Mechanical and Electrical Studies of Silicone Modified Polyurethane–Epoxy Intercrosslinked Networks

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ABSTRACT: A series of intercrosslinked networks (ICNs) based on silicone modified polyurethane (PU)–epoxy resins were developed. In this study, epoxy resin (diglycidyl ether of bisphenol-A) was modified with PU prepolymer and hydroxyl-terminated polydimethylsiloxane (HTPDMS) using γ-aminopropyl triethoxysilane (γ-APS) as silane cross linker and dibutyltindilaurate (DBTL) as catalyst to form ICNs. Aromatic polyamine adduct (A), diethylenetriamine (B) and polyamidoamine (C) were used as epoxy curatives. The final products were obtained in the form of tough films. Changes in chemical structure during ICN formation, mechanical and electrical properties were investigated using FT-IR spectra, tensile, impact and dielectric testing. The mechanical properties were enhanced with incorporation of PU (10 wt %) and silicone (10 wt %) due to the toughening of brittle epoxy matrices. Electrical properties showed a marginally decreasing trend with the incorporation of PU (0–20 wt %) influenced by the polar urethane linkages whereas silicone incorporation (10 wt %) showed an enhancement due to the presence of inorganic –Si–O–Si– linkage. Among the systems studied, the silicone (10 wt %) modified PU (10 wt %)–epoxy cured with "A" exhibited excellent mechanical and electrical characteristics and can be used as coatings and composites for industrial, electrical and marine components.   [DOI 10.1295/polymj.36.848]
      KEY WORDS   Intercrosslinked Network / Epoxy / Polyurethane / Silicone / Coatings / Composites /

Numerous polymeric resins based on epoxy, unsaturated polyester, phenolic and acrylics are available for composite and coating applications, but they are not completely satisfactory from the viewpoint of mechanical and dielectric characteristics. Among them, epoxy resin though possessing good adhesion and chemical resistance, its brittle behavior with low impact strength and dielectric properties restricts the utility for high performance applications.[1,2] Many attempts have been made in the past to toughen the epoxy resin.[3–8] A systematic and detailed study is required to propose suitable chemical modifiers for epoxy resin. Modification *via* blending or the addition of thermoplastic polymers to the thermoset epoxy is a possibility. Among the elastomeric modifiers, polydimethylsiloxane (PDMS) commercially known as silicone is regarded as one of the suitable modifiers owing to its inherent characteristics like good wetting and film forming ability, good dielectric strength and hydrophobic behavior.[9–12] Polyurethane (PU) is another class of favored polymeric modifier owing to its superior impact strength, low curing temperature and abrasion resistant characteristics. PU crosslinked with epoxy reduces phase separation and improves mechanical properties compared to unblended epoxy resins.[8,13–17] Incorporation of a macrodiol such as PDMS into the epoxy matrix is generally difficult because of its poor compatibility with conventional compounds used in epoxy and polyurethane synthesis. These materials exhibit a high degree of phase separation resulting in poor mechanical properties and compositional heterogeneity resulting from poor segmental compatibility.[18] Several techniques were reported in literature to synthesize PDMS based polyurethane and epoxy resins. These techniques include the introduction of polar functionality to PDMS,[19,20] hard segment modification[21] and using silane-coupling agents.[12,22] Introduction of PDMS into the main chain of epoxy impedes surface-enrichment and in order to meet the need for surface modification, a lot of PDMS must be introduced. Concomitantly, the thermo-mechanical properties declined swiftly with increase of the PDMS soft segment. To overcome this limitation, we previously tried amino-terminated PDMS using amino silane coupling agents. Amino-terminated PDMS bonded to the epoxy in the side chain to form a crosslinked structure.[12] Consequently, the thermo-mechanical properties showed an increasing trend with only a small amount (10 wt %) of silicone needed to meet the modification. Stanciu *et al.*[23] reported that hybrid polymeric materials resulting from intercrosslinked network (ICN) mechanism in which two or more polymers are chemically crosslinked in their main or side chains to form a network structure enhance their mechanical and hydrophobicity characteristics than those obtained by blending technique. The technology of ICNs as

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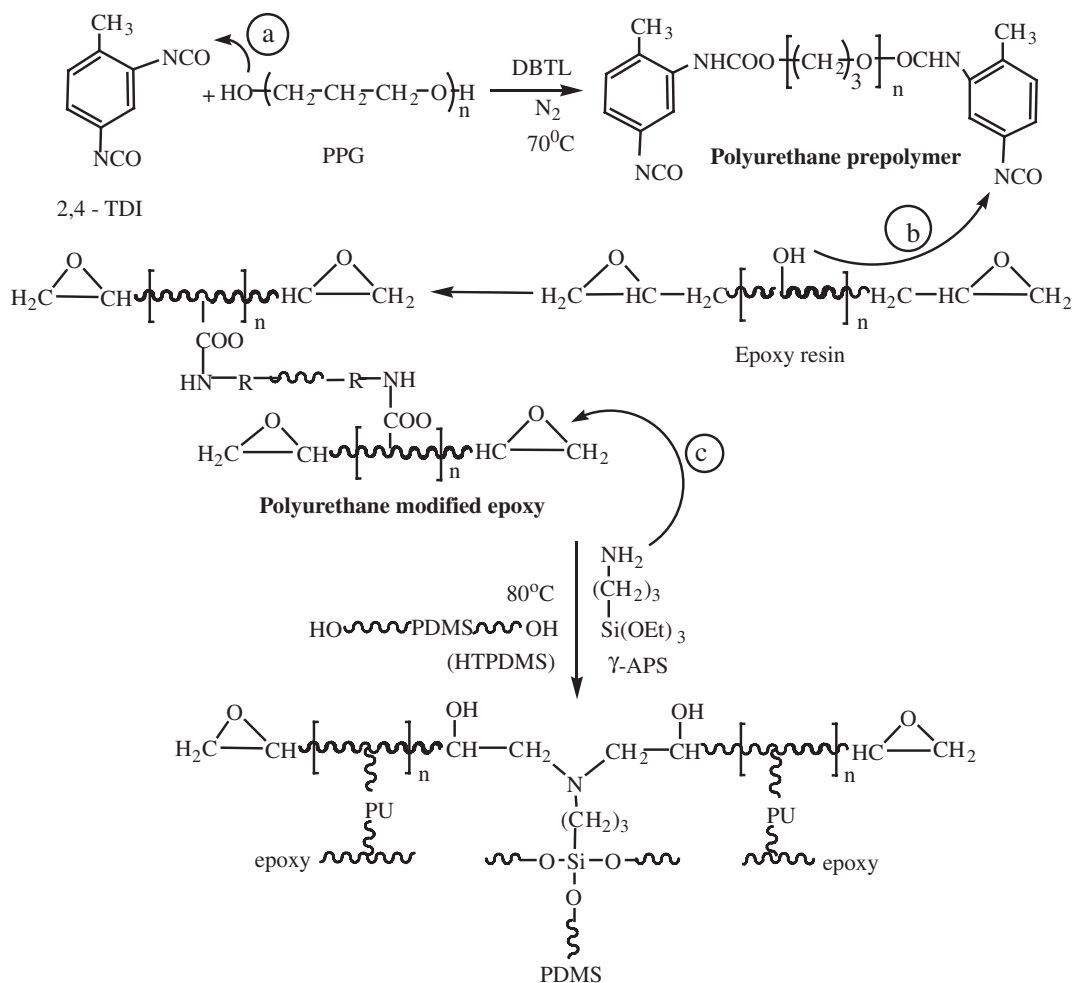
Scheme 1. Formation of silicone modified PU–epoxy ICN.

materials for engineering and electrical applications is presently in a state of emergence.

In the present study, an attempt has been made to develop three different epoxy resins (capable of curing at $<30\,^\circ$C): an unmodified epoxy; a PU–epoxy ICN where NCO-terminated PU prepolymer was cross-linked with pendant hydroxyl groups in epoxy; and a silicone modified PU–epoxy ICN where hydroxyl terminated polydimethylsiloxane (HTPDMS) was crosslinked with oxirane groups in PU–epoxy using an silane coupling agent. Thermoplastic PU and silicone are expected to behave as thermosets when inter-crosslinked with epoxy using silane-coupling agents to form ICNs with improved mechanical and electrical characteristics.

EXPERIMENTAL

Materials

The commercially available epoxy resin, 'GY 250' [DGEBA, Vantico (India); epoxy equivalent $\sim$180–190, viscosity 9000–12000 cP] was used as a base material and is referred as 'X_0'. PU prepolymer

(NCO/OH ratio 1.5) as epoxy modifier was prepared from toluene diisocyanate and polycaprolactone glycol (M_w 1000) as reported earlier[16] and shown in Scheme 1a. The resulting PU prepolymer was stored in airtight containers for further usage. Hydroxyl terminated polydimethylsiloxane (HTPDMS, $M_w \sim$ 1,000) also as epoxy modifier (Elkay Silicones, India), γ-aminopropyl triethoxysilane (γ-APS, Aldrich, USA) as silane cross-linking agent and dibutyltindilaurate (DBTL, Merck, Germany) as catalyst were used as received. HTPDMS was dried at $90\,^\circ$C under vacuum (0.01 Torr) for 4 h prior to usage to remove volatile impurities. Aromatic polyamine adduct (A, HY 2969), diethylenetriamine (B, HY 951) and polyamidoamine (C, HY 840), all obtained from Vantico®, India were used as curatives for the epoxy resin. The nomenclature and stoichiometry of curatives (in parenthesis), crosslinking agent and catalyst are presented in Table I.

Development of Polyurethane Modified Epoxy Resin (X_1)

A typical formulation of epoxy/PU (100/10, AX_1)

Table I. The stoichiometric equivalents of curatives, cross-linking agent and catalyst used in modified epoxy systems

Curatives used	Code	Epoxy/PU/silicone (w/w)			Amine eq/kg	Viscosity at 30 °C (cP)
		100/0/0, X_0	100/10/0, X_1	100/10/10, X_2		
Aromatic polyamine adduct, HY 2969	A	AX_0[a] (60)[b]	AX_1 (54)	AX_2 (48)	4.7–5.0	700–900
Aliphatic amine, HY 951	B	BX_0 (10)	BX_1 (9)	BX_2 (8)	20.6	10–20
Polyamidoamine, HY 840	C	CX_0 (50)	CX_1 (45)	CX_2 (40)	6.6–7.5	10000–15000
γ-APS	—	—	—	1.0	—	—
DBTL	—	—	0.02	0.04	—	—

[a]Nomenclature of modified epoxy systems. [b]Stoichiometric equivalents of curatives added.

was prepared by one-step polyaddition procedure as follows: Calculated amount of PU prepolymer (10 wt %) relative to the epoxy resin (100 w/w) were melt mixed for 10 min at 70 ± 1 °C in the presence of 0.02 wt % of DBTL catalyst, cooled to 30 °C and cured using 54 g of HY 2969 (A). PU prepolymer content was varied as 2.5, 5, 10, 15 and 20 wt % in order to optimize the PU content in epoxy resin. The inter-cross linking reaction between PU and epoxy (Scheme 1b) has been already confirmed.[17] Other PU modified epoxy resins were prepared in similar manner with varying the curatives 'HY 951 and HY 840' and referred as 'BX_1 and CX_1' respectively.

Development of Silicone Modified Polyurethane–Epoxy Resin (X_2)

Optimization of HTPDMS incorporation into epoxy has been reported earlier by the authors.[12] A typical formulation of epoxy/PU/silicone (100/10/10 by wt %, AX_2) was prepared as follows. PU (110 g) modified epoxy was mixed with 10 g of HTPDMS (Scheme 1c) and 1 g of γ-APS followed by 0.04 g of DBTL at 80 ± 1 °C with constant stirring for 10 min, cooled to 30 °C and cured using 48 g of HY 2969. Other silicone modified PU–epoxy resins were prepared in similar manner with varying the curatives 'HY 951 and HY 840' and referred as 'BX_2 and CX_2' respectively. Prior to characterization, the polymer mix was subjected to vacuum to remove the entrapped air and ethanol, which is a byproduct formed during the curing reaction between epoxy and silicone. All the above systems were obtained as tough sheets by casting in a mould at 30 °C, cured at 50 °C in a vacuum oven for 12 h and post cured at 70 °C for 24 h.
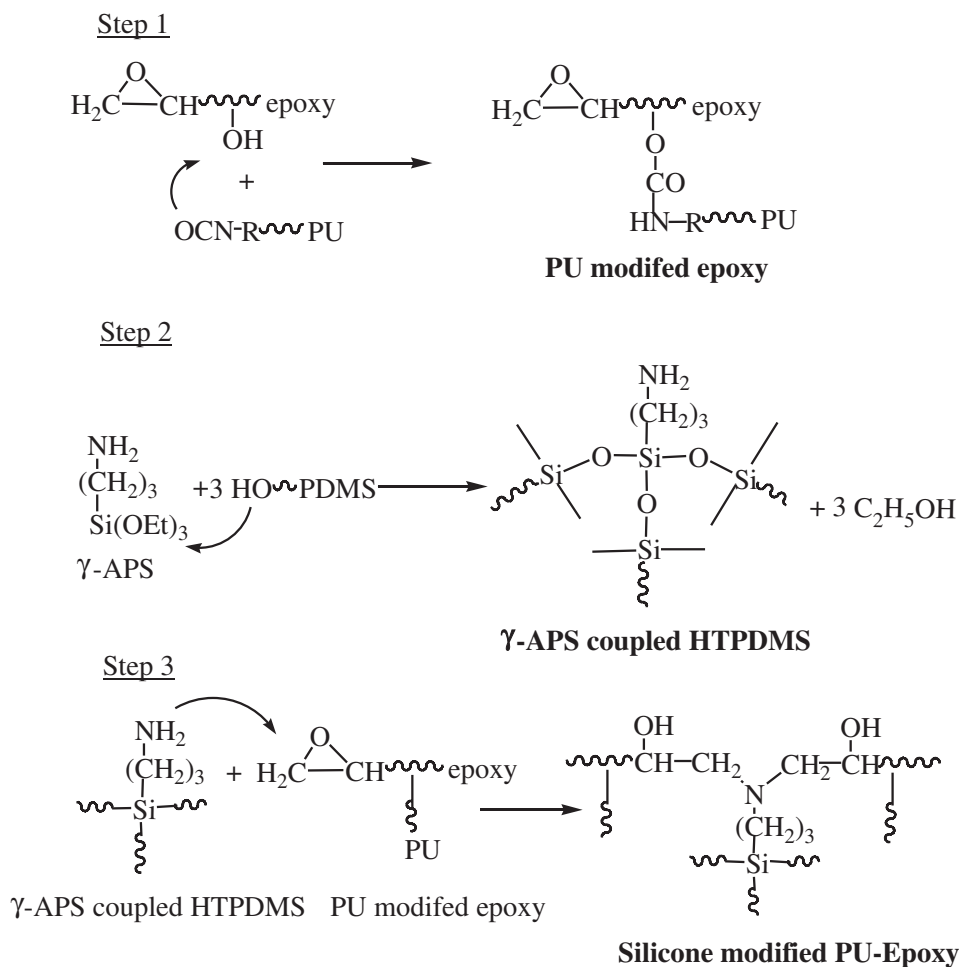
TEST METHODS

The curing mechanism of ICN formation in silicone modified polyurethane–epoxy resin is analyzed using FT-IR spectra obtained using a PerkinElmer Infrared Spectrometer. Tensile properties are studied using dumbbell-shaped specimens ($150 \times 25 \times 3$ mm) as per ASTM D 3039 using an Instron testing machine (Model 6025 UK), at a crosshead speed of 2 mm/min. Izod impact strength of samples ($63 \times 10 \times 3$ mm) was determined as per ASTM D 256-88. Hardness of the material is measured using a Durometer-Type D instrument as per ASTM D 2240. The abrasion resistance was determined by Taber Abrader as per ASTM D 4060 and expressed in terms of weight loss per 1000 number of revolutions under a stated load of 500 g. Dielectric strength of the specimen disks (100 mm in diameter and 4 mm in thickness) was measured according to ASTM D 149-87 using Shearing Bridge, Vettiner, France (accuracy 0.08%) at 250 V and 50 Hz. Arc resistance of the specimens (100 mm in diameter and 4 mm in thickness) was measured according to ASTM D 495 using Arc Resistance Tester (Enamelled Wire Testing Equipments, Pune, India) at 250 V and 50 Hz. Surface and volume resistivities of the samples were measured according to ASTM D 257-83 using disk shaped test specimens (SIGMA MM87, Million Mega Ohm Meter) at 500 V for 60 s at 30 °C. The water absorption property of the samples was tested according to ASTM D570. The cured specimens ($60 \times 60 \times 3$ mm) were immersed in distilled water for 24 h at 30 °C. Specimens were removed; surface water dried using tissue paper and weighed to an accuracy of 0.001 g.

RESULTS AND DISCUSSION

FT-IR Studies

The polymer network formation in silicone modified PU–epoxy proceeds in three steps (Scheme 2). In the first step, the isocyanate group of PU prepolymer reacts with secondary hydroxyl group of the epoxy resin. The disappearance of isocyanate peak at $2270\,cm^{-1}$ and formation of C=O and N–H peaks of urethane group at $1680–1630\,cm^{-1}$ and $1581–1518\,cm^{-1}$ respectively are used to ascertain the completion of the reaction (Figure 1b). The second step involves reaction between the ethoxy group in γ-APS

Step 1

PU modifed epoxy

Step 2

γ-APS coupled HTPDMS

Step 3

γ-APS coupled HTPDMS   PU modifed epoxy

Silicone modified PU-Epoxy

Scheme 2. Stepwise reaction mechanism in silicone modified PU–epoxy ICN.

and the hydroxyl group in HTPDMS. Decrease in intensity of –Si–OCH$_2$CH$_3$ peak at 2850 cm^{-1} and formation of Si–O–Si at 1133 cm^{-1} confirms the reaction between HTPDMS and γ-APS coupled epoxy resin (Figure 1c).[12] The third step, involves the reaction between epoxide of the epoxy resin and amino group of the γ-APS confirmed by the decreased epoxy band intensity at 913 cm^{-1}, increased intensity of hydroxyl group in epoxy at 3420 cm^{-1} and primary amine group in γ-APS at 1495 cm^{-1} (Figure 1d). FT-IR spectra of unmodified epoxy resin as reference is shown in Figure 1a.

Mechanical Studies

The incorporation of PU (0–15 wt %) into unmodified epoxy enhanced the values of tensile strength. However, beyond 15 wt % concentration of PU, further incorporation decreased the values of tensile strength (Table II and Figure 2) due to increased flexibility caused by uncrosslinked PU content.[17] For example, the values of tensile strength of 'AX' systems were increased to 3%, 11%, 24% and 28% with the incorporation of 2.5–15% (w/w) of PU. This is attributed to the formation of ICN structure between elasto-

meric PU and brittle epoxy resulting in toughening of the epoxy matrix. Further increasing the PU content to 20 wt % decreased the tensile behaviour due to increased flexibility and decreased crosslink density in PU–epoxy matrix. The increasing silicone component (0–10 wt %) in 'X$_2$' decreased the values of tensile strength (Table III) when compared to 'X$_1$'. This may be explained due to the weak interfacial boundary between silicone and PU modified epoxy resins. Besides, the siloxane moiety also performs as an internal plasticizer due to its flexible –Si–O–Si– linkage. Among the curatives, polyamidoamine (C) cured systems exhibit lowest tensile value when compared to 'A and B' cured systems (Figure 3). Due to the presence of secondary amino groups in polyamidoamine, the availability of reactive hydrogens is less when compared to other curatives. For example, the tensile value for 'CX$_2$' is 40.2 MPa, whereas that of 'AX$_2$' is 43.3 MPa. The higher value may be attributed to the aromatic nature and the availability of more reactive sites in 'AX$_2$' when compared to 'CX$_2$' cured systems. The values of tensile strength for matrices cured with different curatives follows in the order of A > B > C.
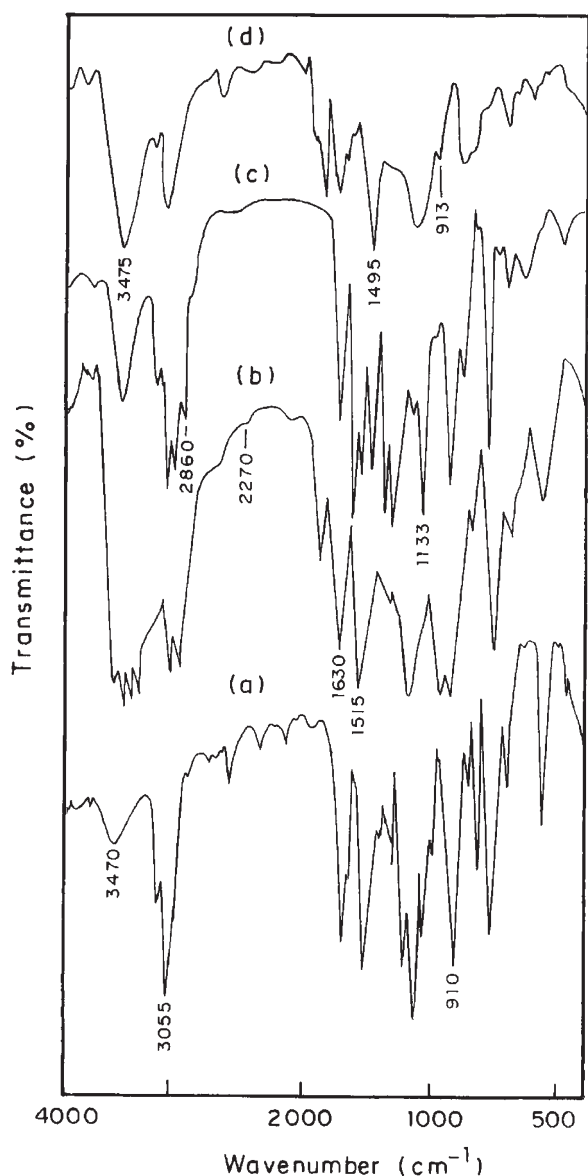
Figure 1. The FTIR absorption profiles of (a) Unmodified epoxy, (b) PU modified epoxy, (c) silicone modified with γ-APS and (d) PU–epoxy coupled with γ-APS.
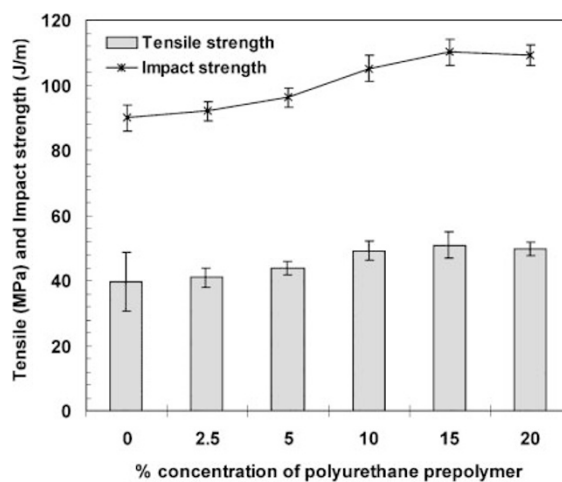

Figure 2. Plot of tensile and impact strength data against % concentration of PU prepolymer in PU modified epoxy (AX) systems.
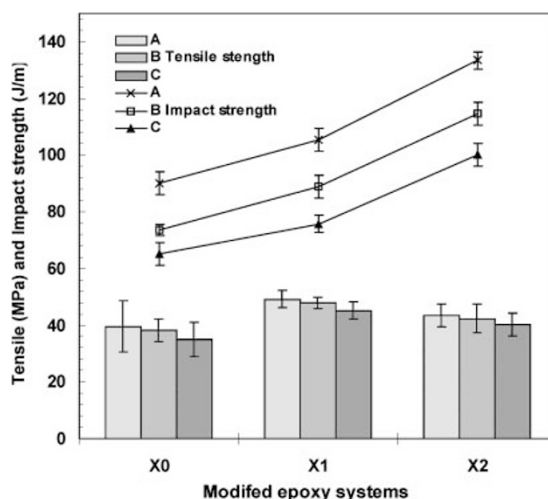

Figure 3. Plot of tensile and impact strength data against modified epoxy systems (X_0—unmodified epoxy; X_1—PU modified epoxy and X_2—silicone modified PU–epoxy).

Table II. Mechanical data of PU modified epoxy (AX) systems

Epoxy/PU (w/w) (AX)	Tensile strength (MPa)	Elongation (%)	Impact strength (J/m)	Abrasion resistance (g)	Hardness (Shore D)	Water absorption (%)
100/0	39.6 ± 9	6.8 ± 5	90.0 ± 4	0.0080	68	0.1201
100/2.5	40.9 ± 3	6.3 ± 2	92.1 ± 3	0.0072	69	0.1215
100/5	43.9 ± 2	5.6 ± 3	96.3 ± 3	0.0064	71	0.1230
100/10	49.1 ± 3	4.8 ± 5	105.2 ± 4	0.0052	73	0.1265
100/15	50.8 ± 4	4.3 ± 2	110.2 ± 4	0.0045	76	0.1225
100/20	49.7 ± 2	4.5 ± 4	109.2 ± 3	0.0049	73	0.1185

The values of elongation of 'AX' systems are decreased with increasing PU (0–15 wt %) content (Table II). However, in the case 20 wt % PU, the value of elongation increases due to increased flexibility imparted by uncrosslinked urethane. With the incorpora-tion of 10 wt % siloxane, the elongation values are fur-ther increased (Table III). This may be explained by the performance of the silicone moiety as an internal plasticizer due to its flexible –Si–O–Si– linkage. Among the curatives, 'C' cured systems exhibit better

Table III. Mechanical data of silicone modified PU–epoxy systems

Sample code	Tensile strength (MPa)	Elongation (%)	Impact strength (J/m)	Abrasion resistance (g)	Hardness (Shore D)	Water absorption (%)
AX_0	39.6 ± 9	6.8 ± 4	90.0 ± 4	0.0080	68	0.1115
AX_1	49.1 ± 3	4.8 ± 5	105.2 ± 4	0.0052	73	0.1185
AX_2	43.3 ± 4	5.8 ± 5	133.4 ± 3	0.0037	67	0.1115
BX_0	38.2 ± 4	7.2 ± 5	71.0 ± 2	0.0081	73	0.1201
BX_1	47.9 ± 2	5.2 ± 2	85.4 ± 4	0.0058	76	0.1265
BX_2	42.3 ± 5	6.0 ± 5	107.3 ± 4	0.0044	72	0.1185
CX_0	35.1 ± 6	7.5 ± 5	65.0 ± 4	0.0084	62	0.1210
CX_1	45.1 ± 3	5.4 ± 4	75.7 ± 3	0.0059	65	0.1288
CX_2	40.2 ± 4	6.2 ± 5	100.2 ± 4	0.0048	60	0.1202

elongation properties when compared with 'A, and B' cured systems due to reduced crosslink density compared to other systems. For example, the percent elongation values for 'CX_2' is $6.2 \pm 5\%$ whereas the 'AX_2' gave a value of $5.8 \pm 5\%$. The values of percentage elongation of matrices cured with different curatives follows the order of C > B > A. The values of impact strength notably increased with the incorporation of PU component (0–20%) in 'X_1' systems due to their elastomeric behaviour (Table II). The values of impact resistance further improved (by 26–50%) in silicone modified polyurethane–epoxy (X_2) due to the resilient and consequent stress dissipating capability of siloxane when compared to 'AX_1' (Table III). Among the curatives, 'A' cured system exhibited increased impact strength values (Figure 3). The values of impact strength follows in the order of A > B > C.

The abrasion resistance increases by 10–44% with incorporation of PU (0–20 wt %) component into unmodified epoxy and this may be due to the low coefficient of friction imparted to epoxy matrix by the PU component (Table II). Abrasion resistance further increased by 19–27% in silicone modified epoxy (X_2) and may be due to the smooth surface character of silicone and its consequent stress dissipating capability (Table III). The abrasion resistance behaviour of different systems followed in the order A > B > C.

Electrical Studies

The values of dielectric strength and arc resistance in PU modified epoxy (AX) systems marginally decreased upto 10 wt % of PU content but decreased appreciably at 15 and 20 wt % (Table IV and Figure 4). The increase in silicone concentration from 0–10 wt % in 'X_2' improved the dielectric and arc resistant char-
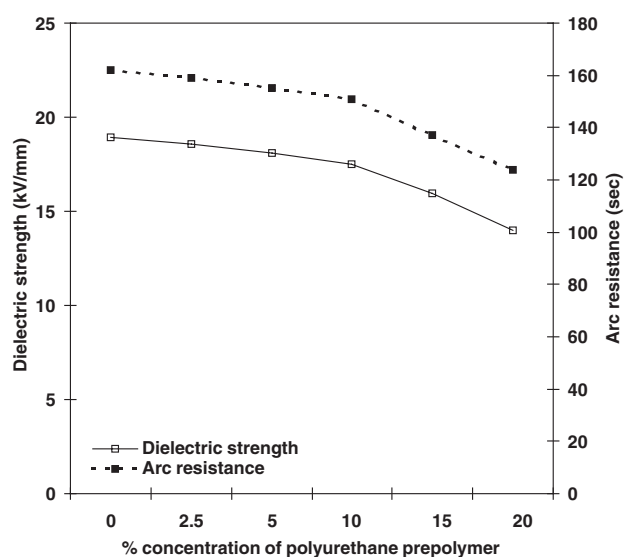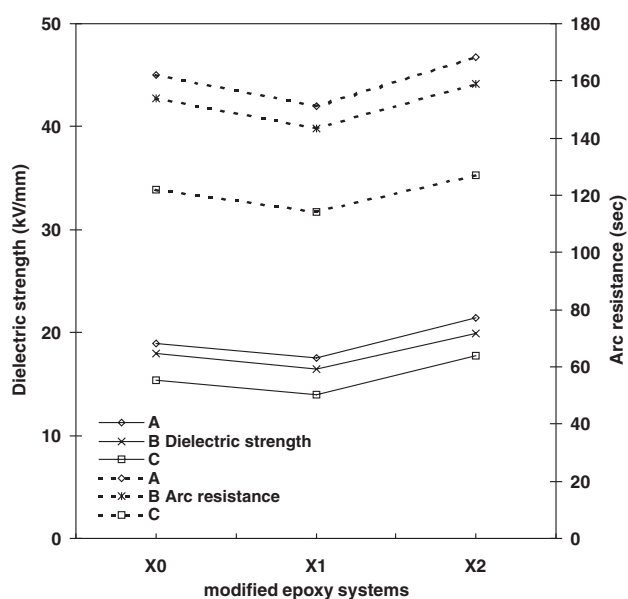

Figure 4. Plot of dielectric strength and arc resistance data against % concentration of PU prepolymer in PU modified epoxy (AX) systems.

Table IV. Electrical data of polyurethane modified epoxy (AX) systems

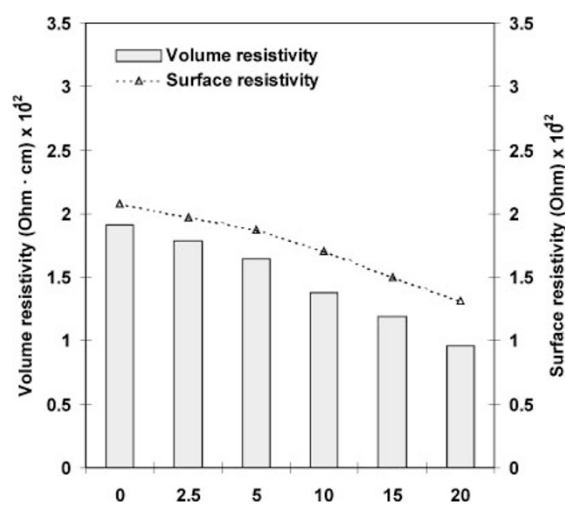| Epoxy/PU (w/w) (AX)	Dielectric strength (kV/mm)	Dielectric constant	Arc resistance (s)	Volume resistivity (Ω cm) $\times 10^{12}$	Surface resistivity (Ω) $\times 10^{12}$	Loss factor
100/0	18.9	8.1	162	1.91	2.07	0.0105
100/2.5	18.6	8.4	159	1.78	1.96	0.0108
100/5	18.1	9.3	155	1.64	1.87	0.0111
100/10	17.5	10.2	151	1.37	1.70	0.0117
100/15	16.0	12.0	137	1.18	1.50	0.0135
100/20	14.0	14.1	124	0.95	1.32	0.0156

Table V. Electrical data of silicone modified polyurethane–epoxy systems

Sample code	Dielectric strength (kV/mm)	Dielectric constant	Arc resistance (s)	Volume resistivity $(\Omega\,cm)\times10^{12}$	Surface resistivity $(\Omega)\times10^{12}$	Loss factor
AX_0	18.9	8.1	162	1.91	2.07	0.0105
AX_1	17.5	10.2	151	1.37	1.7	0.0117
AX_2	21.4	7.1	168	2.91	2.71	0.0091
BX_0	18.0	8.5	154	1.68	1.79	0.0111
BX_1	16.4	10.6	143	1.16	1.55	0.0123
BX_2	19.9	7.6	159	2.48	2.26	0.0096
CX_0	15.4	9.6	122	1.32	1.62	0.0125
CX_1	14.0	11.8	114	0.86	1.36	0.0140
CX_2	17.7	8.9	127	1.77	2.00	0.0114

Figure 5. Plot of dielectric strength and arc resistance data against modified epoxy systems (X_0—unmodified epoxy; X_1—PU modified epoxy and X_2—silicone modified PU–epoxy).

Figure 6. Plot of surface and volume resistivity data against % concentration of PU prepolymer in PU modified epoxy (AX) systems.
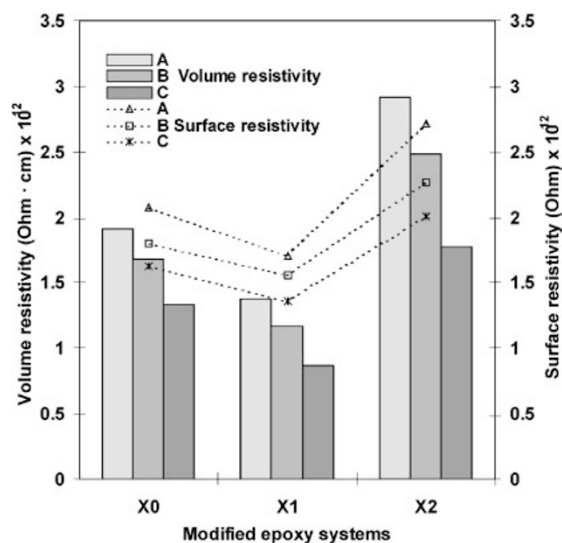
Figure 7. Plot of surface and volume resistivity data against modified epoxy systems (X_0—unmodified epoxy; X_1—PU modified epoxy and X_2—silicone modified PU–epoxy).

acteristics (Table V and Figure 5). Among the curatives used, the values and the dielectric strength and arc resistance are given in the order of A > B > C.

The values of volume and surface resistivities too decreased with increasing PU concentration (Table IV and Figure 6) whereas, incorporation of silicone (10 wt %) improved the values of volume resistivity by 52%, 48% and 33% and surface resistivity values by 30%, 26% and 24% for AX_2, BX_2 and CX_2 systems (Table V and Figure 7). The decrease in electrical properties for PU modified epoxy systems may be explained due to the presence of polar urethane linkages. The increase in values in silicone modified PU–epoxy systems may be due to the presence of inorganic Si–O–Si– linkage, which imparts better dielectric characteristics. The –Si–O–Si– linkage creates a discontinuity and does not allow the formation of continuous carbonized path when the specimens are

subjected to a high voltage. This reduced the leakage or fault path across the surface of the silicone modified PU–epoxy systems. Among the curatives, the poor performance of polyamidoamine (C) curative may be due to its polar and moisture absorbing nature.

Water Absorption

Water absorption behaviour of cured resins affects their mechanical and electrical characteristics. The water absorption behaviour of 'X$_1$' systems show an marginal increase with increasing polyurethane content (0–10 wt %), whereas, a significant increase in water absorption behaviour was noticed for 20 wt % PU due to the presence of uncrosslinked urethane moieties and inadequate crosslinking sites with epoxy (Table II). However, incorporation of silicone (10 wt %) in 'X$_2$' lowered the water absorption tendency when compared to 'X$_1$' (Table III). This behaviour may be attributed to the hydrophobic nature of silicone molecule and its surface enrichment character thereby lowering the permeability to water molecules. Among the curatives, polyamidoamine (C) cured systems exhibited highest water absorption (%) values than other curatives and is attributed due to the influence of polar amide group. 'A and B' cured systems exhibited lower water absorption behaviour due to their high crosslink density and non-polar nature.

CONCLUSIONS

Mechanical and electrical characteristics of PU modified epoxy (X$_1$) systems were studied and compared with silicone modified PU–epoxy (X$_2$). The modification of epoxy resin using PU (10 wt %, X$_1$) improved the mechanical characteristics appreciably due to the toughening nature of PU but marginally decreased the electrical characteristics due to the presence of polar urethane linkages. However, silicone (10 wt %) incorporation into 'X$_1$' improved both mechanical and electrical properties due to its stress dissipating nature and the presence of inorganic Si–O–Si linkage. It was also observed that the resistance to water absorption decreased with increasing PU content but increased with increasing silicone content. Among the systems studied, it can be concluded that the silicone (10 wt %) modified PU (10 wt %)–epoxy cured with aromatic polyamine adduct (HY 2969, AX$_2$) exhibited better mechanical, electrical and hydrophobic characteristics and can be used as coatings and composites for marine, industrial and electrical components.

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