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Ageing Studies of Terminal and Pendant Epoxy Functional Polydimethyl Siloxane Blended DGEBA Resin

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Abstract: In this study, Terminal epoxy functional poly dimethyl siloxane (TEF PDMS) and Pendant epoxy functional PDMS (PEF PDMS) were prepared by hydrosilylation. Hydrosilanes react with compound containing carbon-carbon multiple bonds when catalyzed by transition metal complexes. This is referred to as hydrosilylation. Epoxidised siloxane is used to blend with Diglycidyl ether of bisphenol A (DGEBA). These blends were subjected to ageing studies and the results compared with those of the neat resin. The post-cured samples of the neat DGEBA, DGEBA/TEF PDMS blend (5 wt %) and DGEBA/PEF PDMS 15 wt%) were aged in a temperature controlled air oven kept at 100 °C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for tensile properties, impact strength and water absorption

Keywords: DGEBA, Siloxane, Blending, Ageing, Hydrosilylation

I. INTRODUCTION

Epoxy resins constitute a class of thermosets containing more than one epoxide groups per molecule which are very reactive to many substrates [1]. The first and still the most important, commercial epoxide resins are reaction products of bis-phenol A and epichlorohydrin [2]. 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 [3]-[5]. 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]. Epoxy resins are generally exposed to harsh environment and this leads to aging of epoxy resin [8],[9]. Epoxy resin can be modified by several Methods. 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 [10,11].

Incorporation of PDMS into the epoxy matrix is generally difficult because of the poor compatibility. [12]. 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 [13].

Hydrosilanes react with compound containing carbon-carbon multiple bonds when catalyzed by transition metal complexes. This is referred to as hydrosilylation [14]- [18]. In this study Terminal epoxy functional PDMS was synthesised from terminal hydride functional PDMS and Pendant epoxy functional PDMS was synthesised from Pendant silyl hydride functional PDMS. These siloxanes used to modify DGEBA and post cured samples were aged in temperature controlled oven. After Thermal ageing their mechanical and water absorption properties were studied.

II. EXPERIMENTAL

A. 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 (MW 5364)], TSHF PDMS [Poly(dimethyl siloxane) hydride terminated] (MW 3363, Mn 580)], platinum (0)-1, 3 -divinyl-1, 1, 3, 3-tetramethyl disiloxane complex catalyst and allyl glycidyl ether (99% assay) were supplied by Aldrich. Methanol was supplied by Modern scientific solution.

B. 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.

C. Synthesis of Terminal Epoxy Functional PDMS (TEF PDMS)[5]

1 equivalent of PDMS was mixed with 2 equivalents 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 850°C. 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.

D. Synthesis of Pendant Epoxy Functional Polydimethyl Siloxane (PEF PDMS) [19]

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 850°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.

E. Modification of DGEBA with synthesized Epoxy functional PDMS

Epoxy resin was mixed with 5 wt% functionalized PDMS (PEF PDMS) and stirred well. Then 10wt% 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. The same procedure was repeated to prepare TEF PDMS blended DGEBA

F. Ageing Studies on Epoxy Resin Modified by Epoxidised Siloxanes

The post-cured samples of the neat DGEBA, DGEBA/TEF PDMS blend (5 wt %) and DGEBA/PEF PDMS blend (5 wt%) were aged in a temperature controlled air oven kept at 100 °C for 24, 48, 72, 96 and 120 hours successively. The aged samples were tested for mechanical properties and water absorption.

G. 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.

H. Water Absorption

Water absorption was tested as per ASTM D 570. For the water absorption test, the specimens were dried in an oven for a specified 24hr and 80°C and then placed in a desiccators to cool. Immediately upon cooling, the specimens are weighed. The material is then submerged in water at room temperature for 24 hours. Specimens are removed, patted dry with a lint free cloth, and weighed.

III. RESULT AND DISCUSSION

A. Modification of DGEBA with synthesized Epoxy functional PDMS

Table.1 showing the properties of epoxy PDMS blends. The both DGEBA/PDMS blends showed improved energy absorption improved impact strength and improved water resistance but inferior tensile strength

Table I

Properties Of Siloxane Modified Epoxy Resins

Property	% maximum improvement		
	DGEBA	TEF PDMS	PEF PDMS
Tensile strength (MPa)	55	-12.7	-6.3
Elongation at break (%)	3.01	25	25
Energy absorbed (.J/mm ²)	4.05	62.5	65
Impact strength (J/m)	111.04	51.5	61.43
Water absorption (%)	0.2003	-21.1	-35.09

B. Ageing Studies on Epoxy Resin Modified by Epoxidised Siloxanes

1) *Tensile properties:* The effect of variation of ageing time with tensile strength is shown in Fig.1 Tensile strength decreases during ageing due to the stiffening and thermal degradation of polymer chains. After ageing for 120 hrs the neat resin shows a reduction of 36.6 % in tensile strength while the reduction is 25.4% in the case of DGEBA/TEF PDMS and 24.7% in DGEBA/PEF PDMS blends.

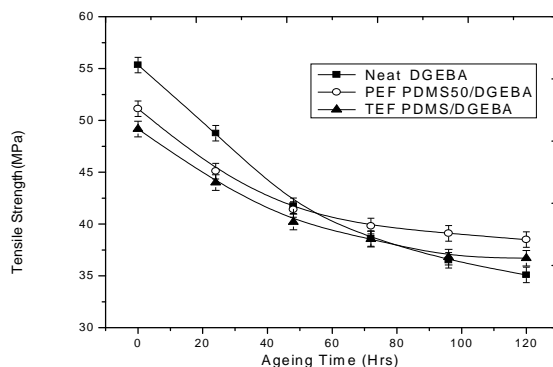


Fig. 1 Tensile strength of modified resin Vs ageing time

Fig.2 depicts the decrease in elongation at break with ageing time, which is attributed to the reduction in flexibility due to increased stiffening of polymer chains. The variation in toughness of cured resin (measured as the energy absorbed to break) with ageing time is given in Fig. 3..The energy absorbed (to break) decreases with ageing time mainly due to reduced flexibility of the chains. While the neat resin shows a reduction of 40% in energy absorption at break, the PEF PDMS and TEF PDMS blends show a reduction of only 19-20%. This suggests the superiority of these siloxanes in improving the ageing characteristics.

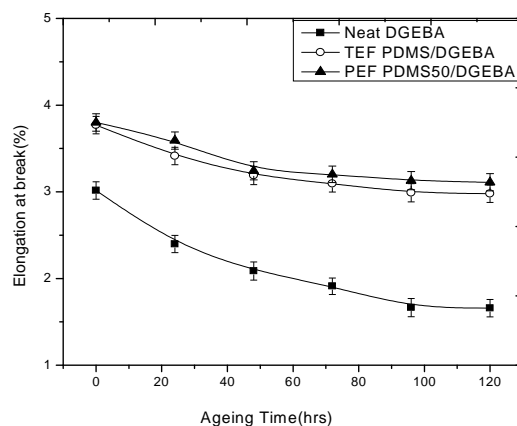


Fig. 2. Elongation at break of modified resin Vs ageing time

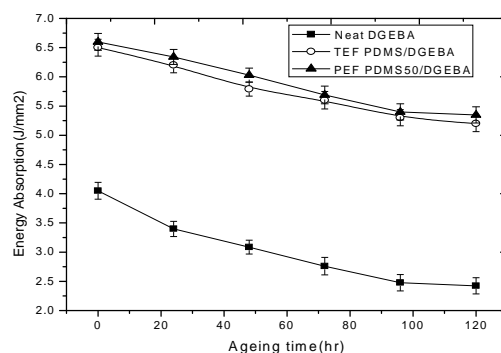


Fig. 3 Energy absorption of modified resin Vs ageing time

- 2) **Impact Strength:** The variation in impact strength of the resins during ageing is given in Fig.4. Impact strength decreases sharply during ageing due to stiffening of the polymer chains. However the extent of decrease is less in the blends (PEF PDMS 22% and TEF PDMS 21%) compared to the unmodified sample (32.5%). This confirms the ability of siloxanes to improve the ageing properties.

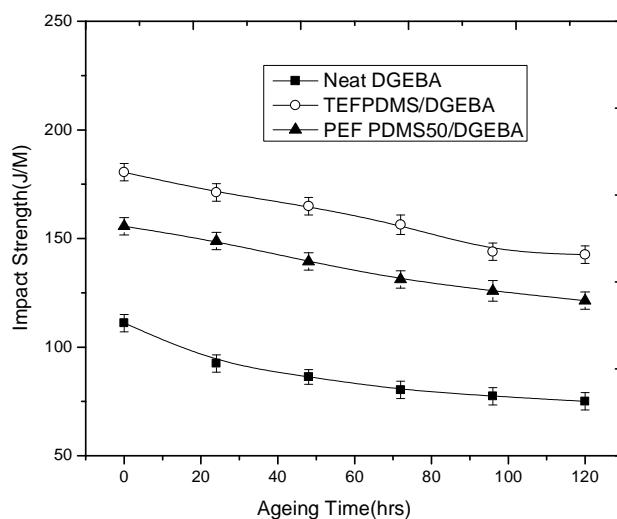


Fig 4 Impact strength of modified resin Vs ageing time

- 3) **Water Absorption:** Water absorption decreases steadily with ageing time (Fig 5). This is due to additional cross-linking accompanying the ageing process. DGEBA/TEF PDMS and DGEBA/PEF PDMS blends show better water resistance than DGEBA resin.

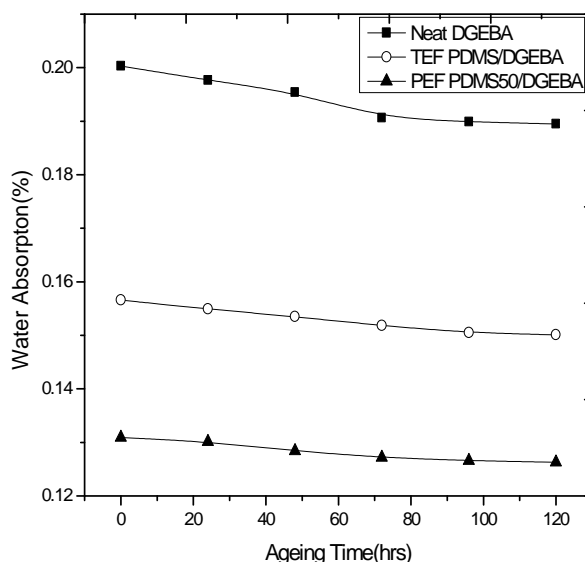


Fig. 5. Water absorption of modified resin Vs ageing time

IV. CONCLUSIONS

Siloxanes can marginally decrease the tensile properties but after ageing for 120 hrs the neat resin shows a reduction of 36.6 % in tensile strength while the reduction is only 25.4% in the case of DGEBA/TEF PDMS and 24.7% in DGEBA/PEF PDMS blends. After ageing the tensile strength values of modified resins are slightly better than that of the aged neat DGEBA. The modified resin retains the mechanical properties to a greater extent than the unmodified resin after ageing.

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