

## Original Article

# Synthesis of pendant epoxy functional polydimethyl siloxane for modification of Diglycidyl Ether of Bis-phenol A

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### Abstract

In this study, pendant epoxy functional poly dimethyl siloxanes were synthesized by the hydrosilylation reaction of pendant silyl hydride functional polydimethyl siloxane with allyl glycidyl ether. The hydrosilylation reaction was characterized by spectroscopic techniques. Samples of pendant epoxy functional poly dimethyl siloxanes and pendant silyl hydride functional polydimethyl siloxane were blended with commercial epoxy resin, diglycidyl ether of bis-phenol A, at various ratios using a polyamine as curing agent. The results show that the addition of functionalised poly dimethyl siloxanes increases the flexibility of the cross linked network and also the thermal stability and water resistance.

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**Key words:** DGEBA; resin; polysiloxanes; hydrosilylation; blending.

### 1. Introduction

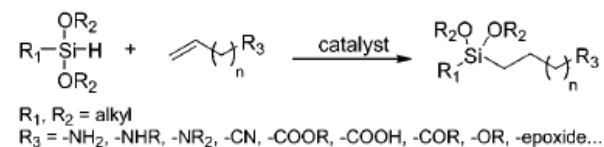
Epoxy resin exhibits many desirable properties, such as high strength and modulus, excellent chemical and solvent resistance, good thermal and electrical properties and outstanding adhesion to various substrates, and easy process ability under various conditions [1-5]. Epoxy resins are also widely used as molding compounds and encapsulation of electronic components. However, their inherent brittleness is a major drawback and limits their use in high performance applications [6, 7]. Among the different elastomeric materials used for toughening of epoxy resin, it is found that hydroxyl terminated polydimethylsiloxane (PDMS) 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].

Incorporation of a macrodiol such as 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 the lack of hydrogen bonding. These materials generally exhibit a high degree of phase separation resulting in poor thermo-mechanical properties and compositional heterogeneity resulting from poor 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 polyhydrosiloxanes [12].

### 1.2. Hydrosilylation

Hydrosilanes react with compound containing carbon-carbon multiple bonds when catalyzed by transition metal complexes. This is referred to as hydrosilylation [13-15]. In this, the key step is the addition of hydrosilanes 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 PSHF PDMS (Pendant Silyl Hydride Functional PDMS).

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.

## 2. Experimental

### 2.1 Materials

Epoxy resin GY 250(WPE 190) and triethylene tetramine hardener (TETA) HY951 were procured from Petro Araldite Pvt. Ltd. Chennai. PSHF PDMS [Poly (dimethylsiloxane-co-methylhydrosiloxane), trimethylsilyl terminated containing 4% methylhydrosiloxane ( $M_w$  5364)], platinum (0)-1, 3 -divinyl-1, 1, 3, 3-tetramethyl disiloxane complex catalyst and allyl glycidyl ether (99% assay) were supplied by Aldrich. 1, 4-dioxane, methyl cellosolve, cresol red indicator and methanol were supplied by Merck India Ltd.

### 2.2 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 100°C for 4 hours.

### 2.3 Curing of epoxy resin modified by siloxane (PSHF PDMS)

Epoxy resin was mixed with 2.5-10 wt % PSHF 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 100°C for 4 hours.

### 2.4 Synthesis of pendant epoxy functional Polydimethyl siloxane (PEF PDMS)

PEF PDMS was functionalised by hydrosilylation reaction using allyl glycidyl ether.

1 mole of PDMS was mixed with 5 moles 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 85°C. The crude product was cooled to room temperature, washed with methanol-water mixture to separate PEF PDMS (Pendant epoxy functional PDMS) from the unreacted allyl glycidyl ether and dried in vacuum.

### 2.5 Modification of epoxy resin with synthesized PEF PDMS

Epoxy resin was mixed with 2.5-10 wt% functionalized PDMS (PEF 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 100°C for four hours.

## 2.6 Characterisation Methods

### a) Weight Per Epoxy (WPE) determination

A 0.2 N HCl / dioxane solution was prepared by placing 12.5 ml of methanol and 4.1 ml of HCl (35%) in a 250 ml volumetric flask, and then adding 1, 4-dioxane to make up 250 ml. NaOH (2g) was dissolved in 50 ml of water in a 500 ml flask; then a mixture of methyl cellosolve (MC, 150 ml) and methanol (350ml) were added into the flask to obtain a roughly 0.1 N NaOH solution.

The sample was dissolved in 20 ml dioxane. HCl/dioxane solution (0.2N, 27ml) was then added and mixed well. The mixture was heated to 40°C for 2hrs and then cooled to room temperature. The obtained solution was titrated with 0.1 N NaOH solution using cresol red as indicator. The same steps were executed with the blank solution and the WPE was calculated using the following equation.

$$WPE = \frac{W \times N_V \times 1000}{(B-A) \times F}$$

where W is the weight of the sample used, g;  $N_V$  the weight of the residue as % of the original weight after heating in an oven at 150°C for 30 min, B the volume of the NaOH solution used in the blank solution, ml; A the volume of the NaOH solution used in the sample solution and F the concentration of the NaOH solution. WPE values of epoxy resin and functionalized PDMS were found to be 190 and 1274.31 respectively

### b) Spectral studies

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

### c) Thermal studies

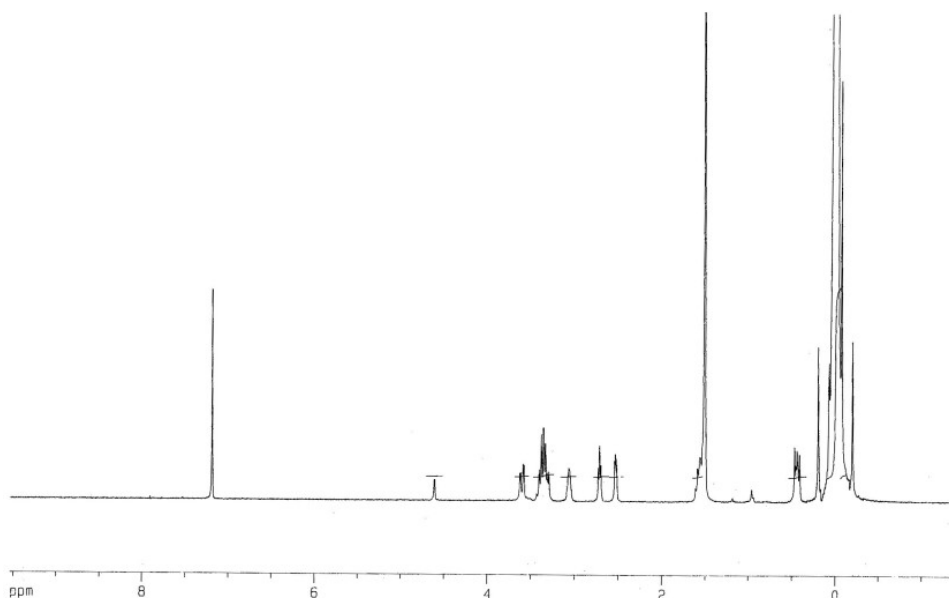
Thermal stability of the neat and modified cured resin samples was assessed using thermo gravimetric analyser (TGA Q50, TA Instruments) over a temperature range from room temperature to 600°C at a heating rate of 10°C/min. The damping qualities were measured by dynamic mechanical analysis (DMA-Q800, 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.

### d) Mechanical properties

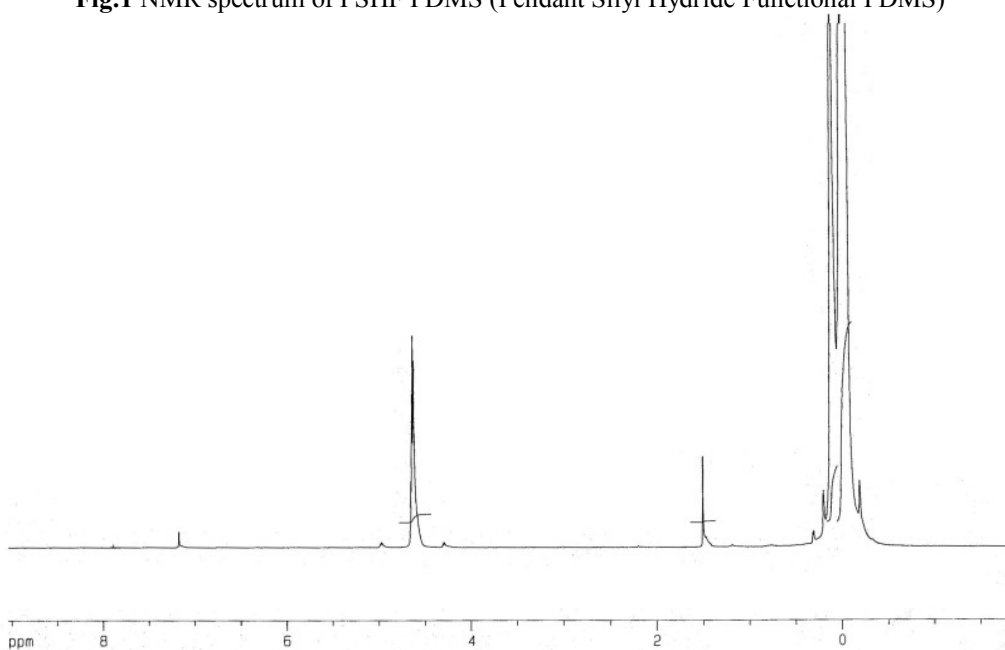
The samples, after post curing, were tested for tensile strength, modulus and impact strength, taking six trials in each case. The tensile properties were determined on a Shimadzu Autograph Universal Testing Machine (ASTM D 638-89) and Izod impact strength was measured on a Zwick impact tester as per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

### e) Water Absorption

Water absorption was tested as per ASTM D 570. For the water absorption test, the specimens were dried in an oven for



**Fig.1** NMR spectrum of PSHF PDMS (Pendant Silyl Hydride Functional PDMS)



**Fig.2** NMR spectrum of PEF PDMS (Pendant Epoxy Functional PDMS)

a specified 24hr and 80<sup>0</sup>C and then placed in a desiccators to cool. Immediately upon cooling, the specimens are weighed. The material is then emerged in water at room temperature for 24 hours. Specimens are removed, patted dry with a lint free cloth, and weighed.

#### **f) Morphological Studies.**

Morphology of the blends studied using scanning electron (SEM) micrographs. The SEM observations reported in the present study were made on the fracture surface of the tensile specimens.

### **3 Results and Discussion**

#### **3.1 Weight per epoxy (WPE) determination**

The WPE of PEF PDMS was found to be 1274.31 which is roughly one by fifth of the molecular weight of the starting material. This indicates that 4 to 5 epoxy group is introduced in to PSHF PDMS. This can be confirmed from spectral data also.

#### **3.2 Spectral studies**

The The <sup>1</sup>H NMR spectrum of PSHF PDMS and PEF PDMS are shown in Fig.1 and Fig.2. The Si – H resonance at

$\delta$  4:7 ppm in PSHF PDMS is almost absent in the spectrum of PEF PDMS. In addition, the peaks at  $\delta$  0.4; 1.5 and 3.4 ppm are the resonance peaks of the silylpropyl group, while those at  $\delta$  2.5; 2.7 and 3.1 ppm represent the resonance peaks of the epoxide group. These results clearly indicate that the hydrosilylation was successful.

### 3.3 Thermal studies

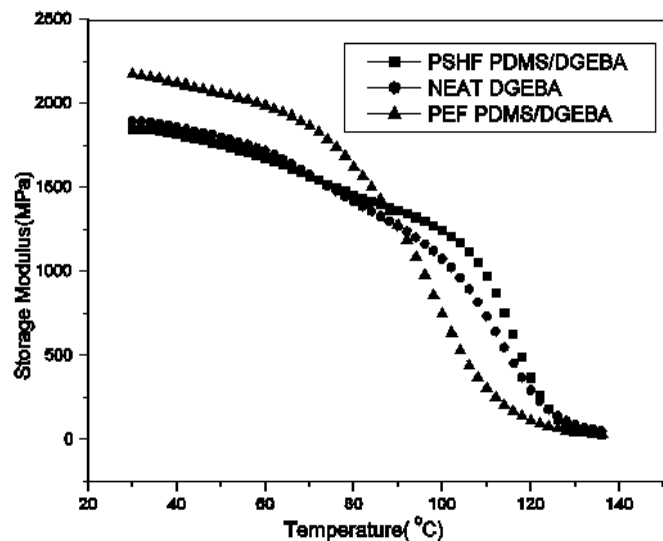
The thermal stability of the cured Neat DGEBA and blends were investigated by TGA. Comparative values of the Onset temperature, temperature at maximum rate and temperature of half loss and residue (%) on using PSHF PDMS and PEF PDMS for modification along with corresponding values for the neat resin 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.

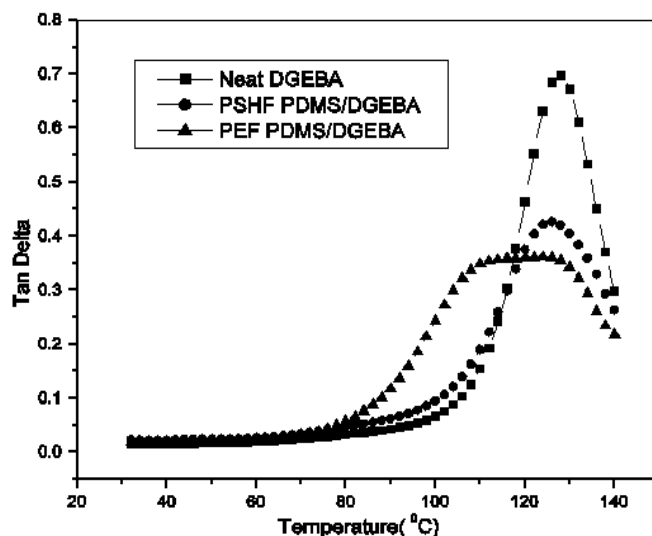
The siloxane segments improve thermal stability probably due to better heat dissipation by the siloxane chains, thus reducing the temperature at the epoxy networks. The thermal stability and the residual weight are improved when greater amount of siloxane segments are incorporated into the cured epoxy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

### 3.4 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.



**Fig.3** Storage modulus of (a) DGEBA (b) PSHF PDMS/DGEBA and (c) PEF PDMS/DGEBA



**Fig.4** Tan  $\delta$  relaxations of (a) DGEBA (b) PSHF PDMS/DGEBA and (c) PEF PDMS/DGEBA

The tan  $\delta$  (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 ( $\tan \delta_{\max}$ ) becomes lower as the distance between the crosslink decreases [26]. The  $\tan \delta_{\max}$  for neat DGEBA decreases on blending with siloxane indicating significant plasticizing effect. The glass transition temperature  $T_g$  corresponding to  $\tan \delta$  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. The  $T_g$  and  $\tan \delta_{\max}$  for the neat DGEBA and the blends are shown in Table III

### 3.5 Mechanical properties

Fig.5 shows the variation of impact strength with the addition of siloxanes. The impact strength increases with increase in concentration of PDMS. 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.

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 functionalised PDMS/ epoxy blends due hydrosilylation which enhances the compatibility with the neat resin

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

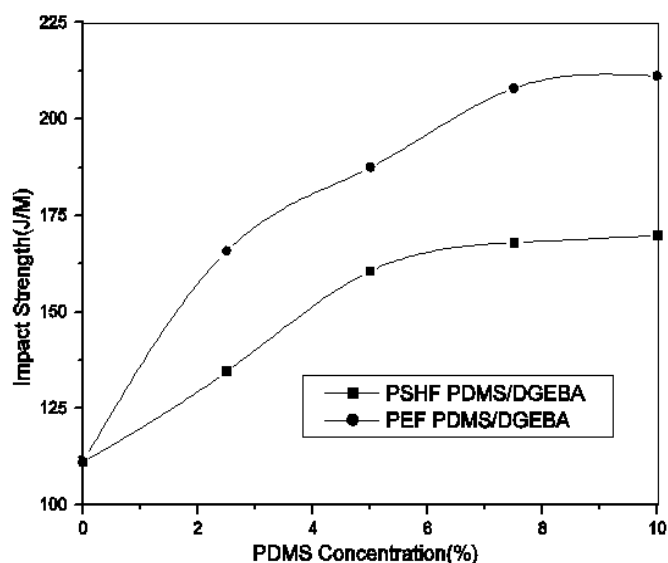


Fig.5 Impact strength of modified resin Vs PDMS concentration

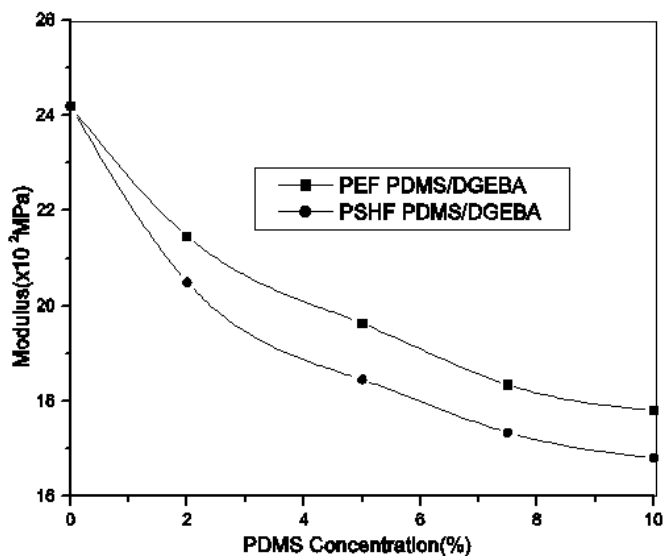


Fig.7 Modulus of modified resin Vs PDMS concentration

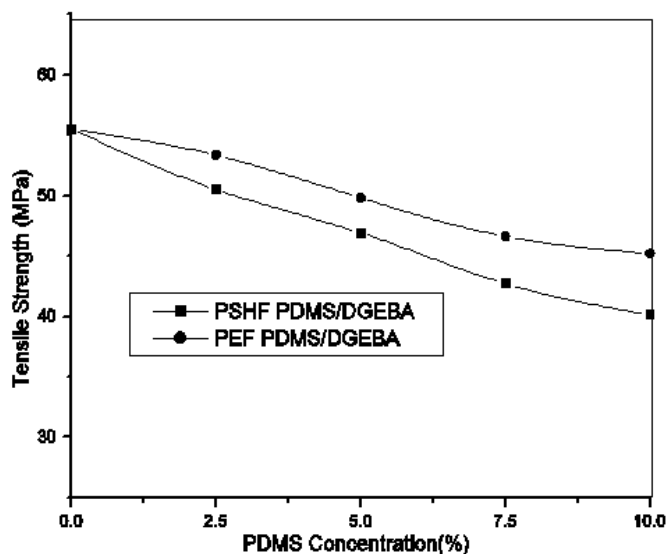


Fig.6 Tensile strength of modified resin Vs PDMS concentration

marginal in the case of functionalised siloxane epoxy blends due to the increased crosslink density.

The variation of energy 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 resulting from functionalisation.

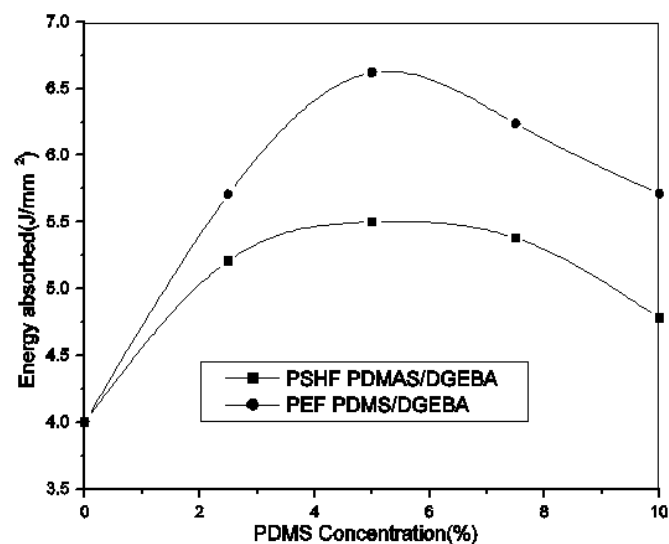


Fig.8 Energy absorbed of modified resin Vs PDMS concentration

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.

### 3.6 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

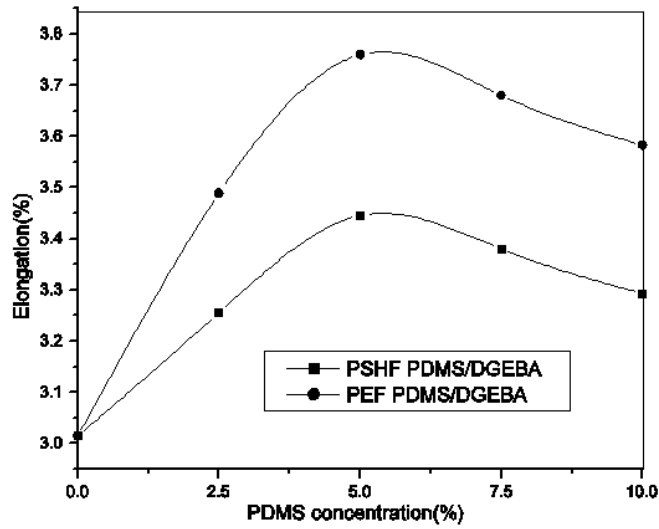


Fig.9 Elongation at break of modified resin Vs PDMS concentration

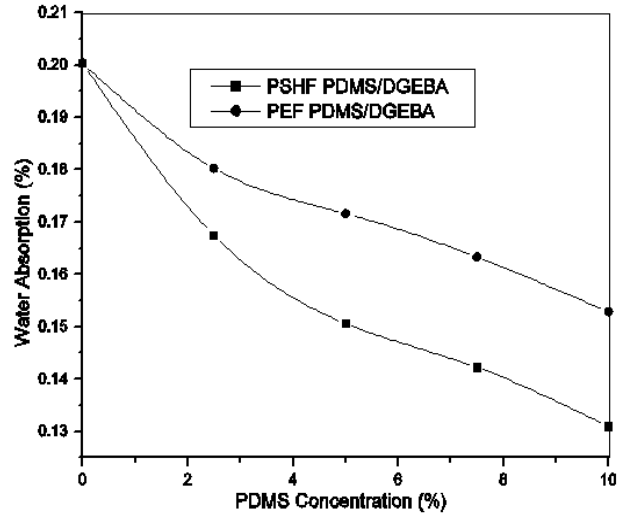


Fig.10 Water absorption versus concentration of PDMS

Table 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	343.02	364.65	378.76	6.68
5%PSHF PDMS / DGEBA	344.23	366.88	380.23	7.94
5% PEF PDMS / DGEBA	346.70	369.83	387.43	8.58

Table II. 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 (%)
2.5% PEF PDMS / DGEBA	343.55	365.21	386.22	7.65
5% PEF PDMS / DGEBA	346.70	369.83	387.43	8.58
7.5% PEF PDMS / DGEBA	347.43	375.35	388.63	9.27
10% PEF PDMS / DGEBA	349.46	376.18	396.43	13.93

Table III. DMA characteristics of blends of DGEBA and functionalized PDMS

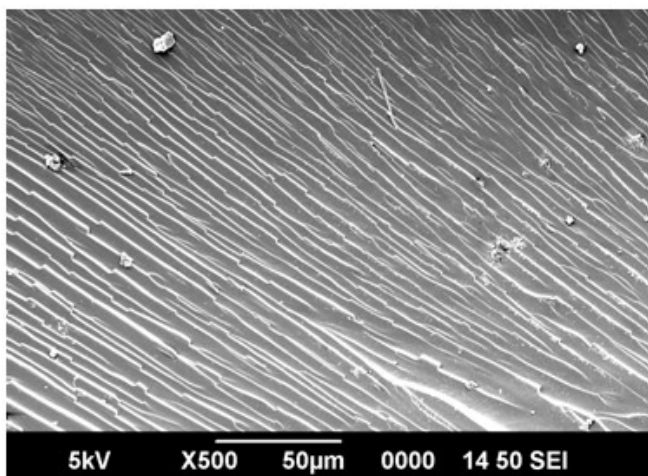
Resin	(Tan δ) <sub>max</sub>	T <sub>g</sub> (°C)
DGEBA	0.6981	128 °C
5 % PSHF PDMS / DGEBA	0.4263	126 °C
5 % PEF PDMS / DGEBA	0.3614	124 °C

water molecules. The functionalised PDMS blend shows increased water resistance.

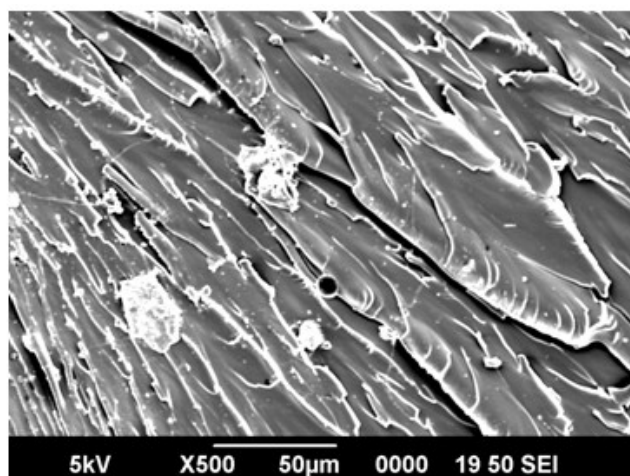
### 3.7 Morphological studies

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

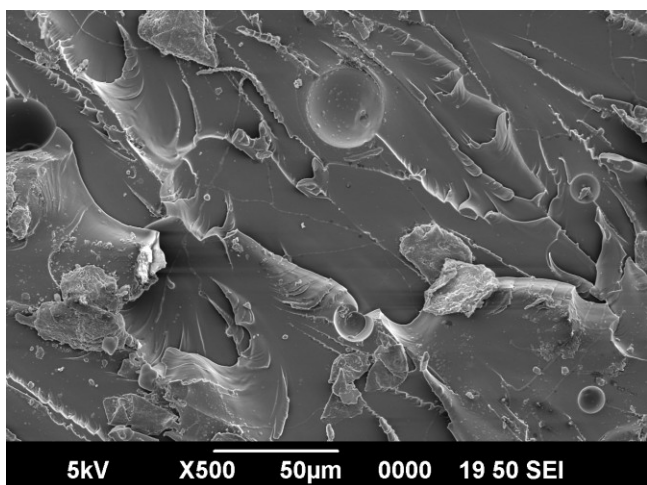
and wavy crests indicate energy absorption on a large scale during failure in the case of terminal silyl hydride functional PDMS (PSHF PDMS/DGEBA) modified epoxy resin (Fig. 11 b). The fracture surface shows furrows and cavitations in the case of terminal epoxy functional PDMS (PEF PDMS/DGEBA) modified epoxy resin. (Fig.11c). The circular depressions represent the sites of rubber domains. Considerable stress whitening is also observed. The rubber particles dissipate the bulk strain energy by cavitations



**Fig 11 (a)** Scanning electron micrographs of the fracture surface of DGEBA



**Fig 11 (b)** Scanning electron micrographs of the fracture surface of PSHS-PDMS/DGEBA



**Fig 11 (c)** Scanning electron micrographs of the fracture surface of PEF-PDMS/DGEBA

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 PEF PDMS modified epoxy are evident from the comparison of micrographs.

#### 4. Conclusions

The pendant epoxy functional siloxanes can be synthesized by hydrosilylation 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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