

SHORT COMMUNICATION

Synthesis and Characterisation of Polyamidoamine-cured DGEBA-siloxane Interpenetrating Polymer Network

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ABSTRACT

A commercially viable polydimethylsiloxane (PDMS)-diglyceryl ether of bisphenol-A (DGEBA) interpenetrating network from hydroxyl-terminated PDMS and DGEBA (GY250-Ciba-Geigy) was synthesised. Epoxy resin was thoroughly mixed with PDMS to get a prepolymer, which was cured with polyamidoamine (HY840, Ciba-Geigy), at 30 °C using γ -aminopropyltriethoxysilane as cross-linker and dibutyltindilaurate as catalyst. It was then post-cured at 70 °C for 10 hr. The interpenetrating network obtained was characterised by SEM, FTIR, DSC, viscosity measurements, and mechanical, electrical and thermal studies. The interpenetrating polymer network has better electrical and thermal characteristics with high impact resistance compared to the virgin epoxy system.

Keywords: Polydimethylsiloxane, siloxane, epoxy resin, DGEBA, interpenetrating polymer network, PDMS, IPN, synthesis, cross-linking agent, prepolymer

1. INTRODUCTION

Elastomeric modification of epoxy resins has been adopted to alleviate its brittle characteristics since advanced composites made from epoxy resins for application in aerospace, automobile, electronic, defence and other industries demand superior impact resistance. Carboxy-terminated butadiene-nitrile (CTBN) rubber, amine-terminated butadiene-nitrile (ATBN)¹⁻⁵ rubber, fluoro-elastomers⁶, polysiloxanes⁷ and acrylate elastomers⁸ have been used successfully to improve the toughness, while only the modest reduction resulted in other important properties. The advantage of using siloxane as modifier is that it improves hydrophobicity and erosion resistance, which makes the material suitable for insulation in

highly adverse environment⁹⁻¹⁰. The PDMS, because of their hydrophobicity^{11,12}, has been widely used for outdoor insulation owing to the flexibility of Si-O linkage and the presence of mobile silicone chains. Low surface energy of siloxanes imparts better hydrophobicity, and hence show very low leakage current in wet conditions even if contaminated¹³⁻¹⁵. Silicone resists moisture, oxidation, chemical attack, biological attack, outdoor weathering, contamination and electrical, mechanical, and thermal stresses¹⁵. Their mechanical properties do not vary much over a wide range of temperature. However, these materials lack good mechanical properties and they are not rigid and self-supporting. To promote substantial enhanced toughness, development of a two-phase morphology is critically important while maintaining or at least

Table 1. Amount of curative, cross-linking agent and catalyst used in IPN

Ratio of epoxy and siloxane	Amount of curative (g)	Cross-linking agent γ -APS (g)	Catalyst DBTDL (g)
100/0	50	-	-
90/10	45	0.20	0.10
80/20	40	0.30	0.15
70/30	35	0.40	0.20

minimising the deterioration in other important properties/parameters, such as modulus and glass transition temperature. The method of compounding incompatible siloxanes and epoxy resins is effective and yet remains the state-of-the-art. Formation of interpenetrating network avoids phase separation, as siloxane is chemically bonded to epoxy resin and provides materials having desired properties and with more consistent results^{16,17}.

In the present study, an attempt has been made to synthesise siloxane-epoxy interpenetrating polymer network (IPN) using polyamidoamine as curing agent and γ -aminopropyltriethoxysilane (γ -APS)¹⁸⁻²⁰. A detailed account of characterisation of the resulting IPN is given here.

2. EXPERIMENTAL PROCEDURE

Calculated percentages of diglycidyl ether of bisphenol-A (DGEBA, GY250, Ciba-Geigy), epoxy equivalent 180-190 eq/kg, viscosity 10,000 cP) and hydroxyl-terminated polydimethylsiloxane [PDMS, viscosity 1000 cP, average molecular weight (M_w) = 1000] were thoroughly mixed (Table 1). Viscosity of the prepolymer was measured using Brookfield viscometer and a Fourier transform infrared (FTIR) spectrum was taken using Perkin-Elmer FTIR spectrometer. To establish the stability of the prepolymer, the sample was allowed to stand in a stability column at 30 °C

Table 2. Thermal, electrical and mechanical properties of IPN

Property	Siloxane (%)			
	0	10	20	30
Pot-life at 30 °C (min)	60	42	36	25
Exotherm (°C)	60	52	47	42
Percentage weight loss by TGA	29	22.004	19.42	12.732
Glass transition temperature by DSC (°C)	69.57	72	73.96	75.79
Heat distortion temperature (°C) [ASTM-D648]	74	77	80	83
Dielectric strength (V/mm) [ASTM-D149]	9.825	18.64	20.31	22.13
Comparative tracking index (V) [ASTM-D3638]	450	450-550	500-550	550
Volume resistivity (Ω -cm) [ASTM-D257]	2.23×10^{14}	$> 10^{14}$	$> 10^{14}$	$> 10^{14}$
Surface resistivity (Ω -cm) [ASTM-D257]	6.82×10^{12}	8.98×10^{13}	3.62×10^{14}	7.35×10^{14}
Arc resistance (s) [ASTM-D495]	104	107	110	113
Tensile strength (psi) [ASTM-D638]	5700	3544	2206	1027
Tensile modulus (psi $\times 10^{-6}$) [ASTM-D638]	2.27	0.2725	0.2526	0.2281
Percentage elongation [ASTM-D638]	5.30	5.88	8.73	10.83
Flexural strength (psi) [ASTM-D790]	12350	8492	6529	4740
Flexural modulus (psi $\times 10^{-6}$) [ASTM-D790]	0.3	0.262	0.176	0.1014
Hardness (Shore D) [ASTM-D2240]	84	75	72	66
Impact strength (kg/cm/cm ²) [ASTM-D256]	11.03	14.8	20.5	25.11

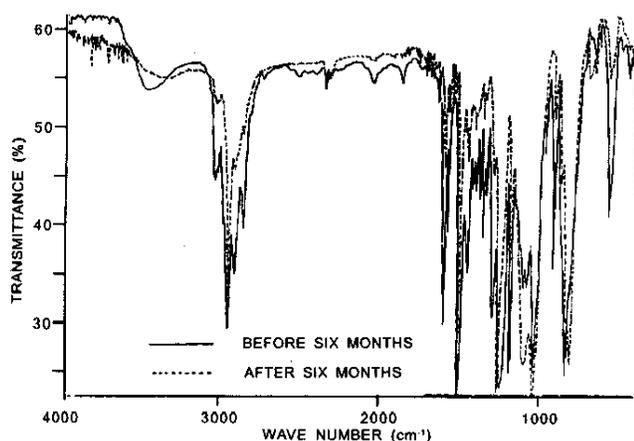


Figure 1. PDMS-DGEBA premix before and after six months of ageing.

for six months and viscosity and spectral studies were made on the sample thereafter. Polyamidoamine hardener (HY840, Ciba-Geigy) were used for curing the epoxy resin. For cross-linking DGEBA and PDMS, γ -APS was used as cross-linking agent with dibutyltindilaurate (DBTDL) as a catalyst. Stoichiometric quantities of polyamidoamine, γ -APS and DBTDL were added sequentially to the prepolymer blend. After evacuating the entrapped air, the resulting product was cast in a mould. Post-curing of the cured material was done at 70 °C for 10 hr.

Thermogravimetric analysis (TGA) was carried out using TGA-Mettler TA3000. Glass transition temperature was determined using a differential scanning calorimeter (DSC, Dupont 2000). The measurements were carried out from 0 °C to 350 °C under nitrogen gas at 25 °C/min. The morphology of the samples was examined by scanning electron microscopy (SEM).

Table 3. Viscosity of the prepolymer mix

Ratio of epoxy and siloxane (w/w)	Viscosity (cP) at 30 °C	
	Initial	After 6 months
0/100	10000	10500
10/90	23000	24500
20/80	39000	40000
30/70	52000	53700

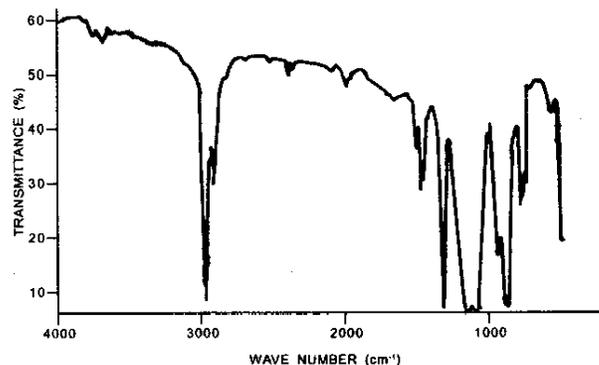


Figure 2. FTIR spectrum of PDMS-DGEBA IPN

Heat distortion temperature, tensile properties, flexural properties, impact strength, hardness (Shore D), dielectric strength, arc resistance, comparative tracking index and surface and volume resistivities were determined as per ASTM standards (Table 2).

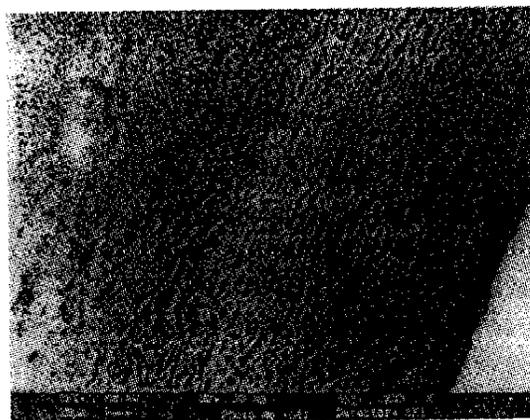
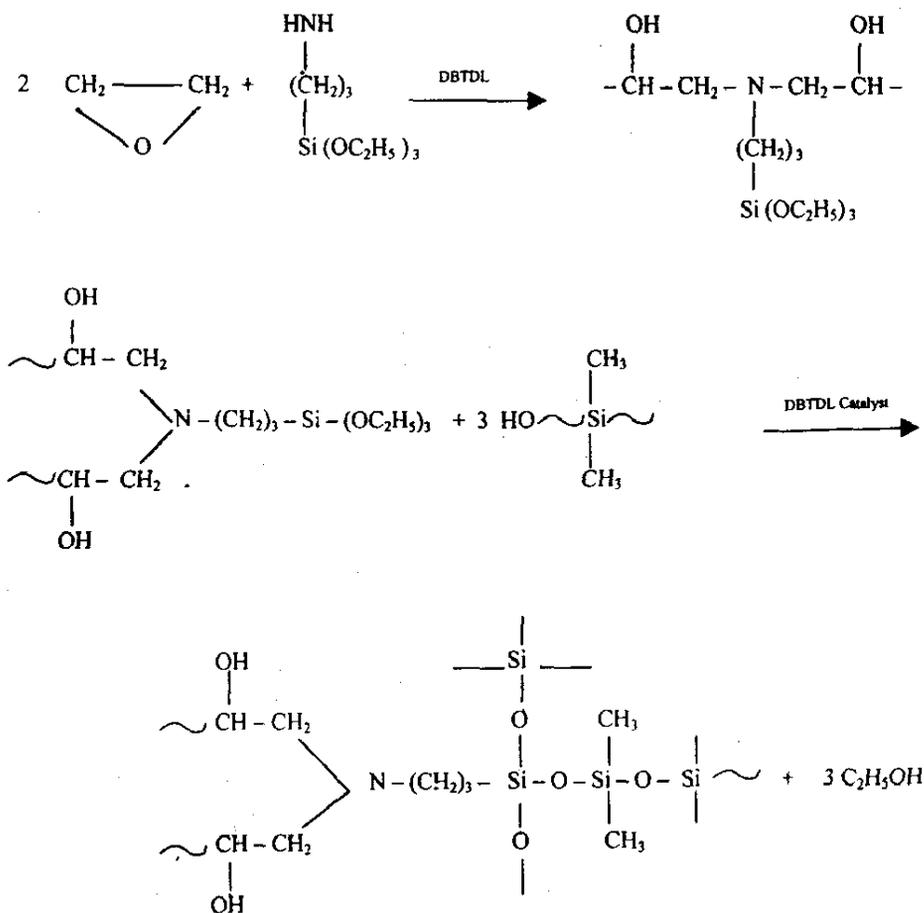


Figure 3. SEM photograph of PDMS-DGEBA IPN

3. RESULTS & DISCUSSION

Viscosity measurements (Table 3) and Fourier transform infrared (FTIR) spectral studies (Fig. 1) confirmed that the PDMS-DGEBA prepolymer was stable after six-month storage at 30 °C in a stability column.

When PDMS-DGEBA is cured, epoxy groups begin to cross-link, PDMS dispersed in the prepolymer on a molecular level also gets bonded to the cross-linked epoxy matrix forming an IPN.



From the FTIR spectral studies, it is evident that the epoxide ring is opened during the formation of network structure which is confirmed by the absence of absorption in the range $860\text{--}770\text{ cm}^{-1}$ and $1280\text{--}1230\text{ cm}^{-1}$ peaks (Fig. 2). The absorption peak between $2980\text{--}2850\text{ cm}^{-1}$ confirms the presence of asymmetric methyl group stretching in Si-CH_3 . Peaks at 1370 cm^{-1} and 960 cm^{-1} confirm the presence of $\text{Si-(CH}_2)_3$ group and residual Si-OH group, respectively. The SEM photographs of the IPN with 10 per cent PDMS (Fig. 3) show that the siloxane micro-domains are distributed all over the epoxy regions. DSC curves obtained for cured epoxy²¹ and siloxane-epoxy IPN show only single glass transition temperature, indicating the formation of a single polymer network (Fig. 4). Glass transition temperature is increased with the incorporation of PDMS (Table 2). Increase in glass transition temperature is attributed to the increase

in cross-link density, due to the presence of γ -APS, which acts as a co-curing agent²² in the presence of DBTDL catalyst.

The TGA data shows that the siloxane-epoxy IPN decomposes exothermally (Fig. 5). The decomposition exotherm follows the same pattern with different percentages of PDMS in the IPN. The decomposition of the cured resins begins at $300\text{ }^\circ\text{C}$ and peaks around $350\text{ }^\circ\text{C}$. It is observed from Fig. 5 and Table 2 that the decomposition exotherm of the IPN increases with increase in siloxane. Higher cross-link density and higher percentage of thermally stable silicone in the IPN play an important role in reducing the decomposition of the organic moiety. Low weight loss is encountered with increase in PDMS content in TGA (Table 2). Due to these factors, the material is suitable for application in high temperature operation inclusive of high voltage insulation, for an insulating material

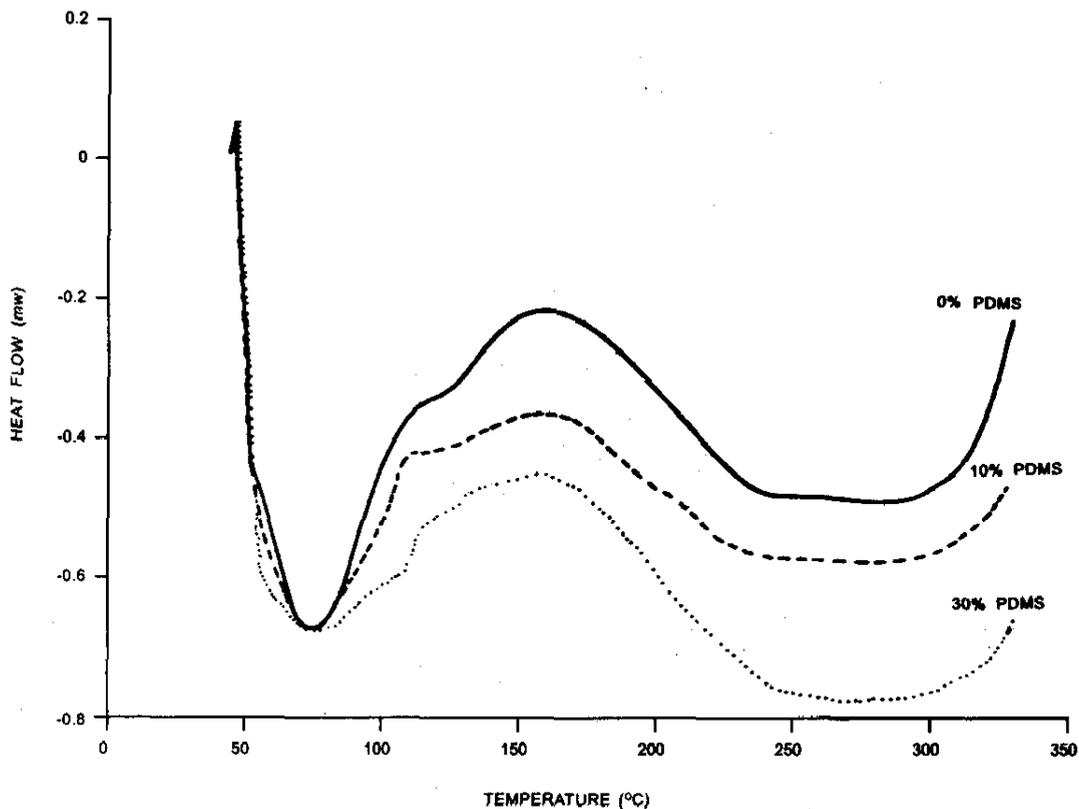


Figure 4. DSC curves of cured IPN

is expected to have high thermal stability to resist any damage due to dielectric heating²³. The heat distortion temperature is increased by the incorporation of siloxane in the matrix (Table 2), which is explained by the higher cross-link density. From the viscosity studies, it is observed that the viscosity increases with the increase in percentage of siloxane in the IPN (Table 1), while pot-life is lowered (Table 2). Low viscous polyamidoamine helps in maintaining the viscosity of the PDMS and there is no reduction in its particle size due to rise in temperature. Curing is initiated by the DBTDL at room temperature. As the curing starts, it is observed that viscosity increases gradually, and hence, there is a possibility of phase separation. However, increase in the cross-link density between PDMS and epoxy resin by the action of γ -APS, which also serves the purpose of a co-curing agent apart from the function of compatibiliser and the catalytic activity of DBTDL, contributes to the lowering of pot-life²⁴. The decrease in exotherm and pot-life reduces the shrinkage and hence lowers the internal stress, which favours the material for

encapsulation purposes to withstand high temperature and high voltage²⁵.

Incorporation of PDMS drastically reduces the tensile and flexural strengths and the hardness as expected (Table 2). This may be due to the large size of the polyamidoamine molecules involved in the cross-linking, elastomeric nature of siloxane, reduction in interlaminar carbon-carbon cross-linking density and lowering of internal stress by siloxane. This also influences the lowering of

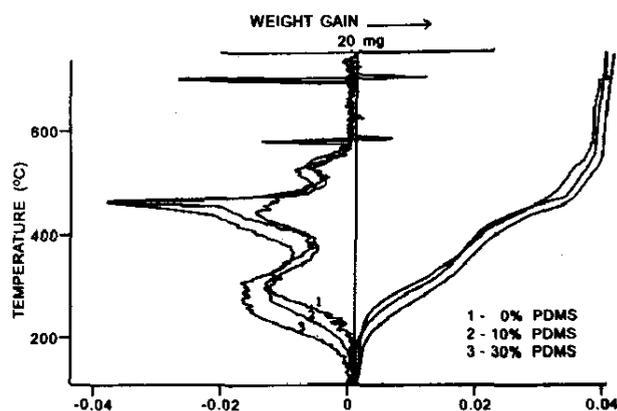


Figure 5. Thermogram (TGA) of IPN

tensile and flexural modulus and increasing the percentage elongation and impact strength (Table 2). The energy dissipating character of the siloxane moiety also increases the impact strength, percentage elongation, and reduces the tensile and flexural strengths.

The presence of PDMS content greatly influences dielectric strength of the IPN. It increases the electric potential gradient of the IPN to withstand without breakdown. Dielectric strength increases with increase in percentage siloxane content in the IPN (Table 2). The organo-inorganic moiety *Si-O-Si*, present in the IPN interrupts the continuity of carbon-carbon linkage, and hence reduces the possibility of forming carbonised path in the organic insulating material. Hence the tracking index is improved (Table 2). This characteristic indicates that the material will exhibit good electrical insulation even in a contaminated environment. From Table 2, it is observed that the volume and surface resistivities of the IPN also increase with the incorporation of PDMS. Hydrophobic nature of the siloxane is responsible for improving the resistivity of the IPN²⁶. It is also observed that increase in PDMS content increases the ability of the IPN to withstand the discharge of high voltage, low current arc across the surface without rendering it conductive²⁷.

Although there is a positive relationship between PDMS fraction and the extent of toughness enhancement²⁸ as expected, other mechanical properties deteriorate. Also, increasing the quantity of PDMS content in the system results in improved electrical and thermal characteristics, as expected. To optimise the benefit of improvement in electrical characteristics with a minimum loss in mechanical characteristics, the percentage of siloxane is minimised²⁹ to 10 per cent²¹.

4. CONCLUSION

PDMS-DGEBA IPN was synthesised from commercially available epoxy resin GY250 (Ciba-Geigy) and hydroxyl-terminated PDMS at room temperature. Polyamidoamine (HY840,

Ciba-Geigy) was used as a curative with γ -APS as a cross-linker and dibutyltindilaurate as a catalyst. The IPN was characterised by FTIR, SEM, viscosity, thermal, mechanical and electrical properties. Incorporation of PDMS in the epoxy matrix increased the viscosity and lowered the exotherm and pot-life. PDMS in the IPN increased both the glass transition temperature and the heat distortion temperature. Percentage weight loss was reduced on exposure to higher temperature conditions. Incorporation of PDMS reduced the tensile and flexural strengths and hardness. By reducing the tensile and flexural modulus, the siloxane moiety reduced the internal stress of the IPN, thereby improving its impact strength and percentage elongation. PDMS present in the IPN improved the dielectric strength, tracking index, arc resistance, and volume and surface resistivities. The siliconised epoxy IPN, with better impact and thermal resistance, may have applications in automobile and aerospace industries to withstand high temperature, and mechanical stress. With the improved electrical characteristics, the 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, and electrical, mechanical and thermal stresses.

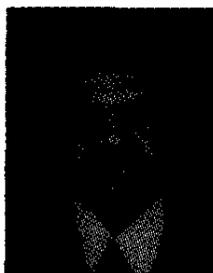
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Dr TV Thanikai Velan obtained his Ph.D. from Anna University in 1998. His areas of research work include: Adhesives, interpenetrating polymer network and composites. Presently, he is engaged in the development of castable engineering polymers.



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