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Synthesis and thermal characterization of phosphorus containing siliconized epoxy resins

S. Ananda kumar [a,*], Z. Denchev [a], M. Alagar [b]

[a] IPC, Institute for Polymers and Composites, Department of Polymer Engineering, University of Minho, Guimarães 4800-058, Portugal
[b] Department of Chemical Engineering, Anna University, Chennai 600 025, India

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Abstract

Siliconized epoxy matrix resin was developed by reacting diglycidyl ethers of bisphenol A (DGEBA) type epoxy resin with hydroxyl terminated polydimethylsiloxane (silicone) modifier, using γ-aminopropyltriethoxysilane crosslinker and dibutyltindilaurate catalyst. The siliconized epoxy resin was cured with 4, 4-diaminodiphenylmethane (DDM), 1,6-hexanediamine (HDA), and bis (4-aminophenyl) phenylphosphate (BAPP). The BAPP cured epoxy and siliconized epoxy resins exhibit better flame-retardant behaviour than DDM and HDA cured resins. The thermal stability and flame-retardant property of the cured epoxy resins were studied by thermal gravimetric analysis (TGA) and limiting oxygen index (LOI). The glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) and the surface morphology was studied by scanning electron microscopy (SEM). The heat deflection temperature (HDT) and moisture absorption studies were carried out as per standard testing procedure. The thermal stability and flame-retardant properties of the cured epoxy resins were improved by the incorporation of both silicone and phosphorus moieties. The synergistic effect of silicone and phosphorus enhanced the limiting oxygen index values, which was observed for siliconized epoxy resins cured with phosphorus containing diamine compound.
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Keywords: Epoxy resin; Siliconized epoxy resin; Curatives; Thermal stability; Flame-retardancy and limiting oxygen index

1. Introduction

Epoxy resins are the focus of the present investigation due to their superior thermo-mechanical properties and excellent processability. The chemical structure of epoxy resins imparts them high chemical resistance against a wide range of severe corrosive conditions. Epoxy resins can be used in both moulding and lamination techniques to make glass fibre reinforced articles with better mechanical strength and electrical insulating properties. Among the various polymer matrices in use, epoxy resins have occupied a dominant position in the development of high performance materials [1–4]. However, their inadequate flame-resistance and

* Corresponding author. Present address: Lecturer, Department of Chemistry, Anna University, Chennai 600 025, India.
E-mail address: sri_anand_72@yahoo.com (S. Ananda kumar).

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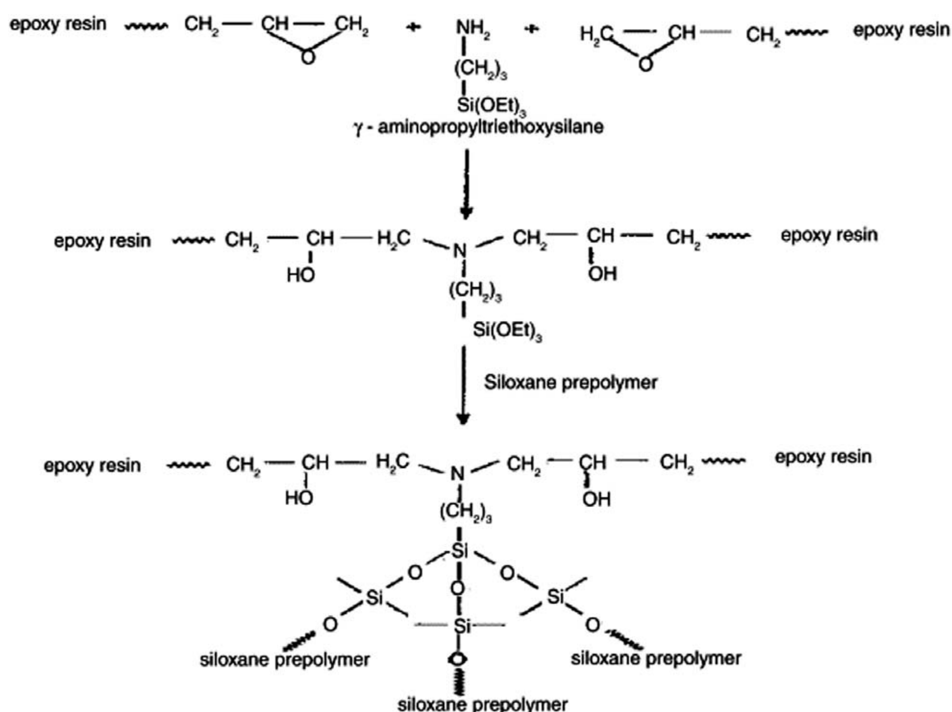
toughness that affect the durability and place a strong constraint on design parameters limit their use. Hence epoxy resins have been modified with flexible polymeric segments like carboxyl terminated butadiene nitrile rubber, hydroxyl terminated butadiene nitrile rubber, amine terminated butadiene nitrile rubber, polyurethanes and silicones [5–8] in order to improve their properties suitable for better utility. Among them, polydimethylsiloxanes (commercially known as silicones) are considered to be one of the best modifiers to improve the thermal properties and impact behaviour of the epoxy resins suitable for high performance applications [9–12]. In our earlier works, we introduced both silicone into epoxy resin and bismaleimide having an ester linkage into polyurethane modified epoxy resin [13–15]. It was found that the incorporation of polyurethane into epoxy resin decreased the thermal stability, glass transition temperature and heat deflection temperature [15]. The incorporation of silicone into the epoxy, on the other hand, enhanced the impact strength, dielectric strength, moisture resistance and corrosion resistance due to its inherent flexibility, constant stress dissipating nature [13,14].

Another important property of epoxy resin that needs to be improved is its flame retardancy. The flame retardancy is the prime requirement in the case of structural materials used for aircraft, motor and vehicle construction, as well as for electrochemical uses and particularly in electrical and electronic applications, due to the danger to human beings and material assets. Therefore, achieving flame retardancy in epoxy resins has received much attention leading to several studies [16–18]. Numerous approaches and techniques have been employed in enhancing the flame retardancy of epoxy resins [19,20]. Among the different classes of flame-retardants available, the development and utilization of fire retardant epoxy resins and phosphorus containing curing agents are feasible [16,21]. Environmental concerns about the use of non toxic, cost effective and halogen free flame-retardants have led to the development of new flame-retardants. In this race, organo-phosphorus flame-retardants are among the leading contenders for enhancing the resistance of epoxy resins to flame and high temperature. It has been found that phosphorus, present either as a constituent of the polymer chain or incorporated as an additive to the polymer system in the form of phosphorus compound, can make polymers flame-retardant and also serve as plasticisers [16,17,22]. Traditionally, flame-retardant polymers are obtained by physically blending a flame-retardant additive with the polymer. However, the major disadvantage of all flame-retardant additives is that they may be lost in processing and during use of the polymer and hence high loadings of flame-retardant additives are initially required. Another way to enhance the flame-retardant property of the polymers is to use a reactive flame-retardant [23–26], which chemically bonds to the polymer backbone. This offers the advantage of permanent attachment of flame-retardant groups to polymer and leads to better flame-retarding efficiency than physically blended flame-retardants. With all these ideas in mind, an attempt has been made in the present investigation to obtain epoxy resin with superior thermal properties and high flame-resistance by simultaneously introducing siloxane and phosphorus moieties into the epoxy skeleton. The synergistic effect of siloxane and phosphorus in enhancing the thermal stability and flame retardancy of the new epoxy resin is studied. The incorporation of siloxane into epoxy resin was performed in a manner well known by art [27–29]. The silicone modified epoxy resin (siliconized epoxy resin) was then cured with different curatives including the reactive flame-retarding phosphorus containing diamine, which was prepared according to the procedure reported by Liu et al. [30–36]. The present work discusses the preparation of siloxane modified epoxy resin, phosphorus containing amine curative, and characterization of their properties with relevance to thermal stability and flame-retardancy of the cured resin systems.

2. Experimental

2.1. Materials

Epoxy resin GY 250 (diglycidyl ether of bisphenol A, DGEBA, with EEW 180–190, viscosity about 10,000 cP) and 4,4-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy. 1,6-Hexanediamine was obtained from Aldrich. Bis (4-aminophenyl) phenylphosphate (BAPP) was prepared by the reported procedure [30]. The hydroxyl-terminated polydimethylsiloxane used in the present study was synthesized in our laboratory from octamethylcyclotetrasiloxane by ring opening polymerization technique [28]. Dibutyltindilaurate catalyst and γ-aminopropyltriethoxysilane (γ-APS) were obtained from Merck (Germany) and Union Carbide (USA)



Scheme 1. Formation of siliconized epoxy TPN structure.

respectively. Phenyldichlorophosphate (PDCP) (Lancaster), *p*-nitrophenol (SD Fine chemicals, India) and copper (I) chloride (Lancaster) were used as received. Tetrahydrofuran (THF) was dried with sodium and distilled before use. Palladium on 10% activated charcoal was obtained from SD fine chemicals (India).

2.2. Preparation of siliconized epoxyprepolymer

Fixed amount of epoxy resin, varying amounts of hydroxyl-terminated polydimethylsiloxane, stoichiometric amount of γ-aminopropyltriethoxysilane (with respect to ethoxy group) and dibutyltindilaurate catalyst were thoroughly mixed at 90 °C for 30 min with constant stirring. The product was then degassed to remove ethanol, which formed during the condensation reaction (Scheme 1) between γ-aminopropyltriethoxysilane and hydroxyl-terminated polydimethylsiloxane [28,29].

2.3. Synthesis of phosphorus containing amine curative

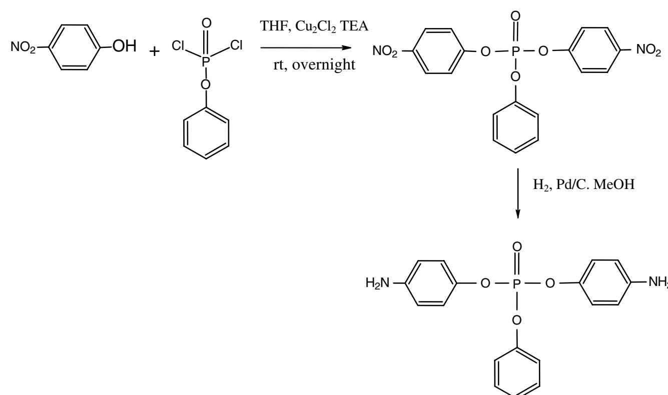
The synthesis of phosphorus based amine curative namely BAPP was obtained by reacting PDCP with hydroxyl derivatives via two-step synthesis route (Scheme 2). The dinitro bis (4-nitrophenyl) phenyl phosphate (BNPP) was first obtained as an intermediate followed by hydrogenation using Palladium on 10% activated charcoal catalyst to get the diamine compound [BAPP].

2.4. Preparation of phosphorus containing siliconized epoxy resin products

The siliconized epoxy pre-polymer after being subjected to degassing process was cured with stoichiometric amounts of three different curing agents namely HAD, DDM, and BAPP to get the corresponding cured products.

2.5. Characterization

The IR spectra were recorded on a Perkin–Elmer 781 infrared spectrometer using KBr pellets for solid samples. NaCl was used for taking IR spectra of viscous liquid samples. H^1 NMR Spectrum was recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer using $CDCI_3$ solvent. Glass transition temperature (T_g) of the samples was determined using DSC 2910 (TA instruments USA) in the temperature range between 50 and 250 °C at a heating rate of 10 °C min^{-1}. Thermal gravimetric analysis



Scheme 2. Synthesis of BAPP.

(TGA) was carried out using Thermal Analyst 2000 (TA instruments USA) at a heating rate of 10 °C min^{-1} in an inert atmosphere. The heat deflection temperature (HDT) and moisture absorption study were carried out as per ASTM D648-72 and ASTM D570 methods respectively. The limiting oxygen index (LOI) test was performed as per ASTM D2836. Furthermore, mechanical properties such as, tensile strength, tensile modulus, flexural strength, flexural modulus, and plain strain fracture toughness of matrix samples were studied as per ASTM standards. The tensile properties were determined using dog bone shaped specimens according to ASTM D3039 method using an Instron testing machine (Model 6025 UK), at a crosshead speed of 2 mm/min. The flexural strength was measured as per ASTM D790. The unnotched Izod impact strength of each sample was tested as per ASTM D256-88. Scanning electron micrographs (SEM) were taken for the samples of fractured matrices from plain strain fracture toughness studies to assess their morphological characteristics. The gold-coated fractured surfaces were examined by a scanning electron microscope, Leica Cambridge, Stereoscan Model 440.

3. Results and discussion

3.1. Spectral analysis

The formation of siliconized epoxy network structure takes place in two steps and was already evaluated by the author by means of IR spectra [28]. The first step involves the opening of oxirane ring of epoxy with amino group of the γ-aminopropyltriethoxysilane (the bonding of γ-aminopropyltriethoxysilane with epoxy resin is given in Scheme 1), is confirmed by the disappearance of epoxy band at 913 cm^{-1} and appearance of hydroxyl band at 3420 cm^{-1}. Appearance of absorption peaks at 2980 cm^{-1} and 2850 cm^{-1}, 1370 cm^{-1} confirms the presence of –Si–O–CH_2CH_3 and –Si–$(CH_2)_3$–, respectively. In the second step, the alkoxy groups present in the γ-aminopropyltriethoxysilane react with hydroxyl groups of hydroxyl-terminated polydimethylsiloxane (Scheme 1).

The IR data for BNPP are as follows. The appearance of the following peaks IR (KBr): 856.3 cm^{-1} (--C–NO_2), 1188.1 cm^{-1} (Ph–O–Ph), 1242.2 cm^{-1} (--P=O), 1350.1 cm^{-1} and 1527.5 cm^{-1} (Ph–NO_2) confirmed the formation of BNPP compound. Peaks appeared at 3513 cm^{-1} and 3409 cm^{-1} correspond to symmetric and asymmetric stretching of aromatic primary amine groups. Moreover, other peaks arising from P–O–Ph at 1191 cm^{-1} and P=O at 1280 cm^{-1} confirm that the phosphate structure is maintained after hydrogenation [29]. ^{1}H NMR Spectrum is presented in Fig. 1 further supports the formation of BAPP. The absorption of amine protons is found at $\delta = 3.45$ ppm. Peaks at $\delta = 6.52$–6.94 ppm and $\delta = 7.09$–7.43 ppm confirm the presence of C_6H_4–NH_2 and P–O–C_6H_5 respectively (see Table 1).

3.2. Glass transition temperature

Glass transition temperatures (T_g) of the cured epoxy and siliconized epoxy systems were determined by differential scanning calorimetry measurements (Table 2). The siliconized epoxy systems exhibit single glass transition temperature (T_g), which in turn confirms the existence of intercrosslinking network structure within the siliconized

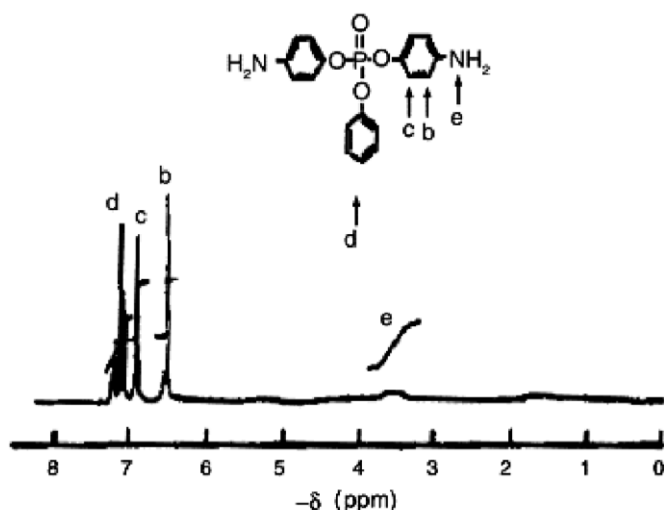


Fig. 1. H^1 NMR Spectrum of BAPP.

Table 1
Composition of resins, curatives, crosslinking agent and catalyst

Matrix system	Epoxy (wt.%)	Siloxane (wt.%)	Curatives	Amount of curative (g)	Crosslinking agent (ml)	Catalyst (g)
A	100	0	DDM	27	–	–
B	100	5	DDM	27	0.05	0.1
C	100	10	DDM	27	0.09	0.1
D	100	15	DDM	27	0.14	0.1
E	100	0	BAPP	49.30	–	–
F	100	5	BAPP	49.30	0.05	0.1
G	100	10	BAPP	49.30	0.09	0.1
H	100	15	BAPP	49.30	0.14	0.1
I	100	0	Hexanediamine	15.83	–	–
J	100	5	Hexanediamine	15.83	0.05	0.1
K	100	10	Hexanediamine	15.83	0.09	0.1
L	100	15	Hexanediamine	15.83	0.14	0.1

Table 2
Data resulted from moisture absorption (%), thermal and flame-retardant studies

Matrix system	Epoxy/siloxane composition	Curatives	Moisture absorption (%)	Heat distortion temperature °C	Glass transition temperature °C	LOI
A	100/00	DDM	0.1101	155	162	20
B	100/05	DDM	0.1062	151	160	22.5
C	100/10	DDM	0.1031	148	158	24
D	100/15	DDM	0.1020	141	156	26
E	100/00	BAPP	0.1045	158	165	32
F	100/05	BAPP	0.1010	155	163	36
G	100/10	BAPP	0.0972	152	161	39.5
H	100/15	BAPP	0.0845	149	160	42
I	100/00	Hexanediamine	0.1115	150	127	17
J	100/05	Hexanediamine	0.1105	148	126	19
K	100/10	Hexanediamine	0.1080	147	125	22
L	100/15	Hexanediamine	0.1062	145	123	23

epoxy systems [28]. In the present study, hybridization of industrially valuable rigid epoxy resin (cured by BAPP having a T_g of 165 °C) with another industrially valuable and flexible functionally terminated poly(dimethylsiloxane) (PDMS) having glass transition (T_g) of about −120 °C is performed.

The incorporation of PDMS into the epoxy resin brings down the T_g of epoxy resin according to the percentage content of PDMS.

However, it has been ascertained that the reduction in T_g for siliconized epoxy material cured by BAPP is insignificant (Table 2) since silicone incorporation does not alter the T_g values of the epoxy resin to a great extent due to its flexible skeleton and ablative behaviour [28]. However, a slight decreasing trend in T_g is observed for siliconized epoxy systems and the values of T_g of hybrid siliconized epoxy materials having 5%, 10% and 15% siloxane content cured by BAPP are l63, 161 and 160 °C respectively. The slight decrease in T_g that may be attributed due to the incorporation of silicone into epoxy resin that might simultaneously increase the free volume and consequently reduces the crosslink density of the cured resins, which in turn have lowered T_g values [37]. The T_g values for epoxy and siliconized epoxy resins are increased when cured with phosphorus diamine based curative, which has rigid aromatic groups in the backbone. The DSC curves of epoxy and siliconized epoxy systems cured with different curatives are presented in Fig. 2 and the values of T_g are presented in Table 2.

3.3. Cure reaction behaviour

The modification of epoxy resin with siloxane (HTPDMS) in the presence of γ-APS proceeds via two steps. The first step involves the reaction between $-NH_2$ groups of γ-APS and oxirane rings of epoxy resin. It is evident from the DSC thermogram (Fig. 2b) that the reaction starts at 95 °C and reaches peak maximum at 125 °C. Furthermore, the reaction between $-OCH_2CH_3$ groups of γ-APS and the hydroxyl groups of HTPDMS also occurs simultaneously and is accelerated during degassing process. In the second step, the $-NH_2$ groups of DDM react with the remaining oxirane rings of epoxy resin. The epoxy-DDM reaction starts at 120 °C and reaches peak maximum at 163 °C (Fig. 2a). The large exotherm obtained for the epoxy-DDM system is due to the following reactions (i) oxirane ring opening reaction with active amine hydrogens of DDM (ii) auto catalytic reaction of oxirane ring with pendent hydroxyl groups of epoxy resin and hydroxyl groups formed during the reaction (i) and it suggests that the reaction proceeds in a homogeneous path. The decrease in peak maximum temperature with siloxane incorporation confirms the reaction between epoxy and siloxane that accelerates the reaction rate and reduces the curing temperature.

3.4. Thermal gravimetric analysis

The thermal stability of epoxy and siliconized epoxy systems was evaluated by thermal gravimetric method. Modification of epoxy with silicone improved thermal stability and enhanced degradation temperature of the epoxy resin according to silicone percentage concentration. This observation can very well be ascertained from Fig. 3. The presence of siloxane moiety in the siliconized epoxy system delays the thermal degradation; apparently high

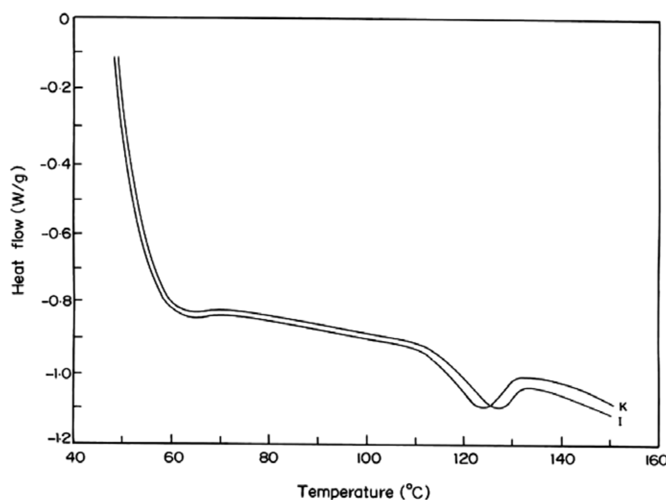


Fig. 2. DSC curves of epoxy and siliconized epoxy resins.

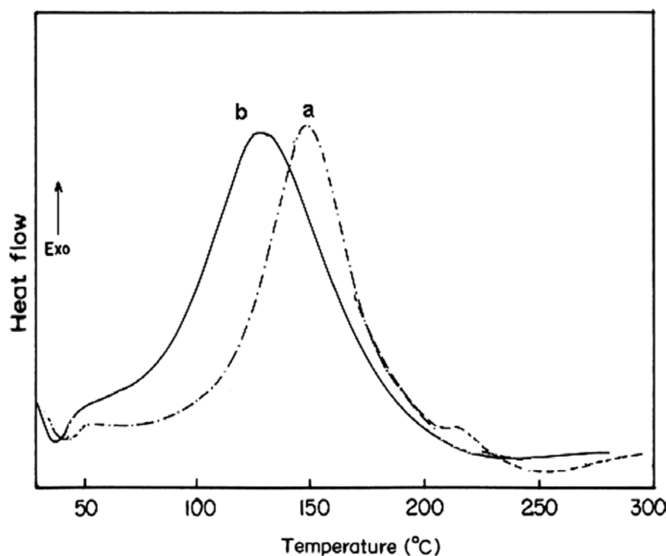


Fig. 2a,b. (a) Reaction between $-OCH_2CH_3$ groups of γ-APS and the hydroxyl groups of HTPDMS and (b) epoxy-DDM reaction.

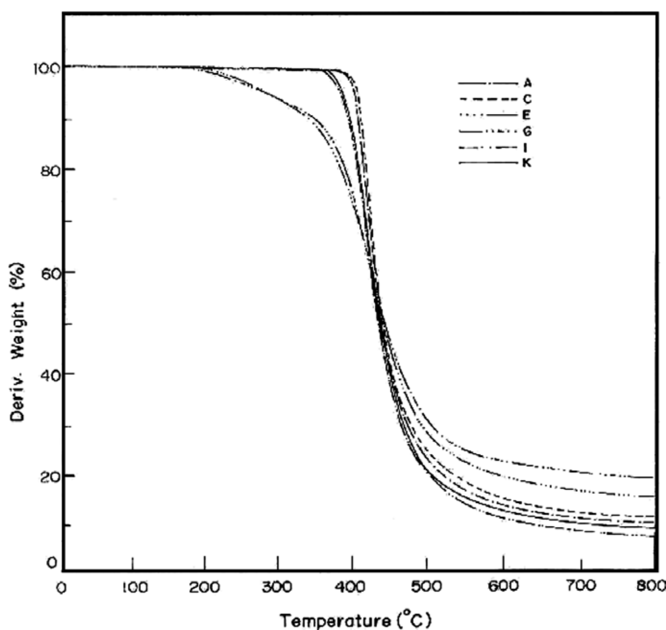


Fig. 3. Thermal degradation patterns of epoxy and siliconized epoxy resins.

amount of thermal energy is required to attain the same weight losses when compared with that of unmodified epoxy system. The delay in degradation caused by the siloxane moiety may be attributed to the stability of the inorganic nature of siloxane structure and its partial ionic nature, which stabilize the epoxy resin from the heat [28]. While heating, low surface energy of silicone renders it to migrate to the surface of the epoxy resin to form a protective self-healing layer [38,39] with resistance to heat and slows down the thermal degradation of the polymer [40–51]. Wu et al. have already vindicated a similar observation for thermosets, especially for epoxy resins [38]. For example, the temperatures required for 10%, 20%, 30% and 50% weight losses of unmodified epoxy resin cured with aromatic amine (DDM) are 375, 391, 401 and 415 °C respectively. Whereas, the temperatures required for attaining the same weight

losses of siliconized epoxy system cured with same curatives having 10% siloxane content are enhanced to 389, 401, 412 and 420 °C. A similar trend is observed for 5% and 15% silicone modified epoxy systems.

It is also observed that the type of curatives and percentage concentration of silicone have specific influence on thermal degradation temperature. For example, thermal degradation temperature of epoxy resin was significantly lowered to 361 °C when cured with phosphorus-containing diamine. The initial weight loss occurred at 222 °C followed by a further weight loss at around 362 °C. Similar trend was observed for siliconized epoxy system cured by phosphorus containing diamine with an improvement in thermal degradation temperature due to the presence of thermally stable siloxane bond. The initial weight loss for siliconized epoxy system occurred at around 239 °C followed by a further weight loss at 378 °C. The decrease in thermal degradation temperature for phosphorus diamine cured epoxy and siliconized epoxy systems may be explained by the decomposition of phosphate group at relatively low temperature region than ordinary polymer chain, owing to the less strength of phosphorus bond [41–43]. However, the phosphorus diamine cured epoxy and siliconized epoxy systems have higher thermal stability than the other systems [44,45].

3.5. Heat distortion temperature (HDT)

HDT measurements are carried out to determine the thermo-mechanical behaviour of matrix systems. HDT values for epoxy and siliconized epoxy systems are presented in Table 2. From the table it is evident that HDT decreased with increasing silicone concentration, this may be attributed due to the presence of flexible –Si–O–Si– linkage. Among the curatives used aromatic amine cured siliconized epoxy systems including the phosphorus containing diamine curative have exhibited higher HDT values. The higher values of HDT for aromatic amine cured systems are due to their rigid-aromatic structure.

3.6. Moisture absorption behaviour

The incorporation of silicone into epoxy resin enhanced the moisture resistant behaviour according to its percentage concentrations (Table 2). The increase in moisture resistant behaviour shown by siliconized epoxy resins may be attributed to the inherent hydrophobic nature of siloxane moiety. Almost all the matrix systems showed good resistance to moisture, however the aromatic amine cured systems have exhibited better moisture resistant values due to rigid aromatic structure and hence less permeability to moisture.

3.7. Limiting oxygen index (LOI)

The LOI is defined as the minimum fraction of oxygen from oxygen–nitrogen mixture, which is sufficient to sustain combustion of the specimens after ignition. The LOI value can be used as an indicator to evaluate the flame-retardancy of polymers. Thus, the flame-retardancy of epoxy and siliconized epoxy resins was evaluated by measuring their LOI values, which are given in Table 2. The LOI values of the epoxy resins, irrespective of the curatives used were increased by silicone incorporation, which may be explained due to the fact that the silicone enhances a significant LOI for polymers with high char yields [46]. For example, the LOI values for the DDM cured systems are increased from 20 to 26 by the incorporation of silicone when compared to unmodified epoxy resin (Table 2). Similar trend was observed with other curatives. Furthermore, a material with a LOI value of 21 or above was rated as flame-retardant materials. Thus incorporating simultaneously silicone and phosphorus into epoxy resin would render these epoxies as flame-retardant polymers. Epoxy and siliconized epoxy materials cured with the phosphorus diamine based curative exhibited the maximum LOI value of 42, which may be due to the consequence of the char enrichment of phosphorus and the char protecting effect of silicone and exhibited the synergistic effect of both silicone and phosphorus on LOI enhancement [47–51].

3.8. Mechanical properties

The enhancement in impact (toughness) behaviour and mechanical characteristics of the cured epoxy resins have already been examined and its importance is discussed below. The incorporation of hydroxyl terminated polydimethylsiloxane (HTPDMS) into epoxy resin improves the toughness of the resulting hybrid siliconized epoxy resin according to the percentage of siloxane incorporation due to its flexible –Si–O–Si– skeleton, resilient behaviour and constant stress dissipating capability

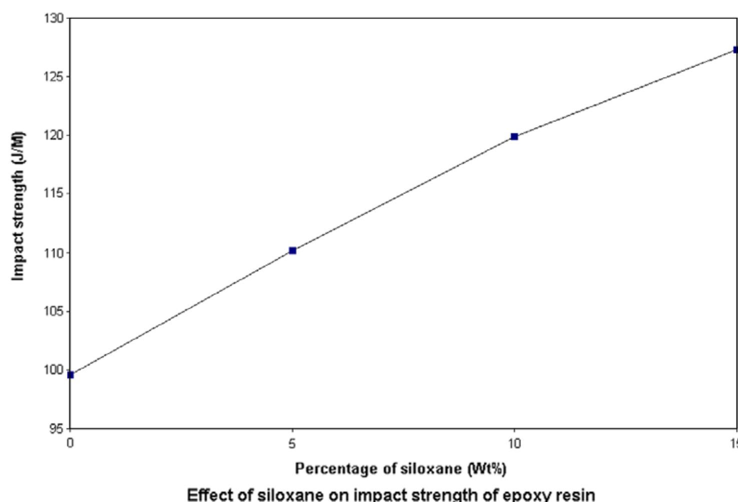


Fig. 4. The enhanced toughness of epoxy resins.

[14]. HTPDMS is one of the most flexible polymer chains known, both in terms of dynamic sense and in the equilibrium sense. The Si–O– skeletal bond has a length of 1.64 Å, which is significantly longer than that of the –C–C– bond (1.53 Å). As a result, steric interferences or intramolecular congestion is diminished. Moreover, the Si–O–Si bond angle of 143° is much more open than the usual tetrahedral bond angle of 110°. These structural features have a profound effect on the impact strength of a polymer and have enough mobility to absorb impact energy thereby increasing the impact resistance of the polymer to a greater extent. The enhanced toughness of the epoxy resin is illustrated in Fig. 4.

Furthermore, the mechanical properties namely tensile strength, tensile modulus, flexural strength and flexural modulus of siliconized epoxy resin decreased with increased percentage incorporation of HTPDMS. The reduction in mechanical properties of siloxane-incorporated epoxy may be explained due to the presence of flexible siloxane linkage, free rotation of –Si–O–Si– bond and weak intermolecular attraction of pendant methyl groups present in the siloxane molecule as well as weak interface boundary between siloxane and epoxy matrix. The data resulted from mechanical studies are presented in Table 3.

3.9. Microscopic investigation

Scanning electron microscope was used to investigate the morphology of unmodified epoxy, siliconized epoxy systems. SEM micrograph of fractured surface of the unmodified epoxy system (Fig. 5a) indicated a smooth, glassy and homogenous microstructure without any plastic deformation. The fractured

Table 3
Mechanical properties of epoxy and siliconized epoxy systems cured by different curatives

Matrix system	Epoxy/HTPDMS/ composition	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Plain strain fracture toughness (K_{IC} MPa m$^{1/2}$)
A	100/00	62.2 ± 9	2750.5 ± 39	112.0 ± 10	1814.8 ± 42	1.16 ± 0.10
B	100/05	52.1 ± 3	2274.7 ± 30	72.6 ± 6	1732.4 ± 39	2.40 ± 0.05
C	100/10	39.6 ± 4	2122.8 ± 29	53.5 ± 4	1713.9 ± 28	2.68 ± 0.04
D	100/15	28.6 ± 5	1858.1 ± 40	47.4 ± 2	1375.4 ± 31	2.98 ± 0.17
E	100/00	66.8 ± 9	2825.4 ± 40	116.5 ± 9	2043.5 ± 41	1.14 ± 0.05
F	100/05	57.2 ± 4	2609.4 ± 35	85.8 ± 4	2070.3 ± 25	1.49 ± 0.08
G	100/10	50.8 ± 3	2550.3 ± 29	76.0 ± 5	1865.9 ± 41	1.58 ± 0.04
H	100/15	46.5 ± 5	2472.2 ± 31	74.2 ± 3	1816.9 ± 29	1.70 ± 0.08
I	100/00	45.1 ± 3	2254.7 ± 30	70.6 ± 6	1732.4 ± 39	2.38 ± 0.05
J	100/05	33.5 ± 4	2110.8 ± 29	50.5 ± 4	1701.9 ± 28	2.49 ± 0.04
K	100/10	25.5 ± 5	1808.1 ± 40	40.4 ± 2	1320.4 ± 31	2.55 ± 0.17
L	100/15	22.6 ± 5	1762.1 ± 40	38.1 ± 2	1293.4 ± 31	2.73 ± 0.15

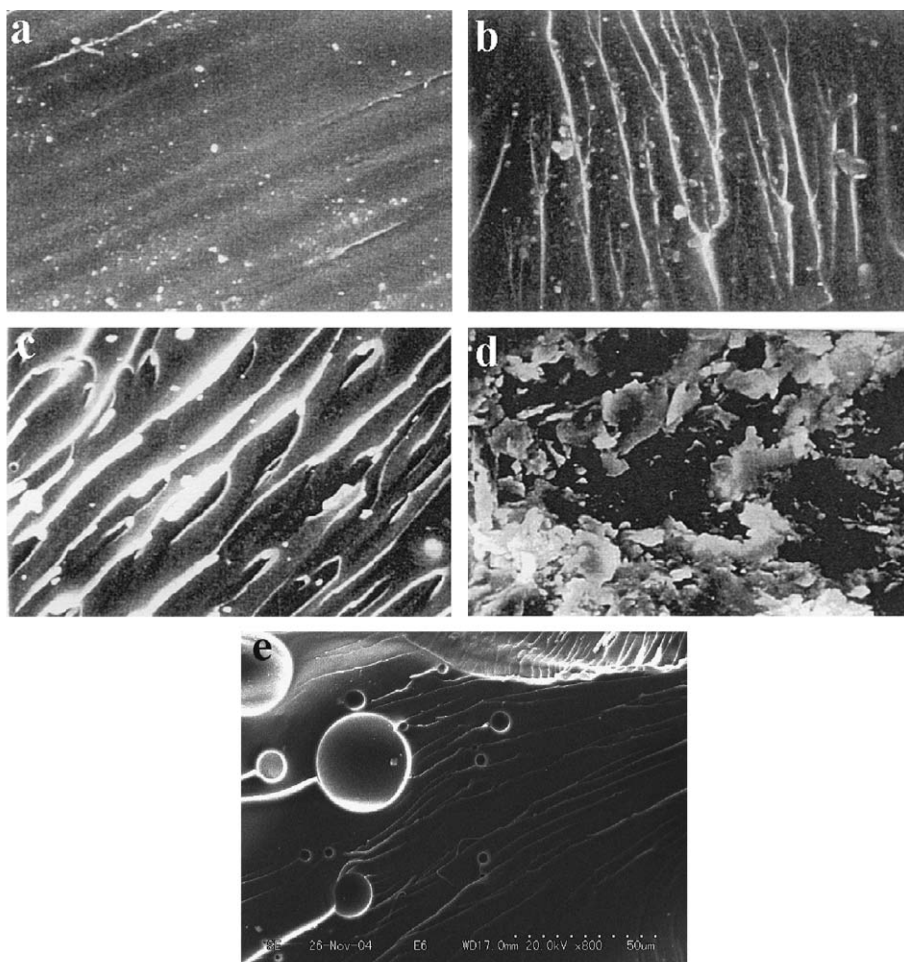


Fig. 5. SEM Micrographs of (a) unmodified epoxy, (b) 5%, (c) 10%, (d) 15% silicone incorporated epoxy resins, (e) siliconized epoxy without γ-aminopropyltriethoxysilane.

surfaces of the siliconized epoxy resin (Fig. 5(b) 5% of siloxane, (c) 10% of siloxane and (d) 15% of siloxane) systems showed the presence of heterogeneous morphology and the siloxane domain size increased according to the siloxane content. However, a significant phase separation occurred without the use of γ-APS (Fig. 5e). It may be concluded that the incorporation of siloxane into epoxy resin was achieved through the chemical linkage between siloxane and γ-aminopropyltriethoxysilane. This observation also confirmed the existence of inter-crosslinked network structure of siliconized epoxy systems [28].

4. Conclusion

The siloxane moiety incorporated epoxy resin, cured with phosphorus containing diamine (BAPP) curative exhibited higher LOI values than unmodified epoxy indicating the flame-retardant behaviour imparted improved by both siloxane and phosphorus to epoxy resin. Siliconization of epoxy resin enhanced the moisture resistant behaviour and decreased the heat deflection temperature due to its inherent hydrophobic nature and flexibility. SEM micrographs of fractured surfaces of siliconized epoxy resin systems showed the progress of heterogeneous morphology with increasing siloxane content. The high flame-retardation efficiency of siliconized epoxy resin cured with phosphorus diamine curative was observed mainly because of the char enrichment of phosphorus and the char protecting effect of silicone to exhibit their synergistic effect on LOI enhancement. Data resulted from different studies indicating the flame-retardant behaviour of the siliconized epoxy resin cured with phosphorus based curative with improved thermal stability and

suggest the suitability of these matrices in the field of advanced electronics, adhesives and coatings for better performance and longevity.

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