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Novel Epoxy resin/Benzedine Polymer network Synthesis with Silicon Powder as Filler and Evaluation of Their Mechanical Strength and thermal stability.

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Abstract

The synthesis of high thermally stable Tetra-di-glycidyl ether bisphenol-A TDGEBA Epoxy resin and Benzidine (BZ) have been synthesized from BZ and DGEBA by in situ polymerization technique to obtain Tetra-di-glycidyl ether bisphenol-A Benzidine TDGEBA/BZ with A purple color developed Epoxy resin and modified with various percentages of Silicon (SI) as a filer to obtain Tetra diglycidyl ether bisphenol-A Benzidine Silicon TDGEBA/BZ -SI, to yield novel epoxy based curing agents. The resultant novel epoxy-based polyamides were cured with triethylenetetramine TETA (hardener) % to obtain highly cross-linked thermosetting polymer. The physical properties of the resulting blends were characterized by by measuring the Impact Strength of (TDGEBA/ /BZ-SI increased more than 33% than the unmodified epoxy resin and the hardness is found to be higher than unmodified DGEBA Epoxy resin. Differential scanning calorimetry (DSC) and thermo gravimetric (TGA) analysis were also cured to assess the thermal behavior of the samples. DSC of the (TDGEBA/BZ Epoxy resin cured with TETA showed exothermic reactions and the glass transition temperature (Tg) shifted from 300˚C to 450˚C compared with unmodified DGEBA epoxy and the thermal stability of the TDGEBA/BZ-SI Epoxy resin modified increased with increasing of Silicon .Scanning Electron Microscopy (SEM) studied the morphology of the samples after un notched impacts on fracture surfaces. These materials exhibited a higher degree of solvent resistance. . These materials exhibited a higher degree of solvent resistance.

Keywords :Epoxy resin . thermal stability . DSC . TGA . SEM ,

1.Introduction

Epoxy resins are a versatile group of crosslinked polymers that have excellent chemical resistance, good electrical insulating properties, good adhesion to glass and metals, and can be easily fabricated. The variety of properties help the Epoxy resins to meet the performance requirements of some demanding applications. These include areas as diverse as construction, electronics, adhesives, and coatings [1-6]. The usefulness of epoxy resins for many applications is often limited due to their inherent brittleness arising from their crosslinked structure. Development of approaches for toughening the Epoxy resins without sacrificing modulus and glass transition temperature (*T*g) would lead to an increase in their applications [7-11].

The use of Epoxy resins in high performance structural materials has increasing recently. Multifunctional epoxiese are used in applications for high performance adhesives and advanced composite matrix materials in the aerospace and electronics industries. The combined mechanical properties of high modulus and high strength at relatively high temperatures make the material suitable for advanced applications

In the present case we have used aliphatic amine and aromatic amine aromatic amine UV- resistance , solvent resistance , chemical resistance high impact strength ,good hardness , highest cross-linking density. Forward, the cured networks are used in electrical insulating materials due to their low polarity and low moisture sorption. Inorganic modifiers have also been considered as toughening agents for epoxy materials [12-15].

In the present study modification is curried on Epoxy resin- Benzidine (BZ) having moderate functionality using silicon as filer , triethylene tetra mine as hardener and penzoylberoxyide as initiator exhibits a superior rigidity for example. In this work, we report the effect of silicon SI on the material properties of the Epoxy resins in an attempt to see the relative effect of organic and inorganic modifiers [16-20.] .

2.Experimental Section

2.1. materials

The following compounds were used for the study: Epoxy resin was procured from Shimo Resin Pvt. Ltd. under the trade name SHIMOREZ- 400, the density at 25^{0}C being 1.11 g/ml viscosity at 25^{0}C, 12000 ± 300 MPaS and Triethylenetetramine as a curing agent was from the Robert Johnson company M.W146.24 and Benzidine Crystalline powder A, R. (Ben) M.Wt/84.24 B-29 100g 7002217 Msz 9527 melting range 127-129 and. Silicon Metal powder sympol Si Mesh At .WT 28.09 AMRUT industrial products chemical House L.B Shastri Marg.P.B No,46 Thana (Mahrashtra) (India) and Chloroform, Methanol, Acetone and Hexane, all these solvents were from Qualigen fine chemicals. Benzoyl peroxide was from Loba. Chemie. Ltd. India.

Synthesis of (TDGEBA/BZ)

The (TDGEBA/BZ) monomer was synthesized by the reaction process of Tetra diglycidyl ether bisphenol A (TDGEBA) with Benzidine BZ by mixing (4.0 mole) of commercial grade of DGEBA with a fixed concentration of Benzidine BZ (1.0 mole) , initially Benzidine was added to the reaction three-neck flasks and heated to 127 ^{o}C until Benzidine melted and mechanical stirring began. After this, DGEBA epoxy resin was added and the temperature was raised from 127˚C to 180˚C over a period of 1 hour under nitrogen atmosphere . The temperature was maintained at 180 ˚C and the reaction was completed after 3 h. The chain-lengthening step is based on the nucleophilic attack of the Amin groups of (BZ) to the less substituted carbon atom of the oxirane ring of TDGEBA, which leads to ring-opening formation of an ether link and generation of a tertar hydroxilic group

The Linear product was purple in color, homogeneous, viscous and transparent in nature. The reaction product was permitted to cool under nitrogen atmosphere and the product initially; the melting of (TDGEBA/BZ) Epoxy resin mixture does show the semi liquid Scheme 1. In the cured of (TDGEBA/ BZ) Epoxy resin with triethylenetetramin (TETA) The chain-lengthening step is based on the nucleophilic attack of the Amin groups of (TETA) to the less substituted carbon atom of the oxirane ring of (TDGEBA/BZ), which leads to ring-opening formation of an (TDGEBA/BZ) soled Epoxy polymer network Scheme2. (TDGEBA/ BZ) cured with (TETA) as a hardener and modified with different ratio of silicon (SI) the soled Epoxy polymer network it be obtained Scheme3.

2.3.Solvent resistance

The Solvent resistance was measured for acetone, chloroform, methanol and hexane by ASTM standards. The apparatus used was made entirely of glass. This was engineered so that the condensed extracting solvent is in contact with the samples and is at temperature not much below its boiling point. Accurately weighted 0.2g samples were placed in a filter paper basket and then introduced in the siphon cup of the Sohxlet and extracted individually with acetone, chloroform, methanol and hexane for 8 hours. The samples were dried after extraction in vacuum oven at 40^{0}Ċ until constant weight was obtained. The solvent unextractable value (X) was calculated [10.,21-25.]

2.4.Mechanical properties

The hardness of samples was measured on a Shore hardness tester. Dunomekes with reference to ASTM standard on an IZOD make ATS faar. S.P. A. Italy. The dimensions of the sample chosen were according to ASTM D256-0 standard [20-25]

2.5.Thermal analysis

The thermal analysis of the samples were performed on TA instrument MAKE; DU-PONT, USA Model; 9900. SPECIFICATON; TGA; the temperature, range varied between ambient was to 1200C Heating rate-was maintained 1-5˚C /min. The samples were analyzed in Nitrogen atmosphere.

2.6.Morphology Analysis

The morphology of the samples was investigated by SEM analysis. The SEM instrument JEOL, JSM-6360A was used for the same

3.RESULT AND DISCUSSION

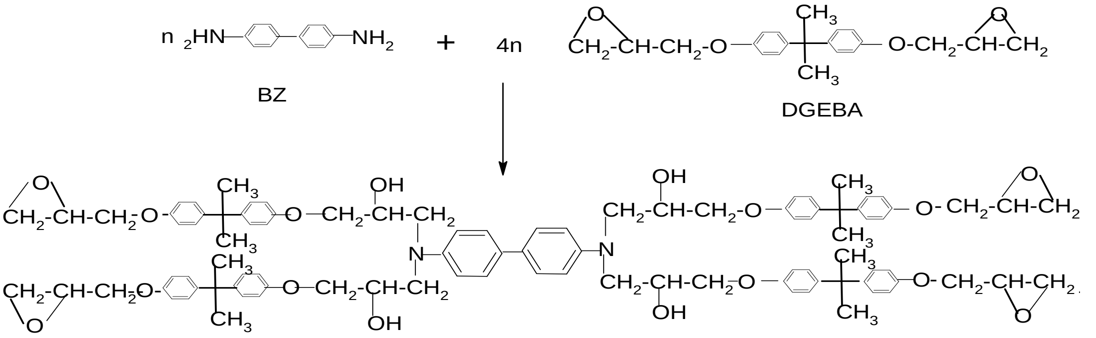
Pure epoxy resins have been observed to have a brittle nature and hence they exhibit poor mechanical properties [5,8,11,26] , However, applications in space industries and extreme conditions require the material to be thermally stable bearing good mechanical properties. In the present work, a novel Epoxy resins have been synthesized by reaction of DGEBA with Benzidine **BZ:**. DSC and TGA using different heating rates investigated the curing reaction of the thermoset Liquid (TDGEBA/BZ) epoxy resin monomer in the presence of TETA. The chemical reactions involved are shown in Scheme 1.

The diamine BZ has two equal amine functions of reactivity and leads to the formation of a liquid epoxy (TDGEBA/BZ) monomers [27 – 29]

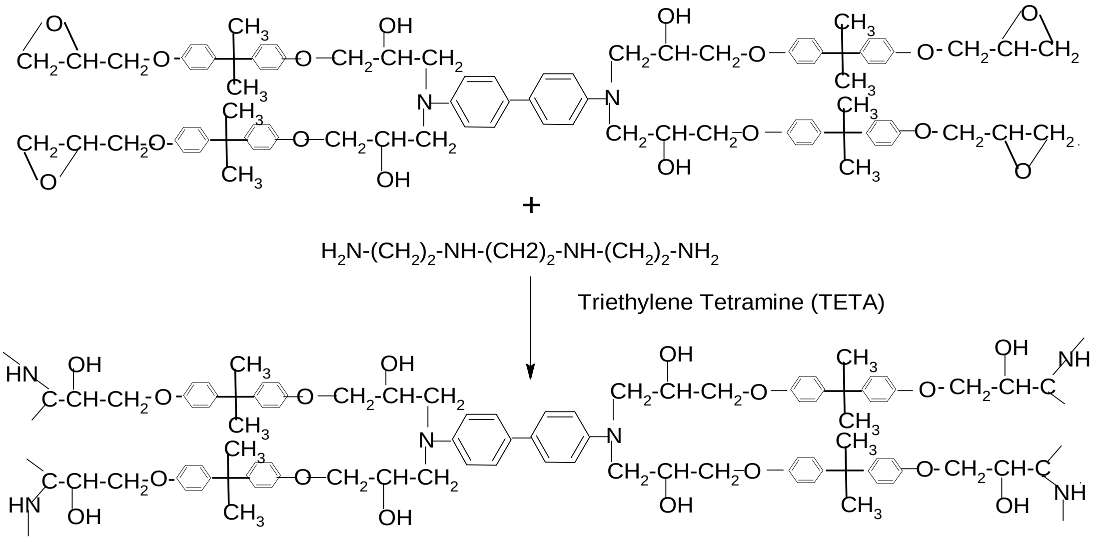
Concerning the liquid Spoxy (TDGEBA/BZ) monomers has been observed to have a brittle nature and hence the exhibit poor mechanical properties comparing with the curing reaction of the TDGEBA/ BZ epoxy monomer with (TETA) like hardener and modified with (SI) as a filer. In the present work, a set of the TDGEBP/ BZ epoxy monomer have been modified by adding various ratio of (SI). The comparison of the results of hardening time, mechanical properties and solvent resistance shown in **Table 2** obtained for each of the sets reveals differences in each case. The chemical structure of the curing of liquid Tetra diglycidyl ether bisphenol-A Benzidine TDGEBA/BZ epoxy monomer with (TETA) is as shown below **Scheme 2**.

In case of liquid epoxy TDGEBP/ BZ, monomers modified with (SI) a set of Epoxy resins samples have been synthesized by adding various ratio of (SI) in the present of (TETA) like hardener **Table 1**. The chemical structure of the modified of liquid TDGEBA/BZ epoxy monomers with (SI) in the present of (TETA) as shown below **Scheme 3**.

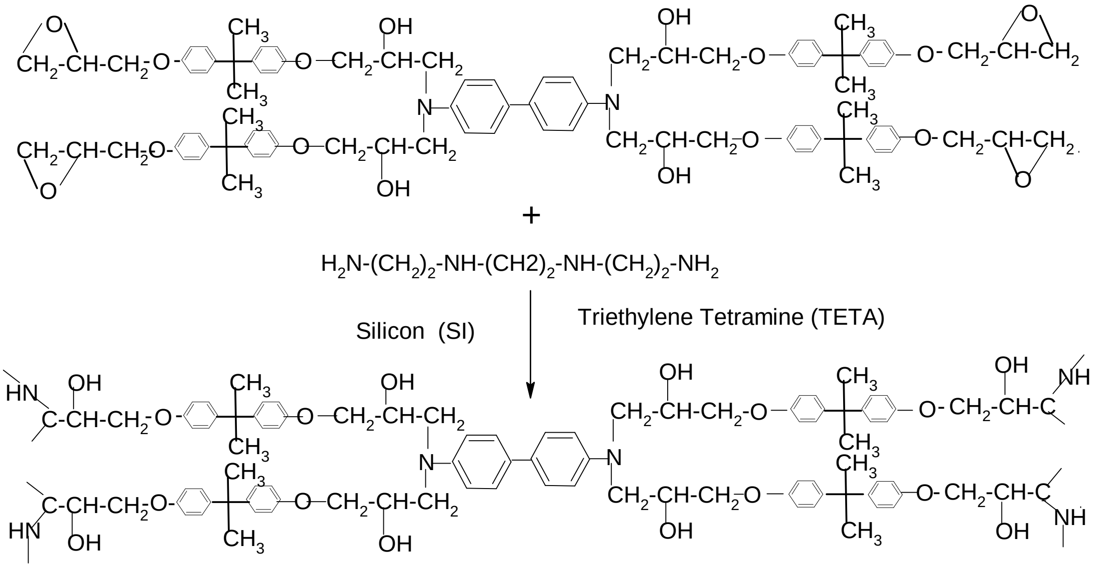
SI being in nature would render or impart rigidity and thermally stable to a greater extent compared to unmodified epoxy resins..



Scheme 1. Tetra-di-glycidyl ether bisphenol-A Benzidine (TDGEBA/ BZ) epoxy resin.



Scheme 2. Curing reaction of TDGEBA/BZ epoxy with (TETA) system..



Scheme 3. Curing of TDGEBA/BZ epoxy resin and modified with Silicon (SI) system.

Table 1. Thermo gravimetric data obtained from the TGA-analysis of neat TDGEBA//BZ (100%) epoxy resin and modified with Silicon SI in presence of benzoyl peroxide as initiator at (85˚C).

Reactant (g)	Temp. of 10% Decomposition (˚C)	Temp. of 20% Decomposition (˚C)	Temp. of 40% Decomposition (˚C)	Tg (˚C)
Neat DGEBA (100%)	250	280	350	250
TDGEBA/BZ (100%)	280	300	370	300
TDGEBA/ BZ-SI (99/1)	290	300	380	350
TDGEBA/ BZ-SI (98/2)	-	-	-	-
TDGEBA/ BZ-SI (97/3)	290	320	395	450
TDGEBA/ BZ-SI (96/4)	-	-	-	-

TDGEBA/ BZ-SI (95/5)	330	360	400	
TDGEBA/ BZ-SI (94/6)	-	-	-	-
TDGEBA/ BZ-SI (93/7)	340	380	420	
TDGEBA/ BZ-SI (92/8)	350	380	430	
TDGEBA/ BZ-SI (91/9)	-	-	-	-
TDGEBA/ BZ-SI (9o/10)	360	400	450	-

Table 2. Hardening time, Solvent resistance and mechanical properties of neat TDGEBA/BZ (100 %) cured with TETA as well as epoxy modified with Silicon in presence of benzoyl peroxide as initiator at (85˚C).

Reactant (g)	Hardening Time (h)	**Solvent Resistance %**				Mechanical Properties	
		Acetone	**Chloroform**	Methanol	**Hexane**	Izod Jm−2	Hardness
Neat DGEBA (100%)	1.30	99.0	98.0	99.0	98.0	**2037.0**	76.0
TDGEBA/BZ (100%)	1.50	100	100	100	100	6741.0	88.0
TDGEBA/ BZ-SI (99/1)	1.50	100	100	100	100	6730.0	86.0
TDGEBA/ BZ-SI (98/2)	1.45	98.0	98.0	99.0	98.0	6691.0	83.0
TDGEBA/ BZ-SI (97/3)	1.40	98.0	98.0	98.0	98.0	6642.0	80.0
TDGEBA/ BZ-SI (96/4)	1.40	98.0	98.0	98.0	98.0	6613.0	77.0
TDGEBA/ BZ-SI (95/5)	1.30	98.0	98.0	98.0	98.0	6600.0	75.0
TDGEBA/ BZ-SI (94/6)	1.20	98.0	98.0	98.0	98.0	5594.0	72.0
TDGEBA/ BZ-SI (93/7)	1.15	98.0	98.0	98.0	98.0	5570.0	70.0
TDGEBA/ BZ-SI (92/8)	1.10	98.0	98.0	98.0	98.0	5531.0	67.0
TDGEBA/ BZ-SI (91/9)	1.05	98.0	97.0	97.0	97.0	5500.0	65.0
TDGEBA/BZ-SI (9o/10)	1.00	97.0	96.0	96.0	96.0	4980.0	63.0

3.1. DSC Experimental Data.

The (DSC) and TGA using different heating rates Figure 1 investigated the curing reaction of DGEBA with TETA. Initially, the melting of the DGEBA curing with TETA mixture does not show the Liquid Crystal (LC) properties since an isotropic liquid is formed above the melting point [30], .Then, as the reaction between epoxy and Benzidine proceeds, a LC texture is developed, which is locked in the crosslinked network by the nematic arrangement. Depending on the heating rate, the DSC Figure

1(a) thermograms of the curing process shows one sharp exothermal peak and two or three endothermal peaks. Generally, the exothermal peaks appear, together with endothermal peaks, when the samples are cured at low heating rates Figure 1(a) shows an example of the DSC thermograms for DGEBA curing with TETA recorded between a temperature range from RT to 600˚C. The first one exothermal peaks at 290 ˚C and the first two endothermal peaks observed in the temperature range between 400˚C and 480˚C are assigned to the melting of the individual components of the mixture studied. With increase of temperature above 500˚C, the DSC curve in Figure 1(a) shows one sharp exothermic peak [31] . Thermal stability of the DGEBA was investigated by TGA, as shown in Figure 1(b). The amine bonds degrade in two steps owing to the initial degradation of the hydroxyl functionalities at 140˚C - 300˚C. The 5% weight loss of amine bound was at 260˚C Table 1.

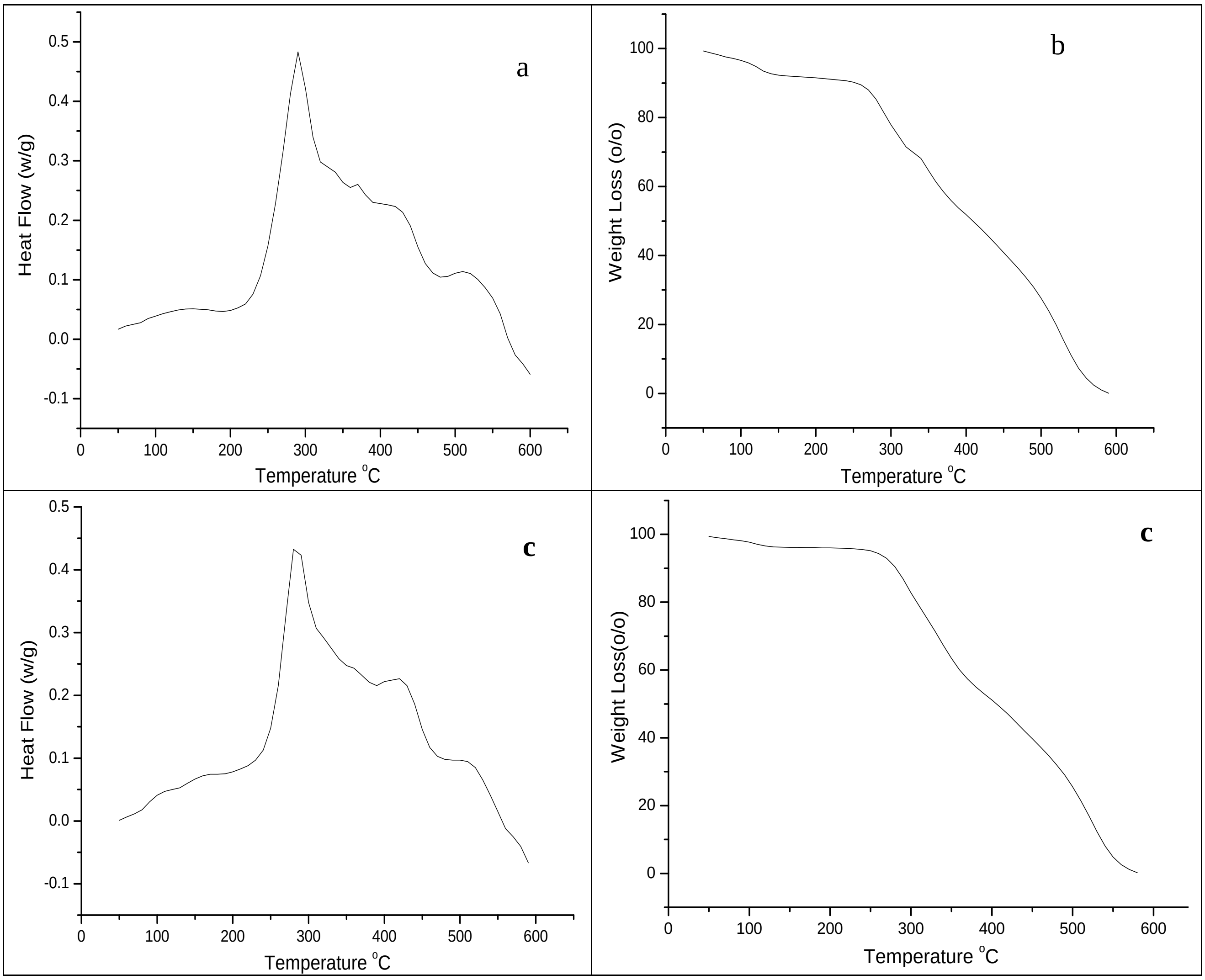


Figure 1. DSC and TGA plots of curing DGEBA epoxy and TDGEBA/ BZ epoxy resin curing with (0.1 g) TETA. (a) curing DGEBA epoxy resin (b) Curing TDGEBA/ BZ epoxy resin; (a) (b) Represent DSC and TGA plots of curing DGEBA epoxy resin respectively; (c) (d) Represent DSC and TGA plots of curing TDGEBA/ BZ respectively, in presence of benzoyl peroxide as initiator at (85˚C).

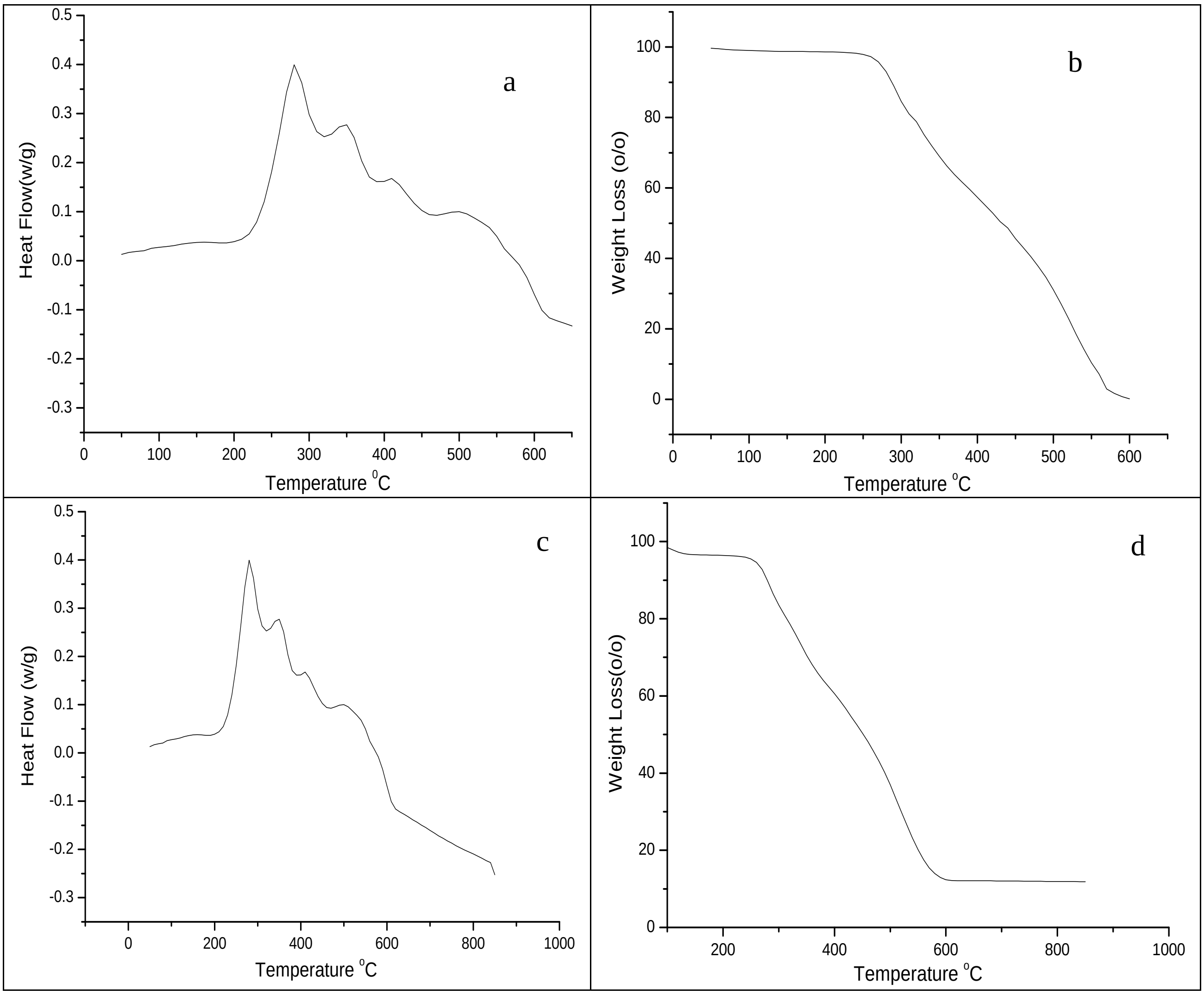


Figure 2. DSC and TGA plots of curing of TDGEBA/BZ epoxy with (1.0 %) TETA. And modified with Silicon (a),(b) Represent DSC and TGA plots of curing of TDGEBA/BZ epoxy with (1.9 %) Silicon) and (c) ,(d), Represent DSC and TGA plots of curing of TDGEBA/BZ epoxy with (3.0 %) Silicon) respectively; in the presence of benzoyl peroxide as initiator at (85˚C).

because of high crosslinking the two aromatic ring crystallenity of benzidine with TDGEBA epoxy cured with TETA.

in case of TDGEBA/ BZ epoxy cured with TETA compared with DGEBA epoxy respectively as shown in Figure 1(d).The thermal stability of the TDGEBA/ BZ mixture using TETA, and superior to that of the TDGEBA/ BZ epoxy mixture which decomposes below 650˚C.

In case of curing reaction, the TDGEBA/ BZ epoxy monomer curing with TETA and modified with SI in the presence of Benzoylperoxide like initiator. In these case a set of TDGEBA/ BZ epoxy monomer have been synthesized by adding SI. The weight percentages of each of them were varied from 1 - 10. Initially, samples were prepared by adding SI during synthesis, small amount 1.0 g, of hardener such as TETA was added

which led to the solidification of the product. The chemical reactions of the TDGEBA/ BZ curing with TETA and modified with SI are shown in Scheme 2. These Samples was investigated by DSC and TGA as shown Figures 2(a)-(d). Incorporation of SI into TDGEBA/ BZ epoxy monomer observed to exhibit overall improves the Tg and thermal stability compeering with the Tg thermal stability of TDGEBA/ BZ epoxy monomer without modified SI as shown above DSC Figure 2(a). For the modified of

TDGEBA/ BZ, epoxy monomer enhances degradation temperature proportionate to its percentage concentrating From Figures 2(a)-(d). It is observed that thermal stability temperature of TDGEBA/ BZ epoxy monomer cured TETA and modified with varies percentage of SI are increase with increasing SI contents compeering with TDGEBA/ BZ epoxy monomer cured with TETA without SI modified. Figures 2(a)-(d) the thermal stability increasing is mainly due to of thermally stable of TDGEBA/ BZ structure network and SI modified.

The DSC and TG plots of degradation temperature of TDGEBA/ BZ epoxy modified system against SI concentration are presented in Figures 2(a)-(d) respectively. In Figure 1(d) TDGEBA/ BZ epoxy cured with TETA without modified SI the temperature required for 10%, 20% and 40% weight losses are 280˚C, 300˚C and 370˚C whereas the temperatures required to attain the same weight losses for modified 5.0% SI ratio Figure 2(a) are found to be increased to 330˚C, 360 and 410˚C respectfully. A similar trend is observed 7.0%,8.0% and 10.0% SI ratio modified TDGEBA/ BZ epoxy. The thermal stability is increase than that of 10 %, SI ratio modified TDGEBA/BZ epoxy. For example, the temperature require for 30 % and 80.0% weight loss of unmodified TDGEBA/ BZ epoxy resin with SI Figure 1(d) are 325˚C and 520˚C comparing with 10.0% SI ratio modified at the same weight loss are found 400˚C and 900˚C respectively, the thermal results of unmodified and modified TDGEBA/SAA epoxy resins are presented in Table 1. From the table it is evident that the thermal stability of modified epoxy resins increasing comparing with unmodified TDGEBA/ BZ epoxy and increasing with of SI concentration comparing with TDGEBA/ BZ epoxy cured with TETA alone This may be explained due to the presence of SI and highly crosslinking of TDGEBA/ BZ epoxy resin polymer network Figures 3(a)-(d).

3.2. Mechanical Properties

In developing high-performance TDGEBA/ BZ epoxy polymer mixtures on two immiscible polymers, the objective is to raise the compatibility of these two components. Compatibilized poly mixtures have finer phase domain size and greater interfacial contact area and interfacial adhesion than the corresponding uncompatibilized mixtures, as shown in the SEM morphologies, so a given stress can be transferred efficiently between phase domains. Unnotched impact strength is commonly used to differentiate toughness change resulting from compatibilization for notch sensitive blends. **Table 2** presents on the impact strength and hardness properties of the DGEBA epoxy systems cured with TETA have been observed to have a brittle nature and hence they exhibit poor mechanical properties. Because of the poor cured DGEBA epoxy systems compatibility between DGEBA and TETA, the impact strength properties of the cured DGEBA epoxy are less than desirable comparing withe TDGEBA/BZ epoxy mixture. The trend of unnotched impact strength for DGEBA epoxy alone and TDGEBA/BZ epoxy mixture unmodified and modified with various amounts of SI is consistent with corresponding hardens properties. the effects of Silicon SI contents exhibits a significant effect on the enhancement of impact strength properties for TDGEBA/ BZ epoxy mixture, which can be attributed to the in situ-formed TDGEBA/ BZ with SI epoxy polymer network molecules anchoring along the interface. A greater number of in situ epoxy polymer network molecules tend to be produced with increasing the quantity of SI and anchor along the interface as the result of chemical reaction.

The SI has demonstrated combination of TDGEBA/ BZ and SI to be an excellent reactive improvement in their impact and hardens strength properties due to internal Stress decreasing of cured TDGEBA/ BZ epoxy modified with (1-5%) SI ratio then slight decries with increasing of SI ratio.

The results on impact resistance, hardness, solvent resistance and hardening time **Table 2** shows the DGEBA epoxy, unmodified TDGEBA/ BZ epoxy and modified tetra diglycidyl ether bisphenol-A Benzidine TDGEBA/ BZ epoxy systems with SI.

In case of unmodified TDGEBA/ BZ, epoxy systems with SI and modified the TDGEBA/ BZ, epoxy systems with SI the solvent resistance and impact strength increased initially up to a TDGEBA/ BZ epoxy resin systems with (1-5%) SI ratio mixture, increased more than 33% than the DGEBA epoxy resin and hardness that is found to be higher than the DGEBA epoxy resin. This can be explained based on characteristically good compatibility of SI with TDGEBA/ BZ, epoxy systems.

The morphological features of some selected samples were investigated with the help of SEM after testing the samples for their impact strength. **Figures** 3 (a) shows the SEM micrographs of pure epoxy.

3.2. Scanning Electron Microscopy (SEM)

Figure 4 exhibits the fracture surface examined using scanning electron microscopy SEM. DGEBA .The Net a DGEBA epoxy as well as TDGEBA/ BZ epoxy resin alone and modified with SI in the presence of TETA morphology of some selected samples is shown in the Figures 4(a)-(d). Which were recorded after testing the samples for unnotched Izod impact strength . In case of neat DGEBA (100%) epoxy sample Figure 4(a) the fracture surfaces shows typical characteristics of brittle fracture and have poor impact properties. These relative to their respective components due to their high interfacial tension, leading to poor control of morphology and stress transfer under loading in solid state. An efficient compatibilizer in the mixture can reduce the interfacial tension or internal stress and enhance the interfacial adhesion between DGEBA and TETA epoxy,

In case of TDGEBA/ BZ, epoxy systems thus improves its impact strength properties. Figures 4(b)-(d) show the unnotched SEM micrograph of the fractured surface of the TDGEBA/ BZ unmodified and modified with (1.0% - 10%) SI ratio. The large dispersed and spherical TDGEBA/ BZ epoxy particles with different dimensions can be easily identified from these uncompatibilized mixtures due to the incompatibility of these two created components.

The morphological features of some selected samples were investigated with the help of scanning electron microscopy after testing the samples for their impact strength. Figures 4(b)-(d) shows the SEM micrographs of net DGEBA epoxy together with TDGEBA/ BZ unmodified and modified with SI. The magnifications were selected depending on the clarity of the morphology that could be observed.

In case of pure DGEBA epoxy sample Figures 4(a) the crystallite size appears to be rather fine with equal fraction of void spaces in between different by sample crystallites indicating poor impact properties or brittleness of sample because of internal stresses. On the other hand, the TDGEBA/ BZ epoxy unmodified with SI exhibits homogeneity in morphology with larger crystallites and lower void space and decreasing of internal stresses as shown in Figures 4(b). This is expected to render better impact strength to the material. Further, modification of TDGEBA/ BZ epoxy with (1.0%) SI ratio depicts agglomerates containing silicon Figure 3 (c) and the morphology appears to be similar as for TDGEBA/ BZ epoxy. On the other hand, modification of epoxy by addition of (5.0%) SI ratio Figure 3 (d). The morphology is seen to improve in this with a homogeneous distribution of large size crystallites. Modification with silicon agglomerates containing silicon can be observed. And the morphology.do is similar as for TDGEBA/ BZ epoxy. The hardness and impact strength measurements also support this feature[31-33],

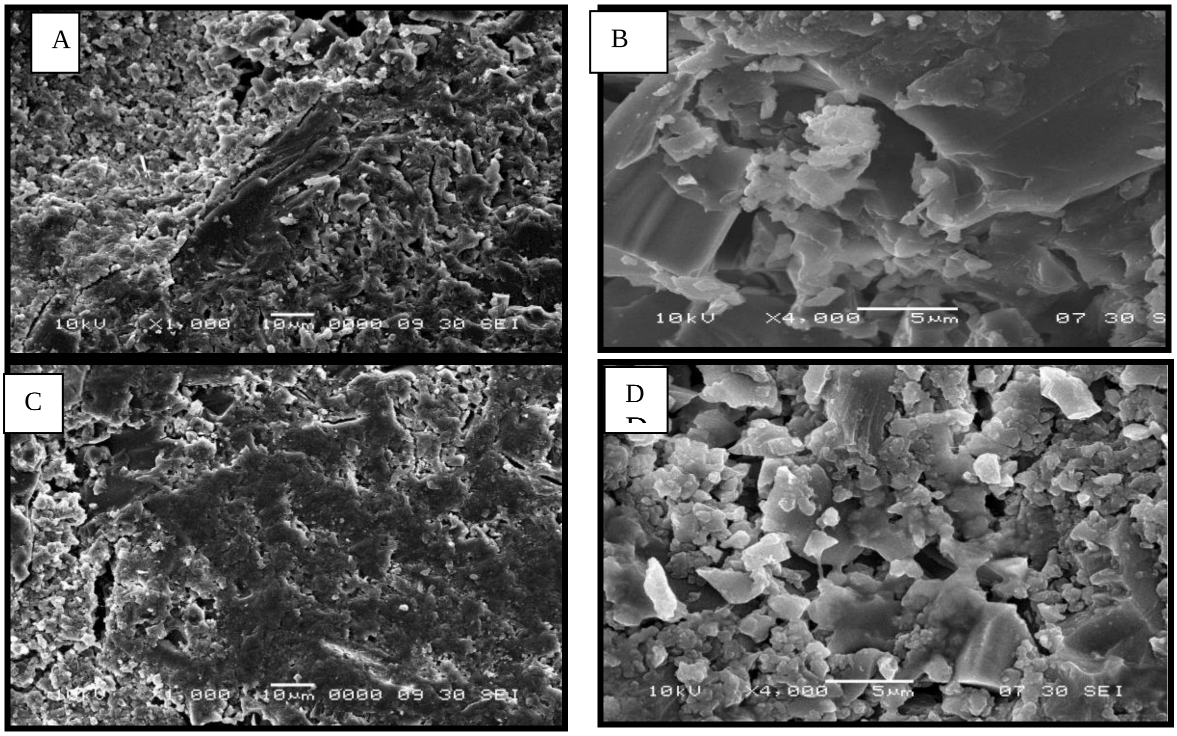


Fig (3) the impact fracture surfaces are examined using scanning electron microscopy (SEM) for (a)Net DGEBA epoxy resin and (b) TDGEBA/BZ Epoxy resin(C) TDGEBA/BZ Epoxy resin modified with 1,0o /o Silicon (D) TDGEBA/BZ Epoxy resin(C) TDGEBA/BZ Epoxy resin modified with 5,0% Silicon

4. Conclusions

The curing of TDGEBA/ BZ epoxy with the reactive TETA and SI modified was found high thermal stability as confirmed by DSC. Viscoelastic analyses showed that the glass transition temperature shifted from 350˚C to 450˚C and higher thermal stability with the increase of Silicon content, which reflected the miscibility between epoxy and Silicon .This product had increase impact strength and excellent solvent resistance, which also proved the formation of the network structure between the epoxy matrix and SI. TGA showed that the cured TDGEBA/ BZ epoxy resins are thermally more stable than the epoxy cured with the traditional diamines.

The increase of the SI content led to increase of the impact strength and thermal stability of the epoxy compared with cured and unmodified DGEBA epoxy resins. The SEM measurements images have shown that TDGEBA/ BZ epoxy resins has a granular morphology and a porous structure.

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