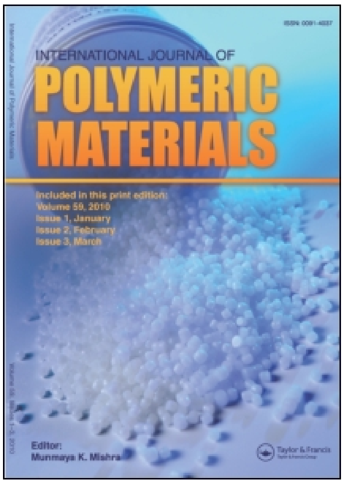

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

MODIFICATION OF SILICONIZED EPOXY RESIN USING MULTIFUNCTIONAL SILANES

M. Alagar[a]; A. Ashok Kumar[a]; A. Anand Prabu[a]; A. Rajendran[a]
[a] Department of Chemical Engineering, Chennai, India

To cite this Article Alagar, M. , Kumar, A. Ashok , Prabu, A. Anand and Rajendran, A.(2004) 'MODIFICATION OF SILICONIZED EPOXY RESIN USING MULTIFUNCTIONAL SILANES', International Journal of Polymeric Materials, 53: 1, 45 — 58

To link to this Article: DOI: 10.1080/00914030490263441

URL: http://dx.doi.org/10.1080/00914030490263441

International Journal of Polymeric Materials, 53:45–58, 2004
Copyright © Taylor & Francis Inc.
ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490263441

MODIFICATION OF SILICONIZED EPOXY RESIN USING MULTIFUNCTIONAL SILANES

M. Alagar
A. Ashok Kumar
A. Anand Prabu
A. Rajendran
Department of Chemical Engineering, Anna University, Chennai, India

Silane coupling agents, namely 3-[(2-aminoethyl)amino]propyltrimethoxysilane (AETMS), 3-[(2-maleicmonoamido)maleicmonoamido]propyltrimethoxysilane (MMTMS) and 3-[(2-maleicdiamido)maleicdiamido]propyltrimethoxysilane (MDTMS), were synthesized and characterized using FT–IR and viscosity studies. The silane coupling agents developed in the present investigation were utilized for coupling hydroxyl terminated polydimethylsiloxane with epoxy matrix and cured with hexamethylenediamine and diaminodiphenylmethane. The siliconized epoxy system developed using MDTMS and cured with diaminodiphenylmethane yielded higher glass transition temperature, better thermal stability and imparts higher crosslinking density due to its higher functionality (pentafunctional) than AETMS and MMTMS (trifunctional). Diamine–cured siliconized epoxy resins coupled with AETMS, MMTMS and MDTMS can be used for the development of high–performance advanced composites.

Keywords: silane coupling agents, siliconized epoxy, epoxy matrix, hydroxyl terminated polydimethylsiloxane

INTRODUCTION

Coupling agents are materials that improve the adhesion of different surfaces, impact strength, wetting and rheology. Coupling agents are

Received 23 November 2001; in final form 17 December 2001.

The authors wish to thank the University Grants Commission, New Delhi for the financial support.

Address correspondence to M. Alagar, Department of Chemical Engineering, Anna University, Chennai 600 025, India. E-mail: mkalagar@yahoo.com

compounds containing both organic and inorganic groups, the organic group compatible with polymer matrix resins and the inorganic group compatible with filler reinforcement. The major consumption of coupling agents [1] is in the manufacture of polyester laminates, epoxy composites and phenolic products. This is mainly to improve the adhesion and compatibility of glass fiber reinforcement and in the modification of the surface of particulate fillers suitable for polymer molding compounds [2].

Among the commercially available coupling agents, silane coupling agents [3] are more versatile and valuable from the industrial point of view [4]. The siloxane bonds involved in mineral surfaces improve the water-resistant characteristics of reinforced composite materials. Silane coupling agents [5, 6] provide significant benefit by modifying the interfacial region. They improve compound rheology [7] and also act as stress transfer agents to transfer stress from the low strength resin to the higher strength inorganic filler reinforcements [8]. In addition to maximizing stress transfer, they also help in maintaining good adhesion and mechanical strength when subjected to adverse environmental conditions [9, 10].

Composite materials developed using silane coupling agents exhibit stable electrical properties, such as dielectric constant, dissipation factor and volume resistivity because of the bonding between filler and reinforcement, which minimizes the ingress of water [11]. Silane coupling agents improve the mechanical and electrical properties of filled and reinforced resins [12, 13]. The lowering of viscosity by coupling agents provides an avenue to increase the reinforcement level for higher strength, and improved flow for higher quality moldings. Silane coupling agents are capable of reducing viscosity significantly in many filled systems, especially thermoplastic and thermosetting systems [9]. Silane coupling agents are used in the modification of glass fiber [14] as sizing agents and they interact with many thermoplastic materials to produce upgraded composites [15].

In the present study, three types of silane coupling agents, namely 3-[(2-aminoethyl)amino]propyltrimethoxysilane referred to as AETMS, 3-[(2-maleicmonoamido)maleicmonoamido]propyltrimethoxysilane referred to as MMTMS and 3-[(2-maleicdiamido)maleicdiamido]propyltrimethoxysilane referred to as MDTMS, were synthesized and used for toughening the epoxy resin LY556 with hydroxyl terminated polydimethylsiloxane (HTPDMS) in the presence of dibutyl tindilaurate as catalyst using hexamethylenediamine and diaminodiphenylmethane curatives.

EXPERIMENTAL

Materials

Epoxy resin (diglycidyl ether of bisphenol-A, DGEBA, LY 556, epoxy equivalent = 180–190, viscosity = 10,000 cP, Ciba-Geigy, India). Octamethylcyclotetrasiloxane (OMCTS, viscosity = 2.5 cP at 25°C, Wacker-Chemie, Germany) was dried over molecular sieves and distilled. Hexamethylenediamine referred to as CA-I (amine equivalent = 29.05 eq/kg, Aldrich Chemicals, USA); Diaminodiphenylmethane referred to as CA-II (HT 972, amine equivalent = 49.5 eq/kg, Ciba-Geigy, India); γ-aminopropyltriethoxysilane (γ-APES), a silane derivative as cross-linking agent for reference, 3-chloropropyltrimethoxysilane (CPTMS, Union Carbide, India) and dibutyl tindilaurate as catalyst (DBTDL, Aldrich Chem. Co., U.S.A) were used as received. Maleic anhydride (MA), ethylenediamine (EDA), maleimide (MI), potassium hydroxide and 2-propanol were purchased from SRL, India and used as supplied.

Apparatus

Viscosity of the samples were determined using an Brookfield viscometer with different capillary sizes over the temperature range of 30°C–80°C ± 0.2% at an interval of 10°C. Infrared spectra were obtained using Perkin-Elmer FT–IR spectrometer to confirm the stability during storage and to study the curing mechanism of interpenetrating polymer network formation. A differential scanning calorimeter (Mettler TA 3000) was used to determine the glass transition temperature. The measurements were carried out from 0°C to 350°C under nitrogen atmosphere with a heating rate of 10°C per minute. Thermogravimetric analysis was carried out in TGA Mettler TA 3000. Morphological studies were done using a Leica Cambridge Stereoscan Model 440 scanning electron microscope.

Synthesis

Preparation of 3-[(2-aminoethyl)amino]propyltrimethoxysilane) (AETMS)

EDA (6 mol) was refluxed with CPTMS (1 mol) at 90°C for about 2–3 h in nitrogen atmosphere. After completion of the reaction, the silane derivative floats over the top layer and subsequent vacuum distillation yielded AETMS.

FT–IR (KBr): 3405 cm^{-1} (Si–O); 3305 cm^{-1} (N–H); 2941 cm^{-1} (C–H); 1465 cm^{-1} (C–Si); 1125 cm^{-1} (C–N).

Preparation of 3-[(2-maleicmonoamido)maleicmonoamido]-propyltrimethoxysilane) (MMTMS)

MMTMS was synthesized by reacting 2 moles of MA with 1 mole of AETMS in 2-propanol at 70°C for about 1 h in nitrogen atmosphere. The resulting solid mass was filtered, purified by recrystallization and neutralized with monoethanolamine to obtain the pure product.

FT–IR(KBr): 3413 cm^{-1} (Si–O), 3400, 1775 & 1685 cm^{-1} (C=O), 3310 cm^{-1} (NH), 2941 cm^{-1} (C–H), 1650 cm^{-1} (3° N–C), 1611 cm^{-1} (C=C), 1482 cm^{-1} (C–Si), 1132 cm^{-1} (C–N).

Preparation of 3-[(2-maleicdiamido) maleicdiamido] propyltrimethoxysilane (MDTMS)

MDTMS was synthesized by reacting 2 moles of MI with 1 mole of AETMS in 2-propanol at 70°C for about 2–3 h in nitrogen atmosphere. The resulting solid mass was filtered and purified.

FT–IR (KBr): 3425 cm^{-1} (Si–O); 3410, 1782 & 1680 cm^{-1} (C=O); 3300 cm^{-1} (NH); 2826 cm^{-1} (O–CH_3); 1672 cm^{-1} (3° N–C); 1642 cm^{-1} (C=C); 3300 cra^{-1} (NH_2); 1479 cm^{-1} (C–Si); 1145 cm^{-1} ($CONH_2$). The synthesis of the substituted propyltrimethoxysilanes is shown in Figure 1.

Synthesis of hydroxyl terminated polydimethylsiloxane (HTPDMS)

HTPDMS used for the development of siliconized epoxy matrix [16] was derived from OMCTS. 1000 ml of OMCTS and potassium hydroxide catalyst (0.22 wt% of OMCTS) were taken in a five-necked, round-bottomed glass reactor. The reaction was carried out under inert atmosphere at 90°C ± 1°C for 4 h in a thermostatically controlled oil bath. After the resulting reaction mixture was cooled to 50°C to avoid frothing, it was stripped of its unreacted OMCTS under vacuum at elevated temperature (180°C). The HTPDMS resulting from the reaction was cooled to room temperature (yield = 62%). The viscosity of the HTPDMS was determined using a Brookfield viscometer. Molecular weight of the polymer was determined using viscosity values (Molecular weight $m_v = 1000$ and viscosity = 40 cP at 25°C). Infrared bands appearing between 1130 and 1000 cm^{-1} and between 3400 cm^{-1} and 3200 cm^{-1} in the FT–IR spectrum confirmed the presence of Si–O–Si and Si–OH linkages respectively (Figure 2).

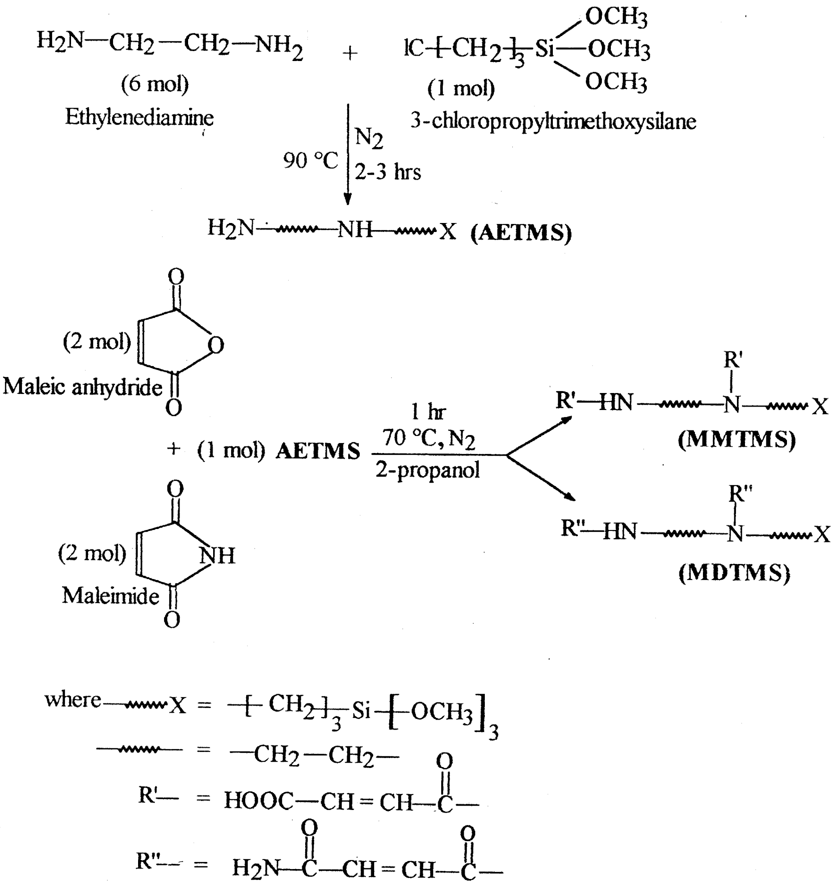

FIGURE 1 Synthesis of substituted propyltrimethoxysilanes-(a) AETMS, (b) MMTMS and (c) MDTMS.

Preparation of Siliconized Prepolymer Mix

A calculated amount (w/w) of HTPDMS prepolymer was thoroughly mixed with a calculated percentage of epoxy resin(LY 556) at 30°C. The prepolymer mix was subjected to vacuum to remove the trapped air inside the prepolymer mix. In order to assess the stability and homogeneity of the prepolymer and to ascertain any chemical change during storage, the prepolymer samples were allowed to stay in a stability column for a period of 6 months at 30°C. No appreciable change in viscosity or in spectral range was observed after a period of

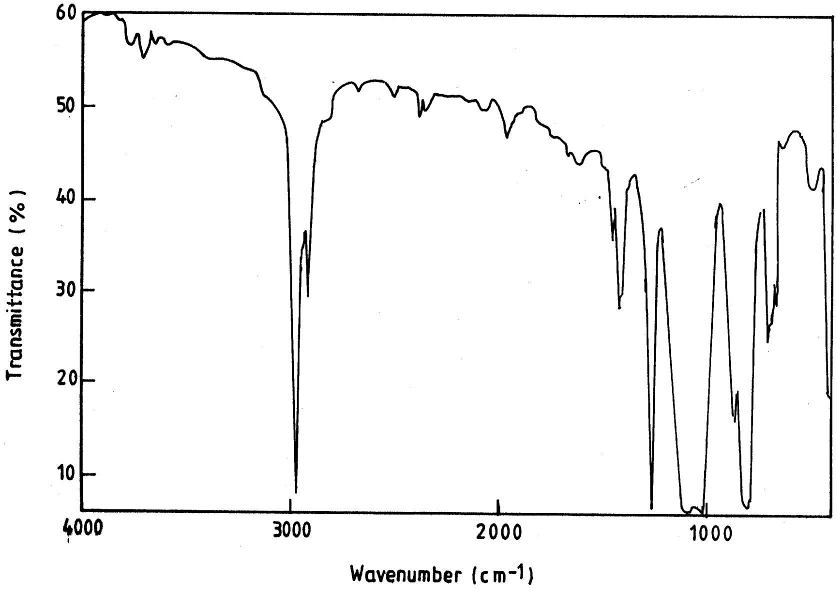

FIGURE 2 Ff–IR Spectrum of hydroxyl-terminated polydimethylsiloxane.

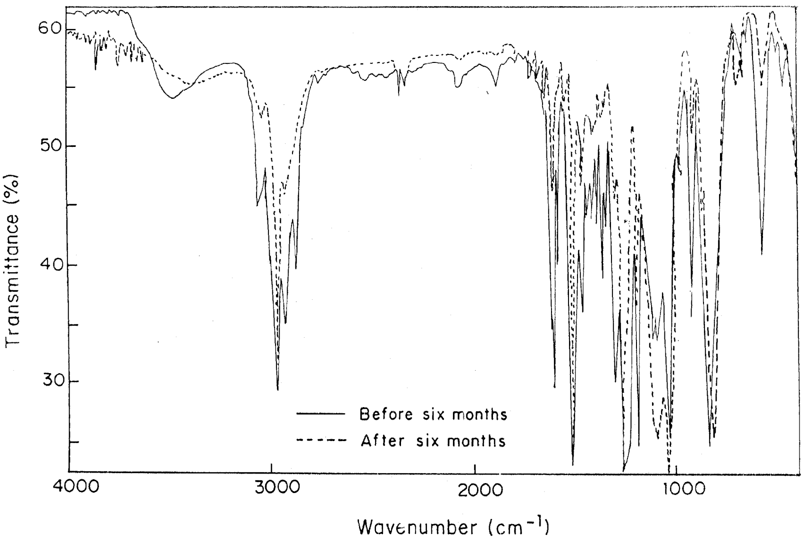

FIGURE 3 FT–IR spectrum of siliconized epoxy (10/90) prepolymer before and after six months ageing–a comparison.

TABLE 1 Comparison of Viscosity of Siliconized Epoxy Prepolymer Before and After 6 Months

	LY566, Viscosity (cP) at 30° C	
Siloxane/epoxy (w/w)	Initial	After 6 months
0/100	10,000	10,000
10/90	17,780	19,200
20/80	28,180	29,250
30/70	39,810	40,700

six months and this confirmed the stability of the prepolymer during that period (Figure 3 and Table 1).

Curing of Siliconized Prepolymer Mix

Varying compositions of the siliconized epoxy LY 556 system with curing agents CA–I and CA–II and catalyst are presented in Table 2. Calculated amounts of the curing agent hexamethylenediamine (CA–I), silane coupling agents and DBTDL catalyst were sequentially added to the prepolymer blend of HTPDMS and epoxy resin (w/w) [16, 17]. After degassing, the resulting product was cast in a mold at 30°C and post cured at 70°C for 10 h. In the case of diaminodiphenylmethane (CA–II), it was melted at 90°C and mixed with siliconized epoxy prepolymer at 120°C, followed by the addition of stoichiometric equivalent of silane coupling agents and DBTDL catalyst. The prepolymer mix and curing agents were thoroughly mixed, cooled to about 60°C and subjected to vacuum treatment to remove trapped air. The mixture was then cast and cured at 70°C for 3 h, post cured at 120°C and 160°C for 2 h and 1 h, respectively.

TABLE 2 Amount of Curatives, Crosslinking Agents and Catalyst Used

	Amount of curing agent (g)		Cross-linking agent (g)			
Siloxane/Epoxy	CA-I	CA-II	AETMS	MMTMS	MDTMS	Catalyst (g)
0/100	16.11	27.0	–	–	–	–
10/90	13.21	24.3	0.2	0.2	0.2	0.10
20/80	10.31	21.6	0.3	0.3	0.3	0.15
30/70	7.41	18.9	0.4	0.4	0.4	0.20

RESULTS AND DISCUSSION

Formation of Interpenetrating Network

Formation of siliconized epoxy interpenetrating polymer network with silane coupling agents in the presence of dibutyl tindilaurate catalyst may occur in two stages. The first stage involves the reaction between the epoxide ring of the epoxy resin and primary and secondary amino groups of AETMS and MDTMS, and secondary amino group and carboxyl group of MMTMS. In the second stage, the methoxy groups of silane coupling agents (AETMS, MMTMS and MDTMS) react with hydroxyl groups of hydroxyl terminated polydimethylsiloxane.

The FT–IR absorption peaks observed for siliconized epoxy (10/90) prepolymer between 1230 cm^{-1} and 1280 cm^{-1} are due to the symmetrical stretching vibration of epoxy ring. The peaks observed between 770 cm^{-1} and 860 cm^{-1} indicate the asymmetric stretching due to the epoxy ring. The absorption peaks observed at 2900 cm^{-1} and between 3390 cm^{-1} and 3400 cm^{-1} show the presence of methylene and hydroxyl groups before the commencement of curing reactions (Figure 3). Absence of absorption peak at 913 cm^{-1} in the representative FT–IR spectrum obtained for AETMS coupled and

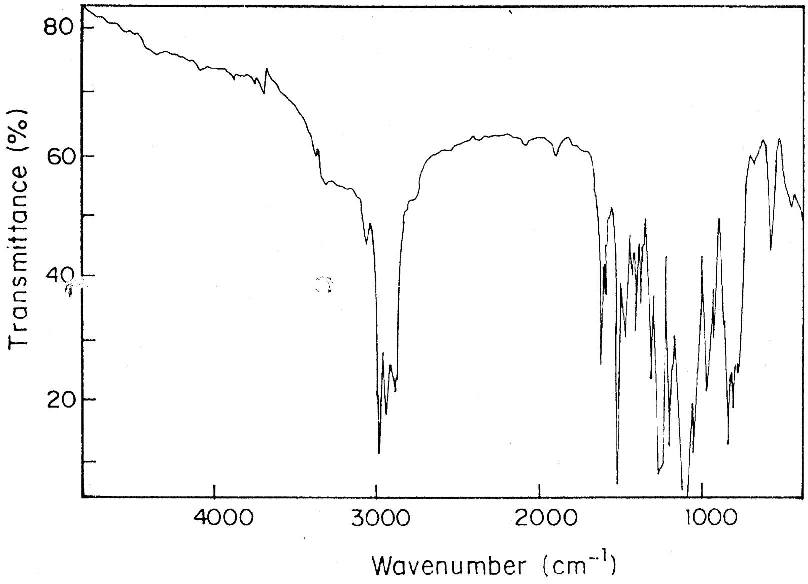

FIGURE 4 FT–IR spectrum of AETMS coupled, CA-I cured siliconized epoxy (10/90) system.

CA–I cured component confirms the disappearance of epoxide group (Figure 4). Absorption peaks present between 2980 cm^{-1} and 2850 cm^{-1} and between 1370 cm^{-1} and 960 cm^{-1} confirm the presence of asymmetric methyl groups stretching in $Si-O-CH_3$, $Si-(CH_2)_3$ group and residual Si–OH groups due to the formation of network.

Si–O strech is sharp at 1200 cm^{-1}. The presence of an intense peak, a triplet at 2874, 2928 and 2970 cm^{-1} is an evidence for existence of $-CH_2$ and $-CH_3$ groups. The peaks that lie in between 1200 cm^{-1} and 1600 cm^{-1} are due to Si–O stretch, CH_2 bands and C–N stretch. The presence of unsaturation in the skeleton ($\sim$CH=CH$\sim$) at 1670 cm^{-1} is confirmed in the cases of MMTMS and MDTMS. The strong peak observed at 1720 cm^{-1} is due to the presence of carbonyl groups in the cases of MMTMS and MDTMS.

Cure Schedule

Cure schedule gives specification of cure time and the cure temperature of any matrix system. The cure schedule data be utilized to assess the suitability of the systems for impregnation, casting, encapsulation, etc., which are to be completed prior to viscosity build up and the approach of gel point [18]. The siliconized epoxy matrix systems developed using AETMS, MMTMS and MDTMS have high crosslink density due to the presence of multifunctional reactive sites. Among them, AETMS and MMTMS exhibit similar reactivity with formation of network structure and their cure behaviour is comparable to γ-APES [19]. MDTMS exhibits higher reactivity than AETMS and MMTMS due to the presence of two electron–rich $-NH_2$ and one >NH hydrogen units (five reactive sites), whereas AETMS has only one $-NH_2$ and >NH– units and MMTMS has only one >NH and two electron–deficient carboxyl hydrogen atoms (three reactive sites).

TABLE 3 Cure Schedule of Siliconized Epoxy Systems LY556

Siloxane/ Epoxy	Pot-life (minutes)						Curing with CA-I-temperature rise (°C)
	CA-I			CA-II			
	AETMS	MMTMS	MDTMS	AETMS	MMTMS	MDTMS	
0/100	37	39	33	440	456	412	90
10/90	28	30	25	270	276	262	75
20/80	25	26	23	195	198	189	64
30/70	19	21	17	150	157	143	58

Exothermal Curing Reaction

The heat evolved during the epoxy curing process causes an exotherm and the reaction proceeds more rapidly [20]. During the chemical reaction between epoxy groups with amino and carboxyl groups of both silane coupling agents and curative, the temperature rises to 120°C and 175°C, respectively, due to the exothermic reacion. The rise in temperature varies according to the nature of curing agent (Table 3) and percentage of siloxane in epoxy resin. In the case of CA–II, heat is required to initiate the reaction between curing agent and siliconized epoxy systems. The bulky benzene ring reduces the molecular mobility needed to orient the reactive end groups for reaction [21].

Pot-Life

The pot-life is the working time available after mixing the resin with curing agent to process them for such applications as impregnation, casting, or other operations that involve "flow". Curing reaction is accelerated by DBTDL at room temperature. As curing starts, the viscosity increases gradually. Network formation depends on the stoichiometric quantities of silane coupling agents AETMS, MMTMS and MDTMS, and they increase the crosslink density and lower the pot–life of the systems.

Incorporation of siloxane into the epoxy systems decreases the pot-life, which is also evidenced from the increase in viscosity (Table 1). In the case of CA–II, the hydroxyl group present in polydimethylsiloxane along with hydrogen donating aromatic group and higher curing temperature increases the rate of the reaction. This is the reason for the abrupt decrease in the pot-life when CA-II is used as curing agent.

Glass Transition Temperature

Differences in the glass transition temperature of siliconized epoxy system with different silane coupling agents such as γ-APTES, AETMS, MMTMS and MDTMS, were too small to show any consistent trend. The single glass transition temperature confirms the presence of a single phase and that the polydimethylsiloxane is a part of it and not in a separate phase.

Thermogravimetric Analysis

Incorporation of HTPDMS into epoxy resin improves its thermal stability and enhances degradation temperature according to its

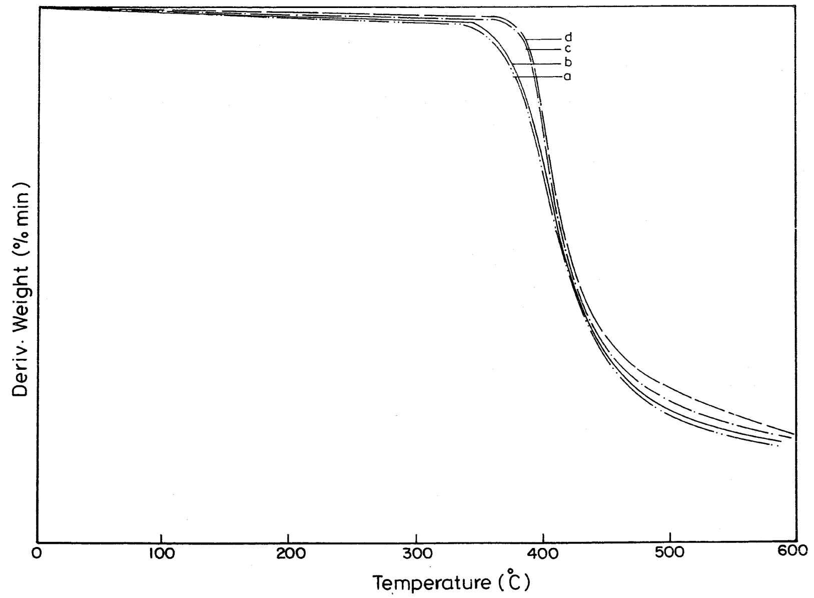

FIGURE 5 TGA curves of siliconized epoxy systems (a) unmodified (b) 5% (c)10% and (d)15% siloxane modified epoxy systems.

percentage concentration. The presence of siloxane skeleton in the system delays the degradation (Figure 5) and high amount of thermal energy is required to attain the same weight loss when compared with that of unmodified system. The delayed degradation may be attributed to the stability of the inorganic nature of siloxane structure, which may stabilize the epoxy resin from the heat [22].

For example, the temperature required for 10%, 30% and 50% weight losses of unmodified epoxy resin cured with CA–II are 375°C, 394°C and 405°C, whereas the temperature required to attain the same weight losses for siliconized epoxy system (epoxy modified with HTPDMS) having 20% siloxane are increased to 408°C, 429°C and 437°C, respectively. A similar trend is observed for the siliconized epoxy system having 10% and 30% of siloxanes. Further, it is also observed that the type of curative system and nature of silane coupling agents have marked influence on thermal degradation. Among the curatives and silane coupling agents studied in the present investigation, the siliconized epoxy system cured with CA–II and crosslinked with MDTMS exhibits higher thermal stability due the hot curing behavior and multifunctionality, and imparts higher crosslink density.

Viscosity

Incorporation of HTPDMS in the epoxy resin increases the viscosity of the systems. Incorporation of 10%, 20% and 30% siloxane in epoxy resin system LY556 increase the viscosity to 17,780 cP, 28,180 cP and 39,810 cP, respectively (Table 1). The enchancement of viscosity may be explained due to association of the molecules by hydrogen bonding. The variation of viscosity with varied percentage of HTPDMS with CA–I along with AETMS, MMTMS and MDTMS are presented in Tables 4–6. From the data, it is observed that the silane-coupling agents have little influence on the effect of enhancement in viscosity during curing reaction according to their functionality and network formation. Among the silane coupling agents studied, the enhance-

TABLE 4 Variation of Viscosity (cP) During the Curing Reaction of Epoxy and Siliconized Epoxy System with CA-I and AETMS

Time (minutes)	LY556	LY556 +10% siloxane	LY556 +20% siloxane	LY556 +30% siloxane
Initial	4200	10800	13600	30000
5	7000	14000	30000	58000
10	14500	28000	86000	230000
15	35000	80000	196000	285500
20	75000	160000	245000	320000
25	140000	324000	375000	–
30	350000	385000	–	–
40	430000	–	–	–

TABLE 5 Variation of Viscosity (cP) During the Curing Reaction of Epoxy and Siliconized Epoxy System with CA-I and MMTMS

Time (minutes)	LY566	LY566 +10% siloxane	LY566 +20% siloxane	LY566 +30% siloxane
Initial	4000	10500	12400	26000
5	6000	12200	26000	52000
10	12000	25000	76000	190000
15	30000	65000	160000	243000
20	70000	142000	224000	296000
25	124000	302000	355000	–
30	348000	378000	–	–
40	388000	–	–	–

TABLE 6 Variation of Viscosity (cP) During the Curing Reaction of Epoxy and Siliconized Epoxy System with CA-I and MDTMS

Time (minutes)	LY556	LY556 +10% siloxane	LY556 +20% siloxane	LY556 +30% siloxane
Initial	4400	11200	15500	32000
5	8000	16000	33000	62000
10	15700	28900	90400	242000
15	37200	82400	208000	360000
20	79000	172000	418000	430500
25	151000	406000	423000	–
30	362000	431000	–	–
35	445000	–	–	–

ment in viscosity is more in the case of MDTMS (Table 6) than other two compounds AETMS and MMTMS (Tables 4 and 5).

Morphological Studies

Scanning electron microscope was used to investigate the morphology of unmodified epoxy system and siliconized epoxy systems. SEM micrograph of fractured surface of the unmodified epoxy system reveals a smooth, glassy and homogeneous microstructure without any plastic deformation. Whereas the fractured surface of the siliconized epoxy resin system show the presence of heterogeneous morphology and the heterogeneity increases with increasing siloxane content.

CONCLUSIONS

Three types of silane coupling agents were synthesized, characterized and used for the toughening of LY556 with HTPDMS. DSC studies reveal that the siloxane incorporation has insignificant improvement in the Tg value. Further, the single Tg obtained for each siliconized epoxy system confirms the presence of a single phase. TGA studies revealed that the incorporation of siloxane improves the thermal stability of siliconized epoxy system according to its percentage concentration. The system cured with CA–II and cross-linked with MDTMS is thermally more stable than AETMS and MMTMS due to higher crosslink density imparted by MDTMS and the presence of rigid aromatic ring in the curative CA–II. The SEM analysis shows homogeneous and heterogeneous morphology for the unmodified epoxy and siliconized epoxy systems, respectively. Among the silane coupling agents developed in the present investigation, silane coupling agent MDTMS is more suitable for the development of advanced siliconized epoxy composites.

REFERENCES

[1] Alagar, M., Thanikaivelan, T.V., Ashok Kumar, A. and Mohan, V. (1999). *Materials and Manufacturing process*, **14**, 67.
[2] Jurai, F. and Stanislav, F. (1993). *Plastics Manufacturing*, **55**, 118.
[3] Plueddemanr, E.P. (1991). *Silane Coupling Agents*, 2nd edition, Plenum Press, New York.
[4] Sounik, D.F. and Malcolm, E.K. (1985). *Polymer Composites*, **6**, 151.
[5] Price, C. C. and Jentung, K. U. (1985). *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 185.
[6] Hamada, H., Ikuta, N., Nishida, N. and Maekawa, Z. (1994). *Composites*, **25**, 512.
[7] Rochette, A., Choplin, L. and Tanguy, P.A. (1988). *Polymer Composites*, **9**, 419.
[8] Po, H.S. and Chein, Y.L. (1997). *Eur. Polym. J.*, **33**, 903.
[9] Gasson, J. and Andrezej, B.K. (1997). *Polymer Composites*, **18**, 179.
[10] Lee, N.J. and Jyonysik, J. (1997). *Composite Science and Technology*, **57**, 1559.
[11] D'Almeida, J.R.M. (1991). *Composites*, **22**, 448.
[12] Alagar, M. (1986). Ph.D Thesis, Anna University, India.
[13] Algar, M., Ponnusamy, M. and Amsavel, A. (1993). *Hungarian J. of Ind. Chem.*, **21**, 19.
[14] Liao, Y.T. (1989). *Polymer Composites*, **10**, 424.
[15] Mcgregor, R.R. (1952). *Silicones and Their Uses*, McGraw-Hill Book Company, New York.
[16] Peerman, D.E., Tolberg, W. and Flayo, D.E. (1957). *Ind. Engg. Chem.*, **49**, 1091.
[17] Bell, J.P. (1970). *J Polym Sci (Part A)*, **6**, 417.
[18] Amdouni, N., Sautereau, H., Gverard, J.F. and Paseault, J.P. (1990). *Polymer*, **31**, 1245.
[19] Culler, S.R., Ishida, H. and Koenig, J.L. (1986). *Polymer-Composites*, **7**, 231.
[20] Gough, L.J. and Smith, I.T. (1960). *J. Appl. Polym. Sci.*, **3**, 362.
[21] Lubin, G. (1982). *Handbook of composites*, Van Nostrand Reinhold, New York.
[22] Lin, S.T. and Huang, S.K. (1997). *Eur. Polym. J.*, **33**, 365.