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1,3-bis(γ-aminopropyl)tetramethyldisiloxane modified epoxy resins: curing and characterization

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Incorporation of siloxane oligomers with reactive organofunctional terminal groups, such as amine, epoxy and carboxy, into the structure of epoxy networks, provides improvements in the fracture toughness, water absorption and surface properties of the resultant systems. 1,3-bis(γ-aminopropyl) tetramethyldisiloxane (DSX) was used as a model curing agent and modifier in bis(4-aminocyclohexyl)methane (PACM-20) cured diglycidyl ether of bisphenol-A (DGEBA) based epoxy resins. Curing reactions followed by differential scanning calorimetry indicated faster reaction rates between DSX and DGEBA as compared with PACM-20 and DGEBA. Mechanical characterization of the modified products showed improvements in tensile and impact strengths as expected. Glass transition temperatures of these materials showed a decrease with an increase in DSX content. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: epoxy curing; epoxy toughening; reactive silicones)

INTRODUCTION

Toughening of epoxy resins with reactive diluents and oligomers has been an active field of research[1–7]. This is due to the broad range of applications of epoxy resins as high performance protective coatings, structural adhesives, low stress IC encapsulants and matrix resins for composites. Most of the earlier work on toughening of epoxy resins has been carried out by utilizing carboxy or amine terminated acrylonitrile–butadiene rubbers (CTBN and ATBN)[3–5]. Other elastomeric materials, such as functionally terminated acrylates, alkylene oxides and siloxanes have also been employed to a lesser extent. More recent approaches include the use of functionally terminated, ductile engineering thermoplastics, such as polyethersulfones, polyimides and polyaryletherketones[8,9] and through the introduction of macropores of controlled size and distribution[10]. Depending on the type, molecular weight, solubility parameter and concentration of the modifier used, structure and reactivity of the curing agent and the temperature of the curing reaction, it is possible to obtain substantial improvements in the fracture toughness of the modified networks. However, in most cases when rubbery modifiers are used there is some sacrifice in the glass transition temperature (T_g) of the network[4,5]. This is more pronounced if the modifier is a low molecular weight flexible molecule[6,7].

When high molecular weight modifiers are used, due to differences in the solubility parameters of the modifier and the epoxy network, the modifier phase separates from the system forming small domains in a continuous epoxy matrix. This is not observed when low molecular weight reactive diluents are used. In phase separated systems, in order to achieve the desired morphology and performance, it has been demonstrated that the modifier must react faster than the curing agent and as a result phase separate from the continuous rigid matrix as the gelation occurs[14].

We are investigating the modification of epoxy networks with reactive polydimethylsiloxane (PDMS) oligomers. Organofunctionally terminated PDMS oligomers, even at fairly low molecular weights, such as $M_n = 500$ g mol^{-1} [or at a $-(CH_3)_2Si-O-$ repeat unit of about 5] are incompatible with epoxy resins for a successful kinetic investigation in bulk. Therefore, in this work we have investigated the use of 1,3-bis(γ-aminopropyl)tetramethyl disiloxane (DSX) as a model reactant, to understand the reactivity of aminopropyl terminated siloxane oligomers with DGEBA (with $n \sim 0.14$) cured with a cycloaliphatic diamine (PACM-20). In addition to the curing kinetics, thermal and mechanical properties of the resultant homogeneous networks were also studied and the compositional range from brittle to ductile transition failure mechanism was determined.

EXPERIMENTAL

Materials

Diglycidylether of Bisphenol-A, (DGEBA), is a product of Shell Chemical Company under the trade name Epon®Resin 828, and has an epoxy equivalent weight of 190 g ($n = 0.14$), as determined by end group titration. Bis(4-aminocyclohexyl)methane (PACM-20), is a product of DuPont and distilled under vacuum before use. 1,3-Bis(γ-aminopropyl)tetramethyldisiloxane (DSX), was obtained from Silar Laboratories Inc., and also distilled under vacuum before use. Chemical structures of these starting materials are given in *Figure 1*.

Differential scanning calorimetry studies on the curing reactions

Curing kinetics of DGEBA with DSX was studied on a Rheometric Scientific PL DSC-Plus. Stoichiometric

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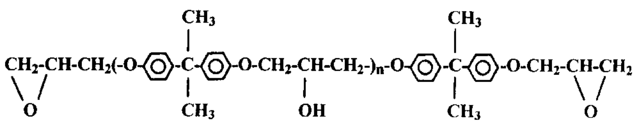
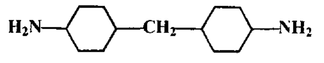
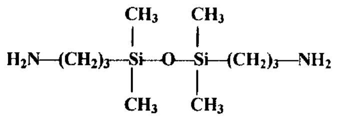


Diglycidylether of Bisphenol-A, (DGEBA), (1)



Bis(4-aminocyclohexyl)methane, (2)



1,3-Bis(γ-aminopropyl)tetramethyldisiloxane, (3)

Figure 1 Chemical structures of the starting materials

mixtures of the epoxy resin and the curing agent were prepared at room temperature and small samples ($\sim$10 mg) were sealed in aluminum sample pans. Differential scanning calorimetry (d.s.c.) scans of curing reactions were conducted under dry nitrogen atmosphere, using both dynamic (constant increasing rate of temperature) and isothermal scanning. Enthalpy calibration of the instrument was done by using indium and tin standards.

In dynamic curing studies, d.s.c. scans were started at room temperature and ended at the point where the curing isotherm merged with the baseline, indicating the completion of the reaction. For isothermal measurements the sample pan was inserted into the d.s.c. cell at room temperature and then quickly heated (100°C min^{-1}) to the desired reaction temperature and held there until the reaction was completed. Curing enthalpies were calculated from the area under the peak.

Sample preparation for thermal and mechanical tests

Calculated amounts of DGEBA and a mixture of PACM-20 and DSX were weighed into separate beakers. PACM-20 and DSX were completely miscible in the composition range studied. Epoxy resin was then placed in a vacuum oven at 60°C for 15 min to remove any trapped air. Following this process the amine mixture and the resin was mixed carefully, until homogeneous and clear, without forming any bubbles. The mixture was again degassed under vacuum for 2 min and poured into hot RTV silicone moulds with proper sample shapes and cured in an oven at 160°C for 150 min. After curing, the samples were cooled down to room temperature and kept in a dessicator until further evaluation and testing. All of the cured samples obtained were transparent.

Characterization of the cured resins

D.s.c. scans were obtained under helium or nitrogen atmosphere between -150 and 200°C with a heating rate of 10°C min^{-1}. TMA penetration curves were obtained on a Perkin Elmer TMS-2, with a load of 0.200 kg and a heating rate of 10°C min $-$ 1. Thermal degradation studies of the samples were conducted under nitrogen atmosphere with a heating rate of 20°C min^{-1} using a Perkin Elmer TGS-2.

Stress–strain tests were carried out on an Instron Model 4411 Tester. Dogbone shaped samples with a thickness of 1.0 mm and a width of 5.0 mm were used during the measurements. Tests were conducted at room temperature with a crosshead speed of 1.0 mm per minute. Impact strengths were determined by a falling weight impact tester. Square samples with dimensions of 5.0 × 5.0 × 0.2 cm were punctured by a hemispherically tipped, 1.00 kg stainless steel dart falling from a fixed height of 1.0 m.

RESULTS AND DISCUSSION

Curing kinetics of DGEBA/DSX system

Curing kinetics of epoxy/amine systems leading to thermoseting networks involve several competing reactions as a function of conversion. At the initial stages of curing, the reactions are mainly between epoxy groups and primary amines which constitute the reaction mixture. As the curing proceeds, epoxy groups start reacting with secondary amines and hydroxyl groups formed in the system. In addition, as the gelation takes place the reaction becomes diffusion controlled which also influences its rate and mechanism. As a result these reactions have a fairly complex kinetics. However, due to the importance of these systems, epoxy/amine curing reactions are thoroughly studied and are well understood[11-13]. A rather complex kinetic model was recently proposed which takes into account all types of reactions as a function of extent of reaction[13].

Curing kinetics of the DGEBA/PACM-20 system were recently studied by d.s.c. and dielectric relaxation spectroscopy, and the relationship between the changes in molecular dynamics and the reaction kinetics was given in detail[14]. We have also investigated the curing kinetics of DGEBA/PACM-20 system previously[15]. Dynamic d.s.c. scans of stoichiometric mixtures of this system between 25 and 200°C yielded an average curing enthalpy (ΔH curing) of -393.7 ± 21.7 J g^{-1} (-95.5 ± 5.3 kJ mol^{-1}). Isothermal scans at 150°C indicated the completion of the curing reaction in about 60 min. Being a cycloaliphatic diamine, curing rates obtained with PACM-20 are much faster than those of aromatic amines at corresponding temperatures. As expected this is due to the stronger basicity of aliphatic amines.

In order to have a direct comparison we performed dynamic and isothermal curing studies of a DGEBA/DSX system similar to that of DGEBA/PACM-20 by using d.s.c. A typical dynamic curing exotherm for this system is given in *Figure 2*. Most epoxy/amine curing exotherms obtained by d.s.c. give unsymmetrical peaks, which usually develop a shoulder as the reaction proceeds. This is explained by a change in the reaction mechanism from kinetic control to diffusion control. This is because of the viscosity increase in the system and densification as the crosslinking proceeds, which continues until vitrification or the transformation of the rubbery network into a glassy solid. Therefore, epoxy curing reactions are usually conducted above the T_g of the fully crosslinked network to ensure complete curing. The peak for the d.s.c. curing exotherm shown in *Figure 2* for DGEBA/DSX is fairly symmetrical, in contrast to that of DGEBA/PACM-20 system[15]. This is due to the lower T_g of the network formed (the T_gs of DSX and PACM-20 cured DGEBA networks are 74 and 148°C respectively) which allows easier diffusion of the end groups even after gelation because of their higher flexibility at the curing temperatures which are well above the T_g of the final network. Also included in *Figure 2* is the percent conversion–temperature

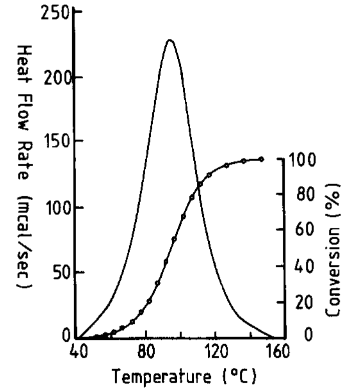


Figure 2 Dynamic curing isotherm and conversion temperature curves for a stoichiometric mixture of the DGEBA/DSX system (heating rate 5°C min^{-1})

Table 1 Enthalpy of curing for the reaction between DGEBA/DSX obtained from dynamic d.s.c. scans

D.s.c. heating rate (°C min^{-1})	ΔH (J g^{-1})	T_o (°C)	T_p (°C)	T_f (°C)
2.5	420.4	35	83	137
5.0	441.2	40	96	152
10.0	402.5	43	112	181

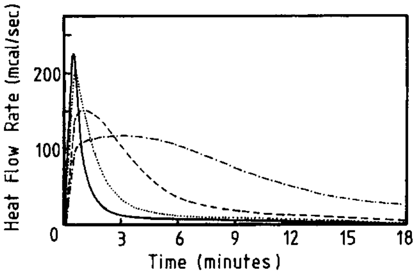


Figure 3 Isothermal d.s.c. curing curves for stoichiometric mixtures of DGEBA/DSX system at different temperatures (•–•, 80°C; - - -, 100°C; ••••, 120°C; and ———, 150°C)

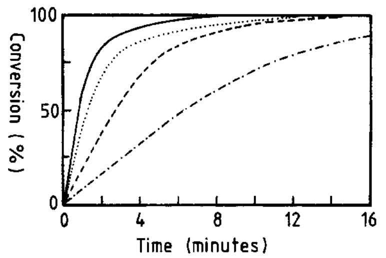


Figure 4 Conversion–time curves for stoichiometric mixtures of DGEBA/DSX system at different curing temperatures (•–•, 80°C; - - -, 100°C; ••••, 120°C; and ———, 150°C)

curve. *Table 1* gives the values of the curing enthalpies obtained for three different dynamic scans with heating rates of 2.5, 5.0 and 10.0°C min^{-1} respectively. Also given in *Table 1* are the initial, peak and final temperatures of the curing exotherms, indicated as T_o, T_p and T_f respectively. The mean value of ΔH_{curing} obtained from these dynamic scans is -421.4 ± 19.4 J g^{-1} (-106.2 ± 4.9 kJ mol^{-1}). This compares well with the curing enthalpy obtained for the DGEBA/PACM-20 system, which is -393.7 ± 21.7 J g^{-1} (-95.5 ± 5.3 kJ mol^{-1})[15].

Table 2 Compositions and glass transition temperatures of DSX modified epoxy networks

Sample No.	Wt% DSX	T_g (°C) (by d.s.c.)	T_i (°C) (by TMA)	T_g(°C) (calculated)
1	0	148	154	148
2	4.0	127	136	133
3	6.8	124	130	125
4	10.0	113	119	115
5	12.1	108	113	107
6	15.0	101	105	100
7	20.2	86	91	85
8	24.5	74	78	74

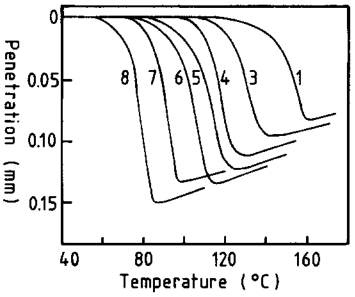


Figure 5 Penetration–temperature behaviour of DSX modified epoxy networks (numbers on curves indicate the sample numbers given in Table 1)

D.s.c. scans of isothermal curing reactions conducted at 80, 100, 120 and 150°C are given in *Figure 3*. Percent conversion–time curves obtained form these isothermal scans are plotted in *Figure 4*. As can be seen from *Figures 3 and 4*, curing reactions are extremely fast, reaching complete conversion in 15 min or less for reactions conducted at 100°C or higher. This clearly shows that the reactivity of DSX towards DGEBA is fairly higher than that of PACM-20. As shown in *Figure 4*, during isothermal curing at 150°C the reaction is completed in about 8 min *versus* 60 min for PACM-20 cured systems[15]. This is most probably due to the stronger basicity of the linear DSX molecule, when compared with PACM-20. In addition, the lower T_g of the network formed and its flexible nature also increase the probability of the reaction of end groups at the curing temperature, even under highly restrained conditions. This is an important observation because it shows that in an epoxy system, where aminopropyl terminated siloxane oligomers are used as modifiers together with conventional aliphatic or aromatic amine curing agents, they will react faster and fulfill the kinetic requirements necessary for obtaining a well phase separated morphology in the modified network.

Thermal characterization of networks

After kinetic studies the physical, thermal and mechanical properties of the networks formed were also investigated. *Table 2* gives the compositional data on the DSX modified networks together with their T_g values obtained from d.s.c. and thermal mechanical analysis (TMA), and calculated from the Flory–Fox equation:

$$1/T_{g_{ab}} = W_a/T_{g_a} + W_b/T_{g_b} \qquad (1)$$

Where (T_{gab}) is the T_g of the modified system and (W_a) and (W_b) are the weight fractions of each component in the network. For our system (T_{ga}) and (T_{gb}) are taken as 148 and 74°C respectively, which were determined experimentally. As can be seen from *Table 2*, the T_g of the samples decreases with an increase in DSX content. They also show almost a perfect fit to the Flory–Fox equation. This is a clear result of the compatibility of the DSX and the curing agent resulting in the formation of a random, miscible network. This is interesting, because when an α,γ-aminopropyl terminated polydimethylsiloxane, a homologue of DSX, with a slightly higher molecular weight is used as the modifier, such as a PDMS with an average molecular weight of 500 g mol^{-1} *versus* that of 248.5 g mol^{-1} for DSX (or with a siloxane backbone of $-[Si(CH_3)_2-O-]_5-Si(CH_3)_2-$ *versus* $-Si(CH_3)_2-O-Si(CH_3)_2-$), the networks obtained show phase separation as proven by thermal analyses and SEM studies[16–18]. TMA penetration studies also clearly indicate this trend in T_g with composition, as shown in *Figure 5*. In addition, the penetration depth decreases as the rigidity of the system increases, as expected. The temperatures corresponding to the inflection points of the penetration–temperature curves, which correspond to T_gs, are tabulated in *Table 2* as T_i. Thermal decomposition profiles of the networks produced were also studied under nitrogen atmosphere by thermogravimetric analysis. The results indicated a slight improvement on the thermal stability of the network as the amount of DSX in the system is increased. The char yield also showed an increase with an increase in the amount of DSX in the system. Both of these are expected, since siloxanes are known to be more thermally stable than hydrocarbons. When higher molecular weight siloxane oligomers are used as modifiers the improvement in thermal stability becomes even more pronounced[16–18].

Mechanical properties of the modified networks

Impact strengths and stress–strain behaviour of the networks obtained were also investigated. *Figure 6* gives the plots of ultimate stress and elongation at break against the DSX present in the network. It is interesting to note that, although their nature and failure mechanisms are different, the ultimate stress at break values for both controls, namely, PACM-20 and DSX cured DGEBA networks are fairly close to each other and are 598 and 576 kg cm^{-2} respectively. However, as the amount of DSX in the system reaches to about 10 wt%, there is a sharp increase in the ultimate stress at break to 748 kg cm^{-2}. After this point, as the amount of DSX is further increased, stress at break starts going down, reaching to 576 kg cm^{-2} for the system containing no PACM-20. This increase in stress at break is mainly due to the elastomeric properties of siloxanes incorporated into the network, which at low levels help to prevent the premature failure by most probably supressing the formation of cracks and/or crazes in the DGEBA/PACM-20 continuous matrix. As the amount of DSX is increased above 10 wt%, there is probably an inversion in the network structure from PACM-20 dominated, high strength, rigid system to a DSX dominated soft system and also a corresponding transition from brittle to a ductile failure mechanism[2,19]. As can be seen in *Figure 6*, elongation at break for the modified samples increases directly with the amount of DSX in the system from 6.8% to slightly over 11%. This is an expected behaviour for such a highly crosslinked network system, which goes gradually from brittle to elastomeric.

The results of the falling weight impact tests are summarized in *Table 3*. As expected, the impact strengths of the networks increase with an increase in the amount of DSX modifier. The sample which is cured with DSX only, shows about 50% improvement in the impact strength when compared with the unmodified, DGEBA/PACM-20 network. This is a fairly good improvement for such highly crosslinked systems.

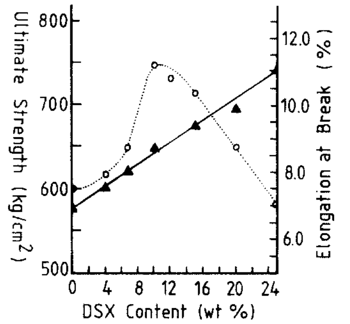


Figure 6 Tensile strength and ultimate elongation as a function of modifier content in DSX modified epoxy networks (○, Ultimate strength; ▲, Elongation at break)

Table 3 Impact strengths of modified networks

Sample No.	Wt% DSX	Impact energy (J mm^{-1})
1	0	0.153 ± 0.027
3	6.8	0.177 ± 0.031
6	15.0	0.202 ± 0.029
8	24.5	0.215 ± 0.029

CONCLUSIONS

A low molecular weight amine terminated siloxane, 1,3-Bis(γ-aminopropyl)tetramethyl disiloxane, was used as a modifier for a cycloaliphatic amine, bis(4-aminocyclohexyl)methane, cured epoxy networks based on DGEBA. At every composition studied, the reaction mixture obtained was completely miscible and clear. Similarly, the cured systems were also transparent and homogeneous.

D.s.c. studies on the curing kinetics of the reaction between DSX and DGEBA indicate that the disiloxane is an effective curing agent for the system, giving considerably higher curing rates than the aliphatic diamine used at corresponding temperatures. This is important regarding the use of higher molecular weight aminopropyl terminated siloxane oligomers as modifiers for DGEBA resins, because this clearly indicates that in a modified system due to their higher reactivities than that of the curing agent, aminopropyl terminated siloxanes will react first and phase separate into smaller domains as the rigid network develops. This fits well to the proposed scheme of rubber modification of epoxy networks.

Characterization of the DSX modified networks by d.s.c. and TMA indicate the formation of homogeneous networks with a single T_g, varying between 74 and 148°C, which follows the Flory–Fox equation for random copolymers. Thermal stability of the modified systems show slight improvement as the amount of DSX in the system is increased. Stress–strain tests show substantial increase on the ultimate strength of the network as the amount of DSX is increased and peaks when about 10 wt% of DSX is incorporated into the system. Elongation at failure increases linearly with the DSX content. Impact strengths of the modified systems also show improvement with increased DSX content of the network.

REFERENCES

1. Sultan, J. N. and McGarry, F., *Polym. Eng. Sci.*, 1973, **13**, 29.
2. Bucknall, C. B., *Toughened Plastics*, Applied Science, London, 1977.
3. Bauer, R. S., ed., *Epoxy Resin Chemistry II*, ACS Symposium Series, No. 221. ACS, Washington DC, 1983.
4. Riew, C. K. and Gillham, J. K., eds, *Rubber Modified Thermoset Resins*, ACS Series, No. 208. ACS, Washington DC, 1984.
5. Riew, C. K. and Kinloch, A. J., eds, *Toughened Plastics I, Science and Engineering*, ACS Series, No. 233. ACS, Washington DC, 1993.
6. Gannon, J., in *Encycl. Chem. Tech.*, Vol. 9. John Wiley, New York, 1994, pp. 730–755.
7. Adams, L. V. and Gannon, J., in *Encycl. Polym. Sci. Tech.*, Vol. 6. John Wiley, New York, 1986, pp. 322–382.
8. Hedrick, J. L., Yilgor, I., Jurek, M., Hedrick, J. C., Wilkes, G. L. and McGrath, J. E., *Polymer*, 1991, **32**, 2020.
9. Recker, H. G., Altstaedt, V., Eberle, W., Folda, T., Gerth, D., Heckman, W., Itteman, P., Tesch, H. and Weber, T., *Sampe J.*, 1990, **26**(2), 73.
10. Kiefer, J., Hillborn, J. G., Manson, J. A. E., Leterrier, Y. and Hedrick, J. L., *Macromolecules*, 1996, **29**, 4158.
11. Chiao, L., *Macromolecules*, 1990, **23**, 1286.
12. Cole, K. C., *Macromolecules*, 1991, **24**, 3093.
13. Cole, K. C., Hechler, J.-J. and Noel, D., *Macromolecules*, 1991, **24**, 3098.
14. Fournier, J., Williams, G., Duch, C. and Aldridge, G. A., *Macromolecules*, 1996, **29**, 7097.
15. Yilgor, I., Yilgor, E., Banthia, A. K., Wilkes, G. L. and McGrath, J. E., *Polym. Bull. (Berlin)*, 1981, **4**, 323.
16. Konczol, L., Doll, W., Buchholz, U. and Mulhaupt, R., *J. Appl. Polym. Sci.*, 1994, **54**, 815.
17. Buchholz, U. and Mulhaupt, R., *Polym. Prepr.*, 1992, **33**(1), 205.
18. Yorkgitis, E. M., Tran, C., Eiss, N. S., Jr., Hu, T. Y., Yilgor, I., Wilkes, G. L. and J. E. McGrath, in *Rubber Modified Thermoset Resins*, ed. C. K. Riew and J. K. Gillham, Adv. Chem. Ser., No 208, Ch. 10. ACS, Washington DC, 1984.
19. Kinloch, A. J. and Young, R. J., *Fracture Behavior of Polymers*. Elsevier Applied Science, Barking, 1985.