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Thermal and Morphological Properties of Silicone-Polyurethane-Epoxy Intercrosslinked Matrix Materials

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Three different types of epoxy resins based on an unmodified epoxy (diglycidyl ether of bisphenol-A), polyurethane (PU) modified epoxy and silicone modified polyurethane-epoxy matrices were developed. Epoxy resin was modified with PU prepolymer and hydroxyl terminated poly (dimethyl siloxane), also referred to as 'silicones' using a silane crosslinking agent and tin catalyst. Aromatic polyamine adduct (A), diethylene-triamine (B) and polyamidoamine (C) were used as epoxy curatives. The formation of intercrosslinked network was confirmed using Fourier transform-infrared (FT-IR) spectra and viscosity data. Thermo gravimetric analysis revealed reduced thermal stability for PU (10 wt%) modified epoxy, whereas the incorporation of silicone (10 wt%) into PU modified epoxy matrix improved their thermal properties. The morphology of silicone modified PU-epoxy was also studied by scanning electron microscopy (SEM).

Keywords polyurethane, silicones, epoxy, intercrosslinked network, thermal stability, morphology

Introduction

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 thermo-mechanical properties.^[1,2] Among them, epoxy resin though possessing good adhesion and chemical resistance, its brittle behavior with low impact strength and elongation restricts the utility for high performance applications. Many attempts have been made in the past to toughen the epoxy resin.^[3–9] 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, polyurethane (PU) is favored due to its superior impact strength, low curing temperature and abrasion resistant characteristics. PU crosslinked with epoxy reduces phase separation and improves thermo-mechanical properties compared to unblended epoxy resins.^[8,10–14] Poly(dimethyl siloxane) (PDMS) commercially known as 'silicone' is another class of modifier due to its

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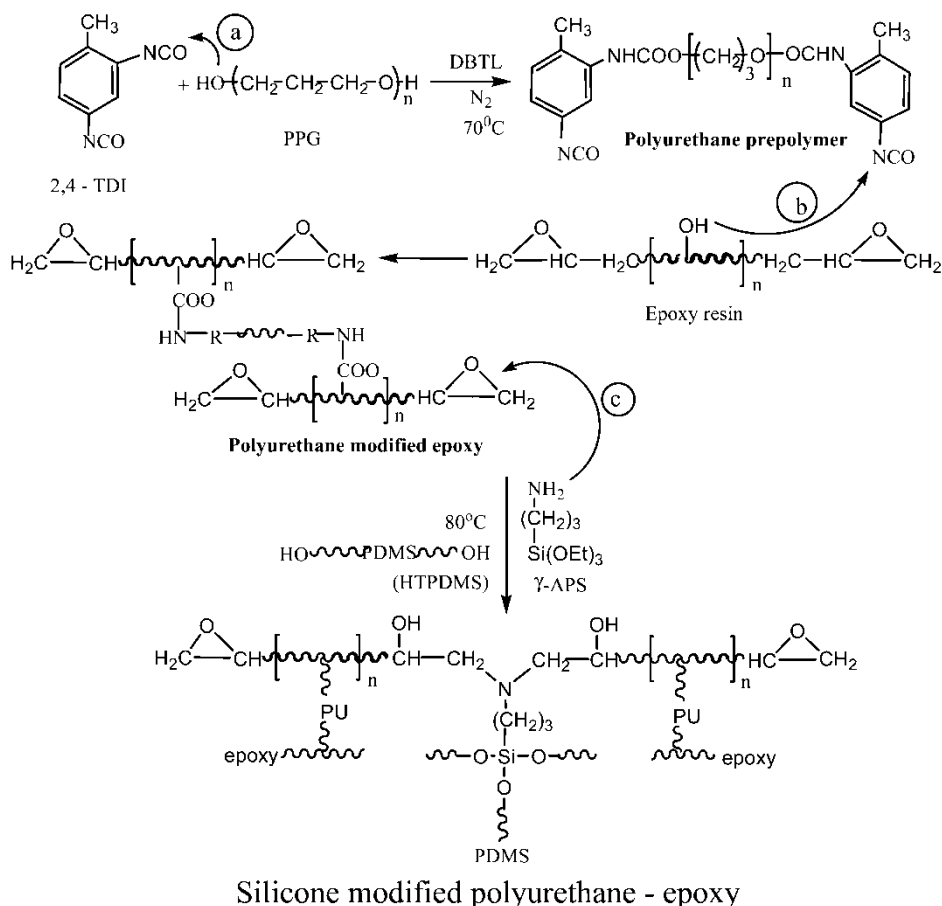
inherent characteristics like good wetting and film forming ability, low temperature flexibility and good hydrophobic behavior.^[15–17] Incorporation of a macrodiol such as PDMS into the epoxy matrix is generally difficult because of the poor compatibility between soft segments of PDMS and polar hard 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.^[18] Several techniques were reported in the literature to synthesize PDMS based polyurethane and epoxy matrices with improved thermo-mechanical properties, which primarily focused on increasing interfacial adhesion between PDMS phase and the hard domains in urethane and epoxy resins. These techniques include the introduction of polar functionality to PDMS^[12,19,20] and using silane coupling agents.^[21,22] 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 an increase of the PDMS soft segment. To overcome this limitation, we previously tried amino-terminated PDMS using amino silane coupling agents.^[12] Amino-terminated PDMS is bonded to the epoxy resin in the side chain to form a crosslinked structure. 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 an intercrosslinked network (ICN) mechanism in which two or more polymers are chemically crosslinked in their main or side chains to form a network structure and exhibit enhanced thermal and morphological characteristics than those obtained by blending technique. The technology of ICNs as materials for engineering 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 $<30^{\circ}\text{C}$): an unmodified epoxy; an PU-epoxy ICN where NCO terminated PU prepolymer was crosslinked with pendant hydroxyl groups in epoxy; and silicone modified PU-epoxy ICN where hydroxyl terminated poly(dimethyl siloxane) (HTPDMS) was crosslinked with oxirane groups in PU-epoxy using an silane coupling agent. Thermal and morphological characteristics of the modified epoxy resins were studied and compared with unmodified epoxy resins.

Experimental

Materials

The commercially available epoxy resin, 'GY 250' [DGEBA, Vantico[®], India; epoxy equivalent $\sim 180\text{--}190$, viscosity $9000\text{--}12,000$ cP] was used as a base material and is referred to as 'X₀'. PU prepolymer (NCO/OH ratio 1.5), as epoxy modifier, was prepared from toluene diisocyanate and polycaprolactone glycol (M.wt. 1000) as reported earlier^[14] and shown in Sch. 1(a). The resulting PU prepolymer was stored in airtight containers for further usage. HTPDMS (M_w ~ 1000) 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. 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 1.



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

Development of Polyurethane Modified Epoxy Resin (X_1)

A typical formulation of epoxy/PU (100/10, AX₁) was prepared by a one-step polyaddition procedure (Sch. 1(b)) as follows: Calculated amount of PU prepolymer (10 wt%) relative to the epoxy resin (100 w/w) were melt mixed for 10 min at $70 \pm 1^\circ\text{C}$ 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. Other PU modified epoxy resins were prepared in a similar manner with varying the curatives 'HY 951 and HY 840' and referred as 'BX₁ and CX₁', respectively (Table 1). X₀ refers to unmodified epoxy resin and used as reference throughout this study.

Development of Silicone Modified Polyurethane-Epoxy Resin (X_2)

HTPDMS was dried at $90 \pm 1^\circ\text{C}$ under a vacuum (0.01 torr) for 4 h prior to usage to remove volatile impurities. A typical formulation of epoxy/PU/silicone (100/10/10 by wt%, AX₂) was prepared as follows. 110 g of PU modified epoxy was mixed with 10 g of HTPDMS (Sch. 1(c)) and 1 g of γ -APS followed by 0.04 g of DBTL at $70 \pm 1^\circ\text{C}$

Table 1
The stoichiometric equivalents of curatives, cross-linking agent and catalyst used in silicone modified PU-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)	5.2–5.6	10,000–15,000
γ-APS	—	—	—	1.0	—	—
DBTL	—	—	0.02	0.04	—	—

^aNomenclature of modified epoxy systems.

^bStoichiometric equivalents of curatives added.

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 'BX₂ and CX₂', respectively (Table 1). 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 films by casting in a mold at 30°C, cured at 50°C for 12 h and post cured at 70°C for 24 h.

Testing Methods

Physico-chemical Studies

The curing mechanism of ICN formation in silicone-modified polyurethane-epoxy is analyzed using FT-IR spectra obtained using a Perkin-Elmer Infrared Spectrometer. The viscosity of the modified epoxy systems was measured at 30°C on a cone and plate viscometer set up with a 2.4-cm cone diameter at a 3° angle. The water absorption property of the samples was tested as per ASTM D 570.

Thermal Studies

The thermal stability of the cured resins was assessed by thermogravimetric analysis (TGA) using a Thermal Analyst 2000 instrument (TA Instruments, USA) at a heating rate of 10°C/min in an inert atmosphere. Glass transition temperature (T_g) of the matrices was determined by differential scanning calorimetry (DSC 2910, TA Instruments, USA) with a temperature range between 50 and 250°C at a heating rate of 10°C/min. The heat distortion temperature (HDT) of the samples was tested as per ASTM D 648-72.

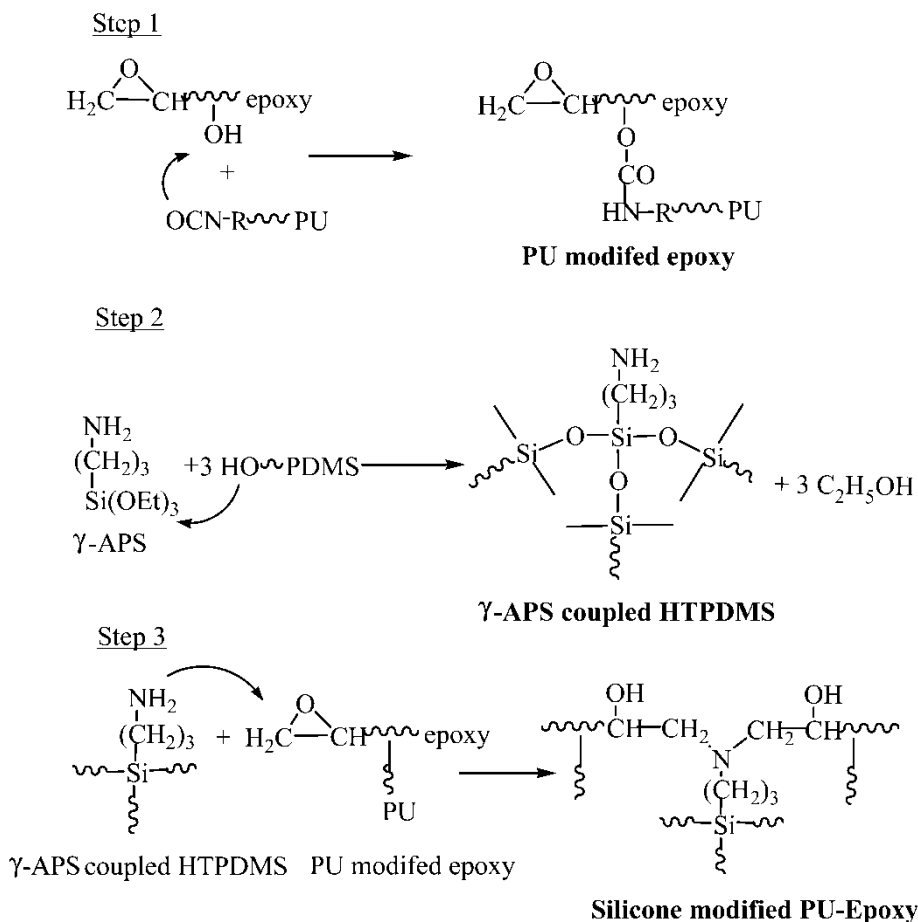
Scanning Electron Microscopy

The morphology of the fractured surface of the samples was observed using a scanning electron microscope (Leica Cambridge, Stereoscan Model 440). The samples were cooled in liquid nitrogen, fractured with a sharp blow, and the fractured section was coated with gold.

Results and Discussion

FT-IR Studies

The polymer network formation in silicone modified PU-epoxy proceeds in three steps (Sch. 2). In the first step, the isocyanate group of PU prepolymer reacts with a secondary hydroxyl group of the epoxy resin. The disappearance of the isocyanate peak at 2270 cm^{-1} and formation of C=O and N-H peaks of urethane group at $1680\text{--}1630\text{ cm}^{-1}$ and $1581\text{--}1518\text{ cm}^{-1}$, respectively are used to ascertain the completion of the reaction (Fig. 1(a)). The second step involves reaction between the ethoxy group in γ -APS and the hydroxyl group in HTPDMS. A decrease in intensity of the $-\text{Si}-\text{OCH}_2\text{CH}_3$ peak at



Scheme 2. Step-wise reaction mechanism in silicone modified PU-epoxy ICN.

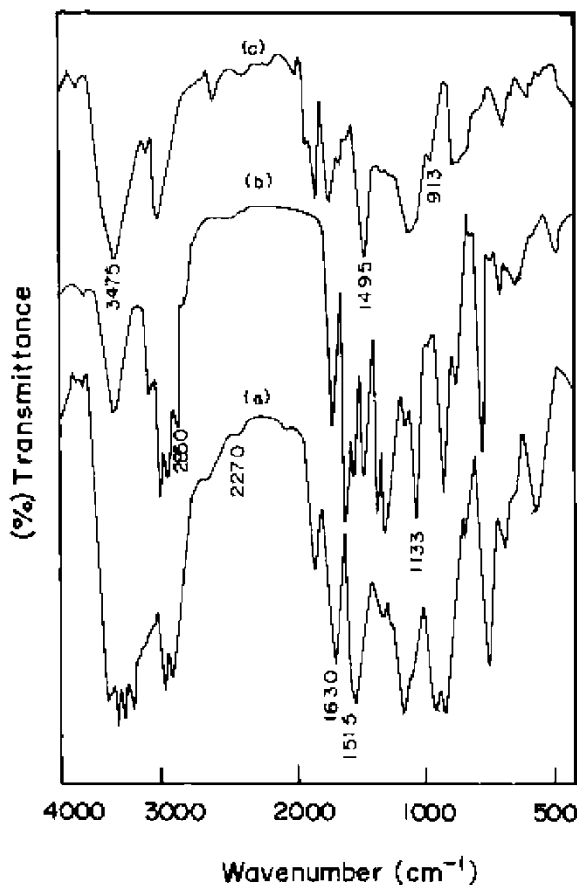


Figure 1. The FTIR absorption peaks of (a) PU modified epoxy, (b) silicone modified with γ -APS and (c) PU-epoxy coupled with γ -APS.

2850cm^{-1} and formation of Si–O–Si at 1133cm^{-1} confirms the reaction between HTPDMS and γ -APS coupled epoxy resin (Fig. 1(b)).^[17] 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 913cm^{-1} , increased intensity of hydroxyl group in epoxy at 3420cm^{-1} and primary amine group in γ -APS at 1495cm^{-1} (Fig. 1(c)).

Viscosity and Cure Schedule

The incorporation of PU (2.5–20 wt%) in unmodified epoxy increased the viscosity according to its concentration (Fig. 2). The further addition of silicone (10 wt%) in 'X₂' also increased the viscosity (Fig. 3). The cure schedule provides information about the working time available after mixing the resin with a curing agent to process them for applications such as impregnation, casting or fabrication operation, which involves 'flow'. The curing reaction of PU modified epoxy was accelerated by the addition of DBTL catalyst with the formation of ICN structure (Table 2). The incorporation of silicone in 'X₂' further accelerated the cure schedule. Among the curatives

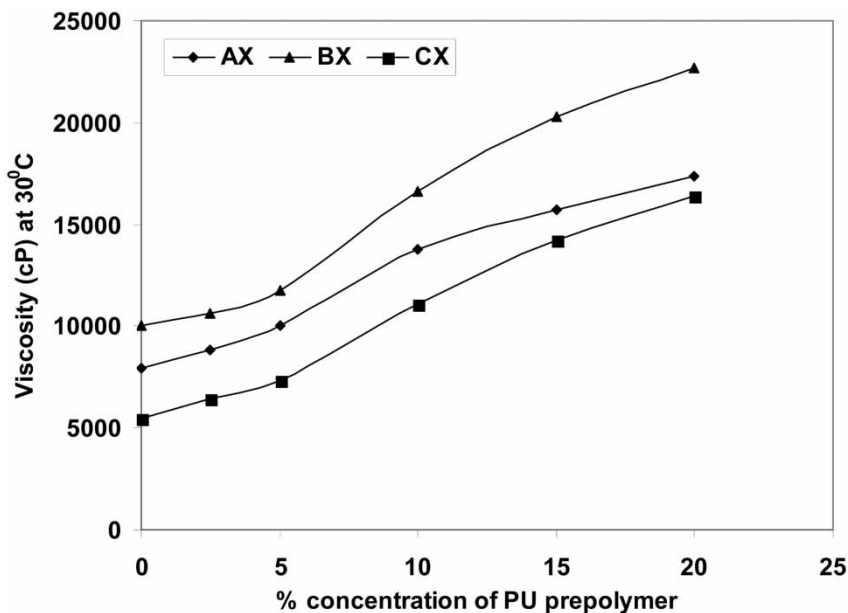


Figure 2. Viscosity studies on PU modified epoxy systems.

used, HY 951 (B) exhibited higher viscosity and minimum curing time than HY 2969 (A) and HY 840 (C).

The increasing viscosity and decreasing cure schedule in “X₁ and X₂” may be attributed to the formation of ICN structure. PU prepolymer and HTPDMS are chemically bonded to

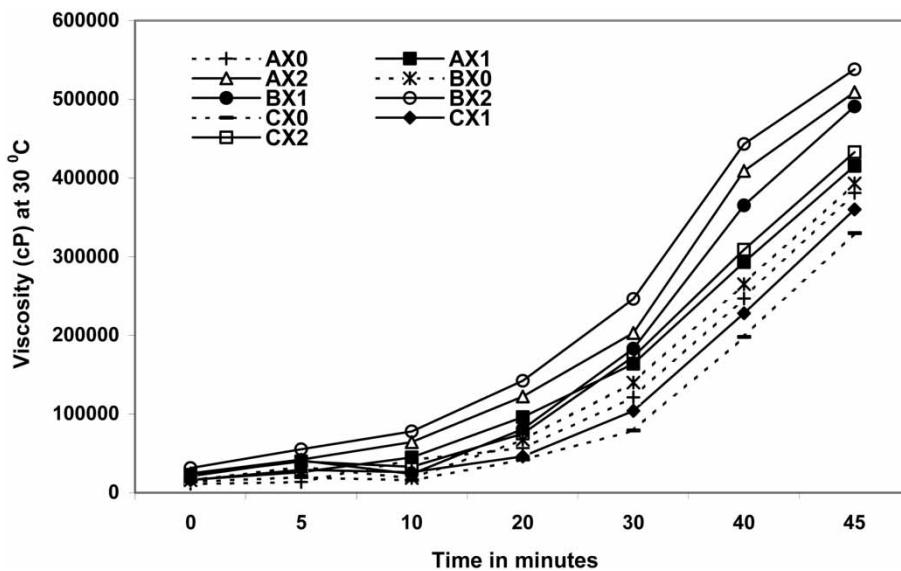


Figure 3. Viscosity studies on silicone modified PU-epoxy systems.

Table 2
Weight loss (%), glass transition (T_g) and heat distortion temperatures (HDT),
cure schedule and water absorption behavior of silicone modified
polyurethane-epoxy systems

Sample codes	AX ₀	AX ₁	AX ₂	BX ₀	BX ₁	BX ₂	CX ₀	CX ₁	CX ₂
10% Wt. loss	374	367	376	371	364	374	358	352	360
30%	402	398	405	395	390	396	381	378	383
50%	415	412	420	408	402	410	395	392	397
T _g (°C)	118	115	102	110	103	100	98	92	88
HDT (°C)	109	103	91	98	89	84	89	80	75
Cure schedule (min)	30	25	18	10	7	5	42	35	30
Water absorption (%)	0.11	0.12	0.09	0.12	0.13	0.10	0.13	0.14	0.11

the epoxy resin through secondary hydroxyl in epoxy and γ -APS, respectively. The order of viscosity and cure schedule for different curatives used followed in the order B < A < C. This may be due to the presence of a shorter aliphatic chain length and unhindered amino groups of curative 'B' resulting in increased reactive sites and high degree of crosslinking.

Thermo Gravimetric Analysis (TGA)

The introduction of 0–20% PU into unmodified epoxy reduced the thermal stability and decreased the degradation temperature (Fig. 4). For example, the temperature required for

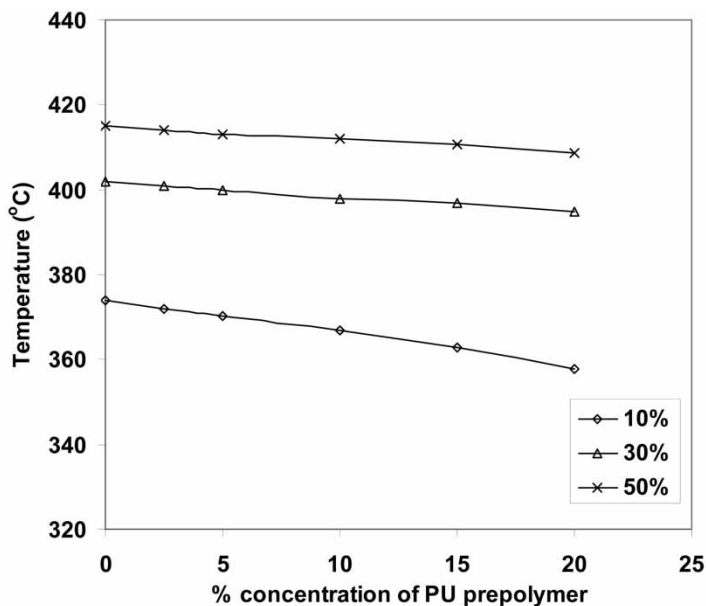


Figure 4. Weight loss (%) curves of PU modified epoxy (AX) systems.

10%, 30%, and 50% weight losses of unmodified epoxy (AX₀) is 374°C, 402°C, and 415°C, respectively. Whereas the temperature required attaining the same % weight losses for PU (10 wt%) modified epoxy (AX₁) decreased to 367°C, 398°C, and 412°C, respectively (Table 2). The incorporation of silicone in 'X₂' improved the thermal stability to a considerable extent (Fig. 5). The thermal stability of different curatives follows in the order A > B > C.

Reduced thermal stability for PU modified epoxy (X₁) compared to unmodified epoxy (X₀) may be attributed to the presence of thermally weak urethane linkages in the PU modified epoxy network.^[14] However, the delay in degradation observed for silicone modified epoxy (X₂) may be attributed to the ablative behavior of silicone moiety, partial ionic nature, high bond energy and thermal stability of -Si-O-Si- linkage in silicone. Among the curatives used, 'A' cured systems exhibited the highest thermal stability due to its thermally stable aromatic structure.

Glass Transition Temperature

DSC thermograms of PU modified epoxy and silicone modified PU-epoxy are presented in Figs. 6 and 7 and the values of glass transition temperature (T_g) are given in Table 2. The incorporation of PU (5–15%) into unmodified epoxy (X₀) slightly reduced their T_g values from 118°C (AX₀) to 115°C (AX₁) (Fig. 6). Incorporation of the silicone moiety further decreased the T_g values to 102°C (AX₂) (Fig. 7 and Table 2).

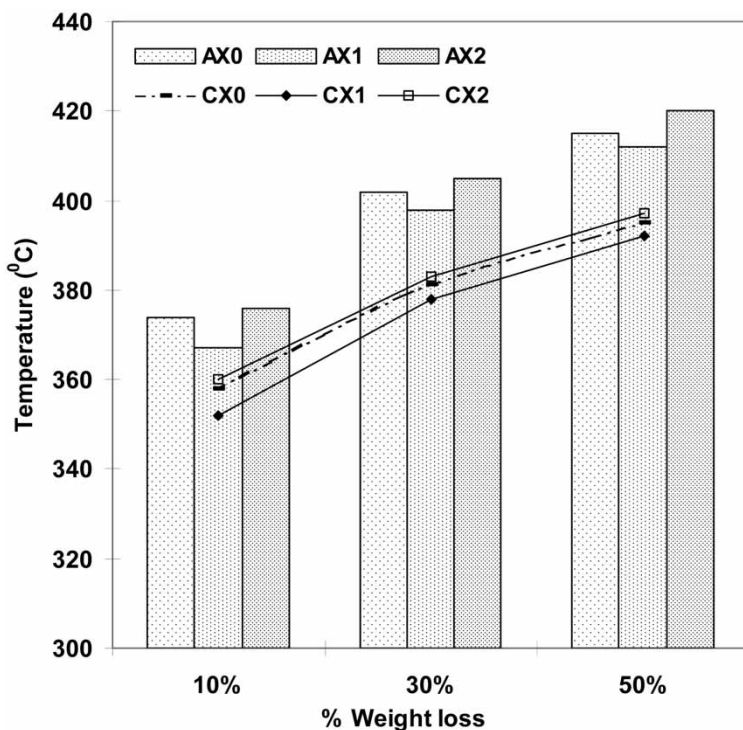


Figure 5. Weight loss (%) curves of silicone modified polyurethane-epoxy (AX and CX) systems.

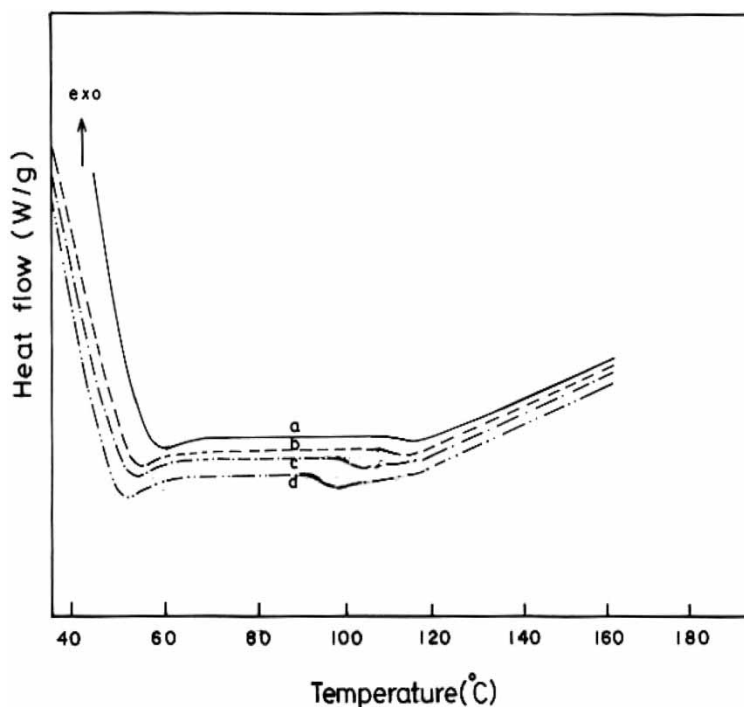


Figure 6. DSC traces of PU modified epoxy (AX) systems (a) unmodified epoxy; (b) 5%; (c) 10% and, (d) 20% PU modified epoxy.

Inter-phase mixing occurs during ICN formation resulting in lower values of T_g in “ X_1 and X_2 ” systems compared to unmodified epoxy (X_0). The flexible urethane linkage plasticize the epoxy matrix internally and creates more available free volume for molecular relaxation and lowers the T_g in “ X_1 ” systems. The presence of flexible $-\text{Si}-\text{O}-\text{Si}-$ linkage acting as a plasticizer also contributes towards lowering the T_g in “ X_2 ” systems. The single T_g values obtained for the “ X_1 and X_2 ” systems indicate that PU and silicone are chemically compatible with the epoxy matrix.

Heat Distortion Temperature (HDT)

HDT is one of the methods to determine the thermo-mechanical behaviour of matrix systems. HDT values of modified epoxy systems are presented in Table 2. It is evident that HDT decreased with increasing PU and silicone concentration. This may be explained due to the presence of flexible urethane and $-\text{Si}-\text{O}-\text{Si}-$ linkages. Among the curatives, aromatic polyamine adduct (A) cured systems exhibited higher HDT values due to the high crosslinking and aromatic structure imparted by the curative.

Scanning Electron Microscope

Scanning electron microscope (SEM) was used to investigate the morphology of modified epoxy systems (Fig. 8). SEM micrographs of the fractured surface of unmodified epoxy

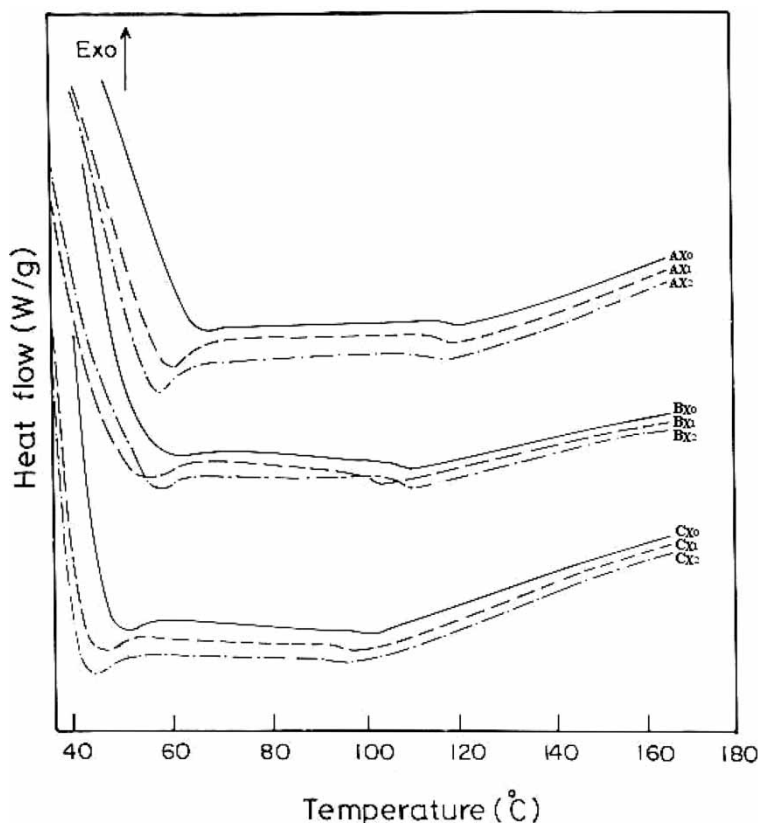


Figure 7: DSC studies on silicone modified PU-epoxy (AX, BX, and CX) systems.

resin cured using “A” reveal a smooth, glassy, and homogeneous microstructure without any plastic deformation (Fig. 8(a)). The fractured surfaces of the PU modified “BX₁” is almost similar to “X₀” systems and revealed a homogeneous morphology due to the efficient interaction between PU and epoxy resin (Fig. 8(b)). The SEM micrograph of the fractured surface of the silicone modified PU-epoxy matrix (AX₂) showed the presence of heterogeneous morphology (Fig. 8(c)). An interesting observation resulting in silicone modified epoxy systems is that the silicone (HTPDMS) did not rise to the top layer, instead, it is uniformly mixed over the whole specimen due to the fact that HTPDMS is chemically bonded to the epoxy resin.

Water Absorption Behavior

The water absorption (%) in “X₁” systems show a marginal increase with increasing polyurethane content (Table 2) due to the moisture absorbing nature of urethane linkages. However, incorporation of silicone (10 wt%) in “X₂” lowered the water absorption tendency when compared to “X₁” systems (Table 2). This behaviour may be attributed to the hydrophobic nature of silicone molecule and its surface enrichment character thereby exhibiting lower permeability to water molecules. Among the curatives used,

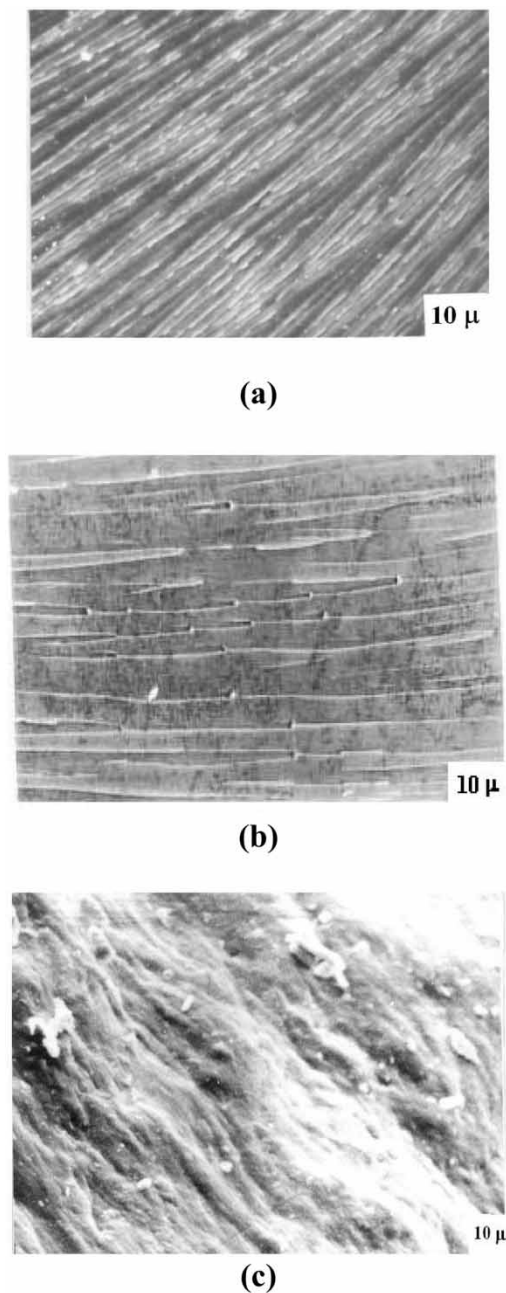


Figure 8. Scanning electron micrographs of (a) Unmodified epoxy, AX₀; (b) PU (10 wt%) modified epoxy, AX₁ and, (c) Silicone (10 wt%) modified PU-epoxy, AX₂.

polyamidoamine (C) cured systems exhibited highest water absorption (%) values than other curatives studied and is attributed due to the influence of polar amide group. “A and B” curatives exhibited lower water absorption (%) due to their high crosslink density and non-polar nature.

Conclusions

Thermal and morphological characteristics of PU modified epoxy (X_1) and silicone modified PU-epoxy (X_2) were studied and compared with unmodified epoxy (X_0). It can be concluded that the incorporation of PU (10 wt%) in " X_1 " marginally reduced its thermal stability, whereas, the incorporation of silicone (10 wt%) in " X_2 " improved its thermal stability. Flexible urethane linkages and free rotation of the Si-O-Si linkages resulted in reduced glass transition temperature (T_g) values for " X_1 and X_2 " systems. The single T_g value obtained for both " X_1 and X_2 " infers that urethane and silicone moieties are chemically incorporated with epoxy matrix in the form of an intercrosslinked network. The SEM analysis of the silicone modified PU-epoxy showed the presence of heterogeneous morphology. It was also observed that the resistance to water absorption decreased with increasing PU content and 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 thermal and morphological characteristics and can be used as thermal barrier coatings and composites for industrial applications.

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