Chapter 3

Effect of hyperbranched polyester generations (G1 to G4) on toughening of epoxy resin

3.1 INTRODUCTION

Epoxy resins which are characterized by the presence of more than one three-membered ring known as the epoxy, epoxide, oxirane, or ethoxyline group, are an important class of polymeric materials. The word “epoxy” is derived from the Greek prefix “ep”, which means over and between, and “oxy”, the combining form of oxygen (Hartman 1984). Bi- or multifunctional epoxies are industrially important epoxy resins. The monofunctional epoxies are primarily used as reactive diluents, adhesion promoters and viscosity modifiers.

Epoxy resins containing aliphatic, cycloaliphatic or aromatic backbones are used in industry as well as in academia with the molecular weight ranging from several hundreds to tens of thousands. Glycidyl ether derivatives of bisphenol A is widely used epoxy resin. The strained epoxy ring in the aforesaid epoxy resin will be cured with different kinds of curatives under diverse temperatures and conditions. Commercialization of epoxy resins was done in the late 1940s and is now utilized in many industries, often in demanding applications due to their better performance with the modest price. However, the usage of aromatic epoxies is limited for exterior applications due to poor ultraviolet light resistance.

Most cured epoxy resins exhibit excellent mechanical strength and toughness; excellent chemical, moisture, and corrosion resistance; good thermal, adhesive, and electrical properties; nonvolatile emission and low shrinkage upon cure; and dimensional stability—a unique combination of properties generally not found in any other plastic material. Because of these superior performance characteristics and diversified formulations versatility and reasonable costs, epoxy resins have gained a wide acceptance as materials of choice for structural and protective coating applications.
3.1.1 HISTORY OF EPOXY RESINS

Around 1947, epoxy resins were commercially introduced into the market. In the United States, the first product was made by the Devoe-Raynolds company. Although 1947 marked the commercial debut of epoxy resins as we know them today, the true beginnings were much earlier. In 1909, the first epoxide synthesis was discovered by the Russian chemist Prileschajew from the reaction between olefins and peroxybenzoic acid. In 1934, German Scientist, Schlack of I.G. Farbenindustrie AG prepared high molecular weight polyamines by the reaction of amines with epoxide compounds containing more than one epoxy group and this was applied for a patent. Unfortunately, Schlack failed to recognize the significance of the latter part of this invention. Epoxy resin which was produced from epichlorohydrin and bisphenol A, was also disclosed that this resin could be hardened with equivalent amounts of amines (May and Tanaka 1973).

The realization of the true value of these products came a few years later. Almost simultaneously and independently two inventors, Pierre Castan of DeTrey Freres Co. in Switzerland and Sylvan Greenlee of DeVoe and Raynolds Co. in the United States, came to the same conclusion. Castan synthesized a low melting epoxy resin from bisphenol A and epichlorohydrin and cured with phthalicanhydride. He anticipated the cured epoxy could be utilized as dental products but the marketing of the resin was unsuccessful initially. The patents were licensed to Ciba AG of Basel, Switzerland and in 1946, the first epoxy adhesive which was applied to a variety of substrates, including metals and siliceous materials, was portrayed at the Swiss Industries Fair and the casted epoxy resins were provided to the electrical industry. In 1936, for synthesizing epoxy resin based on bisphenol A, both the aforementioned persons were given recognition (May and Tanaka 1973).

A series of high molecular weight epoxy resin compositions were patented by Sylvan Greenlee of DeVoe and Raynolds Co. which were synthesized by reaction of bisphenol A and epichlorohydrin for coating applications immediately after World War II. Alkyd type epoxy ester coatings were produced by using the aforementioned epoxy resins which were sold as subsided polyhydroxy ethers by Jones-Dabney Co. with drying oil fatty acids. This epoxy resin was commercialized in major amount as protective
surface coatings and still nowadays it remains a major consumption in the world. Concurrently, Daniel Swern carried out the epoxidation of polyolefins with peroxy acids as an alternative route to epoxy resins (Swern 1949). Meanwhile, the Ciba Products Co. established in the United States, further developed epoxy resins for laminating, casting and adhesive applications. Research on bisphenol A based epoxy resins was carried out by the two US companies, Shell Chemical Co. and Union Carbide Corp. (then Bakelite Co.) in the late 1940s. Numerous multifunctional epoxy resins were generated in 1960s for higher temperature applications. In the late 1960s, Dow chemical commercialized the flame retardant epoxy resins synthesized by using tetrabromobisphenol A for composite and electrical laminate applications. In 1970s, epoxy resins used for water borne coating applications occupied the dominant position in the two markets; ICI-Glidden’s epoxy acrylic interior can coatings and PPG’s cathodic electrodeposition automotive primer. High performance multifunctional epoxy resins prepared using phenolic structures and complex amine is used in composites for defense and aerospace applications in the 1980s. Example for this is trisphenol epoxy novolacs established by Dow Chemical and now commercialized by Huntsman (formerly Ciba) (Pham and Marks 2004).

In 1980s, the progress in the computer and electronics industries required higher performance epoxy resins with higher thermal stability, higher device reliability, etc. Hydrocarbon epoxy novolacs based on dicyclopentadiene was introduced by Dow Chemical Company. One of the crystalline resins such as bisphenol diglycidyl ether was marketed by Japanese epoxy resin industry in 1980s with enhanced electrical properties. In 1990s, the growth of radiation-curable epoxy-acrylates and cycloaliphatic epoxies was significantly improved and used as photoresists and lithographic inks in electronic fields. The hybrid epoxy systems possessing higher glass transition temperature, higher thermal decomposition temperature and lower dielectric constants was developed in 1990s for electrical laminates (Pham and Marks 2004).

The performance of epoxy resins used for structural applications has been improved by epoxy-toughening area. Outstanding thermal, mechanical and chemical properties are improved by using nanocomposites and nanotubes. In 1999, new epoxy-
based thermoplastic resin, BLOX* was introduced by Dow Chemical company for coatings, adhesives and gas barrier applications (Pham and Marks 2004).

Because of the versatility in formulating epoxy resins, it finds a variety of major industrial applications, including surface coatings, aerospace composites and adhesives, painting materials, potting compounds, flooring, structural composites, laminates, semiconductor encapsulates, flooring, printed circuit board (PCB) laminates, molding, automotive primer, castings, light-weight foams and insulating materials for electric devices (May and Tanaka 1973; Pham and Marks 2004; Lee and Neville 1982). New developments continue in the application of epoxy materials.

3.1.2  TOUGHENING OF EPOXY RESIN

Cured epoxy resins are known to exhibit excellent mechanical, thermal, adhesive and electrical properties, outstanding chemical, moisture and corrosion resistance, low shrinkage upon cure and dimensional stability. However, their use in various applications is restricted due to their brittle nature owing to higher crosslinking density which absorb insignificant amount of energy. The cured epoxy resins are associated with poor fracture toughness, low impact behavior and inferior resistance to crack propagation (Srivastava and Singh 2012). This problem can be alleviated by toughening of epoxy resin.

Toughness is a measure of material’s resistance to failure or “a means of reducing the rate of crack growth through an inherently brittle matrix without significantly affecting other properties of the continuous phase”. This leads to an increase in the stress or energy needed to reach an identified failure point. Toughness is usually measured as either the critical stress intensity factor or the energy required failing a specimen under a specific loading condition. The toughened epoxy resins have been widely studied and several toughening mechanisms have been proposed (Kinloach and Hunston 1986; Huang and Kinloch 1992; Raghava 1987; Hedrick et al 1991; Bucknall and Patridge 1983; Hourston and Lane 1991; Hourston and Lane 1992). The microstructure of toughened epoxy can be either homogenous or heterogeneous, according to the miscibility between epoxy resin and the toughening material. In general, a heterogeneous microstructure may
result in a better toughness because the particles can impede the propagation of crack (Haugh and Kinloch).

Toughening of epoxy resins can be done by two methods either (a) by reducing the cross-linked density of the epoxy matrix or (b) by modifying commercially available epoxy resins with secondary components. The secondary components such as a rigid phase (Hsiesh et al 2011), functionally terminated engineering thermoplastics (Yang and Gu 2009; Pearson and Yee 1993; Huang et al 1997), low molecular weight rubbers (Kunz and Beaumont 1981; Levita et al 1985), interpenetrating polymer networks (Hsiesh et al 2001; Chern et al 1994; Prabu and Alagar 2004; Jia et al 2007), to name a few.

3.1.3 LITERATURE SURVEY

Since hyperbranched polymers have low solution and melt viscosities than that of linear analogues because of lack of entanglement (Uppuluri et al 1998), they are used as a modifier (Boogh 1999; Guo et al 2006; Ratna and Simon 2001; Ratna et al 2003; Varley 2004; Zhang and Jia 2006; Decarli et al 2005; Mezzenga and Manson 2001; Mezzenga et al 2001; Zhang et al 2010; Wu et al 1999) for epoxy resins. Hyperbranched polymers were first used as a toughener for epoxy resins by Boogh and his coworkers in 1999 (Boogh et al 1999). The dendritic hyperbranched polymers show not only the excellent performance in toughening the epoxy resin but also maintain the favorable processing of epoxy resin without affecting much the glass transition temperature (Boogh et al 1999). Guo et al (2006) have studied the toughening of epoxy resin by using hyperbranched polyester (Boltron H40) as a toughener using diaminodiphenylmethane as the curing agent. With the addition of 10 wt.-% of hyperbranched polyester (HBP), the cured epoxy is toughened by the presence of discrete HBP domains in the continuous cured epoxy matrix whereas, for 40 wt.-% HBP content, phase separation has occurred. The impact strength of epoxy resin toughened by using hydroxyl functionalized HBP-G5 is increased linearly up to 20 wt.-% of HBP as supported by morphological study (Ratna and Simon 2001). Ratna et al (2003) examined the impact strength of an epoxy-functionalized hyperbranched polymer (Ep-HBP) used for toughening a conventional epoxy resin, diglycidyl ether of bisphenol A (DGEBA) cured with diethylylene-2,6-diamine (DETDA) and observed that the maximum impact strength was achieved at 15 wt.-% of
Ep-HBP concentration. The toughening of two different epoxy resins, DGEBA and tetruglycidyl methylene dianiline (TGDDM) by using Ep-HBP, a carboxy-terminated butadiene rubber and an aminopropyl-terminated siloxane was investigated by Varley (2004). He discovered that the Ep-HBPs can be effectively used to toughen the DGEBA-based systems, with less effect upon viscosity and the gel time while improving the fracture properties at a level of 15 wt.-% of additive and little effect upon the $T_g$. This result was attributed to the phase separation process producing a multi-phase particulate morphology. Zhang and Jia (2006) studied the toughness of DGEBA by using different molecular weight and epoxy equivalent weight of low viscosity liquid Ep-HBP and found that as the content and generation or molecular weight of Ep-HBP is increased, the performance is also increased. DeCarli et al (2005) found that 10 wt.-% of Ep-HBP has been used to toughen a carbon fiber reinforced epoxy anhydride composite. The end groups on the HBP as well as varying the shell surface chemistry play a vital role in deciding the processing which imparts the final properties of the cured epoxy resin (Mezzenga and Manson 2001; Mezzenga et al 2000; Mezzenga et al 2001). The morphology and mechanical measurements of the blends of a tetrafunctional epoxy resin, tetruglycidyl-4,4′-diaminodiphenylmethane (TGDDM) and a HBP (Boogh 1999) using 3,3′-diaminodiphenyl sulfone (DDS) as a curing agent show that cured blends having 15 and 20 phr exhibit a bimodal particle size distribution whereas with 30 phr HBP demonstrates a monomodal particle size distribution and the fracture toughness is increased almost two times than that of unmodified epoxy network with the concentration range 0-30 phr addition of HBP (Zhang et al 2010). Wu et al (1999) examined the toughening of epoxy resin as a function of molar mass and also a function of weight percentage of HBP-G5 and they found that toughness increased only modestly with the molar mass of the HBP. As the weight percentage was increased from 7 to 19 wt.- %, the toughness is increased and decreased with increase of wt.- % of HBP.

Toughening of epoxy is not only done by using either a rigid phase or a rubbery phase, but also by polyurethane (PU) prepolymer as a modifier via interpenetrating polymer network grafting (IPN-grafting). Numerous articles are reported for improving the toughness of epoxy resin by IPN-grafting (Han et al 1990; Wang and Chen 1995; Harani et al 1998; Mahesh and Alagar 2003; Chen and Sun 2006; Prabu and Alagar 2004;
Premkumar et al 2008; Kostrzewa et al 2011; Lin et al 2007). Frisch et al (1974) were the first research group to investigate the properties of PU/epoxy-g-IPNs. Because of the good compatibility of the PU(PBA)-crosslinked DGEBA system in comparing with that of the PU(PTMO)-crosslinked DGEBA system, the former showed higher Izod impact strength with the PU toughened matrix. While comparing the PU(PBA-700)-crosslinked DGEBA with PU(PBA-1000)-crosslinked DGEBA, the shorter soft-segments of PU [ie. PU(PBA700)] exhibited more effective in increasing the Izod impact strength than the longer soft-segments of PU [PU(PBA-1000)], because the shorter soft-segments of PU introduced more of crosslinked structure than the longer soft-segments of PU at the same PU content. The drop in Izod impact strength after 14 wt.-% of PU(PBA700) [or 11 wt.-% of PU(PBA1000)] was due to much soft characteristic having been incorporated into the matrix (Han et al 1990). In 1995, Wang and Chen (1995) compared the toughening of DGEBA epoxy resin by PU prepolymer (10 phr). The two different prepolymer PU such as hydroxyl terminated PU prepolymer (HTPU) and amine terminated PU prepolymer (ATPU) were synthesized using bisphenol-A and 4,4’-diaminodiphenyl sulfone, respectively, as the coupling agents. The polyols used for the aforementioned prepolymer PUs are polytetramethylene glycol and polybutylene adipate (PBA). It had been found that the addition of HTPU resulted in a more effective increase in toughness than for the ATPU and the ester type PBA based PU-modifed epoxy series had little effect on toughness because of homogeneous morphology. Harini et al (1998) found that Desmophen 1200-based PU prepolymer as a modifier at different concentrations within the epoxy resin via grafting chemically has not improved much the mechanical properties. However, by incorporating the chain extender into the PU prepolymer as a modifier into the mixture improved the toughness upto 40 phr content. The toughness is owing to internal cavitation of the modifier particles followed by localized plastics shear yielding proven from SEM analysis. Chen and Sun (2006) found that the mechanical properties such as tensile strength, flexural strength, tensile modulus, flexural modulus and hardness of IPNs formed by reacting epoxy resin and the prepolymer decreased whereas the impact strength of IPNs increased with increase in blocked PU content. Chen et al (2010) prepared a series of graft interpenetrating polymer networks (IPNs) from epoxy resin (EP) and castor oil-based polyurethane. They found that the impact strength
of graft-epoxy IPN decreased beyond 5 wt.-% of PU content whereas the tensile strength of modified epoxy composite was improved (Chen et al 2010). Prabu and Alagar (2004) analyzed mechanical and thermal properties of two different intercross-linked networks (ICN) of siliconized polyurethane-epoxy/unsaturated polyester (UP) coatings. Upto 10 wt.-% of PU and silicone (10 wt.-%) into the epoxy/unsaturated polyester (UP) composite, the mechanical properties were enhanced due to long flexible and resilient nature of PU chain and the stress relieving nature of siloxane moiety. The thermal stability of modified epoxy/UP coating systems were found to be declined due to thermally weak urethane linkage in the case of PU incorporation whereas presence of siloxane in these system retards the degradation process due to the presence of thermally stable Si-O-Si linkage (Prabu and Alagar 2004). Mahesh and Alagar (2003) investigated the mechanical, thermal, and morphological properties of inter-crosslinked networks of bismaleimide (BMI) modified polyurethane–epoxy systems. The incorporation of chain-extended BMI into polyurethane modified epoxy systems increases the thermal stability and both tensile and flexural properties, but decreases the impact strength and glass-transition temperature (Mahesh and Alagar 2003). Toughening of DGEBA upto 15 wt.-% of caprolactam blocked methylenediphenyl diisocyanate (CMDI) as well the aforementioned matrix by using N,N′-bismaleimido-4,4′-diphenylmethane (BMI) were studied by Premkumar et al (2008). The incorporation of caprolactam blocked methylenediphenyl diisocyanate (CMDI) into the epoxy system improved the impact strength to an appreciable extent upto 15 wt.-% of CMDI when compared with that of unmodified epoxy system. The improvement in impact behavior may be explained due to the influence of long molecular chain with flexible group (-NH-CO-) present in CMDI skeleton whereas the impact strength decreased for the incorporation of BMI into both epoxy and CMDI toughened epoxy resin when compared with that of unmodified epoxy system and 10wt.-% CMDI toughened epoxy resin (Premkumar et al 2008). Mechanical and structural properties of DGEBA using polyurethanes (PURs) as modifiers obtained from poly(ethylene glycol)s (PEGs) and polyoxypropylene diols (POPDs) of different molecular weights were examined by Kostrzewa et al (2011). The increase in impact strength and critical stress intensity factor, $K_c$ values as well as the flexural properties of grafted-epoxy-polyurethane composites was obtained by using polyurethanes from PEGs.
(PUR 400 and PUR 600) as well as POPDs (PUR 1002 and PUR 2002) up to 15 wt.-% of PU content (Kostrzewa et al. 2011). Lin et al. (2007) studied the mechanical properties of polyurethane/epoxy-graft-interpenetrating systems (PU/DGEBA-g-IPN) as a function of molecular weights of polyol, poly(tetramethylene adipate)glycol and found that they exhibited improved tensile and izod impact strengths relative to those of neat DGEBA. However, the soft properties of the polyurethanes also caused by the bending and shear strengths of the PU/DGEBA-g-IPN systems decreased upon increasing the PU content as well as increase of polyol molecular weight (Lin et al. 2007).

3.1.4 OBJECTIVE OF THE CHAPTER

While a keen survey of literature, hardly a few citations have been found out regarding the toughening of epoxy resin by physical blending of either hydroxyl-terminated or functionalized- (Acetoxy- or epoxy-terminated) hyperbranched polymers. In the present study, hyperbranched polyester is used as a modifier for epoxy resin by chemical blending through the formation of graft IPNs by reacting it with hexamethylene diisocyanate and epoxy resin. The objective of this chapter is as follows:

a. Hyperbranched polyesters, G1 to G4 (HBP-G1 to HBP-G4) are synthesized by using dipentaerythritol as a core and DMPA as a monomer by pseudo-one-step melt polycondensation method and characterized using spectroscopic (FTIR, NMR, MALDI-TOF), thermal (TGA and DSC) and physical (intrinsic viscosity) methods.

b. Hyperbranched polyester-Polyurethane/Epoxy-g-IPNs are synthesized by reacting HBPs (HBP-G1 to HBP-G4), hexamethylene diisocyanate (NCO/OH (HBP or LP) ratio is 2) and epoxy resin using dibutyltin dilaurate (DBTDL) as a catalyst at 90°C. The aforementioned method is also adopted for synthesizing linear polyol-polyurethane/Epoxy-g-IPN for comparison.

c. The aforesaid IPNs are mixed with the calculated amount of curative and they are cured. The cured epoxy composites as well as neat epoxy samples
are characterized by mechanical measurements, thermal studies and morphological study.

3.2 EXPERIMENTAL

3.2.1 MATERIALS

Dipentaerythritol (DIPE), dimethylolpropionic acid (DMPA), \( p \)-toluenesulphonic acid (\( p \)-TSA), hexamethylene diisocyanate (HMDI), dibutyltin dilaurate (DBTDL), anhydrous CHCl\(_3\) as well as DMF and linear polyol (polyethylene glycol 600) were obtained from Aldrich Chemicals, South Korea and used as received. Epoxy resin (diglycidyl ether of bisphenol-A type, YD-115, epoxide eq. wt. of 180-194) and the curing agent (Polyamidoamine, G-A0533) were obtained from Kukdo Chemicals, Korea.

3.2.2 SYNTHESIS OF HYPERBRANCHED POLYESTERS (G1 TO G4) POLYOLS

Hyperbranched polyesters polyols for different generations from generation one to generation four (HBP-G1 to HBP-G4) were synthesized by pseudo-one-step synthesis (sequential addition of a monomer and each addition corresponds to the stoichiometric amount for the next theoretical generation) (Jana and Raju 2007) by melt polycondensaion as follows: 1 mole of DIPE with 6 mole of DMPA and \( p \)-TSA (0.05 wt.-% of DMPA) were taken in a three-necked flat-bottomed flask placed over an oil bath equipped with a nitrogen inlet, guard tube with calcium chloride and a mechanical stirrer. The temperature was raised from room temperature to 165 °C. The reaction was carried out at 165 °C with a continuous nitrogen flow for about 22 h to complete the esterification reaction. Finally, vacuum was provided for about 1 h to remove the remaining water as well as to increase the molecular weight of the HBP-G1 formed. The above said procedure was adopted for synthesizing HBP-G2 (28 h), HBP-G3 (33 h) and HBP-G4 (42 h) by pseudo-one-step synthesis. For all the generations, 0.05 wt % (of total weight of DMPA) of \( p \)-TSA was taken. Molar ratios for all the generations of HBP were given in the Table 3.1 and the reaction scheme for all the HBPs, was shown in Scheme 3.1.
Dipentaerythritol + 6 HOOC

\[ \text{Dipentaerythritol} + 6 \text{HOOC} \]

\[ \rightarrow \]

\[ \text{p-TSA} \]

165 °C, N₂ atm

\[ \text{DMPA} \]

\[ \rightarrow \]

HPB-G1

\[ \text{Dipentaerythritol} + 18 \text{HOOC} \]

\[ \rightarrow \]

\[ \text{p-TSA} \]

165 °C, N₂ atm

\[ \text{DMPA} \]

\[ \rightarrow \]

HPB-G2
dipentaerythritol + 42 HOOC\textsubscript{2}CH\textsubscript{2}OH

\[ \text{DMPA} \]

\[ \rho\text{-TSA} \]

165 °C, N\textsubscript{2} atm

HBP-G3
Scheme 3.1: Synthesis of HBPs (HBP-G1 to HBP-G4) showing its idealized structures.
Table 3.1: Molar ratios used for synthesizing for different generations of HBPs

<table>
<thead>
<tr>
<th>HBPs generation</th>
<th>DIPE (mole)</th>
<th>DMPA (mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>G2</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td>G3</td>
<td>1</td>
<td>42</td>
</tr>
<tr>
<td>G4</td>
<td>1</td>
<td>90</td>
</tr>
</tbody>
</table>

3.2.3 SYNTEHSIS OF HYPERBRANCHED POLYESTER-POLYURETHANE/EPOXY-GRAFT-INTERPENETRATING POLYMER NETWORKS

Calculated amount of epoxy resin and HBP-G1 were added to 5 ml of anhydrous DMF solvent in a 250 ml round-bottomed flask equipped with nitrogen inlet, mechanical stirrer, guard tube and placed in an oil bath. A homogenous solution was obtained after stirring at 120 °C for 1.5 h and further stirring was continued at 80 °C under reduced pressure to remove moisture, if any. To this reaction mixture, calculated amount of HMDI and DBTDL in anhydrous CHCl₃ solvent was added drop-wise for about 0.5 h at 90 °C under reflux setup and a constant flow of nitrogen with vigorous stirring. The reaction was continued for 3 h and the final product, hyperbranched polyester-polyurethane/epoxy-graft-interpenetrating polymer networks (HBP-PU/Epoxy-g-IPN) (Mahesh and Alagar 2003) is cooled to room temperature. Calculated amount of curative was added to the above mixture under continuous stirring, then poured into a preheated Teflon mold and kept in a vacuum oven at 80 °C for 15 min to remove the entrapped air. Curing and post-curing of HBP(G1)-PU/EP samples were carried out at 80 °C for 14 h and at 120 °C for 2 h, respectively. The aforementioned procedure was adopted in the case of HBP-G2, HBP-G3, HBP-G4 and linear polyol (LP). Composition of the reactants used for preparing the sheets is given in Table 3.2 and the reaction pathway in Scheme 3.2. The NCO/OH (HBP or LP) ratio is maintained at 2 and the amount of HBP-PU in epoxy is maintained at 10 wt.-% irrespective of the generations used and the same weight percentage is used for L-PU sample. The control sample (neat epoxy) was mixed with the curative (50 wt.-% of epoxy) and curing was carried out at 80 °C for 14 h and post-curing at 120 °C for 2 h. Epoxy resin was subjected to vacuum for 2 h at 80 °C prior to synthesis.
Table 3.2: Amount of reactants (gm) used for synthesizing PU/Epoxy-g-IPNs

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Epoxy</th>
<th>Linear Polyol (LP)</th>
<th>HBP polyol (HBP)</th>
<th>HMDI</th>
<th>DBTDL</th>
<th>Curative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>L-PU/EP</td>
<td>90</td>
<td>6.4075</td>
<td>-</td>
<td>3.5925</td>
<td>0.05</td>
<td>45</td>
</tr>
<tr>
<td>G1-PU/EP</td>
<td>90</td>
<td>-</td>
<td>7.3870</td>
<td>2.6130</td>
<td>0.05</td>
<td>45</td>
</tr>
<tr>
<td>G2-PU/EP</td>
<td>90</td>
<td>-</td>
<td>8.7450</td>
<td>1.2550</td>
<td>0.05</td>
<td>45</td>
</tr>
<tr>
<td>G3-PU/EP</td>
<td>90</td>
<td>-</td>
<td>9.3847</td>
<td>0.6153</td>
<td>0.05</td>
<td>45</td>
</tr>
<tr>
<td>G4-PU/EP</td>
<td>90</td>
<td>-</td>
<td>9.6953</td>
<td>0.3047</td>
<td>0.05</td>
<td>45</td>
</tr>
</tbody>
</table>

Scheme 3.2: Reaction pathway for the formation of HBP-PU/Epoxy-g-IPN.
3.2.4 CHARACTERIZATION TECHNIQUES

3.2.4.1 HYPERBRANCHED POLYESTERS POLYOLS

Fourier transform infrared (FTIR) spectra were recorded using a Bruker 66V FTIR spectrophotometer at a resolution of 4 cm\(^{-1}\) with 32 scans at room temperature. The structure of HBPs was confirmed from the \(^1\)H and \(^{13}\)C NMR spectra recorded by using Ascend\(^{TM}\) (Brucker, Germany) 400-MHz spectrometer in hexadeuterated dimethyl sulfoxide (DMSO-d6) with trimethylsilane as an internal standard.

The thermogravimetric analysis (TGA) of HBPs (HBP-G1 to HBP-G4) was carried out by using SDT Q600 V8.3 Build 101 (Korea) at a heating rate of 10 °C/min., under nitrogen (100 ml/min.) atmosphere upto 500 °C. A small amount of sample (around 10 mg) was used for TGA study. Glass transition temperature of HBPs by differential scanning calorimetry (DSC) was carried out using Mettler-Toledo DSC-1 at a heating rate of 10 °C/min. under nitrogen atmosphere (50 ml/min.) in the temperature range from -20 °C to 200 °C. The glass transition temperature was measured from second heating cycle.

Sample for MALDI-MS analysis was prepared by mixing each HBP sample dissolved in DMF with \(\alpha\)-cyano-4-hydroxycinnamic acid matrix. The resulting mixture was spotted onto a freshly cleaned stainless steel MALDI target plate. After air drying, the crystallized spots were processed by using Voyager DE PRO Biospectrometry Workstation (Applied Biosystems, Foster City, CA, USA) MALDI-TOF (time of flight) MS instrument in IIT, Chennai, India. MS was recorded in a linear mode. A pulsed nitrogen laser of 337 nm was used (maximum firing rate: 20 Hz, maximum pulse energy: 300 µJ) for desorption-ionization and TOF was operated in a delayed extraction mode. Ions were accelerated into the analyzer at a voltage of 25 kV. The mass spectra were collected in both the negative and positive ion modes and were averaged for 100 shots.

The viscosity of a solution is a measure of its resistance to flow. Viscosity measurements of synthetic polymer solutions have been used to deduce their molecular weights and degree of branching. By measuring viscosities of polymer solutions at varying concentrations, the intrinsic viscosity of the macromolecule, which reflects the
shape and volume of the macromolecule itself, can be deduced. This technique can be used to measure solution viscosities in the range of 0.35 to 30,000 centipoise for a solution density of ~1 g/mL.

For viscosity measurement in our study, the initial polymer solution was prepared by dissolving 5.025g of HBP-G1 in 100 ml of NMP solvent in a standard measuring flask and kept stirring at 40 °C overnight. The efflux time for the NMP solvent ($t_s$) was measured using Ubbelohde viscometer (AVS 260 Schott–Gerate GmbH) immersed in a water bath thermostated at 25 °C. The stirred polymer solution was filtered using a 25 micrometer PTFE filter and 20 ml of this polymer solution was transferred to the viscometer. The solution was allowed to equilibrate at 25 °C inside the viscometer before starting the experiment. After measuring the efflux time for initial polymer concentration, the apparatus automatically makes four more dilutions by taking neat solvent from the reservoir using a differential pressure. Two photocells detect the change of the refractive index of the solution as it passes through the two marks into the capillary. The signal is sent to a quartz clock that measures the flow time of each solution. For a particular dilution, the flow times agreed within 0.1 s. From the time of flow, the specific viscosity [$\eta_{sp}$] and the relative viscosity [$\eta_r$] of the five solutions (initial solution and four dilutions) were determined. Each experiment was performed for five times (The efflux time for each concentration was calculated from an average of five measurements).

The intrinsic viscosity [$\eta$] (dL/g) was determined as usual as the common intercept of the Huggins and Kramer relationships (eqns. (1) and (2), respectively) using [$\eta_{sp}$] and [$\eta_r$] values obtained with the Ubbelohde viscometer. The concentration of solute, $c$ is expressed in g/dL:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H[\eta]^2 c$$  \hspace{1cm} (1) 

$$\frac{\ln \eta_r}{c} = [\eta] + k_H[\eta]^2 c$$  \hspace{1cm} (2) 

From both equations, the intercept gives the intrinsic viscosity and the slopes (which are of opposite sign) are proportional to [$\eta]^2$. The constant $k_H$ is termed the Huggins constant and has values ranging from 0.3 in good solvents to 0.5 in poor
solvents. Eqns. (1) and (2) are fitted from the minimum squared method and the mean value of the intercepts is taken as the intrinsic viscosity (Bustamant et al 2005).

Similarly, for HBP-G2 (4.028g/dL), HBP-G3 (5.0466) and HBP-G4 (5.0488 g/dL), the aforementioned procedure was carried out for finding the intrinsic viscosity of HBPs.

3.2.4.2 COMPOSITES

Thermal stability of all the composites were measured using SDT Q600 V8.3 Build 101 (Korea) at the heating rate of 10 °C/min., under nitrogen (100 ml/min.) atmosphere upto 600 °C by thermogravimetric analyzer (TGA). A small amount of sample (around 10 mg) was used for TGA study. Differential scanning calorimetry (DSC) was performed using DSC Q1000 V9.9 Build 303 at a heating rate of 10 °C/min. under nitrogen atmosphere (50 ml/min.) in the temperature range from -50 °C to 280 °C. The glass transition temperature was measured from second heating cycle and taken as the midpoint of the heat capacity change. Notched Impact strength of the epoxy and the grafted epoxy sheets were measured by using Tinius Olsen impact tester according to ASTM 256. The dimensions of the samples used were 80 x 10 x 4 mm. The impact test was performed at room temperature. Flexural tests were performed with three point bending mode at a cross head speed of 2 mm/min. according to ASTM 790 using an Instron universal testing machine (model 3382). The dimensions of the samples were 80 x 10 x 4 mm. For both impact and flexural tests, five specimens were tested. Scanning Electron Microscopy images were obtained using Hitachi, Model: S-3400N with a magnification ranging from 5 to 3,00,000x. The izod impact samples were used for SEM analysis and these samples were carbon coated.

3.3 RESULTS AND DISCUSSIONS

3.3.1 CHARACTERIZATION OF HYPERBRANCHED POLYESTERS POLYOLS

Fig. 3.1 shows the FTIR spectra of the synthesized HBPs as a function of varying generations (G1 to G4). The broad band at 3200-3600 cm\(^{-1}\) corresponds to the presence of hydrogen bonded hydroxyl group. The peaks at 2941 and 2884 cm\(^{-1}\) correspond to the
CH\textsubscript{3} and CH\textsubscript{2} stretching vibrations whereas the CH\textsubscript{2} and CH\textsubscript{3} bending deformation vibrations appear at 1472 and 1375 cm\textsuperscript{-1}, respectively. The medium band at 1400 cm\textsuperscript{-1} indicates the existence of OH in-plane bending, while the very weak band at 764 cm\textsuperscript{-1} denotes the presence of OH out-of-plane bending. The bands at 1223 and 1128 cm\textsuperscript{-1} represent the C-O-C=O stretching of ester and C-O-C=O stretching of ester groups, respectively. The C-O stretching of -CH\textsubscript{2}OH groups is detected from the band at 1043 cm\textsuperscript{-1}. Interestingly, the ester carbonyl group exhibit a small but significant shift towards higher wavenumber as observed from the bands at 1729 cm\textsuperscript{-1} (HBP-G1), 1733 cm\textsuperscript{-1} (HBP-G2), 1734 cm\textsuperscript{-1} (HBP-G3) and 1734 cm\textsuperscript{-1} (HBP-G4), which clearly indicates the decrease in the extent of H-bonding between the carbonyl and hydroxyl groups with increasing generations.

Fig. 3.1: FTIR spectra of HBPs as a function of varying generations (G1 to G4).

Figs. 3.2-3.5 represent \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra of HBPs from G1 to G4 generations. The resonance signals of methyl group appear at \approx 0.7-0.1 ppm whereas, methylene groups attached to the reacted hydroxyl groups (CH\textsubscript{2}-O-C=O) and unreacted hydroxyl groups (CH\textsubscript{2}-OH) resonate at 4.1-4.0 and 3.4 ppm, respectively, as shown in Figs. 3.2(a)-3.5(a). The terminal and linear hydroxyl (-OH\textsubscript{T} and -OH\textsubscript{L}) groups show up at \approx 4.6 and \approx 5.0 ppm, respectively [Figs. 3.2(a)-3.5(a)]. The degree of branching and the
expanded zones of methyl groups are presented in Fig. 3.2(a)-3.5(a). The $^{13}$C NMR spectra of HBPs are depicted in Figs. 3.2(b)-3.5(b). The methyl carbons appear in the range of 16-18 ppm whereas quaternary carbons show up in the region between 45 and 51 ppm. Methylene carbons and carbonyl carbons can be detected from the peaks in the range, 62-68 ppm and 170-175 ppm, respectively (Magnusson et al 2000). The expanded form for quaternary carbon and carbonyl carbon groups and their degree of branching by Frechet and Frey as represented by eqns. (3) and (4) (Hawker et al 1991; Hoelter et al 1997) are also shown in the Figs. 3.2(a)-3.5(b). The degree of branching calculated by both methods for HBPs indicate that the polymer formed is highly branched. The peaks at $\approx 49.4$ and $\approx 47.5$ ppm correspond to terminal acid ($T_{acidi}$) and linear acid ($L_{acid}$) units, respectively. Absence of etherification reaction as the side reaction during hyperbranched polymer synthesis could be confirmed from the absence of peak at 49.3 and 47.3 ppm corresponding to linear ether ($L_{ether}$) and dendritic ether ($D_{ether}$), respectively (Zagar and Zigon 2011) in the quaternary region whereas the same could be corroborated from the absence of peak at 72-73 ppm in the methylene region (Zagar and Zigon 2011). The presence of terminal (T), linear (L) and dendritic (D) repeating units of quaternary carbon could be proved from the peaks at 50.2, 48.2 and $\approx 46.2$ ppm, (Zagar and Zigon 2011) respectively, while in the carbonyl carbon region, they could be observed at 174.3, 172.9 and 171.8 ppm for T, L and D, respectively. The signal at 176.6 ppm represents the presence of –COOH group in HBPs. The degree of branching calculated by both methods for HBPs indicate that the polymer formed is highly branched. The structural units found in the HBPs are shown in Scheme 3.3. The degree of branching was calculated by the following equations.

$$DB_{Frechet} = \frac{D+T}{D+L+T}$$  \hspace{1cm} (3)

$$DB_{Frey} = \frac{2D}{2D+L}$$  \hspace{1cm} (4)
Fig. 3.2: (a) $^1$H NMR and (b) $^{13}$C NMR spectra of HBP-G1.
Fig. 3.3: (a) $^1$H NMR and (b) $^{13}$C NMR spectra of HBP-G2.
Fig. 3.4: (a) $^1$H NMR and (b) $^{13}$C NMR spectra of HBP-G3.
Fig. 3.5: (a) $^1$H NMR and (b) $^{13}$C NMR spectra of HBP-G4.
Fig. 3.6 represents the thermal stability of HBPs studied using TGA measurement. An in-depth analysis reveals the measurable weight loss to occur between 230 and 275 °C for all the samples. Below 230 °C, there is no measurable amount of evaporable compounds such as moisture and unreacted monomers. The onset of thermal degradation for HBP-G1 and HBP-G2 was found to be at 314 °C whereas for HBP-G3 and HBP-G4, the weight loss starts occurring at near 325 °C. This clearly indicates that the thermal stability of HBP increases with increasing generations due to the enhancement of backbone structure as well as raised number of end functional groups (Chen and Yin 2002; Baek and Harris 2005; Peng et al 2005). The temperature at which weight loss of 5, 20, 50 and 80 (in %) designated as T5, T20, T50 and T80 (Vukovic et al 2006) was observed to increase with increasing generations as shown in Table 3.3. The increase in thermal stability is more prominent with increasing generation from first to second but reaches a plateau at higher generations. Overall, the increase in degradation temperature with increasing HBP generations is attributed to an increase in molar mass (Hult et al 1999) along with an increase in the number of hydroxyl end groups per macromolecules.
and the formation of intramolecular hydrogen bridges between –OH groups in the same branches (Vukovic et al 2006).

![TGA curves of HBPs (HBP-G1 to HBP-G4).](image)

**Fig 3.6: TGA curves of HBPs (HBP-G1 to HBP-G4).**

**Table 3.3: Degradation temperatures of different HBP generations (G1 to G4)**

<table>
<thead>
<tr>
<th>HBPs</th>
<th>T$_5$ ($^\circ$C)</th>
<th>T$_{20}$ ($^\circ$C)</th>
<th>T$_{50}$ ($^\circ$C)</th>
<th>T$_{80}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBP-G1</td>
<td>283</td>
<td>321</td>
<td>351</td>
<td>419</td>
</tr>
<tr>
<td>HBP-G2</td>
<td>303</td>
<td>333</td>
<td>367</td>
<td>423</td>
</tr>
<tr>
<td>HBP-G3</td>
<td>308</td>
<td>340</td>
<td>377</td>
<td>417</td>
</tr>
<tr>
<td>HBP-G4</td>
<td>310</td>
<td>342</td>
<td>380</td>
<td>417</td>
</tr>
</tbody>
</table>

Thermal properties of hyperbranched polymers are significantly different from those of linear analogous (i.e. linear polymers of the same nature and molar mass). Being amorphous in nature, the highly branched structure of hyperbranched polymer significantly affects the $T_g$, which is one of the most important properties of thermal behavior. Fig. 3.7 shows the DSC curves as a function of varying HBP generations. As the number of generations is increased from first generation (G1) to third generation (G3), the glass transition temperature is also increased due to increase in the branching which restricts the mobility of the backbone. However, it is slightly decreased for the
fourth generation (G4) than that of third generation (G3) due to increase in the end groups as shown in Fig. 3.7. The lowering of $T_g$ is mainly due to increase in free volume by the end groups and also mainly attributed to the reduction of extent of H-bonding by the end groups (Luiani et al 2004). This is already proven by the shift of wavenumber of carbonyl band towards higher frequency with increase in generation number from FTIR data. The second order transition of hyperbranched polymer is mainly due to the translational motion of the molecule which strongly depends on the molecular mobility of the back bone rather than the segmental chain motion (Kim and Webster 1992). It is already indicated that the second order transition of hyperbranched polymer depends not only on the backbone of the structure, but also on the type and number of the end functional groups, number of crosslinks or branching points to some extent and more polarity of the end groups (Inoue 2000; Farrington et al 1998; Wooley et al 1993).

Fig.3.7: Second order transition from DSC curves of different generations of HBPs (G1 to G4).

The intrinsic viscosity, number average ($M_n$) and weight average ($M_w$) molecular weight and the polydispersity index (PDI) of HBPs of different generations are given in Table 3.4. Lower intrinsic viscosity values indicates that HBPs are in globular shape and
its viscosity increases slightly with increase in molar mass or with different generations (Nunez et al 2000; Luciani et al 2004).

Table 3.4: Intrinsic Viscosity and MALDI-TOF data of different HBP generations (G1 to G4)

<table>
<thead>
<tr>
<th>HBPs</th>
<th>Intrinsic Viscosity [η] (dL/g)</th>
<th>(M_n) (g/mol)</th>
<th>(M_w) (g/mol)</th>
<th>PDI = (M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBP-G1</td>
<td>0.0690</td>
<td>525</td>
<td>737</td>
<td>1.40</td>
</tr>
<tr>
<td>HBP-G2</td>
<td>0.0773</td>
<td>1586</td>
<td>2138</td>
<td>1.35</td>
</tr>
<tr>
<td>HBP-G3</td>
<td>0.0915</td>
<td>5330</td>
<td>5469</td>
<td>1.03</td>
</tr>
<tr>
<td>HBP-G4</td>
<td>0.1042</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.3.2 CHARACTERIZATION OF EPOXY COMPOSITES

As discussed in the experimental part, the synthesized HBPs were reacted with epoxy resin through the formation of PU linkages. The IPNs were analyzed for their mechanical properties as a function of varying HBP generations. Fig. 3.8 shows the izod impact strength of epoxy and the modified epoxy samples. Except L-PU/EP sample, all the HBP modified epoxy samples using HBP (represented as G1, G2, G3 and G4) exhibit higher impact resistance than that of the unmodified epoxy sample. However, though the impact strength is decreased for G4-PU/EP modified sample compared to that of G3-PU/EP sample, it is still higher than that of the neat epoxy sample by 6%. Among all the modified samples, the maximum impact strength exhibited by the G3-PU/EP sample (35 J/m, 9.5 % higher than neat epoxy) is attributed to not only the presence of flexible NH\-CO groups in the graft IPN that makes the matrix more ductility but also the formation of covalent bonding between epoxy and polyurethane networks leading to more interpenetration which results in good dispersion of polyurethane in the epoxy matrix. The decrease in impact strength for G4-PU/EP sample is due to the formation of bigger size of rubber particles [Fig. 3.12(g)] whereas the drop in impact strength for L-PU/EP sample when compared to that of neat epoxy sample is attributed to dominance of the macro-separated phase or aggregation of rubber particles rather than the heterogeneous morphology in the matrix proved by the SEM image as shown in Fig. 3.12(b).
Fig. 3.8: Izod impact strength of epoxy and the modified PU/epoxy-g-IPNs of different generations (G1 to G4) of HBP and linear polyol sample.

Fig. 3.9 depicts the flexural properties of neat epoxy and the modified epoxy samples. The flexural strength and modulus of the modified epoxy IPNs is lower than that of neat epoxy sample owing to incorporation of urethane linkages (NH-CO) into the epoxy matrix leading to flexibility of the matrix (Raju et al 2008; Barcia et al 2003; Takao et al 1992). However, the flexural properties of PU/epoxy-g-IPN of hyperbranched polyester samples are lower than that of L-PU/EP sample. As the generation number increases, the flexural strength and modulus is also increased linearly due to increase in the rigidity of the material.
The TG curves for epoxy and the modified epoxy samples are depicted in Fig. 3.10. The thermal stability of the samples is decreased linearly from epoxy to G4-PU/EP sample to some extent owing to thermally weak flexible polyurethane linkage (NH-CO) (Mahesh et al 2003) in the modified epoxy samples. The onset temperature is found to be 339, 333, 323, 321, 318 and 316 °C for Epoxy, L-PU/EP, G1-PU/EP, G2-PU/EP, G3-PU/EP and G4-PU/EP samples, respectively. The temperature at which weight loss of 20, 40 and 60 (in %) designated as $T_{20}$, $T_{40}$, and $T_{60}$ is represented in Table 3.5. The degradation temperature is decreased from Epoxy to its IPN samples indicating the reduction in H-bonding existing between the thermally weak NH-CO groups in the modified samples. Fig. 3.11 represents the glass transition temperature curves of Epoxy and the PU/epoxy-g-IPNs samples. The modified samples exhibit lower glass transition temperature ($T_g$) when compared to that of neat epoxy sample. The lowering of glass transition temperature (Palmese and McCullough 1992; O’Brien et al 2003) in the modified samples is due to the existence of flexible polyurethane linkage which reduces
the effective crosslinking density leading to increase in the free volume for molecular relaxation.

Fig. 3.10: TGA curves for epoxy and the modified epoxy samples (PU/epoxy-g-IPNs).

Fig. 3.11: DSC curves for epoxy and the modified epoxy samples (PU/epoxy-g-IPNs).
Table 3.5: Degradation temperatures for epoxy and its modified samples (PU/epoxy-g-IPNs)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{20}$ (°C)</th>
<th>$T_{40}$ (°C)</th>
<th>$T_{60}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>351</td>
<td>373</td>
<td>393</td>
</tr>
<tr>
<td>L-PU/EP</td>
<td>349</td>
<td>371</td>
<td>391</td>
</tr>
<tr>
<td>G1-PU/EP</td>
<td>342</td>
<td>367</td>
<td>389</td>
</tr>
<tr>
<td>G2-PU/EP</td>
<td>338</td>
<td>365</td>
<td>389</td>
</tr>
<tr>
<td>G3-PU/EP</td>
<td>335</td>
<td>364</td>
<td>391</td>
</tr>
<tr>
<td>G4-PU/EP</td>
<td>337</td>
<td>366</td>
<td>390</td>
</tr>
</tbody>
</table>

Fig. 3.12 shows the SEM images of epoxy and the modified epoxy samples. Fig. 3.12(a) represents the glassy fractured surface with different crack planes indicating the brittle nature of epoxy sample. The modified epoxy samples exhibit heterogeneous morphology (Mahesh et al 2003) with the distribution of rubber particles in thermoset matrix that interprets the modified epoxy samples using HBPs showed better toughness than that of neat epoxy sample. The grafted IPNs formed by G1-PU/EP and G2-PU/EP samples reveal segmental crack growth which reduces the rate of crack propagation in addition to heterogeneous morphology. Besides the heterogeneous morphology, rubber cavitation mechanism indicated by arrow mark as shown in the Fig. 3.12(d) is observed for G2-PU/EP sample while tearing of rubber particles portrayed in Fig. 3.12(e) as well as the moderate size of rubber particles in comparison to that of other modified epoxy samples is responsible for greater toughness in the case of G3-PU/EP sample. The large size of rubber particles is observed in G4-PU/EP sample which reduced the impact strength to some extent in comparison to that of G3-PU/EP sample while L-PU/EP sample revealed the existence of aggregation of rubber particles leading to drop in impact strength in correlation to neat epoxy sample.
Fig. 3.12: SEM images of (a) Epoxy, (b) L-PU/EP, (c) G1-PU/EP, (d) G2-PU/EP, (e) G3-PU/EP and (f) G4-PU/EP samples.
3.4 CONCLUSIONS

Using dipentaerythritol as a core and DMPA as a monomer, four different generations of HBPs (HBP-G1 to HBP-G4) were synthesized by pseudo-one-step melt polycondensation and were characterized by FTIR, NMR, DSC, TGA, MALDI-TOF and intrinsic viscosity measurements. The structure and degree of branching have confirmed the formation of highly branched structure. The toughening of epoxy resin was examined by accomplishing the formation of grafted interpenetrating polymer networks by reacting different generations of HBPs as well as linear polyl with HMDI and epoxy resin. It was found that the modified epoxy samples by HBPs (HBP-G1 to HBP-G4) exhibit better toughness by showing higher impact value than that of neat epoxy sample and L-PU/EP sample. The higher impact strength of G3-PU/EP sample is attributed to the heterogeneous morphology as well as tearing of rubber particles revealed by SEM image when compared to the effect of all the hyperbranched polyesters. SEM micrographs indicate that the toughness is not only due to the presence of heterogeneous morphology but also the segmental crack growth which reduces the rate of crack propagation. The flexural properties of the modified epoxy samples are declined due to the incorporation of polyurethane linkage into the epoxy matrix leading to flexibility of the thermoset epoxy matrix. Thermal stability of the grafted epoxy samples are lowered due to weak flexible urethane linkages with respect to that of neat epoxy sample. The decrease of glass transition temperature of the modified epoxy samples is ascribed to the reduction in crosslinking density of the thermoset matrix.