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SYNTHESIS OF TERMINAL EPOXY FUNCTIONAL SILOXANES FOR MODIFICATION OF DIGLYCIDYL ETHER OF BIS-PHENOL A

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ABSTRACT

In this study, terminal epoxy functional poly dimethyl siloxanes (TEF PDMS) were synthesized by the hydrosilylation reaction of terminal silyl hydride functional with allyl glycidyl ether. The hydrosilylation reaction was characterized by FTIR and NMR. Samples of modified and unmodified PDMS were blended with commercial epoxy resin, diglycidyl ether of bis-phenol A (DGEBA), at various ratios using a polyamine as curing agent. Their damping and thermal properties were studied by DMA and TGA respectively. The tensile and impact properties were also determined. The results show that the addition of functionalised PDMS increases the flexibility of the cross linked network and also the thermal stability and water resistance.

KEYWORDS: DGEBA; resin; polysiloxanes; hydrosilylation; blending.

INTRODUCTION

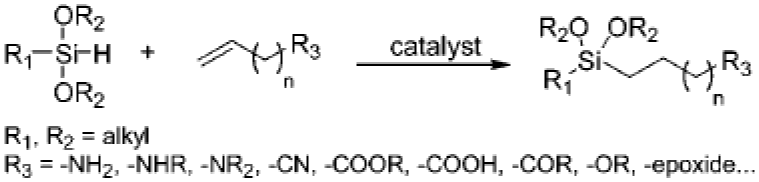
Epoxy resin has excellent mechanical, electrical and adhesion properties and is widely used as a high performance thermosetting material in many industrial and engineering fields [1-5]. Epoxy resins are also widely used for molding purposes and encapsulation of electronic components. Epoxy resins based on bisphenol A and epichlorohydrin (DGEBA) exhibit brittleness and low elongation after cure. This leads to low resistance to crack initiation and propagation. The usefulness of epoxy resins in many engineering applications is often limited by these disadvantages[6, 7].

Epoxies are modified by different methods. Generally, the modifiers can be classified into three types: reactive liquid rubbers, functionally terminated engineering thermoplastics, and inorganic/hybrid particles. Among the different elastomeric materials used for toughening of epoxy resin, it is found that hydroxyl terminated polydimethylsiloxane is the most suitable because of attractive properties like flexibility due to-Si-O-Si- linkage, high thermal and thermo oxidative stability, high moisture resistance, good dielectric properties and excellent UV and chemical resistance [8,9]. Organosiloxanes in general exhibit characteristics such as very low glass transition temperature (-1200C), moisture resistance, good electrical properties, high flexibility, good weatherability and good thermal and oxidative stability. In addition, because of their low surface energy and nonpolar structure polysiloxanes tend to migrate to the air-polymer interface and provide a very hydrophobic surface for the substrate. Therefore, the presence of siloxane should strongly influence the friction and wear behavior of modified epoxy resins.

Incorporation of PDMS into the epoxy matrix is generally difficult because of the poor compatibility between soft segments of PDMS and polar hard segments in epoxy, which largely results from a lack of hydrogen bonding. These materials generally exhibit a high degree of phase separation leading to poor thermo-mechanical properties and compositional heterogeneity due to limited segmental compatibility [10, 11]. So for the incorporation of polysiloxane in epoxy matrix we need to functionalise them. One of the major processes used to functionalize polysiloxanes is hydrosilylation of polyhydridosiloxanes [12].

HYDROSILYLATION

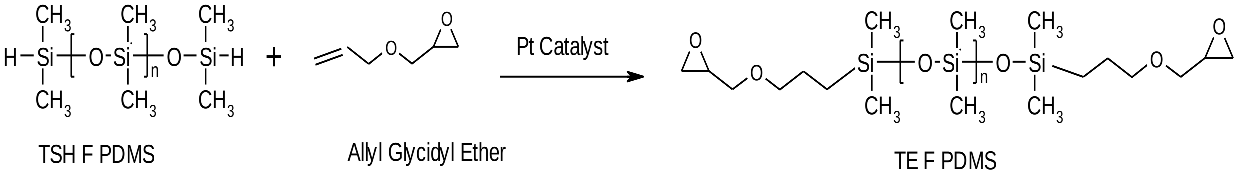
Hydrosilanes react with compound containing carbon-carbon multiple bonds when catalysed by transition metal complexes. This is referred to as hydrosilylation [13-15]. In this, the key step is the addition of hydridosilanes to unsaturated bonds, a topic that has been extensively reviewed [16,17]. The general sequence for hydrosilylation is given in Scheme 1



Scheme 1

A large variety of catalysts including transition metal complexes are available for the hydrosilylation reaction [18-25]. Among all metal catalysts (Pd, Pt, Rh), platinum-based catalysts are the most widely used.

In this study, hydrosilylation of allyl glycidyl ether has been carried out using polydimethyl siloxane (PDMS) and a complex catalyst, platinum (0)-1, 3 -divinyl-1, 1, 3, 3-tetramethyl disiloxane. The PDMS selected is TSHF PDMS (Terminal Silyl Hydride Functional PDMS). The hydrosilylation reactions is shown in Scheme 2



Scheme 2

The strategy adopted is to mix varying amount of these functionalised siloxanes with DGEBA to modify the characteristics of the latter. Since epoxide groups are present in the functionalised siloxanes, they are compatible with the epoxy resin at room temperature. Their damping, thermal, tensile and impact properties were studied.

EXPERIMENTAL

Materials

Epoxy resin GY 250(WPE 190) and triethylene tetramine hardener (TETA) HY951 were procured from Petro Araldite Pvt. Ltd. Chennai. TSHF PDMS [Poly(dimethyl siloxane) hydride terminated] (MW 3363)], platinum (0)-1, 3 -divinyl-1, 1, 3, 3-tetramethyl disiloxane complex catalyst and allyl glycidyl ether (99% assay) were supplied by Aldrich. Sodium hydroxide (M.W= 40, 97% assay) , hydrochloric acid , pyridine , phenolphthalein indicator were supplied by Merck India Ltd.

Curing of neat resin

Epoxy resin was mixed with 10wt% hardener and stirred well to make the mixture homogeneous. The resin was degassed in vacuum, poured into Teflon moulds and allowed to cure for 24 hrs at room temperature. Post curing was done at 100oC for 4 hours.

Curing of epoxy resin modified by siloxane

Epoxy resin was mixed with 2.5-10 wt % TSHF PDMS and the mixture was stirred well. 10wt % hardener was added, stirred and degassed in vacuum. The mixture was poured in to Teflon moulds and cured for 24 hrs at room temperature. Post curing was done at 1000C for 4 hours.

Functionalisation of siloxane (TSHF PDMS)

TSHF PDMS was functionalised by hyrosilylation reaction using allyl glycidyl ether.

I mol of PDMS was mixed with 3moles of allyl glycidyl ether and stirred in a stoppered conical flask using a magnetic stirrer. Platinum catalyst (approximately 100 ppm equivalent) was added and stirred for 20 hrs at a constant temperature of 850C. The crude product was cooled to room temperature, washed with methanol-water mixture to separate TEF

PDMS (Terminal epoxy functional PDMS) from the unreacted allyl glycidyl ether and dried in vacuum.

Modification of epoxy resin with functionalized PDMS

Epoxy resin was mixed with 2.5-10 wt% functionalized PDMS (TEF PDMS) and stirred well. Then 10w% hardener was added, stirred and degassed in vacuum. The mixture was poured into Teflon moulds and cured for 24 hrs at room temperature. Post curing was done at 1000C for four hours.

Characterisation Methods

Epoxy equivalent weight (EEW) determination

Epoxide equivalent (Weight per epoxide)

The epoxy content of liquid resins is frequently expressed as weight per epoxide (wpe) or epoxide equivalent which is defined as the weight of the resin containing on gram equivalent of epoxide. The epoxy content is also expressed as equivalent/Kg of the resin. Weight per epoxide values of the synthesised and commercial epoxy resins samples were determined by the pyridinium chloride method as per ASTM D 1652-73.

0.1 to 0.2 g of the epoxy resin was mixed with 2ml HCl in 25 ml pyridine. The mixture was heated to reflux on a water bath for 45 minutes. The solution was cooled to room temperature and the un-reacted acid present in it was estimated by back titration with standard NaOH solution (0.1N) using phenolphthalein indicator. A blank was also carried out under the same reaction conditions.

Epoxide equivalent =N x V/w, where N is the strength of alkali, V is the volume of alkali used up and w is the weight of the resin. Epoxide equivalent can be obtained as eq/ Kg from which wpe value of the resin can be calculated.

Spectral studies

The extend of hydrosilylation was studied using NMR spectroscopy. NMR spectra of unmodified PDMS (TSHF PDMS) and functionalised PDMS (TEF PDMS) were taken.

Thermal studies

Thermal stability of the neat and modified cured resin samples was assessed using thermo gravimetric analyser (TGA Q50, TA Instruments) over a temperature range from room temperature to 600oC at a heating rate of 10oC/min. The damping qualities were measured by dynamic mechanical analysis (DMA-Q800, Universal V4.0C TA Instruments) using dual cantilever mode over a temperature range from room temperature to 200□C at a heating rate of 3□C/ min and a frequency of 1 Hz.

Mechanical properties

The samples, after post curing, were tested for tensile strength, modulus and impact strength, taking six trials in each case. The tensile properties were determined on a Schimadzu Autograph Universal Testing Machine (ASTM D 638-89) and Izod impact strength was measured on a Zwick impact tester as per ASTM D 256 specifications.

RESULTS AND DISCUSSION

Epoxy equivalent weight determination

The WPE of PEF PDMS was found to be 1655.31 which is roughly half of the molecular weight of the starting material. This indicates that 2 epoxy group is introduced in to PSHF PDMS. This can be confirmed from spectral data also.

Spectral studies

The The 1H NMR spectrum of TSHF PDMS and TEF PDMS are shown in Fig.1and Fig.2. The Si – H resonance at δˆ 4:7 ppm in TSHF PDMS is almost absent in the spectrum of TEF PDMS. In addition, the peaks at δ ˆ 0:5;1.6 and 3.4 ppm are the resonance peaks of the silylpropyl group, while those at δ ˆ 2:5; 2.7 and 3.1 ppm represent the resonance peaks of the epoxide group. These results clearly indicate that the hydrosilyation was successful.

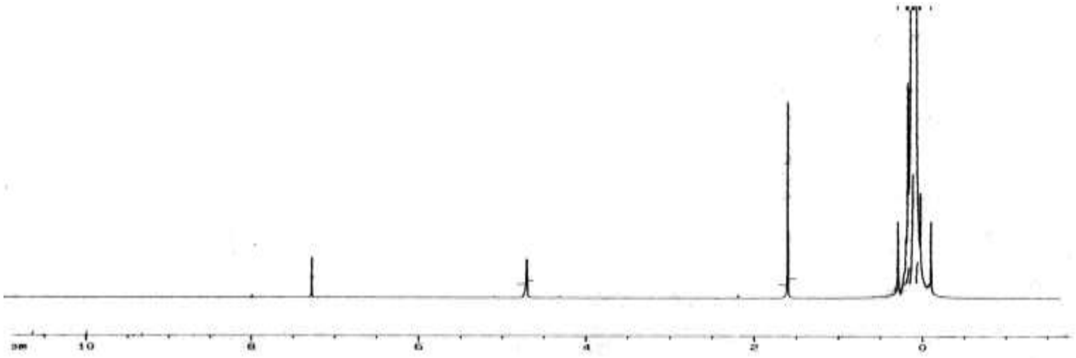


Fig.1 NMR spectrum of TSHF PDMS (Terminal Silyl Hydride Functional PDMS)

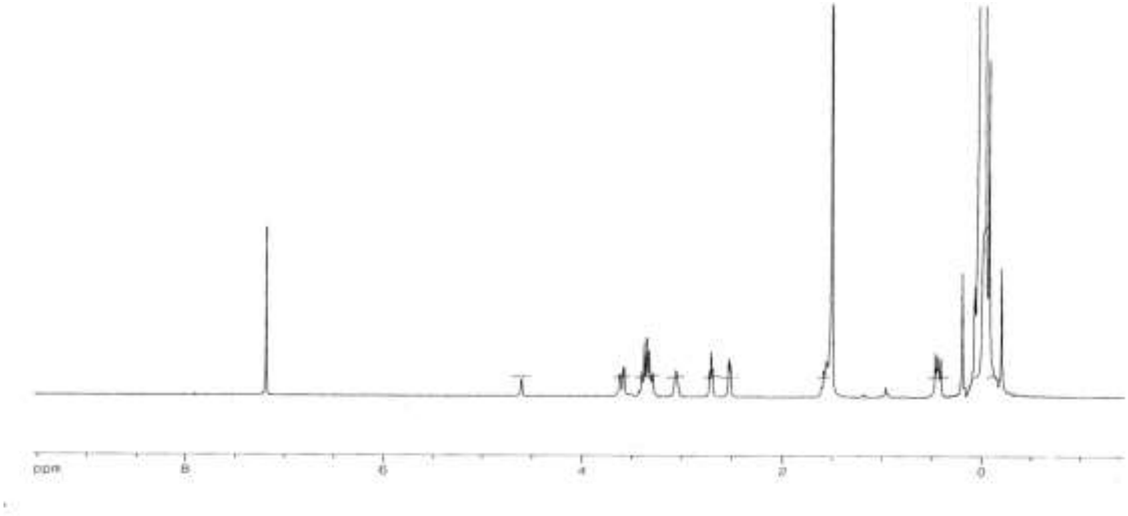


Fig.2 NMR spectrum of TEF PDMS (Terminal Epoxy Functional PDMS)

Thermal studies

The thermal stability of the cured blends was investigated by TGA. Comparative values of the Onset temperature, temperature at maximum rate and temperature of half loss and residue (%) from TGA curve on using TSHF PDMS and TEF PDMS for modification along with corresponding values for the neat resin are given in Table I. The thermal properties of cured blends having different concentrations of functionalised PDMS are given in Table II. Functionalised PDMS/DGEBA blends have marginally better thermal stability.

Table 3.I TGA characteristics of blends of DGEBA, PDMS and functionalised PDMS

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
5% TSHF PDMS/ DGEBA	344	366	379	7.89

5% TEF PDMS/ DGEBA	345	369	382	8.43

Table 3.2 TGA characteristics of blends having different concentrations of functionalised PDMS

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
DGEBA	343	364	378	6.68
2.5% TEF PDMS/ DGEBA	344	366	380	7.36
5% TEF PDMS/ DGEBA	345	369	381	8.43
7.5% TEF PDMS/ DGEBA	346	372	382	9.06
10% TEF PDMS/ DGEBA	349	373	386	11.55

The siloxane segments improve thermal stability probably due to better heat dissipation by the siloxane chains, thus reducing the temperature at the epoxy networks. The thermal stability and the residual weight are improved when greater amount of siloxane segments are incorporated into the cured epoxy networks.

Dynamic Mechanical Analysis

The storage modulus values of blends containing the modified and unmodified PDMS as well as neat epoxy are shown in Fig.3 The functionalized PDMS/DGEBA blends have higher crosslink density due to the cross linking of the epoxide groups of PDMS resulting in higher values of storage modulus.

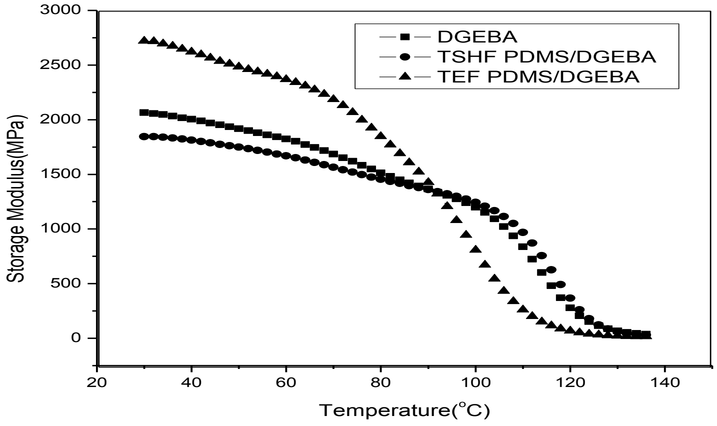


Fig3 Storage modulus of (a) DGEBA (b) TSHF PDMS/DGEBA and (c) TEF PDMS/ DGEBA

The tan δ (loss factor) values are shown in Fig.4. The shape of the loss spectra can give additional information about the nature of the cross linked networks. The amplitude of the damping peak (tan δ_{max}) becomes lower as the distance between the crosslink decreases [26]. The tan δ_{max} for neat DGEBA decreases on blending with siloxane indicating significant plasticizing effect. The glass transition temperature T_g corresponding to tan δ peak of neat DGEBA decreases when functionalized siloxanes are incorporated. The lowering of T_g is due to the flexible siloxane segments in the co- polymer.

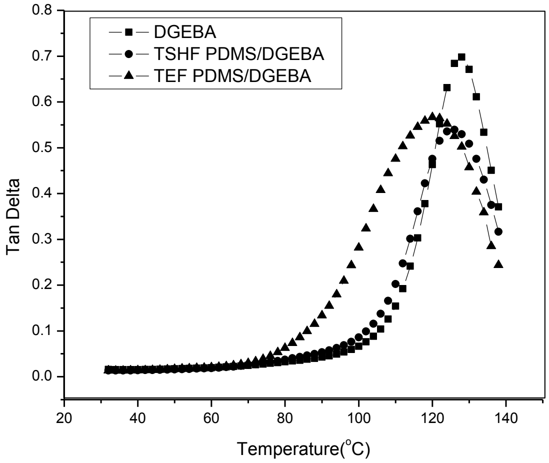


Fig. 4 Tan δ relaxations of (a) DGEBA (b) TSHF PDMS/DGEBA and (c) TEF PDMS/ DGEBA

Mechanical properties

The impact strength increases with increase in concentration as shown in Fig.5. Beyond 5% the increase is marginal. The increase in impact strength is due to the energy dissipation by the soft siloxane segments which occurred during the propagation of the fracture.

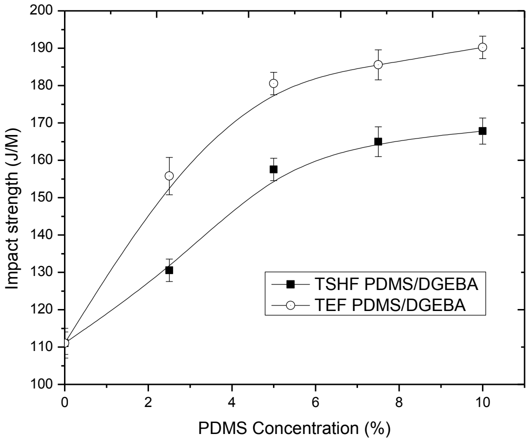


Fig.5 Impact strength of modified resin Vs PDMS concentration

Tensile strength decreases with increase in concentration of PDMS (Fig. 6). This is due to the presence of flexible siloxane segments in the cross linked networks of the epoxy resin blend .The decrease in tensile strength is less pronounced in the case of modified PDMS/ epoxy blends due hydrosilylation which enhances the compatibility with the neat resin

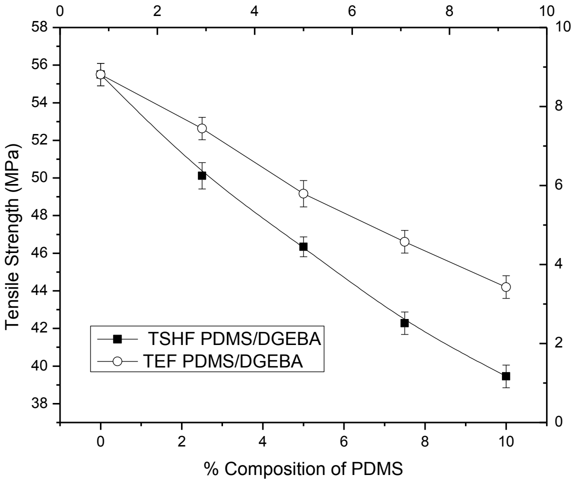


Fig.6 Tensile strength of modified resin Vs PDMS concentration

Fig.7 shows the variation of modulus with concentration of PDMS. The modulus decreases with increase in concentration of PDMS due to the presence of the soft segments of siloxane. The decrease in modulus is marginal in the case of functionalised siloxane epoxy blends due to the increased crosslink density.

The variation of enegy absorption with PDMS concentration is shown in Fig. 8. At 5% PDMS concentration, the energy absorption of the blend is at a maximum. The increase is due to greater energy dissipation by the soft siloxane segments. Energy absorption decreases due to lack of compatibilisation at higher concentrations of PDMS. The increase in energy absorption of functionalised PDMS is due to compatibilisation re+sulting from functionalisation.

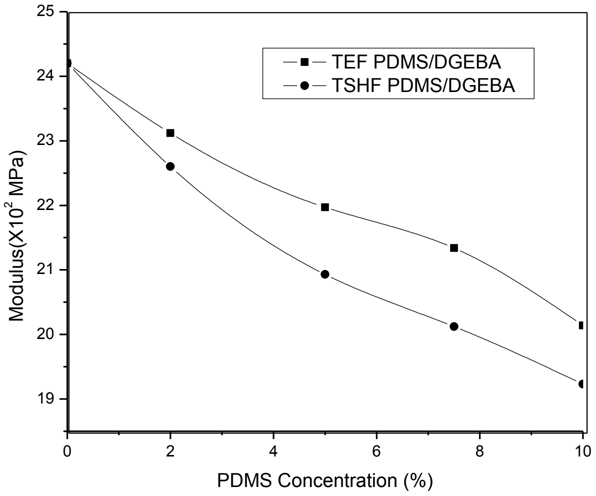


Fig.7 Modulus of modified resin Vs PDMS concentration

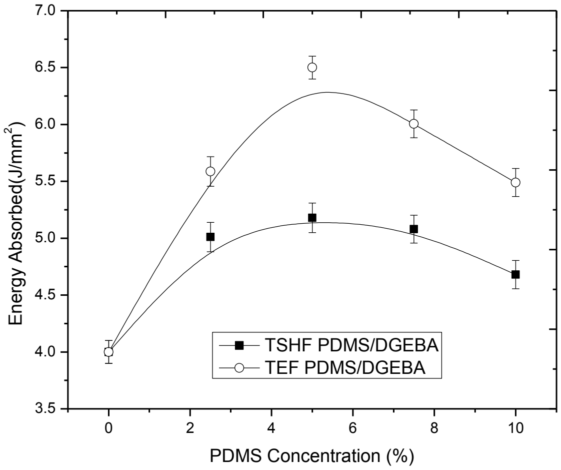


Fig.8 Energy absorbed of modified resin Vs PDMS concentration

At 5% PDMS concentration, the elongation at break of the blend (Fig. 9) is at maximum. The increase is due to the presence of flexible siloxane segments. Elongation decreases due to lack of compatibilisation at higher concentration of PDMS.

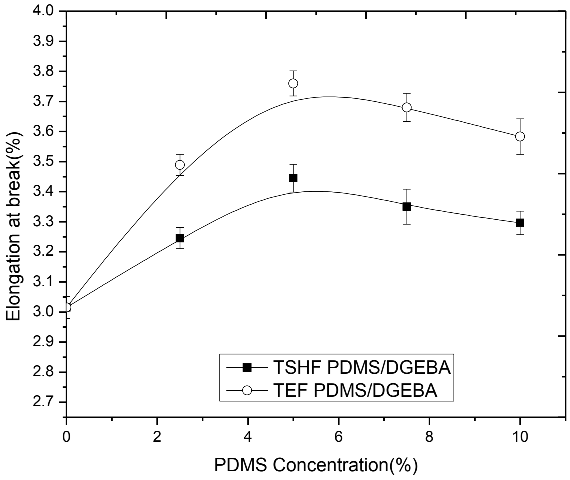


Fig.9 Elongation at break of modified resin Vs PDMS concentration

Water Absorption

The percentage water absorption of the various PDMS/DGEBAs is given in Fig.10. Siloxanes lowered the water absorption of epoxy resin due to the hydrophobic nature of silicon molecule and its surface enrichment character thereby exhibiting lower permeability towards water molecules. The functionalised PDMS blend shows increased water resistance.

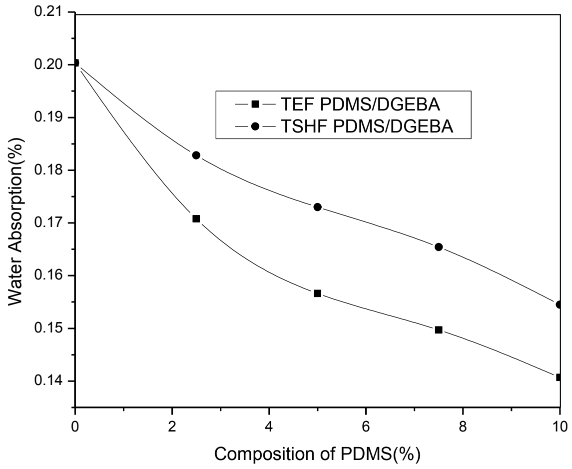
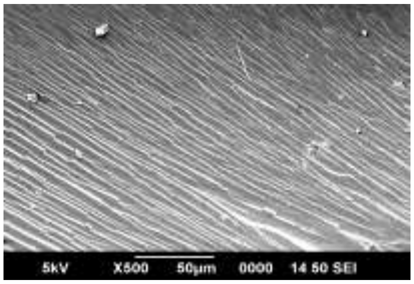


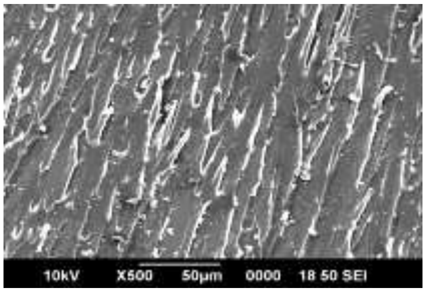
Fig. 10 Water absorption versus concentration of PDMS

Morphological studies

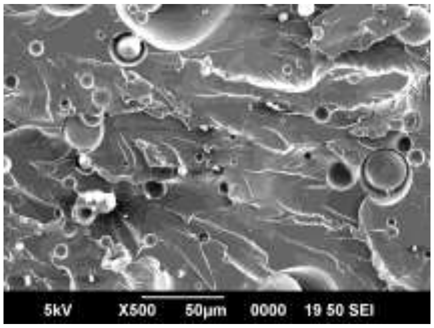
SEM micrograph of the unmodified epoxy resin and modified epoxy resin are given in Fig.11. Fracture SEM micrograph of the unmodified epoxy resin (Fig. 11 a) paths are mostly straight and constitute failure bands. It is a typical case of brittle fracture. Multilevel fracture paths with ridges and wavy crests indicate energy absorption on a large scale during failure in the case of terminal silyl hydride functional PDMS (TSHF PDMS/DGEBA) modified epoxy resin (Fig. 11 b). The fracture surface shows furrows and cavitation in the case of terminal epoxy functional PDMS (TEF PDMS/DGEBA) modified epoxy resin. (Fig.11 c). The circular depressions represent the sites of rubber domains. Considerable stress whitening is also observed. The rubber particles dissipate the bulk strain energy by cavitation leading to reduction of yield stress of the blend. As a result, shear band formation is enhanced by the voids in the matrix caused by cavitated rubber particles. The superior energy absorption characteristics of the TEF PDMS modified epoxy are evident from the comparison of micrographs.



11 (a)



11(b)



11(c)

Fig 11 Scanning electron micrographs of the fracture surface of a) Neat DGEBA (b) TSHS-PDMS/DGEBA (c) TEF-PDMS/DGEBA

CONCLUSIONS

The terminal epoxy functional siloxanes can be synthesized by hydrosililation reaction. The epoxy-functionalised PDMS blends with DGEBA show substantial improvement in thermal stability than neat DGEBA as evident from TGA and damping data. The thermal stability of the blend series improves as a greater amount of siloxane components are incorporated into the cured networks. There is only marginal fall in the mechanical properties due to the addition of PDMS derivatives. The impact strength increases with increase in concentration of PDMS. The epoxy-PDMS blends show appreciable water resistance also.

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