

Thermal properties of siliconized epoxy interpenetrating coatings

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Abstract

This work involves the development of a novel siliconized epoxy interpenetrating coating system using epoxy resin as base, hydroxyl-terminated polydimethylsiloxane (HTPDMS) as modifier, γ -aminopropyltriethoxysilane (γ -APS) as crosslinking agent and dibutyltindilaurate (DBTDL) as catalyst. Polyamidoamine and aromatic polyamine adduct were used as curing agents for the above coating systems. The thermal behaviour, glass transition temperature (T_g) and morphological characteristics of unmodified epoxy and siliconized epoxy coating systems cured by polyamidoamine (B) and aromatic polyamine adduct (D) were studied using thermogravimetric analysis, differential scanning calorimetry and scanning electron microscopy, respectively, and the results are discussed. From the study, it is observed that the thermal stability of epoxy coating systems is enhanced when siloxane is incorporated to them. There is a slight decrease in the glass transition temperature observed for silicone-modified epoxy coatings and SEM analyses reveal that siliconized epoxy coating systems show heterogeneous morphology.

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Keywords: Organic coatings; Siliconized epoxy coatings; Hydroxyl-terminated polydimethylsiloxane; γ -Aminopropyltriethoxysilane; Aromatic polyamine adduct; Thermal characteristics

1. Introduction

The modern technology focuses on the development of reliable high performance coating materials having superior thermal and mechanical properties ideally suitable for adverse environmental conditions. Epoxy resin has been chosen for our present study owing to its exceptional combination of properties such as excellent toughness, adhesion and chemical resistance [1–3]. However, it does not possess adequate thermal and mechanical properties to meet the requirements of high performance structural products. Hence, modification of epoxy resins with flexible polymeric segments like carboxyl-terminated butadiene nitrile (CTBN) rubber, amine-terminated butadiene nitrile (ATBN) rubber, hydroxyl-terminated butadiene nitrile (HTBN) rubber, polyurethanes and silicones is mandatory [4–13] as these modifiers when incorporated with epoxy resin have been proved to improve its thermal and mechanical properties. Hydroxyl-terminated polydimethyl siloxane (fall under the category of silicones) is considered to be one of the best modifiers for epoxy resin among the other modifiers mentioned above, owing to its superior thermal and thermo-oxidative stability, excellent moisture resistance,

partial ionic nature, free rotation about bonds, and high compressivity and dampening action [14,15].

2. Experimental

Epoxy resin (diglycidyl ethers of bis phenol-A, DGEBA) GY 250 with epoxy equivalent of 180–190, viscosity about 10,000 cP was used as base, hydroxyl-terminated polydimethylsiloxane (HTPDMS) as modifier, γ -aminopropyltriethoxysilane (γ -APS) as crosslinking agent and dibutyltindilaurate (DBTDL) as catalyst. Polyamidoamine and aromatic polyamine adduct were used as curing agents for the epoxy and siliconized epoxy coating systems.

2.1. Synthesis of hydroxyl-terminated polydimethyl siloxane

HTPDMS used for the development of siliconized epoxy coatings was derived from octamethylcyclotetrasiloxane (Wacker-Chemie, Germany). Experimental set up used for the synthesis of HTPDMS is given in Fig. 1. One litre of octamethylcyclotetrasiloxane and potassium hydroxide catalyst (0.22% on the weight of octamethylcyclotetrasiloxane) were taken in a four-necked round bottom glass reactor. The reaction was carried out in an inert atmosphere by purging nitrogen. The temperature of the mixture was gradually

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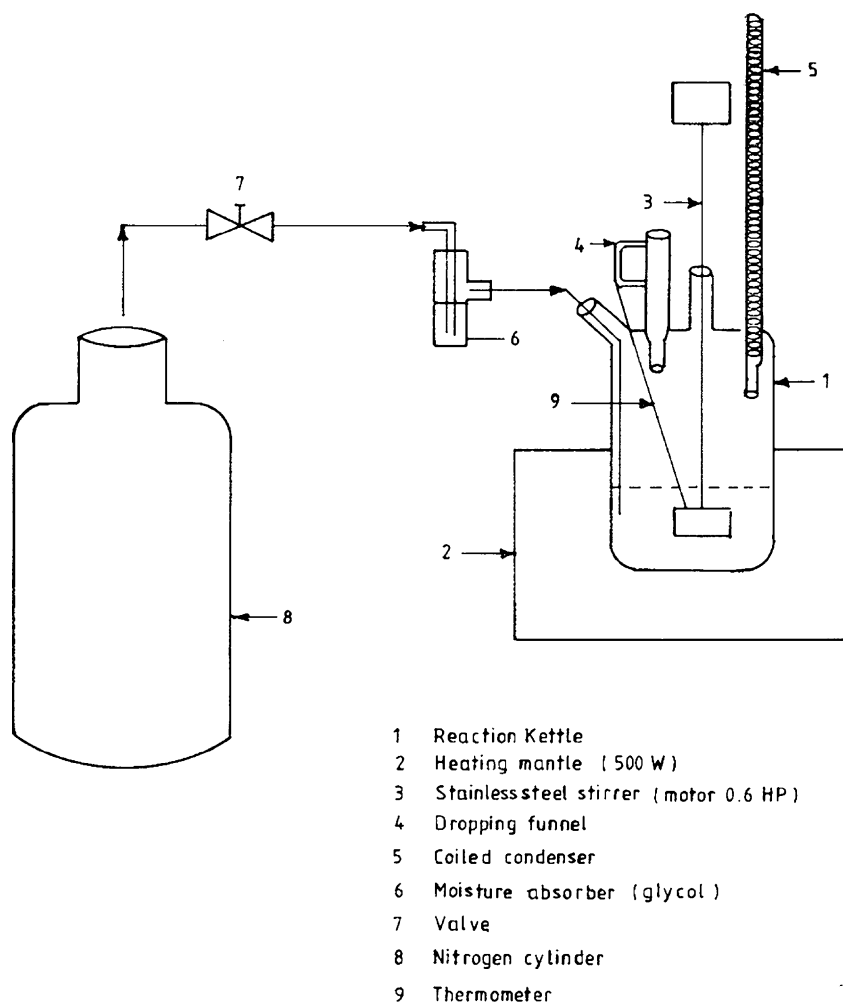


Fig. 1. Experimental set up used for the synthesis of HTPDMS.

raised to $90 \pm 1^\circ\text{C}$ for 4 h in a thermostatically controlled oil bath. The reaction mixture was cooled to about 50°C to avoid frothing. After degassing, the unreacted octamethylcyclotetrasiloxane was removed by distillation, gradually

increasing the temperature to 180°C . The HTPDMS resulted from the reaction was cooled to room temperature. The percentage conversion of octamethylcyclotetrasiloxane to polymer is calculated based on the recovery of

Table 1
Amount of curatives, crosslinking agent and catalyst used in siliconized epoxy coating systems

Siloxane/epoxy ratio (w/w)	Amount of curative (g)		Crosslinking agent (γ -APS) (g)	Catalyst (DBTDL) (g)
	Polyamido amine	Aromatic polyamine adduct		
10/90	45	60	0.1	0.01

Table 2
Nomenclature for siliconized epoxy coating systems

Curatives	Siloxane/epoxy ratio, 0/100 (w/w)	Siloxane/epoxy ratio, 10/90 (w/w)
Polyamidoamine	BX ₁ ^a	BX ₃ ^b
Aromatic polyamine adduct	DX ₁ ^c	DX ₃ ^d

^a Unmodified epoxy coating system cured by B.

^b Siliconized (10%) epoxy coating system cured by B.

^c Unmodified epoxy coating system cured by D.

^d Siliconized (10%) epoxy coating system cured by D.

Table 3

Percentage weight losses of unmodified epoxy and siliconized epoxy coating systems by thermogravimetric analysis

Weight loss (in %)	Temperature required to attain different weight losses of unmodified epoxy coating systems (°C)		Temperature required to attain different weight losses of siliconized epoxy coating systems (°C)	
	BX ₁	DX ₁	BX ₃	DX ₃
10	365	374	376	390
20	379	392	388	402
30	392	402	402	411
50	404	415	414	421

unreacted octamethylcyclotetrasiloxane (yield = 65%). (Yield = $w_2/w_1 \times 100$, where w_1 is the weight of the polymer obtained in the reaction and w_2 the weight of the unreacted octamethylcyclotetrasiloxane.)

2.2. Viscosity

The viscosity of the HTPDMS was determined by Brookfield digital viscometer. Molecular weight of the polymer was determined using viscosity values (molecular weight,

$m_v = 24,000$, refractive index = 1.3968, density = 0.956 g cm^{-3} and viscosity = 800–900 cP at 25 °C).

2.3. Preparation of siliconized epoxy prepolymer mix

Calculated percentage (w/w) of HTPDMS prepolymer, calculated percentage of epoxy resin, stoichiometric equivalent of γ -APS and DBTDL catalyst were thoroughly mixed at 90 °C for 20 min with constant stirring. Prior to characterization, the prepolymer mix was subjected to vacuum with

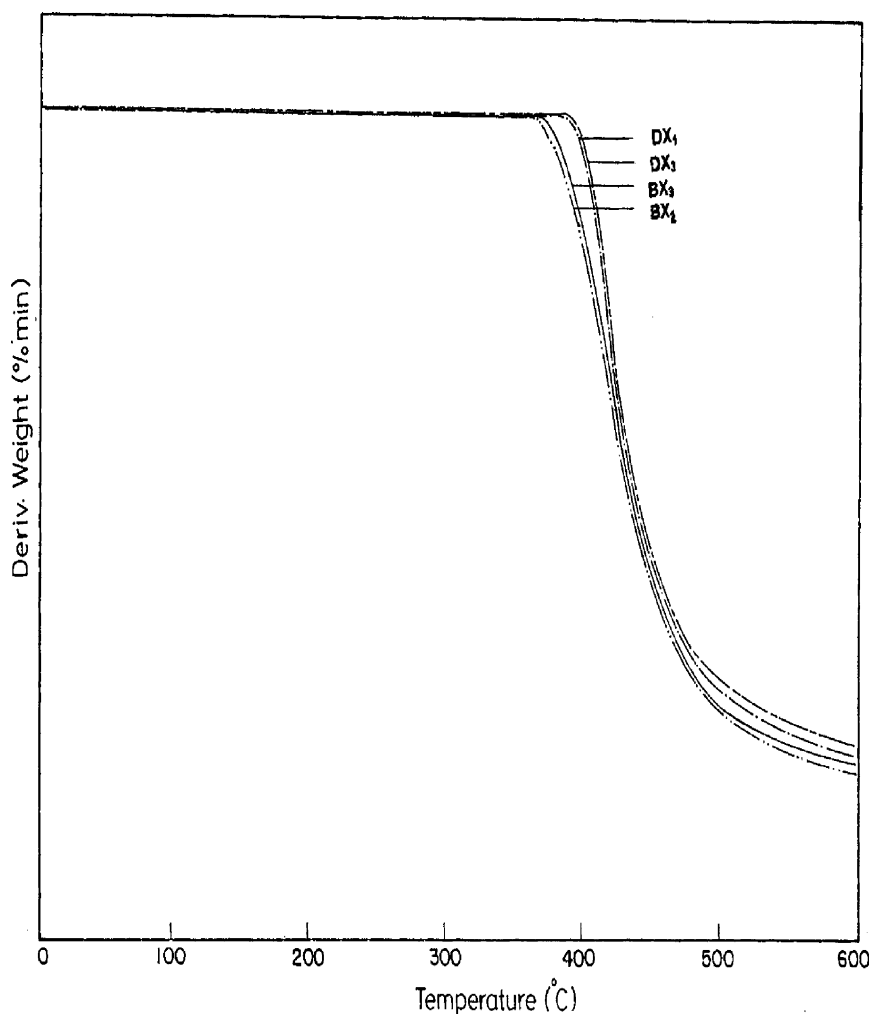


Fig. 2. Thermograms of epoxy and siliconized epoxy coating systems.

the help of vacuum pump to remove the trapped air inside the blend and also to accelerate the condensation reaction between γ -APS and HTPDMS by removal of ethanol formed during degassing process.

2.4. Preparation of siloxane-modified epoxy coating system

Siloxane-modified epoxy IPN coating system was developed using epoxy resin (DGEBA, GY 250, Ciba-Geigy) and is referred to as system X. The curatives polyamidoamine and aromatic polyamine adduct are referred to as systems B and D, respectively. Based on stoichiometric equivalent (Table 1), calculated amount of curatives was sequentially added to the siliconized epoxy prepolymer blend. The resulting products were coated over mild steel specimens at 30 °C after the removal of entrapped air and ethanol by-product formed during the curing reactions and post-cured at 80 °C for 24 h. The nomenclature of epoxy resin, curatives, and the siloxane content in the IPN coating systems are presented in Table 2.

2.5. Siloxane introduction into epoxy coating system

To obtain reasonable improvement in impact, and hydrophobic behaviour of the coating system without sacrificing other characteristics, the tentative requirement of HTPDMS component was taken as 10% (w/w). This has been ascertained from the data obtained from physicochemical, thermal, mechanical, electrical and ageing characteristics of cured siliconized epoxy matrix systems with varied percentages of siloxane content (viz. 10, 20 and 30%) [16].

3. Test methods

The corrosion-resistant behaviour of siliconized epoxy coatings studied by electrochemical methods has already been reported by the authors [17,18]. The thermal stability of unmodified epoxy and siliconized epoxy coating systems cured by B and D was studied using thermogravimetric analyzer (TGA-Mettler TA 3000) at the heating rate of 10 °C/min in an inert atmosphere. Thermogravimetric

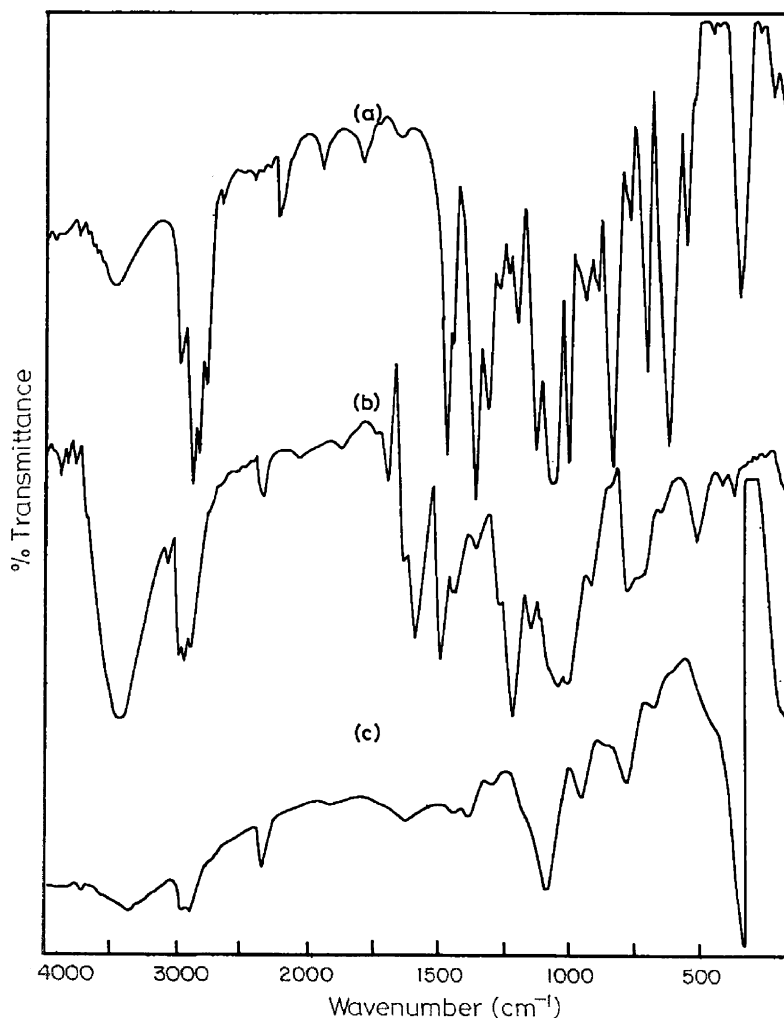


Fig. 3. Infrared spectra of epoxy (a), γ -APS cured epoxy resin (b) and γ -APS (c).

technique is the most important method to assess the thermal stability of polymeric materials. The percentage weight loss of the cured coating materials is presented in Table 3 and the thermograms are presented in Fig. 2.

Glass transition temperature (T_g) of the coating systems 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 thermal stability of the cured coating systems was assessed by thermogravimetric analysis (TGA) using Thermal Analyst 2000 (TA Instruments, USA) at a heating rate of 10 °C/min in an inert atmosphere.

Surface morphological characteristics of the cured coating systems was analysed by scanning electron microscope (SEM, Leica Cambridge, stereo scan model 440). The SEM micrographs were used to study the plain strain fractured surfaces of specimens.

4. Results and discussion

4.1. Spectral analysis

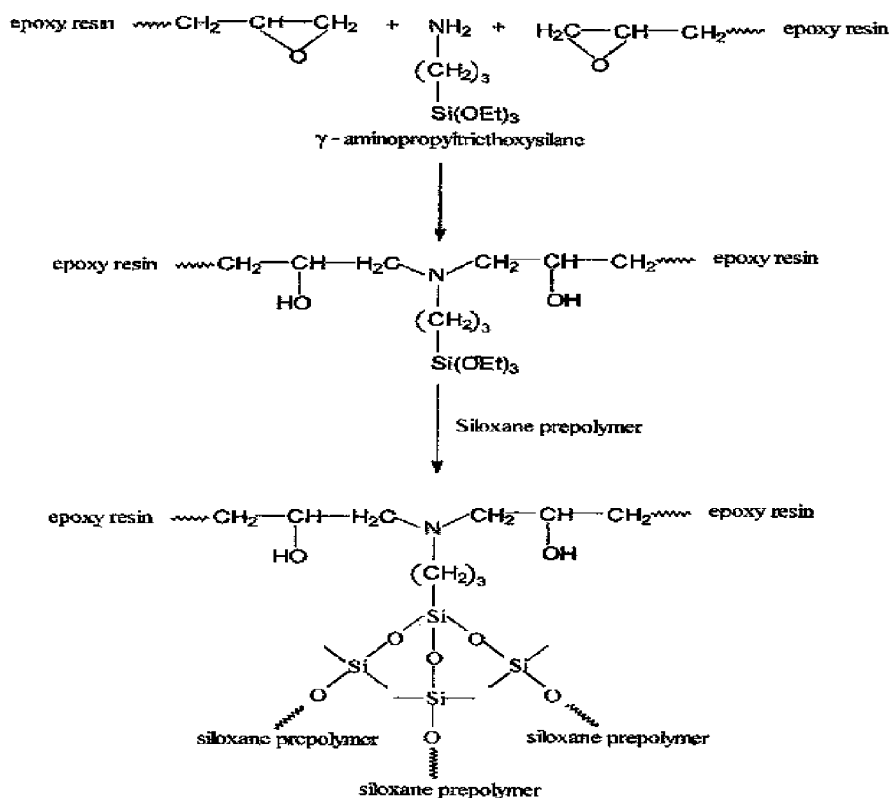
Infrared spectral results suggest that formation of siliconized epoxy interpenetrating network structure proceeds in two steps (Fig. 3 and Scheme 1). The first step involves the reaction between epoxide ring of epoxy resin and amino group of γ -APS that was confirmed by the disappearance of

epoxy band at 913 cm^{-1} and appearance of hydroxyl band at 3420 cm^{-1} . Absorption peaks appeared at 2980, and 2850 and 1370 cm^{-1} confirm the presence of $\text{Si-O-CH}_2\text{CH}_3$ and $-\text{Si}-(\text{CH}_2)_3$, respectively.

In the second step, the alkoxy groups present in the γ -APS react with hydroxyl groups of HTPDMS.

4.2. Thermogravimetric analysis

Incorporation of HTPDMS into epoxy resin improves thermal stability and enhances thermal degradation temperature. The presence of siloxane skeleton in the unmodified epoxy systems delays the degradation (Fig. 2) and high amount of thermal energy is required to attain the same weight losses when compared with that of unmodified epoxy coating systems (Fig. 2). The delay in degradation caused by the siloxane moiety may be attributed to the stability of inorganic nature ($-\text{Si-O-Si}-$) of siloxane structure, which may stabilize the epoxy resin from the heat. The high energy of siloxane bond and its partial ionic nature are clearly responsible for its substantial thermal stability. The siloxane bond energy is significantly greater than those of carbon-carbon and carbon-oxygen bonds [19]. For example, the temperatures required for 10, 20, 30 and 50% weight losses of unmodified epoxy resin cured with aromatic polyamine adduct (curative D) are 374, 392, 402 and 415 °C, respectively. Whereas, the temperatures required for attaining the same weight losses of siliconized epoxy coat-



Scheme 1.

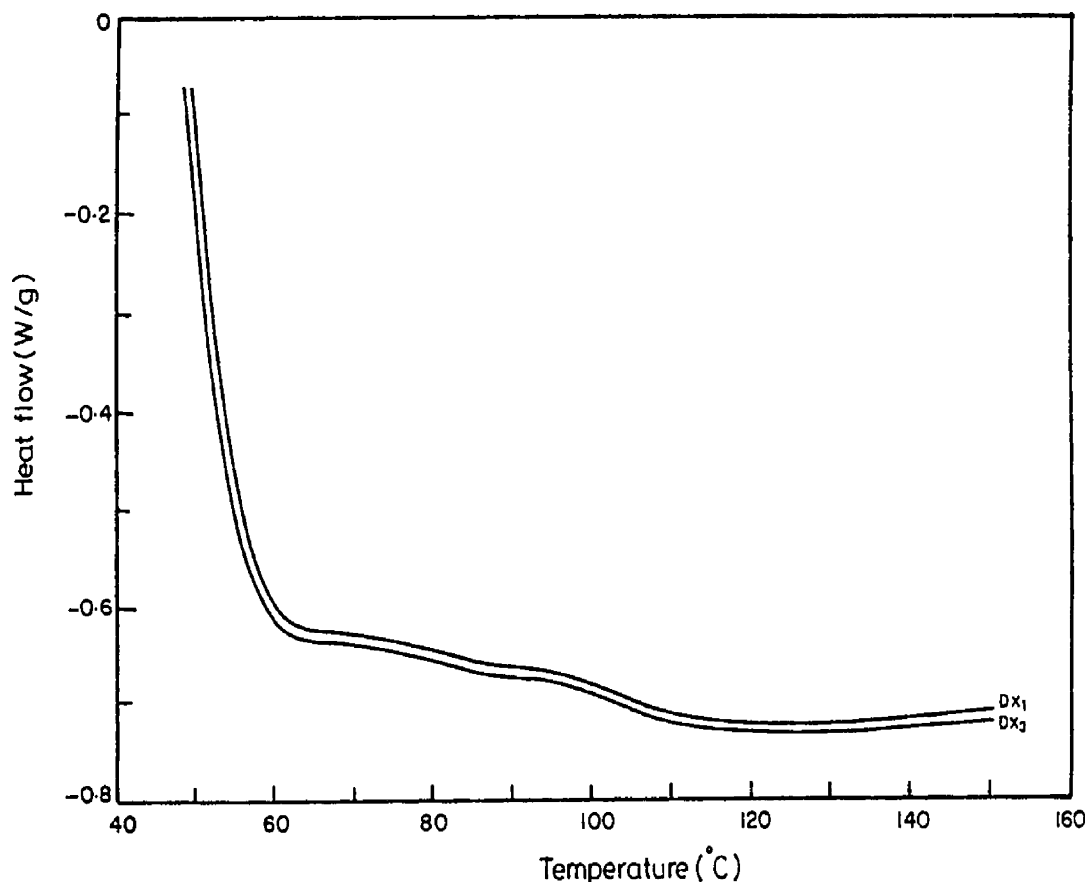


Fig. 4. DSC thermograms of unmodified epoxy and (10%) siliconized epoxy coating systems.

ing systems (epoxy modified with HTPDMS) having 10% siloxane content are enhanced to 390, 402, 411 and 421 °C. Further, it is also observed that the type of curative and percentage concentration of siloxane in the unmodified epoxy coatings have specific influence on thermal degradation. Among the curatives studied in the present investigation (B and D), the siliconized epoxy IPN coating system cured with aromatic polyamine adduct (D) exhibits highest thermal stability due to the thermally stable aromatic structure and formation of inter-crosslinking network structure with epoxy resin.

4.3. Results of differential scanning calorimetry

DSC thermograms of unmodified epoxy and (10%) siliconized epoxy coating systems are presented in Fig. 4. All siliconized epoxy coating systems exhibit single glass transition temperature (T_g), which in turn confirm the presence of inter-crosslinked network structure. The variation of T_g values of siliconized epoxy coating systems is insignificant, since siloxane incorporation does not alter the T_g values due to chain entanglement and its ablative character [20]. However, a slight decreasing trend is observed when siloxane is incorporated into the epoxy coating systems. The values of

glass transition temperatures of unmodified epoxy and siliconized epoxy coating systems cured by B and D are presented in Table 4.

4.4. Morphological studies by SEM

SEM was used to investigate the morphology of unmodified epoxy coating system and siliconized epoxy coating systems (Fig. 5). SEM micrograph of fractured surface of the unmodified epoxy coating system reveals a smooth, glassy and homogeneous microstructure without any plastic deformation. Whereas, the fractured surfaces of the siliconized epoxy coating systems show the presence of heterogenous morphology and the heterogeneity increases with increasing

Table 4
Glass transition temperature (T_g) of unmodified epoxy and siliconized epoxy coating systems

Coating systems	Glass transition temperature (°C)
BX ₁	97.0
BX ₃	95.91
DX ₁	106.0
DX ₃	103.06

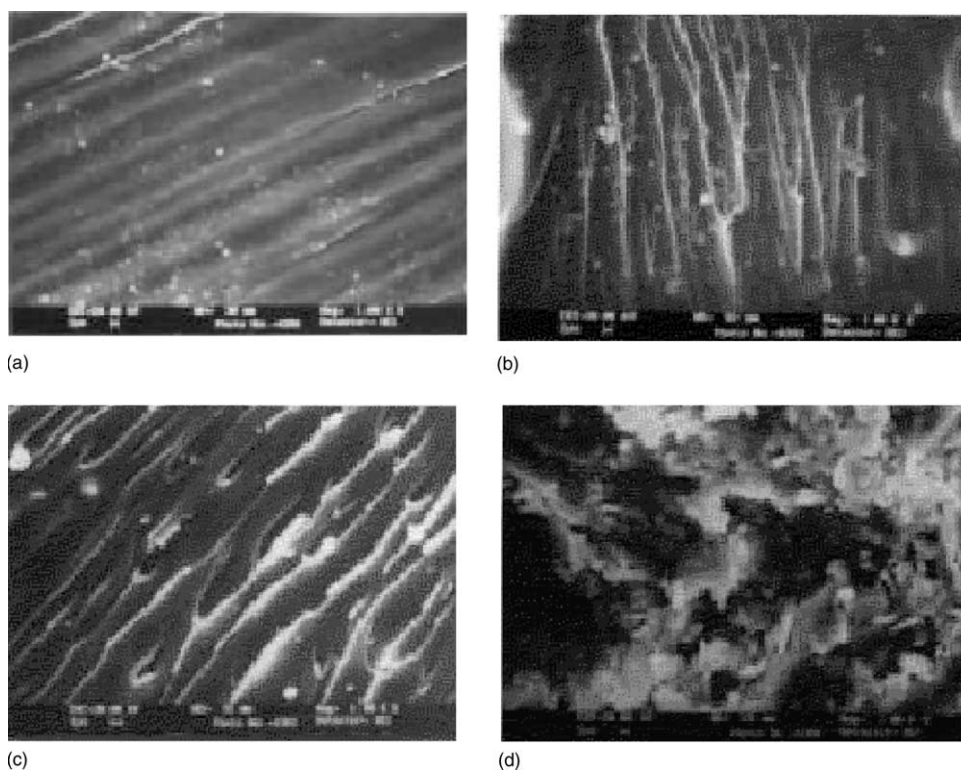


Fig. 5. SEM micrographs of fractured surface of the unmodified epoxy (a) and siliconized epoxy coating systems having 5% (b), 10% (c) and 15% (d) siloxane content.

siloxane content (5–15%). This observation also confirms the existence of inter-crosslinking network structure in siliconized epoxy coating systems [20].

5. Conclusions

Epoxy and siliconized epoxy interpenetrating coating systems were developed. The thermal stability, glass transition temperature (T_g) and morphological characteristics of unmodified epoxy and siliconized epoxy coating systems cured by polyamidoamine (B) and aromatic polyamine adduct (D) were studied using thermogravimetric analysis, differential scanning calorimetry and scanning electron microscopy, respectively. The thermal stability, glass transition temperature (T_g) and morphological characteristics of unmodified epoxy coating systems were compared with siliconized epoxy coating systems. It was found from the study that siliconized epoxy coating systems have greater thermal stability than epoxy coating systems due to their inherent characteristic property and partial ionic nature.

Siliconized epoxy coating systems cured with B and D exhibit single glass transition temperature, which indicates the existence of inter-crosslinked network as confirmed by DSC analysis. The glass transition temperatures of siliconized epoxy coating systems are slightly lower than that of epoxy coatings due to their inherent flexibility and free rotation about bonds.

The SEM micrographs reveal that siliconized epoxy coatings exhibit heterogeneous morphology and heterogeneity increases with increasing percentage of siloxane content, which in turn confirm the formation of inter-crosslinking network with epoxy resin. Hence, siliconized epoxy coatings developed in this investigation can be effectively used as thermal barrier coatings.

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References

- [1] H. Lee, K. Neville, Handbook of Epoxy Resins, McGraw-Hill, New York, 1967.
- [2] A.F. Yee, R.A. Pearson, Toughening mechanism in elastomer-modified epoxies. I. Mechanical studies, *J. Mater. Sci.* 21 (1986) 2462–2474.
- [3] A.J. Kinloch, S.J. Shaw, D.L. Hunston, Deformation and fracture behaviour of rubber toughened epoxy. 2. Failure criteria, *Polymer* 32 (1983) 1341–1344.
- [4] L.H. Sperling, D.W. Friedmann, Synthesis and mechanical behaviour of interpenetrating polymer networks: poly(ethyl acrylate) and polystyrene, *J. Polym. Sci. A-2* 7 (1969) 425–427.
- [5] L.H. Sperling, Recent Advances in Polymer Blends, Grafts and Block, Plenum Press, New York, 1974.

- [6] L.H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981.
- [7] R.F. Boyer, in: R.B. Seymour (Ed.), *History of Polymer Science and Technology*, Marcel Dekker, New York, 1982.
- [8] K.H. Hsieh, J.L. Han, Graft interpenetrating polymer networks of polyurethane epoxy. I. Mechanical behaviour, *J. Polym. Sci. B* 28 (1990) 623–630.
- [9] K.H. Hsieh, J.L. Han, Graft interpenetrating polymer networks of polyurethane epoxy. II. Toughening Mechanism, *J. Polym. Sci. B* 28 (1990) 783–794.
- [10] P.H. Sung, C.Y. Lin, Polysiloxane-modified epoxy polymer networks. I. Graft interpenetrating polymeric networks, *Eur. Polym. J.* 33 (1997) 903–906.
- [11] J.N. Sultan, F.J. McGarry, Effect of rubber particle size on deformation mechanism on glassy epoxy, *J. Appl. Polym. Sci.* 13 (1973) 29–33.
- [12] W.D. Bascom, R.L. Cottingham, R.L. Jones, P.J. Peysen, *J. Appl. Polym. Sci.* 19 (1975) 2425–2432.
- [13] S.J. Wu, T.K. Lin, Shyu, *J. Appl. Polym. Sci.* 75 (2000) 26–34.
- [14] W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York, 1969.
- [15] D.E. Leyden, *Silanes, Surfaces and Interfaces*, Gordon and Breach, New York, 1986.
- [16] T.V. Thanikai Velan, *Studies on synthesis and characterization of E-glass/kevlar 49 reinforced siliconized epoxy matrix composites for high performance engineering applications*, Ph.D. Thesis, Anna University, Chennai, India, 1997.
- [17] S. Ananda Kumar, M. Alagar, V. Mohan, *Surf. Coat. Int. B* 84 (1–90) (2001) 43–47.
- [18] S. Ananda Kumar, M. Alagar, K.P.O. Mahesh, T.S.N. Sankara Narayanan, V. Mohan, *Eur. Coat. J.* 4 (2000) 64–77.
- [19] E.A.V. Ebsworth, in: A.G. MacDiarmid (Ed.), *The Bond to Carbon*, Marcel Dekker, New York, Part 1, 1968, p. 46.
- [20] S. Ananda Kumar, *Development and characterization of siliconized epoxy interpenetrating coatings for high performance corrosion-resistant applications*, Ph.D. Thesis, Anna University, Chennai, India, 2001.