

Synthesis & Characterization of Modified Epoxy Resins and Novel E-Glass/ Spectra Reinforced Composites

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Abstract

This work involves the development of a novel siliconized epoxy interpenetrating system using DGEBA LY556 epoxy resin as base, hydroxylterminated polydimethylsiloxane (HTPDMS) as modifier, γ -aminopropyltriethoxysilane (γ -APS) as crosslinking agent and dibutyltindilaurate (DBTDL) as catalyst. Triethylenetetramine (TETA) was used as curing agent for the above system. Electrical resistant glass (E-glass) and Spectra ultra high molecular weight polyethylene (UHMWPE) reinforced composites are fabricated by hand-lay-up technique using siliconized epoxy matrix systems. The effect of the percentage of siloxanes and the two fibers on the thermal and morphological characteristics of the siliconized epoxy polymer composites are studied using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC). From the study, it is observed that the thermal stability of epoxy systems is enhanced when siloxane is incorporated to them. Morphological studies show that E-glass fiber reinforcement has better intermolecular adhesion to epoxy resin than Spectra reinforcement due to the presence of ionic sites.

Keywords: Siliconized epoxy systems; Interpenetrating network; E-glass/spectra composites; Thermal stability; Glass transition temperature .

1-Introduction

Epoxy resins have widely been used as structural adhesives, and in aviation industries as construction materials (Shieh, et al., 2002) because of their excellent bonding, good adhesion to many substrates, appropriate electrical, thermal and mechanical characteristics (Bouer, 1979 & Buncknall, 1990) . Epoxy resin based composites are used as laminates for printed circuit boards, aerospace, ballistic and engineering hardware components, pollution control equipments, automotive parts, electrical components, rehabilitation products, etc. However, some of its inferior characteristics, such as impact strength, resistant to weather and thermal stability, restrict their use in high performance applications (Sung P, et al., 1997).

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Toughening of epoxy resins (**Adams, et al., 1986**) with reactive diluents and oligomers has been an active field of research. Most of the earlier work on toughening of epoxy resins have been carried out by utilizing carboxy or amine terminated acrylonitrile-butadiene rubbers (CTBN and ATBN) (**Ronald S., 1983 & Riew & Kinloch, 1993**). Other elastomeric materials, such as functionally terminated acrylates (**Wang, et al., 1995**), polyurethanes (**Kemp, et al., 1992**) and siloxanes (**Iijima, et al., 1992**) have also been employed to a lesser extent. When high molecular weight modifiers are used, due to differences in the solubility parameters of the modifier and the epoxy network, the modifier phase separates from the system forming small domains in a continuous epoxy matrix. This is not observed when low molecular weight reactive diluents are used. In phase separated systems, in order to achieve the desired morphology and performance, it has been demonstrated that the modifier must react faster than the curing agent, and as a result, phase separation from the continuous rigid matrix as the gelation occurs (**Fournier, et al., 1996**). An interpenetrating network mechanism provides an effective method of obtaining the matrix materials with single glass transition value when compared with polymer blends, which normally exhibit multiple glass transition values due to thermodynamic incompatibility of the components involved. To overcome the phase separation, interpenetrating network mechanism is favored and can be achieved with the help of multifunctional cross-linkers (**Sung P, et al., 1997**). An attempt has been made to improve the properties of epoxy resin to an appreciable extent by incorporating hydroxyl terminated polydimethylsiloxane as toughening agent. Hydroxyl derivative of polydimethylsiloxane has been preferred as the toughening agent for epoxy resins because of its inherent characteristic properties, constant physical properties over a wide range of temperature, flexible molecular structure, resistance to weather and ozone, good wetting, high thermal stability, good dielectric strength, good hydrophobic and excellent physiological inertness (**Lin, et al., 1996; Gupta, et al., 2011 & Murias 2012**). Advanced composite materials have been used to fabricate many structural parts in engineering applications. This is due to their many attractive characteristics such as light weight, high strength, high stiffness, good fatigue resistance and good corrosion resistance. Also, the ability to manufacture parts with complicated geometry using fewer components enables manufacturers to save cost as compared with the same parts made of conventional metallic materials (**Suong, 2009**).

It has been proven that composites containing aminopropyltriethoxysilane APTES functionalized and silica enriched multiwall carbon nanotubes MWCNTs exhibit better thermal-mechanical properties in terms of higher storage modulus, higher T_g and improved dumping behavior in comparison to neat epoxy resin (**Lavorgna, M., et al., 2013**). The present work focuses on the preparation of siloxane modified epoxy resin/ E-glass and spectra ultra-high molecular weight polyethylene (UHMWPE) fiber composites, and the characterization of their properties with relevance to thermal stability.

2-Experimental

2.1 Materials

Commercially available epoxy resins LY556 DGEBA type having epoxy equivalent 184 with viscosity 10000-12000 cP and triethylenetetramine (TETA) were purchased from Huntsman Co. Dibutyltindilaurate (DBTDL), hydroxylterminated poly(dimethylsiloxane) (HTPDMS) and γ -aminopropyltriethoxysilane (APTES) were purchased from (Sigma Aldrich). High performance spectra fiber (Ultra High Molecular weight Polyethylene, UHMWPE, $M_n = 300,000$ g/mole) m.p = 146°C, was obtained from Akzo-Nobel Co. (Netherlands). E-glass (alumino-borosilicate) bidirectional woven fabric was purchased from OCV reinforcements. E-glass fabric was coated with nano TiN using PVD/PECVD Coating Plant Series NanoFlex 400. It is a "hybrid" high vacuum coating plant, extremely compact and designed for the deposition of thin films according to both the PVD (Physical Vapor Deposition) method and the PECVD (Plasma Enhanced Chemical Vapor Deposition) method, merging two plants in one. The plant is equipped with a PECVD source and 2 different types of PVD sources: a CAE (Cathodic Arc Ion Evaporator) and a couple of MS (Magnetron Sputtering) sources in Dual configuration so it can be used to deposit different types of metals or composite films.

2.2 Synthesis of prepolymer mix (Alagar, et al., 2000; BILAL, et al., 2000 & Ahmad, et al., 2005)

Calculated amounts of epoxy resin of DGEBA and hydroxyl terminated polydimethylsiloxane (HTPDMS) (90/10 wt. ratio) [0.1gm of HTPDMS + 0.9 gm DGEBA] were weighed followed by stirring under vacuum for 15min at 30°C to get rid of the air bubbles.

2.3 Synthesis of cured epoxy resin

Stoichiometric amounts of DGEBA and TETA were mixed thoroughly at room temperature for 15 min and the ratio of resin to hardener, by mass, was 10 : 1 (epoxy: curing agent). The mixture was poured into Al moulds with proper sample shapes and cured in a vacuum oven at 70°C for 120 min.

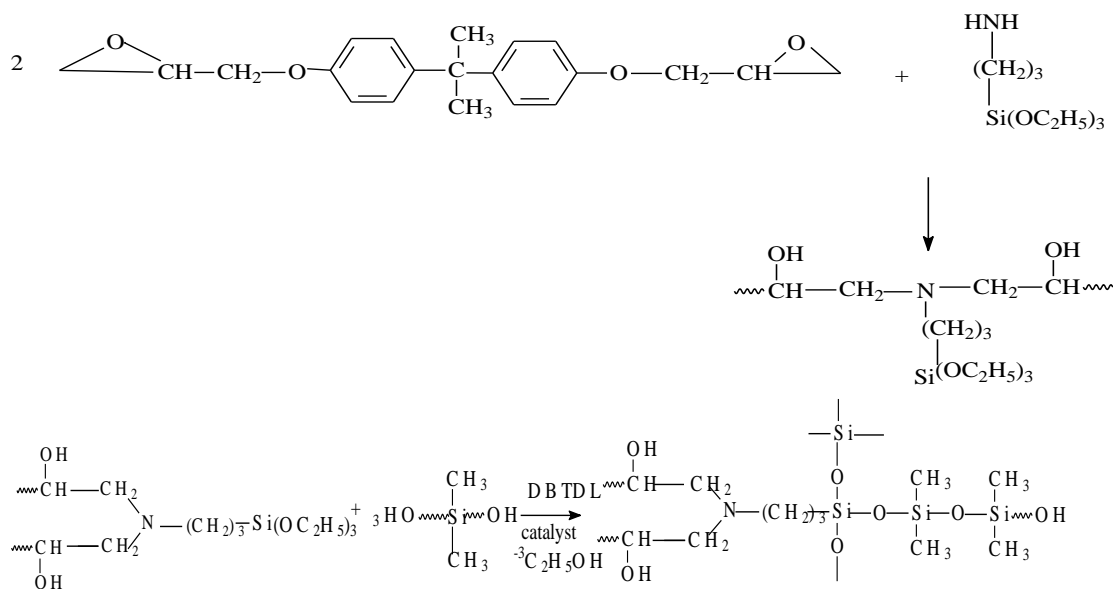
2.4 Synthesis of siliconized epoxy IPN (Alagar, et al., 2000; BILAL, et al., 2000 & Ahmad, et al., 2005)

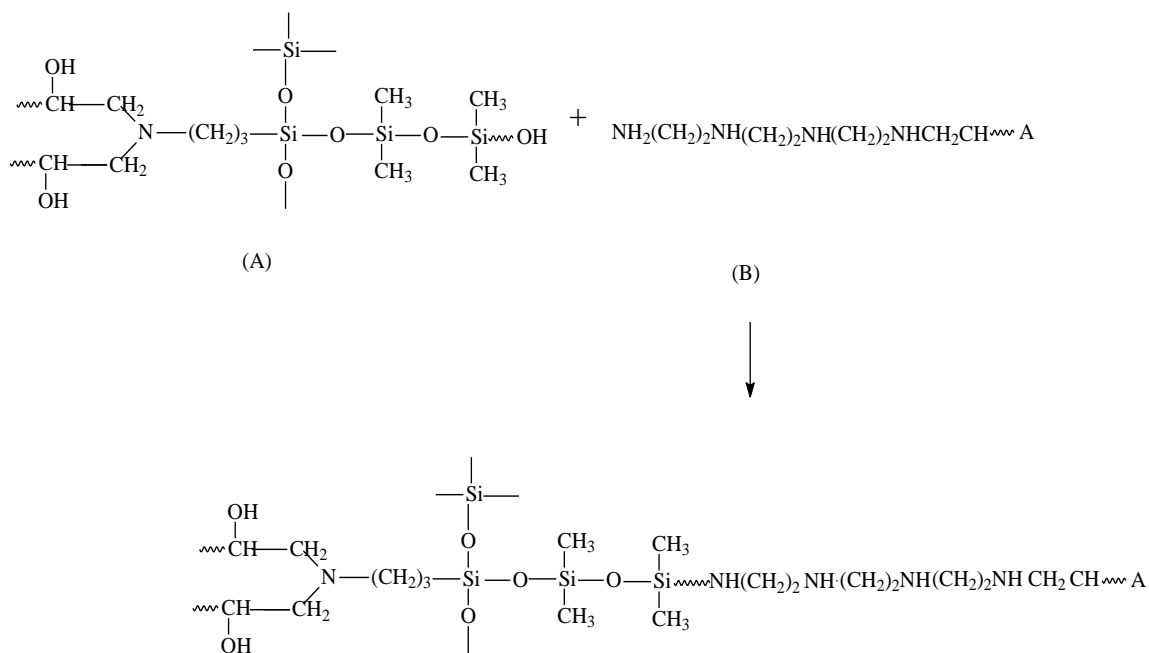
γ -Aminopropyltriethoxysilane (APES) cross-linker, dibutyltindilaurate (DBTDL) and the curing agent (TETA) were added, respectively, on the previous prepared prepolymer mix (DGEBA and HTPDMS) (Table 1). The mixture was mixed carefully under vacuum for degassing for around 30 min. Then, it was poured into Al moulds with proper sample shapes and cast in the mould at 30°C for 1h and post cured in a vacuum oven at 85°C for 120 min. After curing, the samples were cooled down to room temperature and kept in desiccators until further evaluation and testing. The nomenclature of curatives, epoxy resins and the concentration of siloxane present in the hybridized matrix systems are presented in Table 1.

Table1. Amount of curatives, cross-linking agent and catalyst in siliconized epoxy matrix.

Ratio of siloxane/epoxy	Amount of curing agent (g)	Cross-linking agent (g)	Catalyst (g)	Nomenclature of siliconized epoxy matrix system
0/100	0.185	--	--	X ₀
5/95	0.185	0.585	0.025	X ₅
10/90	0.185	0.585	0.027	X ₁₀
15/85	0.185	0.585	0.028	X ₁₅

The formation of siliconized epoxy IPN can be described in the following Scheme1 (BILAL, et al., 2000)





Scheme 1. Formation of siliconized ,IPN structure

Preparation of silconized epoxy fiber composites

2.4.1 Epoxy/E-glass composites

E-glass fabric was heated at 120°C for 2h to get rid of humidity and left to cool to room temperature. The fabric was coated with epoxy resin as well as siliconized epoxy matrix along with the hardener with compositions of [X₀] and [X₁₀] samples, respectively. The fiber to epoxy weight ratio was 30 to 70%, respectively.

2.4.2 Epoxy/E-glass nano TiN composites

E-glass fabric was coated with nanoTiN using PVD/PECVD Coating Plant the fabric was then heated at 120°C for 2h to get rid of humidity and left to cool to room temperature. The fabric was coated with epoxy resin as well as siliconized epoxy matrix along with the hardener [X₀] and [X₁₀], respectively. The fiber to epoxy weight ratio was 30 to 70%, respectively.

2.4.3 Spectra composites

Spectra fibers were washed with benzene, ethanol and water. The specimens were prepared as unidirectional fiber-reinforced composite with epoxy resin as well as siliconized epoxy matrix along with the hardener [X₀] and [X₁₀], respectively. The fiber to epoxy weight ratio was 30 to 70%, respectively. The fabric was coated with nano TiN using PVD/PECVD coating plant but the fiber was deteriorated.

The nomenclature of siliconized epoxy fiber composites can be represented in Table2.

Table 2. Nomenclature of siliconized epoxy fiber composites Characterization techniques

E-glass (30%)	Spectra (30%)	E-glass (30%) coated with nano TiN
AX ₀	BX ₀	ATX ₀
AX ₁₀	BX ₁₀	ATX ₁₀

2.6.1. FT-IR

FT-IR spectra of the neat samples were obtained with Nicolet 205 spectrophotometer (Nicolet, Madison, WI, USA). Transmittance was used and scans were operated from 400 to 4000 cm⁻¹.

2.6.2. ¹H NMR and ¹³C NMR (Sharif Ahmad, 2005)

The ¹H and ¹³C NMR spectra were recorded with a NMR spectrometer (SEOL, Japan). ¹³C NMR spectra were run at 500 MHz using deuterated dimethylsulfoxide (d₆-DMSO), and TMS was used as the internal standard. Chemical shifts are expressed in δ values.

Pure epoxy : (¹H-NMR, DMSO) δ (ppm): 7.07–6.8 (aromatic ring protons), 4.19 (-CH₂-O-Ar), 3.26–3.30 (-CH oxirane), 2.78–2.7 (-CH₂ oxirane), 1.54 (-CH₃).

Epoxy siloxane resin (¹H-NMR, DMSO) δ (ppm): 7.11–6.8 (aromatic ring protons), 4.24–4.22 (CH-OH), 4.18 (CH₂-O-Ar), 5.46 (OH), 3.7–3.27 (-CH oxirane), 2.8–2.67 (-CH₂ oxirane), 2.6 (CH₂-O-Si), 1.52 (-CH₃), 0.074 (-CH₃-Si).) (S.T.Lin, et al, 1996 and R.M. Silverstein, et al, 1991).

Pure epoxy (¹³C-NMR, DMSO) δ (ppm): 50.2 CH₂ (oxirane), 44.28 CH (oxirane), 69.3 (CH₂-O-Ar), 156.4, 143.2, 127.9, 114.3 (aromatic ring carbons), 41.7 (C(CH₃)₂).

Epoxy siloxane resin (¹³C-NMR, DMSO) δ (ppm): 50.3 CH₂ (oxirane), 44.2 CH (oxirane), 69.4 (CH₂-O-Ar), 156.5, 143.2, 128, 114.4 (aromatic ring carbons), 41.7 (C(CH₃)₂), 46.78 (CH₂-O-Si) 26.3 (CH₃-Si). (Keijman, 2000)

2.6.3. SEM measurements

Scanning electron microscope (SEM) (Quanta 250 FEG) was used to investigate the dispersion of siloxane and nano TiN in the epoxy matrix along with the adhesion on the fibers.

2.6.4. DSC measurements

The heat flow data, as a function of temperature and time, were obtained using the area under the peak of the exotherm of the samples using Q 2000 Differential Scanning Calorimeter (TA instruments USA) in the temperature range between 30 and 200°C at a heating rate of 5, 10, 15 and 20°C/min. The glass transition temperature (T_g) was taken as the midpoint of the specific heat capacity.

2.6.5. Thermogravimetric analysis (TGA)

TGA was carried out using Thermal Analyst Q 2000 (TA instruments USA) at a heating rate of 10°C/min. All experiments were conducted from room temperature to 600°C.

3. Results and Discussion

3.1. FTIR Analysis of the Polymers (Ananda kumar S, 2002)

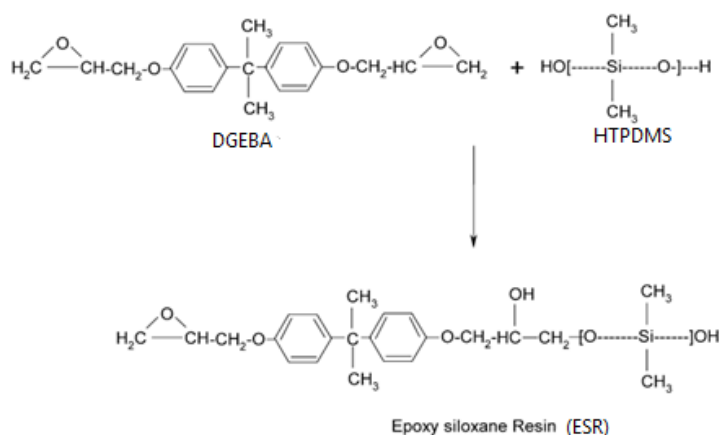
Infrared spectral results suggest that formation of siliconized epoxy interpenetrating network structure proceeds in two steps (Scheme 1). The first step involves the reaction between epoxide ring of epoxy resin and amino group of γ -APS that was confirmed by the disappearance of epoxy band in the range 915- 850 cm^{-1} and the appearance of hydroxyl band at 3459 cm^{-1} . Absorption peaks appearing at 2923, 2855, and 1314 cm^{-1} confirming the presence of $-\text{Si}-\text{O}-\text{CH}_2\text{CH}_3$ 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.

3.2. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (Sharif Ahmad, 2005)

In case of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of prepolymer, characteristics peaks of OH and $\text{CH}_3\text{-Si}$ further support the formation of epoxy siloxane prepolymer by the chemical reaction of DGEBA and HTPDMS. The presence of characteristics peaks in $^1\text{H-NMR}$ spectra (ppm, 2.63 ($\text{CH}_2-\text{O-Si}$), 1.55 ($-\text{CH}_3$), 0.074 ($-\text{CH}_3-\text{Si}$) and $^{13}\text{C-NMR}$ spectra (δ , ppm, 44.28 ($\text{CH}_2-\text{O-Si}$), 26.3 (CH_3-Si)) confirm the formation of epoxy siloxane resin. It is observed that the epoxy siloxane resin ESR has three functionalities per unit molecular chain (Scheme 2), an oxirane ring at one end of ESR, a terminal hydroxyl group of siloxane at another end of the chain and a pendant hydroxyl group.

Formation of these groups can further be attributed to the addition reaction of epoxy with siloxane (J. Chojnowski, 2003). The presence of such polar groups in polymeric resin and chemically bonded silicon in the backbone of the siloxane-modified epoxy resin enhances the stiffness, thermal stability and hydrophobicity of the resin.



Scheme 2. Preparation of epoxy siloxane resin

3.3. Thermogravimetric analysis (TGA)

3.3.1. Siliconized epoxy IPN

The thermal stability of epoxy and siliconized epoxy systems was evaluated by thermal gravimetric method. Modification of epoxy with siloxane improved thermal stability and enhanced degradation temperature of the epoxy resin according to silicone percentage concentration. This observation can be ascertained from Fig. 1. which shows the TGA and TDGA thermograms of cured epoxy and siliconized epoxy IPNs. The presence of siloxane moiety in the siliconized epoxy system delays the thermal degradation. 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 (**Ebsworth, 1968**). Thermal property parameters, namely the onset temperature of weight loss (T_{onset}), which represents the temperature at which the onset of a weight change can be detected, the temperature of the maximum rate of weight loss (T_m), the final decomposition temperature (T_f) and char yield (Y_c %) are given in Table 3. The results showed that the siloxane content has an influence on some thermal parameters. The thermal degradation of the epoxy IPN with 5 wt ratio of siloxane has $T_{onset} = 329^\circ\text{C}$. Pure cured epoxy starting at $T_{onset} = 324^\circ\text{C}$. The thermal degradation of the epoxy resin with 10 wt ratio of siloxane has $T_{onset} = 335^\circ\text{C}$ which starts later than epoxy IPN with 5 wt ratio of siloxane and with higher thermal stability.

There are two factors which have opposite influences on the thermal stability of epoxy-siloxane IPN. Firstly, previous studies have proved that the introduction of siloxane groups into the epoxy network decreases the rigidity of the epoxy network, leading to an increase in the motion of segments of the macromolecules in the DGEBA/HTPDMS IPN. Secondly, the formation of thermally stable three dimensional network through Si-O-Si- linkage of high bond energy this leading to minimizing the weight loss and improving thermal properties (**Velan, et al., 2002; Alagar, et al., 2000; Ebsworth, 1968 & Kumar, et al., 2002**). Comparing the char yield of the epoxy resin and its siliconized IPNs, it's obvious that the char yield increases with increasing siloxane content. Sample containing 15 wt ratio of siloxane having minimum char yield value of IPN which may be attributed to phase separation. It's observed that epoxy with 10 wt ratio siloxane possesses the highest thermally stable IPN of all prepared samples.

Table 3. Thermal property parameters for the investigated samples

Sample code	T_{onset} ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)	Char yield (Y_c %)
X_0	324	369	490	8.6
X_5	329	365	570	21.5
X_{10}	335	376	580	24.1
X_{15}	329	366	575	20.6

3.3.2. Siliconized epoxy fiber composites

TGA was performed for all prepared fiber composites to inspect which fiber composite is of highest thermal stability along with the effect of deposition of nano TiN on the fiber. Figs.2 and 3 show the TGA and TDGA thermograms of cured epoxy and siliconized epoxy IPN [X_0 and X_{10}], respectively; each reinforced with 30% of E-glass [AX_0 , AX_{10}], 30% spectra (UHMWPE) [BX_0 , BX_{10}] and E-glass with a layer of deposited nano TiN fibers [ATX_0 , ATX_{10}]. From these figures one may notice that the siloxane-epoxy IPN composites decompose exothermally at higher temperatures than unmodified corresponding ones.

Spectra composites decompose at much lower temperatures than E-glass composites which is attributed to the high melting point of E-glass around 800°C and for spectra 140°C.

The coupling agents can combine with both the glass fiber and the polymer matrix material to form a separate phase called the interphase. This interphase may have different properties from either the glass or the polymer material (Staab, 1999). However, the inorganic skeleton of siloxane units intimately bonds and efficiently wets the inorganic nature of silicates present in the E-glass reinforcement. Effect of siloxane is much more pronounced with spectra fiber by increasing T_m 11%, it increased thermal stability for E-glass fiber too. TiN didn't have the expected effect to enhance decomposition temperature. Thermal parameters were not enhanced which may be attributed to electrostatic interaction between TiN nano particles and polymeric chain of the siliconized IPN, developing the strain among the bonds of the polymers, which leads to the decomposition of composites at lower temperatures (Table 4).

Table 4. Thermal property parameters for the investigated fiber composites

Sample code	$T_{on\ set}$ (°C)	T_m (°C)	T_f (°C)	Residue (Yc%)
AX_0	316	364	599	37.7
BX_0	308	360	580	10.94
ATX_0	329	370	597.5	29.6
AX_{10}	319	370	598	60
BX_{10}	310	450	568	24
ATX_{10}	336	371	599	39.5

Figure 1. TGA (a) and DTGA (b) thermograms of cured epoxy resin and its siliconized IPN containing different weight ratios of siloxane recorded at heating rate 10°C/min.

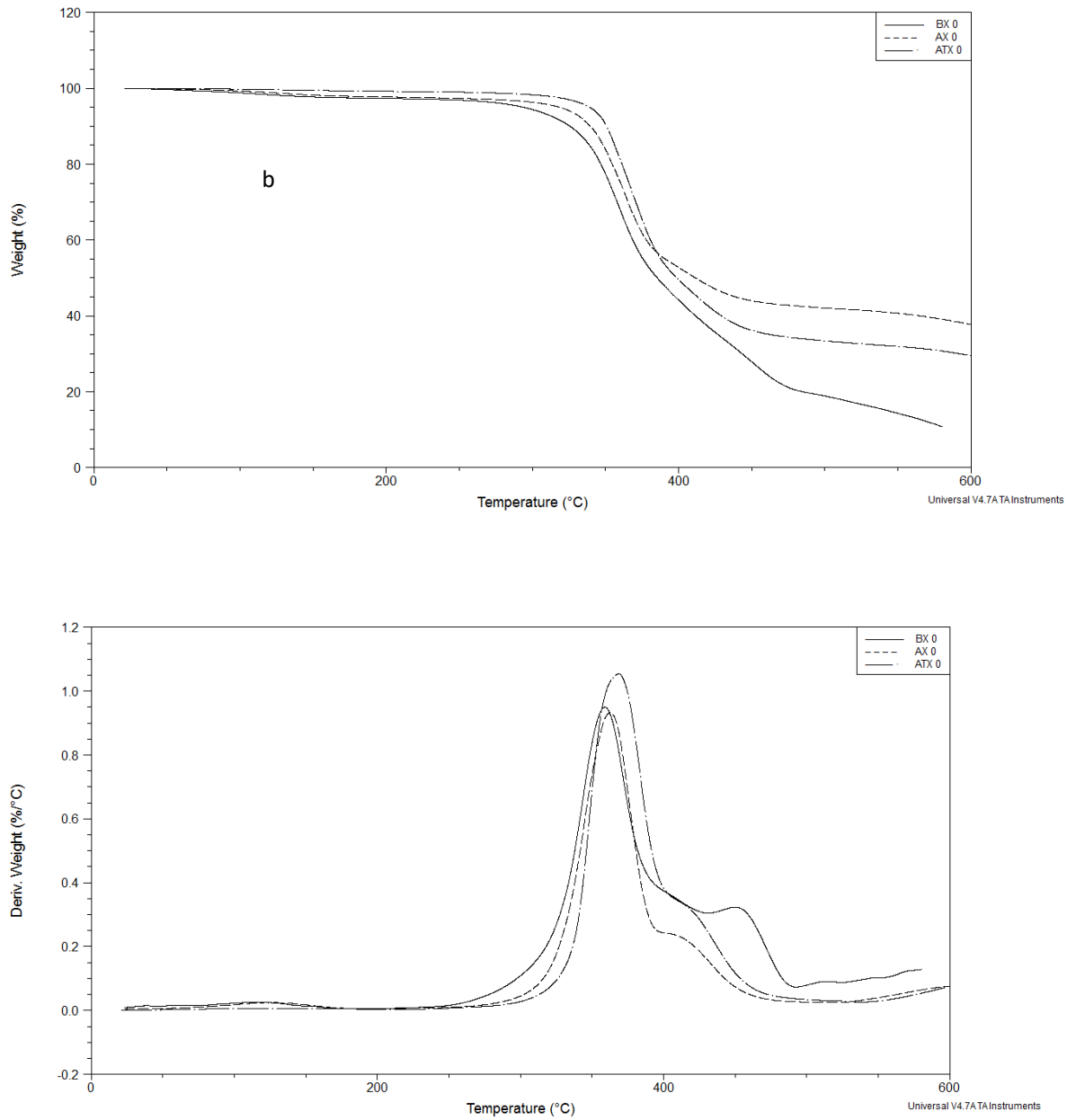


Figure 2. TGA (a) and DTGA (b) thermograms of cured epoxy resin fiber composites recorded at heating rate 10°C/min.

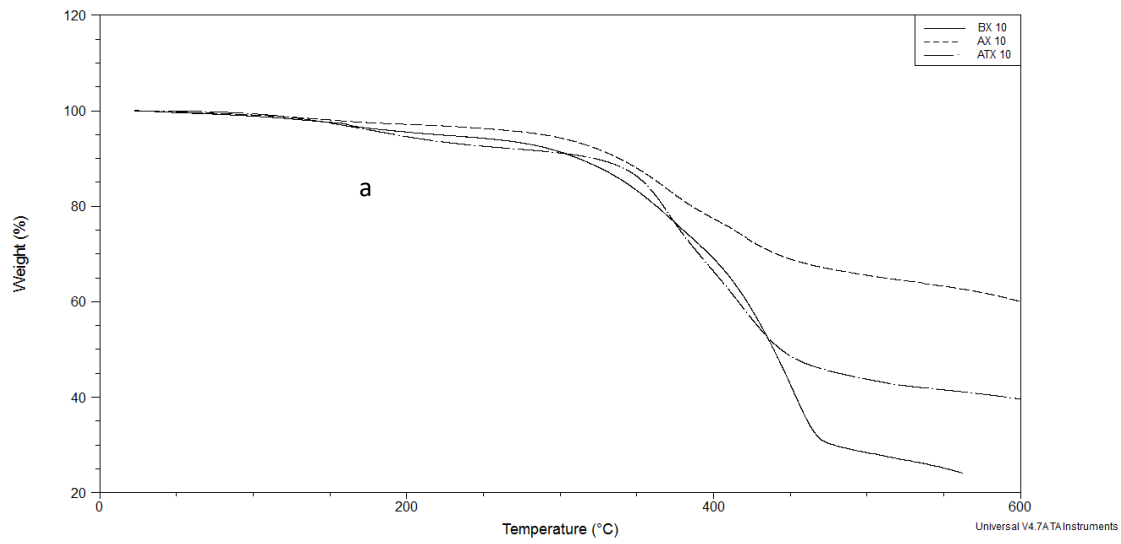


Figure 3.TGA (a) and DTGA (b) thermograms of siliconized epoxy resin IPN with 10 wt ratio of siloxane fiber composites recorded at heating rate 10°C/min.

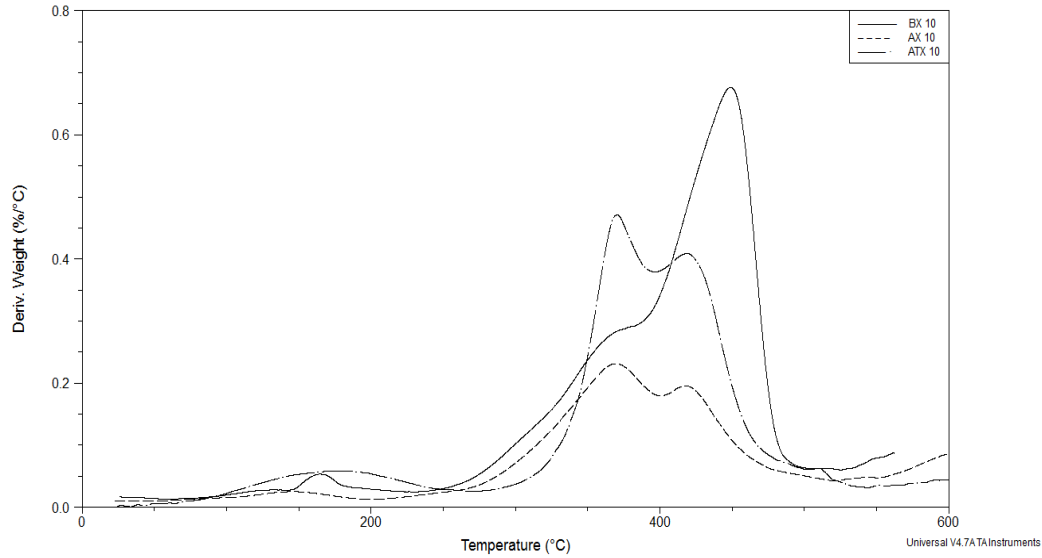


Figure 4. DSC curves of epoxy resin DGEBA with TETA [Xo] at different heating rates

3.4. Differential scanning calorimeter (DSC)

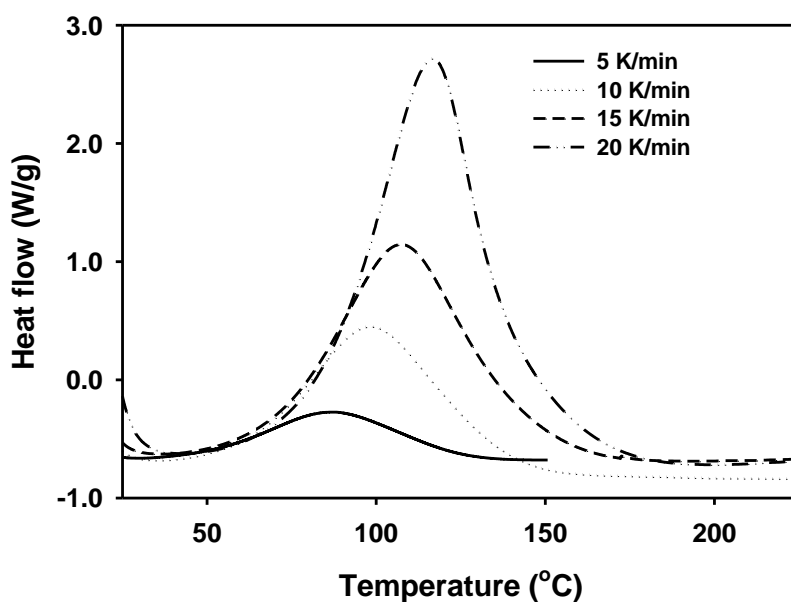
3.4.1. DSC study of curing reactions

The curing behavior of DGEBA/HTPDMS formulations with TETA as curing agent was studied using DSC (the chemical reactions that took place in this stage are presented in Scheme 1). Figures 4 and 5 present the typical DSC curves for DGEBA/TETA and on the addition of (10 wt. ratio HTPDMS) [X_0 and X_{10}], respectively were recorded at four heating rates. The samples present one thermal stage with symmetrical exothermic peaks. As seen from these figures, the trends of the curves are similar to all the formulations studied and one exothermic peak is observed in DSC curves were obtained for cured epoxy and siloxane-epoxy. The heating rate shows a great influence on the curing process. The initial and the peak temperatures of curing reaction increase with increasing the heating rate. As a first approximation, this allows that the reactions of primary and secondary amine hydrogen atoms of TETA and γ -APTES condensate product with epoxy occur simultaneously.

3.4.2. Activation-energy

The activation energy of the curing reactions (E_a) were calculated by means of Ozawa's method from plotting $\ln(\beta)$ versus $(1/T_p)$, (Figs. 6a and 7a) and Kissinger's method from the plotting of $\ln(\beta/T_p^2)$ versus $(1/T_p)$ (Figs. 6b and 7b) for all the formulations. There is a linear fit in all cases, indicating that the experimental data fit the Ozawa and Kissinger models quite well. From the slopes of these plots, the corresponding values of the overall activation energies are calculated and listed in Table 5. It can be observed that the apparent activation energy of the epoxy resin loaded with siloxane has a slightly lower (E_a) than that of epoxy without siloxane. The slight decrease in (E_a) for the X_{10} sample suggests that the reaction between epoxy and siloxane accelerates the reaction rate and reduces the curing temperature.

The activation energies obtained by the Kissinger approach (Table 5) differ from average values obtained by the Ozawa approach. This can be explained by the differences in assumptions and mathematical approach between the two models.



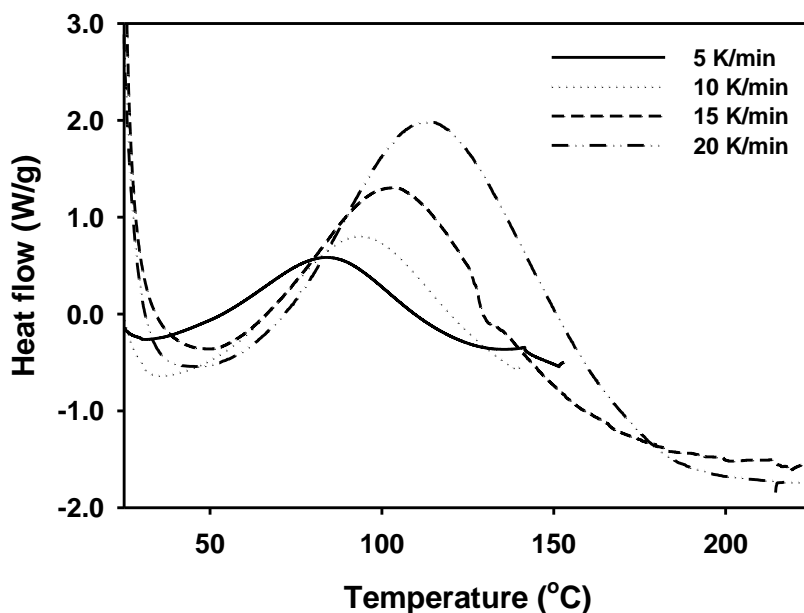


Figure 5. DSC curves of Epoxy resin DGEBA loaded with 10wt ratio siloxane [X₁₀] at different heating rates

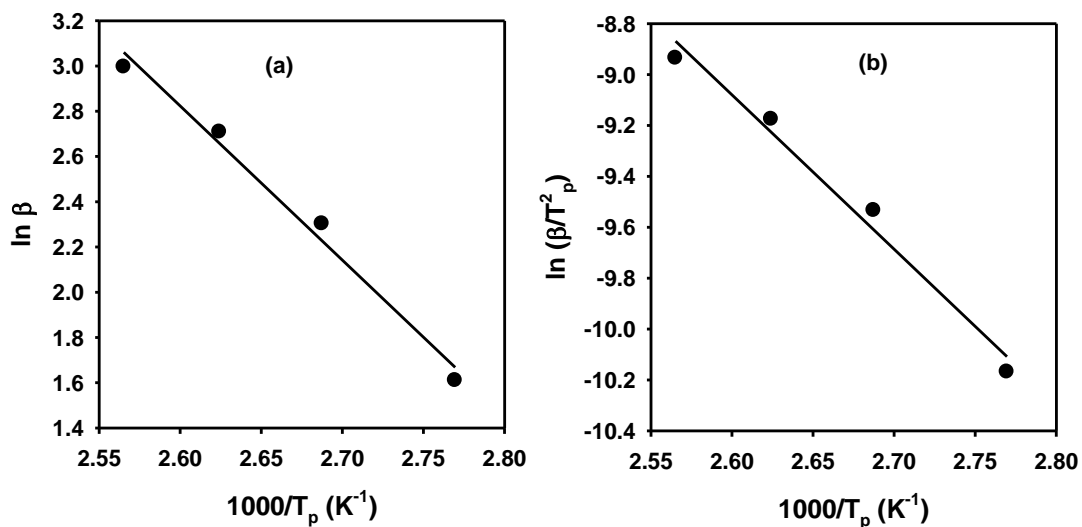


Figure 6. (a) Plot of the Ozawa equation $\ln(\beta)$ versus $(1/T_p)$, (b) plot of the Kissinger equation $\ln(\beta/T_p^2)$ versus $(1/T_p)$ for DGEBA cured with TETA

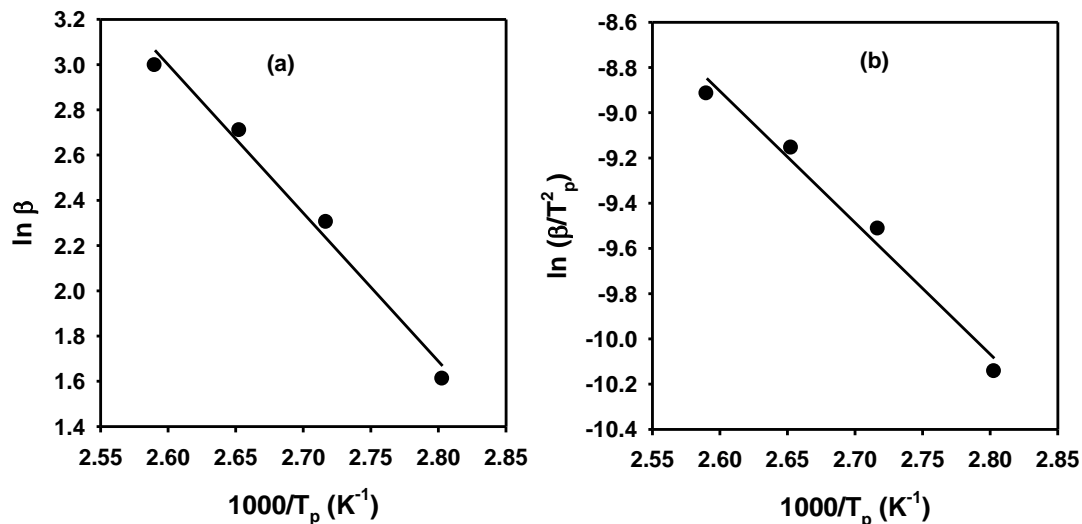


Figure7 (a) Plot of the Ozawa equation $\ln(\beta)$ versus $(1/T_p)$, (b) plot of the Kissinger equation $\ln(\beta/T_p^2)$ versus $(1/T_p)$ for DGEBA loaded with 10 wt % siloxane.

Table 5. The activation energy obtained by Ozawa and Kissinger methods.

Sample code	Ea(kJ/mol) Ozawa	Ea(kJ/mol) Kissinger
X ₀	50.4	53.85
X ₁₀	51.8	48.33

3.4.3. Glass transition temperature

Glass transition temperatures (T_g) of the cured epoxy and siliconized epoxy systems were determined by differential scanning calorimetry measurements (Table 6). The siliconized epoxy systems exhibit single glass transition temperature (T_g), which in turn confirms the existence of intercrosslinking network structure within the siliconized epoxy resin glass transition temperature is not highly affected by the incorporation of PDMS.

There are two factors affecting the influence of siloxane on glass transition temperature of epoxy resin: (Alagar, et al., 2000 & BILAL, et al., 2000)

a-Increase in glass transition temperature is attributed to the increase in cross-link density, due to the presence of γ -APS, which acts as a co-curing agent in the presence of DBTDL catalyst.

b-Flexibilizer introduction into the epoxy system, generally plasticizes the resin system and is expected to increase the free volume and to lower the glass transition-temperature values

of the system. Further, the long siloxane molecule favors chain entanglement and induces the formation of an interpenetrating network structure with an enhanced cross-link density between epoxy matrix and siloxane component through γ -aminopropyltriethoxysilane. In case of epoxy resin loaded with 5, 10 wt ratio siloxane the first factor might be the dominant due to the increase of T_g which is attributed to the increase in the crosslinked network, whereas for epoxy with 15 wt ratio of siloxane the second factor is presumably the dominant.

Table 6. Glass transition temperatures of siliconized epoxy matrices

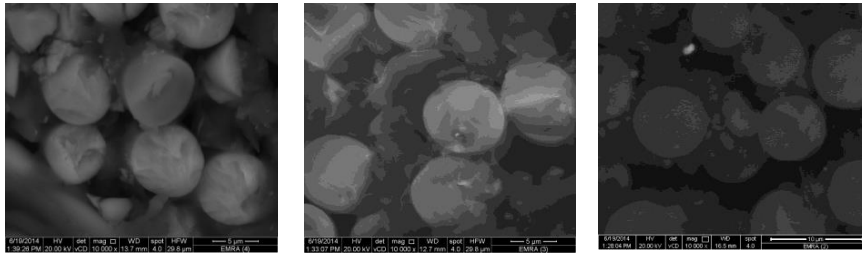
No.	Sample	T_g °C
1	X_0	89
2	X_5	90
3	X_{10}	97
4	X_{15}	90

3.5. Scanning electron microscope (SEM)

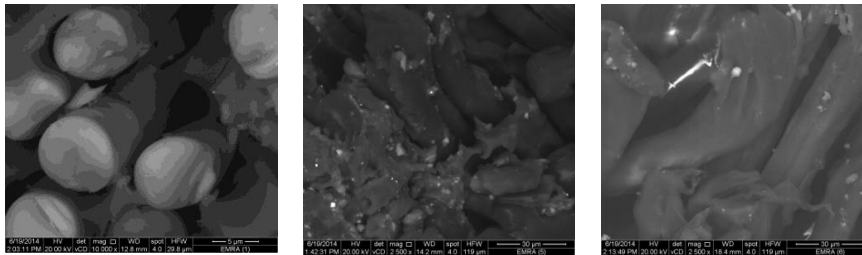
Scanning electron microscope was used to investigate the diversity of fiber wetting along with effect of siliconization of epoxy on it. The SEM micrographs of siliconized epoxy fiber composites are shown in Fig.(8). From Fig. (8a-8d), it is observed that epoxy and siliconized epoxy IPN system reinforced with E-glass show better wetting than that of spectra composites (Fig.8e,8f). This may be explained due to the strong polar active sites present on the surface of glass fiber imparted by ionic sites of silicon and oxygen atoms and are responsible for the formation of strong intermolecular adhesion between E-glass and matrix resin, which is absent on the surface of spectra because of the long organic polymer chain with a smooth crystal structure. The aligned crystalline morphology, the absence of nonpolar groups and absence of chemical groups as ester, amides or hydroxyls from spectra are responsible for the limited adhesion between fiber and matrix. Siloxane introduction into the epoxy skeleton improves wettability of reinforcements including spectra, as siloxane possesses low surface tension, better wetting and spreading characteristics even over smooth polished surfaces.

Figure 8. The SEM images of fracture surface of siliconized epoxy fiber composites

- (a) epoxy resin loaded with 30% E-glass fiber[AX₀],
- (b) epoxy resin IPN loaded with 30% E-glass fiber [AX₁₀],
- (c) epoxy resin siliconized IPN(loaded with 30% E glass fiber coated with nano TiNdeposit) [ATX₁₀],
- (d) epoxy resin (loaded with 30% E glass fiber coated with nano TiN deposit) [ATX₀],
- (e) epoxy resin siliconized IPN loaded with 30% Spectra fiber [BX₁₀],
- (f) epoxy resin loaded with 30% Spectra fiber [BX₀].



c



d

e

f

4. Conclusion

The present work deals with the study of cure reaction kinetics and thermal degradation of epoxy/siliconized IPN and their fiber composites prepared using hydroxyl terminated

polydimethyl siloxane with γ -aminopropyltriethoxysilane as cross-linker with dibutyltindilaurate catalyst and cured by aliphatic amine (TETA). The new prepared E-glass and spectra fiber composites were modified by nano TiN deposition. The formation of siliconized epoxy IPN was confirmed by FTIR, ^1H and ^{13}C NMR measurements. A series of epoxy/fiber composites were prepared using a diglycidyl ether of bisphenol A (DGEBA) and aliphatic amine (TETA), as a curing agent, with different loading of siloxane (0, 5, 10 and 15 wt ratio). The activation energy of the cure of the epoxy and its siliconized IPN with 10 weight ratio of siloxane was studied using dynamic DSC. It was found that the onset temperature, the peak temperature, and the final cure temperature shift to higher values with increasing the heating rate for epoxy resin and its siliconized IPN. The curing kinetics of these epoxy systems were modeled by Kissinger and Ozawa methods. The apparent activation energy (E_a) for the cure was found to be approximately the same. The glass-transition temperature (T_g) of the cured epoxy and its siliconized IPN was determined from DSC. It was found that siliconized epoxy exhibits a slightly higher T_g compared with that of epoxy resin without siloxane. The thermal behavior and stability of epoxy fiber composites were studied by thermo gravimetric analysis (TGA). The results showed that siliconized epoxy samples loaded with 10 wt. ratio of siloxane is the most thermally stable matrix. SEM shows that siloxane introduction into the epoxy skeleton improves wettability of reinforcements including spectra, as siloxane possesses low surface tension and better wetting and spreading characteristics even over smooth polished surfaces.

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الملخص العربي

تحضير و توصيف راتنجات الإيبوكسي المحورة ومواد مركبة جديدة من الألياف الزجاجية ومادة سبكترا

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يشتمل هذا العمل على تطوير مركبات إيبوكسي سيلوكسان (siliconized epoxy) جديدة باستخدام راتنجات الإيبوكسي من DGEBA LY556 كقاعدة، Hydroxy terminated polydimethyl siloxane (HTPDMS) كمحسن ، aminopropyltriethoxysilane (γ-APS) كعامل تشابك و dibutyltindilaurate (DBTDL) كعامل حفاز. وقد استخدم Triethylenetetramine (TETA) كعامل تصلد. كما تم تحضير مواد مركبة جديدة من الألياف الزجاجية E-glass والألياف السبكترا (البولي إيثيلين فائق الوزن الجزيئي) (UHMWPE) مع متراكبات إيبوكسي سيلوكسان المحورة باستخدام تقنية وضع المتابعة (Hand lay-up). تم دراسة تأثير نسبة السيلوكسان وكلا الألياف (الزجاجية و السبكترا) على الخصائص الحرارية والتركييب الشكلى للمركبات الناتجة للإيبوكسي باستخدام التحليل الوزنى الحرارى (TGA) و المسح الحرارى التفاضلي (DSC) و من خلال هذه الدراسة، لوحظ أن أنظمة الإيبوكسي عندما يتم دمجها بالسيلوكسان تعزز من الثبات الحرارى. و قد أظهرت دراسة التراكيب الشكلية للمترابكات المحضرة أن الألياف الزجاجية تلتصق بجزيئات راتنجات الإيبوكسي أفضل من ألياف السبكترا بسبب وجود مواقع أيونية بالألياف الزجاجية.