition, processing parameters, and thermomechanical properties of epoxy network glasses investigated in this study

	POSS content (wt%)	Epoxy monomer	Amine monomer	Curing temp. (°C)	Curing time (h)	T_g (°C)	E' at 30 °C (GPa)	E' at Rubbery Plateau (MPa)
DJ00	0	DGEBA	Jeffamine®	100	12	84	3.7	30
DJ04	0.4	DGEBA	Jeffamine®	100	12	91	3.3	32
DJ10	1.0	DGEBA	Jeffamine®	100	12	91	3.1	25
TJ00	0	TGDDM	Jeffamine®	150	12	137	4.3	80
TJ04	0.4	TGDDM	Jeffamine®	150	12	148	3.6	76
TJ10	1.0	TGDDM	Jeffamine®	150	12	148	3.5	77
DD00	0	DGEBA	Dytek®A	100	12	98	2.6	29
DD02	0.2	DGEBA	Dytek®A	100	12	115	2.6	36
DD04	0.4	DGEBA	Dytek®A	100	12	122	1.7	29
DD06	0.6	DGEBA	Dytek®A	100	12	118	2.3	38
DD08	0.8	DGEBA	Dytek®A	100	12	122	2.0	36
DD10	1.0	DGEBA	Dytek®A	100	12	123	1.8	30
TD00	0	TGDDM	Dytek®A	150	12	167	2.6	78
TD02	0.2	TGDDM	Dytek®A	150	12	214	2.5	97
TD04	0.4	TGDDM	Dytek®A	150	12	218	2.6	123
TD06	0.6	TGDDM	Dytek®A	150	12	219	2.8	125
TD00_LTC	0	TGDDM	Dytek®A	100	24	198	2.5	126
TD04_LTC	0.4	TGDDM	Dytek®A	100	24	207	3.0	144
TD10_LTC	1.0	TGDDM	Dytek®A	100	24	222	2.5	172
DD00_IR	0	DGEBA	Dytek®A	60	N/A	N/A	N/A	N/A
DD04_IR	0.4	DGEBA	Dytek®A	60	N/A	N/A	N/A	N/A

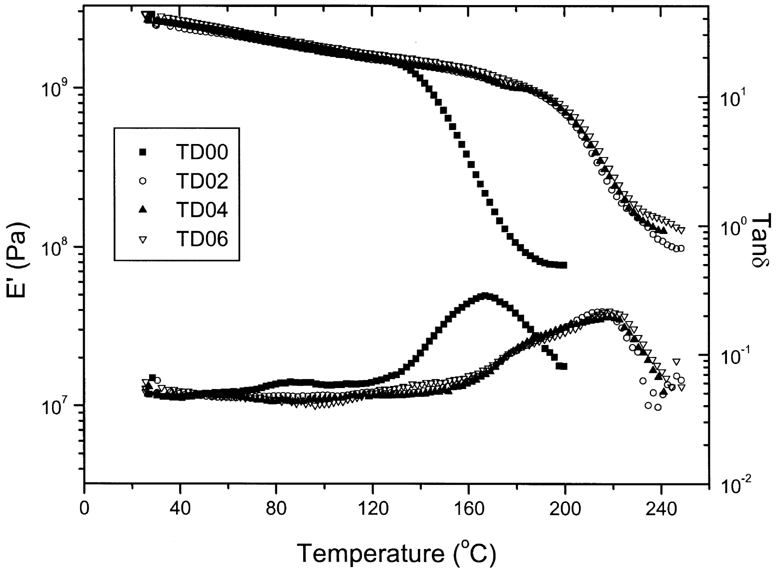

Fig. 2. Storage modulus (E') and tan δ versus temperature for various weight percent POSS-triol containing TGDDM cured with Dytek®A at 150 °C for 12 h. (■) TD00 (0% POSS); (○) TD02 (0.2 wt% POSS); (▲) TD04 (0.4 wt% POSS); (▽) TD06 (0.6 wt% POSS).

contain not yet reacted moieties. This is not surprising since the curing temperature T_c used was lower than T_g observed. As shown in Fig. 2, we observe an increase of 40 °C in the value of T_g for samples containing POSS-triol. It is known that a trace amount of hydroxyl groups can affect the curing kinetics of epoxy resin. This is presumed to be caused by hydrogen bonding effects assisting in the opening of epoxy ring [3]. The hydroxyl groups that are produced by the primary-amine reaction (i.e. the first active hydrogen in the amine) could accelerate the reaction. The activity of the hydrogen group in the catalyst usually plays a significant role. For example, the greater activity of the hydrogen in phenol makes it a more effective catalyst compared to aliphatic hydroxyl groups [3]. Although the OH group is not directly attached to the phenyl groups in the case of phenyl-trisilanol POSS, the silanol groups are still more acidic than aliphatic silanols and aliphatic hydroxyl groups. Thus, we postulate the presence of POSS-triol affects the curing kinetics of the epoxy amine reaction. It is known that the activity of the hydrogen in phenol is increased in the presence of a basic medium [3]. Similarly, the activity of silanol groups in the phenyl-trisilanol POSS is also influenced by the basicity of the amine used.

Representative DMA results for TGDDM cured with Jeffamine®D230 at 150 °C for 12 h are shown in Fig. 3. It was observed that the value of T_g increased by 11 °C due to the presence of POSS-triol, which was much less than the 40 °C increase observed when cured with Dytek®A. Table 1 summarizes the values of T_g. For both systems of TGDDM cured with Dytek®A or Jeffamine®D230, the improvement of T_g seems independent of POSS-triol concentration. Due to small amount of POSS-triol used in system, i.e. 0.2 wt%, this increase in T_g for TGDDM cured with Dytek®A or by Jeffamine®D230 was attributed to the silanol groups in POSS-triol which are acting as a Lewis acid catalyzing systems rather than due to any filler effect induced by the incorporation of POSS-triol.

Furthermore ^{29}Si NMR data indicates that the POSS-triol descrambles in the presence of the amine forming a resin-like structure, which implies POSS-triol no longer exists as a cage-like structure [9]. This reiterates that the POSS-triol does not have any particulate shape that affects the epoxy-amine network; rather it indicates the increased local availability of the silanol groups for catalyzing the epoxy-amine reaction.

The presence of Lewis acid catalysts can affect the epoxy-amine reaction in either chemical control or diffusion control stage or both. However, from the results presented in the above observations indicates reactions occurred in the diffusion controlled stage is more likely to be impacted by the POSS-triol since the curing temperature T_c was significantly lower than the T_g obtained for the case of TGDDM cured with Dytek®A as compared to TGDDM cued with Jeffamine®D230. To further elucidate this phenomenon, we cured TGDDM with Dytek®A at an even lower temperature (100 °C, which was approximately 100 °C lower than T_g) for 24 h. The results were shown in Fig. 4. As seen, the addition of 0.4 wt% POSS-triol (TD04_LTC) showed 9 °C increase in T_g as compared to the neat epoxy. Furthermore with addition of 1% of POSS-triol (TD10_LTC), the value of T_g is the same as those cured at 150 °C for 12 h (see Table 1).

Representative results of TGDDM containing 1 wt% of POSS-triol cured with Dytek®A at two different conditions are shown in Fig. 5. From the isothermal time–temperature-transformation cure diagrams [14], by curing at lower temperatures and for longer time, the time for diffusion-control reaction is increased. As observed from Fig. 5, the value of T_g from tan δ curves is higher for sample cured at 100 °C for 24 h. This additional promotion of T_g for

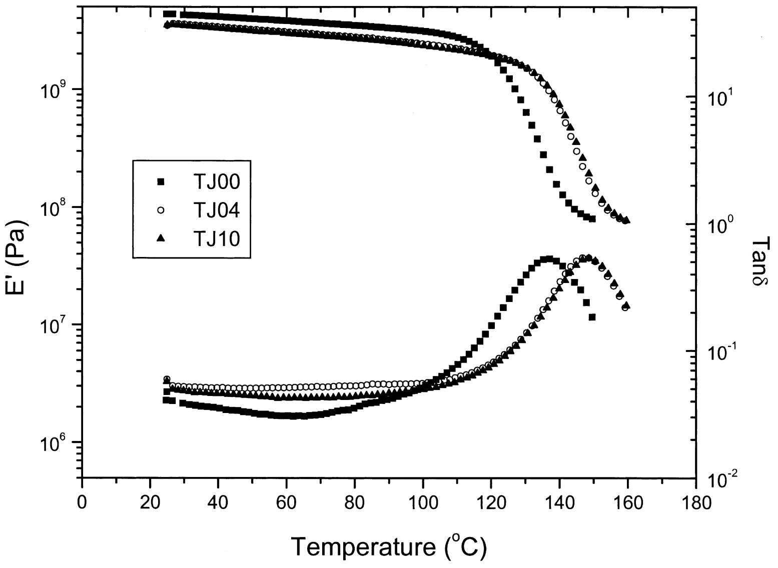

Fig. 3. Storage modulus (E') and tan δ versus temperature for various weight percent POSS-triol containing TGDDM cured with Jeffamine®D230 at 150 °C for 12 h. (■) TJ00 (0% POSS); (○) TJ04 (0.4 wt% POSS); (▲) TJ10 (1 wt% POSS).

epoxy-amine systems cured at low temperatures and for longer times can be attributed to the amount of time where the crosslinking reaction was under diffusion control.

Fig. 6 shows DMA results for POSS-triol containing DGEBA cured with Dytek®A at 100 °C for 12 h. The value of T_g for DGEBA cured with Dytek®A at 100 °C for 12 h is 98 °C, since T_g is less than T_c the reaction occurred mostly under chemical control condition. But when small amount of POSS-triol was added and cured under identical conditions, the observed T_g was around 120 °C. Again, this observation suggested that there was a promotion of additional reaction by POSS-triol in the diffusion control regime, i.e. when T_g of the system becomes greater than T_c.

Although, we observed an enhancement in T_g in the case of DGEBA cured with Dytek®A by the addition of POSS-triol, it is not as significant as in the case of TGDDM cured with Dytek®A. The appreciable increase of T_g in TGDDM samples as compared to that of DGEBA samples (T_g values are summarized in Table 1) was due to the promotion of additional reaction by POSS-triol in the diffusion control condition. This is because of a higher ΔT ($T_g - T_c$) in the case of TGDDM and ΔT ($T_g - T_c$) is the main driving force in the diffusion control reaction.

Three major observations were derived from our results. (1) The T_g enhancement was caused by POSS-triol. (2) Epoxy (DGEBA and TGDDM) cured with Dytek®A

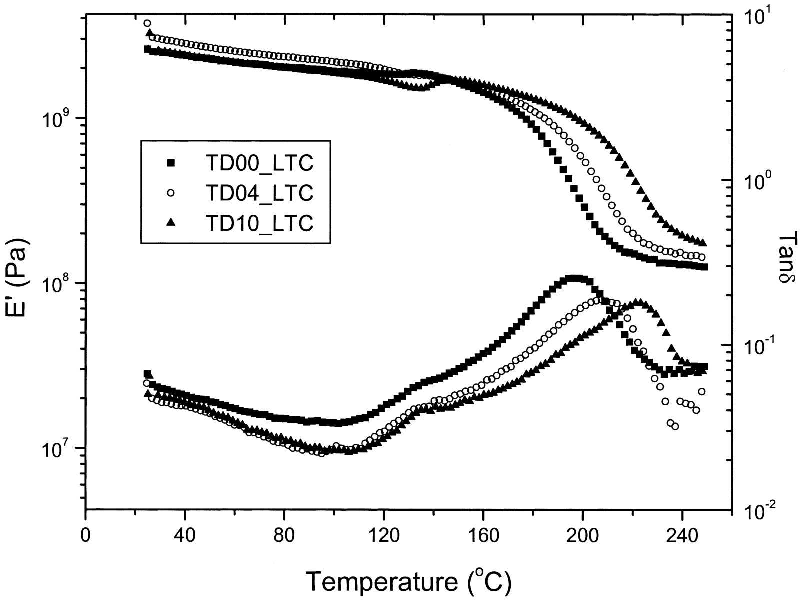

Fig. 4. Storage modulus (E') and tan δ versus temperature for various weight percent POSS-triol containing TGDDM cured with Dytek®A at 100 °C for 24 h. (■) TD00_LTC (0% POSS); (○) TD04_LTC (0.4 wt% POSS); (▲) TD10_LTC (1 wt% POSS).

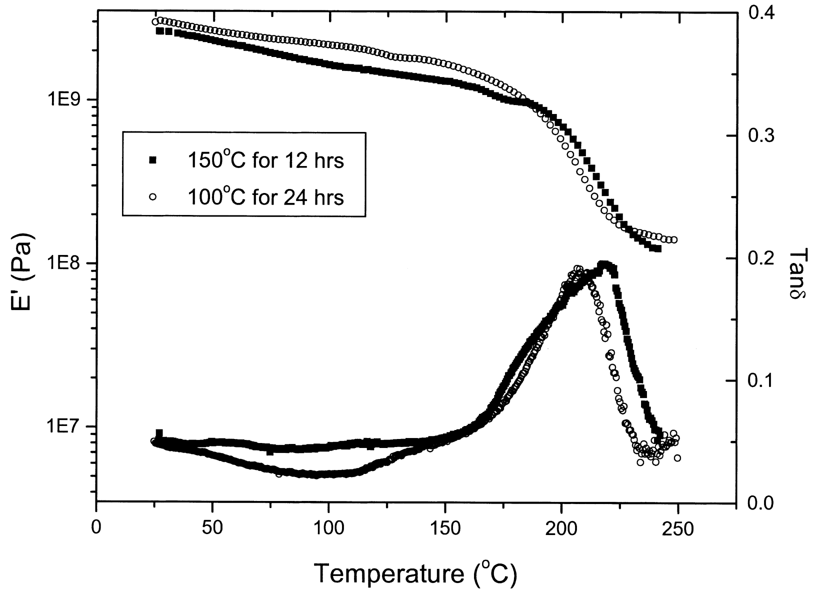

Fig. 5. Storage modulus (E') and tan δ versus temperature for TGDDM containing 1 wt% POSS-triol cured with Dytek®A at 150 °C for 12 h and 100 °C for 24 h. (■) 150 °C for 12 h; (○) 100 °C for 24 h.

showed a greater amount of increase in T_g than epoxy cured with Jeffamine®D230. (3) The T_g enhancement in tetra-functional epoxy, TGDDM, cured with Dytek®A is more significant than in di-functional epoxy, DGEBA, cured with Dytek®A. In observation one, the acidity of molecularly dispersed phenyl-trisilanol POSS promotes additional reactions between epoxies and linear aliphatic amines. These additional crosslinks causing an enhancement in T_g. The observations two and three, clearly suggested that the catalytic effect of POSS-triol was more effective in promoting additional reaction when the chemical reaction occurred in the diffusion control regime (T_c less than T_g), where the use of POSS-triol became more beneficial in enhancing thermomechanical performance of epoxy network glasses.

For some industrial applications, it may be desirable for a cure additive plays none or little effect on the kinetics at the initial stage. For example in processing large composite structures using RTM method, it is important to maintain the low viscosity for a period of time until the mold is filled and voids can escape from the closed mold. The DMA results presented before indicates that POSS-triol enhances the network formation in the diffusion-controlled region in epoxy-amine reaction. To investigate that POSS-triol does

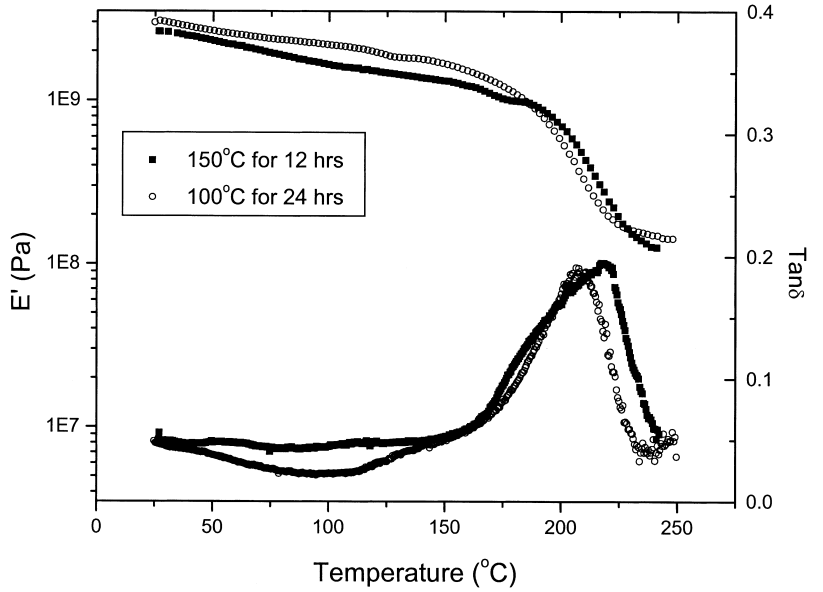

Fig. 6. Storage modulus (E') and tan δ versus temperature for various weight percent POSS-triol containing DGEBA cured with Dytek®A at 100 °C for 12 h. (■) DD00 (0% POSS); (○) DD02 (0.2 wt% POSS); (▲) DD04 (0.4 wt% POSS); (▽) DD06 (0.6 wt% POSS); (◆) DD08 (0.8 wt% POSS); (+) DJ10 (1 wt% POSS).

not affect the initial pre-gelation process, the epoxies were cured with amines at just above the onset of reaction temperature where the reaction is under chemical control.

3.3. Effects of POSS-triol on gelation stage curing process

Epoxy-amine cured systems were studied by using an FT-IR where a better understanding of the initial reaction mechanism can be obtained. To ensure the reaction occurs mostly within the initial pre-gelation regime, all curing processes were conducted at temperature just above the onset temperatures of epoxy-amine reaction. FT-IR was used to study the curing kinetics of DGEBA cured with Dytek®A. Dytek®A was used because the effect of POSS-triol is more predominant than in the case of Jeffamine®D230. Two samples were studied in the experiments: DD00_IR and DD04_IR. Fig. 7 shows the FT-IR spectra of sample DD04_IR cured at 60 °C. The detailed peak assignment can be found in the literature [3,15]. In this study, we used the aromatic C=C stretching peak (1510 cm^{-1}) as the internal standard. We note that because the POSS-triol molar ratio was very small in sample DD04_IR, the contribution from the phenyl groups of POSS-triol was negligible. The etherification peak (1070 cm^{-1}) was found to be insignificant in both DD00_IR and DD04_IR samples, which indicates the etherification effect is negligible in this study. Hydroxyl group at 3450 cm^{-1} was observed in both DD00_IR and DD04_IR samples. Since the contribution of silanol group should be low for its low molar ratio, the hydroxyl peak should be due to the backbone of the epoxy resin that contained the hydroxyl group [16]. The intensity of hydroxyl group showed barely little difference between DD00_IR and DD04_IR. The conversion of epoxide in the curing process of sample DD00_IR and DD04_IR was calculated and compared in Fig. 8. The conversion of epoxide was calculated using the area of epoxide peaks (914 cm^{-1}) at different curing time and normalized with the area of epoxide peak immediately after mixing. As shown, the conversion of epoxide showed rapid increase during the first 15 min. After that, the conversion of epoxide only slightly increases. After 16 h, the total conversion of epoxide was 28% in sample DD00_IR and 22% in sample DD04_IR as shown in Fig. 8. This low conversion value ensures that the epoxy-amine reaction remain at the initial, pre-gelation stage. Though we study the epoxide conversion for 16 h it is the initial slope of the epoxide conversion curve which is of interest. As shown in Fig. 8, the conversion of epoxide in DD04_IR was always lower than DD00_IR. This observation shows that the presence of phenyl-trisilanol POSS did not affect during the gelation stage of epoxy-amine reaction. We note that in a separate measurement, the initial conversion rate of epoxide showed almost no difference in DD00_IR and DD04_IR cured at 100 °C, which clearly suggests that phenyl-trisilanol POSS did not affect the epoxy-amine reaction at gelation stage.

The above FT-IR results suggest that the presence of POSS-triol in epoxy resins did not significantly affect the reaction rate during the gelation stage. Instead, the presence of POSS-triol promoted additional crosslinks during the diffusion controlled stage of epoxy-amine reaction, this resulted in a higher crosslinked epoxy network. The FT-IR results agree with our previous hypothesis as demonstrated using DMA results.

3.4. Effects of POSS-triol on the glassy-state modulus and rubbery plateau modulus

For TGDDM or DGEBA cured with Dytek®A (shown in Figs. 2 and 3, respectively), the addition of POSS-triol

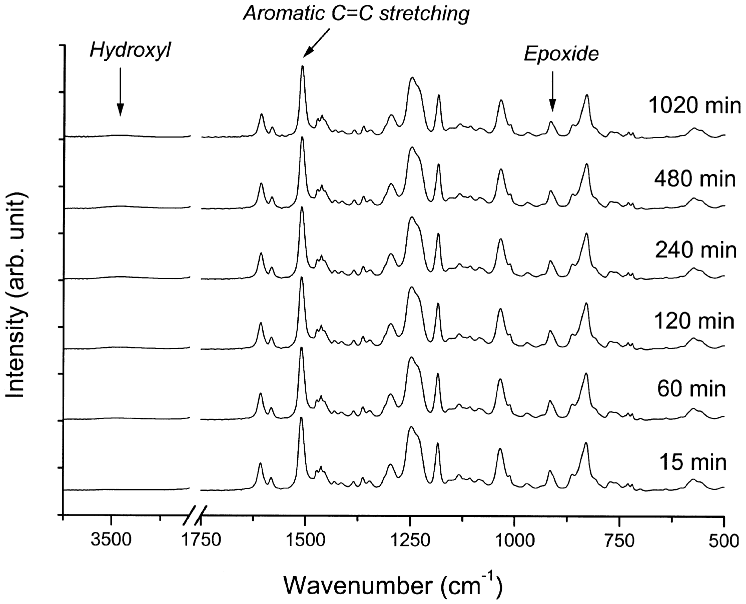

Fig. 7. FT-IR spectra of sample DD04_IR (DGEBA cured with Dytek®A, 0.4 wt% of POSS-triol) cured at 60 C.

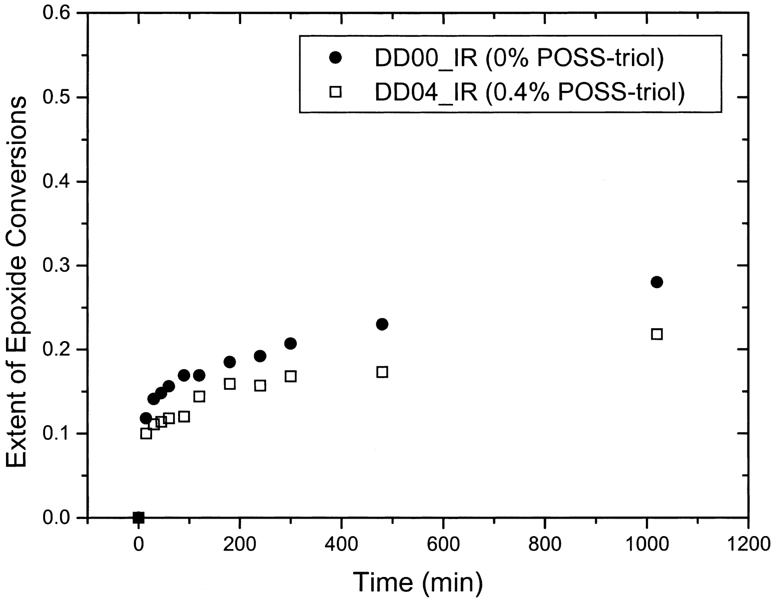

Fig. 8. Extent of epoxide conversions versus time in sample DD00_IR (DGEBA cured with Dytek®A without POSS) and DD04_IR (0.4 wt% POSS-triol) cured at 60 °C.

showed a slight increase in glassy state modulus. In the case of DGEBA cured with Dytek®A the rubbery plateau modulus, was slightly enhanced with the addition of POSS-triols (increased from 29 to 38 MPa). However, the addition of POSS-triol was found to have more significant impact to the rubbery plateau modulus of TGDDM cured with Dytek®A. As seen in Fig. 5, the rubbery plateau modulus was 78 MPa for sample TD00. After addition of 0.2–0.6 wt% POSS-triol, the rubbery plateau modulus increased to as much as 127 MPa, in correspondence with increasing T_g. Furthermore, we observed systematic increases in rubbery plateau modulus with increasing amount of POSS-triol additives. For systems cured at a lower temperature (100 °C, shown in Fig. 4), the rubbery plateau modulus increased substantially after adding 0.4 and 1.0 wt% POSS-triol.

For TGDDM or DGEBA cured with Jeffamine®D230 (shown in Figs. 5 and 6, respectively), the addition of POSS-triol showed a slight decrease in its glassy-state modulus. The rubbery plateau modulus of the networks was found to be almost the same in both systems, indicating that the degree of crosslinking was not significantly changed during the curing process. The rubbery plateau modulus can be related to the degree of crosslinking [1,17]. For network with higher degree of crosslink density, the rubbery plateau modulus is usually higher. In epoxy cured with Jeffamine®D230, the rubbery plateau modulus of POSS-triol containing samples was not significantly changed, which indicates that the addition of POSS-triol did not significantly change the degree of crosslinking. In epoxy cured with Dytek®A, the large increase of the rubbery plateau modulus of POSS-triol containing samples indicates higher degrees of crosslinking, which is also consistent to our T_g observations. Moreover, the increase of rubbery plateau modulus was much more significant in the case of TGDDM cured with Dytek®A than DGEBA cured with Dytek®A. Since, the tetra-functional TGDDM is more sterically constrained than DGEBA, therefore the diffusion-controlled stage of reaction is more important to the thermomechanical properties of TGDDM, which is in complete agreement with the FT-IR observations.

4. Conclusions

In this study, we demonstrated that the addition of soluble POSS-triol, POSS-triol, can be used to improve the crosslinking of epoxy-amine networks. DMA results showed that the epoxy containing POSS-triol cured with linear aliphatic diamine had a higher T_g than the neat epoxy-amine networks. However, due to its size, the POSS-triol did not seem to assist the reaction during the pre-gelation stage, but rather promoted additional crosslinking during post-vitrification where the reaction is diffusion control. Hence, we were able to produce higher T_g epoxy network glasses without using high curing temperatures. FT-IR results clearly showed that addition of POSS-triol did not accelerate epoxy-amine reaction in the pre-gelation stage.

The influence of POSS-triol on epoxy-amine reaction depends mostly on the magnitude of ΔT ($T_g - T_c$) used. Since T_g for epoxy cured with Dytek®A was higher than T_g of the same epoxy cured with Jeffamine®D230, when cured at the same temperature, epoxy cured Dytek®A showed a greater improvement in the value of T_g. Moreover, the addition of POSS-triol in TGDDM cured with Dytek®A also increases the rubbery plateau modulus. On the other hand, the glassy state modulus was retained (no change) in all epoxy systems. The T_g improvement was caused by the promotion of the diffusion-controlled epoxy-amine reaction, hence, this promotion worked better in a network with a higher ΔT ($T_g - T_c$).

Moreover, the addition of small amount of POSS-triol ensured the consistency of the thermomechanical properties of epoxy networks with high degree of steric constraints (high epoxy functionality monomer), as evidenced by several parallel experiments. Because the addition of such small amount of POSS-triol does not increase the viscosity of the epoxy resins, and does not accelerate the reaction in the pre-gelation stage, we believe this technology is of significant importance when use in the fabrication of fiber reinforced epoxy composites using rapid processing method such as RTM or vacuum assisted RTM.

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References

[1] May, CA. Epoxy resins: chemistry and technology. New York: Marcel Dekker; 1988.

[2] Smith IT. Polymer 1961;2:95.

[3] Lee H, Neville K. Epoxy resins. New York: Mcgraw-Hill; 1957.

[4] Goh Y, Iijima T, Tomoi M. J Polym Sci Polym Chem 2002;40:2689.

[5] Kim WG, Yoon HG, Lee JY. J Appl Polym Sci 2001;81:2711.

[6] Altmann N, Halley PJ, Cooper-White J, Lange J. Macromol Symp 2001;169:171.

[7] Halley PJ. J Appl Polym Sci 1997;64:95.

[8] Iijima T, Sekine S, Kakiuchi H. J Thermosetting Plast Jpn 1987;8:73.

[9] Namani M. Thesis of Master of Science, Michigan State University, 2003.

[10] Manna AK, De PP, Tripathy DK. J Appl Polym Sci 2002;84:2171.

[11] Dijkstra TW, Duchateau R, Van Santen RA, Meetsma A, Yap GP. J Am Chem Soc 2002;124:9856.

[12] Lee A, Lichtenhan JD. Macromolecules 1998;31:4970.

[13] Li GZ, Wang L, Toghiani H, Daulton TL, Koyama K, Pittman Jr CU. Macromolecules 2001;34:8686.

[14] Enns JB, Gillham JB. J Appl Polym Sci 1983;28:2567.

[15] Don TM, Bell JP. J Appl Polym Sci 1998;69:2395.

[16] Ochi M, Takahashi R. J Polym Sci Polym Phys 2001;39:1071.

[17] Shan L, Verghese KNE, Robertson CG, Reifsnider KL. J Polym Sci Part B: Polym Phys 1999;37:2815.