# ABA AND ABC TYPE THERMOPLASTIC ELASTOMER TOUGHENING OF EPOXY MATRICES AND ITS EFFECT ON CARBON FIBER REINFORCED COMPOSITES

By

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#### ABSTRACT

## ABA AND ABC TYPE THERMOPLASTIC ELASTOMER TOUGHENING OF EPOXY MATRICES AND ITS EFFECT ON CARBON FIBER REINFORCED COMPOSITES

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Epoxy-matrices have high modulus, strength, excellent creep resistance, but lacks ductility. One approach to improve the mechanical toughness is the addition of thermoplastic elastomers (TPEs). The TPEs investigated here are triblock copolymers of styrene-butadiene-methyl methacrylate (SBM) and methylmethacrylate-butylacrylate-methylmethacrylate (MAM) of the ABC and ABA type, respectively. The effect of concentration (1-12.5 wt %) of these TPEs on a diglycidyl ether of bisphenol-A (DGEBA) epoxy cured with metaphenylenediamine (mPDA), has been investigated. The TPE-DGEBA epoxies were characterized by TGA, DMA, SEM and impact. The flexural modulus, flexural strength and thermal resistance remained unaffected up to 5 wt% loading of TPEs, and exhibited less than 10% decrease at higher weight percent.  $T_g$  was unaffected for all concentrations. Fracture toughness was improved ~250% and up to ~375% (when non- stoichiometric amount of curing agent was used) with TPE addition to epoxy/mPDA matrix. A SBM(1phr)EPON system was chosen to be the matrix of choice for a fiber reinforced composite system with a 4wt% aromatic epoxy sizing on a AS4 (UV-treated) carbon fiber. The 0° and 90° flexural modulus and strength of a SBM modified system was compared with the neat and their fracture surfaces were analyzed. A 89% increase in flexural strength was observed in a 90° flexural test for the modified system when compared with the neat. Novel sizing agents were also developed to enhance interfacial shear strength (IFSS) and the fiber-matrix adhesion and their birefringence pattern were analyzed.

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# KEY TO ABBREVIATIONS

TPE	Thermoplastic elastomer
FRC	Fiber reinforced composites
CFRC	Carbon fiber reinforced composites
DGEBA	Diglycicdyl ether of bisphenol-A
m-PDA	meta-phenylene diamine
EPON	Trade name for DGEBA-EPON 828 material from Miller-stephenson
ASTM	American Society for Testing materials
CFRP	Carbon fiber reinforced composite
SEM	Scanning Electron Microscopy
SBM	Polystyrene, Polybutadiene, Poly methyl methacrylate triblock copolymer
MAM/ MBM	Polymethyl methacrylate, polybutadiene, Polymethyl methacrylate triblock copolymer
FT-IR	Fourier transform infra-red
TGA	Thermo-gravimetric analysis
DMA	Dynamic mechanical analysis
DSC	Dynamic scanning calorimetry
PS	Polystyrene
PB	Polybutadiene
PMMA	Poly methyl methacrylate
PBuA	Ppoly butyl accrylate
СТ	Compact tension
BDMA	Benzyl dimethylamine

rfacial shear strength

- PEI Polyetherimide
- TGPAP Triglycidylether of para-aminophenol
- TGDDMTetraglycidyl 4,4'-diaminodiphenylmethane
- DDS 4,4'-diaminodiphenylsulfone

#### CHAPTER 1 INTRODUCTION AND LITERATURE REVIEW

#### **1.1. ROLE OF MATRICES IN A COMPOSITE**

Composite materials are sought after by the aerospace industry for their light weight and strength properties. Polymer composites, with epoxy resins as matrix material, are widely used in the aerospace industry owing to its chemical resistance, strength, low shrinkage during cure, ease of processing, solvent resistance and good mechanical properties [1]. Epoxy resins vary based on their functionality, with the more crosslinked multifunctional systems being used for advanced applications involving harsher environments. Table 1 lists the commonly used epoxy resins on the basis of their functionality. The fracture toughness of these cured matrices control damage tolerance and toughness of a composite [2]. Despite these advantages, epoxies are inherently brittle. Brittleness increases with crosslink density and ultimately hampers toughness [3]. Among several materials used to improve the fracture toughness of brittle epoxies, rubber materials likes CTBN (Carboxyl Terminated Butadiene Acrylonitrile) are the most studied. Addition of rubber produces two phase morphology after phase separation. Phase separated material contains small rubber particles (0.1-2µm) dispersed in the matrix that increases toughness by inducing shear yielding and cavitation [1]. However, any enhancement of fracture toughness (K<sub>Ic</sub>) and fracture energy (G<sub>Ic</sub>) by the addition of rubber to lightly crosslinked systems is accompanied with a decrease in thermal, mechanical and chemical stability of the system [1]. This decrease is due to agglomerates during rubber phase separation, stress concentration effects. All these result in an inability of rubbers to be used in high crosslink density systems for advanced applications. An alternate approach to toughen highly crosslinked epoxy matrices was made possible by the advent of stable, tough and ductile thermoplastic materials. Their morphology in an epoxy matrix can be co-continuous, particulate, and homogenous or phase inverted (via reaction induced phase

separation). In contrast to rubber toughening, these materials toughen the epoxy matrix without deteriorating other mechanical and thermal properties.

Tuble 1.1. Epoxy results of varying functionality					
Epoxy type	Hardener	K <sub>Ic</sub>	Tg	Epoxide	
		(MPa.m <sup>0.5</sup> )	(°C)	content(mole/100g)	
DGEBA-difunctional [6]	PIP	1.0	180	0.52-0.55 [7]	
TGDDM-tetrafunctional[8]	DDS	0.61	256	0.75-0.85 [7]	
TGPAP-trifunctional [9]	DDS	0.79	262	0.94-1.05 [7, 10]	

Table 1.1. Epoxy resins of varying functionality

#### 1.1.1. Nanocomposites in terms of Aerospace applications

Nature presents us with efficient composite materials. Right from wood, teeth etc. composites exists but with anisotropy [4]. Composites, in essential are designed to yield synergistic properties. In recent years, with the advent of nanotechnology, nano-composites have entered the fray. When these are used in conjunction with polymers, these form polymeric nanocomposites [4]. Polymer nanocomposites offer us hybrid materials that in today's world provide us with low cost, easy to design, high performance materials. Industrial composites are classified based on its matrix: Polymer Matrix Composites or Metal matrix Composites; Thermoset or Thermoplastic. Reinforcements are added in the form of glass/ceramic fibers/carbon materials/nanoparticles to enhance stiffness. Since 1986, polymer matrix fiber composites have been in use, and its application rapidly rising. 19% of the structural weight in the F-18 fighter aircraft is made of polymer composites and 70% of GENx90 is made of composites [5].

Designing a composite requires a thorough understanding of the micro and macro aspects, physical and chemical properties. Morphology, density, thermal properties (conductance expansion etc.), stiffness, strength, toughness, load sharing of reinforcement with matrix, are all important. For advanced applications and components like that in aircrafts, multicomponent systems, hybrid materials or composites are mandated. Graphite/epoxy composites, for eg. are used in truss elements, antennas, parabolic reflectors, bus panels, wave guides [6]. Strength in the interface, dispersion, agglomeration, high mobility, and toughness (involves interfaces) are major properties of concern when dealing with nanocomposites [8].

Matrix	Density, ρ (gmm <sup>-3</sup> )	Young's modulus , E (GPa)	Tensile Strength, σ (MPa)	Fracture toughness $(K_{Ic})$ MPa $(m)^{1/2}$	Thermal Conductivity, K (Wm <sup>-1</sup> K <sup>-1</sup> )	Failure strain € (%)
Thermosets- epoxies	1.1-1.4	3-6	35-100	0.5	0.1	1-6
Thermoplast ic-Nylon	1.14	1.4-2.8	60-70	4.0	0.2	40-80
Metal (Al)	2.7	70	200-600	40-140	24	6-20
Ceramic- Al <sub>2</sub> O <sub>3</sub>	3.8	380	500	4	30	0.1

Table 1.2. Various matrices for FRC's [9]

#### 1.1.2. Mechanical properties and toughening mechanisms

With the help of a physical testing machine, properties like Young's modulus and Tensile Strength, Failure to strain (ASTM D638), Flexural strength and modulus could be measured experimentally (ASTM D790). The addition of fillers leads to enhancement of modulus. Homogenous mixture of polymer nanocomposites is required to cast into molds to maketest specimens. The Halpin Tsai model tells us a way to predict the modulus of composite[8]. In addition to these mechanical properties, crack propagation, fatigue and ultimately failure of the material must be tested. The most important property in terms of Aerospace applications for epoxy matrices is toughness,  $K_{Ic}$ ,  $G_{Ic}$  [9, 11-14]. It has been reported that failure of the materials could be due to the failure of the matrix, or, failure at fiber matrix interface, failure between reinforcing and the matrix and filler. Some of the different modes of fracture and/or failure and a few of the toughness mechanisms with respect to epoxy-filler materials are described [12]. To get a complete picture of mechanical properties, the samples have to be tested under static, cyclic and dynamic loading conditions.

In practice a lot of events happen at the interface and depends on structure and stresses generated, plastic deformation of the matrix, and ultimately point of failure [15]. Crack bridging mechanism is characterized by a fiber bridging zone when a crack tip is produced. When energy is dissipated, Pullout of materials with matrix happens [8]. Faber et. al suggested a phenomena for crack deflection, that when a crack encounters a particle it could be twisted out of the place, could bend around them or is merely tilted. This increase the total fracture area which could be measured by AFM, which analyses rough surfaces [8, 11, 16-17].

Crazing, on the other hand forms denser regions which generate fibrils under tension [11, 18]. This mechanism increases the fatigue crack growth. Lange *et.* al proposed the mechanism for a crack pinning process [12-14, 16-18]. As the crack grows, there is a bowing between the filler materials. A parameter called the Crack Opening displacement has to happen, which means the particles should be larger than CNTs. Pinning marks are observed to show plastic zone in front of cracks.In simpler words, a) crack deflection b) crack branching. C) crack pinning/bowing, d) particle bridging are all "On fracture plane processes"; while, e) particle debonding, 2) crazing 3) inelastic deformation of matrix are all "Off-fracture place process" [8, 15-19]. Plastic void growth is also common in epoxy composites. Initiated by debonding of particles. Irwin's model gives relation between, yield strength, plastic zone size and K<sub>le</sub>. Void growth mechanism

4

contributes to matrix plastic deformation which talks about void growth, shear bonding. Dilation of matrix could be observed too. Shear banding is common in both rubber and micron glass bead filled epoxy composites. It is also an energy absorption mechanism. Plastic flow when a stress is applied, at 45 degree angle might produce isolated shear bands [17, 19]. For an epoxy matrix with a modifier, the toughness will be determined by the manner in which the crack goes through it and the resistance provided by the system to this crack.

1) Crack pinning: Small filler particles (<1µm) toughen using this mechanism. Forceful crack bowing and change in crack length, consuming energy during the process owing to the rigidity and impenetrable nature of the particle is the idea behind this mechanism. The crack front changes length once it approaches an inhomogeneous particle. This is explained by crack pinning mechanism[2].

2) Particle bridging: Large filler particles (>5 $\mu$ m) toughen using this mechanism. Particles fill up the crack surfaces, decrease traction to reduce stress at crack tip and deform the particles [2].

3) Crack path deflection: Large filler particles (>10 $\mu$ m) toughen using this mechanism. The filler increases toughness by acting like a rigid particle and deflects the crack away thus creating a new surface for the crack [2].

4) Particle yielding and induced shear banding: Rubber particles toughen by this mechanism. The particles yield when the crack passes through the material. This decreases the modulus, and concentrates stresses at the compliant rubber site, thus inducing shear banding in the matrix [22].5) Microcracking: This mechanism is predominant in filler materials that possess poor adhesion with the matrix. It lowers the stress intensity of the material around the crack tip [2, 22].

#### 1.1.3. Components

Increase in toughness with or without reinforcements, always has a negative modulus influence. A thermoset material is that in which the liquid is converted to a hard rigid solid by

chemical cross-linking, to produce a 3-D network. Lengths of chain, density of units that make up the network, decide the properties. Shrinkage during cure, thermal contraction on cooling, leads to residual stress in the component. Epoxy is tough to handle this. Hence it is better than vinyl esters of polyurethane [9]. Thermoset materials like epoxy, are used in aerospace industry due to their high specific strength [16]. Epoxy having low ductility and low damage tolerance, gives scope for researchers to try and improve this system [20]. Epoxy cure chemistry, kinetics, cure cycle, chemistry, curing agent flexibility are all among reasons to pick epoxy matrix. Epoxies have been used due to their advantage of high strength, high adhesive strength, hardness, weight savings, and cost, resistance to corrosion, fatigue and mechanical damage, low creep, use in high temp [17, 21]. These come in handy esp., when using fiber reinforced composites for aerospace applications. Considerable brittleness, low resistance to crack initiation and propagation restricts them to be kept away from applications that require high toughness and strengths. Epoxies also have a low resistance to crack propagation. Thermoplastic materials and rubber have been added to epoxy to negate this problem. But these decrease strength, modulus [17]. Thermoplastic matrix polymers are reversibly pliable at or above a specific temperature. They possess excellent chemical and creep resistance. But, at high temperatures, the entanglements that also serve as crosslinks change from solid to liquid fairly easily. Processing becomes difficult too. Metal matrices, though possess good properties are reactive to oxygen and hence are ruled out for aerospace and toughening mechanisms.

#### **1.2 THERMOPLASTIC TOUGHENING**

Owing to their inherent high modulus, high glass transition temperatures ( $T_g$ ) and good ductility, thermoplastics have advantages over standard rubbers at higher loading levels [23]. Fracture toughness is a function of morphology which is a function of modifier content and cure conditions [12] [24]. A good thermoplastic modification would achieve the following, a)

improved mechanical properties, b) have a hydrophobic component that would reduce water sorption, c) provide a low-friction surface by altering surface properties [28]. A thermoplastic modified matrix possesses the following general characteristics:

- 1. Morphology varies as the cure temperature is varied [25].
- 2. Varying modifier content increases system viscosity and affects phase separation.
- 3. Phase separation and crosslinking due to polymerization are competing processes that affect morphology and hence toughness [26, 27].
- The addition of thermoplastic can affect the T<sub>g</sub> of a system and cure reaction, by reacting with certain components from the epoxy network [29].
- 5. Solubility parameters serve as a good initial mode of modifier selection. Thereafter, the phase separation process is governed by curing agent used and cure kinetics and its effect on the mobile separating phase [30].

Thermoplastic toughening of epoxies through the addition of PC, PMMA, PES, PSF, and PPO is reviewed here. Polycarbonate (PC with number average molecular weight, M<sub>n</sub>=12000), Polymethyl Methacrylate (PMMA) are miscible in epoxy and display UCST (Upper critical solution temperature) behavior [31]. PMMA was chosen as a toughening agent owing to its transparency and its inertness in epoxies up to 230°C. Solubility parameters of PMMA and 22.7J<sup>1/2</sup> cm<sup>-3/2</sup> and 23.1J<sup>1/2</sup> cm<sup>-3/2</sup>, respectively [32]. PC reacts chemically with the epoxy, which might prevent it from phase separation. However, PC modified material has advantages like minimal loss in modulus at 20wt% loading , G<sub>Ic</sub> increase (7 times) , through shear yielding and crack blunting mechanism of toughening without phase separation over the entire composition range [33-35]. An increase in strain rate decreases toughness due to reduced plastic deformation in these materials. For a PMMA system, change in curing conditions and precure temperature

yields miscible transparent system/opaque system with incomplete miscibility. This could be explained by considering the physico-chemical factor between matrix and modifier. PMMA reacts with curing agent and its addition decreases crosslink density, thus decreasing  $T_g$  [36]. Addition of PMMA reduces reaction rate and heat of polymerization due to steric hindrance [37]. At high loading levels of 20wt%, some phase separation could be seen with PMMA particles of 0.1-0.5µm. Particles of this size do not enhance toughness.

PMMA and PC work well only in systems of low crosslink density. PMMA is generally not preferred to toughen epoxies because of its low  $T_g$  of 105°C and its tendency to become brittle at room temperature [32]. Use of a high molecular weight PMMA ( $M_n$ =232000) produces phase inversion @9wt% PMMA, by moving critical concentrations to low values. For these modifiers toughening mechanism is through ductile drawing and crack path deflection. When  $M_n$ =58000 only a miscible system is produced. Only at 16.6wt% PMMA, few particles of 0.1-1µm in size are found. High molecular weight PMMA shifts critical point to very small loading rates [32]. An amine curing agent reduced reaction rate at 20% additions while anhydride does not, implying that the choice of curing agent is important. Such a dependence is also found for DGEBA/PES systems, with only a few curing agents producing phase separation. Table 2 gives a complete list of values for thermoplastically modified epoxies with different curing agents used.

#### **1.2.1.** Polyphenylene oxide (PPO)

PPO has a refractive index (1.6) similar to that of epoxies (1.4) and this generates transparent materials [23, 38]. Particulate morphology was observed when PPO (34000g/mol) was added to DGEBA. With up to 20wt% addition of PPO, K<sub>Ic</sub> and yield stress increases. No dilation effect was seen prior to yielding; suggesting shear deformation is the dominating mechanism at the center of a specimen for PPO-epoxy systems. Further, microcracking and crack bifurcation was observed and pointed out to be dominant at the crack tip. The damage zone

width increased with increase in PPO content, and this increased toughness. These cracks were seen even in the elastic-plastic interface, which is the region of maximum hydrostatic tensile stress. Attempts were then made to increase toughness by inducing shear banding at crack tip and cavitation by adding rubber particles that vary largely in modulus with epoxy resin. Triaxial stresses are the reason for microcracking [39]. According to this mechanism, the PPO particles form the microcracks and rubber addition to this increases the density of these microcracks per particle by initiating crazes in the PPO phase, which propagate into resin, consequently increasing toughness. In addition, bifurcation of crack tip acts as a shielding mechanism. Particle bridging of PPO may play a part in microcrack zone size control and its stabilization [38].

#### **1.2.2.** Polysulfone (PSF)

PSF is a highly stable, tough, high modulus material with good chemical resistance [39-40]. A blend of PSF/DGEBA/DDM (diaminodiphenylmethane) is homogenous, single phase, miscible upto 280°C. The miscibility is owing to the low molecular wt. of DGEBA and its entropy contribution. When cured, PSF sterically hinders the crosslinked structure, and reduces T<sub>g</sub>. A homogenous system is obtained when gelation of a cured epoxy occurs before phase separation. Homogenous systems could result in interpenetrating network (IPN) formation. No toughening mechanisms were observed when PSF forms IPN with epoxy. While a DDM cured PSF is miscible, a DDS (diaminodiphenylsulfone) cured PSF is immiscible. This illustrates the influence of curing agent on phase behavior, and hence toughness. Bucknall *et al.* proposed a system of hydroxyl functionalized PSF/DGEBA/DDS with Mn of 6400 and 10000 [25, 39]. Hydroxyl terminated groups of the PSF could react with the epoxide rings of the epoxy, thus introducing heterogeneity in the sample. This heterogeneity is the cause for phase inversion. At 15wt% phase particulate/co-continuous morphology is observed and at 20wt% inversion could

be seen. K<sub>Ic</sub> and G<sub>Ic</sub> increase upto 300% due to increase in molecular weight and loading rate [41].

Flexural modulus also increases with increase in molecular weight and toughness increased in these systems due to chain extension and entanglements effect [42]. Chemical reaction and network formation are achieved by the solubility of these thermoplastics in epoxies at initial stages (solubility parameters: epoxy-9.4, bis-A-PSF-10.2). They are transparent in initial stages. During curing, as  $M_n$  increases, the thermoplastic component phase separates to form a secondary dispersed phase. Particle sizes vary from  $0.3\mu m$  for  $M_n$ =5300g/mol to 0.6 $\mu m$  for 10000g/mol. Phase separation increases with increase in molecular weight. With increase in rate of loading, particle frequency increases, and its stress fields interact to improve K<sub>Ic</sub>.

Amine terminated polysulfone (NH<sub>2</sub>-PSF in Table 2) showed two phase morphology when appropriate  $M_n$  (10000 g/mol) was used. This had smaller size particles because of the absence of chain extension. Kinetic effects control domain size in these materials. Thermal coefficients of modified PSF and epoxy are similar and thus there is no chance for dilation of particle during phase separation, as observed in rubber toughening. Concentration of stress plastically deforms the area around these particles. The ductile deformation (stretching and tearing) of the PSF oligomer particles, its crack pinning and the plastic deformation of the epoxy matrix around these particles were the main energy absorbing processes that increased its toughness [25]. Thus, from the behavior of PSF, PC and PMMA, it could be inferred that a miscible homogenous system is not the best for achieving increased toughness.

#### **1.2.3.** Polyetherimide (PEI)

PEI is a tough thermoplastic material that is often used, owing to its good adhesion (without functionalization) with the epoxy matrix (works well with trifunctional epoxies too). PEI thermoplastic shows high  $K_{Ic}$  values through a ductile tearing and crack bridging mechanism.

PEI is a tough thermoplastic material and its morphology is related to the fracture data via the toughening mechanism [43]. In a PEI/TGAP (triglycidyl-p-aminophenol) /DDS system, maximum  $K_{Ic}$  was observed at15wt% where morphology was co-continuous. A Phase inversion occurs at 30wt%. Enhanced properties are achieved at all loading rates when the morphology is co-continuous [26-27]. Morphology could be fixed during early stages of phase separation to produce spinodal decomposition and hence co-continuous morphology by varying curing conditions. Further morphology control beyond phase inversion varies epoxy domain size in a continuous PEI matrix. Large epoxy domains (3-5 $\mu$ m) confine the crack to continuous PEI phase at 30wt% or greater. This is achieved by modifying curing conditions [26, 41]. Phase inverted PEI with large epoxy domains gives better  $K_{Ic}$  values than co-continuous PEI in epoxy [26, 38-39].

Increasing molecular weight from 5200 to 12000 PEI increases  $K_{Ic}$  from 0.5MPa.m<sup>0.5</sup> to 1.5MPa. m<sup>0.5</sup> at 25wt% PEI [15]. At low concentration, PEI forms spherical particles of ~2µm size. At 20phr, there are irregular shaped domains [6, 38]. Further increase in molecular weight to 18000 g/mol causes phase inversion at lower loadings. Epoxy domains exist, and crack flows around these. Honeycomb morphology is observed at 20wt% via phase inversion [39, 44]. Ductile tearing/drawing and crack bridging by PEI are the toughening mechanisms that increase  $K_{Ic}$  values at high loading rates. A phase inverted PEI toughens by yielding. At lower loading rates the increase is due to the deformation resulted from localized yielding of PEI. Ductile tearing is only exhibited in materials like PEI, which possess high yield stress [27, 33, 41]. Unmodified PEI shows this behavior despite not having good adhesion with the matrix.

Commercial PEI was unfunctionalized and gave better results with higher crosslinked systems than functionalized PES/PSF [39, 43]. When PEI is nitrated, the imide groups formed

makes the backbone even stronger and stiffer, due to the bulky polar groups added. This increases molecular weight and  $T_g$  of the system. But, NI-PEI (Nitro group modified PEI) produces a miscible system, thus showing no toughness increases [Table 2]. Unreacted epoxy usually plasticizes a system and this could be offset by post curing. Post curing increases the strength at the matrix particle interface beyond 15wt% due to weakening of PEI-epoxy interface at lower loadings [43]. Post cure temperature is chosen in such a way that, it is over the  $T_g$  of modifier to permit some diffusion. Post curing TGDDM with PEI increases the  $T_g$ , but decreases  $K_{lc}$  due to decreases the plasticizer content and crosslinks due to graft polymerization of PEI with itself [43, 48]. PEI adhesion after post cure could be investigated by soxhlet extraction [30]. PEI was unable to be extracted indicating that after post cure. This shows that PEI has good adhesion with epoxy, despite being unfunctionalized [8].

#### **1.2.4.** Polyethersulfone (PES)

PES was one of the first thermoplastics that were synthesized with reactive end groups. PES showed no  $K_{lc}$  improvements with a functionalized end group eg. NH<sub>2</sub>-PES(M-PES) [Table 2]. PES thermoplastic works well only with di-functional and tri-functional epoxies. An unfunctionalized PES ( $M_n$ : 24000) and a functionalized PES were compared, and it was observed unfunctionalized PES gave better results [Table 2] [49]. The synthesized PES was amine and hydroxyl functionalized PES with  $M_n$ =11000,  $M_n$ =13000. Increasing the molecular weight of the modified PES (M-PES) increases  $K_{lc}$ . High thermoplastic loading, forces these materials to act as diluents, inhibiting reaction and reducing rate of heat liberation and cure times. The presence of reactive end groups decreases the heat release in reaction with increase in loading. Functionalized PES did not show enhanced  $K_{lc}$  at all loading rates. M-PES results in small number yet a broader distribution of occluded phases of small size (0.1-1 $\mu$ m) that do not increase  $K_{lc}$ . A mismatch in linear coefficient of thermal expansion (LCTE) between

functionalized PES (55m/m/°C) and anhydride cured tetra functional epoxy (70m/m/°C) also decreases  $K_{Ic}$ . The effect of -OH terminated PES on the highly crosslinked resin was improved by not more than 10% at all temperature ranges [50]. Moreover, the M-PES did not react with the epoxy matrix. Also, the stresses of these modified PES-tetra functional epoxy interface are tensile, which makes it susceptible to cracks.

Advantage of PES inclusions offer 1) larger ductility, 2) more concentration of larger particles than its low molecular weight counterpart, hence can absorb more energy on fracture, 3) multiple toughening mechanisms, 4) reduces resin crosslink density, 5) larger elongation at break [50]. Theoretically, high molecular weight modifiers are very helpful for increasing K<sub>1c</sub> in highly crosslinked resins [51]. But, the effect of increased molecular weight could go either ways: the end chains (if not functionalized) could act as stress concentrators, or it could decrease crosslink density by preventing the amine-epoxy reaction and thereafter increase the ductility (dilution effect) [51]. PES addition has no effects with tetrafunctional epoxies despite high molecular weights due to the crosslink density being too high to make a brittle matrix to give K<sub>lc</sub> benefits and its elongation is very low [51].

Distance between phases separated particles increase with curing temperature. Slow heating rate between cure results in a shorter periodic distance (0.2µm) between phase separated particles. Single cure temperature, produces two phase morphology with large periodic distance (3µm) [51]. Phase separation in PES happens due to specific interaction between the PES molecule and tertiary amines of the glycidyl amine epoxies [18]. Spinodal decomposition in a PES/epoxy/curing agent system shows a LCST (lower critical solution temperature) behavior [49, 51]. A PES/TGDDM/DDM system produces a miscible blend that does not increase toughness. Mackinnon *et.al* report morphology of their PES/TGAP/DDS modified matrix to be

co- continuous (spinodal) at 20wt% loading, where maximum  $K_{Ic}$  improvements were observed [49]. Particulate and other morphologies were observed until 15wt% loading. Only modest  $K_{Ic}$  increase was observed at these levels. A PES of  $M_n$ =142000 was used with this system, and particles of size 1-5µm were phase separated. Crack arrest, fracture at the particles, pullout are the toughening mechanisms observed.

Material	Mn	K <sub>Ic</sub> , at	Morphology	T <sub>g</sub> at	Е,
		20wt%	beyond 20%	20wt%,	(GPa)
		$(MPa.m^{0.5})$	-	(°C)	
PC/DER 438/MNA <sup>34</sup>	12000	1.2 (0.5)*	homogenous	170 (170)*	2.8 (3.0)*
PMMA/DGEBA/MTHA <sup>24,30</sup>	232000	At 7wt% 0.94 (0.65)	phase inversion at 7wt%	105 (117)	2.45(2.4 )
PSF/DGEBA/DDM <sup>25, 49, 52</sup>	8200 5300	1.3 (1.0) 0.9 (1.0)	co-continuous	184 (178) 185 (178)	3.4 (3.2) 3.3(3.2)
NH <sub>2</sub> -PSF/DGEBA/DDS <sup>52</sup>	10000	-	inversion	190 (193)	3.1 (3.2)
PEI/TGPAP/DDS <sup>43</sup>	24000	1.9 (0.9)	co-continuous	229 (232)	-
NI-PEI/TGPAP/DDS <sup>43</sup>	-	1.7 (0.9)	co-continuous	238 (232)	-
PES/TGPAP/DDS <sup>49</sup>	24000	1.5 (0.6)	co-continuous	-	3.5 (3.7)
PES/TGPAP/DDS <sup>49</sup>	11000	1.2 (0.6)	co-continuous	-	3.7 (3.7)

Table 1.3. Thermoplastic modified epoxies and their properties

\*- Values in paranthesis correspond to unmodified resin with curing agent.

From the literature review above, it can be inferred that the factors that could affect toughening are: 1) interfacial adhesion, 2) solid solution formation, 3) molecular entanglements, 4) ductility, 5) sensitivity to triaxial stresses, 6) any differences in coefficient of linear expansion at interface, 7) stress concentration at interface, 8) difference in young's moduli and poisons ratio of 2 materials, 9) if plastic deformation cud be caused, 10) loading rate [23, 36, 39, 41, 45-47]. An important observation from Table 1.3 is that an unmodified PEI system provides the highest

 $K_{Ic}$  values amongst the materials evaluated. Functionalization of thermoplastics has been reported to deter  $K_{Ic}$  [43]. But, a clear inference cannot be reached until blends of modified, unmodified thermoplastics in epoxy systems are evaluated. Also, amine functionalization should be evaluated for compatibility in an amine cured epoxy system. Increasing the molecular weight generally increases  $K_{Ic}$ ,  $G_{Ic}$  accompanied by an increase in viscosity.

#### **1.3. SECONDARY PHASE FILLER MATERIAL**

Mixing of phases occurs in a small scale length scale. Layered and intercalated silicates offer good mechanical properties [19-21]. Volume fraction, shape and orientation, chemical bonding are important factors when reinforcements are used. Historically, defect free micron size nano whiskers (0.1-1  $\mu$ m in diameter) were thought to yield the best mechanical properties. Now we have a plethora of nanofiller (0.1-100nm) that are cheap, easy to handle process and possess high surface areas, and aspect ratios. When reinforcement is in contact with a matrix, wetting takes place, adhesion is promoted by Vander Waals forces. Surface roughness also contributes to wetting. The adhesive strength depends on the nature of the bond [9]. Adhesive strength in turn depends on the nature of the bond. Heat treatment increases adhesive and bond strength due to the oxidation of surface layers.

#### 1.3.1. Si based materials

According to higher loading of Si (>3wt %) leads to a deterioration in properties (modulus). These points out the size and volume fraction play an important role in determining properties. These nanoparticles ~20nm are small enough to go through roving's in an epoxy system [44, 48][14, 18]. This increases the number of particles zone, and the materials toughen by particle matrix debonding, and localized deformation in the plastic zone ahead of the crack tip [52][53]. Silane functionalization in silica was not very efficient given that it caused agglomeration. This reported 2 fold increases in K<sub>Ic</sub> numbers. This leads us to hypothesize that

agglomerates are not always detrimental. They act as crack deflectors in a dynamic fatigue test. Another plausible inference is that different toughening mechanisms were observed for static and dynamic cases. Batistella et al. describe a sol gel process that helps in the preparation of agglomerate free silica of ~25nm [9, 14]. Uniform dispersion, quasi spherical shape, narrow particle size distribution are characteristic of sol-gel method [4, 38]. Plasticizing effect of uncured epoxy, absorbed moisture, extra free volume at matrix-filler interface, weak adhesion lead to a decrease in Tg. Smaller particles of SiO2 with increased surface area, 12nm particle with 220 sq. /g as opposed to 40nm particle with 50 sqm/g, and observed that strength values were enhanced [17]. With the density of Si being very close to that of GnP, these behavioral trends could serve as the basis of the use of Graphene Nanoplatelets. Strong interaction between resin and particle would not have any effect on Tg [21,53]. Modulus increases when interparticle distance is small [54]. This stemmed from initial toughness enhancements obtained by the addition of 1-5 mi.m rubber particles @5-20wt% loading that tends to form a secondary micro phase upon curing [4, 38]. Crack pinning, crack deflection, immobilized polymer are all discounted. Debonding and increased plastic void growth are hypothesized to be the reason. Both the above are Consistent with literature. Rubber particles reduced brittleness and increased impact resistance. Thus rubber toughening by itself would have reduced the modulus, hence nanofiller are added. Lower levels of rubber and nanoparticles seem to yield the best results. Rubber modified epoxies toughen by cavitation that induce plastic matrix deformation [54]. Studies have been done to observe effects of particle size and vol% on fracture toughness, which was found to be proportional to the square root of the interparticle distance. (Adachi Model). Agglomerated Nano silica in CTBN lead to no increase in toughness.

## **1.3.2.** Clay-epoxy composites

Clay-polymer composites maybe of 3 categories: conventional, intercalated, and exfoliated. In conventional clay there is absence of polymer in the clay. Intercalated polymer insertion into clay occurs in a crystallographic fashion. Exfoliated counterparts have much lesser clay in the matrix. Polymer layered silicate composites have high aspect ratios, surface areas, and high strengths at low loading and possess barrier properties and flame retardancy in addition to mechanical and thermal properties [55,58]. Organic surfactant was added to make clay oraganophilic. Various authors report inability of clay to be exfoliated to 100% and suggested that to be a reason for not having improvements in stiffness, modulus and strength. Combination of intercalation and exfoliation did not yield good results either. This led to the use of "Slurry compounding technique "using solvents for dispersing clay in epoxy matrix, because there was not a good interaction otherwise. Glass transition temperature is reduced as a result [56]. The viscosity of a clay-epoxy system is very high, and it becomes very difficult to process [57]. DCB technique seems to provide more information regarding fracture mechanism, because we could have more control over it. Development of micro cracks, initiated between the clay layers and not the epoxy clay interface, and STEP formation, i.e. micro deformation are the dominant toughening mechanisms in an epoxy-clay composite [56]. The crack initiation process in the epoxy/S-clay nano-composites happens in a few steps. Sample is subjected to a load; stress concentrates around the clay tactoids due to the difference of Young's modulus and Poisson's ratio of clay and epoxy. "The clay interlayer strength is weaker than the epoxy-clay interfacial bonding strength and the cohesive strength of epoxy, interlaminar debonding takes place". Subsequently, micro cracks form [57].

### 1.3.3. Carbon Nanotubes (CNTs)/Graphite Nanoplatelets (GnPs) as filler materials

Silica particles do not provide adequate strong interface for introducing crosslinks in a matrix. Clay nanoparticles provide orientation benefits, but still, could not be completely exfoliated, and was difficult to process in the matrix system. Carbon Nanotubes have a high modulus, surface area, conductivity, fracture strength. [58]

The fact that both GnPs and CNTs possess similar properties, due to their similar sp2 deformed hybridized structure, and the fact that GnPs could be synthesized in a cost effective way, and are much cheaper than CNTs to synthesize, we would look at these materials as a filler material. Graphite nanoparticles are synthesized in the following way:

- Graphite flakes  $\rightarrow$  Intercalated with strong acids(4:1)
- Forms GIC after 16hrs of reaction, filtered and washed to pH 6
- This is then subjected to 1050C in a microwave for reduction (exfoliation step) for 15-30s.
- This rapid heating caused expansion of GNP to 100 times along thickness due to evaporation of initial intercalant.
- This is then sonicated and broken into platelets called Graphene Nanoplatelets [21, 59-61].

## **1.4. SCOPE**

Materials used for aerospace applications should possess good damage tolerance in all environments. As shown in the background, thermoplastic materials work well for toughening high crosslink density epoxy resins, but usually at high loading rates. Rubber toughening has been proven to work well for lightly crosslinked matrices even at low loading rates. Multicomponent systems in the form of polymer blends and/or hybrid composites that could combine the properties of thermoplastics and rubbers to be used in all environments at lower loading rates could be deemed useful. This is in fact possible by a class of materials called thermoplastic elastomers (TPEs). The ductile TPEs are independent of matrix ductility and hence could be used even in highly crosslinked epoxy systems.



Figure 1.1. A schematic of ABC type TPE (schematic in figure is a SBM copolymer)



#### Figure 1.2. A schematic of ABA type TPE (schematic in figure is a MAM/MBM copolymer)

Literature shows evidence of molecular weight increase in a system reflecting in K<sub>lc</sub> increase [25, 49, 52]. Adhesion is deemed important for a modifier-resin system. The role of functionalization in improving adhesion and hence K<sub>lc</sub> has not been suggested clearly [43, 49, 52] [Table 2]. Future approach involves modifying a TPE material by a) increasing its molecular weight b) functionalizing this TPE and determining its role in adhesion and k<sub>lc</sub> improvements and c) using this in a thermoplastically modified epoxy matrix to result in a hybrid system. TPEs combines the ease of processing of thermoplastics with the properties of rubbers. They are of different types, with the styrene-elastomer block copolymers being the most widely used. Recently, commercially available triblock copolymers, SBM (Styrene Butadiene Methacrylate block copolymer-ABC type) addition to a lightly crosslinked DGEBA/DDS system has been evaluated [39].

With the increase in demand from modified epoxy materials for aerospace applications this thesis reviews the subject of toughening of epoxy composites [38, 46-47]. The toughening mechanism and chemistry behind toughening are two important concepts that are briefly discussed. PES (polyethersulfone), diglycidyl ether of bisphenol-A (DGEBA) modified PSF (polysulfone), PEI (polyetherimide) are the most commonly used and studied thermoplastics. Their addition to epoxy is reviewed in detail. The addition of polycarbonate (PC), polymethyl methacrylate (PMMA), poly phenylene oxide (PPO) to epoxy is also reviewed. The efficacy of toughening provided by these materials is explained in terms of morphology, particle size, adhesion and distribution with the matrix, molecular weight. The effect of functionalized thermoplastics and curing conditions are also discussed along with commonly used epoxy resins that vary in functionality and the effect of thermoplastics in these highly cross-linked resins. The mechanism of toughening governing thermoplastics, and the role of functionalizing thermoplastics in epoxies are an active area of research with many contradicting theories [39, 43, 49, 52]. Hence, the aim of this thesis was to connect the aforementioned properties to the toughness of the epoxy matrix, and establish a set of conditions that could be employed in the future for a hybrid polymer composite system.



### Figure.1.3. Toughening approaches for epoxy-filler composites

The above chart shows a summary of various attempts made to toughen epoxy composites [1]. The subsequent chapters will detail mainly the matrix modification route and the various effects it (viz. processing, shear, flexural and impact properties, morphology) has on an TPE-EPON-mPDA composite. Fractographic analyses were also performed to attempt to determine toughening mechanism(s). The best combination of matrix properties were chosen and employed in a FRC system.
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# CHAPTER 2 ABA TYPE THERMOPLASTIC ELASTOMER TOUGHENING OF EPOXY MATRICES 2.1. ABSTRACT

The mechanical properties, morphology and fracture performance of an amine cured epoxy resin modified with a thermoplastic elastomer was investigated in bulk form. The effect of TPE addition to the bulk matrix and its overall effect on a carbon fiber reinforced composite was also preliminarily investigated through single fiber fragmentation tests on dogbone coupons. The TPEs investigated here are triblock copolymers of methylmethacrylate-butylacrylatemethylmethacrylate (MAM) of the ABA type. The effect of concentration (1-15 wt %) of these TPEs on a diglycidyl ether of bisphenol-A (DGEBA) epoxy cured with metaphenylenediamine, has been investigated. The TPE-DGEBA epoxies were characterized by thermo gravimetric analysis (TGA), Dynamic Mechanical Analysis (DMA), impact, rheology and Scanning Electron Microscopy (SEM). The TPEs micro-phase separated when the DGEBA-mPDA reaction took place based. A linear increase with up to 60% in Izod impact strength was observed with increased concentration of TPEs upto 15wt%. In addition, fracture toughness was improved ~250% with TPE addition to epoxy/mPDA matrix. The flexural modulus and strength was unaffected up to 5 wt% loading of TPEs, and exhibited less than 10% decrease at higher weight percent. Tg remained unaffected upto 15wt% TPE addition to the bulk matrix. Electron microscopy revealed localized plastic deformation, ductile and shear yielding as the primary toughening mechanisms.

### **2.2. INTRODUCTION**

Epoxy-matrix composites have found widespread use in the aerospace, adhesive, and coating fields. The cured bulk matrix in itself provides high modulus and strength, but lacks ductility and are inherently brittle [1]. Literature has suggested the addition of a second phase

into the epoxy matrix. These range from core shell rubber particles, carboxyl terminated butadiene-acrylonitrile, carbon nanotubes to hybrid particles employing glass, silica nanoparticles [2, 3]. However, any enhancement of fracture toughness (K<sub>Ic</sub>) and fracture energy (G1c) by the addition of rubber to lightly crosslinked systems is accompanied with a decrease in thermal, mechanical and chemical stability of the system [3, 4]. One approach to improve the mechanical toughness is the addition of thermoplastic elastomers (TPEs). The TPEs possess the combined advantages of the ease of processing of thermoplastics and the ductility of rubbers. This approach is attractive since TPEs possess ductility accompanied by improved strength and stiffness without compromising the visco-elastic properties. The mechanical and thermal properties that result are also affected by the processing technique and cure cycle [2–21]. The efficacy of toughening provided by these materials is explained in terms of morphology, particle size, adhesion and distribution with the matrix, toughening mechanism. The repulsive nature of the middle block with the terminal blocks, and the miscibility of the endblocks with DGEBA earned these materials their consideration [22]. The mechanism of toughening governing thermoplastic elastomers in epoxies are an active area of research with many contradicting theories [1, 3, 5, 12-13]. Hence, the aim of this chapter was to connect the improvements in mechanical, themomechanical and viscoelastic properties to the toughness of the epoxy matrix for a MAM/MBM type TPE, and establish a set of conditions that could be employed as the matrix for a composite system and carbon fiber reinforced polymers (CFRP) for the aerospace industry.

### **2.3. MATERIALS**

An aromatic amine cured epoxy was used in this study. A DGEBA epoxy from Miller Stephenson of EEW 185 g/eq was used for the matrix/resin material. The aromatic amine was meta-Phenylene diamine (m-PDA) which is solid at room temperature and has a melting point of

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68 °C was obtained from Sigma Aldrich. m-PDA has four reactive hydrogens and for all epoxide groups of DGEBA to react and the stoichiometric amount of 14.5 phr of mPDA curing agent was added. Thermoplastic elastomers (TPEs), SBM and MAM were used in this study. These were obtained from Arkema Inc. (powdered form) with the trade name Nanostrength E21 and M53, respectively. Their molecular weights are 50,000 and 100,000 g/mole, respectively. The polarity, middle block, molecular weight differs greatly between the aforementioned TPEs.

# 2.4. PROCESSING OF COMPOSITES

Processing of the bulk composite was achieved by flacktek mixing followed by magnetic stirring (Figure 2.1).

- For a set quantity of EPON 828 add MAM rubber @10phr
- Flack tek the mixture for 10 minutes at 3000rpm
- MAM rubber is dispersed in EPON by magnetic stirring on a hot plate at 80°C for ~3hrs, then at 150°C for 2hrs
- Degas the sample (~30min) at 80°C in a vacuum oven
- Add mPDA @ 14.5phr and flack tek for 2min @3000rpm
- Degas the sample in vacuum oven (~10 min to avoid any reaction with mPDA) @ 80°C and cast

The desired quantity of curing agent is melted at 75°C and hand mixed with the degassed epoxy TPE mixture utilizing a Flacktek mixing step. This mixture of curing agent, TPE and DGEBA was degassed for 10-15 minutes prior to casting coupons in preheated Room Temperature Vulcanizing (RTV) silicone molds. The curing cycle employed is 75°C (2 h) and 125°C (2 h)



Figure 2.1. Processing of bulk matrix composites

The processing time and the added step of flacktek mixing had a large impact on the mechanical properties of the ABA type TPE-EPON composites. Based on the time and temperature employed for mixing, agglomerates of varying sizes where identified while evaluating the morphology of fractured surfaces.



Figure 2.2. <u>Processing of MAM-epoxy composites:</u> (left) MAM (10phr) + epoxy after stirring for 3hrs @80°C, (center) MAM (10phr) epoxy after stirring for 3hrs @80°C & 2hrs @150°C, (right) MAM (10phr) + epoxy after degassing, prior to mPDA addition

Figure 2.2 shows you the various staged of MAM processing in the epoxy resin. Upon initial mixing the solution is turbid, and as the processing steps continue, the turbidity vanished and a more translucent solution results. The degassing steps breaks down the air bubbles/voids generated from processing. The choice of processing technique had an influence on the level of dispersion of the TPE in epoxy. This in turn had an effect on mechanical properties and morphology of the TPE-epoxy composite. Figures 2.3-2.4 show the effect of mixing (5hrs in total) on a MAM (10phr) EPON system @ 14.5phr mPDA. The increased temperature mixing helped breakdown the particles into smaller aggregates and gave a larger time for the PMMA to be miscible in the epoxy system. This is also indicated by the transparency in Figure 2.2. Moreover, isolated crack initiation sites could be observed in Figure 2.4. This could also be the result of particle toughening in these systems. The particle sizes are rather large in the 10um range. This could be due to aggregated PBuA blocks that we self assembled or phase separated depending on the curing agent used. In our case, it was macrophase separated and was not able to be broken down it nanophases.



Figure 2.3. <u>5hrs-mixing SEM of MAM (10phr) EPON @14.5phr mPDA (higher</u> <u>magnification):</u> (left) No agglomeration, (right) Non-Phase separated particles of 2 µm is seen



Figure 2.4. <u>5hrs-mixing SEM of MAM (10phr) EPON @14.5phr mPDA</u>: (left) MAM rubber distribution, (right) Particle toughening along a 10 µm agglomerate



Figure 2.5. 20min mixing at 150 °C SEM of MAM (10phr) EPON @14.5phr mPDA, 20 minute mixing at 150 °C: (left) Inefficient rubber deagglomeration, (right) Non-Phase separated particles of 2-5μm is seen

Figure 2.5 shows the bimodal distribution of particles for the quicker dispersion method employed. Large rubber particles, 20 µm size, can be seen where there are parts of the sample where the PBUA blocks have block have macrophase separated in the epoxy matrix, in which PMMA is miscible. These particles are in the the 2-3 µm range. This method was trialled upon Arkema Inc.'s suggestions that a faster mixing time at elevated temperatures upto 135°C, could give us a good mechanical properties. Figure 2.6 explains the scenario with a 4hour mixing step. This mixing step was performed at 80°C. The miscibility of PMMA chains in the epoxy resin certainly helped in achieving a better dispersion without the use of added steps like vacuum agitation. The only downside of this method was the fact that some particles settled to the bottom of the flexural sample during curing owing to its molecular weight of 100,000g/mol. These were agglomerates that were larger than 30 µm in size. This is shown in Figure 2.7.



Figure 2.6. <u>4hr mixing: SEM of MAM (10phr) EPON @ (14.5phr) mPDA (higher</u> <u>magnification):</u> (left) good dispersion with particles of 1-2 μm, (right) Isolated cracks, and stress whitening can be seen



Figure 2.7. <u>4hr mixing: SEM of MAM (10phr) EPON @ (14.5phr) mPDA:</u> (left) good dispersion with particles of 1-2 μm, (right) large particles settled to bottom of flexural sample



Figure 2.8. <u>5hr mixing: SEM of MAM (10phr) EPON @ (14.5phr) mPDA:</u> (left) shows isolated particle toughening with particles of 1-2μm, (right) shows good dispersion overall

Overall, the 20-minute mixing resulted in non uniform distribution of rubber particles of various sizes. PMMA is ideally supposed to be miscible in epoxy matrix. The mixing time of 20 minutes did not seem sufficient to yield a translucent mixture prior to casting. The occurrence of isolated cracks was reduced and the stress whitening zone width was reduced too. A longer processing time for the MAM rubber particles (especially at higher temperature) has shown good dispersion and distribution of rubber particles. This is evident as shown in Figure 2.8. What we hypothesize to be the toughening mechanism is shear yielding in the stress whitening zone for a critical particle size. This is to be further investigated. A critical particle size exists for these materials to show the above mechanism For the MAM rubber in epoxy, this seems to be of the order of 0.8-3µm. A processing technique had been optimized for the MAM rubber dissolution in DGEBA-mPDA mixture for future loading studies. The above micrographs showed the effect of mixing time with MAM material. This was identified to be three hours at 80°C and 2 hours at

150°C. The mechanical properties and Tg associated with the aforementioned property changes is

detailed in Table 2.2

(Tophi) El OT composites (d(14.5phi) in Di Todung				
Materials	Flexural	Flexural	Tg	Izod Impact
(cured with 14.5phr mPDA)	modulus(GPa)	Strength(MPa)	(°C)	strength (J/m)
Neat EPON828 @14.5phr mPDA	3.2 (±0.1)	124 (±4)	157.12	23.4 (±1.1)
MAM (10phr) EPON - 20 minute magnetic stir at 150°C	2.8 (± 0.05)	110.4 (±3.2)	153.56	28.7 (±1.7)
MAM(10phr) EPON - 4hrs magnetic stir at 80°C	2.85 (± 0.23)	112.4 (±6.6)	154.12	30 (±2)
MAM(10phr) EPON - magnetic stir, 3hrs at 80°C, 2hrs at 150°C	2.82 (± 0.12)	107.1 (±1.1)	157.75	34.2 (±1.1)

Table 2.1. Effects of processing time and temperature on the mechanical properties of MAM (10phr) EPON composites @(14.5phr) mPDA loading

The effect of Flacktek mixing was also studied as a part of the processing trials. This is because the flacktek mixing is known to breakdown the bubbles. Figure 2.9 shows the effects of not flacktek mixing the MAM particles in an EPON matrix. Table 2.1 shows the flexural and impact properties of such a process. As can be seen from the table, there is not a massive advantage gained in properties from Flacktek mixing. The fact that it facilitates the absence of globs on the surface as shown in Figure 2.9 and aids in uniform distribution led us to employ this method.

8				
	Material tested	Flexural modulus (GPa)	Flexural Strength (MPa)	Izod Impact strength (J/m)
Cure cycle: 75°C for 2hrs, 125°C for 2 hrs	Neat EPON at (14.5phr) mPDA	3.2	124	23.3
	MAM(10phr)EPON –with flacktek	2.85	112.4	30.2
	MAM(10phr)EPON –with flacktek	2.76	104.9	30.7

Table 2.2. Effects of Flacktek mixing on MAM (10phr) EPON composites @14.5phr mPDA loading





Figure 2.9. <u>Effect of flacktek mixing:</u> (left) globs of TPE material can be seen on surface of Izod sample (When not flacktek mixed), (right) undissolved material can be seen, prior to making samples

## **2.5. RHEOLOGY**

Rheology tests were conducted to observe the gelation point in the resin with and without TPE addition. The tests were conducted on an ARES Rheometer with a sample that has been processed through the technique mentioned above prior to casting. All samples were kept at room temperature for 300 seconds prior to test. This is to facilitate similar conditions for comparison, adequate time for loading the sample and for it to be workable within the torque tolerances of the system. A parallel plate setup was used with 25mm aluminum plates and a gap of 1mm. Tests were performed at a frequency of 1Hz at isothermal conditions of 80°C with a time sweep for 3000-12000s (depending on system). The gelation point of various weight percent of TPEs (MAM/MBM) is shown in Figure 4. It can be seen that at lower concentrations the gelation point does not vary a great deal with TPE addition. This shows that the viscosity and hence polymerization does not drastically increase with TPE addition. This ensures that we have a workable system that would make it suitable for use in CFRPs at these low TPE additions. The gelation time does, however, increase for increased TPE addition (>5 wt%). This is due to the

addition of high molecular weight and MAM particles (~100,000g/mole), which delays possible TPE-epoxy-mPDA adduct formation. Such systems also show non-Newtonian behaviors, which show increased viscosities at increased weight percent due to particle-particle interaction and particle-matrix interactions.



Figure 2.10. Rheology of MAM-EPON at various wt% of MAM

## 2.6. MECHANICAL, THERMO-MECHANICAL AND VISCO-ELASTIC PROPERTIES

Flexural three-point bending tests were performed according to ASTM D790 [14]. A bar of rectangular cross section of 3.2E-3 m x 12.8E-3 m (thickness x width) was used. A support span-to-depth ratio of 16:1 was used and rate of crosshead motion is determined from the formulae mentioned in the ASTM standards. The tests were performed on a Universal Testing Machine. The flexural modulus and strength were calculated from the standard. Five samples were tested for each formulation.

$$R = \frac{ZL^2}{6d}; \sigma f = \frac{3PL}{2bd^2}$$
[1]

L is the support span (m), b is the width of beam tested, d is the depth of beam (m), Z is 0.01, R is the rate of crosshead motion (m/min), P is the load at a point on load deflection curve, and  $\sigma f$ 

is the stress at the midpoint (MPa). Notched Izod impact test was performed in accordance with Test Method A in ASTM D256 [15]. The samples were conditioned at room temperature for two days before being tested. A 53.4 J/m hammer was used for sample of 0.01143 m width. Five prenotched specimens were tested for each composition. All samples resulted in complete failure and the impact strength was reported in J/m. Compact tension (CT) tests were performed to determine plane-strain fracture toughness (K<sub>1c</sub>) in accordance with ASTM D5045 [16]. Test specimens with a size 0.02 x 0.009 x 0.009 m were notched with a fresh razor blade to obtain an a/w ratio ~0.45. Tests were performed on a MTS Machine at a displacement rate of 1 mm/min. Five samples were tested for each formulation and fracture toughness was calculated using the fracture load. DMA was used to measure the Tg (peak of tan delta curve vs. temperature), storage modulus and the loss modulus. The values of Tg, flexural modulus and strength, Izod impact strength, K<sub>1c</sub> fracture toughness and loading study for MBM/MAM TPEs are listed in Table 2.3. The unmodified matrix has values that agree with literature [7].

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Material	$T_g(^{\circ}C)$	Flexural	Flexural Strength	Izod Impact
		modulus(GPa)	(MPa)	Strength(J/m)
Neat –(RC)	156	$3.2 \pm 0.1$	$124 \pm 4$	$23.4 \pm 1.1$
MAM1-(RC)	156	$3.2 \pm 0.3$	$122.3 \pm 6$	$25.1 \pm 0.6$
MAM2.5-(RC)	157	$3.1 \pm 0.3$	$120 \pm 4$	$28 \pm 2$
MAM5-(RC)	155	$3.0 \pm 0.1$	$122 \pm 4$	$27.5 \pm 1.5$
MAM7.5-(RC	154	$2.9 \pm 0.1$	$115 \pm 0.5$	$32.3 \pm 2$
MAM10-(RC)	155	$2.8 \pm 0.1$	$108 \pm 2$	$34.2 \pm 1$
MAM12.5-(RC)	153	$2.8 \pm 0.1$	$106 \pm 1$	$37.4 \pm 4$

Table 2.3. T<sub>g</sub>, Flexural Modulus and Strength, Notched Izod Impact strength for MAM in EPON matrix

The  $K_{Ic}$  values of the matrix kept increasing on MAM/MBM addition indicating that there was not a threshold needed in terms of dispersity. However the  $K_{Ic}$  values started leveling off at (10phr) loading. SBM was well dispersed and compatible in the matrix until this point. However, the viscosity increases were apparent [23]. Figure 2.11 clearly shows this increase in  $K_{Ic}$  with increasing percentages of MAM/MBM rubber added.



K1c Fracture Toughness of MAM Modified Composites

Figure 2.11. KIc increase in MAM/EPON with upto 12.5wt% addition of TPE

The values of  $T_g$  does are within experimental error for all composites indicating complete microphase phase separation of PBUA aggregates. Generally if PMMA remains dissolved in the matrix an increase in  $T_g$  would be observed because its  $T_g$  is higher than the DGEBA/mPDA mixture. The partial de-swelling of the PMMA block and presence of Polybutadiene moeity leads to a decrease of 2-3°C in  $T_g$  for most systems. Figure 2.12 shows the thermal stability of various TPE-modified epoxy matrices. All TPE-EPON matrices are thermally stable up to 400°C.



Figure 2.12. <u>Thermal Stabilities of MAM (10phr) EPON (a)</u> (14.5phr) mPDA Vs. Neat <u>DGEBA-mPDA</u>



Figure 2.13. <u>Storage modulus and tan δ curves for MAM-epoxy composites:</u> various weight percentages of MAM-EPON composites @ (14.5phr) mPDA Vs. Neat DGEBAmPDA

Material	Tg	Storage	Storage	Crosslink	
	(°C)	Modulus at	Modulus at	density, $\rho$ [24]	
		T=Tg+30°C	T=35°C		
		(MPa)	(MPa)		
Neat EPON @(14.5phr) mPDA	157.12	36.84	2570	0.962713	
$\frac{1111011}{MAM (1phr) FPON @}$					
(14.5phr) mPDA	157.38	33.19	2269	0.866841	
MAM (2.5phr) EPON	155.2	31.7	2367	0.832336	
@ (14.5phr) mPDA	155.2	51.7	2507	0.052550	
MAM (5phr) EPON @	156.20	31.04	2261	0.813071	
(14.5phr) mPDA	150.27	51.04	2201	0.015071	
MAM (7.5phr) EPON	153 70	31.01	2072	0.816268	
@ (14.5phr) mPDA	155.79	51.01	2072	0.810208	
MAM (10phr) EPON	157 75	26.14	2480	0.682164	
@ (14.5phr) mPDA	137.73	20.14	2409	0.082104	
MAM (12.5phr) EPON	152 75	20.01	2256	0.812707	
@ (14.5phr) mPDA	155.75	30.71	2230	0.013/0/	

Table 2.4. Variation in apparent crosslink density for MAM-EPON composites at various loading percentages

Two separate peaks indicating phase separation are not observed in Figure 2.13 because of the similar range of temperature for the DGEBA-mPDA relaxation and MAM-DGEA-mPDA relaxation [22]. Broadening of tan delta peaks were observed due to distribution in molecular weight between crosslinks or general heterogeneity. Table 2.4 displays the variation in crosslink density for a neat and a TPE modified system. The crosslink density,  $\rho$ , was also calculated in accordance with the studies done by Iijima et al.

$$\rho = \frac{G'}{\phi RT}$$
[24]

They suggested that  $\rho$  is the crosslink density, and was calculated from the equilibrium storage modulus, G' in the rubber region over the  $\alpha$ -relaxation temperature. R is the universal gas constant.  $\Phi$  is the front factor which is assumed to be unity in this case. T in the absolute temperature in the rubber region. In our case of equilibrium storage modulus T is taken at T<sub>g</sub>+30°C. The extensibility of the network would be decreased for system having G' > 10<sup>7</sup> Pa

and the theory of rubber elasticity might no longer hold. But the (21.5phr) system show G' less than  $10^7$  Pa and moreover according to studies done by LeMay et al. the rubber modulus could be used to determine crosslink-link density for short chain epoxy systems like that of DGEBA/mPDA [25, 26]. The MAM10-(RC) system possesses a higher molecular weight between crosslinks at a given amine concentration [27, 28]. This shows that the TPEs interact with the resin and curing agent and reduced the crosslink density [10, 11]. Thus, a system of low crosslink density provides us with the improved K<sub>Ic</sub> values due to the ability for such a system to shear yield.

Table 2.3 summarizes the loading study for MAM TPE in EPON matrix. The selfassembly of TPEs may occur during TPE dispersion in DGEBA, and hence the processing technique used is important. Moreover, the aggregation of these spherical particles occurs during processing [8]. It is this aggregation that results in a decrease in modulus and strength at higher loading. At lower loadings it can be seen that the modulus and strength properties do not vary, but the impact strength and toughness values increase. The (2.5 wt%) system offers unique potential for a modified matrix as shown by the morphological examination in the next section. An exponential increase of K<sub>Ic</sub> fracture toughness (~200%) is reported due to the microseparated TPE particles in the EPON matrix. The TPE modified matrices also show enhanced strain indicating its ability to delay crack propagation. Chen and Taylor [3] reported a microseparation for Nanostrength M52 and Nanostrength M52N materials up to (7 wt %) and a cocontinuous microstructure thereafter. These results show a micro-separated structure up to (12.5 wt% owing to the choice of an aromatic amine curing agent and cure cycle. Up to a 200% increase is observed for MAM10-(RC) in an EPON matrix with ~10% loss in modulus and strength. The PBuA middle block that in immiscible is epoxy is a soft rubbery segment that

decreases the modulus and strength values while imparting toughness enhancements. Although K<sub>Ic</sub> was largely improved, it did not exhibit a strain softening behavior.

# 2.7. FRACTOGRAPHY

Fractured ASTM D790 samples and ASTM D5045 samples were examined using a SEM EVO scanning electron microscope at an acceleration voltage of 3kV. Samples were coated with a 5nm layer of tungsten to make the surface conductive for examining the surface. Figures 2.14-2.17 show SEM micrographs from flexural fracture for MAM 1phr – 10phr in DGEBA-mPDA matrix.



Figure 2.14. SEM micrograph of MAM (1phr) EPON-mPDA system



Figure 2.15. <u>SEM micrograph of MAM (2.5phr) EPON system: (</u>left) MAM (2.5phr) EPONmPDA system, (right) Deagglomerated phase separated particles



Figure 2.16. <u>SEM micrograph of MAM (5phr) and (7.5phr systems) EPON system:</u> (left) MAM (5phr) EPON-mPDA system, (right) MAM(7.5phr) EPON-mPDA system



Figure 2.17. <u>SEM micrograph of MAM (10phr) EPON system:</u> (left) MAM (10phr) EPONmPDA system showing uniform dispersion, (right) MAM (10phr) EPON-mPDA system showing particle sizes at 2μm

SEM micrographs indicate a presence of macroscopic phase separation which induces different toughening mechanism than the ones usually seen, i.e., debonding and matrix plastic deformation. Fibrils without evidence of debonding due to epoxy disruption around the particles are seen that could indicate enhanced adhesion between DGEBA-mPDA system and the phase separated particles [8]. This is because the TPE-DGEBA/mPDA system mentioned here did not facilitate debonding. Matrix dilation and matrix roughness can be seen, which could add to the

increases in K<sub>lc</sub>. The step changes along crack plane and river marks on a small-scale indicate that not all of the energy in dissipated. Excess energy absorption is indicated by the multi-planar nature of the fracture surface [3]. The aggregation of the particles in this case creates overlapping stress fields that enhance matrix deformation and the epoxy traces present in between the aggregates change the stress state to plastically deform the matrix. One or both of these phenomenon may occur [2]. The MAM 10phr-EPON-mPDA resembles the morphology of a macro vesicle formed. The tendency to form aggregates of sphere on spheres increases with increase in amount of TPE added. Small cavities to the tune of 1um were found on the fracture surface. The roughness of the fracture surface also seems to increase with increase in MAM added. Figures 2.14-2.17 confirm cavitation within particles and matrix deformation due to epoxy disruption around the TPEs. The Microphase separation leads to the formation of the stress whitened zones and the mechanisms from fracture seen in the SEM micrographs above. Cavitation and subsequent plastic void growth is the mechanism that initiates plastic deformation in matrix, leading to the K<sub>lc</sub> results we see.

#### **2.8. CONCLUSIONS**

An aromatic amine cured epoxy polymer was modified using MAM thermoplastic elastomers. The microstructure, thermo-mechanical and fracture properties, and toughening mechanisms were identified. The MAM-DGEBA/mPDA systems display a semi-brittle/ductile behavior. PMMA and PBuA are the nanostructuring blocks in MAM. These self-assembling triblock copolymers in a cured DGEBA/mPDA matrix lead to micro-phase separated structures. The amine-epoxy cure extent dictates morphology and hence mechanical properties. Optimum mixing was required to insure complete dissolution of the polymers into the epoxy matrix. The addition of TPE to this DGEBA-mPDA system displays the ability to delay crack propagation. The optimum results depend on matrix morphology, interfacial adhesion, choice of cure agent, and are cure schedule dependent. The fracture toughness increased upto 200% for a 10phr MAM-EPON system without affecting  $T_g$ . Only a modest 10% decrease in modulus was observed. Mechanisms that govern the increase in critical stress intensity factors include crack deflection of spherical/vesicular aggregates and large interfacial zones between two phases, cavitation of PB middle block of the TPE particles and subsequent plastic, matrix deformation caused by these particles. The Izod and K<sub>Ic</sub> values could be further enhanced by using curing agents like Jeffamine, but was beyond the scope of this study. Molecular weight determination of MAM (~100000g/mol) would give us further details on the role of this material in toughening. Variation in butadiene content could also affect toughness values. Future work includes using TPE modified matrix in fiber-reinforced composites for the aerospace industry.

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## CHAPTER 3 MECHANICAL, THERMAL AND VISCOELASTIC STUDY OF ABC TYPE THERMOPLASTIC ELASTOMER TOUGHENING OF EPOXY MATRICES

# PART I: EFFECT OF PROCESSING AND CURE IN BULK MATRIX 3.1. ABSTRACT

Epoxy-matrices form a highly-cross linked microstructure upon curing. This structure provides high modulus and strength, excellent creep resistance, but lacks ductility. One approach to improve the mechanical toughness in epoxy matrices is the addition of thermoplastic elastomers (TPEs). This approach is attractive since TPEs possess ductility accompanied by improved strength and stiffness with little/no compromise in the thermal, mechanical and viscoelastic properties. The TPEs investigated here are triblock copolymers of styrene-butadienemethyl methacrylate (SBM) of the ABC type. The choice of processing conditions and/or technique, curing agent stoichiometry and cure cycle used all had an impact on the mechanical, thermal and the morphological properties that resulted. The choice of processing technique (magnetic stirring, paddle mixing, ultrasonication, vacuum agitation) produced different levels of shear that also had an effect on the transparency of the system. The effect of concentration (1-12.5wt%) of these TPEs on a diglycidyl ether of bisphenol-A (DGEBA) epoxy cured with metaphenylenediamine (mPDA) has been investigated. The glass transition temperature  $(T_g)$  was unaffected at all concentrations. A non-linear increase up to 60% in Izod impact strength was observed with increased concentration of TPEs and showed increases up to  $\sim 90\%$  when non stoichiometric amount of curing agent was used. In addition, the plane strain critical stress intensity (K<sub>Ic</sub>) was improved ~250% with SBM addition (10wt%) to epoxy/mPDA matrix at stoichiometric amounts and up to ~400% when non-stoichiometric amounts of curing agent was used. The flexural modulus and strength was unaffected up to 5wt% loading of TPEs, and

exhibited less than 10% decrease at higher weight percent. The TPE-DGEBA epoxies were also characterized by Thermo Gravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA), rheology and Scanning Electron Microscopy (SEM). The TPEs phase separated and self-assembled into micro or nano-domains upon DGEBA-mPDA cure in the thermoset matrix.

## **3.2. INTRODUCTION**

Composite materials are sought after by the aerospace industry for their light weight and strength properties. Polymer composites, with epoxy resins as matrix material are widely used in the aerospace industry owing to their chemical resistance, strength, low shrinkage during cure, ease of processing, solvent resistance and good mechanical properties [1]. The fracture toughness of cured epoxy matrices control damage tolerance and toughness of a composite [2]. Despite these advantages, epoxies are inherently brittle. Brittleness increases with crosslink density and ultimately hampers toughness [3]. Among several materials used to improve the fracture toughness of brittle epoxies, rubber materials like Carboxyl Terminated Butadiene Acrylonitrile (CTBN) are the most studied. The addition of rubber produces two phase morphologies after phase separation. Phase separated material contains small rubber particles (0.1-2µm) dispersed in the matrix that increases toughness by inducing shear yielding and cavitation [1]. However, any enhancement of fracture toughness ( $K_{Ic}$ ) and fracture energy ( $G_{Ic}$ ) by the addition of rubber to lightly crosslinked systems is accompanied by a decrease in thermal, mechanical and chemical stability of the system [1]. This decrease is due to agglomerate formation during rubber phase separation and stress concentration effects. These factors greatly limit the usage of rubbers in high crosslink density systems for advanced applications. An alternate approach to toughen highly crosslinked epoxy matrices was made possible by the ABC type thermoplastic elastomeric toughening of epoxies. Their morphology in an epoxy matrix can be spherical [4-5], worm-like [6], particulate [7], vesicle formation [8-9] or phase inverted. In contrast to rubber toughening,

these materials toughen the epoxy matrix without drastically reducing other mechanical and thermal properties.

This chapter explores thermoplastic toughening of epoxy with a focus on ABC type thermoplastic elastomers [10-11]. The toughening mechanism, mechanical properties and fractography are briefly discussed. PES (polyethersulfone), diglycidyl ether of bisphenol-A (DGEBA) modified PSF (polysulfone), PEI (polyetherimide) are the most commonly used and studied thermoplastics. CTBN is also a well-studied elastomeric material. The TPEs possess the combined advantage of the ease of processing of thermoplastics and the ductility of rubbers. Their addition to epoxy is reviewed in detail. The efficacy of toughening provided by these materials is explained in terms of morphology, particle size, adhesion and distribution with the matrix, toughening mechanism.

The repulsive nature of the middle blocks with the terminal blocks, and the miscibility of the endblocks with DGEBA earned these materials their consideration [8]. The synergy between processing and curing conditions, curing agent stoichiometry has also been investigated. The mechanism of toughening governing thermoplastic elastomers, has also been discussed [1,12-13]. Hence, the aim of this chapter was to connect the improvements in mechanical, themomechanical and viscoelastic properties to the toughness of the epoxy matrix and establish a set of conditions that could be employed in the future for a hybrid polymer composite system and carbon fiber reinforced polymers (CFRP) for the aerospace industry.

#### **3.3. EXPERIMENTATION**

#### 3.3.1. Materials

An aromatic amine cured epoxy was used in this study. A DGEBA epoxy from Miller Stephenson of epoxide equivalent weight (EEW) of 185g/eq was used for the matrix/resin material. The aromatic amine was meta-Phenylene diamine (m-PDA), which is a solid at room temperature and has a melting point of 68°C was obtained from Sigma Aldrich. m-PDA has four reactive hydrogens and for all epoxide groups of DGEBA to react and the stoichiometric amount of 14.5phr of mPDA curing agent was added. Thermoplastic elastomers (TPEs), i.e. SBM used in this study. These were obtained with molecular weights of 50,000g/mole from Arkema, under the tradename Nanostrength E21. The polarity, middle block, molecular weight differs greatly between different grades of SBM TPEs.

### 3.3.2. Mechanical Testing

Flexural three-point bending tests were performed according to ASTM D790 [14]. A bar of rectangular cross section of 3.2E-3 m x 12.8E-3 m (thickness x width) was used. A support span-to-depth ratio of 16:1 was used and rate of crosshead motion is determined from the formulae mentioned in the ASTM standards. The tests were performed on a Universal Testing Machine. The flexural modulus and strength were calculated from the standard. Five samples were tested for each formulation.

$$R = \frac{ZL^2}{6d}; \sigma f = \frac{3PL}{2bd^2}$$
[1]

where L is the support span (m), b is the width of beam tested, d is the depth of beam (m), Z is 0.01, R is the rate of crosshead motion (m/min), P is the load at a point on load deflection curve, and  $\sigma f$  is the stress at the midpoint (MPa). Notched Izod impact test was performed in accordance with Test Method A in ASTM D256 [15]. The samples were conditioned at room temperature for two days before being tested. A 53.4J/m hammer was used for sample of 0.01143m width. Five pre-notched specimens were tested for each composition. All samples resulted in complete failure and the impact strength was reported in J/m. Compact tension (CT) tests were performed to determine plane-strain fracture toughness (K<sub>Ic</sub>) in accordance with a fresh

razor blade to obtain an a/w ratio ~0.45. Tests were performed on a MTS Machine at a displacement rate of 1mm/min. Five samples were tested for each formulation and fracture toughness was calculated using the fracture load. Density tests were performed to determine the molecular weight between crosslinks. The molecular weight between crosslinks was calculated from the expression [2] using the G' above the  $\alpha$  transition and using the density,  $\rho$ . The density was calculated using a density picnometer in accordance with ASTM D792

$$\log_{10} G' = 7 + 293 \frac{\rho}{M_c}$$
[2]

#### 3.3.3. Effect of processing on mechanical properties and morphology

Material (All samples tested with 14.5phr mPDA)	Abbreviation
Neat EPON 828, 75 °C(2 h) and 125 °C(2 h) @ 14.5phr mPDA	Neat-S(RC)
SBM(10phr) EPON, 75 °C(2 h) and 125 °C(2 h), magnetic stirring	SBM10-(RC)-MS
SBM(10phr) EPON, 75 °C(2 h) and 125 °C(2 h), sonication	SBM10-(RC)-SO
SBM(10phr) EPON, 75 °C(2 h) and 125 °C(2 h), sonication, high power	SBM10-(RC)-SOHP
SBM(10phr) EPON, 75 °C(2 h) and 125 °C(2 h), solvent sonication	SBM10-(RC)-SSO
SBM(10phr) EPON, 75 °C(2 h) and 125 °C(2 h), paddle mixing	SBM10-(RC)-PM
SBM(10phr) EPON, 75 °C(2 h) and 125 °C(2 h), magnetic stirring +Vacuum agitation	SBM10-(RC)-MS+VA
Neat EPON 828, 125C(5h)	Neat-(MC1)
Neat EPON 828, 125C(14h)	Neat-(MC2)
Neat EPON 828, 75 °C(2 h) and 125 °C(2 h) @ 21.5phr mPDA	Neat-NS(RC)

Table 3.1. The processing variations of ABC type TPE employed and their abbreviations

The choice of processing technique had an influence on the level of dispersion of the TPE in epoxy. This in turn had an effect on mechanical properties and morphology of the TPE-epoxy composite. Table 3.1 summarizes the different conditions employed as a part of the
processing study and relates to the thermal, mechanical and morphological analysis (from SEM fracture surface examination standpoint). The SEM analysis was performed on samples post three point flexural bending test to determine morphology, particle size, dispersion and toughening mechanism. The processing variations of the bulk matrix in terms of the values of flexural modulus, strength, Izod impact strength and the toughening mechanisms are also presented and discussed. This becomes an important study for the epoxy matrix synthesis in a CFRP system.

Processing of the bulk composite was achieved by different methods viz, magnetic stirring, paddle mixing, and sonication (Figure 3.1). All the processing methods discussed here used 10phr TPE for evaluation and comparison purposes. A processing change which resulted in remarkably improved properties was achieved with the addition of a vacuum mixing step prior to casting the coupons. The preferred processing technique is as follows: Flacktek mix was done at at 2500-3000rpm with the required quantity of TPE in epoxy resin. This mixture was then magnetic stirred at 100-120 °C for 12-14 hrs to ensure proper mixing and dispersion, followed by vacuum degassing until trapped gas bubbles were removed. The desired quantity of curing agent was melted at 75 °C and hand mixed with the degassed epoxy TPE mixture utilizing a Flacktek mixing step. This mixture of curing agent, TPE and DGEBA was degassed for 10-15 minutes prior to casting coupons in preheated Room Temperature Vulcanizing (RTV) silicone molds. A vacuum agitation step was added to the TPE-DGEBA/mPDA mixture prior to the casting step by agitating the sample at 500 rpm under vacuum condition at 60 °C in a whipmix bowl followed by the protocol identified in Figure 3.1. The improvements in mechanical properties obtained from such a change are shown in Table 3.2.



## Figure 3.1. Processing of bulk matrix composites

## **3.3.3.1.** Magnetic stirring

Mixing time and temperature also had a bigger effect on the mechanical properties and the toughening mechanisms involved in TPE-EPON composite synthesized via magnetic mixing. The procedure for making composites via magnetic stirring is detailed below.

- For a set quantity of EPON 828(100g) SBM rubber @10phr (10g) was added
- The mixture was Flacktek mixed for 10 minutes at 3000 rpm
- SBM rubber was dispersed in EPON by magnetic stirring on a hot plate at 80°C for ~2hrs. It was further stirred on a hot plate for 2 hours@ 140°C
- The sample was degassed (~30-45min) at 80°C in a vacuum oven
- mPDA @ 14.5phr was added and flack tek mixed for 2min @3000rpm
- The sample was degassed in a vacuum oven (~15 min to avoid any reaction with mPDA) @ 80°C and then casted
- The cure cycle employed was : 75°C for 2hrs, 125°C for 2hrs

Figure 3.2 gave us an overall idea of the fracture surface of a SBM (10phr)-EPON composite prepared via magnetic stirring. It was initially found that a 4 hour magnetic stirring time at 80°C yielded large 15-20µm size TPE particles in a three-point flexural bending test coupon (Figure 3.3). The domination mechanism here was isolated particle toughening around flocculated SBM particles. Figure 3.4. shows that dispersion improved with magnetic stirring at 100rpm for 14 hours and eliminated the 15-20µm size agglomerates and broke down the SBM particles to the order of 1µm. Shear yielding and particle toughening were dominant mechanisms in this case. Table 3.2 showcases the mechanical properties from this process.

Table 3.2. Flexural modulus, flexural strength and impact strength results from processing variations

Material	Flexural Modulus (GPa)	Flexural Strength (MPa)	Izod Impact Strength (J/m)
Neat –(RC)	3.2±0.1	124±4	$23.4 \pm 1.1$
SBM10-(RC)-MS	3.0 ±0.1	$117.3 \pm 0.9$	$32.8 \pm 1.0$
SBM10-(RC)-MS+VA	$3.5 \pm 0.2$	$132.5 \pm 3$	$35.5 \pm 1.8$
SBM10-(RC)-SO	$2.8 \pm 0.1$	$109.3 \pm 4$	$27.4 \pm 0.8$
SBM10-(RC)-SOHP	2.8 ±0.1	$112 \pm 3$	$30.9 \pm 1.0$
SBM10-(RC)-SSO	$2.7 \pm 0.3$	$109.1 \pm 8$	$30.8 \pm 0.6$
SBM10-(RC)-PM	$2.7 \pm 0.05$	$113 \pm 3$	$29.5 \pm 1.6$



Figure 3.2. Overall view of the flexural fracture surface of a sample processed via magnetic <u>stir</u>



Figure 3.3. <u>Magnetic stirring:</u> (left) Particle toughening exists, (right) agglomerates of 10-20um can be seen



Figure 3.4. Dispersion via magnetic stirring: (left) shows the improved SBM dispersion, (right) SBM flocculates broken down to the order of 1µm

# 3.3.3.2. Paddle mixing

Listed below the procedure for paddle mixing. Paddle mixing is been performed by a

- ECG paddle mixer at ~200rpm. Procedure for paddle mixing is detailed below.
- For a set quantity of EPON 828(70g) add SBM rubber @10phr (7g). Flack tek the mixture

for 10 minutes at 3000 rpm

- SBM rubber is dispersed in EPON by magnetic stirring on a hot plate at 80°C for ~2hrs, then mixed with the paddle mixer @150°C for 2hrs. Degas the sample (~30min) at 80°C in a vacuum oven
- Add mPDA and flack tek for 2min @3000rpm
- Degas the sample for 15min @80°C in a vacuum oven to eliminate trapped voids
- After adding mPDA and degassing in vacuum oven, an overwhelming amount of trapped air) that existed (that arises due to shear) gets degassed.
- Flack tek the material for 5 min @3000rpm
- Cast the sample using the following cure cycle : 75°C for 2hrs, 125°C for 2hrs



Figure 3.5<u>. Processing via paddle mixing:</u> (left) ECG Paddle mixer, (center) SBM (10phr) after mixing for 2hrs @ 80C, (right) SBM (10phr) after mixing for 2hrs @ 80°C and 2hrs @150°C

Unpolished side – under tension



Polished side - under compression

Figure 3.6. Overall view of the flexural fracture surface of a sample processed via magnetic stir followed by paddle stirring



Figure 3.7. Paddle mixing dispersion: (left) overall distribution of SBM particles in epoxy matrix, (rift) agglomerates of 25µm still exist and particle toughening happens around this



Figure 3.8. <u>SBM distribution via paddle mixing:</u> (left) Hackles can be seen, (right) bottom of flexural sample, and several agglomerates can be seen.'

TPE particle sedimented in a three-point flexural bending test coupon, and yielded low strength and stiffness value when compared to other processing techniques. A paddle mixing technique with two baffles rotating at 200rpm also had a similar result, and such a process caused increased shear in the sample, but increased bubbling as shown in Figure 3.5. Table 3.2 showcases the mechanical properties from this process.

## 3.3.3.3. Sonication

The sonication process was utilized with the premise that better the shear, better the breakdown of SBM rubber agglomerates. Sonication should do a good job to break down agglomerates. Sonication was performed at 80W with a 5s pulse using the procedure detailed below

- For a set quantity of EPON 828 (70g) add SBM rubber @10phr (7g)
- Flack tek the mixture for 10 minutes at 3000rpm
- SBM rubber is dispersed in EPON by magnetic stirring on a hot plate at 80°C for ~1hr, then sonicated @80C for 0.5hrs and for 0.5hrs at 150°C (with and without acetone as solvent)
- Degas the sample (~30min) at 80°C in a vacuum oven
- Add mPDA @ 14.5phr and flack tek for 2min @3000rpm
- Degas the sample for 15min @80°C in a vacuum oven to eliminate trapped voids
- Flack tek the material for 5 min @3000rpm
- The materials became transparent indicating rubber miscibility after just 1hr sonication.
- Cast the sample. Cure cycle : 75C for 2hrs, 125C for 2hrs

Unpolished side - under tension



Polished side – under compression

# Figure 3.9. Overall view of the flexural fracture surface of a sample processed via magnetic stir followed by sonication



Figure 3.10. **Distribution of SBM particles via sonication:** (left) Multiple crack initiated at the rubber sites, (right) Rubber particles have been deagglomerated well owing to solvent sonication



Figure 3.11. <u>Toughening mechanisms exhibited by SBM in epoxy matrix:</u> (left) Crack initiations similar to these are at rubber particle sites, (right) Isolated Crack initiation and propogation from a rubber-agglomerated site

Figures 3.9-3.11 showcase the morphology of the SBM (10phr) EPON composite. Table 3.2 showcases the mechanical properties from these processes. It can be seen from Figure 3.11 that sonication breaks down the particles at the conditions mentioned above. Yet, there are agglomerates/flocculates at the 10µm size range. When sonicated in the presence of acetone as solvent, SBM particles show multiple crack initiation sites with shear yielding and isolated

particle toughening mechanisms. Sonication with a solvent does yield a fully dispersed composition due to shear and good interaction with the modifier/resin structures. It was inferred that the level of shear mixing had an influence on the dispersion of the ensuing TPE-epoxy composites. Ultrasonication resulted in a bimodal distribution of particles of 2-4 µm and 400-500 nm in size, but the presence of solvent did not deem it feasible to be used for FRC synthesis. Magnetic stirring was selected as the preferred mixing technique. Table 3.2 highlights the results from various sonication trials.

#### 3.3.3.4. Vac-u-mixing

Table 3.2 and Figure 3.14. also highlights the results from the vacuum agitation technique and compositions and conditions employed. It was hypothesized that owing to the exothermic nature of the TPE-DGEBA/mPDA reaction, trapped gas might be present in the mixture that could impair mechanical properties. To overcome this, a vacuum agitation technique was employed for two minutes followed by subsequent degassing and casting of coupons. Chong et al. [5] and Hydro and Pearson [7] report optically translucent and opaque samples, coupled with decreases in modulus at all loading percentages. Although their choice of curing agent differed, the observation that the same Nanostrength E21 performs differently with different curing agents in a DGEBA composite highlights the important role of the curing agent. The data shows that the vacuum agitation technique has increased the flexural modulus and strength by ~5% and the Notched Izod impact strength by  $\sim 70\%$ . The opaqueness of the resin suggested that miscibility was prevalent in uncured resin [7]. The vacuum mixing technique, however, led to translucent samples compared to the previously obtained opaque samples. Fig. 3 highlights these differences. The system shows an increase of Tg with respect to the neat epoxy system is said to be completely phase separated [7]. This translucent character maybe due to the fact the  $T_g$  has decreased slightly, ensuring some miscibility of the PMMA in uncured resin.



Figure 3.12. <u>Miscibility improvements via vac-u-mixing:</u> (left) TPE material is frothy when degassed under vacuum even after 10 min, (right) after the sample has been agitated in vacuum + 2min degas in vacuum

SBM Epon composites with other processing techniques were synthesized with trapped ٠

gas bubbles

- These seemed unavoidable owing to the nature of flocculent TPEs ٠
- Agitating the SBM-epoxy-mPDA mixture under vacuum removed trapped air bubbles ٠
- This translated to enhanced modulus and toughness ٠
- Future experiments could be evaluated with this procedure ٠





Figure 3.13. Vac-u-mixing setup



#### NOtched IZOD Impact Strength of SBM modified composites - Effect of processing after mPDA addition on composites

## Figure 3.14. Notched Izod Impact Strength for SBM (10phr) EPON Composites owing to Processing changes after Curing Agent Addition

The effect of degas post addition of curing agent, with or without the addition Flacktek mixing step was evaluated to verify if flacktek is dispersing the bubbles in the material. It was found that this did not have a huge impact on properties (morphology, flexural, Izod) for the processing methods used. It is also noteworthy to note that soxhlet extracted samples with vacuum agitation yielded nano-phase separated particles with a raspberry morphology. With the ease of processing of a CFRP in mind this processing method was eliminated.

#### **3.4. THERMAL ANALYSIS AND RHEOLOGY**

Rheology tests were conducted to observe the gelation point in the resin with and without TPE addition. The tests were conducted on an ARES Rheometer with a sample that has been processed through the technique mentioned above prior to casting. All samples were kept at room temperature for 300 seconds prior to test. This is to facilitate similar conditions for comparison, adequate time for loading the sample and for it to be workable within the torque

tolerances of the system. A parallel plate setup was used with 25 mm aluminum plates and a gap of 1 mm. Tests were performed at a frequency of 1 Hz at isothermal conditions of 80 °C with a time sweep for 3000-12000 seconds (depending on system).

The gelation point of various weight percent of SBM is shown in Figure 3.15. It can be seen that at lower concentrations the gelation point does not vary a great deal with SBM addition. This shows that the viscosity and hence polymerization does not drastically increase with SBM addition. This ensures that we have a workable system that would make it suitable for use in CFRPs at these low SBM additions. The gelation time does, however, increase for increased SBM addition (>5 wt%). This is due to the addition of high molecular weight SBM particles (~50,000 g/mole) which delays possible TPE-epoxy-mPDA adduct formation. Such systems also show non-Newtonian behaviors, which show increased viscosities at increased weight percent due to particle-particle interaction and particle-matrix interactions.



Figure 3.15. Gelation point Vs. ABC type TPE loading

## 3.5. EFFECT OF POST CURE CYCLE ON MECHANICAL PROPERTIES AND Tg

The choice of curing cycle, and in turn the kinetics of amine reaction, may disrupt the formation of spherical/vesicle like aggregates that shows much lower improvements in  $K_{lc}$  than otherwise observed. Varying extent of PMMA vitrification could also contribute to this [4]. Tian et al. showed that increasing or decreasing the rate of cure, can increase the ductility in the system [27]. With MC1 and MC2 cure cycles the primary amines are thought to be consumed in the first hour of cure itself, and the secondary amines react fast to vitrify the system in the next 2-3 hours. This results in a system of high  $T_g$ , but results in a glassy matrix [22]. No stress whitening was observed for these particles that were cured with a different schedule which supports the glassy matrix theory.

Material	T <sub>g</sub> (°C)	Flexural modulus(GPa)	Flexural Strength (MPa)	Izod Impact Strength(J/m)	K <sub>Ic</sub> (MPa m <sup>0.5</sup> )
Neat –S(RC)	156	$3.2 \pm 0.1$	$124 \pm 4$	23.4 ±1.1	$0.76 \pm 0.1$
Neat –S(MC1)	156	$2.9\pm0.3$	$121 \pm 6$	24.7±0.7	$0.96 \pm 0.1$
Neat –S(MC2)	156	3.0 ±0.3	125 ±9	$23.8 \pm 0.6$	-
SBM10-S(RC)	155	2.9 ±0.1	$115 \pm 5$	$32.8 \pm 1$	$2.82 \pm 0.2$
SBM10- S(MC1)	155	2.9 ± 0.2	116±3	24.5 ± 1.3	1.41 ±0.1
SBM10- S(MC2)	155	2.7 ±0.1	$107 \pm 2$	35.5 ± 2.5	-

Table 3.3. Variation of properties with varying cure schedule for SBM-epoxy composites

Good adhesion and free volume generation could reduce the mechanical properties and  $K_{Ic}$  values. Table 3.3 shows the variation of properties with varying cure schedule. Drzal et. al suggested that increase in upper temperature of cure increases  $T_g$ . Since there was no secondary post cure to higher temperatures, and since the samples belonging to all cure cycles were cooled by switching off the curing oven, the molecular chains remain frozen at  $T_g$ , to the same extent for

both the cure cycle [19]. Hence a spike in  $T_g$  is not observed for the modified cure cycles. Thus the RC cure has been established to provide a good balance between conversions,  $T_g$ , and deformable matrix. Table 3.3 shows the effects of varying cure cycle on SBM-epoxy composites. A (10phr) loading was selected as a standard recipe.

## **3.6. THERMOMECHCANICAL PROPERTIES**

The values of  $T_g$ , flexural modulus and strength, Izod impact strength, K<sub>Ic</sub> fracture toughness and loading study for SBM TPEs are listed in Table 3.4. Fractured ASTM D790 samples and ASTM D5045 samples were examined using a SEM EVO scanning electron microscope at an acceleration voltage of 3 kV. Samples were coated with a 5 nm layer of tungsten to make the surface conductive for examining the surface. DMA was used to measure the  $T_g$  (peak of tan delta curve vs. temperature), storage modulus and loss modulus.

Material	Tg(°C)	Flexural modulus (GPa)	Flexural Strength (MPa)	Izod Impact Strength (J/m)	K <sub>Ic</sub> (MPa m <sup>0.5</sup> )
Neat –(RC)	156	$3.2 \pm 0.1$	$124 \pm 4$	$23.4 \pm 1.1$	$0.76 \pm 0.1$
SBM1-(RC)	158	$3.2 \pm 0.3$	$128.3 \pm 7$	27.1 ±3	$1.41 \pm 0.1$
SBM2.5-(RC)	155	$3.2 \pm 0.3$	$123.2 \pm 9$	$34.8 \pm 5$	1.84±0.3
SBM5-(RC)	156	$3.0 \pm 0.1$	$122 \pm 4$	28.1 ±0.5	-
SBM7.5-(RC)	156	$2.9 \pm 0.2$	$116.1 \pm 1.3$	$32.3 \pm 2$	-
SBM10-SRC)	155	2.9 +/- 0.1	$115 \pm 5$	$32.8 \pm 1$	$2.82 \pm 0.2$
SBM12.5-(RC)	155	2.8 ±0.1	$105 \pm 2$	35 ±0	-

Table 3.4. Tg, Flexural Modulus and Strength, Notched Izod Impact strength, K<sub>Ic</sub> for SBM in EPON matrix

The unmodified matrix has values that agree with literature [4]. The values of  $T_g$  does are within experimental error for all composites indicating complete phase separation. Generally if PMMA remains dissolved in the matrix an increase in  $T_g$  would be observed because its  $T_g$  is higher than the DGEBA/mPDA mixture. The partial de-swelling of the PMMA block leads to a

decrease of 2-3 °C in  $T_g$  for most systems. Figure 5 shows the thermal stability of various TPEmodified epoxy matrices. All TPE-EPON matrices are thermally stable up to 400 °C. Two separate peaks indicating phase separation are not observed because of the similar range of temperature for the DGEBA-mPDA relaxation and SBM-DGEA-mPDA relaxation [8]. Broadening of tan delta peaks were observed due to distribution in molecular weight between crosslinks or general heterogeneity. Fig. 6 displays the variation in crosslink density for a neat and a TPE modified system. The SBM10-(RC) system possesses a higher molecular weight between crosslinks at a given amine concentration [18-19]. This shows that the TPEs interact with the resin and curing agent and reduced the crosslink density [20-21]. Thus, a system of low crosslink density provides us with the improved K<sub>Ic</sub> values due to the ability for such a system to shear yield.



Figure 3.16.<u>T<sub>g</sub> and TGA curves for TPE-EPON composites:</u> (left) Variation of T<sub>g</sub> (measured via DMA) for various SBM loading %; (right) Comparison of thermal stability of TPE-EPON composites

Table 3.4 summarizes the loading study for SBM TPE in EPON matrix. The selfassembly of TPEs may occur during TPE dispersion in DGEBA, and hence the processing technique used is important. Moreover, the aggregation of these spherical particles occurs during processing [6]. It is this aggregation that results in a decrease in modulus and strength at higher loading. At lower loadings it can be seen that the modulus and strength properties do not vary, but the impact strength and toughness values increase. The 2.5 wt% system offers unique potential for a modified matrix as shown by the morphological examination in the next section. An exponential increase of  $K_{Ic}$  fracture toughness (~275%) is reported due to the microseparated TPE particles in the EPON matrix. The TPE modified matrices also show enhanced strain indicating its ability to delay crack propagation. Table 3.4 shows about the results of a similar loading study for SBM TPE in EPON matrix.

## **3.7. FRACTROGRAPHY**

The following figures shows SEM micrographs from flexural fracture for a regular cure SBM-epoxy composite at various loading percentages. The goal was to identify the morphology, correlate filler behavior to mechanical properties and idientify a critical particle size that is responsible for the toughening mechanism that gives the enhanced properties seen in these materials.



Figure 3.17. Neat epon @(14.5phr) mPDA-morphology: (left) Neat EPON-mPDA fracture surface, (right) neat EPON-mPDA fracture surface showing hackles

The objective here was to analyze the fracture surface of neat EPON-mPDA composite and relate microstructural changes and morphology to the mechanical properties, and its effects after TPE addition. Figure 3.17. shows the smooth fracture surface of a neat epoxy sample and its

catastrophic failure due to the absence of any crack deflection mechanism. What we see are shear cusps and hackles on the epoxy fracture surface.



# Figure 3.18. SBM (1phr) EPON fracture surface

At 1phr loading, the goal was to explore feasibility for use in a FRC system. This system as shown earlier, has a very low gelation point, with a 15% increase in Izod impact strength, 100% increase in  $K_{Ic}$  without affecting the flexural modulus and strength. This makes it an ideal choice as a matrix for a FRC. Particle sizes are <600nm. They are well de-agglomerated.



Figure 3.19. SBM (2.5phr) EPON fracture surface

A great combination of properties, unaffected gelation point and  $T_g$ , flexural modulus and strength coupled with ~45% increased Izod impact strength and ~85% increased K<sub>Ic</sub> leads us to propose this as the ideal candidate for a future FRC system. Isolated particle toughening and the micro-phase separated and flocculated SBM particles in the EPON matrix in the size range of 800-1000nm makes it show enhanced toughness. Areas of plastic void growth were also seen similar to the ones reported by Chen et al [26]. The 5phr system on the other hand, with its microphase separated particles in the order of ~2-3µm lead to a modest 20% increase in Izod impact strength. On observing the overall morphology of the surface this system showed cavitation, and did not show as much resistance to a crack propagation like a (2.5phr) system did, albeit the surface showed increase in surface roughness as shown in figure 3.24.





Figure 3.20. SBM (5phr) EPON fracture surface



# Figure 3.21. SBM (7.5phr) EPON fracture surface

The 7.5phr SBM-EPON system although showed a rougher surface (Figure 3.24), did show ~40% increased Izod impact strength. The system also showed ~a 10% reduction in flexural modulus which has been consistent with rubber toughening [4, 7, 11]. The T<sub>g</sub> of this system was unaffected which still showcased miscibility of the PMMA network in the epoxy. The decreased strengths could be attributed the presence of rather large agglomerates in the size range of 15-20um. This could be owing to the processing conditions employed, in this case magnetic stirring. For future work, the proposed vacuum mixing technique would be used. Shear yielding and isolated particle toughening around the block copolymers was attributed to be the major toughening mechanism. Some void growth could also be seen in this case [figure 3.21

## (right)].



# Figure 3.22. SBM (10phr) EPON fracture surface

This system showed a 90% increase in Izod impact strength without a change in  $T_g$  [28]. From Figure 3.22, it can be seen that cavitation inside the particles leads to the formation of the stress whitened zones and the mechanisms from fracture seen in the SEM micrographs.



## Figure 3.23. SBM (12.5phr) EPON fracture surface

The (12.5phr) SBM-EPON system had showed ~100% increase in Izod impact strength, but at this loading, the viscosity of the system increases drastically, and would make it almost impossible to serve as the matrix for a FRC system.

a. Critical particle size for enhanced adhesion is ~700um.

- b. The self assemble particles were interconnected on a micr-scale, and no fibrils are present
- c. Debonding together with SBM internal rupture increases and allows for plastic void growth
- d. Adhesion of particles increases with increase in phase separated particle size and enhances  $K_{Ic}$
- e. Despite plastic deformation, no fibrils were observed, contrary to Dean, et al. Instead, particles agglomerated to increase adhesion with base matrix and increased K<sub>Ic</sub>

Figures 3.18-3.23 indicated the morphology of SBM-EPON composite with increase in TPE loading upto (12.5phr) SBM addition. For the sake of consistency all samples were synthesized via magnetic stirring method per the procedure mentioned in section 3.3.



Figure 3.24. <u>Surface roughening in SBM-EPON composites:</u> Shows roughening increases from SBM (1phr) EPON composite (top left), to SBM (12.5phr) EPON composite (bottom right)

Figure 3.24 above also shows increase in roughness with increase in loading of SBM. This could be attributed to very rough surfaces and more step changes in the plane of crack propogation shows increased plastic deformation, usually when this is observed, yield strength decreases [5], but in this case it contributes to less than 5% decreases, and due to other toughening mechanisms and selective way of phase separation. It can be seen that the increase in roughness has contributed to the toughness improvements as well. The fracture surface of a neat epoxy appears smooth, and that of the toughened matrices appears rough as the SBM content increases. This in turn increases the level of plastic deformation in the matrix. Up to 15phr of SBM loading, no phase inversion was observed. Good stress transfer can be seen as a result of the good adhesion between the SBM particles and the epoxy matrix. Absence of debonding, is also indicative of good adhesion of the TPE's in an epoxy matrix.

SEM micrographs indicate a presence of macroscopic phase separation which induces different toughening mechanism than the ones usually seen, i.e., debonding and matrix plastic deformation. Fibrils without evidence of debonding due to epoxy disruption around the particles are seen that could indicate enhanced adhesion between DGEBA-mPDA system and the phase separated particles [6]. This is because the TPE-DGEBA/mPDA system mentioned here did not facilitate debonding. Matrix dilation and matrix roughness can be seen, which could add to the increases in K<sub>1c</sub>. The aggregation of the particles in this case creates overlapping stress fields that enhance matrix deformation and the epoxy traces present in between the aggregates change the stress state to plastically deform the matrix. One or both of these phenomenon may occur [5].The SBM2.5-(RC) resembles the morphology of a macro vesicle formed. The tendency to form aggregates of sphere on spheres increases with increase in amount of TPE added. Figures 3.18-3.23 confirms cavitation within particles and matrix deformation due to epoxy disruption around the TPEs. Cavitation is the mechanism that initiates plastic deformation in matrix, leading to the K<sub>1c</sub> results we see. Figure 10 shows crack deflection mechanism for SBM10-(RC)

in addition to cavitation and that leads to the  $K_{Ic}$  increases. This is contrary to literature [5–7]. Gerard *et al.* [4] explains that crack deflection could contribute significantly to high levels of toughness.



Figure 3.25. SEM Micrograph of CT specimen for SBM10-(RC)

## **3.8. CONCLUSIONS**

An aromatic amine cured epoxy polymer was modified using SBM and MAM thermoplastic elastomers. The microstructure, thermo-mechanical and fracture properties, and toughening mechanisms were identified. The SBM-DGEBA/mPDA system display a semi-brittle/ductile behavior. PMMA is the nanostructuring block in SBM. These self-assembling triblock copolymers in a cured DGEBA/mPDA matrix lead to micro-phase separated structures. The amine-epoxy cure extent dictates morphology and hence mechanical properties. Optimum mixing was required to insure complete dissolution of the polymers into the epoxy matrix. The addition of TPE to this DGEBA-mPDA system displays the ability to delay crack propagation.

The optimum results depend on matrix morphology, interfacial adhesion, choice of cure agent, and are cure schedule dependent. Mechanisms that govern the increase in critical stress intensity factors include crack deflection of spherical/vesicular aggregates and large interfacial zones between two phases, cavitation of PB middle block of the TPE particles and subsequent plastic, matrix deformation caused by these particles. The processing variations and toughening of the bulk matrix are discussed followed by matrix toughening in terms of thermo-mechanical properties, rheology, degree of cure and cure conditions established. The values of flexural modulus, strength, K<sub>Ic</sub>, Izod impact strength and the toughening mechanisms are also presented and discussed. Fractographic studies were performed to identify the chief toughening mechanisms and to correlate these to the K<sub>Ic</sub> increases observed. Future work includes using TPE modified matrix in fiber reinforced composites for the aerospace industry.

- From the SEM micrographs it can be seen that the magnetic stirring method gives us a much more uniform distribution of particles
- SBM (2.5phr) system was processed for the same length of time as the 10phr system
- Smaller amount of particles give these more time to phase separate without agglomeration during cure owing to several events of isolated cracks
- With the addition of more rubber particles larger domains of rubber phase separates
- If this is less than 1µm size, it seems to be more conducive for toughness but impairs modulus and strength values as shown in the data

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## CHAPTER 4 MECHANICAL, THERMAL, VISCOELASTIC AND MORPHOLOGICAL STUDY OF ABC TYPE THERMOPLASTIC ELASTOMER TOUGHENING OF EPOXY MATRICES

#### PART II: EFFECT OF STOICHIOMETRY IN BULK MATRIX

#### 4.1. ABSTRACT

Epoxy-matrices form a highly cross-linked microstructure upon curing. This structure provides high modulus and strength, excellent creep resistance, but lacks ductility. One approach to improve the mechanical toughness in epoxy matrices is the addition of thermoplastic elastomers (TPEs). In this chapter we talk about means to improve the toughness of epoxy matrices by a combination of TPE and stoichiometric variations in curing agent addition. The plane strain critical stress intensity ( $K_{Ic}$ ) was improved ~250% with SBM addition (10wt%) to epoxy/mPDA matrix at stoichiometric amounts (14.5phr) of mPDA and up to ~375% when non-stoichiometric amount (21.5phr) of curing agent was used owing to decreased cross-linked density. The thermal resistance and glass transition temperature of this system when blended with SBM at non-stoichiometric, suffered a modest sacrifice. This is compensation by an enhancement in other properties at the matrix level. It is noteworthy to point out that the overall properties of a SBM-EPON system at (1phr) loading and (2.5phr) loadings give us the overall balance of properties and would serve to be the matrix of choice for a fiber reinforced composite.

## **4.2. INTRODUCTION**

The highly cross-linked structure of epoxy thermoset polymers gives it good mechanical properties but also makes it inherently brittle. Several methods have been employed in literature to toughen epoxy thermoset polymers. Tian *et al.* suggest the toughening of an epoxy crosslinking network by controlling the topological structure [1]. This does however require polymer synthesis capabilities and a fine level of control of initiator BDMA through a chain-

wise-polymerization reaction. Guerrero et al. used variations in epoxy-amine ratio to enhance toughness. The competitive etherification and esterification in their TGDDM/THPA mixtures give them the best properties in an epoxy rich stoichiometry. Their studies focused on a stoichiometric dependence on Tg and dynamic mechanical properties [2]. Meyer et al. studied stoichiometry on a high molecular weight harder (DDS) - epoxy system [3]. Drzal et al. showed how variations in molecular weight between crosslinks related to crosslink density and how post curing conditions also had an effect on toughness of the polymer network [4]. Downey et al. also employed aliphatic epoxy to toughen an aromatic epoxy system such as DGEBA-mPDA system. Such a system showed improved properties upto 77% with no decrease on  $T_g$  [5]. Crosslink density variation has been known to have an effect on toughness. Various approaches have been taken to reduce crosslink density and toughen a matrix. Kinloch et al. varied the cure time and temperature to reduce cross-link density. Pearson et al. varied epoxy equivalent weights [6] [8] [9]. Other attempts include, varying molecular weight of starting epoxy resin, usage of hybrid curing agents, aliphatic curing agents etc [10]. Epoxy resin blending with reactive and nonreactive rubbers such as ATBN and CTBN have also been extensively studied. In these cases, the rubber particles phase separate in the 2-5µm range, increases the molecular weight in the system and thus tremendously decreases glass transition temperature and flexural strength and modulus [6]. The advent of block copolymers made it feasible to produce copolymer-epoxy composites with increased fracture toughness without reduction of glass transition temperature. Most of this work was done at stoichiometric conditions using low molecular weight amines like Jeffamine [7], [8] [9]. Ren et al. controlled the reactivity of the block copolymer for a DGEBA/DDM system and showed toughening increases up to 150% via innovative reactive blending [10].

In this chapter, crosslink density variation was achieved by varying the amount of curing agent added. i.e. an excess of primary and secondary amines in mPDA. The curing agent added in excess of stoichiometry contributes to large scale motion of polymer chains and the cured thermoset material has a higher molecular weigh between crosslinks [10] [24]. Crosslink Density of DGEBA was controlled by varying amounts of a single hardener, mPDA. The TPEs were effective as modifiers for an epoxy matrix. The addition of 10phr SBM led to a 250% increase in K<sub>Ic</sub> of resin cured with mPDA. This resulted from a system of lower crosslink density. Takao et.al. suggested a toughened epoxy matrix with elastomers that were terpolymerized. Their system however resulted in a decrease of Tg when KIc was increased. The morphology of the resulting TPEs via vacuum agitation broke down larger aggregates, and resulted in micro phase separated particles that had a lower crosslink density than the neat matrix system without compromising  $T_g$  even at 250%  $K_{Ic}$  increases. In this chapter some of the advances made in literature were employed on a SBM-EPON-mPDA system and its plane strain fracture toughness (K<sub>Ic</sub>) was determined for both stoichiometric and amine rich groups. The reasons for enhanced toughness were determined and its morphology was examined under SEM to correlate toughness increases with a toughening mechanism.

#### **4.3. PROCESSING**

Both the neat matrix and the SBM modified matrix were treated with non-stoichiometric amount of curing agent and their effects on thermal, mechanical and viscoelastic properties were studied. These composites were processed as detailed in Chapter 3.3. Henceforth stoichiometric and non-stoichiometric addition of curing agent attributes to addition of (14.5phr) mPDA and (21.5phr) mPDA respectively, to the epoxy and the SBM modified composite.

4.4. MECHANICAL AND VISCOELASTIC PROPERTIES AT STOICHIOMETRIC AND NON-STOICHIOMETRIC ADDITIONS OF CURING AGENT Flexural three-point bending tests were performed according to ASTM D790 [14]. A bar of rectangular cross section of 3.2E-3m x 12.8E-3m (thickness x width) was used. A support span-to-depth ratio of 16:1 was used and rate of crosshead motion is determined from the formulae mentioned in the ASTM standards. The tests were performed on a Universal Testing Machine. The flexural modulus and strength were calculated from the standard. Five samples were tested for each formulation.

$$R = \frac{ZL^2}{6d}, \sigma f = \frac{3PL}{2bd^2}$$
[11]

L is the support span (m), b is the width of beam tested, d is the depth of beam (m), Z is 0.01, R is the rate of crosshead motion (m/min), P is the load at a point on load deflection curve, and  $\sigma f$  is the stress at the midpoint (MPa). Notched Izod impact test was performed in accordance with Test Method A in ASTM D256 [15]. The samples were conditioned at room temperature for two days before being tested. A 53.4J/m hammer was used for sample of 0.01143m width. Five prenotched specimens were tested for each composition. All samples resulted in complete failure and the impact strength was reported in J/m. Compact tension (CT) tests were performed to determine plane-strain fracture toughness (K<sub>Ic</sub>) in accordance with ASTM D5045 [16]. Test specimens with a size 0.02 x 0.009 x 0.009m were notched with a fresh razor blade to obtain an a/w ratio ~0.45. Tests were performed on a MTS Machine at a displacement rate of 1mm/min. Five samples were tested for each formulation and fracture toughness was calculated using the fracture load. Density tests were performed to determine the molecular weight between crosslinks was calculated from the expression [2]

using the G' above the  $\alpha$  transition and using the density,  $\rho$ . The density was calculated using a density picnometer in accordance with ASTM D792

$$\log_{10} G' = 7 + 293 \frac{\rho}{M_c}$$
[4]

The crosslink density,  $\rho$ , was also calculated in accordance with the studies done by Iijima et al.

$$\rho = \frac{G'}{\phi RT}$$
[12]

They suggested that  $\rho$  is the crosslink density, and was calculated from the equilibrium storage modulus, G' in the rubber region over the  $\alpha$ -relaxation temperature. R is the universal gas constant.  $\Phi$  is the front factor which is assumed to be unity in this case. T in the absolute temperature in the rubber region. In our case of equilibrium storage modulus T is taken at T<sub>g</sub>+30°C. The extensibility of the network would be decreased for system having G' > 10<sup>7</sup> Pa and the theory of rubber elasticity might no longer hold. But the (21.5phr) system show G' less than 10<sup>7</sup> Pa and moreover according to studies done by LeMay et al. the rubber modulus could be used to determine crosslink-link density for short chain epoxy systems like that of DGEBA/mPDA [12], [14].

Table 4.1. T<sub>g</sub>, Flexural Modulus and Strength, Notched Izod Impact strength, K<sub>Ic</sub> for stoichiometric and non-stoichiometric matrices (neat & modified)

Material	T <sub>g</sub> (°C)	Flexural	Flexural Strength	Izod Impact	K <sub>Ic</sub> (MPa
		modulus(GPa)	(MPa)	Strength(J/m)	m^0.5)
Neat –S(RC)	156	$3.2 \pm 0.1$	124 +/- 4	23.4 ± 1.1	$0.76 \pm 0.1$
Neat –NS(RC)	134	$3.2 \pm 0.3$	$127 \pm 5$	32± 4.1	$0.91 \pm 0.1$
SBM2.5-S(RC)	155	3.2±0.3	123.2 ±9	34.8±5	1.74±0.3
SBM10-S(RC)	155	$2.9 \pm 0.2$	$115 \pm 5$	$32.8 \pm 1$	2.82 ±0.2
SBM10-NS(RC)	127	$3.1 \pm 0.1$	$126 \pm 1$	$43.9 \pm 4$	3.56 ±0.2



Figure 4.1. <u>Stoichiometric addition of mPDA:</u> (left) Fracture toughness testing for EPONmPDA system at stoichiometric amount of curing agents; (right) Fracture toughness testing for EPON-mPDA system at non-stoichiometric amount of curing agents



Figure 4.2. <u>Non-stoichiometric addition of mPDA:</u> (left) Fracture toughness testing for SBM(10phr)EPON-mPDA system at stoichiometric amount of curing agents; (right) Fracture toughness testing for SBM(10phr)- EPON-mPDA system at non-stoichiometric amount of curing agents

Table 4.1 shows the variation of flexural modulus, flexural strengths, Izod impact strengths and  $K_{Ic}$  at stoichiometric vs non-stoichiometric amounts of curing agent addition. While the SBM-10phr modified composite shows ~5% decrease in flexural modulus and strength when compared to the base matrix at stoichiometric amounts of curing agent, at non-stoichiometric addition of curing agent the flexural modulus and strength show no decrease when compared to the base system. Another interesting point to note is that at non-stoichiometric

additions of curing agent to both the base matrix and the modified system shows increased modulus and strengths than their stoichiometric counterparts.

It can be seen from Figure 4.1 that an amine reach, non-stoichiometric amount of curing agent added, delayed the crack propagation. The average displacement increased from about 0.2mm to about 0.4mm in a neat epoxy system with no fillers. This increase is purely due to the increase in molecular weight between the cross links of amine rich system in an epoxy-amine polymer system. For the same reasons, Figure 4.2 shows increased in displacement from 0.4mm to ~1.6mm and in some cases no sample break was found from testing the compact tension specimens. Figure 4.3 gives us an overall snapshot of axial force vs. displacement. In the latter case, the SBM-epoxy composites further increase the molecular weight between crosslinks and in turn reduce the crosslink density. Fracture toughness measurements were also used to study the 1<sup>st</sup> drop in load for the TPE modified samples with respect to the neat resin. For the purpose of comparison, let us evaluate the neat and the modified matrix at a stoichiometric amount and non-stoichiometric amount of curing agent addition. The first drop in load is an indication of the ability of the matrix to withstand the plane strain fracture toughness condition until the matrix is adversely affected. At stoichiometric amounts, the matrix can absorb almost four times as much energy before a drop in load when compared to the base matrix. For a non-stoichiometric SBM modified system these values increase to ten times increase in resistance before the first drop in load when compared to a neat matrix at stoichiometric amounts of curing agent. These values also correlate to the increase in K<sub>Ic</sub> values observed, which in turn is due to a system with reduced crosslink density. Another noteworthy test was performed to read the displacement values for an applied load. A neat sample at both stoichiometric and non stoichiometric amounts of curing agent, led to a failure at the first drop in load indicating the brittle nature of the sample.

However, when the modified samples at non-stoichiometric amounts of curing agent were tested to failure, the sample asymptotically would approach complete failure, but theoretically never failed owing to the enhance crack absorption capability of the matrix.



# Figure 4.3. Force vs displacement of neat epoxy (to first drop in load) and TPE-epoxy composites on a CT specimen



Figure 4.4. <u>Fracture toughness results and sample appearance:</u> (left) K<sub>Ic</sub> improvements from stoichiometric and non-stoichiometric addition of curing agent to SBM (10phr) EPON composite; (right) Fracture surfaces of SBM-EPON compact tension samples


Figure 4.5. The effect of lowering of crosslink density in a modified matrix

Figure 4.5 indicates the molecular weight between crosslinks for a neat and a SBM modified matrix at stoichiometric and non-stoichiometric additions of curing agent (mPDA). The crosslink density of the system was merely controlled by varying amount of curing agent added and without the addition of any secondary hardener that acted as chain extenders [12]. From the graph, it can be seen that both the neat and the modified matrix show increase in the molecular weight between crosslinks, i.e., decreased crosslink density based on ASTM D736. There was no chemical reaction that had taken place between the SBM and the epoxy/curing agent during cure. These values were not calculated from the epoxy resin quantity, and hence can be considered as a good semi quantitive analysis of crosslink density. The SBM particles being rubbery in nature act as chain extenders when added to a DGEBA/mPDA system and contribute to the increase in molecular weight between crosslinks, thus slightly reducing rigidity due to the chain rotation and molecular motion. The toughening thus satisfied the two conventional requirements viz, existence of micro-phase separated particles and interfacial bonding between two incompatible phases (middle block and DGEBA/PMMA/PS, [13]). The increase in molecular weight of the epoxy oligomers also confirms phase separation during curing [14] [13]. The added fact is that the composition in its liquid state is transparent and when cured, is opaque. The absence of transparency through cure could also explain the phase separation behavior. The phase separation in these cases is unlike that of CTBN.

Curing conditions have an impact on morphology. Hence, an attempt was made to cure the matrix at different conditions to try and produce various morphologies and observe impacts on adhesion/toughening mechanisms in Chapter 3. Shorter periodic distance dispersion was attempted but no other morphology was seen, indicating the adhesion was not compromised [15]. One of the objectives of this chapter was to associate K<sub>Ic</sub> improvements with Viscoelastic properties of the tri-block copolymers, which in turn could be attributed to the primary toughening mechanism in these materials. Figure 4.4 (right) shows the presence of intense stress whitening, localized shear bands and plastic deformation. The morphology of these samples would be analyzed via SEM later in the chapter. Crosslink density reduction, slightly reduces the flexural strength for a TPE-epoxy system. But for the (2.5phr) system, there was no negative effect on the bulk matrix. This was accompanied by an increase)e in K<sub>Ic</sub>. (2.5phr system @ (21.5phr) mPDA, and varies in the nature of phase separation prior to gelation or vitrification compared to 10phr system @ (21.5phr) mPDA. This could be owing to the (10phr) system having a higher crosslinked system than (2.5phr) [12]. The (1phr) and (2.5phr) system physically acted like reinforcements with no reduction in mechanical and Viscoelastic properties and still results in a 100% K<sub>Ic</sub> improvement compared to the neat matrix. Mechanical property retention of the (2.5phr) system could be attributed to the reinforcement of the matrix[16]. No decrease in flexural properties nor Tg was soon, could be attributed to ill-defined dispersed particles in the epoxy matrix and this could be in agreement in morphological and viscoelastic behavior. The illdispersed particles give rise to more than one domination toughening mechanism and considerably increase K<sub>Ic</sub>.

# 4.5. THERMAL AND VISCOELASTIC PROPERTIES AT STOICHIOMETRIC AND NON-STOICHIOMETRIC ADDITION OF CURING AGENT

Table 4.2 clearly indicates the heat of exotherm reduces with the stoichiometrically different formulations and for a (10phr) SBM addition. For a SBM-EPON system, the PMMA only shows physical adsorption in the matrix and hence is non-reacting. This is shown by a decrease in the enthalpy and hence the degree of polymerization for a non-stoichiometric system is lower than its stoichiometric counterpart. The degree of polymerization is also lower for a (10phr) system as opposed to a (2.5phr) system owing to the increased concentration of PMMA is the copolymer blend. The rate of reaction is reduced and a concentration dilution effect in the blend takes place with non reactive TPE additions [14] [17]. The hardener mPDA had the secondary amine that systematically controls crosslink density [12].

composites					
Materials	Enthalpy	$T_g(^{\circ}C)$	Displacement	Storage	Cross-link
	(J/g)		(mm)	modulus	density, p [12]
				(MPa), at	
				$T = T_g + 30^{\circ}C$	
Neat EPON @	372.6	156	0.17	35.98	0.94
(14.5phr) mPDA					
Neat EPON @	256.0	134	0.32	14.92	0.41
(21.5phr) mPDA					
SBM (10phr) EPON	220.9	155	0.57	28.27	0.74
@ (14.5phr) mPDA					
SBM (10phr) EPON	202.9	127	No break	9.63	0.27
@ (21.5phr) mPDA			(>1.2mm)		
SBM (1phr) EPON	-	158	0.31	37.01	0.95
@ (14.5phr)mPDA					
SBM (2.5phr) EPON	417.6	158	0.40	36.24	0.94
@ (14.5phr) mPDA					
SBM (2.5phr) EPON	-	151	-	27.34	0.72
@ (21.5phr) mPDA					

Table 4.2. Apparent crosslink density and degree of polymerization of various SBM-EPON composites



Figure 4.6. <u>Storage modulus of SBM (10phr) EPON composites at stoichiometric and non-</u> stoichiometric mPDA compared to its Neat EPON equivalent

Table 4.2 documents the storage modulii from Figure 4.6. These values are used in apparent crosslink density calculations. At ambient conditions, the storage modulii for the modified and neat epoxy systems (a) (21.5phr) mPDA additions showed less than a 10% decrease. And the values of the modified system vs. neat system at similar mPDA additions were unaffected. The decrease is considered acceptable considering the impact,  $K_{Ic}$  improvements provided by the system.



Figure 4.7. <u>Tan δ of SBM (10phr) EPON composites at stoichiometric and non-</u> stoichiometric mPDA compared to its Neat EPON equivalent

The tan delta peak signifies the ratio of the dissipated energy to the energy stored per cycle of sample deformation at the glass transition temperature, determined by DMA. Tan delta is the ratio of loss to the storage and is called damping. Decreasing Tan delta means that your material acts more elastic now and by applying a load, it has more potential to store the load rather than dissipating it. This also explains the increase in  $K_{1c}$  for a non-stoichiometric system, and is enhanced futher by the presence of thermoplastic elastomer, SBM. The degree of cure increases when the tan delta peak decreases [18]. This is true for the 21.5phr systems. A single peak in tan delta, and a single glass transition temperature, indicates efficient mixing and a homogenous solution [14]. The decrease in  $T_g$  for system of non-stoichiometric mPDA addition could be attributed to the PMMA chains' penetration into the EPON-mPDA crosslink structure. The PMAA chains are soft in comparison to the epoxy networks and hence show a plasticization effect [19]. The decrease in  $T_g$  for an SBM system at (21.5phr) mPDA, could also be attributed

to the differential segregation of the epoxy and hardener to the TPE rich phases. The TPE copolymers micro-phase separated prior to gelation [17].

The alpha transition relates to the  $T_g$  and hence large scale movement of molecular segments. Adding compatible polymers to the bulk matrix is one way to lower crosslink density in the system, among others. An SBM system, being of a higher molecular weight in itself increases the molecular weight between crosslinks, lowers the crosslink density and imparts ductility to the system. The alpha transitions are virtually unaffected [4]. Figure 4.7 shows the tan delta peak is broader and shifts to lower temperature when compared to the neat epoxy system at (21.5phr) loading [16]. Tg naturally decreases with increase in amine content [4], [16]. The decrease in Tg with SBM addition is rather small when compared it to neat epoxy counterpart, and this decrease is attributed to the increase in molecular weight between the crosslinks via SBM addition. The phase separation and hence the presence of two peaks in a tan delta curve are highly dependent on the type of curing agent and processing method used for a DGEBA/EPON resin system [17]. For the system employed here, a two phase morphology was not prevalent nor were there two or more peaks in the tan delta curve. Figure 4.8. shows the thermal stability of a SBM(10phr) EPON system at non stoichiometric amounts of curing agent addition against its neat epon counterpart. It can be seen that throughout the range of temperatures the TPE modified system shows stability. This could be attributed to the physical adhesion between the SBM particles and the epoxy network.



Figure 4.8. <u>Thermal Stabilities of SBM (10phr) EPON @ (21.5phr) mPDA Vs.</u> <u>Neat EPON system @ (21.5phr) mPDA</u>

### 4.6. FRACTOGRAPHY



Figure 4.9. Fracture surface of a Neat EPON system @ (14.5phr) mpDA from a CT specimen



Figure 4.10. Fracture surface of a SBM (10phr) EPON system @ (14.5phr) mpDA from a <u>CT specimen</u>



Figure 4.11. <u>CT specimen SBM-EPON toughening:</u> (left) Toughening mechanim of a SBM (10phr) EPON system @ (14.5phr) mpDA from a CT specimen (right) Fracture surface of a SBM (10phr) EPON system @ (14.5phr) mpDA showing traces of Microphase separated particles



Figure 4.12. Fracture surface of a SBM (10phr)EPON system @ (21.5phr) mpDA from a CT specimen



Figure 4.13. <u>CT specimen SBM-EPON toughening non-stoichiometric system:</u> (left) Toughening mechanim of a SBM (10phr) EPON system @ (21.5phr) mpDA from a CT specimen (right) Fracture surface of a SBM(10phr)EPON system @ (21.5phr) mpDA showing debonding/void growth

The unmodified resin had one phase and was transparent, independent of hardener composition. The TPE modified resins had a spherical morphology with Microphase separated particles with varying levels of agglomeration. The efficiency of SBM modifiers could be due to the high extent of dispersion of fine particles less than 1um. The fracture surfaces are rough. The particles micro-phase separated and were fixed by the curing reaction but a two phase morphology, like traditional rubbers was not observed. A peak for PS was not observed at 75°C either. A prenotched and precracked CT specimen subjected to a hydrostatic force, the SBM particles cavitate and interact with each other. The crack tip is blunted owing to these shear bands by large scale plastic deformation of the matrix. The SBM particles then tear after its elongation on increasing the hydrostatic forces and void growth (in some cases) and crack deflection dominate as toughening mechanism, depending on the particle/agglomerate size [16]. This is true in both the SBM (10phr)- EPON systems at (14.5phr)mPDA and (21.5phr) mPDA. In the nanostructured thermosets PB blocks aggregate into spherical domains at the interface between the epoxy-rich matrix and spheres formed by the PS blocks [20]. However, while the former case shows plastic deformation and crack deflection as the major toughening mechanism, the latter demonstrates crack deflection, debonding and/or void growth.

Toughning is attributed to the stress concentrators that cavitate and interact upon application of hydrostatic pressure at crack tip. The plastic shear deformation of the matrix diffuses these interaction that induces shear band near crack tip. Crack deflection then elongates and tears particles when the hydrostatic pressure is increased [12]. Though the morphologies aren't too different between system (14.5phr) mPDA system and the 21.5phr mPDA system for the SBM-EPON composite., the crosslink density of the system may lead to different levels of plastic shear deformation that could directly impact K<sub>Ic</sub>. SBM creates a ductile matrix, that impairs plastic shear deformation that has an effect on toughening of DGEBA/mPDA systems. Our results agree with literature in that [19], [21], [20] microphase separation occurs on PB and then microphase separation occurs from demixing of PS sphere from PB blocks. In our case the viscosity increases are so large that it prevents the demixing of these two immiscible middle blocks. The Microphase separated PB could be demixed from previously self assembled from nanophases of PS, or vice-versa [21]. This is not the case since we did not find any particles in the 100nm range.

#### **4.7. FTIR STUDIES**

Drzał et al. suggested that for any amount of mPDA added, hydroxyl concentration increased with added mPDA and the concentration of epoxide group containing molecules decreases. In no case did the epoxide band completely vanish, which indicated that at (14.5phr) mPDA addition or (21.5phr) mPDA, the epoxy-amine reaction never went to completion. This meant that there is a possibility of PMMA-epoxy hydroxyl reaction which does not seem to be the case from FTIR results. There are no new peaks formed to indicate this chemical reaction. The reason for this could be two fold, either the reaction is physical in nature; or at the temperature at which the mixing and curing was carried on the rate of viscosity increase happened faster than the rate of the chemical reaction [23]. Primary amines in mPDA react with the resin at extremely high rates at lower temperatures. As the cure duration and temperatures supported by the fact that a complete reaction of epoxy and secondary amine was not observed. The cure cycle that is employed here sterically hinders the reactive functional groups-epoxide reaction and hence the progress of the epoxy-secondary amine reaction [22].



agents

The FT-IR spectra also shows that for the (21.5phr) system the O-CH3 (2850–2950 cm<sup>-1</sup>) band is very weak, which supports our above theory that the viscosity increase suppresses the chemical reaction on an otherwise slower reaction rate that is caused by TPE addition in the case of non-stoichiometric SBM-EPON system. Increasing the heating time does not induce any shift or modification of the O–CH3 (2850–2950 cm<sup>-1</sup>) and the C=O (1725 cm<sup>-1</sup>) peaks of PMMA [17]. If there were excess epoxy, like in the case of an epoxy rich system, PMMA interaction via hydrogen bonding between its carbonyl group and the epoxy's hydroxyl group could be possible. Our systems are amine rich or stoichiometrically balanced for this reaction to take place. Hence the FTIR shows no additional groups formed [14][17].



Figure 4.15. <u>ATR studies 500 to 2500 cm<sup>-1</sup> : (left)</u> ATR studies on various SBM-EPON composites at varying amounts of curing agents in the 500-1500 cm<sup>-1</sup> wavelength range, (right) 1500-2500 cm<sup>-1</sup>





#### **4.8. CONCLUSIONS**

The ductility and crack deflection of the matrix contributed greatly to the toughening of epoxy resin with TPEs. From the FT-IR results, we can conclude that no hydrogen bonding

exists between PMMA and DGEBA and that no trans-esterification reaction occurs. Transesterification reaction could also be studied via tracking molar masses, which had not been performed and was out of the scope in this case. The opaqueness of the samples are shown to be obtained as a result of the procure and curing conditions employed because gelation hindered phase separation [24]. This again shows the PBu phase separated particles are fixed during curing and PMMA is merely miscible and non-reactive with the epoxy. When a system has two immiscible components, like in the case of SBM, the formation of microstructures in our case could be attributed to the tandem reaction induced microphase separation in the DGEBA/mPDA matrix. The final morphology of the thermosets is strongly dependent on the competitive kinetics involving curing reaction, phase separation and connectivity of phases [21]. In our case, it has been biomodal spherical structure. Deeper investigation into the curing kinetics, conversion and intercomponent interaction parameters had not been studied.

Changes in solubility parameters affect miscibility in TPE-EPON systems. Therefore, in our case it is judged that the copolymers follow a reaction induced Microphase separation rather than a self-assembly process [25]. Bimodal distribution of TPEs, owing to coagulation of smaller particles into larger particles, is beneficial to toughening [12]. Any slight decrease in flexural strength could be attributed due to SBM addition could be attributed to lack of chemical interfacial adhesion. This could be proved via FTIR, and as it can be seen, no new groups are formed. The decrease in rather low 10% and this could be fixed by synthesizing a fuctional SBM terpolymer [26]. The addition of SBM to this DGEBA-mPDA system displays the ability to delay crack propagation. The optimum results depend on matrix morphology, interfacial adhesion, choice of cure agent, and are cure schedule dependent. Increases upto ~260% in  $K_{Ic}$  were observed for a SBM (10phr) EPON system at stoichiometric addition of curing agent, and

upto 375% was observed for a non-stoichiometric system. In the former case  $T_g$  was unchanged, and in the latter case  $T_g$  reduced by 20% when compared to a neat epoxy system at stoichiometric additions of curing agent. Mechanisms that govern the increase in critical stress intensity factors in the case of a SBM (10phr) EPON system @ (14.5phr) mPDA, include crack deflection of spherical/vesicular aggregates and large interfacial zones between two phases, cavitation of PB middle block of the TPE particles and subsequent plastic, matrix deformation caused by these particles. Mechanisms that govern the increase in critical stress intensity factors in the case of a SBM (10phr) EPON system @ (21.5phr) mPDA include plastic void growth/debonding, crack deflection, isolated crack propogation and plastic deformation. Future work includes using TPE modified matrix in fiber-reinforced composites for the aerospace industry which limits any large scale viscosity increase.

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#### CHAPTER 5 MECHANICAL AND MORPHOLOGICAL STUDY OF ABC TYPE THERMOPLASTIC ELASTOMER TOUGHENING OF EPOXY MATRICES

# PART III: EFFECT OF TPE MODIFICATION IN MATRIX AND SIZING ON FRC'S 5.1. ABSTRACT

This chapter addresses the use of thermoplastic elastomers (TPE) as a sizing agent in addition to an aromatic epoxy. The use of TPE's as a modifier in the matrix has been discussed in Chapters 3 and 4. This chapter narrows down the exact amount of modifier to be added to the matrix keeping in mind the ease of processing in the case of a FRC. The performance of the sizing has been evaluated using the single fiber fragmentation test to quantify interfacial shear strength (IFSS). The matrix modification in the composite was compared first. The addition of TPE (1wt%) modifier to the neat epoxy matrix had no effect on the IFSS for a ABC type TPE modifier (SBM) and increased the IFSS by 11% for a ABA type TPE modifier (MAM) addition to the DGEBA based epoxy matrix at stoichiometric addition of curing agent, mpDA. The IFSS increased by  $\sim 27\%$  when an aromatic sizing (4% EPON sizing) was added to a UV-treat AS-4 carbon fiber in a SBM(1wt%) modified EPON matrix at stoichiometric addition of curing agent, mPDA, when compared to a SBM (1%) modified DGEBA matrix with no sizing agent. The IFSS increased by ~25% when a SBM(1wt%)+aromatic epoxy(4wt%) sizing was added to a neat epoxy matrix at stoichiometric addition of curing agent. The addition of sizing agent, aromatic, aliphatic(1wt%)+aromatic(4wt%), were also studied for a SBM(1wt%) modified DGEBA matrix. A FRC was then made with a 4wt% aromatic epoxy sizing, and the 0<sup>o</sup> and 90<sup>o</sup> flexural modulus and strength were compared for a neat epoxy matrix at 14.5phr mPDA addition, against a SBM(1wt%) modified epoxy matrix at 14.5phr mPDA addition. The birefringence pattern for these various combinations were analyzed. Mechanical tests were also performed on the fiber

reinforced composites. A 11% and a 17% increase in flexural modulus and strength respectively was observed in a 0° flexural test for a SBM(1wt%) modified epoxy matrix in comparison to a neat epoxy matrix at 14.5phr mPDA addition. A 8% and a 89% increase in flexural modulus and strength respectively was observed in a 90° flexural test for a SBM(1wt%) modified epoxy matrix in comparison to a neat epoxy matrix. The fracture surfaces of these fibers were analyzed.

#### **5.2. INTRODUCTION**

The properties of fiber reinforced composites is largely dependent on the matrix, the choice of sizing agent and the performance and morphology of the fiber-matrix interphase. With the overall objective of weight reduction or lightweighting in mind, all the aforementioned aspects are gaining increasing attention in both the automobile and the aerospace industries. The fiber imparts the increased modulus and load bearing ability to the composite, the sizing agent promotes adhesion between the fiber and the matrix, and, the matrix aides in load transfer. A better adhesion at the interface enhances delamination resistance in a composite [1], [2]. Strength of unidirectional composites in the off-axis direction could be enhanced by a chemical or a physical bond between the fiber and matrix, a layer called the interhpase [1]. Transcrystallization, macromolecular orientation, strong adsorption and grafting are some of the ways to enhance adhesion at the interphase [3]. The sizing also positively affects the fiber during winding but also affects the mechanical properties based on the amount picked up during impregnation [4]. Polymer composites, with epoxy resins as matrix material are widely used in the aerospace industry owing to their chemical resistance, strength, low shrinkage during cure, ease of processing, solvent resistance and good mechanical properties. The fracture toughness of cured epoxy matrices control damage tolerance and toughness of a composite. Despite these advantages, epoxies are inherently brittle [5]. Brittleness increases with crosslink density and ultimately hampers toughness [6]–[9]. Among several materials used to improve the fracture

toughness of brittle epoxies, rubber materials like Carboxyl Terminated Butadiene Acrylonitrile (CTBN) are the most studied. In this chapter, thermoplastic elastomers (TPE's) were used to toughen the matrix.[6], [9]–[13] [14]. The TPE's, owing to its increased molecular weight increase the viscosity in the material and also increase the ability of the epoxy matrix to absorb energy prior to failure or fracture. The loading study for these TPE materials (SBM, MAM) is reported elsewhere [14]. Chapters 2-4 in this thesis also discuss this in greater detail. The concentration of TPE's for our composite was carefully chosen to be 1-2.5wt% loading of TPE to achieve the best balance of properties. At these concentrations, the flexural modulus, strength and T<sub>g</sub> was unaffected when compared to the neat resin. For a modified system with 2.5wt% SBM, the Notched Izod impact strength and the plane strain fracture toughness (K<sub>Ic</sub>) increased by ~21% and 88% respectively when compared to the neat DGEBA matrix at stoichiometric additions of curing agent.

#### **5.3. CHOICE OF MATRIX**

The processing methods for SBM and MAM materials in an epoxy matrix have been detailed in chapters 2-4 and elsewhere [14]. The use of non-stoichiometric amount of curing agent for low concentration of SBM material has been explored in Chapter 4 and its viscoelastic properties have been shown in Figure 5.1 and Figure 5.2. The T<sub>g</sub> and storage modulus of a modified system with (2.5phr) SBM addition remain unchanged for a non-stoichometric and stoichiometric amount of curing agent added, when compared to the neat matrix.



Figure 5.1. <u>Storage modulus of a SBM (2.5phr) EPON system vs. a Neat EPON system at</u> <u>stoichiometric and non-stoichiometric addition of curing agent</u>



Figure 5.2. <u>Tan δ curves and T<sub>g</sub> of a SBM (2.5phr) EPON system vs. a Neat EPON system</u> <u>at stoichiometric and non-stoichiometric addition of curing agent</u>



Figure 5.3. <u>Storage modulus and Tan δ curves of a SBM (1phr) EPON system vs. a Neat</u> <u>EPON system at stoichiometric addition of curing agent</u>

At 1, 2.5wt% systems, the viscosity increase is small, that the PB-PS exist as separate sphere in the micron range [15]–[17]. Figure 5.3 indicates how a modified SBM(1wt%)-epoxy matrix behaves when compared to a neat matrix. For such a system the storage modulus and  $T_g$  remain unchanged. The gelation point for such a system is very similar to that of the neat matrix as well. This would indicate that such a system could be readily deployed in for a bath during the impregnation phase of a carbon fiber reinforced composite.

Matrix	T <sub>g</sub> (°C)	Flexural Modulus (GPa)	Flexural Strength (MPa)	Notched Izod impact strength (J/m)	K <sub>Ic</sub> Fracture toughness (MPa.m <sup>0.5</sup> )	Viscosity	Appearance
Neat EPON @14.5 mPDA	158	3.2	124.6	23.2	0.75	Baseline	Baseline - Clear
SBM (2.5phr ) EPON @ 14.5 mPDA	158	3.15	123.2	34	>1.41	Gel point- ~No change	~80% Clear
SBM (1phr) EPON @ 14.5	157	3.26	128.3	28.1	1.41	Gel point- ~No change	~90% Clear

Table 5.1. Matrix of choice for FRC's

mPDA

#### 5.4. MECHANICAL PROPERTIES OF FIBER REINFORCED COMPOSITES





Figure 5.4 shows a schematic of a carbon-fiber reinforced composite. The matrix is indeed a critical component of the composite. The carbon fibers were wound through a sizing bath of 4wt% epoxy at 7.5phr mPDA, in N-methyl pyrollidine (NMP) solution at 75°C. This

solution was mixed for 1hr in a hot plate prior to its addition to the sizing tower's bath. The fiber tow then passed through two drying towers, one was maintained at 175°C and the other at 160°C. The fiber tow speed and hence the speed of collection spool was regulated at 35m/h. The sized fibers were dried at 60°C overnight in a convection oven to dry off any residual NMP. The sizing mass was determined by weighing the fibers in the spool before applying sizing, and after overnight drying off of the solvent in an oven. A pre-pregger was then used to use the fibers in a spool and process it into a pre-preg. Two composites and hence you prepreg's were prepared in our case, one with neat epoxy matrix at stoichiometric addition of curing agent, and another with SBM(1wt%) epoxy matrix at stoichiometric addition of curing agent. This mixture was then added to a resin reservoir which is held at 100°C. The 12k tow was then pulled through a slit die of dimensions of 0.220"x0.00675" at 1.5rpm, and then collected on a rotating drum rotation fixed at 28 and the carriage movement fixed at 18m/min. This yielded a pre-preg that was 190cmx30cm tape. The tape was then laid into a 18-ply composite unidirectionally [2], [18].

The pre-preg is now staked on a steel base of dimensions 9"x12" over a vacuum bag. A non-porous Teflon sheet is placed between layers 9 and 10 of the fiber ply. The autoclave layup is as follows: A steel plate, a non-porous teflon sheet, tape to create a cork dam (6"x6"), a sheet of porous teflon , a bleeder sheet and topped off with a non-porous teflon sheet. Tacking tape and another steel plate is placed over the vacuum bag. The vacuum bag with cut holes under bottom plate is sealed with blue tape. A wrinkle-free layup in a sealed vacuum bag is now ready to be autoclaved. The autoclave drew vacuum at 0.82atm during initial ramp to draw out any trapped gases, and thereafter vented to atmospheric pressure. The cycle employed to cure the composite in the autoclave was 2hrs at 75°C and 2 hrs at 125°C with a ramp rate of 3°C/min [18][19]. After the composite was cooled it was cutting using a felker saw blade to samples of appropriate

dimensions based on the ASTM D790 test. Atleast 5 samples for each composition were cut to 114x12.5x3mm in dimension for both the 0° and 90° flexural tests.

A 11% and a 17% increase in flexural modulus and strength respectively was observed in a  $0^{\circ}$  flexural test for a SBM(1wt%) modified epoxy matrix in comparison to a neat epoxy matrix. The fiber reinforced composites with a toughened matrix at low concentrations of TPE addition was compared with a composite with neat epoxy matrix, both at stoichiometric additions of curing agent. To facilitate ease in comparison, both composites were processed under the same set of conditions. Surface treatment also increases the surface energy on the carbon fiber surface. Hence, the AS4 fibers (12k tow) were treated surface treated with Ulltraviolet (UV)-oxygen [19]–[23] and with a 4wt% aromatic epoxy sizing agent with 7.5phr mPDA. Since the processing conditions were same for both composites, any results observed could be correlated directly to the ability of the modified matrix to absorb energy. Figure 5.5 shows the effect of the composite to a 0<sup>o</sup> flexural test, in the longitudinal direction. This test tells us a lot about the fiber properties. This increase could also be attributed to the stiffer fiber-matrix interphase with larger contributions from the matrix interphase interface [1]. Figure 5.5 shows the how the  $0^{\circ}$  flexural modulus and strength for a AS4 (UV-treated) CF with 4% epon sizing, varies for an SBM (1phr) EPON @14.5phr mPDA matrix vs. neat EPON matrix. Figure 5.6 shows the how the 90° flexural modulus and strength for a AS4 (UV-treated) CF with 4% epon sizing, varies for an SBM (1phr) EPON @14.5phr mPDA matrix vs. neat EPON matrix. The longitudinal flexural properties are also insensitive to the fiber-matrix adhesion, which further alludes these increases to the modified matrix [24]. The improvements in strength in the modified matrix  $(0^{\circ})$  could be due to the ability of the interface to suppress interlaminar failure and that of the stiffness is due to the brittle matrix interphase interface. For all the flexure tests conducted in this study, the aspect

ratio was chosen to be about 60. The flexure stress in the outer fibers at the midspan was calculated from Equation (1):

$$\sigma_{\rm b} = \frac{3PS}{2Wt^2}$$

All the curves are fairly linear to failure. The flexural modulus was quite uniform. The flexural modulus was calculated from the load-deflection curves. Without taking into account the machine compliance, the deflection was assumed to be the same as crosshead displacement. From the slope of the load-deflection curves, the flexural modulus was calculated from Equation (2):

$$E_{\rm b} = \frac{S^3 m}{4Wt^3}$$

where S is the span length, m is the slope of the load deflection curve, and W and t are the specimen width and thickness respectively.



Figure 5.5. <u>0° flexural modulus and strength for a AS4 (UV-treated) CF (4% epon sized)</u> with SBM (1phr) EPON @ (14.5phr) mPDA matrix vs. neat EPON matrix



#### Figure 5.6. <u>90° flexural modulus and strength for a AS4 (UV-treated) CF (4% epon sized)</u> with SBM (1phr) EPON @ (14.5phr) mPDA matrix vs. neat EPON matrix

A 8% and a 89% increase in flexural modulus and strength respectively was observed in a 90° flexural test for a SBM(1wt%) modified epoxy matrix in comparison to a neat epoxy matrix. The 90° flexural bending test investigates the properties of a unidirectional composite in the transverse direction. This test is sensitive to the the fiber/matrix adhesion. The increased modulus could be due to the stiffer interphase. With all conditions including the quantity of sizing agent kept constant, the increase in properties could be attributed in part to the ability of the modified matrix to absorb energy from the fracture. This could also indicate that such as system could have increased interfacial shear strength. The increased strength observed in the 90° flexural test indicates that despite the interlaminar failure possessed by these composites due to intermediate IFSS, the increased fracture absorption ability and toughness for the modified matrix is the major reason for the increased properties in the transverse direction. Comparisons of the 0° and 90° flexural tests with various other sizing agents were not made as a part of this study. Although, the effect of various sizing agents on the interfacial shear strength (IFSS) was evaluated in section 5.6.

## 5.5. FRACTOGRAPHY



Figure 5.7. Overall fracture surface: A) SEM of 0°flex – Baseline [AS4 (UV-treated-w/ 4% EPON sizing) with Neat EPON matrix @14.5mPDA] composite vs. B) SEM of 0°flex – [AS4 (UV-treated-w/4% EPON sizing) with SBM (1phr) EPON matrix @14.5mPDA] composite

In this section the fracture surfaces from the transverse (90°) and the longitudinal (0°) tests were examined using using a SEM EVO scanning electron microscope at an acceleration voltage of 3 kV. Samples were coated with a 5 nm layer of tungsten to make the surface conductive for examining the surface.



Figure 5.8. <u>SEM of 0° fracture – interfacial adhesion</u>: A) Baseline [AS4 (UV-treated-w/ 4% EPON sizing) with Neat EPON matrix @14.5mPDA] composite vs. B) Modified [AS4 (UV-treated-w/4% EPON sizing) with SBM (1phr) EPON matrix @14.5mPDA] composite



Figure 5.9. <u>SEM of 0° flex fracture – mechanism:</u> A) Baseline [AS4 (UV-treated-w/ 4% EPON sizing) with Neat EPON matrix @14.5mPDA] composite vs. B) Modified [AS4 (UV-treated-w/4% EPON sizing) with SBM (1phr) EPON matrix @14.5mPDA] composite

Figure 5.7-5.9 shows the morphology from the fracture surface of a 0<sup>o</sup> flexural test for a baseline composite which has a neat epoxy matrix (EPON @14.5phr mPDA) vs. a modified composite with SBM(1wt%)EPON at 14.5phr mPDA. From figure 5.7 it could be inferred that the modified composite definitely shows greater surface roughness than its baseline counterpart. The presence of rough surfaces and more step changes in the plane of crack propogation shows increased plastic deformation, usually when this is observed, yield strength decreases, but in this case it does not. This indicates that there may be other toughening mechanisms coming into play. Figure 5.7A) shows there are 2 modes of failure on this sample; tensile side showing matrix failure and the compressive side showing interfacial failure due to loss of matrix between fibers. The sample did not break into two. Figure 5.7B) on the other hand did break into two halves at maximum load and shows matrix failure due to the tightly held fibers admist the toughened matrix. Figure 5.8 indicates that the fracture surface has a lot of loosely held fibers, and fibers that have been pulled out for the baseline sample (with neat epoxy matrix). This baseline matrix

shows large internal damage in the form of fiber pullout, fiber delamination, a poor ability for the stressed fibers to transfer load, and finally poor load bearing ability of the matrix and its inability to plasticize. For the modified matrix, however, the fibers are intact with the matrix and fibers showing good interfacial adhesion. No loose fibers can be seen, hence these sample had not experienced severe internal damage. The baseline sample with the neat matrix shows an inability of the matrix to hold all fibers together. Figure 5.9 indicates that there is still some matrix pieces adhered to the fibers.



Figure 5.10. <u>Overall 90° flex fracture surface:</u> A) SEM of 90° flex – Baseline [AS4 (UVtreated-w/ 4% EPON sizing) with Neat EPON matrix @14.5mPDA] composite vs. B) SEM of 90° flex – [AS4 (UV-treated-w/4% EPON sizing) with SBM (1phr) EPON matrix @14.5mPDA] composite



Figure 5.11. <u>SEM of 90° flex fracture surface - pullout:</u> A) Baseline [AS4 (UV-treated-w/ 4% EPON sizing) with Neat EPON matrix @14.5mPDA] composite vs. B) Modified [AS4 (UV-treated-w/4% EPON sizing) with SBM(1phr) EPON matrix @14.5mPDA] composite



Figure 5.12. <u>SEM of 90° flex fracture surface – interfacial adhesion</u>: A) Baseline [AS4 (UV-treated-w/ 4% EPON sizing) with Neat EPON matrix @14.5mPDA] composite vs. B) Modified [AS4 (UV-treated-w/4% EPON sizing) with SBM (1phr) EPON matrix @14.5mPDA] composite

Figure 5.10-5.12 shows the morphology from the fracture surface of a 90° flexural test

for a baseline composite which has a neat epoxy matrix (EPON @14.5phr mPDA) vs. a modified

composite with SBM(1wt%)EPON at 14.5phr mPDA. Extensive fiber-matrix separation and

loose fibers can be seen in the baseline sample which indicates poor fiber-matrix properties. The sizing and the "interphase" is the same for both the composites, and hence the load bearing abilities and failure modes and mechanisms of the matrix interphase interface could be the reason for the improved properties in the transverse direction, listed in figure 5.6. the fibers are much more "tightly-packed" by the SBM modified epoxy matrix than the neat epoxy matrix. This can be seen in figure 5.11 and 5.12. Very limited fiber breaks and fiber pulling was observed in the case of the baseline composite. Fiber breakage happens when the IFSS is intermediate, and fiber pulling causes when the fibers to pull away before they could break. No fiber pulling and very limited fiber breakage is observed for the SBM modified matrix. The modified matrix is compatabile with the composite system (with its sizing agent), that very few fibers exist without being covered by matrix material. In the baseline sample interfacial failure can be seen with broken fibers, and in the modified matrix, both matrix failure and interlaminar failure was seen.

#### 5.6. INTERFACIAL SHEAR STRENGTH (IFSS) WITH MODIFIED SIZING AGENTS

Various sizing materials were trialed on AS4 (UV tr.) carbon fibers to improve IFSS and material properties. The AS4(UV-treatment) themselves when used in modified matrices with SBM and MAM at 14.5phr mPDA were compared to a neat epoxy matrix and a non-uV treated fiber in Figure 5.13. It can be seen that the matrix modification with SBM does not adversely affect the IFSS. In the meantime the matrix toughness (K<sub>Ie</sub>) is increased as shown earlier in Chapters 3 and 4, by 90%. Upto a 15% increase in interfacial shear strength (IFSS) was observed in a single fiber fragmentation test (SFFT) with AS4-UV treated carbon fiber at 1wt% MAM addition to the bulk matrix and its debonding characteristics were observed with cross-polarized light. The fiber-matrix IFSS was affected by major failure modes and toughening mechanisms [24]. Figure 5.14 shows the various attempts made to address improvements in the fiber matrix interface. 5.14A) and 5.14B) show the EPON sizing at 4wt% with 7.5phr mpDA.

5.14C) and 5.14D) was sized using an aliphatic epoxy, poly-diglycidyl ether of bisphenol-A [20] [25] in addition to a 4wt% EPON sizing with 7.5phr mpDA. 5.14E) and 5.14F) was sized using the 1wt% SBM in addition to a 4wt% EPON sizing with 7.5phr mPDA. Figure 5.15 shows the IFSS of various composites made using these sizing agents on the carbon fibers, by means of a single fiber fragmentation test (SFFT) [2], [18], [19], [21]–[24]. An optical microscope was used to measure the fiber diameter and was averaged over three points. The SFFT samples, which are similar to a dog bone sample, were then mounted in a tensioning device with a dial gauge extensometer. While extending the tension at certain intervals, fractures were created on the fiber surface. These were evaluated under polarized and non-polarized light. The critical fracture length and interfacial shear strength was calculated when no more fiber breaks/fractures were seen when increasing dial on the gauge extensometer. IFSS was then calculated using Equation (3) [22], [26].

$$\tau = \frac{\delta_f d}{2l_c}; \ l_c = \frac{4l_{\text{average}}}{3} \tag{3}$$

where,

 $\tau$ : Interfacial shear strength [MPa]

d<sub>f</sub>: Fiber tensile strength [MPa]

d: Fiber diameter [m]

lc and laverage : Critical fiber length [m], and average fiber length [m], respectively



Figure 5.13. IFSS of various FRC's



Figure 5.14. <u>Novel sizing materials on AS4(UV tr.) carbon fibers:</u> A), B) (4wt%) EPON sizing; C), D) PDGE (1%), (4wt%) EPON sizing; E), F) SBM (1%), (4wt%) EPON sizing


#### Figure 5.15. Single fiber fragmentation tests (SFFT) on various composites

Figure 5.15 shows the performance of the sizing that has been evaluated using the single fiber fragmentation test to quantify interfacial shear strength (IFSS). Both matrix and fiber sizing was modified and tested through a single fiber fragmentation test (SFFT). The IFSS increased by ~27% when an aromatic sizing (4% EPON sizing at 7.5wt% mPDA) was added to a UV-treated AS-4 carbon fiber in a SBM(1wt%) modified EPON matrix at stoichiometric addition of curing agent, mPDA, when compared to a SBM (1%) modified DGEBA matrix with no sizing agent. The IFSS for a AS-4 UV-treated composite increased by ~25%, when a SBM(1wt%)+aromatic epoxy(4wt%) sizing was added to a neat epoxy matrix at stoichiometric addition of curing agent when compared to a composite with a neat epoxy matrix and no sizing agent . The addition of sizing agent, aliphatic(1wt%)+aromatic(4wt%), were also studied for a SBM(1wt%) modified DGEBA matrix. This sizing agent increased the IFSS by ~14% when compared to an unsized

fiber in a modified epoxy matrix. The explanations to the results obtained above could be addressed via birefringence pattern analysis from the SFFT.



Figure 5.16. <u>AS4(UV treated) CF (no sizing) in SBM(1phr)EPON @ (14.5phr) mPDA</u> <u>composite:</u> A) 50x unpolarized light; B) 20x unpolarized light; C) 20x polarized light; D) 5x polarized light



Figure 5.17. <u>AS4 (UV treated) CF with (4%EPON sizing) in SBM (1phr) EPON @</u> (14.5phr) mPDA composite: A) 50x unpolarized light; B) 20x unpolarized light; C) 20x polarized light; D) 5x polarized light



Figure 5.18. AS4 <u>(UV treated) CF with (PDGE1%, EPON 4% sizing) in SBM (1phr) EPON</u> <u>matrix @ (14.5phr) mPDA composite:</u> A) 50x unpolarized light; B) 20x unpolarized light; C) 20x polarized light; D) 5x polarized light



Figure 5.19. <u>AS4(UV treated) CF with (SBM1%, EPON 4% sizing) Neat EPON matrix @</u> <u>14.5phr mPDA composite:</u> A) 50x unpolarized light; B) 20x unpolarized light; C) 20x polarized light; D) 5x polarized light

Figure 5.16 shows a unsized AS-4 (UV-treated) carbon fiber in a neat epoxy matrix. The composite shows a frictional sliding mechanism and hence low IFSS. The shear failure happened near the fiber surface. This signals low fiber matrix adhesion. This could also be partly due to the fact that there might be some defects on CF surface. The generated interfacial crack would travel fast through such a system without the absence of any toughening mechanism. Also, the debonded fibers do not transfer the load to the matrix. Om The birefringence pattern in Figure 5.17 shows intermediate fiber/matrix adhesion. The modified matrix with SBM (1wt%) showed a failure locus for this system to be a matrix failure showing crack growth into the matrix, with the fiber fracture in a direction perpendicular to the of the interface. This resulted in an interphase of less plasticity [2], [21]. The interfacial crack in Figure 5.18 and 5.19 shows the interfacial crack grows parallel to the fibers. When this happens, the stress is transferred to neighboring less stressed area and arrests the crack, thereby distributing the stress more uniformly. This phenomena occurs for both aliphatic 1wt% + aromatic sizing (4wt%) and TPE sizing (wt%)+aromatic sizing (4wt%) in a SBM modified matrix and a neat matrix respectively. This shows a structurally sound surfaces in both these composites. Both these systems in Figure 5.18 and 5.19 also showed a small crack growth into the matrix indicating a combination of interfacial and matrix failures imparting a slight increase in IFSS. In figures 5-17-5.19, the IFSS is rather higher, and this is indicated when fibers start breaking, and the crack is initiated perpendicular to the fiber axis, thereby increasing the notch sensitivity. This could be called a "brittle failure".

### **5.7. CONCLUSION**

The experimental results dictated that when a SBM (1wt%), EPON (4wt%) sizing agent was used in a neat matrix, the IFSS was increased by 20% for a neat matrix. When an EPON wt% sizing was used in a modified matrix with SBM 1wt% EPON at 14.5phr mPDA, the IFSS increased by 20%. The EPON (4wt%) sized AS4 (UV-treated) CF in a SBM modified matrix

increased the IFSS by 20% when compared to an unsized AS4 (UV-treated fiber) CF was used in a SBM modified matrix processed under similar conditions. The effect of a SBM sizing on a SBM modified matrix was not evaluated and needs to be investigated. Matrix interaction is increased. It could be said that the composites with the higher flexural modulus (upto 11% and 8% in 0° and 90°, respectively), has higher fiber matrix adhesion [19]–[21], [24]. These composites also possess a brittle interphase due to the fact that the sizing agent is offstoichiometry. But this is constant between both the neat and the modified composites. Such an affect shows up more in the transverse flexural test, due to the added influence of interlaminar axial and shear modulii. The flexural strength increase (upto 17% and 89% in 0° and 90°, respectively) does not translate to large IFSS increases, because the failure in these cases were not strictly interfacial [24]. A matrix failure is observed, when the IFSS is too large, which was not observed either. Hence, it can be inferred that the system has intermediate IFSS but excellent matrix toughening properties owing to the TPE modifications. REFERENCES

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#### CHAPTER 6 CONCLUSIONS AND FUTURE WORK

#### **6.1. CONCLUSIONS**

Composite materials are sought after by the aerospace industry for their light weight and strength properties. Polymer composites, with epoxy resins as matrix material, are widely used in the aerospace industry owing to its chemical resistance, strength, low shrinkage during cure, ease of processing, solvent resistance and good mechanical properties. Despite these advantages, epoxies are inherently brittle. Brittleness increases with crosslink density and ultimately hampers toughness. There are several methods identified in literature to toughen epoxy thermoset based composites. Of these several methods, SBM and MBM/MAM modified aromatic amine cured epoxy polymer, was one of them. The MAM-DGEBA/mPDA systems displayed a semibrittle/ductile behavior. PMMA and PBuA are the nanostructuring blocks in MAM/MBM. These self-assembling triblock copolymers in a cured DGEBA/mPDA matrix lead to micro-phase separated structures. The amine-epoxy cure extent dictates morphology and hence mechanical properties. Optimum mixing was required to ensure complete dissolution of the polymers into the epoxy matrix. The addition of TPE to this DGEBA-mPDA system displays the ability to delay crack propagation. The optimum results depend on matrix morphology, interfacial adhesion, choice of cure agent, and are cure schedule dependent. The fracture toughness and impact strength increased upto 190% and 47% respectively, for a (10phr) MAM-EPON system without affecting T<sub>g</sub>. Only a modest 10% decrease in flexural modulus was observed. The microstructure, thermo-mechanical and fracture properties, and toughening mechanisms were identified. Mechanisms that govern the increase in critical stress intensity factors include crack deflection of spherical/vesicular aggregates and large interfacial zones between two phases, cavitation of PB middle block of the TPE particles and subsequent plastic and matrix deformation caused by these particles. The Izod and  $K_{Ic}$  values were identified to be further enhanced by using curing agents like Jeffamine, but was beyond the scope of this study. Molecular weight determination of MAM (~100000 g/mol) would have given us further details on the role of this material in toughening and could be considered as a part of the future work. Variation in butadiene content could also affect toughness values. There are several grades of TPE's available to accomplish this, and could be considered a part of the future work as well.

The choice of processing technique had an influence on the level of dispersion of the TPE in epoxy. This in turn had an effect on mechanical properties and morphology of the TPE-epoxy composite. The level of shear and hence the mixing technique used to process the thermoplastic elastomer had a major impact on the flexural modulus, flexural strength and morphology of the composite. It was initially found that a 4 hour mixing time at 80 °C yielded large 15-20  $\mu$ m size particle sediments in a three-point flexural bending test coupon, and yielded low strength and stiffness value when compared to other processing techniques. A paddle mixing technique with two baffles rotating at 200 rpm also had a similar result. A dispersion with magnetic stirring at 100 rpm for 14 hours resulted in a much better dispersion and eliminated the 15-20  $\mu$ m size agglomeration. The addition of a vacuum mixing step in conjunction with magnetic stirring gave us the best combination of properties

The ductility and crack deflection of the matrix contributed greatly to the toughening of epoxy resin with TPEs. From the FT-IR results, we can conclude that no hydrogen bonding exists between PMMA and DGEBA and that no trans-esterification reaction occurs. Transesterification reaction could also be studied via tracking molar masses, which had not been performed and was out of the scope in this case. The opaqueness of the samples are shown to be obtained as a result of the procure and curing conditions employed because gelation hindered phase separation. This again shows the PBu phase separated particles are fixed during curing and PMMA is merely miscible and non-reactive with the epoxy. When a system has two immiscible components, like in the case of SBM, the formation of microstructures in our case could be attributed to the tandem reaction induced microphase separation in the DGEBA/mPDA matrix. The final morphology of the thermosets is strongly dependent on the competitive kinetics involving curing reaction, phase separation and connectivity of phases. In our case, it has been biomodal spherical structure. Deeper investigation into the curing kinetics, conversion and intercomponent interaction parameters had not been studied.

Changes in solubility parameters affect miscibility in TPE-EPON systems. Therefore, in our case it is judged that the copolymers follow a reaction induced Microphase separation rather than a self-assembly process. Bimodal distribution of TPEs, owing to coagulation of smaller particles into larger particles, is beneficial to toughening. Any slight decrease in flexural strength could be attributed due to SBM addition could be attributed to lack of chemical interfacial adhesion. This could be proved via FTIR, and as it can be seen, no new groups are formed. The decrease in rather low 10% and this could be fixed by synthesizing a functional SBM terpolymer. The addition of SBM to this DGEBA-mPDA system displays the ability to delay crack propagation. The optimum results depend on matrix morphology, interfacial adhesion, choice of cure agent, and are cure schedule dependent. Increases upto ~260% in  $K_{Ic}$  were observed for a SBM(10phr) EPON system at stoichiometric addition of curing agent, and upto 375% was observed for a non-stoichiometric system. In the former case  $T_g$  was unchanged, and in the latter case Tg reduced by 20% when compared to a neat epoxy system at stoichiometric additions of curing agent. Mechanisms that govern the increase in critical stress intensity factors in the case of a SBM(10phr) EPON system @ 14.5phr mPDA, include crack deflection of spherical/vesicular aggregates and large interfacial zones between two phases, cavitation of PB middle block of the TPE particles and subsequent plastic, matrix deformation caused by these particles. Mechanisms that govern the increase in critical stress intensity factors in the case of a SBM(10phr) EPON system @ (21.5phr) mPDA include plastic void growth/debonding, crack deflection, isolated crack propogation and plastic deformation. The plastic deformation zone expands for the SBM(10phr) EPON system @ (21.5phr) mPDA due to the decrease in crosslinkdensity. Future work includes using TPE modified matrix in fiber reinforced composites for the aerospace industry which limits any large scale viscosity increase. Overall, a system with lower crosslink density has been shown to enhance fracture toughness of SBM epoxy composites by 400% by being able to delay crack propagation and was shown via crack displacement experiments conducted. A more pragmatic system readily employable as a matrix has been identified to be SBM(1phr) and SBM(2.5phr) EPON system at (14.5phr) mPDA or (21.5phr) mpDA which gave us the best combination of thermal, mechcanical and viscoelastic properties. The TPE's were also evaluated as sizing agent for a carbon fiber to enhance fiber matrix adhesion. The experimental results dictated that when a SBM(1wt%, EPON4wt%) sizing agent was used in a neat matrix, the IFSS was increased by 20% for a neat matrix. When an EPON sizing was used in a modified matrix with SBM(1phr)EPON at 14.5phr mPDA, the IFSS increased by 20%. The (4wt%) EPON sized AS4 (UV-treated) CF in a SBM modified matrix increased the IFSS by 20% when compared to an unSized AS4 (UV-treated fiber) CF was used in a SBM modified matrix processed under similar conditions. The effect of a SBM sizing on a SBM modified matrix was not evaluated and needs to be investigated. Matrix interaction is increased. It could be said that the composites with the higher flexural modulus (upto 11% and 8% in 0° and 90°, respectively), has higher fiber matrix adhesion. These composites also possess

a brittle interphase due to the fact that the sizing agent is off-stoichiometry. But this is constant between both the neat and the modified composites. Such an affect shows up more in the transverse flexural test, due to the added influence of interlaminar axial and shear modulii. The flexural strength increase (upto 17% and 89% in 0° and 90°, respectively) does not translate to large IFSS increases, because the failure in these cases were not strictly interfacial. A matrix failure is observed, when the IFSS is too large, which was not observed either. Hence the system has intermediate IFSS but excellent matrix toughening properties owing to the TPE modifications. Overall a fiber reinforced composite was produced with intermediate IFSS with a toughened matrix, with a novel sizing agent, with easier processing at both the matrix and the composite level, with enhanced flexural properties at low loadings (1wt%) of SBM.

## **6.2. FUTURE WORK**

At the matrix level:

- Synergistic effects of PDGE (an aliphatic toughening agent) and SBM are not shown at both high and low loading levels of both components
- The PDGE and its network impair to a certain extent the phase separation ability of SBM rubber
- Synergistic effect with GnP and SBM would impart a stiff and tough material
- Trial polyols, which offer a good way to toughen the system without a loss in mechanical properties and T<sub>g</sub>.
- Crosslink density and chemistry is to be studied carefully while using these systems
- To functionalize GnP, reduce agglomeration, improve adhesion, ball Milling of GnP with dry ice with a pre-sonication step with acetic acid, and then refluxed with a mild acid treatment
- · Amine functionalization using aminobenzoic acid and polyphosphoric acid

• <u>Hypothesis</u>: The above steps will increase the oxygen and/or amine content in the edge groups and will provide enhanced bonding as a filler

At the composite level:

- Future work includes using TPE modified matrix in fiber reinforced composites for the aerospace industry
- Attempting to use TPE materials as sizing agents in a TPE modified matrix

Fiber Reinforcement/Sizing	Matrix to be analyzed	Property increase expected
Functionalized GnP (3wt%)-	EPON 828 @(14.5phr) mPDA	+10% increase in toughness
AS4 (UV-treated) CF		
Functionalized GnP (3wt%)-	SBM(1phr) EPON @(14.5phr)	+60% increase in toughness
AS4 (UV-treated) CF	mPDA	+20% increase in IFSS
SBM(1phr) epoxy - AS4	SBM(1phr) EPON @(14.5phr)	+80% increase in toughness
(UV-treated) CF	mPDA	+20% increase in IFSS
SBM(1phr) epoxy - AS4	SBM(2.5phr) EPON	+100% increase in toughness
(UV-treated) CF	@(14.5phr) mPDA	+20% increase in IFSS
EPON 4%sizing in AS4 (UV-	SBM(2.5phr) EPON	+90% increase in toughness
treated) CF	(a)(14.5 phr)  mPDA	+20% increase in IFSS

# Table 6.1: Summary of future work