Aliphatic amine cured PDMS–epoxy interpenetrating network system for high performance engineering applications—Development and characterization

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Abstract. A siliconized epoxy interpenetrating network (IPN) was synthesized from commercially available DGEBA epoxy resin GY250 (Ciba-Geigy, epoxy equivalent = 182–192, viscosity = 9000–12000 cP) and hydroxyl terminated polydimethylsiloxane (PDMS). PDMS and GY250 were thoroughly mixed at 30°C to get the prepolymer. Stoichiometric amounts of PDMS–epoxy prepolymer, *g*-aminopropyltriethoxysilane, aliphatic amine curing agent (HY951), and dibutyltindilaurate catalyst, were thoroughly mixed and cast in a mould after evacuating the entrapped air. The cured material was then taken out and post cured at 70°C for 10 h. IPN was characterized by FTIR spectroscopy, SEM, DSC, TGA and viscosity measurements. Incorporation of PDMS in the epoxy matrix increased the viscosity and lowered the exotherm and pot-life. PDMS in IPN increased T_g, heat-distortion temperature and reduced the percentage weight loss with increase in temperature. Incorporation of PDMS drastically reduced the tensile and flexural strengths and hardness. By reducing the tensile and flexural modulus, the siloxane moiety effectively reduced the internal stress of IPN thereby improving its impact strength and percentage elongation. PDMS increased the electric potential gradient of IPN to withstand without breakdown. An increase in the tracking index and arc resistance of IPN were observed, because of the presence of Si–O–Si, which minimized the possibility of forming carbonized path. Volume and surface resistivities of IPN also increased with the incorporation of PDMS. The siliconized epoxy IPN, with better impact and thermal resistance, may be used in automobile and aerospace applications to withstand high temperature, and mechanical stress. The PDMS–epoxy IPN may be used for encapsulation, high temperature and high voltage application due to their low shrinkage and lesser internal stress. With the improved electrical characteristics, IPN may be used for high performance electrical insulation, insulator housings, and encapsulation to withstand high voltage, moisture, oxidation, chemical attack, biological attack, outdoor weathering, contamination, electrical, mechanical and thermal stress.

Keywords. PDMS; siloxane; epoxy; siliconized epoxy matrix; interpenetrating network.

1. Introduction

Any insulating material in service is exposed to moisture, oxidation, chemical attack, biological attack, outdoor weathering, contamination, electrical, mechanical and thermal stress. Polymers are better insulating materials for high performance applications in contaminated environments (Looms 1990). However, these materials also deteriorate due to multiple stresses encountered in service and aging. No single polymer or polymer blend has the necessary properties for an outdoor insulating material to provide the desired mechanical or electrical characteristics. Desired performance and service life over a diverse range of service conditions may be achieved by synthesizing materials with complex formulations.

Polymeric materials with good hydrophobicity and erosion resistance are preferred for better insulation applications.

Materials having such properties usually lack good mechanical characteristics. They are not rigid and self-supporting and hence are modified to improve their mechanical characteristics for high performance applications (Bascom *et al* 1975; Mackevich and Shah 1997). Silicones, owing to their hydrophobicity (Gorur *et al* 1991; Looms 1990; Karady *et al* 1995) have been much widely used for outdoor insulation. The hydrophobicity is due to the presence of flexible Si–O linkage and mobile silicone chains. Low surface energy of silicone imparts better hydrophobicity and hence silicones show very low leakage current in wet conditions even if contamination is present (Simmons *et al* 1997). Their mechanical properties do not vary much over a wide temperature range. However, they possess very poor mechanical characteristics. Epoxy resins possess good mechanical and electrical characteristics. However, they have comparatively less hydrophobicity and impact strength (Gutman *et al* 1997). They are often modified to improve their hydrophobicity, weathering characteristics and impact strength for

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high-tech applications (Sultan and Mc Garry 1973; Bascom *et al* 1975).

Polymer blends usually exhibit separate T_g values due to thermodynamic incompatibility. Siloxane is made to chemically bond with epoxy resin to form the interpenetrating network with desired characteristics and avoid phase separation (Nguyen and Suh 1984; Frisch 1985). Compounding the incompatible siloxane with epoxy resin is effective in achieving the desired characteristics, yet the method of compounding remains the state of the art. In this study, an attempt was made to synthesize and characterize a siliconized epoxy IPN, by cross-linking epoxy resin and hydroxyl-terminated polydimethylsiloxane (PDMS), using *g*-aminopropyltriethoxysilane (*g*-APS) as cross-linking agent, dibutyltindilaurate (DBTDL) as catalyst, and an aliphatic amine (HY951, Ciba-Geigy) as curing agent (Serier *et al* 1991).

2. Experimental

Commercially available epoxy resins GY250 (DGEBA, Ciba-Geigy) having epoxy equivalent about 182–192 with viscosity 9000–12000 cP was used in this study. The silicone component of interpenetrating network system was derived from octamethylcyclotetrasiloxane (Wacker-Chemie, Germany). Octamethylcyclotetrasiloxane (OMCTS) and potassium hydroxide catalyst (0·22% on the weight of OMCTS) were taken in a five-necked round-bottomed flask. The temperature of the mixture was gradually raised to 90°C over a period of 45 min and maintained at 90°C ± 1°C for 4 h, using thermostatically controlled oil bath and an inert atmosphere was maintained in the reaction medium by purging nitrogen. The reaction mixture was slowly cooled to about 50°C to avoid frothing. After degassing, the unreacted oligomer was removed by gradually increasing the temperature to 180°C. Molecular weight of the polymer was evaluated from the viscosity of the PDMS, which was determined using Brookfield viscometer.

PDMS and DGEBA were thoroughly mixed at 30°C to get the prepolymer. The prepolymer was degassed before characterization. Viscosity of the prepolymer was measured using Brookfield viscometer and a FTIR spectrum was taken using Perkin-Elmer FTIR spectrometer.

Diethylenetriamine (HY951, Ciba-Geigy) with an amine equivalent = 20·6 eq./g was used as the curing agent.

Table 1. Amount of curing agent, cross-linking agent and catalyst used in synthesis of siliconized epoxy system.

Ratio of epoxy/PDMS	Amount of curing agent (g)	Cross-linking agent (g)	Catalyst (g)
100/0	10	–	–
90/10	9	0·2	0·10
80/20	8	0·3	0·15
70/30	7	0·4	0·20

Diethylenetriamine at 95 index of siliconized epoxy prepolymer, calculated amounts of silane adhesion promoter and dibutyltindilaurate catalyst, were added sequentially to the prepolymer blend (table 1). The resulting product was cast in a mould after evacuating the entrapped air. The cured material was then taken out and post cured at 70°C for 10 h.

Heat distortion temperature was determined using S.C. Day Heat Distortion Temperature apparatus as per ASTM 648. Thermogravimetric analysis was carried out using TGA-Mettler TA3000. A differential scanning calorimeter (Dupont 2000) was used to measure the glass transition temperature (T_g) of a specimen. The measurements were carried out from 0°C to 350°C, with a heating rate of 10°C/min under nitrogen gas. The morphology of the samples was examined by scanning electron microscopy. Mechanical properties (tensile strength, tensile modulus, percentage elongation, flexural strength and flexural modulus) were studied using an Instron Model 8502 machine as per ASTM procedure. Impact strength was tested as per ASTM procedure (ASTM D256). Hardness of the specimen was tested using Durometer (Shore D) as per ASTM D2240.

Dielectric strength was determined by step by step test as per ASTM D149. Comparative tracking index was determined as per ASTM D3638 on the surface of a specimen. Volume and surface resistivities were determined as per ASTM D257 on the flat surface of a specimen. Arc resistance was measured as per ASTM D495.

3. Results and discussion

Molecular weight of PDMS synthesized from OMCTS was evaluated using viscosity values (M_n = 1000 g/mol, refractive index = 1·3985, density = 0·97 g/cm³, viscosity 100 cP at 25°C).

Prepolymer obtained by mixing PDMS and DGEBA was allowed to stand in a stability column for a period of 6 months at 30°C, in order to assess its stability and homogeneity and to ascertain any chemical change during storage.
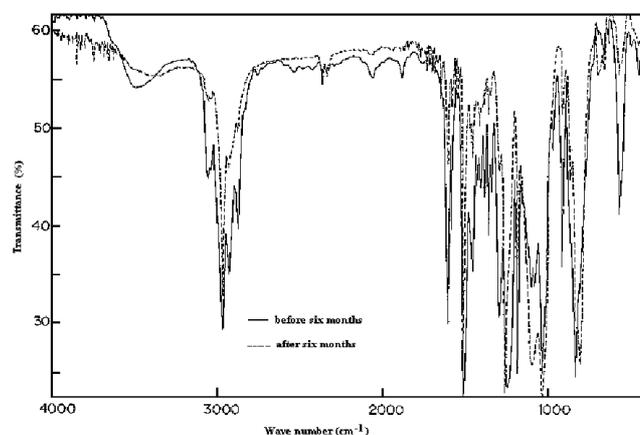
Figure 1. FTIR spectrum of siliconized epoxy prepolymer before and after six months ageing.

Table 2. Properties of siliconized epoxy system.

| Property	Percentage PDMS			
	0	10	20	30
Pot life (min)	40	35	28	23
Exotherm (°C)	70	50	42	38
Percentage weight loss (TGA)	45·03	43·65	41·25	37·00
T_g (°C)	64·1	68·8	75·1	79·2
HDT (°C)	85	88	91	93
Dielectric strength (V/mm)	11·16	18·99	20·21	21·89
Comparative tracking index (V)	400	450	500	550
Volume resistivity (Ω cm^2)	$3\cdot56 \times 10^{12}$	$2\cdot16 \times 10^{14}$	$> 10^{14}$	$> 10^{14}$
Surface resistivity (Ω cm)	$3\cdot8 \times 10^{9}$	$5\cdot0 \times 10^{12}$	$5\cdot8 \times 10^{13}$	$6\cdot6 \times 10^{14}$
Arc resistance (sec)	83	87	92	98
Tensile strength ($\times 10^6$N/m^2)	42·45	26·09	24·62	16·22
Tensile modulus ($\times 10^{-3}$N/m^2)	22·33	2·37	2·21	2·16
Percentage elongation	1·35	1·92	2·11	4·72
Flexural strength ($\times 10^6$N/m^2)	103·38	62·67	28·70	24·73
Flexural modulus ($\times 10^{-3}$N/m^2)	2·48	2·43	2·01	1·30
Hardness (shore D)	86	79	73	68
Impact strength (kg/cm/cm^2)	5·1	8·32	14·15	20·73

No appreciable change in viscosity or in the FTIR spectral ranges was observed which confirmed the stability of the prepolymer (figure 1 and table 2).

In the FTIR spectrum of the prepolymer (figure 2), absorption peaks at 1232 cm^{-1} and 831 cm^{-1} indicate the symmetrical stretching vibration and asymmetric stretching due to the presence of epoxy ring, respectively. These peaks are absent after the curing reaction, which confirms the opening of epoxide group (figure 3). The absorption peaks at 2969 cm^{-1}, 2830 cm^{-1} and 1385 cm^{-1} are due to the asymmetric methyl group stretching confirming the presence of Si–O–CH$_3$ and Si–(CH$_2$)$_3$ groups (figures 2 and 3). Absence of peak at 3500 cm^{-1} for the OH stretching indicates the absence of free OH group of the hydroxyl terminated PDMS, which has taken part in the network formation (figure 3). However, the peak at 960 cm^{-1} confirms the presence of residual Si–OH groups respectively. Absence of free NH$_2$ group of the *g*-APS is evident by the absence of N–H stretching at 3300 cm^{-1}. Scanning electron micrograph for the siliconized epoxy IPN with 10% PDMS is given in figure 4.

Formation of siliconized epoxy IPN with *g*-APS in the presence of DBTDL catalyst may be explained in two stages.
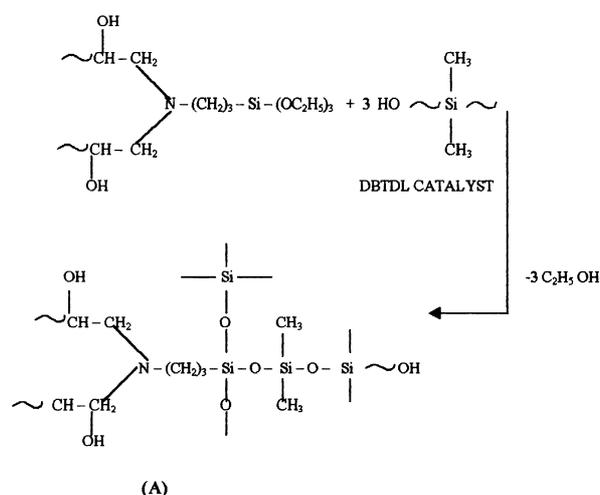
Stage I:

The first stage involves the reaction between the epoxide ring of the epoxy resin and amino group of the *g*-APS.
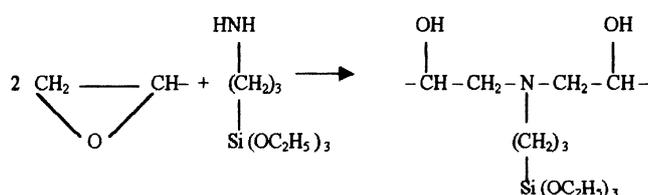

Stage II:

In the second stage, the reaction between epoxy and PDMS is promoted by the alkoxy group of *g*-aminopropyltriethoxysilane. This compatibilizes the siloxane (10 parts w/w) with the DGEBA.

(A)

Reaction with curing agent:

The diamine-curing agent reacts with the major portion of the DGEBA and opens the ring of the epoxy group. The amino groups react with the hydroxyl group of the siloxane as well as the hydroxyl group formed in the resin during the ring opening reaction.

(B)

(A)
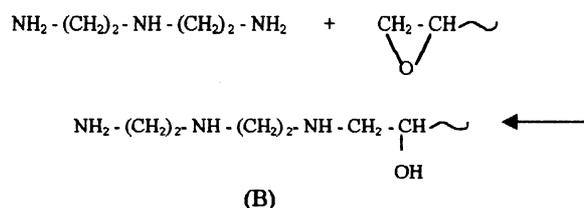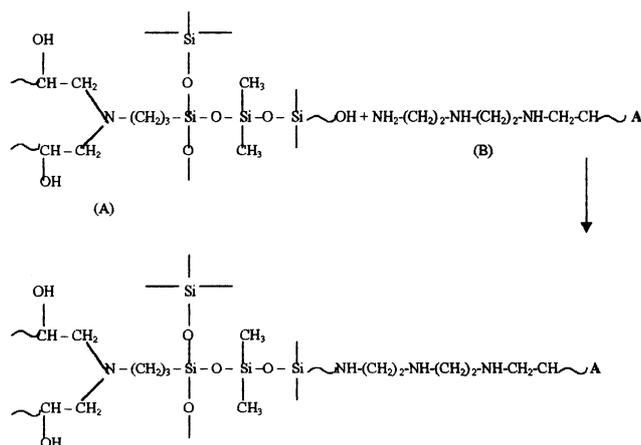
DSC curves for PDMS–IPN are given in figure 5. It is observed from the sharp peaks that IPN systems have single glass transition temperature (T_g). Incorporation of PDMS increased the T_g, which further increased with additional increments of PDMS content in IPN. TGA data show that the PDMS–epoxy IPN decompose exothermally (table 2). The decomposition exotherm peaks around 350°C. The decomposition of the cured resins begins at 300°C and follows the same pattern in all the cases. It is also observed that the decomposition temperature increased with increase in PDMS content (figure 5). The heat distortion temperature of IPN increased with increase in percentage PDMS (table 2). Percentage weight loss in the cured resin was lowered by increasing PDMS content.

Viscosity increased with increase in percentage PDMS in IPN (table 2). However, this lowered the exotherm and pot-life. The decrease in exotherm and pot-life accounts for reduction in shrinkage and hence lowering the internal stress. Incorporation of PDMS drastically reduced the tensile and flexural strengths, and hardness. This is due to the elastomeric nature of PDMS, reduction in cross-linking density and lowering of internal stress by PDMS. This greatly influences the tensile and flexural modulus, percentage elongation and impact strength. The energy dissipating character of the
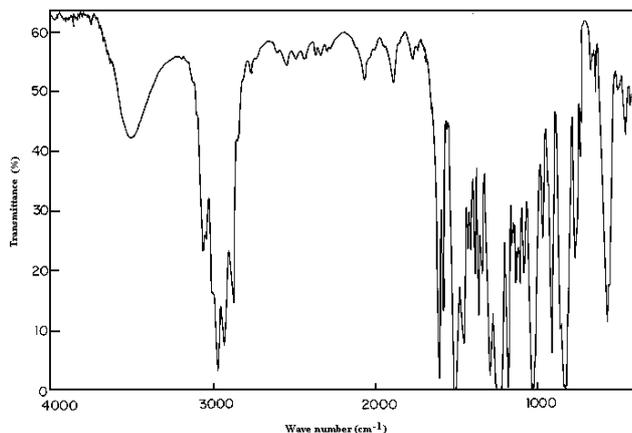
siloxane moiety contributes mainly to the increase of impact strength, percentage elongation and decreases the tensile and flexural modulus. By reducing the tensile modulus, the siloxane moiety effectively reduces the internal stress of IPN (Sung and Lin 1997).

Dielectric strength is highly influenced by the presence of PDMS in IPN. PDMS increases the electric potential gradient of IPN to withstand without breakdown. The dielectric strength increases with an increase in percentage PDMS content in IPN. PDMS present in IPN increases the tracking index by reducing the possibility of forming carbonized path in the organic insulating material, when high voltage current is passed. Because of the presence of Si–O–Si linkage, there is a discontinuity in the carbon chain, which does not allow the formation of continuous carbonized path and reduces the leakage or fault path, across the surface of IPN (Simmons *et al* 1997) (table 2). Hence, the material may be used for electrical insulation with a reliable performance even in salty humid conditions (Sung and Lin 1997). From table 2, it is observed that the volume and surface resistivities of IPN also increase with the incorporation of PDMS. Arc resistance of IPN is improved by the incorporation of PDMS. Increase in PDMS content increases
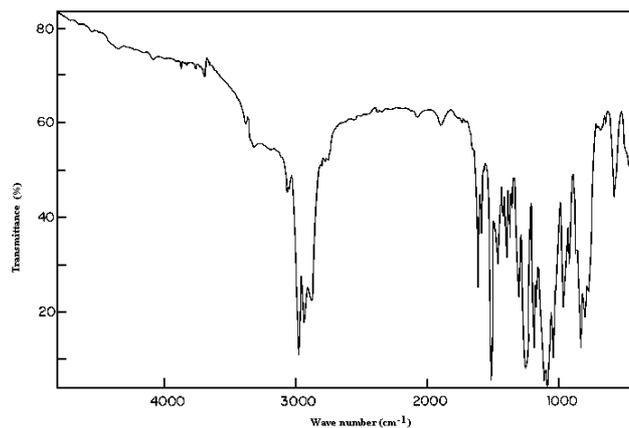

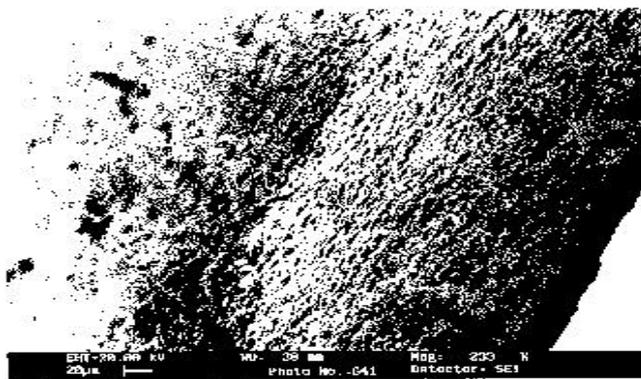**Figure 3.** FTIR spectrum of cured siliconized epoxy (10/90) prepolymer.

Figure 4. SEM photograph of PDMS–epoxy IPN.

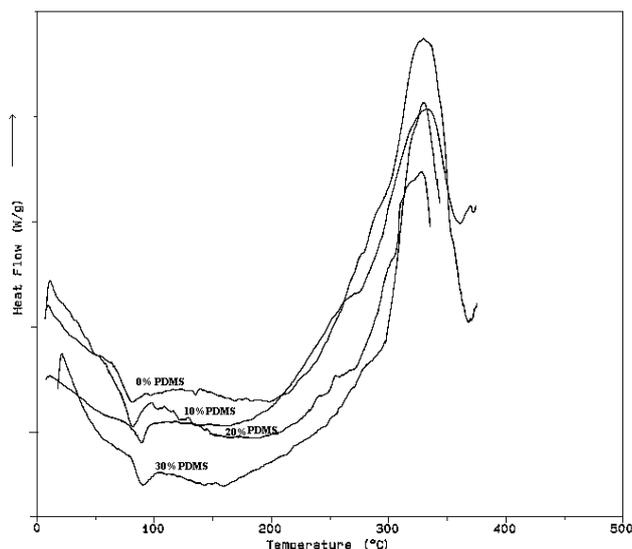**Figure 2.** FTIR spectrum of siliconized epoxy prepolymer.

Figure 5. DSC curves of epoxy and PDMS–epoxy systems.

the ability of IPN to withstand the discharge of high voltage, low current arc across the surface without rendering it conductive. The discontinuity in the carbon chain due to the incorporation of siloxane units is responsible for improved arc resistance.

4. Conclusion

PDMS–epoxy interpenetrating network, synthesized from commercially available epoxy resin GY250 (Ciba-Geigy) and hydroxyl-terminated PDMS at room temperature using aliphatic amine curing agent HY951 (Ciba-Geigy) was used along with dibutyltindilaurate catalyst and g-APS as cross-linking agent. IPN was characterized by FTIR, viscosity, thermal, mechanical and electrical stu-

dies. IPN has better electrical and thermal characteristics with high impact resistance compared to the virgin epoxy system. The PDMS epoxy IPN may be used for encapsulation, high temperature and high voltage application due to their low shrinkage and lesser internal stress. It is suggested that IPN with better electrical and thermal characteristics with improved impact resistance may be used in high performance electrical insulation, encapsulation, insulator housings and aerospace applications to withstand high voltage, moisture, oxidation, chemical attack, biological attack, outdoor weathering, contamination, electrical, mechanical and thermal stress.

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