# FRACTURE BEHAVIOR OF BLOCK COPOLYMER AND GRAPHENE NANOPLATELET MODIFIED EPOXY AND FIBER REINFORCED/EPOXY POLYMER COMPOSITES

By

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#### ABSTRACT

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Glass and carbon fiber reinforced/epoxy polymer composites (GFRPs and CFRPs) have high strength-to-weight and stiffness-to-weight ratios. Thus, GFRPs and CFRPs are used to lightweight aircraft, marine and ground vehicles to reduce transportation energy utilization and cost. However, GFRP and CFRP matrices have a low resistance to crack initiation and propagation; i.e. they have low fracture toughness. Current methods to increase fracture toughness of epoxy and corresponding GFRP and CFRPs often reduce composite mechanical and thermomechanical properties. With the advent of nanotechnology, new methods to improve the fracture toughness and impact properties of composites are now available.

The goal of this research is to identify the fracture behavior and toughening mechanisms of nanoparticle modified epoxy, GFRPs and CFRPs utilizing the triblock copolymer poly(styrene)-block-poly(butadiene)-block-poly(methylmethacrylate) (SBM) and graphene nanoplatelets (GnPs) as toughening agents.

The triblock copolymer SBM was used to toughen the diglycidyl ether of bisphenol-A (DGEBA) resin cured with m-phenylenediamine (mPDA) and corresponding AS4-12k CFRPs. SBM self assembled in epoxy to form nanostructured domains leading to larger increases in fracture toughness,  $K_Q$  (MPa\*m<sup>1/2</sup>) than the traditional, phase separating carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber. Additionally, SBM increased the mode-I fracture toughness,  $G_{Ic}$  (J/m<sup>2</sup>) of CFRPs without corresponding reductions in composite three-point flexural properties and glass transition temperature (T<sub>g</sub>). Fractography of SBM modified epoxy and CFRPs via scanning electron microscopy (SEM) showed that sub 100 nm spherical micelles cavitated to induce void growth and matrix shear yielding toughening mechanisms. Furthermore, SBM did not suppress epoxy T<sub>g</sub>, while CTBN decreased T<sub>g</sub> with both increasing concentration and acrylonitrile content.

Graphene nanoplatelets (GnPs) consist of a few layers of graphene sheets, which are a single atomic layer of sp<sup>2</sup> hybridized carbon atoms arranged in a honeycomb lattice. GnPs have excellent thermal, electrical and mechanical properties and are thus attractive fillers for composite materials.

GnPs with a basal plane diameter of 5  $\mu$ m were incorporated between lamina in GFRPs made via vacuum assisted resin transfer molding (VARTM). At only 0.25 wt%, GnPs improved GFRP flexural strength and G<sub>Ic</sub> by 29 and 25%, respectively. GnPs also improved the low velocity drop weight impact properties of the GFRP laminates. Ultrasonic C-scans and dye penetration experiments on impacted laminates showed that the impact-side damage area decreased with increasing concentration of GnPs, while the back-side damage area increased. The addition of GnPs improved absorption and dissipation of impact energy throughout GFRP laminates.

Additionally, GnPs were investigated as toughening agents in epoxy and corresponding AS4-12k CFRPs. In epoxy and CFRPs, GnPs activate a crack deflection toughening mechanism, resulting in increased fracture surface area and fracture energy. Hybrid GnP/SBM modified epoxy and CFRPs were also investigated. Copyright by NICHOLAS T. KAMAR 2016 Dedicated to my wife Danielle, our daughter Eleanor, my parents, grandparents and Lucy

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# **TABLE OF CONTENTS**

LIST OF TABLES	X
LIST OF FIGURES	. xi
CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW	1
1.1 Motivation	1
1.2 Epoxy polymers	2
1.3 Fracture toughness and linear elastic fracture mechanics (LEFM)	6
1.4 Toughening epoxy	11
1.4.1 Rubber toughening of epoxy	11
1.4.2 Block copolymer modified epoxy	16
1.4.3 Rigid particle toughening of epoxy	24
1.5 GFRPs and CFRPs	30
REFERENCES	34
CHAPTER 2: MICRON AND NANOSTRUCTURED RUBBER TOUGHENED EPOXY: A DIRECT COMPARISON OF MECHANICAL, THERMOMECHANICAL	
AND FRACTURE PROPERTIES	40
Abstract	40
2.1 Introduction	41
2.2 Methods.	47
2.2.1 Materials	47
2.2.2 Production of CTBN and SBM modified epoxy	47
2.2.3 Flexural testing	48
2.2.4 Dynamic mechanical analysis	49
2.2.5 Molecular weight between cross-links	49
2.2.6 Fourier infrared transmission spectroscopy of epoxy and modified epoxy	50
2.2.7 Fracture toughness testing	50
2.2.8 Fractography by scanning electron microscopy	50
2.3 Results and Discussion	51
2.3.1 CTBN modified epoxy: mechanical, fracture and thermomechanical	
properties	51
2.3.2 SBM modified epoxy: mechanical, fracture and thermomechanical	
properties	62
2.3.3 The role of interparticle distance in CTBN and SBM modified epoxy	72
2.3.4 Influence of curative concentration on mechanical, fracture	
and thermomechanical properties of epoxy	75
2.4. Conclusion	83
REFERENCES	85

CHAPTER 3: NANOSCALE TOUGHENING OF CARBON FIBER	
REINFORCED/EPOXY POLYMER COMPOSITES USING A TRIBLOCK	
COPOLYMER	89
Abstract	89
3.1 Introduction	
3.2 Methods	
3.2.1 Composite manufacturing	
3.2.1.1 Fiber sizing	
3.2.1.2 Prepreg and autoclave	
3.2.2 Void volume and fiber volume fraction	
3.2.3 Flexural testing	
3.2.4 Dynamic mechanical analysis	100
3.2.5 Mode-I fracture toughness testing	100
3.2.6 Fractography of CFRPs by scanning electron microscopy	101
3.3 Results and Discussion	102
3.3.1 Summary	102
3.3.2 Fracture toughness	103
3.3.2.1 Mode-I fracture toughness	103
3.3.2.2 Relationship between matrix and composite toughness	106
3.3.3 Flexural properties	109
3.3.4 Thermomechanical properties	115
3.4 Conclusion	117
REFERENCES	118
CHAPTER 4: INTERLAMINAR REINFORCEMENT OF GLASS FIBER/EPO	DXY
POLYMER COMPOSITES WITH GRAPHENE NANOPLATELETS	124
Abstract	124
4.1 Introduction	125
4.2 Methods	128
4.2.1 Materials	128
4.2.2 Coating process and Raman spectroscopy	128
4.2.3 Composite production	129
4.2.4 Composite testing	130
4.2.4.1 Flexural testing	130
4.2.4.2 Mode-I fracture toughness testing	130
4.2.4.3 Low velocity drop weight impact testing	131
4.2.4.4 Dye penetration inspection	132
4.2.4.5 Ultrasonic c-scans	132
4.3 Results and Discussion	133
4.3.1 Dispersion and Raman spectroscopy of graphene nanoplatelets	133
4.3.2 Mechanical and fracture properties of GFRPs	135
4.3.3 Low velocity drop weight impact properties of GFRPs	141
4.4 Conclusion	152
REFERENCES	154

CHAPTER 5: HYBRID GRAPHENE NANOPLATELET (GNP)/TRIBLOCK	
COPOLYMER MODIFIED EPOXY AND CARBON FIBER REINFORCED/EPO	OXY
POLYMER COMPOSITES (CFRPS)	158
Abstract	158
5.1. Introduction	159
5.2 Methods	163
5.2.1 Materials	163
5.2.2 Raman and X-ray photoelectron spectroscopy	163
5.2.3 Production of neat, modified and hybrid modified epoxy	164
5.2.4 Characterization of epoxy	165
5.2.4.1 Flexural testing	165
5.2.4.2 Dynamic mechanical analysis	166
5.2.4.3 Compact tension specimen testing	166
5.2.4.4 Fractography via scanning electron microscopy	167
5.2.5 Composite manufacturing	167
5.2.5.1 Fiber sizing	167
5.2.5.2 Prepreg and autoclave	168
5.2.6 Characterization of CFRPs	169
5.2.6.1 Void volume and fiber volume fraction	169
5.2.6.2 Flexural testing	170
5.2.6.3 Dynamic mechanical analysis	170
5.2.6.4 Mode-I fracture toughness testing	171
5.2.6.5 Fractography via scanning electron microscopy	172
5.3 Results	172
5.3.1 Graphene nanoplatelets and SBM	172
5.3.2 SBM, GnP and SBM/GnP hybrid modified epoxy	176
5.3.3 GnP and SBM modified epoxy: fracture, mechanical and	
thermomechanical properties	179
5.3.4 GnP modified CFRPs: Summary	191
5.3.5 GnP modified CFRPs: fracture, mechanical and thermomechanical	
properties	192
5.4 Conclusions	200
REFERENCES	202
CHAPTER 6: CONCLUSIONS AND FUTURE WORK	207
6.1 Conclusions	207
6.2 Future work	210

# LIST OF TABLES

<b>Table 2.1:</b> Glass transition temperature and the value of the rubbery plateau modulus (G') at $T_a + 40$ °C of neat epoxy and 5–10 and 15 phr CTBNx9 (a) and CTBNx13 (b)
modified epoxy, respectively [9]
<b>Table 2.2:</b> Functional group assignments for spectra shown in Figure 8 for neat DGEBA and 15 phr CTBNx9 modified DGEBA [9]
<b>Table 2.3:</b> Glass transition temperature and the value of the rubbery plateau modulus (G') at $T_g + 40$ °C of and 5, 10 and 15 phr SBM modified epoxy made with 140 and 165 °C pre-cure mixing temperatures, respectively [9]
<b>Table 2.4:</b> Interparticle distance $(D_p)$ and corresponding fracture toughness values for 5,10 and 15 phr CTBN and SBM modified epoxy, respectively [9]74
<b>Table 3.1:</b> Summary of composites including sizing, matrix, fiber volume fraction (FVF) and void content for each panel made in this work       102
<b>Table 4.1:</b> Low velocity impact results for pristine, 0.25 and 1.0 wt% GnP specimenstested at 20, 40, 60 and 80J of impact energy, respectively [21]
<b>Table 5.1:</b> XPS C1s spectrum measured binding energies and corresponding functional groups
Table 5.2: Hansen solubility parameters for acetone, SBM blocks and GnPs [27] and         [28]
<b>Table 5.3:</b> Summary of composites including sizing composition, matrix, fiber volume fraction (FVF) and void content for each panel evaluated in this work
<b>Table 5.4:</b> Average Tg of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs

# LIST OF FIGURES

Figure 1.1: Chemical structures of DGEBA (1a) and mPDA (1b)
<b>Figure 1.2:</b> A description of the rubber toughening mechanisms occurring within the plastic zone of the crack tip (reproduced with permission) [28] 12
<b>Figure 1.3:</b> Fracture toughness of DGEBA of varying epoxy monomer MW cured with DDS (circles) and the same systems containing CTBN (reproduced with permission) [29]
<b>Figure 1.4:</b> Morphology of amphiphilic diblock copolymers in epoxy as a function of the volume fraction of the epoxy miscible block (reproduced with permission) [36]
<b>Figure 1.5:</b> Description of the self assembly of SBM in amine cured DGEBA (reproduced with permission) [37]
Figure 1.6: Chemical structure of a graphene nanoplatelet (GnP)
<b>Figure 1.7:</b> Fracture toughness of nano modified epoxy normalized with respect to the neat epoxy (reproduced with permission) [22]
<b>Figure 1.8:</b> A plot of fiber reinforced composite $G_{Ic}$ versus the corresponding resin $G_{Ic}$ for thermoset, toughened thermoset and thermoplastic modified resin systems (reproduced with permission) [58]
<b>Figure 2.1:</b> Chemical structures of diglycidyl ether of bisphenol-A (DGEBA, n=0.2) (a), m-phenylenediamine (mPDA) (b), carboxyl-terminated butadiene-acrylonitrile (CTBN) (c) and the triblock copolymer poly(styrene)-block-poly(butadiene)-block-poly(methylmethacrylate) (SBM) (d) [9]
<b>Figure 2.2:</b> Flexural strength of neat epoxy and 5, 10 and 15 phr CTBNx9 and CTBNx13 modified epoxy, respectively [9]
<b>Figure 2.3:</b> Flexural modulus of neat epoxy and 5, 10 and 15 phr CTBNx9 and CTBNx13 modified epoxy, respectively [9]
<b>Figure 2.4:</b> Fracture toughness (MPa*m <sup>1/2</sup> ) of neat epoxy and 5, 10 and 15 phr CTBNx9 and CTBNx13 modified epoxy, respectively [9]
<b>Figure 2.5:</b> Scanning electron microscopy (SEM) images of neat epoxy and 5, 10 and 15 phr CTBNx9 (18% acrylonitrile) modified epoxy compact tension specimen fracture surfaces [9]

<b>Figure 2.6:</b> SEM images of 5, 10 and 15 phr CTBNx13 (26% acrylonitrile) modified epoxy compact tension specimen fracture surfaces [9]
<b>Figure 2.7:</b> Storage modulus (G') and Tan $\delta$ as determined by dynamic mechanical analysis (DMA) of neat epoxy and 5, 10 and 15 phr CTBNx9 modified epoxy [9] 58
<b>Figure 2.8:</b> Storage modulus (G') and Tan $\delta$ as determined by dynamic mechanical analysis (DMA) of neat epoxy and 5, 10 and 15 phr CTBNx13 modified epoxy [9] 59
Figure 2.9: FTIR spectra of neat DGEBA (a) and 15 phr CTBNx9 modified DGEBA (b)         [9]       61
<b>Figure 2.10:</b> Flexural strength of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 140 and 165 °C pre-cure mixing temperatures [9]
<b>Figure 2.11:</b> Flexural modulus of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 140 and 165 °C pre-cure mixing temperatures [9]
<b>Figure 2.12:</b> Fracture toughness of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 140 and 165 °C pre-cure mixing temperatures, respectively [9]
<b>Figure 2.13:</b> Scanning electron microscopy (SEM) images of 5, 10 and 15 phr SBM modified epoxy compact tension specimen fracture surfaces. Surfaces are from specimens produced at 140 °C pre-cure mixing temperature [9]
<b>Figure 2.14:</b> Scanning electron microscopy (SEM) images of 5, 10 and 15 phr SBM modified epoxy compact tension specimen fracture surfaces. Surfaces are from specimens produced at 165 °C pre-cure mixing temperature [9]
<b>Figure 2.15:</b> Storage modulus (G') and Tan $\delta$ as determined by dynamic mechanical analysis (DMA) of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 140 °C pre-cure mixing temperature [9]
<b>Figure 2.16:</b> Storage modulus (G') and Tan $\delta$ as determined by dynamic mechanical analysis (DMA) of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 165 °C pre-cure mixing temperature [9]
<b>Figure 2.17:</b> Flexural strength of DGEBA cured with varying concentration of mPDA
<b>Figure 2.18:</b> Flexural modulus of DGEBA cured with varying concentration of mPDA
<b>Figure 2.19:</b> Fracture toughness, $K_Q$ (MPa*m <sup>1/2</sup> ) of DGEBA cured with varying concentration of mPDA

<b>Figure 3.10:</b> Transverse flexural strength (MPa) (a) and modulus (GPa) (b) of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM modified CFRPs
<b>Figure 3.11:</b> Scanning electron micrographs of UVO and UVO-S CFRP longitudinal flexural failure surfaces. Specimens tested at $L/D = 60$
<b>Figure 3.12:</b> Scanning electron micrographs of UVO-S-5, 10 and 15 phr SBM CFRP longitudinal flexural failure surfaces. Specimens were tested at $L/D = 60$
<b>Figure 3.13:</b> Storage modulus G' (MPa) and Tan $\delta$ of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM CFRPs
<b>Figure 3.14:</b> Average glass transition temperature (T <sub>g</sub> ) of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM CFRPs
<b>Figure 4.1:</b> Exfoliated graphene nanoplatelets (GnP) after sonication in 2-isoproponol [21]
Figure 4.2: Raman spectra of GnP M5 before and after sonication in 2-isopropanol [21]
<b>Figure 4.3:</b> Four-point flexural test results for pristine and 0.10, 0.25 and 0.50 wt% GnP samples [21]
Figure 4.4: Flexural strength of pristine and 0.10, 0.25 and 0.50 wt% GnP samples [21]
<b>Figure 4.5:</b> Mode-I fracture toughness (G <sub>Ic</sub> ) results of pristine and 0.25 and 1.0 wt% GnP samples [21]
<b>Figure 4.6:</b> Scanning electron microscopy (SEM) image of a pristine mode-I fracture surface. Image (a) shows a macrovoid and images (b) and (c) are progressively higher magnifications of the void edge, as indicated by the colored boxes [21]
<b>Figure 4.7:</b> Scanning electron microscopy (SEM) image of a mode-I fracture surface of a 0.25 wt% GnP sample. Image (a) shows a typical channel region and image (b) shows GnPs on the fibers [21]
<b>Figure 4.8:</b> Inter-tow region of a 0.25 wt% GnP nanocomposite showing cavitated rubbery adducts and aggregation of GnPs [21]
<b>Figure 4.9:</b> Force-time histories of pristine, 0.25 wt% and 1.0 wt% GnP specimens at 20, 40, 60 and 80J impact energies, respectively [21]
<b>Figure 4.10:</b> Energy-time histories of pristine, 0.25 wt% and 1.0 wt% GnP specimens at 20, 40, 60 and 80J impact energies, respectively [21]

<b>Figure 4.11:</b> Force-deflection histories of pristine, 0.25 wt% and 1.0 wt% GnP specimens at 20, 40, 60 and 80J impact energies, respectively [21] 145
<b>Figure 4.12:</b> Dye-penetration inspection (DPI) images of the impact side (12a) and back side (12b) of nanocomposites with various concentrations of GnP tested at 20, 40, 60 and 80J of impact energy, respectively [21]
<b>Figure 4.13:</b> C-scan images of the impact-side of nanocomposites with 0, 0.25 wt% and 1.0 wt% GnP tested at 20, 40, 60 and 80J of impact energy, respectively [21] 148
<b>Figure 4.14:</b> C-scan images of the back-side of nanocomposites with 0, 0.25 wt% and 1.0 wt% GnP tested at 20, 40, 60 and 80J of impact energy, respectively [21] 149
<b>Figure 4.15:</b> Damage area (mm <sup>2</sup> ) of nanocomposites with 0, 0.25 wt% and 1.0 wt% GnP tested at 20, 40, 60 and 80J of impact energy, respectively [21]
Figure 5.1: Scanning electron micrographs of graphene nanoplatelets       172
Figure 5.2: Raman spectrum of graphene nanoplatelets (GnPs) 173
Figure 5.3: Scanning electron micrographs of GnPs coated with SBM 175
Figure 5.4: Scanning electron micrographs of GnP modified epoxy cross-sections 177
Figure 5.5: Photograph of 3 wt% SBM modified epoxy flexural coupons overlaid onto a laboratory notebook       178
Figure 5.6: Fracture toughness, K <sub>Q</sub> (MPa*m <sup>1/2</sup> ) of neat, SBM, GnP and SBM/GnP hybrid modified epoxy
Figure 5.7: Scanning electron micrographs of CT specimen fracture surfaces
<b>Figure 5.8:</b> Depiction of a toughened epoxy compact tension specimen fracture surface (a) and scanning electron micrographs of slow (A1 and A2) and fast (B1 and B2) fracture regions on 3 wt% SBM modified epoxy compact tension specimen fracture surfaces 184
<b>Figure 5.9:</b> Scanning electron micrographs of GnP modified epoxy compact tension specimen fracture surfaces. Images A1 and A2 show GnP modified epoxy made with the 3RM method, while B and C show GnP and SBM/GnP hybrid modified epoxy made via the son. method, respectively
<b>Figure 5.10:</b> Flexural strength (MPa) of neat, SBM, GnP and SBM/GnP hybrid modified epoxy
Figure 5.11: Flexural modulus (GPa) of neat, SBM, GnP and SBM/GnP hybrid modified epoxy

<b>Figure 5.12:</b> Storage modulus, G' (MPa) as a function of temperature (°C) of neat, SBM, GnP and SBM/GnP hybrid modified epoxy
<b>Figure 5.13:</b> Tan δ as a function of temperature (°C) of neat, SBM and GnP and SBM/GnP hybrid modified epoxy
Figure 5.14: Scanning electron micrographs of UVO-AS4-12k carbon fibers sized with epoxy and GnPs       192
<b>Figure 5.15:</b> Mode-I fracture toughness, G <sub>Ic</sub> (J/m <sup>2</sup> ) of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs
Figure 5.16: Scanning electron micrographs of UVO-S, UVO-S-GnP and UVO-S-GnP         SBM CFRP mode-I fracture surfaces
<b>Figure 5.17:</b> Transverse (90°) flexural strength (MPa) (a) and modulus (GPa) (b) of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs
<b>Figure 5.18:</b> Longitudinal (0°) flexural strength (MPa) (a) and modulus (GPa) (b) of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs
<b>Figure 5.19:</b> Scanning electron micrographs of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRP longitudinal flexural failure surfaces. Specimens were tested at $L/D = 60$
<b>Figure 5.20:</b> Storage modulus, G' (MPa) and Tan δ of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs

## **CHAPTER 1: INTRODUCTION AND LITERATURE REVIEW**

### **1.1 Motivation**

Materials define the age in which we live. Indeed, the periodization of history is sectioned into ages by materials used to make tools at the time: the stone, bronze and iron ages divide the time of civilizations. We are now in the polymer composite age.

A composite is a material resulting from the combination of two or more materials on a macroscopic scale. The composite is formed such that a constituent with superior properties acts as the reinforcement, while another constituent acts to support the reinforcement [1]. Under this definition, composites are ubiquitous. In particular, fiber reinforced polymer composites are of interest as a structural material, since these composites offer high strength-to-weight and stiffness-to-weight ratios. Fibers can be glass or carbon (graphite or aramid) and the polymer supporting the reinforcement can be a thermoplastic or thermoset [1]. Cured epoxy resins have good mechanical, thermal and electrical properties and are thus used as matrix material in advanced, continuous fiber reinforced/epoxy polymer composites (FRPs). Although continuous glass fiber and carbon fiber reinforced/epoxy polymer composites (GFRPs and CFRPs) can have high strength-to-weight and stiffness-to-weight ratios, their epoxy matrices can be brittle. Thus, laminated composites consisting of plies or 'lamina' stacked together to make a composite are susceptible to delamination by crack growth initiated at a defect in the material under an applied load or impact event. Researchers have explored methods to improve GFRP and CFRP fracture and impact properties. Typically, these methods involve incorporation of an additional phase(s) into the composite, which can serve to

activate toughening mechanisms ahead of the crack tip or in the wake of a propagating crack. However, incorporation of an additional phase often detriments FRP mechanical and thermomechanical properties. Therefore, methods to improve GFRP and CFRP fracture and impact properties without corresponding reductions in mechanical and thermal properties should be explored and developed. Additionally, the adhesion between the fiber and the polymer matrix and the interphase that forms between the fiber/matrix interface and the region where the polymer properties match those of the bulk polymer can influence composite mechanical and fracture properties [1], [2], [3], [4], [5] and [6]. Therefore, this dissertation investigates 'nanoengineering' GFRPs and CFRPs in particular composite regions to improve their mechanical, fracture and/or impact properties. Specifically, the composite interphase, polymer matrix and/or interlaminar regions are nanoengineered to better understand the influence of nanoadditives on composite fracture behavior.

The following introductory sections review the chemistry and properties of amine cured epoxies, linear elastic fracture mechanicals (LEFM) for the determination of polymer and composite fracture 'toughness' and the state of the art in toughening epoxy and GFRPs and CFRPs.

## **1.2 Epoxy polymers**

Epoxy polymers have variable chemical structures, good mechanical properties, resistance to solvent attack and high electrical resistivity [7]. A common epoxy resin is diglycidyl ether of bisphenol-A (DGEBA), which is formed by reaction between bisphenol-A and epichlorohydrin under basic conditions. The DGEBA monomer is

shown in **Figure 1a**. For DGEBA monomers, the value of n varies from 0.03 to 10. At n = 0, DGEBA is a solid and n = 0.5 gives a liquid [8]. Values of n greater than 0.5 give an amorphous solid having a glass transition temperature ( $T_g$ ) between 40 and 90 °C [9].



Figure 1.1: Chemical structures of DGEBA (1a) and mPDA (1b).

DGEBA is a *bifunctional* epoxy resin, since the molecule contains two reactive epoxide rings. Tetrafunctional epoxy resins can be synthesized as well, including N,N,N'N'-tetraglycidyl-4'4'-methylene dianiline (TGMDA).

Epoxide rings are strained and reactive towards nucleophilic functional groups. Curing agents containing nucleophilic moieties are reacted with DGEBA under a ring opening mechanism to form a polymer network; a network can form if at least one of the monomers has a functionality greater than 2. Acids and bases can be used to cure epoxy, with basic amines used to form networks with a wide range of properties [7]. For example, m-phenylenediamine (mPDA) shown in **Figure 1b** is tetrafunctional having 4 reactive amine hydrogens. Other amine curatives include aliphatic and cycloaliphatic amines. Due to steric effects, the reactivity of amines with epoxy is influenced by curative structure, with aliphatic amines being the most reactive, followed by cycloaliphatic and aromatic types [7] and [8]. Primary (1°) amines are more reactive than

secondary (2°) amines [7]. Aliphatic amines are used in low T<sub>g</sub> adhesives, whereas aromatic amines are used for FRPs requiring matrices with good mechanical and thermal properties [8].

Gelation and vitrification can occur during cure of epoxy resins and are separate phenomena [7] and [8]. Gelation is observed when the polymer viscosity tends to infinity. The epoxy polymer network forms across the material, resulting in an increase in crosslink density and elastic modulus. On the other hand, vitrification occurs when the  $T_g$  of the network is greater than or equal to the reaction temperature. This can occur in either isothermal or non-isothermal conditions and can happen before or after gelation [7]. Beyond the gel point, epoxy can no longer flow.

Cross-link density can be defined as the inverse of the molecular weight (MW) between cross-links ( $M_c$ ) and has units of MW<sup>-1</sup>.  $M_c$  can be determined by dynamic mechanical analysis (DMA) of the cured epoxy. DMA involves applying an oscillatory strain to a specimen at a particular frequency, amplitude and temperature. Polymers are viscoelastic and thus the response of a polymer to an applied strain lies somewhere between completely elastic and completely viscous behavior [10]. DMA can also be used to determine epoxy  $T_g$  by keeping frequency and amplitude constant while ramping the temperature at a controlled rate, say 3 °C/min.

In DMA, a complex modulus (G\*) can be defined:

$$G^* = G' + iG'',\tag{1}$$

where G' is the storage modulus (Pa) and G'' is the loss modulus (Pa) [10]. G' is the elastic part, and represents recoverable energy. G'' is the viscous part and corresponds to energy lost due to heating. The transition from glassy to rubbery behavior of the polymer will correspond to a sharp decrease in G'. This sharp decrease corresponds to the main transition, where the polymer chains have overcome local barriers to motion. The Tan  $\delta$ , or the damping factor, is defined as the ratio of loss and storage moduli:

$$Tan \,\delta = \frac{G''}{G'}.\tag{2}$$

The temperature corresponding to the maximum value of Tan  $\delta$  is also a measure of T<sub>g</sub>. Other methods to determine the T<sub>g</sub> of epoxy include differential scanning calorimetry (DSC), where the amount of heat required to increase the temperature of a polymer is measured against that of a reference material.

DMA can be used to determine  $M_c$  by the classical theory of rubber elasticity, where the storage modulus in the rubbery plateau is inversely proportional to  $M_c$ :

$$G' = \frac{\rho RT}{M_c}.$$
(3)

In **Equation (3)**,  $\rho$  is the density (kg/cm<sup>3</sup>), R is the ideal gas constant (cm<sup>3</sup>MPa/mol\*K) and T is the absolute temperature (K) [11]. As the M<sub>c</sub> increases, the T<sub>g</sub> of the epoxy decreases [7] and [12].

In this dissertation, a temperature sweep in DMA is used to determine the  $T_g$  of epoxy, modified epoxy and corresponding CFRPs. The  $T_g$  is defined as the temperature

corresponding to the maximum value of Tan  $\delta$ . DMA is also used to determine M<sub>c</sub> for DGEBA cured with varying concentrations of mPDA to determine the role of cross-link density on the mechanical, thermomechanical and fracture properties of DGEBA cured with mPDA. The DGEBA + mPDA system is used throughout this work since it has been used previously as matrix material in composites to study the role of fiber/matrix adhesion on the mechanical and fracture properties of CFRPs [2], [3], [4] and [5]. Moreoever, the difunctional DGEBA resin gives a network with intermediate T<sub>g</sub> (154 °C) that can respond to rubber and particulate toughening. On the other hand, the trifunctional and tetrafunctional epoxy resins are less susceptible to toughening since they have a greater cross-link density and therefore exhibit less shear yielding [13].

### **1.3 Fracture toughness and linear elastic fracture mechanics (LEFM)**

Fracture toughness is defined as a material's ability to resist crack initiation and propagation. In general, polymers are more brittle than ceramics and metals [14]. They also have lower density and greater specific strength than metals, which makes them useful for light-weighting applications. In particular, the cross-linked chemical structure of epoxies gives a brittle material with low fracture toughness [7], [8], [15]. The fracture surfaces of epoxy appear smooth and glassy, with some striations visible due to defects in the material and resulting plastic deformation of the polymer. Crack growth within epoxy can be stable or unstable, showing stick slip behavior indicated by bands on the fracture surface corresponding to crack arrest [15]. For epoxies and toughened epoxies (discussed in **Section 1.5**), the linear elastic fracture mechanics (LEFM) approach is used to measure fracture toughness.

Fracture mechanics is based on the observation that the strength of most solids is based on flaws [16]. There are two approaches to understanding the fracture of solid bodies. The first is based on Griffith's work, which provides a measure of energy required to extend a crack over unit area [14] and [16]. Thus, G<sub>c</sub>, or a critical strain energy release rate is measured. Another approach is based on Irwin's model, which describes the stress intensity at a sharp crack in a linear elastic body [14]. In this view, K<sub>c</sub> is measured, which is the critical value of the stress intensity factor, or K, required for fracture to occur.

The energy balance approach says that during fracture of a body containing a flaw, the work done by an external force F on the body and the elastic energy U stored in the body are converted into a surface free energy,  $\gamma$  [14]. Thus,

$$\frac{\partial}{\partial a}(F-U) \ge \gamma \frac{\partial A}{\partial a},\tag{4}$$

where  $\partial A$  is a growth in crack area resulting from crack growth,  $\partial a$  [14]. Because the fracture of polymers involves fracture of both van der Waals and covalent chemical bonds, the energy required to fracture a polymer is larger than  $2\gamma$ . Also, for a plate of thickness b,  $\partial A = \partial b^* \partial a$ . Thus, we can write

$$\frac{1}{b}\frac{\partial}{\partial a}(F-U) \ge G_c,\tag{5}$$

where  $G_c$  is the strain energy release rate. If a material exhibits Hookean behavior, then a solution to **Equation (5)** can be found by application of linear elastic fracture mechanics (LEFM). For a growing crack in an elastic body, we can write

$$\partial(F - U) = \frac{1}{2}(P\partial\Delta - \Delta\partial P),\tag{6}$$

where P is the applied load, and an infinitesimal crack growth  $\partial a$  causes a change in displacement  $\partial \Delta$  and load  $\partial P$ . We can then combine **Equations (5)** and **(6)**:

$$G_c = \frac{1}{2b} \left( \frac{P \partial \Delta}{\partial a} - \frac{\Delta \partial P}{\partial a} \right). \tag{7}$$

The compliance is defined as the ratio of displacement to the load:

$$C = \frac{\Delta}{P}.$$
(8)

An expression for  $\partial \Delta$  can be written by differentiating **Equation (8)**:

$$\partial \Delta = P \partial C + C \partial P. \tag{9}$$

## Finally, substituting Equation (9) into Equation (7) gives

$$G_c = \frac{P_c^2}{2b} \frac{\partial C}{\partial a},\tag{10}$$

where  $P_c$  is the load corresponding to crack propagation. Thus,  $G_c$  can be determined by measuring both  $P_c$  and  $\frac{\partial c}{\partial a}$  experimentally. This approach is used to calculate  $G_{Ic}$  of unidirectional FRPs, as discussed in ASTM D5528, "the standard test method for mode-I interlaminar fracture toughness of unidirectional fiber-reinforced polymer matrix composites". In this dissertation, ASTM D5528 is used to determine the  $G_{Ic}$  of GFRPs and CFRPs.

Building on Westergaard's work, Iwrin introduced a parameter K called the stress intensity factor [15]. Therefore, the stress intensity at a sharp crack is directly related to the applied load and specimen geometry. Thus,

$$K = f(\sigma, a),\tag{11}$$

where  $\sigma$  is the applied stress and a is the crack length. Iwrin hypothesized that for a crack to grow in a material under mode-I loading conditions, the following condition must be met:

$$K_I \ge K_{Ic},\tag{12}$$

where  $K_{Ic}$  is the critical stress intensity factor and is a material property. The critical stress intensity factor for mode-I crack growth is

$$K_{Ic} = Q\sigma_c a^{1/2},\tag{13}$$

where Q is a function of the specimen geometry. Solutions of the R.H.S. of **Equation** (13) for particular specimen geometries are tabulated in texts and testing standards on the fracture of polymers [14]. This approach is used to calculate  $K_{Ic}$  of polymers and is outlined in ASTM D5045, "the standard test method for plain-strain fracture toughness and strain energy release rate of plastic materials". This research uses the compact tension specimen geometry to determine  $K_{Ic}$  of epoxy and modified epoxy.

Although different descriptions of fracture behavior of brittle solids, the critical strain energy release rate and the critical stress intensity factor are related. For mode-I fracture under plane strain conditions

$$G_{lc} = \frac{K_{lc}^2}{F} (1 - \nu^2), \tag{14}$$

where E is the Young's modulus and v is Poisson's ratio.

This dissertation focuses on the mode-I fracture toughness of epoxies and GFRPs and CFRPs. This is because for most materials and for polymers in particular, the mode-I tensile failure is the most brittle failure mode. Additionally, this work focuses on developing new methods to increase the resistance to crack propagation in laminated composite materials. Delamination in composite materials can result in reduced mechanical and/or impact properties and catastrophic failure of a composite part [17]. Therefore, the delamination resistance of GFRPs and CFRPs, or G<sub>Ic</sub>, is a critical material property.

### **1.4 Toughening epoxy**

Methods to toughen epoxy include blending with reactive liquid rubbers, core-shell rubber particles, block copolymers and rigid particles like nanosilica, carbon nanotubes and graphene nanoplatelets [18], [19], [20], [21] and [22]. Factors that influence the toughness of modified epoxy include matrix ductility, particle concentration, particle size, particle size distribution, interparticle distance and the physical processes induced by the additive upon fracture of the modified epoxy to absorb fracture energy [18]. These processes are called 'toughening mechanisms' and are often identified by optical or scanning electron microscopy (SEM) of a coupon fracture surface.

### 1.4.1 Rubber toughening of epoxy

Incorporation of phase separating rubbers in epoxy is the most extensively studied and commonly used method to toughen epoxy [18]. Sultain and McGarry were the first to investigate rubber toughening of epoxy by blending carboxyl-terminated butadieneacrylonitrile (CTBN) rubber with epoxy resin [23]. Initially, CTBN is miscible with the epoxy at elevated temperatures. During cure of the network, the molecular weight (MW) of the network increases, which reduces the free energy of mixing of the epoxy and the rubber additive [13]. As a result, the CTBN phase separates from the epoxy to form a uniform dispersion of spherical, rubbery adducts with particle diameters on the order of  $1-5 \mu m$ . The microstructure is fixed at gelation. Since then, researchers have explored methods to generate different morphologies to better understand the influence of rubber particle morphology on fracture toughness of rubber modified epoxies. Previously, researchers believed that tearing of the rubber particles in the wake of the crack absorbed

fracture energy [24]. This hypothesis could not explain the fact that more ductile epoxy matrices are more 'toughenable' than more tightly cross-linked networks with higher  $T_g$ [25]. Currently, researchers agree that the rubber particles in an epoxy matrix act as stress concentrators and that during fracture of the rubber modified epoxy, shear bands are formed between particles in the plastic zone of the crack tip [25], [26] and [27]. The rubber particles cavitate ahead of the propagating crack, which induces plastic deformation of the epoxy, inducing void growth and shear yielding toughening mechanisms [27]. Huang and Kinloch's description of the rubber toughening mechanism is shown in **Figure 2** [28].



**Figure 1.2:** A description of the rubber toughening mechanisms occurring within the plastic zone of the crack tip (reproduced with permission) [28].

The model in **Figure 2** shows cavitation of rubber particles within the plastic zone of the crack tip. Shear bands develop by interactions between particles. As a result, the polymer responds by plastically deforming and blunting the propagating crack.

Since the 'matrix shear yielding' toughening mechanism is responsible for the increases in toughness of rubber modified epoxies, the ductility of the epoxy itself governs its 'toughenibility' [13] and [18]. Epoxy polymer networks with higher cross-link densities are more difficult to toughen with phase separating rubbers than networks with lower cross-link densities. Pearson and Yee varied the cross-link density of DGEBA cured with 4,4'-diamino diphenyl sulphone (DDS) by varying epoxy equivalent weight [29]. The G<sub>Ic</sub> of the neat and modified epoxies versus monomer MW is shown in **Figure 3** [29].



**Figure 1.3:** Fracture toughness of DGEBA of varying epoxy monomer MW cured with DDS (circles) and the same systems containing CTBN (reproduced with permission) [29].

The plot shows only a slight increase in epoxy fracture toughness (G<sub>Ic</sub>) with increasing epoxy monomer MW, or decreasing cross-link density. However, addition of CTBN increased the fracture toughness sharply with the increase in monomer MW. They identified the toughening mechanisms in the rubber modified epoxy via scanning electron microscopy (SEM) of the single edge notched (SEN) fracture surfaces as cavitation of the rubbery adducts, followed by void growth and shear yielding of the epoxy. Later, Levita et al. showed that for DDS cured DGEBA, the K<sub>Ic</sub> of the CTBN modified epoxy decreased with increasing cross-link density [30].

Morphological parameters including concentration, particle size distribution and interparticle distance ( $D_p$ ) also play a role in rubber toughening of epoxy. Pearson and Yee investigated the influence of particle size and particle size distribution on the fracture toughness of rubber modified epoxy [31]. They found that methacrylated butadienestyrene (MBS) core shell rubber particles gave larger values in fracture toughness than CTBN modified epoxy. The MBS particle diameter was 0.2 µm, while the CTBN particle size ranged from 1 - 200 µm, depending on the acrylonitrile content within the CTBN additive. They found that when the particle size is smaller than the size of the plastic zone, cavitation, void growth and shear yielding toughening mechanisms are responsible for the increases in fracture toughness. This finding is consistent with the description given by Huang and Kinloch in **Figure 2** above. Larger particles with diameters greater than 20 µm were less effective towards toughening epoxy, since they could not cavitate and only induced a crack bridging toughening mechanism. When combined with smaller 1-2 µm CTBN particles, the larger rubber particles were found to interact with one

another by inducing cavitation of the smaller particles. No synergy in fracture toughness was observed for bimodal particle size distributions.

Azimi et al. examined the fatigue crack propagation (FCP) in MBS and CTBN modified epoxy, respectively [32]. They found that the smaller MBS particles 0.2  $\mu$ m in diameter gave an order of magnitude improvement in FCP over the larger, 1.5  $\mu$ m diameter CTBN particles. They showed that the 0.200  $\mu$ m MBS particles were somewhat aggregated, while the CTBN particles were better distributed throughout the epoxy. Later, Bagheri and Pearson expanded on their earlier work on rubber toughened epoxy to explain the increases in fracture toughness with decreasing interparticle distance (D<sub>p</sub>) [27]. They found that rubber modified epoxies experience a 'brittle-to-tough' transition as the particle size is decreased. A decrease in particle size results in a decrease in D<sub>p</sub>. The observed transition from brittle to ductile behavior does not occur at a particular particle size. Rather, the authors hypothesized, the epoxy in the vicinity of the cavitated particles goes from a plane strain to a plane stress state, which encourages plastic deformation of the matrix. This explains the observation that more ductile epoxies are more amenable to rubber toughening.

The concentration of the rubber additive also has an influence on the fracture toughness of rubber modified epoxy [18], [25], [27] and [32]. Typically, an optimum concentration giving the largest values of fracture toughness is obtained somewhere near 10 phr rubber, but tends to vary depending on the rubber additive type and the epoxy system [18] and [33]. Below the optimum concentration, a linear increase in fracture toughness with increasing concentration of rubber is observed. Beyond the optimum concentration, the fracture toughness of the epoxy remains constant. This plateau effect

occurs in both MBS and CTBN toughened epoxy, where the particle sizes ranged from 0.2 to 0.7  $\mu$ m [25]. For microvoid toughened epoxy, the fracture toughness decreases beyond the optimum concentration, although the cavitation and matrix shear yielding toughening mechanism is operative [25].

Preformed particles, otherwise known as 'core shell particles' (CSPs), consist of a rubbery core surrounded by a glassy shell and have been used to toughen epoxy and CFRPs [33]. CSPs offer a better control of particle size and maintenance of epoxy T<sub>g</sub> since the particles are pre-formed and do not phase separate upon cure of the epoxy matrix [19] and [33]. CSPs cavitate and induce void growth and matrix shear yielding toughening mechanisms in epoxy [33]. However, some authors have shown that pullout and matrix shear yielding toughening mechanisms are operative in CSP modified epoxy as well [19].

#### **1.4.2 Block copolymer modified epoxy**

Another method to increase the fracture toughness of epoxy is by incorporation of a block copolymer to form a nanostructured thermoset. A block copolymer consists of long MW polymer chains of dissimilar chemical functionality bound together by covalent chemical bonds [34]. Diblock copolymers have two distinct blocks, while tribock copolymers have three. Triblock copolymers can be symmetric or asymmetric, with ABA or ABC forms, etc. An amphiphilic diblock copolymer can self assemble in epoxy if one of the blocks is miscible with the epoxy, while the other block is immiscible [35] and [36]. The self assembly of the diblock copolymer can form vesicles and wormlike or spherical micelles,

depending on the volume fraction of the epoxy miscible block [35] and [36]. A description of the transition from spherical micelles to vesicles is shown in **Figure 4**.



**Figure 1.4:** Morphology of amphiphilic diblock copolymers in epoxy as a function of the volume fraction of the epoxy miscible block (reproduced with permission) [36].

Vesicles have a block copolymer shell surrounding an epoxy core. On the other hand, spherical micelles have a core of the epoxy immiscible block surrounded by a more polar, epoxy miscible block. Bates et al. found that for toughening an amine cured epoxy with diblock copolymers, a vesicular morphology gives larger values of  $G_{Ic}$ , as compared to the wormlike or spherical micelle morphologies [36]. They also found that functionalization of the epoxy miscible block with epoxide groups can give better adhesion between the block copolymer and the epoxy. SEM of compact tension specimen fracture surfaces of diblock modified epoxy showed that the nonreactive vesicles debonded from the matrix, while the reactive vesicles remained attached to the epoxy by fibrils that were stretched by the fracture event. For larger interparticle distance/particle

diameter ratios, the reactive block copolymer improved the fracture resistance more so than the nonreactive block copolymers. However, as the ratio of interparticle distance/particle diameter decreased, the differences were negligible. The toughening mechanism was identified as debonding of vesicles, followed by plastic deformation of the matrix. As the as the ratio of interparticle distance/particle diameter decreased, the stress field around the particles may have overlapped, or the epoxy between the particles went from a plane strain to a plain stress state. Regardless, 3-fold increases in G<sub>c</sub> were observed for concentrations of block copolymers at 5 wt%, which is a low loading compared to traditional rubber or thermoplastic modified epoxies.

Toughening epoxy with block copolymers differs from the rubber toughening method described in **Section 1.5.1**. For rubber or thermoplastic modified epoxy, the additive is initially miscible with the epoxy monomers. Cure of the network increases epoxy MW and the rubber or thermoplastic will phase separate from the network. Block copolymers, on the other hand, self assemble in the epoxy prior to cure to form nanostructures with various morphologies as described above. In addition to diblock copolymers, triblock copolymers containing an epoxy miscible block and a soft, rubbery block have been explored as toughening agents for epoxy resins. In particular, the triblock copolymer poly(styrene)-block-poly(butadiene)-block-poly(methylmethacrylate) (SBM) has explored as a toughening agent for epoxy resins [37], [38], [39], [40] and [41].

Ritzenthaler et al. examined the morphological, rheological and fracture properties of SBM modified DGEBA [37] and [38]. They made SBM modified DGEBA using 4,4'-methylenebis-[3-chloro 2,6 diethylaniline] (MCDEA) and 4,4'-

diaminodiphenyl sulfone (DDS) curatives. They found that the MCDEA cured SBM modified DGEBA gave a nanostructured thermoset, while DGEBA cured with DDS resulted in a bicontinuous structure and flocculation of SBM micelles. The former system led to transparent samples, even at concentrations of SBM up to 50 wt%, while the modified epoxy cured with DDS gave opaque specimens. The DGEBA cured with MCDEA is a better solvent for the poly(styrene) (PS) block and thus the extent of cure will be greater prior to microphase separation, as compared to the DDS cured system which encouraged macrophase separation of SBM [37]. The PMMA block within SBM remained miscible in the epoxy throughout the entire cure cycle for the MCDEA cured DGEBA and thus the formation of well dispersed nanoscale micelles. The authors also note that anionically synthesized SBM contains about 1/5<sup>th</sup> SB diblock. Films of 'asreceived' SBM containing the diblock and SBM purified from cyclohexane were cast from THF. Transmission electron microscopy (TEM) of the films showed that the pure SBM formed a cylinder of PS surrounded by a helix of poly(butadiene) (PB). TEM of the SBM containing SB diblocks showed the formation of a lamellar structure, with some regions revealing macrophase separation of the SB diblocks. In the modified epoxy, a spheres-on-spheres, or 'raspberry' morphology was generated, which consisted of PS spheres surrounded by smaller PB spheres. The SBM triblock copolymer was able to incorporate the SB diblocks. The authors proposed a model describing the morphology of the micelles before and after cure of the epoxy network. The model is shown in **Figure 5**.



**Figure 1.5:** Description of the self assembly of SBM in amine cured DGEBA (reproduced with permission) [37].

DMA of the SBM modified DGEBA cured with MCDEA showed a distinct shoulder corresponding to the PMMA and the authors claimed that some of the PMMA chains were expelled from the epoxy, forming a dry brush. The authors also state that the PMMA blocks are long compared to the PB block and thus much of the PMMA blocks remain swelled in the epoxy. As a result, the T<sub>g</sub> of the epoxy decreased by incorporation of SBM. Finally, the authors showed that the SB diblocks alone macrophase separate to form micron scale adducts.

In another report, Ritzenthaler et al. examined the morphology and fracture toughness of SBM modified DGEBA cured with MCDEA [38]. In their report, the SBM was used 'as-received' from the manufacturer and contained about 1/5<sup>th</sup> SB diblocks. The authors found that mixing at 135 °C for 12 hours was required to completely dissolve SBM in DGEBA monomers. At 10 wt% additive, the fracture toughness of SBM modified DGEBA was greater for the SBM containing a larger PB block. These systems resulted in an onion'-like morphology, with PS and PB blocks surrounded by a PMMA shell. However, as the concentration of SBM increased beyond 10 phr, the raspberry
morphology gave larger values of fracture toughness. The spheres-on-spheres morphology was observed for SBM additives containing less PB. These authors did not identify the toughening mechanisms responsible for the increases in fracture toughness.

After Ritzenthaler's work, Rebizant et al. examined the influence of a carboxyl functionalized PMMA block in SBM modified DGEBA cured with different types of curing agents [39]. Their work showed that the MCDEA curative gives a uniform distribution of both neat and functionalized SBM in DGEBA. This result is consistent with the aforementioned work done by Ritzenthaler et al. Rebizant et al. also examined DDS cured DGEBA with both neat and functionalized SBM. They found that carboxyl functionalized SBM gave a better dispersion of SBM micelles. This effect was attributed to ether linkages formed between the carboxyl groups and the epoxy, which were found to form before gelation to prevent macrophase separation. In general, the fracture toughness was increased by incorporation of SBM performed better than neat SBM for a variety of curatives, but did not show any standard deviations on their data. Moreover, these authors did not investigate the fracture surfaces or otherwise identify the toughening mechanism(s) for any of their SBM modified epoxies.

In an effort to better understand the toughening mechanism for SBM modified, lightly cross-linked epoxy, Hydro and Pearson modified DGEBA cured with aminoethylpiperazine (AEP) and piperidine (PIP) with SBM [40]. DGEBA cured with AEP and PIP had M<sub>c</sub> of 725 and 550 g/mol, respectively; these values of M<sub>c</sub> correspond to network Tg's of 109 and 103 °C, respectively. They investigated two SBM additives from Arkema, namely SBM E20 and E40. The SBM E20 had more PB than E40 (the exact

MW of the blocks was not given in their report). At 10 phr, SBM E40 decreased T<sub>g</sub> of AEP and PIP cured DGEBA by 16 and 1 °C, respectively. At the same concentration, E20 SBM decreased the T<sub>g</sub> of AEP and PIP cured DGEBA by 2 and 0 °C, respectively. Thus, it appears that AEP cured DGEBA may be a better solvent for SBM. The SBM modified epoxy with more PB gave lower modulus composites, as evidenced by DMA results. In addition, the SBM E40 with less PB gave significantly smaller improvements in fracture toughness (K<sub>Ic</sub>), as compared to E20, which contained more PB. For each type of block copolymer investigated, the modified DGEBA cured with AEP and PIP gave similar values of fracture toughness. The morphology of the modified DGEBA before and after fracture was investigated by TEM and SEM, respectively. In these epoxy systems, both the E20 and E40 SBM types gave an aggregated morphology of worm-like micelles. Interestingly, the fracture surfaces of the SBM modified epoxy resemble those of amine cured DGEBA containing MBS particles. The SBM appears highly aggregated, with aggregates of SBM surrounded by matrix rich regions. The authors claim that some degree of flocculation of rubbery particles may be beneficial for toughening epoxy. Although difficult to discern, the toughening mechanism appears to be cavitation of the micelles and concomitant matrix shear yielding, or the same as that observed for CTBN modified epoxy.

Chong and Taylor investigated SBM modified DGEBA cured with an accelerated methylhexahydrophtalic acid anhydride [41]. They used E21 and E41 SBM, with E21 containing more PB than E41, but having lower MW than E20 SBM investigated by Hydro and Pearson. The E21 SBM modified DGEBA cured with the anhydride resulted in highly aggregated SBM micelles, while the E41 SBM macrophase separated to form

large particles with a diameter on the order of 1 micron. Similar to the aforementioned work by Hydro and Pearson, the fracture surfaces of the E21 SBM modified epoxy showed matrix rich regions of epoxy and micron scale aggregates of SBM micelles. However, in this case, the authors indicate that the E21 SBM debonds from the matrix to induce void growth. This is difficult to observe on the fracture surfaces, since even at 5 phr SBM E21 it appears a kind of massive phase separation has occurred giving a soft, interconnected SBM phase surrounded by an epoxy phase. In this case, the E21 SBM was not a better toughening agent than CTBN, which forms individual particles that individually cavitate and induce void growth and matrix shear yielding toughening mechanisms. The E41 SBM gave micron scale spheres, which debonded from the matrix upon fracture and did not cavitate to induce plastic void growth of epoxy.

The literature has shown that SBM can increase the fracture toughness of more lightly cross-linked DGEBA. Additionally, macrophase separation of SBM can be prevented by using MCDEA as a curative because this particular system solubilizes the PMMA block during the entire cure cycle. However, this results in decreases in modified epoxy  $T_g$ . Other systems encourage macrophase separation of SBM resulting in micron scale toughening adducts and increases in fracture toughness comparable to those already observed for CTBN modified epoxy. Thus, this dissertation explores SBM as a toughening agent in the DGEBA + mPDA system, which is a classical aerospace grade epoxy with intermediate  $T_g$  and good mechanical properties. The resulting nanostructured thermoset is then used to toughen CFRPs.

### 1.4.3 Rigid particle toughening of epoxy

Rigid, inorganic particles can be incorporated into epoxy to increase fracture toughness. Inorganic particles used to toughen epoxy include nanosilica, nanoclays, carbon nanotubes (CNTs) and graphene nanoplatelets (GnPs) [42], [43], [44] and [45]. In general, the toughening mechanisms identified for rigid fillers in epoxy differ from those observed in rubber modified epoxy. The toughening mechanisms identified for rigid fillers depend on their concentration in the matrix, particle shape, particle size and chemistry.

Johnsen et al. showed that nanosilica particles with a mean particle diameter of 20 nm and a narrow particle size distribution toughen epoxy by debonding and void growth toughening mechanisms [42]. They also discounted crack deflection and crack pinning toughening mechanisms previously attributed to nanosilica modified epoxy. In the crack pinning toughening mechanism, a particle pins a propagating crack, increasing crack length and fracture energy [45]. In the case of nanosilica particles, the particle size ( $\sim 20$ nm) is significantly smaller than the crack opening displacement of epoxy ( $\sim$ 7.5 µm ) and thus the particles are not able to pin a propagating crack. Crack deflection occurs when a propagating crack turns around a particle, increasing crack area and fracture energy [45]. This mechanism results in rough fracture surfaces due to substantial deformation of the polymer in the vicinity of the rigid particles. Nanosilica modified epoxy did not show a rougher fracture surface than neat epoxy. However, debonding of the particles and nanoscale void growth was observed at higher magnification on the fracture surfaces and accounts for the 4 fold increase in fracture toughness of nanosilica modified epoxy at 14.8 wt% filler. On the other hand, the literature shows that GnPs with a basal plane

diameter on the micron scale and a thickness on the nanoscale, toughen epoxy by crack pinning and crack deflection mechanisms at substantially lower concentrations than nanosilica [22], [45] and [46].

GnPs consist of stacks of graphene, which is a single atomic layer of sp<sup>2</sup> hybridized carbon atoms arranged in a honeycomb lattice [47]. Graphene has outstanding mechanical, thermomechanical and electrical properties [48]. However, single layer graphene is difficult to isolate or produce, requiring micromechanical cleavage with scotch tape or growth via chemical vapor deposition [47]. Thus, for composite materials, GnPs present an alternative to single layer graphene. The structure of a GnP is shown in **Figure 6**.



Figure 1.6: Chemical structure of a graphene nanoplatelet (GnP).

The individual graphene sheets stack together via van der Waals interactions. The interlayer d spacing between sheets in pristine GnPs (non-chemically functionalized) is about 0.355 nm, or three times the length of a carbon-carbon bond [45]. The edges of pristine GnPs contain OH, CO and COOH functional groups, while the basal plane is relatively clean containing mostly sp<sup>2</sup> hybridized carbon atoms [48]. Graphene and GnPs

have a modulus of about 1 TP and excellent thermal and electrical properties and thus are attractive fillers for composite materials [49] and [50].

Graphite can also be exfoliated into graphite oxide (GO) by an oxidative process developed from Brodie's, Hummer's and Staudinger's work [48]. This process exfoliates graphite into single and few layer GO, which is hydrophilic in nature due to the large concentration of mostly epoxide and hydroxyl groups on the basal plane, with carbonyl and carboxyl groups at the edges [48]. Thus, GO is readily dispersed in water at concentrations of 1 mg/mL. However, the oxidative process disrupts the sp<sup>2</sup> bonding structure on the basal plane by introducing sp<sup>3</sup> sites. This disruption in sp<sup>2</sup> bonding results in decreased mechanical, thermal and electrical properties that make graphene an attractive material for many applications [48]. Additionally, the conversion of sp<sup>2</sup> bonded carbon atoms to sp<sup>3</sup> on the basal plane causes the GO to appear wrinkled on the nanoscale. GO can be reduced back to RGO, which can have properties similar to those of pristine graphene [48]. Some authors have claimed that for graphene modified epoxy, wrinkled GO can provide a mechanical interlocking between the particles and the matrix [46].

Chemical functionalization of GnPs using traditional organic chemistry methods has been explored as well. Edge selective functionalization can be achieved using the Diels-Alder cycloaddition reaction, where  $4\pi + 2\pi e^{-1}$  combine to form two covalent bonds and a new  $\pi$  bond [51], [52], [53]. The edge selectively functionalized GnPs can improve the strength and stiffness of epoxy at concentrations as low as 2 wt% [53]. Other methods can be used to functionalize GnPs as well [52]. However, methods to

functionalize GnPs are expensive, time consuming and can have low yields. Thus, these methods are not yet attractive for industrial applications.

For composite applications, GnPs need to be well dispersed into a host polymer. Due to their chemical structure, GnPs tend to aggregate via van der Waals interactions and are difficult to disperse. In GnP modified epoxy, researchers use sonication and solution casting, high shear rate mixing or some combination of the two methods to disperse the nanoplatelets. Research has shown that dispersion of GnPs in epoxy is a critical factor governing GnP epoxy nanocomposite properties. Tang et al. compared sonication and ball milling methods to produce GnP modified DGEBA cured with an accelerated 4-methylhexahydrophtalic anhydride [54]. They found that using sonication alone gave 'poorly dispersed' RGO, while the ball milling could more effectively disperse RGO in epoxy. Aggregation of the GnPs was observed using either production method, however. The poorly dispersed RGO increased modified epoxy Tg by 2 °C at 0.2 wt% filler, while the milled RGO modified epoxy showed an 11  $^{\rm o}\rm{C}$  increase in  $T_g$  at the same concentration. The poorly dispersed RGO modified epoxy had epoxy rich and RGO rich regions and thus was not as effective in increasing the epoxy Tg. The dispersed RGO gave larger increases in fracture toughness at each concentration investigated. The poorly dispersed RGO formed aggregates that were less effective towards activating platelet pullout and crack bridging across the fracture surface. In either case, however, poor bonding between the platelets and the matrix was observed on the fracture surfaces. This may explain why the moduli of the more aggregated and well-dispersed RGO modified epoxies were similar.

Other researchers have shown that crack deflection and crack bridging toughening mechanisms are operative for GnP modified epoxy. Crack deflection occurs when the crack is forced to go around the toughening particles, resulting in an increase in fracture surface area and fracture energy [45]. This toughening mechanism results in rough fracture surfaces, since the polymer yields significantly in the vicinity of the toughening agent, often tilting or twisting away from the crack plane. Chatterjee et al. used a three roll mill calendaring technique to disperse GnPs into DGEBA cured with an aromatic diamine [55]. They investigated GnPs with flake sizes of 5 and 25 µm, respectively. Chatterjee et al. found that GnPs with a larger basal plane diameter (25 µm) gave larger values of fracture toughness than smaller GnPs for concentrations ranging from 0.1 to 2 wt% filler. The authors hypothesized that larger GnPs were better able to deflect and bridge a propagating crack. However, no investigation of the fracture surfaces was performed and thus the toughening mechanism was not identified experimentally. They also found that the larger platelets increased the modulus more than the smaller platelets for each concentration, which was attributed to the higher aspect ratio of the GnP with the larger basal plane diameter. Further, the authors coated GnPs with CNTs and found a synergy in modulus at a CNT/GnP ratio of 9/1. The synergy in modulus was attributed to enhanced dispersion of the GnPs by the CNTs, but no microscopy was performed to analyze the state of dispersion in epoxy before or after cure in these hybrid systems. No synergy in fracture toughness was observed between GnPs and CNTs.

To better understand the toughening mechanism in graphene modified epoxy, Chandrasekaran et al. used three-roll milling to make CNT, GnP and thermally reduced GO (TRGO) modified epoxy, respectively [22]. They found that both GnPs and TRGO

gave larger increases in fracture toughness than CNTs at the same loading level (0.1 to 0.5 wt%), while TRGO gave larger increases than GnPs. The CNTs debonded from the epoxy matrix to increase fracture toughness and the GnPs and TRGO activated crack pinning and deflection toughening mechanisms, which were accompanied by bifurcation of the crack tip and separation of platelets, respectively. SEM of mounts of the composites showed that at 0.3 wt%, CNTs and GnPs tended to aggregate, while the TRGO was better dispersed throughout the epoxy.

Chandrasekaran et al. conducted a literature review of nanoclay, CNT and GnP modified epoxy. Their plot of normalized fracture toughness as a function of concentration for nanoclay, CNT and GnP modified epoxy is shown in **Figure 7** [22].



**Figure 1.7:** Fracture toughness of nano modified epoxy normalized with respect to the neat epoxy (reproduced with permission) [22].

Their literature review shows that nanoclay toughens epoxy at higher loading levels than CNTs and GnPs. The CNTs can toughen epoxy to the same degree, but at loading levels one order of magnitude smaller than for nanoclay. GnPs tend to give higher values of fracture toughness across all loading levels investigated.

The literature shows that GnPs can improve the fracture toughness of epoxy at low loading levels. However, it is an open question as to whether there exists a synergy in hybrid GnP and block copolymer modified epoxy. Therefore, **Chapter 5** explores this question by investigating the fracture toughness and fracture behavior of GnP and SBM modified epoxy, as well as their combination in the baseline system used in this dissertation.

#### 1.5 GFRPs and CFRPs

GFRPs and CFRPs can be manufactured using infusion and prepregging/autoclave methods. Infusion methods include resin transfer molding (RTM) and vacuum assisted resin transfer molding (VARTM) whereby a glass or carbon fiber fabric 'pre-form' is infused with epoxy resin and the system is cured in a hot press or convection oven to form a composite. Prepregging involves pulling glass or carbon fibers through an epoxy resin using a dye to 'pre-impregnate' the fiber tows with resin. The prepreg dye is used to control the resin pickup and to ensure complete infiltration of the fiber tow. The resulting prepreg 'tapes' are then laid up, vacuum bagged and autoclaved to make a composite. Although more labor and energy intensive, the prepregging, layup and autoclave method can be used to make high quality composite parts with less than 2% void content used for aerospace applications. Although GFRPs and CFRPs have high strength-to-weight ratios, their matrices can be brittle and have low fracture toughness. Thus, these laminated composites are susceptible to delamination under an applied load or impact event. Researchers have investigated toughened resin systems to improve composite fracture and impact properties [33] and [56]. As one may hypothesize, the toughening mechanisms identified for rubber modified epoxy are also observed for rubber modified GFRPs and CFRPs [57]. However, the toughness improvements in rubber modified epoxy are not completely manifested in FRPs made with the toughened resin system [57] and [58].

Hunston et al. plotted CFRP  $G_{Ic}$  against the corresponding resin  $G_{Ic}$  for composites made using similar manufacturing conditions and for a wide range of fracture toughness values to better understand the relationship between composite and resin fracture toughness [58]. The plot of CFRP  $G_{Ic}$  versus resin  $G_{Ic}$  is shown in **Figure 8**.



**Figure 1.8:** A plot of fiber reinforced composite  $G_{Ic}$  versus the corresponding resin  $G_{Ic}$  for thermoset, toughened thermoset and thermoplastic modified resin systems (reproduced with permission) [58].

This plot shows that for brittle resins, the fracture toughness of the CFRP is larger than the resin alone. The increase in fracture toughness in the composites is due to additional toughening mechanisms like fiber breakage and fiber pullout. However, for tougher resin systems, the rigid fibers constrain plastic deformation of the polymer matrix and only about a third of the resin toughness is transferred to the composite.

More recently, Sprenger et al. made a similar plot for GFRPs and CFRPs manufactured with hybrid CTBN/nanosilica modified epoxy resins [57]. The plot shows the same trends as those observed by Hunston in **Figure 8**. That is, for brittle resins, the  $G_{Ic}$  of the composite is larger than the resin alone. For tougher resins, the gradient is smaller and the data is non linear. A plot of the % increase in composite  $G_{Ic}$  versus resin  $G_{Ic}$  showed that only about 18% of the toughness increases are transferred to the composite for hybrid CTBN/nanosilica systems.

The general trends in fracture toughness for rubber modified thermosets and thermoplastics, as well as for hybrid CTBN/nanosilica modified FRPs have been identified. However, the influence of a nanostructured thermoset formed via self assembling block copolymers in epoxy on the fracture toughness of CFRPs has not yet been determined. Therefore, **Chapter 3** explores SBM at varying loading levels in the epoxy matrix on the mechanical, thermomechanical and fracture properties of CFRPs. The toughening mechanisms are identified via scanning electron microscopy of double cantilever beam fracture surfaces and a transfer factor is determined by comparison between SBM modified bulk resin and CFRP G<sub>Ic</sub> values.

**Chapters 4** and **5** evaluate the influence of GnPs on the properties of GFRPs and CFRPs, respectively. The GnPs are incorporated into the FRPs using a sizing applied to

glass fiber laminates and carbon fiber tows. In particular, the toughening mechanisms induced by the GnPs in the FRPs is explored. Finally, **Chapter 5** investigates the fracture toughness and fracture behavior of hybrid SBM/GnP modified CFRPs.

REFERENCES

#### REFERENCES

- [1] L. T. Drzal, "The interphase in epoxy composites," in *Epoxy Resins and Composites II*, K. Dušek, Ed. Springer Berlin Heidelberg, 1986, pp. 1–32.
- [2] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: I. Inplane and Interlaminar Shear Behavior of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 25, no. 8, pp. 932–957, Aug. 1991.
- [3] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: II. Longitudinal (0°) and Transverse (90°) Tensile and Flexure Behavior of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 25, no. 8, pp. 958–991, Aug. 1991.
- [4] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties. III. Longitudinal (0°) Compressive Properties of Graphite/Epoxy Composites," J. Compos. Mater., vol. 26, no. 3, pp. 310–333, Mar. 1992.
- [5] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: IV. Mode I and Mode II Fracture Toughness of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 26, no. 7, pp. 936–968, Jul. 1992.
- [6] L. T. Drzal and M. Madhukar, "Fibre-matrix adhesion and its relationship to composite mechanical properties," *J. Mater. Sci.*, vol. 28, no. 3, pp. 569–610, Feb. 1993.
- [7] H. Lee and K. Neville, "Handbook of Epoxy Resins," 1967.
- [8] J.-P. Pascault and R. J. J. Williams, "General Concepts about Epoxy Polymers," in *Epoxy Polymers*, J.-P. Pascault and R. J. J. Williams, Eds. Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 1–12.
- [9] J.-P. Pascault and R. J. J. Williams, Epoxy Polymers. John Wiley & Sons, 2009.
- [10] J. D. Ferry, Viscoelastic Properties of Polymers. John Wiley & Sons, 1980.
- [11] G. R. Palmese and R. L. McCullough, "Effect of epoxy-amine stoichiometry on cured resin material properties," *J. Appl. Polym. Sci.*, vol. 46, no. 10, pp. 1863– 1873, Dec. 1992.

- [12] E. Crawford and A. J. Lesser, "The effect of network architecture on the thermal and mechanical behavior of epoxy resins," *J. Polym. Sci. Part B Polym. Phys.*, vol. 36, no. 8, pp. 1371–1382, Jun. 1998.
- [13] D. Ratna and A. K. Banthia, "Rubber toughened epoxy," *Macromol. Res.*, vol. 12, no. 1, pp. 11–21, Feb. 2004.
- [14] A. J. Kinloch and R. J. Young, *Fracture behaviour of polymers*. London : New York: Applied Science Publishers ; Elsevier Science Publishing Co. [distributor], 1983.
- [15] A. J. Kinloch, S. J. Shaw, D. A. Tod, and D. L. Hunston, "Deformation and fracture behaviour of a rubber-toughened epoxy: 1. Microstructure and fracture studies," *Polymer*, vol. 24, no. 10, pp. 1341–1354, Oct. 1983.
- [16] A. A. Griffith, "The Phenomena of Rupture and Flow in Solids," *Philos. Trans. R. Soc. Lond. Math. Phys. Eng. Sci.*, vol. 221, no. 582–593, pp. 163–198, Jan. 1921.
- [17] Y. Tang, L. Ye, Z. Zhang, and K. Friedrich, "Interlaminar fracture toughness and CAI strength of fibre-reinforced composites with nanoparticles – A review," *Compos. Sci. Technol.*, vol. 86, pp. 26–37, Sep. 2013.
- [18] R. Bagheri, B. T. Marouf, and R. A. Pearson, "Rubber-Toughened Epoxies: A Critical Review," *Polym. Rev.*, vol. 49, no. 3, pp. 201–225, Aug. 2009.
- [19] G. Giannakopoulos, K. Masania, and A. C. Taylor, "Toughening of epoxy using core-shell particles," J. Mater. Sci., vol. 46, no. 2, pp. 327–338, Aug. 2010.
- [20] T. H. Hsieh, A. J. Kinloch, K. Masania, A. C. Taylor, and S. Sprenger, "The mechanisms and mechanics of the toughening of epoxy polymers modified with silica nanoparticles," *Polymer*, vol. 51, no. 26, pp. 6284–6294, Dec. 2010.
- [21] Y. Geng, M. Y. Liu, J. Li, X. M. Shi, and J. K. Kim, "Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites," *Compos. Part Appl. Sci. Manuf.*, vol. 39, no. 12, pp. 1876–1883, Dec. 2008.
- [22] S. Chandrasekaran, N. Sato, F. Tölle, R. Mülhaupt, B. Fiedler, and K. Schulte, "Fracture toughness and failure mechanism of graphene based epoxy composites," *Compos. Sci. Technol.*, vol. 97, pp. 90–99, Jun. 2014.
- [23] J. N. Sultan and F. J. McGarry, "Effect of rubber particle size on deformation mechanisms in glassy epoxy," *Polym. Eng. Sci.*, vol. 13, no. 1, pp. 29–34, Jan. 1973.
- [24] S. Kunz-Douglass, P. W. R. Beaumont, and M. F. Ashby, "A model for the toughness of epoxy-rubber particulate composites," *J. Mater. Sci.*, vol. 15, no. 5, pp. 1109–1123, May 1980.

- [25] R. Bagheri and R. A. Pearson, "Role of particle cavitation in rubber-toughened epoxies: 1. Microvoid toughening," *Polymer*, vol. 37, no. 20, pp. 4529–4538, Sep. 1996.
- [26] R. Bagheri and R. A. Pearson, "The use of microvoids to toughen polymers," *Polymer*, vol. 36, no. 25, pp. 4883–4885, 1995.
- [27] R. Bagheri and R. A. Pearson, "Role of particle cavitation in rubber-toughened epoxies: II. Inter-particle distance," *Polymer*, vol. 41, no. 1, pp. 269–276, Jan. 2000.
- [28] Y. Huang and A. J. Kinloch, "Modelling of the toughening mechanisms in rubbermodified epoxy polymers," J. Mater. Sci., vol. 27, no. 10, pp. 2763–2769, Jan. 1992.
- [29] R. A. Pearson and A. F. Yee, "Toughening mechanisms in elastomer-modified epoxies," J. Mater. Sci., vol. 24, no. 7, pp. 2571–2580, Jul. 1989.
- [30] G. Levita, S. D. Petris, A. Marchetti, and A. Lazzeri, "Crosslink density and fracture toughness of epoxy resins," J. Mater. Sci., vol. 26, no. 9, pp. 2348–2352, May 1991.
- [31] R. A. Pearson and A. F. Yee, "Influence of particle size and particle size distribution on toughening mechanisms in rubber-modified epoxies," *J. Mater. Sci.*, vol. 26, no. 14, pp. 3828–3844, Jul. 1991.
- [32] H. R. Azimi, R. A. Pearson, and R. W. Hertzberg, "Fatigue of rubber-modified epoxies: effect of particle size and volume fraction," *J. Mater. Sci.*, vol. 31, no. 14, pp. 3777–3789, Jan. 1996.
- [33] B. S. Hayes and J. C. Seferis, "Modification of thermosetting resins and composites through preformed polymer particles: A review," *Polym. Compos.*, vol. 22, no. 4, pp. 451–467, Aug. 2001.
- [34] A.-V. Ruzette and L. Leibler, "Block copolymers in tomorrow's plastics," Nat. Mater., vol. 4, no. 1, pp. 19–31, Jan. 2005.
- [35] J. M. Dean, P. M. Lipic, R. B. Grubbs, R. F. Cook, and F. S. Bates, "Micellar structure and mechanical properties of block copolymer-modified epoxies," J. Polym. Sci. Part B Polym. Phys., vol. 39, no. 23, pp. 2996–3010, Dec. 2001.
- [36] J. M. Dean, R. B. Grubbs, W. Saad, R. F. Cook, and F. S. Bates, "Mechanical properties of block copolymer vesicle and micelle modified epoxies," *J. Polym. Sci. Part B Polym. Phys.*, vol. 41, no. 20, pp. 2444–2456, Oct. 2003.
- [37] S. Ritzenthaler, F. Court, L. David, E. Girard-Reydet, L. Leibler, and J. P. Pascault, "ABC Triblock Copolymers/Epoxy–Diamine Blends. 1. Keys To Achieve Nanostructured Thermosets," *Macromolecules*, vol. 35, no. 16, pp. 6245–6254, Jul. 2002.

- [38] S. Ritzenthaler, F. Court, E. Girard-Reydet, L. Leibler, and J. P. Pascault, "ABC Triblock Copolymers/Epoxy–Diamine Blends. 2. Parameters Controlling the Morphologies and Properties," *Macromolecules*, vol. 36, no. 1, pp. 118–126, Jan. 2003.
- [39] V. Rebizant, A.-S. Venet, F. Tournilhac, E. Girard-Reydet, C. Navarro, J.-P. Pascault, and L. Leibler, "Chemistry and Mechanical Properties of Epoxy-Based Thermosets Reinforced by Reactive and Nonreactive SBMX Block Copolymers," *Macromolecules*, vol. 37, no. 21, pp. 8017–8027, Oct. 2004.
- [40] R. M. Hydro and R. A. Pearson, "Epoxies toughened with triblock copolymers," J. Polym. Sci. Part B Polym. Phys., vol. 45, no. 12, pp. 1470–1481, Jun. 2007.
- [41] H. M. Chong and A. C. Taylor, "The microstructure and fracture performance of styrene–butadiene–methylmethacrylate block copolymer-modified epoxy polymers," *J. Mater. Sci.*, vol. 48, no. 19, pp. 6762–6777, Jun. 2013.
- [42] B. B. Johnsen, A. J. Kinloch, R. D. Mohammed, A. C. Taylor, and S. Sprenger, "Toughening mechanisms of nanoparticle-modified epoxy polymers," *Polymer*, vol. 48, no. 2, pp. 530–541, Jan. 2007.
- [43] W. Liu, S. V. Hoa, and M. Pugh, "Fracture toughness and water uptake of highperformance epoxy/nanoclay nanocomposites," *Compos. Sci. Technol.*, vol. 65, no. 15–16, pp. 2364–2373, Dec. 2005.
- [44] F. H. Gojny, M. H. G. Wichmann, U. Köpke, B. Fiedler, and K. Schulte, "Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content," *Compos. Sci. Technol.*, vol. 64, no. 15, pp. 2363–2371, Nov. 2004.
- [45] Y. T. Park, Y. Qian, C. Chan, T. Suh, M. G. Nejhad, C. W. Macosko, and A. Stein, "Epoxy Toughening with Low Graphene Loading," *Adv. Funct. Mater.*, vol. 25, no. 4, pp. 575–585, Jan. 2015.
- [46] M. A. Rafiee, J. Rafiee, I. Srivastava, Z. Wang, H. Song, Z.-Z. Yu, and N. Koratkar, "Fracture and Fatigue in Graphene Nanocomposites," *Small*, vol. 6, no. 2, pp. 179– 183, Jan. 2010.
- [47] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nat. Mater.*, vol. 6, no. 3, pp. 183–191, Mar. 2007.
- [48] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide," *Carbon*, vol. 45, no. 7, pp. 1558– 1565, Jun. 2007.

- [49] C. Lee, X. Wei, J. W. Kysar, and J. Hone, "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene," *Science*, vol. 321, no. 5887, pp. 385–388, 2008.
- [50] H. Wu and L. T. Drzal, "Graphene nanoplatelet paper as a light-weight composite with excellent electrical and thermal conductivity and good gas barrier properties," *Carbon*, vol. 50, no. 3, pp. 1135–1145, Mar. 2012.
- [51] C. K. Chua and M. Pumera, "Friedel–Crafts Acylation on Graphene," Chem. Asian J., vol. 7, no. 5, pp. 1009–1012, May 2012.
- [52] C. K. Chua and M. Pumera, "Covalent chemistry on graphene," *Chem. Soc. Rev.*, vol. 42, no. 8, p. 3222, 2013.
- [53] K.-S. Kim, I.-Y. Jeon, S.-N. Ahn, Y.-D. Kwon, and J.-B. Baek, "Edgefunctionalized graphene-like platelets as a co-curing agent and a nanoscale additive to epoxy resin," *J. Mater. Chem.*, vol. 21, no. 20, p. 7337, 2011.
- [54] L.-C. Tang, Y.-J. Wan, D. Yan, Y.-B. Pei, L. Zhao, Y.-B. Li, L.-B. Wu, J.-X. Jiang, and G.-Q. Lai, "The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites," *Carbon*, vol. 60, pp. 16–27, Aug. 2013.
- [55] S. Chatterjee, F. Nafezarefi, N. H. Tai, L. Schlagenhauf, F. A. Nüesch, and B. T. T. Chu, "Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites," *Carbon*, vol. 50, no. 15, pp. 5380–5386, Dec. 2012.
- [56] D. L. Hunston, "Composite interlaminar fracture Effect of matrix fracture energy," *Compos. Technol. Rev.*, pp. 176–180, Jan. 1984.
- [57] S. Sprenger, "Fiber-reinforced composites based on epoxy resins modified with elastomers and surface-modified silica nanoparticles," *J. Mater. Sci.*, vol. 49, no. 6, p. 2391+, Mar. 2014.
- [58] D. Hunston, R. Moulton, N. Johnston, and W. Bascom, "Matrix Resin Effects in Composite Delamination: Mode I Fracture Aspects," in *Toughened Composites*, N. Johnston, Ed. 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959: ASTM International, 1987, pp. 74–74–21.

# CHAPTER 2: MICRON AND NANOSTRUCTURED RUBBER TOUGHENED EPOXY: A DIRECT COMPARISON OF MECHANICAL, THERMOMECHANICAL AND FRACTURE PROPERTIES

#### Abstract

Phase separating rubbers are a well-documented toughening additive to epoxies. However, their effectiveness begins to plateau as the loading approaches 10 phr. To better understand this phenomenon, the mechanical, thermomechanical, fracture properties and toughening mechanisms of the diglycidyl ether of bisphenol-A (DGEBA)/ m-phenylenediamine (mPDA) system ( $T_g = 154$  °C) toughened with carboxyl-terminated butadiene-acrylonitrile (CTBN) and the triblock copolymer poly(styrene)-blockpoly(butadiene)-block-poly(methylmethacrylate) (SBM) were compared directly. The SBM formed a nanostructured thermoset and thus was a more efficient toughening agent than CTBN, which forms micron scale, rubbery inclusions in the epoxy. At 10 phr SBM, the fracture toughness (MPa\* $m^{1/2}$ ) was increased by 220%, while the 10 phr CTBN modified epoxy containing 18 and 26% acrylonitrile showed 60 and 80% increases, respectively. Unlike the CTBN modified epoxy, SBM increased the fracture toughness with increasing concentration. Fracture surface analysis of the SBM modified epoxy via scanning electron microscopy (SEM) identified the toughening mechanism as cavitation of  $\sim 100$  nm spherical micelles, void growth of the epoxy and concomitant matrix shear yielding. While both the CTBN and SBM modified epoxy exhibit similar toughening mechanisms, the nanoscopic SBM particles had an interparticle distance one order of magnitude smaller than that of the CTBN modified epoxy. Thus, a finer dispersion of

nanoscopic, spherical micelles resulted in massive plastic deformation of the epoxy upon activation of cavitation, void growth and matrix shear yielding toughening mechanisms. Finally, dynamic mechanical analysis indicated that SBM did not decrease epoxy  $T_g$ , while the  $T_g$  of CTBN modified epoxy decreased with both increasing concentration and acrylonitrile content.

Additionally, this chapter examines the influence of stoichiometry on the mechanical, fracture and thermomechanical properties of DGEBA cured with mPDA. The influence of cross-link density on the fracture toughness of SBM modified epoxy is determined as well.

Sections 1-3.3 and 4 of this chapter can be found in N. T. Kamar and L. T. Drzal, "Micron and nanostructured rubber toughened epoxy: A direct comparison of mechanical, thermomechanical and fracture properties," Polymer, vol. 92, pp. 114–124, Jun. 2016 (doi:10.1016/j.polymer.2016.03.084).

# 2.1 Introduction

Epoxy resins have high strength and stiffness, good resistance to solvent attack and high electrical resistivity, which makes them useful for potting materials for electronics and as matrices for carbon fiber reinforced polymer composites (CFRPs) [1]. However, cured epoxies are brittle, i.e. they have a low resistance to crack initiation and propagation. Therefore, research over the last 40 years has been done to improve their fracture toughness, which involves the incorporation of additional phase(s) of material to form a composite [2].

Methods to improve the fracture toughness of epoxies include blending with reactive rubbers, incorporation of solid particles, or some combination of the two [2], [3], [4]. The addition of nanosilica and glass microspheres can increase the fracture toughness of epoxy resins by debonding and void growth toughening mechanisms [5]. Also, incorporation of carbon nanotubes (CNTs) and graphene nanoplatelets (GnPs) can increase fracture toughness of epoxy [6], [7], [8]. However, the addition of solid particles to epoxy resins can increase viscosity of the resin, which may complicate infusion based composite production processes [5]. Further, the solid particles could be filtered out by the preform during an infusion, resulting in the formation of an additive concentration gradient in the final part. In any case, rubber toughened epoxies can be used for infusion or prepregging composite production processes, depending on the concentration of rubber additive and its particular influence on the resin viscosity.

Blending epoxy resins with reactive, telechelic rubbers containing butadieneacrylonitrile backbones terminated with carboxyl (CTBN), amine (ATBN) or epoxide (ETBN) functional groups has been studied extensively [2], [3]. This method involves dissolving CTBN into diglycidyl ether of bisphenol-A (DGEBA) epoxy resin prior to the addition of curative [3]. The chemical structures of DGEBA and CTBN are shown in **Figure 1a** and **1c**, respectively.



**Figure 2.1:** Chemical structures of diglycidyl ether of bisphenol-A (DGEBA, n=0.2) (a), m-phenylenediamine (mPDA) (b), carboxyl-terminated butadiene-acrylonitrile (CTBN) (c) and the triblock copolymer poly(styrene)-block-poly(butadiene)-blockpoly(methylmethacrylate) (SBM) (d) [9].

The cure reaction increases epoxy molecular weight (MW) and decreases the thermodynamic miscibility between the rubbery additive and the epoxy resin [3]. The rubber then phase separates to form spherical adducts in the matrix with particle size on the order of 1-5 microns [10]. The most agreed upon toughening mechanism in rubber modified epoxy is 'matrix shear yielding', where cavitation of rubber particles ahead of the crack tip induces void growth and plastic deformation of the matrix [2], [3], [10], [11]. Since this toughening mechanism relies on the ability of the matrix itself to plastically deform, traditional rubber toughening is more effective for lightly cross-linked epoxies than for intermediate or high  $T_g$  epoxy networks [2]. Further, the fracture toughness of rubber modified epoxy versus additive concentration shows a plateau at

about 10 phr additive [2], [10]. It is hypothesized that since increasing the concentration of rubber additive increases the number of particles and particle size per unit area, there is less epoxy matrix available for plastic deformation required to increase fracture toughness [2]. Furthermore, incomplete phase separation of the rubber additive plasticizes the matrix, leading to reductions in thermomechanical properties required for high performance applications.

More recently, block copolymers defined as long MW polymer alloys of chains with dissimilar functionality bound by covalent chemical bonds have also been explored as additives to epoxy resins [12], [13], [14], [15], [16]. In contrast to random block, telechelic rubber additives, block copolymers can self assemble in epoxy resins prior to addition of the curative; cure of the network then fixes the nanostructure [17]. This self assembly mechanism, driven by steric repulsions between blocks of dissimilar chemistry, leads to the formation of a 'nanostructured thermoset' [17]. Among others, spherical micelles, spherical vesicles, spheres-on-spheres and worm-like vesicles with submicron particle size have been observed in epoxy resins [12], [14]. In particular, the ABC triblock copolymer poly(styrene)-block-poly(butadiene)-block-poly(methylmethacrylate) (SBM), which can be synthesized on an industrial scale, has shown promise towards increasing the fracture toughness of cured epoxy [14], [15]. The chemical structure of SBM is shown in **Figure 1d**.

More lightly cross-linked epoxy networks are more amenable to rubber toughening and thus most of the studies on SBM modified epoxy involve toughening lower T<sub>g</sub> networks. Gerard et al. toughened DGEBA cured with Jeffamine T403® (T<sub>g</sub> of 92 °C) using CTBN and SBM at 10 phr [13]. They found that the fracture toughness was

increased more by the addition of SBM (292%) than CTBN (81%). Interestingly, they reported that no plastic deformation was observed for the CTBN/epoxy composites, while the fracture surfaces of SBM/epoxy composites showed plastic deformation. Further, they found that the more interconnected structure observed in the triblock copolymer modified epoxies improved the fracture toughness, as compared to nanostructured thermosets containing individual nanoparticles. Hydro and Pearson used SBM of different molecular weights to toughen DGEBA cured with aminoethyl-piperzine and piperidine (Tg of 109 °C and 103 °C, respectively) [14]. They found that SBM of larger MW increased the fracture toughness by over 300% for both epoxy systems investigated, while SBM containing less poly(butadiene) was less effective for toughening. The toughening mechanism for the SBM modified epoxies was identified as matrix shear yielding, which is the toughening mechanism observed in CTBN modified epoxies [2]. Rebizant et al. toughened DGEBA cured with a variety of curatives with both reactive and non-reactive SBM, where the reactive SBM triblock contained carboxylic acid functionality to form an ether linkage with DGEBA terminal oxirane groups, analogous to toughening with CTBN [15]. Their results showed that the improvement in  $K_{Ic}$  decreased with increasing network cross-link density, or decreasing Tg, in agreement with the literature on rubber toughened epoxy [2]. The influence of SBM additive on the strength and modulus of the SBM modified epoxy was not investigated in this study. More recently, Chong et al. examined the toughening mechanisms in SBM modified DGEBA cured with an accelerated methylhexahydrophthalic acid anhydride, which has a neat Tg of 157 °C [18]. They examined the fracture toughness, fracture surface morphology and toughening mechanisms of Arkema® E20 and E40 SBM modified epoxy. The E20 SBM has a larger

MW and therefore more poly(butadiene) than E40. Their results showed that the SBM E20 phase separated to form micron scale spherical micelles, which tended to flocculate to form an interconnected network in the epoxy, even at concentrations as low as 5 wt%. The fracture surfaces showed the formation of ligaments, indicative of good adhesion between the block copolymer and the epoxy matrix [12]. Further, CTBN led to larger increases in fracture toughness in the same thermoset system (130% at 9 wt% CTBN). Chong *et al.* hypothesized that since the SBM formed a more interconnected structure in this case, the amount of surface area to form voids during fracture was minimized and therefore the triblock additive was less efficient for toughening than CTBN, which forms isolated spheres. On the other hand, the lower MW E40 showed evidence of phase inversion at concentrations greater than 7.5 phr, which led to larger increases in fracture toughness (160% at 10 phr) than the CTBN additive (130 wt% at 9 phr CTBN).

Lightly cross-linked epoxy networks can be toughened more effectively by SBM than CTBN owing to the nanoscopic particles formed from the triblock additive self assembly, which results in more particles present in the matrix over an equivalent surface area to interact with a proceeding crack [2]. However, there are a lack of studies comparing traditional toughening with CTBN and SBM at variety of concentrations and processing conditions for intermediate  $T_g$  networks. Therefore, this work directly compares the mechanical properties, thermomechanical properties, fracture toughness and toughening mechanisms of CTBN and SBM modified epoxy made with the DGEBA + m-phenylenediamine (mPDA) (**Figure 1b**) system ( $T_g = 155$  °C). Furthermore, the influence of curative concentration on the mechanical, thermomechanical and fracture properties, as well as 'toughenibility' of DGEBA + mPDA is explored.

#### 2.2 Methods

#### 2.2.1 Materials

Diglycidyl ether of bisphenol-A (DGEBA) was used as the epoxy resin (n = 0.2) and was from Momentive (Epon 828). The curing agent was m-phenylenediamine (mPDA) from Acros Organics. Emerald Performance Materials supplied the carboxyl-terminated butadiene-acrylonitrile (CTBN). Two types of CTBN were investigated, namely Hypro CTBN 1300x9 (CTBNx9) and Hypro CTBN 1300x13 (CTBNx13), which contain 18 and 26% acrylonitrile, respectively. The triblock copolymer poly(styrene)-blockpoly(butadiene)-block-poly(methylmethacrylate) (SBM) was supplied by Arkema (E21 SBM).

### 2.2.2 Production of CTBN and SBM modified epoxy

To make neat samples, mPDA was melted at 75 °C and mixed by hand with DGEBA at 75 °C for two minutes. The resin mixture was then degassed (27 inHg) at 75 °C for 5 minutes, cast into silicone molds and cured in a convection oven at 75 °C for 2 hours followed by a post cure at 125 °C for 2 hours.

CTBN modified epoxies were made as follows. A measured mass of CTBN was added to DGEBA and the mixture was heated to 140 °C with magnetic stirring for 6 hours. Melted mPDA was then added to the mixture at 75 °C and stirred by hand until a clear solution was obtained. The resin mixture was then degassed (27 inHg) at 75 °C for 5 minutes, cast into silicone molds and cured under the cycle described for the neat specimens. To make SBM modified epoxy, SBM powder was added to DGEBA and placed into a 150 DCA FlackTek mixer for 3 minutes at 3,000 rpm. The mixture was then heated to either 140 °C or 165 °C and stirred for at least 12 hours. The solution was degassed (27 inHg) for 5 minutes at 75 °C or until foaming subsided. Melted mPDA was added to the SBM modified resin mixture and mixed by hand for 1 minute. The reactive mixture was then added to a WhipMix® bowl, placed under vacuum (27 inHg) and mixed with a rotary drill operated paddle for 2-3 minutes. This mixture was then degassed (27 inHg) at 75 °C for 5 minutes, cast into silicone molds and cured under the cycle described for the neat specimens.

Prior to testing, the samples sets were polished with SiC paper on an Abramin Struers polishing wheel to a 1200 grit finish.

## 2.2.3 Flexural testing

Three-point flexural specimens were prepared and tested in accordance with ASTM D-790, "the test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials". At least four samples were tested for each sample type. The nominal thickness and width of the specimens was 3.00 mm and 12.7 mm, respectively. A 16:1 span-to-depth ratio was used with a loading rate determined for each specimen according to the standard. The nominal loading rate was 1.30 mm/min. Values of flexural strength were calculated at 5.0% strain.

#### 2.2.4 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 DMA using single cantilever beam specimens. The sample dimensions (length x width x thickness) were 17.4 mm x 12.4 mm x 3.00 mm. An amplitude of 20  $\mu$ m at a frequency of 1 Hz was applied to the specimens under a temperature ramp (3 °C/min) from 25 to 250 °C. The storage modulus (G'), loss modulus (G'') and the Tan  $\delta$  as a function of temperature were calculated from the data.

# 2.2.5 Molecular weight between cross-links

The density ( $\rho$ ) of Epon 828 cured with 14.5 phr mPDA was measured on the basis of ASTM D792, or the standard test method for density and specific gravity (relative density) of plastics. At least three specimens of each type were measured. The value of the equilibrium storage modulus (G') at T<sub>g</sub> + 40 °C in the rubbery plateau was determined by DMA and **Equation 1** was used to approximate the molecular weight between cross-links (M<sub>c</sub>):

$$Log(G') = 6.5 + \frac{293\rho}{M_c}.$$
 (1)

Since values of G' were larger than  $10^7$  Pa, **Equation (1)** was used to approximate M<sub>c</sub> instead of the theory of rubber elasticity, which tends to under-estimate M<sub>c</sub> for tightly cross-linked networks [19], [20], [21].

#### 2.2.6 Fourier infrared transmission spectroscopy of epoxy and modified epoxy

Potassium bromide (KBr) pellets were made using a Midvale-Heppenstall press and KBr stored in a dry room. The pellets were placed into a Perken Elmer Spectrum One Fourier infrared transmission (FTIR) spectrometer and the background was collected via 32 consecutive scans. One to two drops of epoxy or modified epoxy resin were scraped onto one side of the pellet and spectra were collected using 32 scans.

## 2.2.7 Fracture toughness testing

Compact tension (CT) specimens were prepared and tested in accordance with ASTM D5045, "the standard test method for plane-strain fracture toughness and strain energy release rate of plastic materials". Cured epoxy samples were polished and their dimensions recorded. A sharp pre-crack was generated by placing a fresh razor blade into the molded slot and dropping a stainless steel tube down a guide column onto the razor blade. Care was taken to ensure a level starter crack was formed and the crack length was made such that plane strain conditions were maintained during fracture testing. The nominal specimen thickness was 8.00 mm and the width was 32.0 mm. The CT specimens were then mounted onto a Materials Test System (MTS) 810 using clevis grips and loading pins. The samples were leveled, equal and opposite tensile forces were applied to fracture the specimens and the load-displacement data was recorded for analysis. The loading rate was 10 mm/min. The fracture toughness, K<sub>Q</sub> (MPa\*m<sup>1/2</sup>), was calculated as follows:

$$K_Q = \frac{P_Q}{BW^{1/2}} f(x),$$
(2)

where  $P_Q$  is the maximum load (kN) sustained by the specimen, B is the specimen thickness (cm), W is the specimen width (cm) and f(x) is a geometric form factor:

$$f(x) = \frac{(2+x)(0.886+4.64x-13.32x^2+14.72x^3-5.6x^4)}{(1-x)^{3/2}}$$
(3)

with  $x = \frac{a}{w}$  where a is the total crack length (cm). The crack length 'a' was maintained such that the crack was properly constrained, i.e. the condition  $0.45 \le \frac{a}{w} \le 0.55$  was met for all samples used in the analysis. At least five samples were tested for each sample set, with the pre-crack length being conveniently measured after the testing the samples under mode-I opening.

### 2.2.8 Fractography by scanning electron microscopy

After fracture toughness testing, compact tension specimen fracture surfaces were coated with a 1-3 nm layer of tungsten, mounted onto a scanning electron microscopy (SEM) stage with carbon tape and ground to the stage with copper tape. The stage was then placed into a Carl Zeiss Auriga Dual Column FIB SEM for analysis.

# 2.3 Results and Discussion

**2.3.1 CTBN modified epoxy: mechanical, fracture and thermomechanical properties** The flexural strength and flexural modulus of neat epoxy, 5, 10 and 15 phr CTBNx9 and CTBNx13 modified epoxy are shown in **Figures 2 and 3**, respectively. A statistically significant reduction in flexural strength was not observed until the addition of 10 and 15 phr CTBNx9 (20% decrease) and CTBNx13 (30% decrease). Similarly, the flexural modulus of 10 phr CTBNx9 and x13 modified epoxy decreased by 20%, while the 15 phr CTBNx9 and x13 modified epoxy flexural modulus decreased by 30%. The decreases in flexural strength and modulus of CTBN modified epoxy with increasing rubber additive concentration were due to incomplete phase separation of CTBN and the presence of soft poly(butadiene) in the rubber additive [22]. Although the error bars overlap for the flexural strength and modulus of CTBNx9 and CTBNx13 at 10 and 15 phr, larger values of flexural strength and modulus were observed for CTBNx13 at 5 phr, as compared to CTBNx9. The CTBNx13 additive contains more acrylonitrile than CTBNx9 and thus forms a more rigid toughening adduct resulting in a composite with higher modulus.



**Figure 2.2:** Flexural strength of neat epoxy and 5, 10 and 15 phr CTBNx9 and CTBNx13 modified epoxy, respectively [9].



**Figure 2.3:** Flexural modulus of neat epoxy and 5, 10 and 15 phr CTBNx9 and CTBNx13 modified epoxy, respectively [9].

The fracture toughness of neat epoxy, 5, 10 and 15 phr CTBNx9 and CTBNx13 modified epoxy is shown in **Figure 4**. The 5 phr CTBN modified epoxy showed a 60% increase in fracture toughness. Although larger values of fracture toughness were observed at 10 and 15 phr concentrations for both CTBNx9 and CTBNx13, further increases in concentration did not show statistically significant increases in fracture toughness. Thus, a proportional increase in fracture toughness with increasing concentration of additive was not observed. Other researchers have observed this plateau in the fracture toughness of rubber modified and core-shell rubber modified epoxies [2], [10], [23].



**Figure 2.4:** Fracture toughness (MPa\*m<sup>1/2</sup>) of neat epoxy and 5, 10 and 15 phr CTBNx9 and CTBNx13 modified epoxy, respectively [9].

Representative scanning electron microscopy (SEM) images of the neat epoxy and CTBNx9 modified epoxy fracture surfaces are shown in **Figure 5**, while CTBNx13 modified epoxy fracture surfaces are shown in **Figure 6**. The fracture direction is identified by the white arrow overlaid onto each image (left to right). The neat epoxy fracture surfaces reveal a mostly smooth fracture surface, representative of brittle failure. There is some plastic deformation indicated by striations originating from defects in the epoxy. Increasing the concentration of CTBNx9 in the epoxy tended to increase the width of the stress whitening zone, as shown in **Figures B1**, **C1**, and **D1**. The phase separated rubber particles had good adhesion to the matrix, possibly the result of a pre-reaction between CTBN terminal carboxyl groups and the epoxy monomers prior to addition of the curative (see green arrows). The higher magnification images in **Figure 5 B-3**, **C-3**  and **D-3** showed evidence of rubber particle cavitation followed by void growth of the epoxy, which induced matrix shear yielding to absorb fracture energy. Histograms of the voids on the fracture surface of the CTBNx9 modified epoxies revealed a bimodal void size distribution. At 5 phr CTBNx9, most of the void diameters were within the ranges of 400-450 and 700-750 nm. The void size on the fracture surfaces increased with increasing concentration. At 10 phr CTBNx9, most of the void diameters ranged from 800-850 nm and 2.65-2.70  $\mu$ m. At 15 phr CTBNx9, the void diameters ranged from 1.70-2.00  $\mu$ m to 2.60-2.65  $\mu$ m.



**Figure 2.5:** Scanning electron microscopy (SEM) images of neat epoxy and 5, 10 and 15 phr CTBNx9 (18% acrylonitrile) modified epoxy compact tension specimen fracture surfaces [9].

As was the case for the CTBNx9 modified epoxy, the CTBNx13 modified epoxy fracture surfaces shown in **Figure 6** displayed evidence of rubber particle cavitation, void growth of the epoxy and concomitant matrix shear yielding. The CTBNx13 modified epoxy fracture surfaces showed a smaller void size than those shown in **Figure 5** for the
CTBNx9 modified epoxies. This is because the CTBNx13 contains more acrylonitrile than the CTBNx9 and thus phase separated at a later time in the cure cycle to form smaller rubber particles in the epoxy. Further, the voids on the fracture surfaces of the CTBNx13 modified epoxies remained constant at each concentration investigated, with an average diameter of  $600 \pm 200$  nm.



Figure 2.6: SEM images of 5, 10 and 15 phr CTBNx13 (26% acrylonitrile) modified

epoxy compact tension specimen fracture surfaces [9].

The storage modulus (G') and Tan  $\delta$  as a function of temperature of CTBNx9 and CTBNx13 modified epoxy at 5, 10 and 15 phr are shown in **Figure 7** and **Figure 8**, respectively.



**Figure 2.7:** Storage modulus (G') and Tan  $\delta$  as determined by dynamic mechanical analysis (DMA) of neat epoxy and 5, 10 and 15 phr CTBNx9 modified epoxy [9].



**Figure 2.8:** Storage modulus (G') and Tan  $\delta$  as determined by dynamic mechanical analysis (DMA) of neat epoxy and 5, 10 and 15 phr CTBNx13 modified epoxy [9].

It was observed that the G' shifts to lower values with increasing concentration of CTBN, in agreement with the literature on rubber modified epoxy [24]. At the same concentration of additive, the CTBNx13 containing 26% acrylonitrile shifted the Tan  $\delta$  more than CTBNx9, which contained 18% acrylonitrile. The CTBN containing more acrylonitrile was more miscible with the DGEBA and thus phase separated later in the cure cycle. If the phase separation of CTBN took place later in the cure cycle, then the diffusion of CTBN was slowed due to the increased viscosity of the network resulting in a greater degree of plasticization of the matrix [24]. As shown in **Table 1**, the glass transition temperature (T<sub>g</sub>), defined as the maximum of the Tan  $\delta$ , decreased more for the CTBNx13 modified epoxies than for the CTBNx9 modified epoxies at the same concentration of additive.

**Table 2.1:** Glass transition temperature and the value of the rubbery plateau modulus (G') at  $T_g + 40$  °C of neat epoxy and 5, 10 and 15 phr CTBNx9 (a) and CTBNx13 (b) modified epoxy, respectively [9].

Sample Type	$T_{g}(^{o}C)$	<b>G'</b> $(T_g + 40^{\circ}C)$ (MPa)
Neat epoxy	154.4	38.2
5 phr CTBNx9	153.1	35.5
10 phr CTBNx9	151.9	30.1
15 phr CTBNx9	151.1	26.6
5 phr CTBNx13	152.0	33.3
10 phr CTBNx13	150.5	31.6
15 phr CTBNx13	149.9	29.1

Further, the value of G' in the rubbery plateau at  $T_g + 40^{\circ}$ C decreases with increasing concentration of additive for CTBNx9 and CTBNx13 modified epoxies. The molecular weight between cross-links (M<sub>c</sub>) of the neat cured epoxy was estimated using **Equation 1** of **Section 2.5** above. A value of 325.0 g/mol was calculated, which is in agreement with literature on the Epon 828 + mPDA epoxy system [21]. The M<sub>c</sub> of the rubber modified epoxies produced in this work was not determined using **Equation 1**, since the rubber influences both the network structure and the modulus of the modified epoxy.

The reaction between CTBN and DGEBA, which results in the formation of linear aliphatic ester functional groups, was confirmed by Fourier transform infrared spectroscopy (FTIR) of the reacted CTBN and DGEBA blend. The FTIR spectra of the neat DGEBA and 15 phr CTBNx9 modified epoxy are shown in **Figure 8a** and **8b**, respectively. The peaks and their corresponding functional groups were identified and are shown in **Table 2** [25].



**Figure 2.9:** FTIR spectra of neat DGEBA (a) and 15 phr CTBNx9 modified DGEBA (b) [9].

The presence of the peak at 1738.9 cm<sup>-1</sup> in the CTBNx9 modified epoxy confirms the formation of the linear aliphatic ester by an addition reaction between the CTBN terminal carboxyl hydroxyl group and terminal epoxide rings of DGEBA [26]. Additionally, a decrease in the oxirane peak relative to the hydroxyl, C-H aliphatic and C-H aromatic

peaks in the modified epoxy provides further confirmation of the ring opening reaction. The covalent chemical bonding between CTBN and the epoxy led to good adhesion between the rubbery adducts and the epoxy matrix in the final composites, as shown by the green arrows in **Figures 5** and **6**.

 Table 2.2: Functional group assignments for spectra shown in Figure 8 for neat DGEBA

 and 15 phr CTBNx9 modified DGEBA [9].

<b>Functional Group</b>	Neat DGEBA (cm <sup>-1</sup> )	DGEBA + 15 phr
		$\mathbf{CTBNx9}\ (\mathbf{cm}^{-1})$
C-O-C (oxirane)	915.3	916.4
C=C (1,4	1508.8	1511.7
substituted)		
R-COO-R	-	1738.9
CN	-	2237.1
C-H (aliphatic)	2872.4	2873.6
C-H (aromatic)	3056.3	3054.9
O-H	3508.0	3501.8

#### 2.3.2 SBM modified epoxy: mechanical, fracture and thermomechanical properties

The flexural strength and flexural modulus of neat epoxy, 5, 10 and 15 phr SBM modified epoxy manufactured with 140 and 165 °C pre-cure mixing temperatures, respectively, are shown in **Figures 10** and **11**. At 140 °C pre-cure mixing temperature, a statistically significant reduction in flexural strength was not observed until the addition of 10 (10% decrease) and 15 phr (20% decrease) SBM. At 165 °C pre-cure mixing temperature, reductions in flexural strength at 10 and 15 phr SBM (20%) were also observed. Further, the flexural modulus tended to decrease with increasing concentration of SBM. At 140 °C pre-cure mixing temperature, the flexural modulus was decreased by

20% at 10 and 15 phr SBM. At 165 °C pre-cure mixing temperature, the 10 and 15 phr SBM modified epoxies had a 20 and 30% decrease in flexural modulus, respectively. As was observed for CTBN modified epoxy, the presence of soft and flexible poly(butadiene) in the toughening agent leads to decreases in flexural strength and modulus of SBM modified epoxy.



**Figure 2.10:** Flexural strength of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 140 and 165 °C pre-cure mixing temperatures [9].



**Figure 2.11:** Flexural modulus of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 140 and 165 °C pre-cure mixing temperatures [9].

The fracture toughness (MPa\*m<sup>1/2</sup>) of neat epoxy, 5, 10 and 15 phr SBM modified epoxy manufactured with 140 and 165 °C pre-cure mixing temperatures, respectively, are shown in **Figure 12.** At 5 phr SBM additive, an increase of 80% in fracture toughness was observed. Compared to the results for CTBN modified epoxy shown in **Figure 4**, a concentration of 15 phr CTBNx13 was required to increase the fracture toughness by 90%. Unlike the CTBN modified epoxy, increasing concentration of SBM in the matrix increased the fracture toughness of the composites. At 140 °C precure mixing temperature, the fracture toughness was increased by the addition of 10 phr (140%) and 15 phr (170%) SBM. These increases were not found to be linearly proportional to concentration, but indicated that the optimum, or plateau concentration of SBM in DGEBA cured with mPDA could be larger than 15 phr, or at least three times that observed for the more traditional CTBN toughening agent (section 3.1 above). The fracture toughness of SBM modified epoxy made with 165 °C pre-cure mixing temperatures showed a different trend. In this case, the optimum concentration was 10 phr in the matrix, yielding a 220% increase in toughness. The increase in fracture toughness at 15 phr (using 165 °C pre-cure mixing temperature) was 190%. For specimens processed using a higher pre-cure mixing temperature (165 °C), it may be that the plateau in fracture toughness was closer to that observed for CTBN modified epoxy, albeit with substantially larger increases in fracture toughness at the same concentration.



**Figure 2.12:** Fracture toughness of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 140 and 165 °C pre-cure mixing temperatures, respectively [9].

Compact tension specimen fracture surfaces were investigated using SEM to determine the microstructure and toughening mechanisms of the SBM modified epoxy.

The fracture surfaces of SBM modified epoxy produced at 140 and 165 °C pre-cure mixing temperatures are shown in **Figures 13** and **14**, respectively. The direction of fracture is indicated by the white arrow overlaid onto each image (right to left).



**Figure 2.13:** Scanning electron microscopy (SEM) images of 5, 10 and 15 phr SBM modified epoxy compact tension specimen fracture surfaces. Surfaces are from specimens produced at 140 °C pre-cure mixing temperature [9].

The first column of images in **Figure 13** shows the slow growth fracture regions, or stress whitening zone on the fracture surfaces. The size of the slow growth fracture region increased with increasing concentration of additive, resulting from increased plasticity of

the SBM toughened epoxies. At 5 phr (**Figure 13 A1 - A3**), the SBM self assembled into ~100 nm spherical micelles, which were well dispersed in the matrix. Further, the SBM micelles tended to flocculate, with 2-3 individual micelles aggregating together in the matrix. The toughening mechanism was identified as cavitation of SBM micelles and void growth of epoxy with concomitant matrix shear yielding.

As shown in **Figure 13 B1-B3** and **Figure 13 C1-C3**, increasing the concentration of SBM in the matrix increased the ability of the matrix to plastically deform during fracture. Interestingly, at 10 phr, many of the SBM micelles remained fixed in the matrix and did not undergoe cavitation to induce void growth in the epoxy. The micelle size was also increased to ~200 nm. Regardless, an increase in plasticity and fracture toughness (140%) was observed. Larger 800 nm adducts also formed in the matrix, as shown in **Figure 13 B3**. A similar fracture surface morphology was observed by Hydro and Pearson for Arkema E40 SBM at 10 phr in epoxy (T<sub>g</sub> of 109 °C) [14]. Arkema E40 SBM has a smaller MW than Arkema E21 SBM. In this work, as the concentration of SBM was increased to 15 phr, the SBM formed an interconnected network of ~100 nm spherical micelles. Even though the micelles aggregated, they could individually cavitate ahead of the crack tip to induce void growth and shear yielding of the epoxy.

Representative fracture surfaces of the SBM modified epoxy made with 165 °C pre-cure mixing temperature are shown in **Figure 14**. The first column of the images shows the stress whitening zone, which tended to increase with increasing concentration of SBM. At 5 phr SBM, the 100 nm micelles were well dispersed throughout the matrix. The image in **Figure 14 A-3** reveals evidence of nanocavitation and void growth, which

induced matrix shear yielding to absorb fracture energy. More void growth was observed on the fracture surfaces of the SBM modified epoxy made with a 165 °C pre-cure mixing temperature than at 140 °C. Compared to the 10 phr SBM modified epoxy made with 140 °C pre-cure mixing temperature, the 10 phr SBM modified epoxy made with higher precure mixing temperature revealed more evidence of nanocavitation and void growth on the fracture surface. Thus, greater increases in fracture toughness (MPa\*m<sup>1/2</sup>) were observed (**Figure 12**).



**Figure 2.14:** Scanning electron microscopy (SEM) images of 5, 10 and 15 phr SBM modified epoxy compact tension specimen fracture surfaces. Surfaces are from specimens produced at 165 °C pre-cure mixing temperature [9].

The storage modulus and Tan  $\delta$  of neat epoxy, 5, 10 and 15 phr SBM modified epoxy manufactured with 140 and 165 °C pre-cure mixing temperatures, respectively, are shown in **Figure 15** and **16** 



Figure 2.15: Storage modulus (G') and Tan  $\delta$  as determined by dynamic mechanical analysis (DMA) of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 140 °C pre-cure mixing temperature [9].



**Figure 2.16:** Storage modulus (G') and Tan  $\delta$  as determined by dynamic mechanical analysis (DMA) of neat epoxy and 5, 10 and 15 phr SBM modified epoxy made with 165 <sup>o</sup>C pre-cure mixing temperature [9].

As was observed for the CTBN modified epoxy in **Figures 7** and **8**, the storage modulus before the main transition decreased with increasing concentration of SBM. These decreases are due to the presence of the soft, flexible poly(butadiene) block in the terpolymer. As shown in **Table 3**, the  $T_g$  of SBM modified epoxy does not decrease with increasing concentration of SBM under the processing conditions used in this work.

The SBM terpolymer is designed to form spherical micelles in the epoxy resin prior to cure, with the PMMA blocks forming the corona of the micelles and the poly(styrene) and poly(butadiene) blocks forming the core. Subsequent cure of the triblock/epoxy blend fixes the nanostructure. Previous research has shown that the PMMA blocks may not completely deswell from epoxy networks upon cure. For example, Ritzenthaler *et al.* found that SBM decreased the T<sub>g</sub> of DGEBA cured with 4,4' methylenebis-[3-chloro 2,6

diethylaniline] (MCDEA). They indicated that the epoxy miscible PMMA chains could not completely deswell from the cured network in the regions close to poly(butadiene), which is immiscible with the network [27]. Contrarily, Liu *et al.* found that for DGEBA extended with bisphenol-A (BPA) and cured with 1,1,1-tris(4-hydroxyphenyl) ethane (THPE), the addition of the amphiphilic block copolymer poly-(ethylene-alt-propylene)b-poly(ethylene oxide) (PEP-PEO) did not influence the T<sub>g</sub> for either spherical or wormlike nanorubber morphologies [28]. In this work, the PMMA blocks of the SBM may not completely deswell from the network upon cure. This phenomena does not influence the T<sub>g</sub> up to 10 phr SBM. However, at 15 phr SBM the T<sub>g</sub> increases, which may result from PMMA chains occupying free volume and restricting chain motion during the main transition.

**Table 2.3:** Glass transition temperature and the value of the rubbery plateau modulus (G') at  $T_g + 40$  °C of and 5, 10 and 15 phr SBM modified epoxy made with 140 and 165 °C pre-cure mixing temperatures, respectively [9].

Sample Type	Т <sub>g</sub> (°С)	G' $(T_g + 40^{\circ}C)$ (MPa)
Neat epoxy	154.4	38.2
5 phr SBM (140 °C)	154.1	35.7
10 phr SBM (140 °C)	155.3	32.2
15 phr SBM (140 °C)	155.8	29.3
5 phr SBM (165 °C)	153.8	37.5
10 phr SBM (165 °C)	154.9	32.3
15 phr SBM (165 °C)	157.0	26.0

#### 2.3.3 The role of interparticle distance in CTBN and SBM modified epoxy

The compact tension testing results, the corresponding SEM imaging and the dynamic mechanical analysis (DMA) results in **sections 3.1** and **3.2** clearly establishes SBM as a more efficient toughening agent than CTBN for mPDA cured DGEBA. SBM self assembles on the nanoscale to form spherical micelles in DGEBA, which are fixed in the network by the curing process. Although increasing the concentration of SBM in the DGEBA + mPDA system results in flocculation of the micelles, they can individually cavitate ahead of the crack tip to induce epoxy void growth and shear yielding toughening mechanisms. On the other hand, dissolved CTBN phase separates from the growing DGEBA + mPDA network upon cure to form micron scale, rubbery adducts, which cavitate ahead of the crack tip to induce void growth and matrix shear yielding toughening mechanisms. Thus, the toughening mechanism in both systems is similar, with the SBM modified epoxy having significantly larger fracture toughness values than CTBN modified epoxy at the same loading levels.

To explain the differences in toughness for each type of modified epoxy produced in this work, we measured the center-to-center, nearest neighbor interparticle distance  $(D_p)$  between particles on the fracture surfaces. To make the measurement using imaging software (Image Pro 5.0), it was assumed that the center of the dilated voids on the fracture surfaces represents the central location of the particles. The  $D_p$  for SBM and CTBN modified epoxies and the corresponding measured fracture toughness values are displayed in **Table 4**.

The CTBN modified epoxy showed a  $D_p \sim 1-2 \mu m$ , while the SBM modified epoxy had a  $D_p$  of ~0.1-0.2  $\mu m$ , or an order of magnitude smaller than that for CTBN.

The CTBNx9 phase separated with a bimodal particle size distribution with larger, micron scale particles surrounded by smaller, submicron scale particles. Thus, the scatter on the D<sub>p</sub> measurements for CTBNx9 modified epoxy was large. We also note that increasing the concentration of CTBNx9 from 5 to 15 phr did not increase the fracture toughness. On the other hand, CTBNx13 phase separated to form a uniform particle size distribution, resulting in a sharper void size distribution on the fracture surfaces. The measured D<sub>p</sub> decreased as a function of concentration for CTBNx13 modified epoxy; correspondingly, the fracture toughness increased as the loading level increased.

Sample Type	D <sub>p</sub> (μm)	K <sub>1c</sub> (MPa*m <sup>1/2</sup> )
Neat epoxy		$1.3 \pm 0.1$
5 phr CTBNx9	$1.2 \pm 0.3$	2.1 ± 0.2
10 phr CTBNx9	$2.5 \pm 0.7$	$2.0 \pm 0.2$
15 phr CTBNx9	$2.4 \pm 0.5$	$2.3 \pm 0.2$
5 phr CTBNx13	$1.2 \pm 0.3$	2.1 ± 0.3
10 phr CTBNx13	$1.0 \pm 0.2$	$2.3 \pm 0.1$
15 phr CTBNx13	$0.8 \pm 0.1$	$2.5 \pm 0.1$
5 phr SBM (140 °C)	$0.15 \pm 0.09$	$2.4 \pm 0.1$
10 phr SBM (140 °C)	$0.18\pm0.04$	3.1 ± 0.2
15 phr SBM (140 °C)	$0.12 \pm 0.04$	$3.5 \pm 0.2$
5 phr SBM (165 °C)	$0.21 \pm 0.11$	$2.3 \pm 0.1$
10 phr SBM (165 °C)	$0.15 \pm 0.05$	$4.1 \pm 0.4$
15 phr SBM (165 °C)	$0.14 \pm 0.04$	3.8 ± 0.1

**Table 2.4:** Interparticle distance  $(D_p)$  and corresponding fracture toughness values for 5, 10 and 15 phr CTBN and SBM modified epoxy, respectively [9].

Analysis of the SBM modified epoxy was more difficult, since the nanoscopic spherical micelles tend to flocculate in DGEBA at higher concentrations (10 and 15 phr). However, the flocculated SBM micelles were mostly individually distinguishable via SEM at high magnification and thus the interparticle distance can be measured. Even though the SBM particles were aggregated at higher concentrations in the epoxy (10 and 15 phr), they individually cavitated ahead of the crack tip. The resulting finer dispersion of SBM micelles in the nanostructured thermoset resulted in a decreased  $D_p$  and a better interaction with the proceeding crack, as compared to the larger, micron scale CTBN adducts. Others factors including particle number density and particle/matrix adhesion may also contribute to the fracture toughness in both systems, but are beyond the scope of this work.

## 2.3.4 Influence of curative concentration on mechanical, fracture and

### thermomechanical properties of epoxy

Rubber toughening of epoxy requires plastic deformation of the epoxy itself. The observation that epoxy networks with larger  $M_c$  are more amenable to rubber toughening supports this hypothesis [29]. For amine cured DGEBA, the concentration of curative influences the  $M_c$  and consequently, the mechanical, thermomechanical and fracture properties of the thermoset network as well [21] and [30]. To establish connections between network structure and bulk mechanical, fracture and thermomechanical properties of DGEBA cured with mPDA, the concentration of mPDA was varied and the cured epoxies were analyzed. Finally, SBM was used to modify networks cured with excess mPDA to explore the influence of  $M_c$  on the toughenibility of amine cured DGEBA.

The flexural strength and modulus of DGEBA (n = 0.2) cured with 11, 12.75, 14.5, 18 and 21.5 phr mPDA are shown in **Figures 17** and **18**, respectively. The maximum flexural strength and modulus was observed for networks cured with less-than-stoichiometric amounts of amine, or 11 phr mPDA. Vanlandingham et al. proposed that

off-stoichiometric concentrations of amine curative form a more linear polymer network with lower cross-link density [30]. The more linear network has a higher effective aspect ratio, which provides more efficient load transfer and thus the larger values of flexural strength and modulus. The more linear network forms because the primary amines react faster than the secondary amines, which are by definition bound into the network and more sterically hindered [1]. A related hypothesis called 'antiplasticization' says that the addition of non-reacted species can increase the modulus of epoxy by reducing the space available for chain motion [31].



Figure 2.17: Flexural strength of DGEBA cured with varying concentration of mPDA.



Figure 2.18: Flexural modulus of DGEBA cured with varying concentration of mPDA.

The fracture toughness of DGEBA cured with 11, 12.75, 14.5, 18 and 21.5 phr mPDA is shown in **Figure 19**. Specimens cured with less-than-stoichiometric concentrations of curative did not show statistically significant differences in fracture toughness compared to specimens cured at stoichiometry (14.5 phr mPDA). Compact tension specimen coupons showed brittle failure for those specimens cured at stoichiometry or less-than-stoichiometric concentrations of mPDA. Excess amine, however, increased the fracture toughness of 14.5 phr mPDA cured DGEBA by 25% at 18 phr mPDA and 35% at 21.5 phr mPDA. These increases may result from an increase in a soft phase resulting from the excess amines [30]. Vanlandingham et al. found that the fracture toughness of DGEBA cured with bis (para-amino cyclohexyl) methane (PACM 20) increased as a result of excess amine and hypothesized that the increase in a softer phase in the microstructure could enable more plastic deformation during fracture.



Figure 2.19: Fracture toughness,  $K_Q$  (MPa\*m<sup>1/2</sup>) of DGEBA cured with varying concentration of mPDA

The  $T_g$  and  $M_c$  determined via **Equation 1** for DGEBA cured with 11, 12.75, 14.5, 18 and 21.5 phr mPDA are shown in **Figure 20**. DGEBA cured at stoichiometry shows a maximum in  $T_g$  and a minimum in  $M_c$ . Network polymers with a higher cross-link density will have a higher  $T_g$ , since more thermal energy is required for the network polymer chains to overcome local barriers to motion in the transition from glassy to rubbery behavior. As the concentration of mPDA deviates from stoichiometry, the  $T_g$  decreases because the  $M_c$  is increased.



Figure 2.20: Glass transition temperature  $(T_g)$  and molecular weight between cross-links  $(M_c)$  of DGEBA cured with varying concentration of mPDA.

Since DGEBA cured with excess mPDA gave larger values of fracture toughness, SBM was used to modify the network cured with excess mPDA. The flexural strength and modulus of neat epoxy and 10 phr SBM modified epoxy cured at stoichiometry and with excess mPDA (21.5 phr mPDA), are shown in **Figures 21** and **22**, respectively. SBM modified epoxy cured at stoichiometry or with excess amines shows a decrease in flexural strength and modulus as previously described. The 10 phr SBM modified epoxy cured at 21.5 phr mPDA has a larger flexural strength than that cured at stoichiometry. This could arise from the aforementioned reinforcing effect observed for offstoichiometric quantities of mPDA. However, there is no change in modulus, as shown in **Figure 22**.



**Figure 2.21:** Flexural strength of neat epoxy and 10 phr SBM modified epoxy cured with mPDA at stoichiometry (14.5 phr) and at excess (21.5 phr).



**Figure 2.22:** Flexural modulus of neat epoxy and 10 phr SBM modified epoxy cured with mPDA at stoichiometry (14.5 phr) and at excess (21.5 phr).

The fracture toughness of neat epoxy, 10 phr SBM modified epoxy cured at stoichiometry and with excess mPDA (21.5 phr) is shown in **Figure 23**. Addition of 10 phr SBM and excess mPDA increased the fracture toughness by 300%. Hydro and Pearson observed similar increases in fracture toughness for SBM modified DGEBA cured with AEP and PIP, where the neat AEP and PIP cured DGEBA had glass transition temperatures of 109 and 103 °C, respectively [14]. The M<sub>c</sub> for the AEP and PIP cured DGEBA was 550 and 725 g/mol, respectively. In this work, DGEBA cured with 21.5 phr mPDA had a M<sub>c</sub> of 500 g/mol and a T<sub>g</sub> of 137.5 °C.



**Figure 2.23:** Fracture toughness of neat epoxy and 10 phr SBM modified epoxy cured with mPDA at stoichiometry (14.5 phr) and at excess (21.5 phr).



**Figure 2.24:** Scanning electron microscopy (SEM) images of 10 phr SBM modified epoxy cured with excess mPDA compact tension specimen fracture surfaces.

SEM images of compact tension specimen fracture surfaces of 10 phr SBM modified epoxy cured with excess mPDA are shown in **Figure 24**. The SEM images show void growth of the epoxy resulting from cavitation of the SBM micelles. The extent of void growth for the epoxy with larger M<sub>c</sub> appears qualitatively larger than for SBM modified epoxy cured at stoichiometry (see **Figures 13** and **14**). The observation that for CTBN modified epoxy, the value of M<sub>c</sub> governs the 'toughenibility' of the epoxy also holds for the SBM modified epoxy, even though only one third of the copolymer consists of a rubbery block.

#### 2.4. Conclusion

CTBN and SBM were directly compared as toughening agents for an intermediate  $T_g$  (154 °C) epoxy network. The SBM terpolymer increased the fracture toughness of the epoxy with increasing concentration of additive, while CTBN was only effective up to 5 phr. Scanning electron microscopy (SEM) of the SBM modified epoxy compact tension specimen fracture surfaces revealed cavitation of 100 nm SBM micelles, followed by void growth and shear yielding of the epoxy. While the CTBN and SBM additives exhibited a similar toughening mechanism in epoxy, the larger, micron scale CTBN adducts were less effective towards increasing fracture toughness. SEM imaging of the fracture surfaces qualitatively supports these results. Additionally, measurement of the center-to-center, nearest neighbor interparticle distance ( $D_p$ ) within the modified epoxies showed that the SBM had a  $D_p$  smaller by one order of magnitude, as compared to CTBN. The finer distribution of nanoscopic SBM micelles results in a decrease in  $D_p$  and

an improved interaction with the crack tip resulting in massive plastic deformation of the epoxy upon fracture.

Dynamic mechanical analysis showed that SBM does not decrease the  $T_g$  of the epoxy network at 5, 10 or 15 phr. The SBM self assembles into spherical micelles in the epoxy and the nanostructure is fixed by the curing process. Thus, SBM does not plasticize the network and decrease the epoxy  $T_g$ , even up to 15 phr loadings. On the other hand, phase separation and diffusion of CTBN to form rubbery adducts results in unprecipitated CTBN, which plasticizes the network. Further, it was found that CTBN reacts with terminal DGEBA epoxide rings prior to cure and therefore the cross-link density of the CTBN modified epoxy may be reduced leading to decreases in  $T_g$ 

Finally, the influence of curative concentration on the mechanical, thermomechanical and fracture properties of DGEBA cured with mPDA was explored. The flexural strength and modulus goes through a minimum near stoichiometry and has larger values for epoxy cured with less-than-stoichiometric concentrations of curative. This is attributed to the formation of a more linear polymer network, which results from the differences in reactivity of primary and secondary amines. More linear networks, however, were found to have a lower  $T_g$  due to the increases in M<sub>c</sub>. Additionally, the fracture toughness of the epoxy itself and its toughenibility was increased by addition of excess mPDA.

REFERENCES

#### REFERENCES

- [1] H. Lee and K. Neville, "Handbook of Epoxy Resins," 1967.
- [2] R. Bagheri, B. T. Marouf, and R. A. Pearson, "Rubber-Toughened Epoxies: A Critical Review," *Polym. Rev.*, vol. 49, no. 3, pp. 201–225, Aug. 2009.
- [3] D. Ratna and A. K. Banthia, "Rubber toughened epoxy," *Macromol. Res.*, vol. 12, no. 1, pp. 11–21, Feb. 2004.
- [4] A. J. Kinloch, R. D. Mohammed, A. C. Taylor, C. Eger, S. Sprenger, and D. Egan, "The effect of silica nano particles and rubber particles on the toughness of multiphase thermosetting epoxy polymers," *J. Mater. Sci.*, vol. 40, no. 18, pp. 5083– 5086, Sep. 2005.
- [5] B. B. Johnsen, A. J. Kinloch, R. D. Mohammed, A. C. Taylor, and S. Sprenger, "Toughening mechanisms of nanoparticle-modified epoxy polymers," *Polymer*, vol. 48, no. 2, pp. 530–541, Jan. 2007.
- [6] Y. Geng, M. Y. Liu, J. Li, X. M. Shi, and J. K. Kim, "Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites," *Compos. Part Appl. Sci. Manuf.*, vol. 39, no. 12, pp. 1876–1883, Dec. 2008.
- [7] X. Wang, J. Jin, and M. Song, "An investigation of the mechanism of graphene toughening epoxy," *Carbon*, vol. 65, pp. 324–333, Dec. 2013.
- [8] S. Chandrasekaran, N. Sato, F. Tölle, R. Mülhaupt, B. Fiedler, and K. Schulte, "Fracture toughness and failure mechanism of graphene based epoxy composites," *Compos. Sci. Technol.*, vol. 97, pp. 90–99, Jun. 2014.
- [9] N. T. Kamar and L. T. Drzal, "Micron and nanostructured rubber toughened epoxy: A direct comparison of mechanical, thermomechanical and fracture properties," *Polymer*, vol. 92, pp. 114–124, Jun. 2016.
- [10] R. Bagheri and R. A. Pearson, "Role of particle cavitation in rubber-toughened epoxies: 1. Microvoid toughening," *Polymer*, vol. 37, no. 20, pp. 4529–4538, Sep. 1996.
- [11] R. Bagheri and R. A. Pearson, "Role of particle cavitation in rubber-toughened epoxies: II. Inter-particle distance," *Polymer*, vol. 41, no. 1, pp. 269–276, Jan. 2000.
- [12] J. M. Dean, R. B. Grubbs, W. Saad, R. F. Cook, and F. S. Bates, "Mechanical properties of block copolymer vesicle and micelle modified epoxies," *J. Polym. Sci. Part B Polym. Phys.*, vol. 41, no. 20, pp. 2444–2456, Oct. 2003.

- [13] P. Gerard, N. P. Boupat, T. Fine, L. Gervat, and J.-P. Pascault, "Toughness Properties of Lightly Crosslinked Epoxies Using Block Copolymers," *Macromol. Symp.*, vol. 256, no. 1, pp. 55–64, Sep. 2007.
- [14] R. M. Hydro and R. A. Pearson, "Epoxies toughened with triblock copolymers," J. Polym. Sci. Part B Polym. Phys., vol. 45, no. 12, pp. 1470–1481, Jun. 2007.
- [15] V. Rebizant *et al.*, "Chemistry and Mechanical Properties of Epoxy-Based Thermosets Reinforced by Reactive and Nonreactive SBMX Block Copolymers," *Macromolecules*, vol. 37, no. 21, pp. 8017–8027, Oct. 2004.
- [16] C. Declet-Perez, L. F. Francis, and F. S. Bates, "Deformation Processes in Block Copolymer Toughened Epoxies," *Macromolecules*, vol. 48, no. 11, pp. 3672–3684, Jun. 2015.
- [17] A.-V. Ruzette and L. Leibler, "Block copolymers in tomorrow's plastics," Nat. Mater., vol. 4, no. 1, pp. 19–31, Jan. 2005.
- [18] H. M. Chong and A. C. Taylor, "The microstructure and fracture performance of styrene–butadiene–methylmethacrylate block copolymer-modified epoxy polymers," *J. Mater. Sci.*, vol. 48, no. 19, pp. 6762–6777, Jun. 2013.
- [19] L. E. Nielsen, "Cross-Linking–Effect on Physical Properties of Polymers," J. Macromol. Sci. Part C, vol. 3, no. 1, pp. 69–103, Jan. 1969.
- [20] G. Levita, S. D. Petris, A. Marchetti, and A. Lazzeri, "Crosslink density and fracture toughness of epoxy resins," J. Mater. Sci., vol. 26, no. 9, pp. 2348–2352, May 1991.
- [21] V. B. Gupta, L. T. Drzal, C. Y.-C. Lee, and M. J. Rich, "The temperaturedependence of some mechanical properties of a cured epoxy resin system," *Polym. Eng. Sci.*, vol. 25, no. 13, pp. 812–823, Sep. 1985.
- [22] S. Sprenger, "Epoxy resins modified with elastomers and surface-modified silica nanoparticles," *Polymer*, vol. 54, no. 18, pp. 4790–4797, Aug. 2013.
- [23] D. Quan and A. Ivankovic, "Effect of core-shell rubber (CSR) nano-particles on mechanical properties and fracture toughness of an epoxy polymer," *Polymer*, vol. 66, pp. 16–28, Jun. 2015.
- [24] C. W. Wise, W. D. Cook, and A. A. Goodwin, "CTBN rubber phase precipitation in model epoxy resins," *Polymer*, vol. 41, no. 12, pp. 4625–4633, Jun. 2000.
- [25] A. Cherdoud-Chihani, M. Mouzali, and M. J. M. Abadie, "Study of crosslinking acid copolymer/DGEBA systems by FTIR," J. Appl. Polym. Sci., vol. 87, no. 13, pp. 2033–2051, Mar. 2003.

- [26] X. Ramis, J. M. Salla, C. Mas, A. Mantecón, and A. Serra, "Kinetic study by FTIR, TMA, and DSC of the curing of a mixture of DGEBA resin and γ-butyrolactone catalyzed by ytterbium triflate," *J. Appl. Polym. Sci.*, vol. 92, no. 1, pp. 381–393, Apr. 2004.
- [27] S. Ritzenthaler, F. Court, E. Girard-Reydet, L. Leibler, and J. P. Pascault, "ABC Triblock Copolymers/Epoxy–Diamine Blends. 2. Parameters Controlling the Morphologies and Properties," *Macromolecules*, vol. 36, no. 1, pp. 118–126, Jan. 2003.
- [28] J. (Daniel) Liu *et al.*, "Toughening of Epoxies with Block Copolymer Micelles of Wormlike Morphology," *Macromolecules*, vol. 43, no. 17, pp. 7238–7243, Sep. 2010.
- [29] R. A. Pearson and A. F. Yee, "Toughening mechanisms in elastomer-modified epoxies," J. Mater. Sci., vol. 24, no. 7, pp. 2571–2580, Jul. 1989.
- [30] M. R. Vanlandingham, R. F. Eduljee, and J. W. Gillespie Jr., "Relationships between stoichiometry, microstructure, and properties for amine-cured epoxies," J. *Appl. Polym. Sci.*, vol. 71, no. 5, pp. 699–712, Jan. 1999.
- [31] G. R. Palmese and R. L. McCullough, "Effect of epoxy-amine stoichiometry on cured resin material properties," J. Appl. Polym. Sci., vol. 46, no. 10, pp. 1863– 1873, Dec. 1992.

# CHAPTER 3: NANOSCALE TOUGHENING OF CARBON FIBER REINFORCED/EPOXY POLYMER COMPOSITES (CFRPS) USING A TRIBLOCK COPOLYMER

#### Abstract

This work explored the incorporation of a triblock copolymer in carbon fiber reinforced epoxy polymer composites (CFRPs) to improve their mode-I fracture toughness, G<sub>Ic</sub> (J/m<sup>2</sup>). The triblock copolymer poly(styrene)-block-poly(butadiene)-blockpoly(methylmethacrylate) (SBM) was used to modify the CFRP matrix at 5, 10 and 15 phr concentrations, respectively. Before manufacture of the CFRPs, the carbon fibers used in this study were treated using an in-house, patented UV-ozone (UVO) treatment process to enhance composite interfacial properties. CFRPs with UVO treated fibers, sized UVO treated fibers and sized UVO treated fibers with SBM modified matrices were made using an in-house sizing tower system, prepregger, vacuum bag and autoclave method. Mode-I fracture toughness testing revealed a 290% increase in G<sub>Ic</sub> by incorporation of the reactive sizing on the fibers and 10 phr SBM in the matrix. Scanning electron microscopy of the SBM modified CFRP fracture surfaces showed that well distributed, sub 100 nm spherical micelles of SBM underwent cavitation and induced void growth and shear yielding toughening mechanisms to absorb fracture energy. It is noteworthy that longitudinal and transverse composite three point flexural testing showed that the SBM modified matrix did not decrease CFRP strength and stiffness up to 10 phr additive. Further, dynamic mechanical analysis revealed that SBM at 10 phr decreased the glass transition temperature ( $T_g$ ) of CFRPs by only 2.9 °C; the  $T_g$  was then recovered

at 15 phr SBM. Finally, the SBM modified CFRP  $G_{Ic}$  was compared to the neat matrix  $G_{Ic}$  at 0, 5, 10 and 15 phr SBM to develop a 'transfer factor' for SBM modified composites. It was found that only 10% of the increased matrix toughness was transferred from the SBM modified epoxy to the CFRPs. The presence of the rigid carbon fibers constrains plastic deformation of the modified epoxy and limits the toughness transfer in the composite.

#### 3.1 Introduction

Since the 1970s, utilization of carbon fiber reinforced epoxy polymer composites (CFRPs) has grown in a wide range of applications from aerospace to sporting equipment. CFRPs have a high strength-to-weight ratio and can be manufactured as high quality parts using autoclave and resin transfer molding processes. More recently, CAFE standards imposed on light duty vehicles to reduce fuel consumption and carbon footprint have incentivized manufacturers to explore adopting new materials for 'light-weighting'. With a reduction in production cost of carbon fibers and shorter composite manufacturing times, CFRPs for automotive applications are an attractive and viable means to achieve fuel economy goals.

Although CFRPs have high strength-to-weight ratios, epoxy matrices may be brittle and have a low resistance to crack initiation and propagation. Thus, CFRPs are susceptible to delamination which can reduce mechanical performance of a composite part [1]. In fact, for structural materials, toughness and not strength is often the limiting material property [2]. Methods to improve the fracture toughness of CFRPs include *z*pinning/stitching to form a three dimensional composite, interleaving a toughened thin

film as an additional layer in a laminate, application of a sizing to the fibers to enhance interphase performance, or toughening the epoxy matrix itself [1], [3], [4], [5] and [6]. Z-pinning/stitching and interleaving can reduce CFRP in-plane mechanical properties and thus toughening the matrix itself presents an attractive alternative to these methods [1].

Methods to improve fracture toughness of epoxy include blending with reactive, phase separating rubbers like carboxyl-terminated butadiene-acrylonitrile (CTBN), nanosilica particles, or carbonaceous nanoparticles like graphene nanoplatelets and graphene oxide [7], [8] and [9]. In CTBN modified epoxy, micron scale rubbery domains cavitate ahead of the crack tip to induce void growth of epoxy and concomitant matrix shear yielding toughening mechanisms [10], [7], [11] and [12]. Interestingly, nanosilica modified epoxy exhibits a similar toughening mechanism, where spherical particles on the order of 30 nm induce localized plastic shear banding and debond from the epoxy to induce plastic void growth [13] and [14]. On the other hand, rigid platelet like fillers such as graphene nanoplatelets and graphene oxide pin, deflect and bifurcate a propagating crack, with separation of the nanoplatelet sheets observed as well [15] and [16].

With the advent of new synthesis methods, block copolymers (BCPs) consisting of long MW chains of dissimilar chemistries connected via covalent chemical bonds can be synthesized on an industrial scale [17]. BCPs self assemble in a host solvent or polymer due to steric repulsions between polymer chains of dissimilar chemistry and the surrounding media [17]. The asymmetric triblock copolymer poly(styrene)-blockpoly(butadiene)-block-poly(methylmethacrylate) (SBM, see **Figure 1** for chemical structure) has been shown to increase fracture toughness of epoxy [18], [19], [20], [21] and [22]. SBM self assembles into spherical micelles in epoxy resin (monomers) prior to

cure. During cure, the nanostructure may become fixed in place being solubilized in the matrix or macrophase separation of the block copolymer will occur depending on the solubility of the PMMA block in the epoxy/amine solution throughout the entire cure cycle [23]. SBM can toughen both lightly cross-linked epoxy networks with a glass transition temperature ( $T_g$ ) near 100 °C as well as intermediate  $T_g$  networks ( $T_g = 154$  °C) used as matrix material in CFRPs [22].

Although the fracture toughness of epoxy resins can be improved by the incorporation of a second phase rigid particle or rubbery adduct, the observed toughness increases in the modified epoxy are not always completely transferred to the fiber reinforced composite [1]. Hunston et al. studied the mode-I fracture toughness (G<sub>Ic</sub><sup>c</sup>) of CFRPs modified with epoxy and thermoplastic matrices having a wide range of resin fracture toughness  $(G_{Ic}^{m})$  [24]. They found that for brittle epoxy resins (i.e.  $G_{Ic}^{m} < 0.200$ kJ/m<sup>2</sup>),  $G_{Ic}^{c}$  was greater than  $G_{Ic}^{m}$  due to fiber breakage, fiber nesting, fiber bridging and fiber/matrix debonding toughening mechanisms. However, as G<sub>Ic</sub><sup>m</sup> increased beyond about  $0.700 \text{ kJ/m}^2$ , only a third of the increase was transferred to the composite. The authors hypothesized that during interlaminar fracture, the rigid fibers constrained the plastic deformation zone ahead of the crack tip and thus the maximum ductility of the tougher epoxies could not be achieved. More recently, Sprenger published a review on toughening glass and carbon FRPs with phase separating elastomers and nanosilica particles [25]. Sprenger showed that the trends observed by Hunston et al. are also observed for rubber/nanosilica hybdrid toughened FRPs. A plot of G<sub>Ic</sub><sup>c</sup> vs. G<sub>Ic</sub><sup>m</sup> showed an initial, linear increase until resin toughness became greater than  $0.200 \text{ kJ/m}^2$ , where a decreased slope and non linear trends in the data were observed.
Research on toughening CFRPs with nanostructured thermosets formed via self assembling block copolymer additives is quite limited. Chong *et al.* used SBM to toughen anhydride cured DGEBA and quasi-isotropic CFRP panels made from resin infusion under flexible tooling (RIFT) [21]. They found that the SBM macrophase separates from the anhydride cured DGEBA, forming an interconnected structure of SBM in the epoxy to increase neat epoxy  $G_{le}^{m}$  from  $0.096 \pm 0.009 \text{ kJ/m}^2$  to  $0.511 \pm 0.038 \text{ kJ/m}^2$  at a 15 wt% loading. However, increases in  $G_{le}^{c}$  peaked at only 2.5 wt% SBM additive and then decreased with increasing concentration of SBM. The decrease in  $G_{le}^{c}$  was attributed to the macrophase separation of SBM, the restriction of the plastic zone size of the crack tip by the rigid fibers and a reduction in fiber bridging. Quaresimin *et al.* applied a coating of dissolved SBM onto carbon fibers and then manufactured CFRPs using a vacuum bag and press method [26]. The  $G_{le}^{c}$  was decreased by the addition of SBM, which was attributed to the poor quality of the laminates and macrophase separation of the SBM. The authors did not provide a measure of the void content in the laminates.

To date, the role of a nanostructured thermoset on the fracture toughness of CFRPs has not yet been explored. In **Chapter 2**, it was found that SBM forms a nanostructured thermoset in the Epon 828 (DGEBA, n = 0.2) + 14.5 phr m-phenylenediamine (mPDA) system ( $T_g = 154$  °C) (see **Figure 1** for chemical structures) [22]. In addition to the large increases in K<sub>Q</sub> (220% at 10 phr SBM additive), the modified epoxy  $T_g$  was not decreased by the presence of the sub 100 nm spherical micelles at 5, 10 and 15 phr additive. Thus, this work explores the influence of both a reactive epoxy/amine sizing and an SBM modified matrix on the mechanical, thermomechanical and fracture properties of UVO treated carbon fiber (UVO-AS4-12k)/

epoxy (DGEBA + 14.5 phr mPDA) composites modified with 5, 10 and 15 phr SBM additive, respectively.





diglycidyl ether of bisphenol-A (DGBEA)

m-phenylenediamine (mPDA)

poly(styrene)-block-poly(butadiene)-blockpoly(methylmethacrylate) (SBM)

**Figure 3.1:** Chemical structures of digylcidyl ether of bisphenol-A (DGEBA ) monomer, m-phenylenediamine (mPDA) curative and triblock copolymer poly(styrene)-blockpoly(butadiene)-block-poly(methylmethacrylate) (SBM).

# 3.2 Methods

# 3.2.1 Composite manufacturing

# 3.2.1.1 Fiber sizing

AS4-12k carbon fiber tows were treated using an in-house, patented UV-ozone (UVO) treatment process (US 6,649,225 B2). The UVO treatment process increases the quantity of surface oxygen on the fibers and removes a weak surface layer from the fiber to improve the tensile strength of the fibers and interfacial shear strength in epoxy [27]. After UVO treatment, the fibers were pulled through the fiber sizing system shown in **Figure 2** to apply a thin uniform sizing coating. The carbon fibers were drawn through a

sizing bath containing a 1 wt% solution of DGEBA (Epon 828, Momentive) + 9 phr mphenylenediamine (mPDA, Acros Organics) in 2-propanol at a line speed of 40.5 m/hr.



**Figure 3.2:** Fiber sizing tower system. The fibers follow the direction of the black arrows overlaid onto the image: the fibers go through the bath, up drying tower (1), down drying tower (2) and are collected onto a stainless steel core for further processing. The sizing solution is re-circulated from a reservoir using a peristaltic pump to mitigate evaporation of isopropanol during sizing.

The sizing bath solution was prepared as follows. DGEBA was dissolved in 3L of isopropanol with magnetic stirring and solid mPDA flakes (9 phr) were added to the solution. After the mPDA was dissolved, the reacting mixture was stirred for 1 hr before beginning the sizing process. The polar protic isopropanol catalyzes the epoxy/amine reaction, which consumes most of the epoxide groups within 1 hr when reacted at stoichiometry [28].

The sized fibers then pass through two drying towers at 75.0  $^{\circ}$ C and are wound onto a stainless steel core. The core containing the sized fibers was transferred to a convection oven and heated at 60  $^{\circ}$ C for 3 hrs to remove any residual solvent from the fibers.

# 3.2.1.2 Prepreg and autoclave

A Research Tool drum winding prepregger was used to make unidirectional prepreg tapes. The resin pot, flattening pins and guide roller were set to 52.0 °C. The neat epoxy or SBM modified epoxy was then added to the resin pot and the fibers were pulled through the bath at 2.2 RPM to make unidirectional tapes 0.30 m wide and 1.8 m long.

The neat epoxy was blended as follows: DGEBA and mPDA were heated separately in a convection oven at 75 °C until the mPDA melted. The epoxy and curative were then mixed at stoichiometry (14.5 phr) by hand for 2 min. The mixture was degassed in a vacuum oven at 75 °C under 27 mmHg for 5 min prior to prepregging.

For SBM modified epoxy blends, SBM powder (Arkema, E21 SBM) was added to DGEBA and then stirred at 150 °C for 12 hrs. The mixture was then cooled to 75 °C and then degassed for 30 min to remove air entrapped during the pre-cure blending stage. Melted mPDA (75 °C) was then added to the modified epoxy and the mixture was stirred by hand for 1 min. The modified resin was transferred to a Whipmix® bowl, pulled under vacuum and mixed with a paddle using a rotary motor for 2 minutes. Finally, the SBM modified epoxy was degassed in a vacuum oven at 75 °C under 27 inHg for 5 min prior to prepregging.

The prepreg tapes were cut, laid up in unidirectional configuration, vacuum bagged and autoclaved under 0.59 MPa (85 psi) at 75 °C for 2 hrs and 125 °C for 2 hrs. Vacuum (27 inHg) was applied to the bag for 30 min into the first hold. A schematic of the layup is shown in **Figure 3**. Flexural panels had a length and width of 0.30 m and 0.15 m, respectively. Mode-I panels had a length and width of 0.15 m. 8-ply panels used for mechanical and thermomechanical testing and were nominally 1.3 mm thick, while 18-ply panels used for fracture toughness testing were 3.4 mm thick. A 60 mm long, 0.15 m wide Teflon® peel ply was placed between the middle plies of the mode-I panels at one edge to form 50 mm pre-crack after removal of 10 mm of the panels edges with a diamond bonded composite saw blade.



**Figure 3.3:** Schematic of the layup and vacuum bag for autoclaving CFRPs. The tooling plate and caul sheet were wrapped in non-porous Teflon® prior to layup.

## **3.2.2** Void volume and fiber volume fraction

Cross-sections ( $0^{\circ}$ ) of each panel were mounted in clear epoxy and polished to a 4,000 grit finish. The polished surfaces were etched for 30 min using a Plasma Science O<sub>2</sub> plasma reaction chamber to remove a small amount of the epoxy matrix to enhance microscopic observation of the carbon fibers. The polished and etched surfaces were coated with a 1.5 nm layer of tungsten using a Leica EM MID020 sputter coater. The

mounts were then ground to a metal stage with copper tape and imaged using a Zeiss EVO scanning electron microscope (SEM). At least two cross-sections were investigated for each panel and 8 images were taken for each cross-section. Adobe Photosphop® was used to determine the void volume, since the voids contrast strongly from the fibers and marix. This optical method is safer than acid digestion, which can also be difficult to perform experimentally.

To measure the FVF, the density of the matrix and of the CFRPs was measured according to ASTM D792, "the standard test method for density and specific gravity (relative density) of plastics by displacement". Rule of mixtures was used to calculate the FVF ( $V_f$ ) using **Equation (1)**:

$$V_f = \frac{\rho_c - \rho_m}{\rho_f - \rho_m},\tag{1}$$

where  $\rho_c$ ,  $\rho_m$  and  $\rho_f$  are the density (g/cm<sup>3</sup>) of the composite, polymer matrix and carbon fiber, respectively.

# 3.2.3 Flexural testing

Three-point flexural testing was performed on a UTS screw-driven load frame according to ASTM D790, "the standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials". The ASTM standard indicates that larger span-to-depth ratios may be needed for accurate determination of the flexural modulus for highly orthotropic specimens. Therefore, span-to-depth ratios (L/D) of both 32:1 and 60:1 were used for each specimen type. The coupons were 1.3 mm thick and

12.7 mm wide. To ensure no more than 10% overhang was allowed for each specimen, the length of the specimens tested at L/D = 32 and 60 were 47 mm and 90 mm, respectively. The loading rates for the specimens tested at L/D = 32 and 60 were 2.54 mm/min and 9.4 mm/min, respectively. At least 5 coupons of each composite type were tested at each span-to-depth ratio for both longitudinal (0°) and transverse (90°) fiber directions. For specimens tested at L/D = 32:1, **Equation (2)** was used to calculate the flexural strength at 5% strain:

$$\sigma = \frac{3PL}{2bd^2},\tag{2}$$

where  $\sigma$  is the stress in the outer fibers at the midpoint (MPa), P is the load (N), L is the support span (mm), b is the beam width (mm) and d is the depth (mm). For specimens tested at larger L/D (60 mm), **Equation (3)** was used to account for the larger deflection observed in the specimens:

$$\sigma = \frac{3PL}{2bd^2} \left[ 1 + 6\left(\frac{D}{L}\right)^2 - 4\left(\frac{d}{L}\right)\left(\frac{D}{L}\right) \right],\tag{3}$$

where D is the deflection of the specimen at middle of the support span. The bending modulus was calculated using **Equation (4)**:

$$E_B = \frac{L^3 m}{4bd^3},\tag{5}$$

where  $E_B$  is the modulus of elasticity in bending (MPa) and m is the slope of the tangent to the initial straight-line portion of the load-displacement curve (N/mm).

#### **3.2.4 Dynamic mechanical analysis**

A TA Instruments DMA 800 was used to perform single cantilever dynamic mechanical analysis (DMA) of the CFRPs. The samples were 1.3 mm thick and 12.4 mm wide. The distance between clamps was 17.6 mm. The specimens were strained at a frequency of 1.0 Hz at an amplitude of 20  $\mu$ m under a temperature ramp (3 °C/min) from room temperature to 250 °C. The storage modulus (G'), loss modulus (G'') and the Tan  $\delta$  were calculated from the data. At least 3 transverse (90°) specimens were tested for each composite type.

#### **3.2.5 Mode-I fracture toughness testing**

Mode-I fracture toughness testing was performed according to ASTM D5528, "the standard test method for the mode-I interlaminar fracture toughness of unidirectional fiber-reinforced polymer matrix composites". Double cantilever specimens were machined from the 18-ply mode-I panels such that the pre-crack was 50 mm. The specimens were nominally 3.4 mm thick and 21 mm wide. Piano hinges were mounted to the ends of the specimens using J-B Weld® adhesive and could freely rotate after bonding to the CFRPs. The hinge point was mounted along the edge of specimen for simpler attachment.

The specimens were gripped on a Materials System 810® servo hydraulic load frame and loaded at a rate of 5 mm/min. A Cannon® EOS Rebel® T4i camera was used

to record the propagating crack and the load-displacement data was collected for analysis. The strain energy release rate,  $G_{Ic}$  (J/m<sup>2</sup>) was calculated using the modified beam theory method via **Equation (6)**:

$$G_{Ic} = \frac{3P\delta}{2ba},\tag{6}$$

where P is the load (N),  $\delta$  is the crack opening displacement (m), 'b' is the specimen width (m) and 'a' is the crack length (m) corresponding to a particular P and  $\delta$ . At least 5 specimens were tested for each composite type. To mitigate the influence of the starter crack in AS4-12k/DGEBA unidirectional composites, propagation values of fracture toughness were determined for each specimen (G<sub>Ic</sub>) [4].

# **3.2.6 Fractography of CFRPs by scanning electron microscopy**

CFRP mode-I cantilever beam fracture surfaces were shortened using a Felker ® saw with a diamond bonded blade. Care was taken to ensure that the cut corresponded to the end of the test and the specimens were not damaged during their preparation. The mode-I fracture surfaces were coated with a 1-3 nm layer of tungsten using a Leica EM MID020 sputter coater, mounted onto a scanning electron microscope (SEM) stage with carbon tabe and grounded to the stage with copper tape. The stage and specimens were placed into a Carl Zeiss Auriga Dual Column FIB SEM for microscopy.

# **3.3 Results and Discussion**

## 3.3.1 Summary

A summary of the composites is shown in **Table 1**. The fiber type, sizing, matrix and modification (if applicable), number of plies, fiber volume fraction (FVF) and void volume are listed for each panel. The fiber volume fraction (FVF) and void volume of the panels are in agreement with values previously reported for AS4-12k/Epon 828 + 14.5 phr mPDA composites produced using similar manufacturing conditions [29].

**Table 3.1:** Summary of composites including sizing, matrix, fiber volume fraction (FVF) and void content for each panel made in this work.

Panel Name	Fiber	Sizing	Matrix	# of Plies	Fiber Volume Fraction (%)	Void Content (%)
UVO-CFRP	UVO-AS4-12k	N/A	Epon 828 + 14.5 phr mPDA	8	$65.0 \pm 2.0$	0.65 ± .20
UVO-CFRP	UVO-AS4-12k	N/A	Epon 828 + 14.5 phr mPDA	18	$67.0~\pm~1.0$	$0.18 \pm 0.07$
UVO-S-CFRP	UVO-AS4-12k	Sized	Epon 828 + 14.5 phr mPDA	8	63.8 ± 1.0	0.87 ± 0.22
UVO-S-CFRP	UVO-AS4-12k	Sized	Epon 828 + 14.5 phr mPDA	18	66.9 ± 0.9	$0.24\pm0.05$
UVO-S- 5 phr SBM CFRP	UVO-AS4-12k	Sized	Epon 828 + <b>5 phr SBM</b> + 14.5 phr mPDA	8	56.2 ± 2.0	$1.1 \pm 0.10$
UVO-S- 5 phr SBM CFRP	UVO-AS4-12k	Sized	Epon 828 + <b>5 phr SBM</b> + 14.5 phr mPDA	18	63.0 ± 0.6	$0.23\pm0.2$
UVO-S- 10 phr SBM CFRP	UVO-AS4-12k	Sized	Epon 828 + <b>10 phr SBM</b> + 14.5 phr mPDA	8	61.2 ± 2.0	$0.65 \pm 0.17$
UVO-S- 10 phr SBM CFRP	UVO-AS4-12k	Sized	Epon 828 + <b>10 phr SBM</b> + 14.5 phr mPDA	18	63.0 ± 2.6	$0.08\pm0.05$
UVO-S- 15 phr SBM CFRP	UVO-AS4-12k	Sized	Epon 828 + <b>15 phr SBM</b> + 14.5 phr mPDA	8	58.8 ± 2.3	0.62 ± 0.05
UVO-S- 15 phr SBM CFRP	UVO-AS4-12k	Sized	Epon 828 + <b>15 phr SBM</b> + 14.5 phr mPDA	18	58.3 ± 2.9	0.17 ± 0.14

# 3.3.2 Fracture toughness

## 3.3.2.1 Mode-I fracture toughness

The mode-I fracture toughness of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM CFRPs is shown in **Figure 4**. Fiber bridging was observed for all specimens during the mode-I test and appeared qualitatively similar for each composite. The reactive sizing applied to the fibers prior to prepregging increased the fracture toughness of the composites ( $G_{Ic}^{c}$ ) by 80%, while the application of the sizing and the incorporation of 5 phr SBM in the matrix increased  $G_{Ic}^{c}$  by 200%. At 10 phr SBM, the UVO-S CFRPs reached a plateau in fracture toughness (290% increase). The fibers constrained the extent of matrix plastic deformation required to increase CFRP toughness with increasing concentration of SBM. Increasing the concentration of SBM in the CFRPs beyond 10 phr did not show any further increase in  $G_{Ic}$  beyond 290%.



**Figure 3.4:** Mode-I fracture toughness of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM CFRPs.

To identify the toughening mechanisms in sized and SBM modified CFRPs, mode-I double cantilever beam (DCB) specimen fracture surfaces were examined using SEM. Representative fracture surfaces of UVO and UVO-S CFRP mode-I DCB specimens are shown in **Figure 5**.



**Figure 3.5:** Scanning electron micrographs of UVO and UVO-S CFRP mode-I double cantilever beam fracture surfaces. Fracture is from right to left.

The fracture direction is from right to left in each image. The UVO CFRP fracture morphology shows evidence of "cusps", which result from brittle matrix failure [30]. "Ribbons" were also observed, which tended to peel away from the fiber/matrix interface. On the other hand, the UVO-S CFRPs showed fewer cusps between fibers and more ribbons, which showed less evidence of peeling than for the UVO CFRPs. The SBM CFRPs exhibited different fracture morphology, as compared to the UVO and UVO-S CFRPs. Representative images of UVO-S-5, 10 and 15 phr SBM CFRPs are shown in **Figure 6**.



**Figure 3.6:** Scanning electron micrographs of UVO-S-5, 10 and 15 phr SBM CFRP mode-I double cantilever beam fracture surfaces. Fracture is from right to left.

The fracture direction is from right to left in each image. Column A shows lower magnification images of the fracture surfaces, while columns B and C show higher magnification images focusing on the fiber/matrix interface (green arrows) and plastic deformation of the matrix. The images in column A and B show intimate contact between

fiber and matrix, which is a qualitative indicator of good adhesion between the SBM modified matrix and the sized carbon fibers. Examination of the resin rich regions between fibers in the UVO-S-5 phr SBM CFRPs identifies nanoscale cavitation, concomitant void growth and matrix shear yielding toughening mechanisms. Thus, the toughening mechanisms observed for the neat SBM modified DGEBA (+14.5 phr mPDA) epoxy matrix were transferred to the SBM CFRPs [22]. The UVO-S-10 phr SBM CFRPs show two levels of toughening: 1. Nanocavitation of the SBM micelles induces plastic deformation of the matrix and 2. Micron scale deformation of the matrix between fibers absorbs additional fracture energy (see black arrows in Figure 6 (A) S-10 phr). This larger scale deformation may also result from good fiber/matrix adhesion. The 15 phr SBM CFRPs show a similar toughening mechanism, with greater aggregation of SBM micelles in the matrix. Thus, the morphology and fracture behavior of SBM modified DGEBA (+14.5 phr mPDA) was retained after incorporation of the carbon fibers to form a composite [22]. The extent of plastic deformation of the matrix between fibers in the toughened SBM CFRPs reported here appears to be more extensive than in CTBN, nanosilica or hybrid nanosilica/CTBN modified CFRPs [14].

### 3.3.2.2 Relationship between matrix and composite toughness

The relationship between modified resin and CFRP interlaminar fracture toughness is important for composite designers and manufacturers and thus for composite lightweighting applications [25]. To examine this relationship for SBM modified epoxy and the corresponding CFRPs, **Figure 7** shows the toughness of the SBM CFRPs ( $G_{Ic}^{c}$ ) versus the toughness of the SBM modified DGEBA matrix  $(G_Q^m)$  as a function of SBM concentration.



**Figure 3.7:** UVO-S and UVO-S-5, 10 and 15 phr SBM modified CFRP  $G_{Ic}$  (J/m<sup>2</sup>) vs. neat and 5, 10 and 15 phr SBM modified epoxy  $G_{Ic}$ , respectively.

The  $G_Q^m$  values for 5, 10 and 15 phr SBM modified DGEBA (+14.5 phr mPDA) were determined via the corrected energy method from compact tension testing curves used to calculate  $K_Q$  for SBM modified epoxy previously [22]. The neat mPDA cured DGEBA had a  $G_Q^m$  of 0.288 kJ/m<sup>2</sup>, while the  $G_Q^m$  of the 5, 10 and 15 phr SBM modified epoxy was 2.21 kJ/m<sup>2</sup>, 3.14 kJ/m<sup>2</sup> and 4.01 kJ/m<sup>2</sup>, respectively. These results agree with the finding that SBM increases the fracture toughness ( $K_Q$ ) of mPDA cured DGEBA with increasing concentration and provides larger values of toughness than CTBN modified epoxy at the same loading levels [22]. A linear fit to the data was used to examine the relationship between  $G_{Ic}^{c}$  and  $G_Q^{m}$ .

The slope of the line in **Figure 7** indicates that large improvements in fracture toughness in the SBM modified epoxies are not completely transferred to the SBM CFRPs; only about  $1/10^{\text{th}}$  of the matrix toughness is transferred to the composites. A plot of % increase in  $G_{Ic}^{C}$  vs.  $G_{Ic}^{m}$  in **Figure 8** shows a plateau in improvement at 10 phr. Beyond 10 phr SBM no further toughness improvements in the matrix are transferred to the CFRPs.



**Figure 3.8:** Increase in fracture toughness (%) of UVO-S CFRP vs. increase in fracture toughness of neat resin by incorporation of SBM at 5, 10 and 15 phr.

Sprenger et al. calculated a transfer factor for hybrid nanosilica/elastomer modified CFRPs of 0.18 [25]. In this work, the transfer factor is lower due to the tougher nature of the SBM modified epoxy, as compared to CTBN, nanosilica or nanosilica/CTBN hybrid modified epoxy [22], [25].

Often, significant improvements in the fracture toughness of CFRPs are accompanied by reductions in composite mechanical and/or dynamic mechanical properties. Therefore, the mechanical and dynamic mechanical properties of UVO, UVO-S and UVO-S SBM CFRPs are discussed in the following sections.

# **3.3.3 Flexural properties**

The three-point flexural test was used to evaluate the CFRP mechanical properties in the longitudinal (0°) and transverse fiber directions (90°). The 0° flexural strength and modulus normalized for FVF of UVO, UVO sized (-S) and UVO-S- 5, 10 and 15 phr SBM CFRPs is shown in **Figure 9** and the 90° flexural strength and modulus for the same composite types are shown in **Figure 10**.



**Figure 3.9:** Longitudinal flexural strength (MPa) (a) and modulus (GPa) (b) of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM modified CFRPs.

The ASTM specification for flexural properties of reinforced plastics indicates that a large span-to-depth (L/D) ratio may be necessary for determination of flexural modulus due to the development of shear in highly orthotropic composites tested at lower values of L/D. Zweben et al. showed that for Kevlar® 49 aramid fibers in a polyester matrix, the flexural modulus determined by three point bending asymptotically approached the tensile modulus with increasing values of L/D [31]. They recommend an L/D of 60 to determine the CFRP modulus and a lower value to determine the strength. Therefore, each specimen type was tested at L/D = 32 and 60 to ensure accurate determination of the flexural strength and modulus of the CFRPs made in this work.



**Figure 3.10:** Transverse flexural strength (MPa) (a) and modulus (GPa) (b) of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM modified CFRPs.

As shown in **Figures 9** and **10**, the specimens tested at L/D = 60 showed similar trends in the modulus data as those tested at L/D = 32, but with larger values in modulus

for most of the CFRP types. The increases in modulus by increasing L/D were small relative to those observed by Zweben, which implies that the 32:1 span-to-depth ratio is sufficient to mitigate the influence of shear in the flexural specimens. Increasing the concentration of SBM in the matrix did not reduce the longitudinal modulus for either 32:1 or 60:1 span-to-depth ratios since the longitudinal flexural modulus is fiber dominated and thus incorporation of SBM, which contains one-third soft and flexible poly(butadiene) block, did not decrease the modulus of the CFRPs.

The sizing was applied to the fibers prior to prepregging to improve the fiber/matrix adhesion. Previous work on A4 carbon fiber/Epon 828 + 14.5 phr mPDA composite system reported the relationship between interfacial shear strength (IFSS) and composite mechanical and fracture properties [4], [29], [32] and [33]. A surface treatment and sizing was found to improve the IFSS by removal of a weak boundary layer on the surface of the carbon fibers and by the formation of an interphase, which has distinct properties compared to the bulk matrix [34]. In this work, both the longitudinal and transverse flexural strength increased after applying the reactive sizing. The increases were larger and statistically significant for specimens tested at L/D = 60 compared to those tested at L/D = 32.

The sizing pickup on the fibers was  $0.53 \pm 0.04$  wt%. After sizing and before prepregging, the fibers were heated to 60 °C to remove residual solvent. This heating step vitrifies the reactive epoxy sizing on the fibers. During cure of the CFRP, the reactive sizing will swell or dissolve into the matrix, forming an interphase around the fibers and thus the increases in flexural strength [32]. The combination of the reactive sizing applied to the fibers and SBM in the matrix led to larger values of transverse flexural strength.

However, the large error bars on the strength measurement suggest that the differences are statistically insignificant and thus it can only be concluded that SBM does not have a deleterious effect on the interfacial and interlaminar strength of the CFRPs.

The longitudinal flexural specimens tested at L/D = 32 and 60 had different failure modes. For specimens tested at L/D = 32, the specimens failed by delamination and/or failure initiation on the compressive or tensile side of the coupons. For the specimens tested at L/D = 60, failure initiated on the tensile side, followed by a sudden and complete fracture at the centerline of the coupons. This difference in failure mode is due to the larger deflection observed in the specimens tested at L/D = 60. For each composite type, flexural specimens tested at L/D = 60 had a maximum deflection four times greater than those tested at L/D = 32. For example, the UVO-S CFRPs had a deflection at failure of  $0.32 \pm 0.02$  cm and  $1.24 \pm 0.16$  cm at L/D = 32 and L/D = 60, respectively. The UVO-S-15 phr SBM CFRP had similar values of deflection at failure, with  $0.31 \pm 0.01$  cm and  $1.13 \pm 0.04$  cm at L/D = 32 and L/D = 60, respectively. The concentration of SBM did not have an influence on the flexural failure mode of the CFRPs, even up to 15 phr additive for either L/D = 32 or 60.

To examine the influence of the sizing and the presence of SBM on fiber/matrix adhesion, the 0° flexural coupon failure surfaces were examined with scanning electron microscopy (SEM). The 0° coupons were analyzed since the failure of these specimens initiated on the tensile side and the coupons catastrophically fractured. The UVO and UVO-S CFRP flexural fracture surfaces in **Figure 11**, column A show the compressive and tensile failure of the flexural coupons and columns B-D show the tensile side at increasing magnification where failure initiated.



**Figure 3.11:** Scanning electron micrographs of UVO and UVO-S CFRP longitudinal flexural failure surfaces. Specimens tested at L/D = 60.

Fiber pullout is observed for both UVO and UVO-S CFRPs. The flexural failure surfaces of UVO-S-5, 10 and 15 phr SBM CFRPs are shown in **Figure 12**.



**Figure 3.12:** Scanning electron micrographs of UVO-S-5, 10 and 15 phr SBM CFRP longitudinal flexural failure surfaces. Specimens were tested at L/D = 60.

The UVO-S-SBM CFRPs also show evidence of fiber pullout, with the UVO-S-15 phr SBM CFRP coupons exhibiting the most pullout. The higher magnification images in **Figure 12** column D show evidence of matrix shear yielding by cavitation of SBM micelles, which may be limited due to the high rate of fracture and the constraining nature of the fibers.

# **3.3.4** Thermomechanical properties

Previously, it was found that the glass transition temperature ( $T_g$ ) of DGEBA (+14.5 phr mPDA) was not suppressed by the presence of SBM up to 15 phr additive [22]. SBM self assembles in the epoxy prior to cure and, unlike CTBN, does not randomly cross-link into or plasticize the network. Therefore, it is anticipated that for CFRPs modified with SBM, a similar behavior should be observed where the composite glass transition temperature is unaffected by the presence of SBM.

The storage modulus G<sup>2</sup> (MPa) and the Tan  $\delta$  of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM CFRPs is shown in **Figure 13**.



**Figure 3.13:** Storage modulus G' (MPa) and Tan  $\delta$  of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM CFRPs.

Prior to the main transition, the G' of the UVO-S CFRP is lower than that of the UVO CFRPs. Increasing concentration of SBM decreases G' further, which is due to the

presence of the soft, flexible poly(butadiene) block making up one third of the additive. The main transition of the decay in the storage modulus, however, occurs at a similar onset point for each composite type. Thus, the poly(butadiene) block lowers the modulus of the composite, but the SBM micelles do not have a major influence on the mobilization of the polymer backbone as the material transitions from glassy to rubbery behavior.

Tan  $\delta$ , the damping factor, increases in peak height with increasing concentration of additive. In dynamic mechanical analysis of CFRPs, an increase in the damping has been attributed to poorer fiber/matrix adhesion [35] and [36]. In this work, however, the transverse flex test showed larger values of strength for all specimens containing sized fibers and SBM in the matrix, as compared to the baseline UVO CFRPs. Therefore, the increases in damping are not due to poorer adhesion between the fibers and the matrix by the presence of the nanostructured thermoset. The increases may be due to a confinement effect, where vibrational energy is dissipated in the vicinity of the toughening micelles in the matrix between the fibers.

The average  $T_g$ , which is defined as the temperature corresponding to the maximum of the Tan  $\delta$ , of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM CFRPs is shown in **Figure 14**.



**Figure 3.14:** Average glass transition temperature (T<sub>g</sub>) of UVO, UVO-S and UVO-S-5, 10 and 15 phr SBM CFRPs.

There is a slight decrease (2.9 °C) in CFRP  $T_g$  at 10 phr SBM, which is recovered at 15 phr SBM. As hypothesized, the SBM micelles, even up to 15 phr in the matrix, do not have a substantial influence on the  $T_g$  of the CFRPs.

## 3.4 Conclusion

The asymmetric triblock copolymer SBM was used to form a nanostructured thermoset capable of increasing the mode-I fracture toughness of CFRPs by 290% with no corresponding decrease in flexural properties or  $T_g$ . The increases in fracture toughness is due to a combination of nanoscale cavitation, void growth and concomitant matrix shear yielding toughening mechanisms, which also enhanced micron scale toughening mechanisms previously observed in CFRPs. The mode-I fracture toughness of the SBM CFRPs ( $G_{Ic}^{c}$ ) when compared to that of the bulk modified SBM ( $G_Q^{m}$ ) generates a

transfer factor for this composite system of about 10%. Although only 10% of the toughness increases in  $G_{Ic}$  are transferred to the CFRP by incorporation of SBM in the matrix, those increases (290% at 10 phr additive) in fracture toughness of CFRPs are important for composite manufacturers and designers.

REFERENCES

#### REFERENCES

- Y. Tang, L. Ye, Z. Zhang, and K. Friedrich, "Interlaminar fracture toughness and CAI strength of fibre-reinforced composites with nanoparticles – A review," *Compos. Sci. Technol.*, vol. 86, pp. 26–37, Sep. 2013.
- [2] M. E. Launey and R. O. Ritchie, "On the Fracture Toughness of Advanced Materials," *Adv. Mater.*, vol. 21, no. 20, pp. 2103–2110, May 2009.
- [3] M. Hojo, S. Matsuda, M. Tanaka, S. Ochiai, and A. Murakami, "Mode I delamination fatigue properties of interlayer-toughened CF/epoxy laminates," *Compos. Sci. Technol.*, vol. 66, no. 5, pp. 665–675, May 2006.
- [4] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: IV. Mode I and Mode II Fracture Toughness of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 26, no. 7, pp. 936–968, Jul. 1992.
- [5] X. Zhang, X. Fan, C. Yan, H. Li, Y. Zhu, X. Li, and L. Yu, "Interfacial Microstructure and Properties of Carbon Fiber Composites Modified with Graphene Oxide," ACS Appl. Mater. Interfaces, vol. 4, no. 3, pp. 1543–1552, Mar. 2012.
- [6] A. J. Kinloch, R. D. Mohammed, A. C. Taylor, S. Sprenger, and D. Egan, "The interlaminar toughness of carbon-fibre reinforced plastic composites using 'hybridtoughened' matrices," *J. Mater. Sci.*, vol. 41, no. 15, pp. 5043–5046, May 2006.
- [7] R. Bagheri, B. T. Marouf, and R. A. Pearson, "Rubber-Toughened Epoxies: A Critical Review," *Polym. Rev.*, vol. 49, no. 3, pp. 201–225, Aug. 2009.
- [8] S. Sprenger, "Epoxy resin composites with surface-modified silicon dioxide nanoparticles: A review," J. Appl. Polym. Sci., vol. 130, no. 3, pp. 1421–1428, Nov. 2013.
- [9] J. R. Potts, D. R. Dreyer, C. W. Bielawski, and R. S. Ruoff, "Graphene-based polymer nanocomposites," *Polymer*, vol. 52, no. 1, pp. 5–25, Jan. 2011.
- [10] D. Ratna and A. K. Banthia, "Rubber toughened epoxy," *Macromol. Res.*, vol. 12, no. 1, pp. 11–21, Feb. 2004.
- [11] R. Bagheri and R. A. Pearson, "Role of particle cavitation in rubber-toughened epoxies: 1. Microvoid toughening," *Polymer*, vol. 37, no. 20, pp. 4529–4538, Sep. 1996.

- [12] R. Bagheri and R. A. Pearson, "Role of particle cavitation in rubber-toughened epoxies: II. Inter-particle distance," *Polymer*, vol. 41, no. 1, pp. 269–276, Jan. 2000.
- [13] T. H. Hsieh, A. J. Kinloch, K. Masania, A. C. Taylor, and S. Sprenger, "The mechanisms and mechanics of the toughening of epoxy polymers modified with silica nanoparticles," *Polymer*, vol. 51, no. 26, pp. 6284–6294, Dec. 2010.
- [14] S. Sprenger, M. H. Kothmann, and V. Altstaedt, "Carbon fiber-reinforced composites using an epoxy resin matrix modified with reactive liquid rubber and silica nanoparticles," *Compos. Sci. Technol.*, vol. 105, pp. 86–95, Dec. 2014.
- [15] S. Chandrasekaran, N. Sato, F. Tölle, R. Mülhaupt, B. Fiedler, and K. Schulte, "Fracture toughness and failure mechanism of graphene based epoxy composites," *Compos. Sci. Technol.*, vol. 97, pp. 90–99, Jun. 2014.
- [16] F. Wang, L. T. Drzal, Y. Qin, and Z. Huang, "Enhancement of fracture toughness, mechanical and thermal properties of rubber/epoxy composites by incorporation of graphene nanoplatelets," *Compos. Part Appl. Sci. Manuf.*, vol. 87, pp. 10–22, Aug. 2016.
- [17] A.-V. Ruzette and L. Leibler, "Block copolymers in tomorrow's plastics," Nat. Mater., vol. 4, no. 1, pp. 19–31, Jan. 2005.
- [18] P. Gerard, N. P. Boupat, T. Fine, L. Gervat, and J.-P. Pascault, "Toughness Properties of Lightly Crosslinked Epoxies Using Block Copolymers," *Macromol. Symp.*, vol. 256, no. 1, pp. 55–64, Sep. 2007.
- [19] R. M. Hydro and R. A. Pearson, "Epoxies toughened with triblock copolymers," J. Polym. Sci. Part B Polym. Phys., vol. 45, no. 12, pp. 1470–1481, Jun. 2007.
- [20] V. Rebizant, A.-S. Venet, F. Tournilhac, E. Girard-Reydet, C. Navarro, J.-P. Pascault, and L. Leibler, "Chemistry and Mechanical Properties of Epoxy-Based Thermosets Reinforced by Reactive and Nonreactive SBMX Block Copolymers," *Macromolecules*, vol. 37, no. 21, pp. 8017–8027, Oct. 2004.
- [21] H. M. Chong and A. C. Taylor, "The microstructure and fracture performance of styrene–butadiene–methylmethacrylate block copolymer-modified epoxy polymers," *J. Mater. Sci.*, vol. 48, no. 19, pp. 6762–6777, Jun. 2013.
- [22] N. T. Kamar and L. T. Drzal, "Micron and nanostructured rubber toughened epoxy: A direct comparison of mechanical, thermomechanical and fracture properties," *Polymer*, vol. 92, pp. 114–124, Jun. 2016.
- [23] S. Ritzenthaler, F. Court, L. David, E. Girard-Reydet, L. Leibler, and J. P. Pascault, "ABC Triblock Copolymers/Epoxy-Diamine Blends. 1. Keys To Achieve

Nanostructured Thermosets," *Macromolecules*, vol. 35, no. 16, pp. 6245–6254, Jul. 2002.

- [24] D. Hunston, R. Moulton, N. Johnston, and W. Bascom, "Matrix Resin Effects in Composite Delamination: Mode I Fracture Aspects," in *Toughened Composites*, N. Johnston, Ed. 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959: ASTM International, 1987, pp. 74–74–21.
- [25] S. Sprenger, "Fiber-reinforced composites based on epoxy resins modified with elastomers and surface-modified silica nanoparticles," *J. Mater. Sci.*, vol. 49, no. 6, p. 2391+, Mar. 2014.
- [26] M. Quaresimin and R. J. Varley, "Understanding the effect of nano-modifier addition upon the properties of fibre reinforced laminates," *Compos. Sci. Technol.*, vol. 68, no. 3–4, pp. 718–726, Mar. 2008.
- [27] M. J. Rich, P. Askeland, and L. T. Drzal, "Photo-oxidative treatment of carbonaceous fibers to promote adhesion in polymer matrix composites," *Carbon Conf. Brown Univ. R. I. USA*, Jul. 2004.
- [28] L. Shechter, J. Wynstra, and R. P. Kurkjy, "Glycidyl Ether Reactions with Amines," *Ind. Eng. Chem.*, vol. 48, no. 1, pp. 94–97, Jan. 1956.
- [29] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: I. Inplane and Interlaminar Shear Behavior of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 25, no. 8, pp. 932–957, Aug. 1991.
- [30] K. Friedrich, *Application of Fracture Mechanics to Composite Materials*. Elsevier, 2012.
- [31] S. W. Tsai and American Society for Testing and Materials, Eds., Composite materials, testing and design (fifth conference): a conference sponsored by the American Society for Testing and Materials, New Orleans, La., 20-22 March 1978: [papers]. Philadelphia: American Society for Testing and Materials, 1979.
- [32] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: II. Longitudinal (0°) and Transverse (90°) Tensile and Flexure Behavior of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 25, no. 8, pp. 958–991, Aug. 1991.
- [33] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties. III. Longitudinal (0°) Compressive Properties of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 26, no. 3, pp. 310–333, Mar. 1992.

- [34] L. T. Drzal, "The interphase in epoxy composites," in *Epoxy Resins and Composites II*, K. Dušek, Ed. Springer Berlin Heidelberg, 1986, pp. 1–32.
- [35] R. Chandra, S. P. Singh, and K. Gupta, "Damping studies in fiber-reinforced composites a review," *Compos. Struct.*, vol. 46, no. 1, pp. 41–51, Sep. 1999.
- [36] S. Dong and R. Gauvin, "Application of dynamic mechanical analysis for the study of the interfacial region in carbon fiber/epoxy composite materials," *Polym. Compos.*, vol. 14, no. 5, pp. 414–420, Oct. 1993.

# CHAPTER 4: INTERLAMINAR REINFORCEMENT OF GLASS FIBER/EPOXY POLYMER COMPOSITES WITH GRAPHENE NANOPLATELETS

## Abstract

This chapter investigated the ability of graphene nanoplatelets (GnPs) to improve the interlaminar mechanical properties of glass-reinforced multilayer composites. A novel method was developed for the inclusion of GnPs into the interlaminar regions of plain-weave, glass fabric fiber reinforced/epoxy polymer composites (GFRPs) processed with vacuum assisted resin transfer molding (VARTM). Flexural testing showed a 29% improvement in composite flexural strength with the addition of only 0.25 wt% GnP. At the same concentration, mode-I fracture toughness testing revealed a 25% improvement. Additionally, low-velocity drop weight impact testing showed improved energy absorption capability with increasing concentration of GnPs. Ultrasonic C-scans and dye penetration inspection of the impact- and back-sides of the specimens qualitatively support these results. Finally, the impact damage area was quantified from the C-scan data. These results showed that the impact-side damage area decreased with increasing concentration of GnP, while the back-side damage area increased.

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#### 4.1 Introduction

Recently, in an effort to reduce CO<sub>2</sub> emissions, the Environmental Protection Agency (EPA) and the National Highway Traffic Safety Administration (NHTSA) have introduced strict fuel economy standards for light duty vehicles [1]. Light-weighting vehicles with high performance, fiber reinforced/epoxy polymer composites (FRPs) will likely play a major role in continuing to meet or exceed EPA and NHTSA standards. Compared to steel, FPRs offer higher specific strength and stiffness at a low density. However, FRPs are brittle materials, owing to their cross-linked polymer matrices and strong and stiff fibers [2]. Therefore, over the last four decades researchers have investigated the incorporation of micron and more recently nanoscale materials to improve FRP toughness [3].

Due to their outstanding thermal, electronic and mechanical properties, carbonaceous nanomaterials have shown considerable promise as functional additives to epoxy and FRPs [4] and [5]. These materials include carbon nanotubes (CNTs), buckminsterfullerene (C<sub>60</sub>) and more recently graphene nanoplatelets (GnPs) [4] and [6]. In particular, CNTs as additives to polymer matrices have been explored extensively [7]. Their high aspect ratios and high specific strength and stiffness have been shown to improve strength, stiffness and toughness of resulting epoxy and FRP nanocomposites; of course, their beneficial effects are contingent on the degree of their dispersion throughout the composite polymer matrix [8]. Chemical functionalization of CNTs can provide enhanced dispersion and improved interfacial interaction between the polymer matrix and functionalized nanotubes [7]. The beneficial incorporation of CNTs into epoxy has been demonstrated.

However, good quality CNTs are expensive, available at a cost of about 100 US dollars per gram [9]. Therefore, to enhance epoxy properties in a cost effective manner, researchers have investigated the incorporation of GnPs, which share CNT's outstanding thermal, electronic and mechanical properties at about 1/500<sup>th</sup> of the cost [10]. These materials are conceptually different from graphene oxide (GO), which is produced via an oxidative process that disrupts the sp<sup>2</sup> basal plane hybridization, effectively reducing graphene's outstanding properties; reduced graphene oxide (rGO) shares these effects [11], [12] and [13]. Furthermore, GnPs share nanoclay's layered structure, where graphene sheets are held together by weak van der Waals forces. As such, GnPs have been intercalated and exfoliated in epoxy [14], [15].

Different methods to disperse GnP into epoxy resins have been discussed in the literature. For example, Li et al. achieved a 1 wt% percolation threshold in Epon 828 epoxy resin cured with m-phenylenediamine through optimization of solution casting, sonication and high shear rate mixing parameters [16]. Low concentrations of UVO treated GnP (2 wt%) showed enhancements in glass transition temperature (Tg) (20 °C), flexural modulus (17 %) and decreased electrical resistivity of EPCs (by about 5.5 x 10<sup>6</sup> times from 0.2 wt% GnP to 2 wt% GnP). Size distribution and image analysis showed the GnPs had a thickness of about 3 nm and a basal diameter of about 46 µm. Zaman et al. showed improvements in fracture toughness (200%) and Tg (14 °C) of a polyoxyalkyleneamine cured diglycidyl ether of bisphenol A (DGEBA) epoxy with acid treated GnP and 4,4'-methylene diphenyl diisocyanate functionalized GnP at loadings of 4 wt% [17]. Compared to the 'as-received' GnP, the isocyanate functionalized GnP

showed better matrix adhesion, which was attributed to covalent bonding between the epoxy and GnP isocyanate groups. Further, the size of the GnP 'clusters' in epoxy decreased from about 2  $\mu$ m for the non-treated GnPs to 1  $\mu$ m for the isocyanate treated GnPs. Chandrasekaran et al. investigated both solution casting and three roll milling (3RM) methods to disperse GnPs (12-15 nm thick by 20-50  $\mu$ m in diameter) in epoxy [18]. They found that 3RM provided a better dispersion than sonication methods. The optimum concentration in this system was 1.0 wt%, providing a 43% increase in the critical stress intensity factor (K<sub>1c</sub>). Collectively, these results encourage exploration of GnP as additives to GFRPs.

Two primary methods to introduce nanoparticles into laminate composite materials made via resin transfer molding (RTM) are described in the literature. One method involves dispersing the nanoparticles into a resin system, followed by resin infusion of the laminate plies. However, the high surface area and aspect ratio of the nanoparticles can result in significant increases in resin viscosity [19]. Furthermore, filtration of the nanoparticles at the resin inlet by the fiber reinforcement can prevent their homogeneous dispersion. Another method involves coating/ sizing the nanoparticles directly onto the fiber surfaces, followed by resin infusion, which can eliminate problems created with the first technique [20].

The strengthening and toughening mechanisms of graphene nanoplatelets in epoxy have been reported [14], [15]. However, to the best of the authors' knowledge, the existing literature does not describe the incorporation of pristine GnPs in the interply regions of FRPs made with vacuum assisted resin transfer molding (VARTM). As such, this work will investigate the dispersion of GnPs onto the surface of plain-weave glass

fabric prior to infusion with a two-part diglycidyl ether of bisphenol A (DGEBA) epoxy resin system. The influence of inter-ply GnP concentration on nanocomposite flexural properties, mode-I fracture toughness and low-velocity impact properties are described in the following sections.

# 4.2 Methods

## 4.2.1 Materials

A low viscosity, two-part resin system, namely Applied Polymeric SC-15 epoxy resin (SC-15A) and SC-15 amine hardener (SC-15B) was used in both the coating and VARTM processing. The fiber reinforcement was Owens-Corning ShieldStrand S2-glass in plain-weave with an areal-specific weight of 832 g/m<sup>2</sup>. Exfoliated graphene nanoplatelets (xGnP-5) with a mean diameter of 5 µm and a thickness of 5-7 nm were provided by XG Sciences in Lansing, MI.

# 4.2.2 Coating process and Raman spectroscopy

To disperse the GnPs into a solvent for subsequent coating onto glass fabric, measured quantities of GnPs were added to a solution of 30.0g of SC-15A, 2.25g SC-15B and 5.0 x  $10^2$  mL of isopropanol. The mixture was then stirred for 5 minutes, followed by tipsoncation at 30W power (35% amplitude) for 1 hour with a pulse of 10 seconds on, 5 seconds off. After sonication, aliquots of the mixture were weighed and brushed onto the surface of S2-glass fabrics such that the final composite laminate panels had concentrations of 0.10, 0.25, 0.50 and 1.00 wt% GnP, respectively. The coated fabrics were degassed in a fume hood for 12-15 hours prior to infusion.
Drops of the coating solution were placed onto a silicon substrate to determine the degree of exfoliation and size distribution of GnPs in isopropanol. Once the solvent was evaporated from the substrate, the GnPs were analyzed under scanning electron microscopy (SEM). The GnPs were also analyzed under Raman spectroscopy using a LabRAM Aramis Raman spectrometer with a HeNe laser (514 nm) at room temperature.

# 4.2.3 Composite production

Glass fabrics with dimensions of 30.48 cm by 30.48 cm (for flexural and fracture toughness test specimens) and 60.96 cm by 30.48 cm (for impact test specimens) were infused with the SC-15 resin system using the VARTM process, where the stoichiometry of epoxy and curing agent was 100:30 by weight. A 4-ply layup was used to manufacture flexural and impact test specimens, while 8-ply layups were used to produce fracture toughness test specimens. The cured sample thicknesses are provided in the testing section. Further, a 140 mm impervious Teflon<sup>®</sup> peel-ply material, which spanned the length of the panel, was folded in half and placed between the 4<sup>th</sup> and 5<sup>th</sup> plies of the fracture toughness test specimens. The infusion system consisted of a 91.44 cm by 60.96 cm steel tooling plate with a single injection port and a single vacuum port. The two-part resin system was mixed with proper stoichiometry and degassed for 20 minutes under 27 inHg vacuum. The layup consisted of a tooling plate, a small quantity of liquid mold release, pristing glass or sized (as described in 2.2 above) fabric, release ply material and distribution media. The layup was vacuum bagged under 0.2 kPa and the infusion was completed within two to four minutes. The infusion system was then placed into a convection oven for cure at 60 °C for 2 hours and post cure at 94 °C for 4 hours.

# 4.2.4 Composite testing

# 4.2.4.1 Flexural testing

Four-point bending flexural specimens were prepared and tested in accordance with ASTM D-6272, "the test method for flexural properties of unreinforced and reinforced plastics by four-point bending". Sample testing was performed on a Materials Test System (MTS) 810 in conjunction with a laser extensometer to accurately measure sample displacement. The coupons were 12.7 mm by 60.0 mm with an average thickness of 2.60 mm. Each coupon was carefully placed onto the support bars to ensure symmetric and level sample loading. The load span was taken as 1/3 of the support span and was based on sample thickness using a 16:1 span-to-depth ratio. A 20N pre-load was applied at the beginning of each flexural test. A 1.215 mm/min cross-head speed, as calculated from the support span and sample thickness, was applied to each specimen. The specimens were tested until failure and their load-displacement data was recorded for analysis.

# 4.2.4.2 Mode-I fracture toughness testing

Eight-ply panels with a folded 70 mm impervious Teflon® peel-ply material insert located between the 4th and 5th middle plies were manufactured for mode-I testing. Specimens were prepared and tested on the basis of ASTM 5528, "the test method for mode-I interlaminar fracture toughness of unidirectional fiber reinforced polymer matrix composites", except that the piano hinges were rotated 180° for simpler attachment. Since the standard calls for a 50 mm starter crack, the panel edge with 70 mm Teflon® insert was cut with a diamond bonded saw to ensure standard specifications. Piano hinges with a width of 25.4 mm were attached with a 5-minute cure Quickset® epoxy to the ends of the 25.4 mm wide and 152.4 mm long samples. The average sample thickness was 4.85 mm. A clean razor blade was then carefully used to remove the starter crack Teflon® material and the sample was placed onto the MTS grips for testing. A constant loading rate of 5 mm/min was applied to open the samples under mode-I and a Cannon® EOS Rebel® T4i was used to record the crack event. The drawing program Corel® was used to determine the crack length for each specimen. Mode-I fracture toughness (G<sub>Ic</sub>) values were calculated according to modified beam theory, as shown in Equation 1:

$$G_{lc} = \frac{3P\delta}{2ba} \tag{1}$$

where P is the load (N),  $\delta$  is the load point displacement (m), b is the specimen width (m) and a is the delamination length (m).

# 4.2.4.3 Low velocity drop weight impact testing

A Drop-Weight Dynatup 8250 impact machine was used for impact testing. The machine setup consists of a 12.7 mm diameter instrumented tup mounted on a crosshead with a provision for the attachment of weights. To perform an impact test, the 11.8 kg impactor is released along stiff, smooth guide columns and singularly impacts a mounted composite sample. The samples were 12.7 cm by 12.7 cm and were clamped at the base of the test fixture by 8 bolts. The energy of impact is governed by the drop height; four different energy levels were used for testing: 20, 40, 60 and 80J, respectively. Load-time

curves were recorded for analysis and energy and displacement curves were calculated from the data using Newton's equations of motion.

# **4.2.4.4 Dye penetration inspection**

Dye penetration inspection (DPI) was performed to investigate the extent of surface/ interlaminar damage in the top layers due to the low-velocity impact event. This damage is usually not visible to the naked eye and hence the DPI measurements. Zyglo Penetrant ZL-27A fluorescent inspection dye was sprayed onto the impact- and back-sides of the impacted specimens. After 30 minutes, excess penetrant was removed and Zyglo Developer Z9-9F was added to provide contrast. Each side of the sample was irradiated by UV-light and the fluorescence was captured by a digital camera.

# 4.2.4.5 Ultrasonic c-scans

To evaluate the internal structure of the impacted specimens, ultrasonic C-scanning was performed using the Pulse-Eco method. An ultrasonic ULTRAPAC II system with a 5 MHz, 12.7 mm transducer was used for data acquisition and UTwinTM® software was used for imaging and analysis. The scan area was selected by choosing the x and y position that would result in complete scanning of the specimen. To evaluate the reflected signal amplitude changes through the back of each specimen, an electronic gate was set on the back surface echo to digitize the signal. For each impacted specimen, scanning was carried out for both the front- (impact-side) and back-sides. Histograms of the pixel values from the C-scan data files were made in MATLAB. A common threshold value was determined from the histograms. The number of pixels above the threshold for each image was counted and represented the pixelated damage area. The damage area in pixels was then converted to mm<sup>2</sup> using a conversion factor from the UTwinTM® software.

# 4.3 Results and Discussion

# 4.3.1 Dispersion and Raman spectroscopy of graphene nanoplatelets

GnPs were examined under SEM after their sonication dispersion in isopropanol. A representative SEM image is shown in **Figure 1**. Size distribution analysis of multiple images showed that the GnPs had a mean basal plane diameter of  $5.1 \pm 2.5 \,\mu\text{m}$  under the sonication parameters used in this study. Since the sonication power was at a relatively low 30W, there was a minimal amount of size reduction of xGnP-5, which, according to the manufacturer, has a nominal basal plane diameter of 5  $\mu$ m.



**Figure 4.1:** Exfoliated graphene nanoplatelets (GnP) after sonication in 2-isoproponol [21].

Raman spectroscopy can be used to examine order in carbon nanostructures. The so-called 'disorder' (D), 'G' and '2D' peaks provide information about the relative order within single layer graphene, multilayer GnPs and graphite [21]. Raman spectra of the GnPs before and after sonication dispersion in isopropanol are shown in **Figure 2** and the peaks are labeled accordingly. The spectra in **Figure 2** also show  $I_D/I_G$  ratios of 0.1 and 0.03 for GnPs before and after sonication dispersion, respectively. As such, the GnPs retain a large degree of order under the processing conditions used in this study. Also, it appears that sonication of the GnPs in isoproponal may have removed some defects in the material, as the  $I_D/I_G$  ratio decreased by an order of 10 for the GnPs after sonication dispersion.



Figure 4.2: Raman spectra of GnP M5 before and after sonication in 2-isopropanol [21].

# 4.3.2 Mechanical and fracture properties of GFRPs

The stress-strain behavior of the GnP nanocomposites with concentrations of 0 ("pristine"), 0.10, 0.25 and 0.50 wt% interlaminar GnP is shown in in **Figure 3**. The slope of the elastic region at each concentration was linear until the first load drop. This point was used to calculate the flexural strength for each specimen. The largest flexural strengths were observed for samples with low loadings of GnPs, namely 0.10 and 0.25 wt%. Once the concentration of GnPs reached 0.50 wt%, the specimen stress-strain response closely resembled that of the pristine samples. These trends were observed for all samples tested.



**Figure 4.3:** Four-point flexural test results for pristine and 0.10, 0.25 and 0.50 wt% GnP samples [21].

The summary of flexural strength results for various GnP concentrations is presented in **Figure 4**. Pristine specimen flexural strength values were found to be larger than those reported in the literature for the S2-glass/ SC-15 system [22]. Haque et al. reported a value of flexural strength at 298 MPa [22], while experimental results in this work yielded  $324.8 \pm 31.6$  MPa. For the nanocomposites developed in this work, the GnP concentration was found to be optimal at 0.25 wt%, resulting in a 29% increase in flexural strength relative to the pristine specimens. At 0.50 wt% GnP, the nanocomposite flexural strength showed a less dramatic increase relative to the improvement found at 0.25 wt%. At 1.0 wt% GnP, the error bars between the pristine and GnP samples overlap, and no improvement was observed. Furthermore, these enhancements in flexural strength are comparable to those reported by Haque et al [22], but at ¼ wt% of nanofiller. It appears that GnPs are more efficient nano-additives than intercalated and phase separated montmorillonite clay in the S2-glass/ SC-15 system.





The concentration of GnP had an effect on the failure mode of the samples during flexural testing. Those samples with lower concentrations of GnP (0.10 and 0.25 wt%) failed on the tension side, while those samples with higher concentrations of GnP (0.50 and 1.0 wt%) failed on the compression side or by composite delamination. At lower concentrations of GnP, the polymer matrix was better able to transfer stress to the rigid GnPs and the fiber reinforcement. However, when the concentration of GnPs became too large the interlaminar adhesion decreased leading to delamination and microbuckling on the compressive side.

Mode-I fracture toughness (G<sub>Ic</sub>) testing results for pristine, 0.25 wt% and 1.00 wt% GnP specimens are shown in **Figure 5**. Similar to flexural tests, the mode-I fracture toughness (G<sub>Ic</sub>) showed maximum enhancement (25%) at GnP concentrations of 0.25 wt%. This reinforces the possibility that 0.25 wt% may be the most optimal concentration for enhancement in multiple properties (in this case, flexural and G<sub>Ic</sub>). Furthermore, the 1.00 wt% GnP specimens indicated a substantial decrease in G<sub>Ic</sub> values, which could be due to agglomeration of GnPs at the fiber/matrix interface. In addition to acting as stress concentrators, such aggregates can form a path for crack propagation [23].



**Figure 4.5:** Mode-I fracture toughness (G<sub>Ic</sub>) results of pristine and 0.25 and 1.0 wt% GnP samples [21].

Mode-I fracture surfaces of specimens with varying concentrations of GnPs were analyzed under SEM. A variety of details, including micron and sub-micron scale voids, are visible at both low and high magnifications of pristine and GnP-doped samples. For all specimens, the SEM images indicated that the propagating crack was limited to the region between the middle plies.

Resin transfer molding processes (RTM), in which a fabric pre-form is infused with a two-part resin system, can introduce voids which are possibly due to mechanically entrapped air or matrix constituents. Infused fabrics in plane-weave have two regions in which voids can form: the smaller region between the individual fibers within a tow and the larger region between individual tows where the warp and fill cross over one another; voids formed in these regions are called "tow voids" and "channel voids", respectively [24]. Channel voids were found at the warp and fill cross-over regions, as determined by inspection of the fracture surfaces. One such void is shown in **Figure 6a**; this void has a diameter on the order of 1 mm. **Figures 6b** and **6c** show progressively higher magnification views of the color mapped boxed areas. The wavy pattern in **Figure 6c** indicates a free surface confirming the channel void in **Figure 6a**.



**Figure 4.6:** Scanning electron microscopy (SEM) image of a pristine mode-I fracture surface. Image (a) shows a macrovoid and images (b) and (c) are progressively higher magnifications of the void edge, as indicated by the colored boxes [21].

In addition to larger scale channel voids, the fracture surfaces show sub-micron scale cavities throughout the polymer matrix. One such cavity is highlighted with a white arrow in **Figure 6b**. These cavities likely result from the proprietary toughening agent present in the Applied Polymeric SC-15 resin system [25], [26], [27]. During fracture of the cured specimens, the phase separated particles cavitate inducing void growth of the matrix resulting in sub-micron and micron-scale voids on the fracture surfaces of toughened epoxies [28]. In addition to cavitation, the left side of **Figure 6b** shows a

rough fracture surface due to matrix shear yielding induced by cavitation of the phaseseparated rubber domains [29].



**Figure 4.7:** Scanning electron microscopy (SEM) image of a mode-I fracture surface of a 0.25 wt% GnP sample. Image (a) shows a typical channel region and image (b) shows GnPs on the fibers [21].

Samples containing inter-ply, dispersed GnP exhibit different fracture surface morphologies at the warp and fill cross over regions. For example, **Figure 7a** shows that the channel regions in the 0.25 wt% GnP specimens have a rougher morphology than channel regions in the pristine specimens shown in **Figure 6**. In fracture surface studies of matrix morphology, a smooth, featureless fracture surface is attributed to brittle failure, while rougher fracture surfaces are attributed to tougher nanocomposites. The rough surfaces of matrix regions in 0.25 wt% GnP incorporated composites compliment the experimental findings of high G<sub>Ic</sub> values. **Figure 7b** shows a closer view of the 0.25 wt% GnP mode-I fracture surface fibers. GnPs present on these surfaces appear to be aggregated to some extent. Resin rich regions of the 0.25 wt% GnP fracture surfaces are shown in **Figure 8**. A GnP aggregate is highlighted with a green box in **Figure 8a** and a closer view of this aggregate is shown in **Figure 8b**. Also, **Figure 8a** shows cavitation of the rubber toughening agent in SC-15A, as previously described [29].



**Figure 4.8:** Inter-tow region of a 0.25 wt% GnP nanocomposite showing cavitated rubbery adducts and aggregation of GnPs [21].

# 4.3.3 Low velocity drop weight impact properties of GFRPs

The impact test results for pristine, 0.25 and 1.0 wt% GnP specimens are presented in

Figures 9-11 and the corresponding peak loads are shown in Table 1.

Impact Energy	Pristine		0.25 wt% GnPs		1.0 wt% GnPs	
	Peak load (kN)	Absorbed Energy (J)	Peak load (kN)	Absorbed Energy (J)	Peak load (kN)	Absorbed Energy (J)
20	$0.77 \ge 10^{1}$	$0.47 \ge 10^1$	0.75 x 10 <sup>1</sup>	$0.62 \ge 10^1$	$0.69 \ge 10^1$	$1.12 \times 10^{1}$
40	$1.14 \text{ x } 10^1$	$1.66 \ge 10^1$	$1.15 \times 10^{1}$	1.79 x 10 <sup>1</sup>	$0.93 \times 10^{1}$	$2.67 \times 10^{1}$
60	$1.30 \ge 10^{1}$	$4.83 \times 10^{1}$	$1.21 \times 10^{1}$	$4.34 \times 10^{1}$	$1.17 \text{ x } 10^1$	$4.45 \times 10^{1}$
80	$1.39 \ge 10^{1}$	$7.84 \times 10^{1}$	$1.45 \times 10^{1}$	$7.86 \times 10^{1}$	$1.17 \text{ x } 10^1$	$7.56 \ge 10^1$

**Table 4.1:** Low velocity impact results for pristine, 0.25 and 1.0 wt% GnP specimens tested at 20, 40, 60 and 80J of impact energy, respectively [21].

The peak loads represent the amount of force the composite can withstand before significant damage. The force-time histories of pristine, 0.25 and 1.0 wt% GnP specimens impacted at 20, 40, 60 and 80J, respectively, are shown in **Figure 9**.



**Figure 4.9:** Force-time histories of pristine, 0.25 wt% and 1.0 wt% GnP specimens at 20, 40, 60 and 80J impact energies, respectively [21].

At 20J of impact energy, the specimen responses are symmetric about the peak load for both pristine and GnP-reinforced composite laminate plates, which indicates a lack of prominent damage. Peak loads for the pristine specimens are larger than those reported in the literature for the S2-glass/ SC-15 system [29]. However, the peak load decreased with increasing GnP concentration, which could result from minor interlaminar damage and/or debonding between the polymer matrix and GnP nanoparticles. At 40J impacts, the specimen responses exhibited a slight asymmetry about the peak load, indicating the presence of damage in the specimens. It is also interesting to note that at 40J, the 1.0 wt% specimens exhibited a sharp load drop at about 7.8 kN, followed by a climb up to peak load. This load drop at 7.8 kN was also present for the 1.0 wt% samples at 60 and 80J, but was not visible in the 1.00 wt% specimens tested at 20J. This abrupt load drop is attributed to the first interlaminar failure in the specimens. The subsequent load increase may be due to other phenomena, including tortuosity and crack diversion contributions by GnP in the epoxy matrix.

At 60 and 80J, the load-time specimen responses were substantially asymmetric about the peak load. Beyond this load-point, several subsequent load drops occurred prior to the saturation level; the number of load drops was found to increase with increasing energy level. Each load drop indicates some damage, which may be due to fiber breakage on front and back surfaces, matrix cracking and/or interfacial delamination. For both 60 and 80J energy levels, the area under the load-time curves up to saturation increased with increasing concentration of GnPs, which implies that energy absorption performance is enhanced with increasing GnP concentration.

The energy-time histories of pristine, 0.25 wt% and 1.0 wt% GnP specimens impacted at 20, 40, 60 and 80J, respectively, are shown in **Figure 10** and the corresponding absorbed energies are noted in Table 1.



**Figure 4.10:** Energy-time histories of pristine, 0.25 wt% and 1.0 wt% GnP specimens at 20, 40, 60 and 80J impact energies, respectively [21].

Absorbed energy is defined as the difference between the impact and rebound energies and is shown schematically in **Figure 10**. At 20 and 40J impact energies, energy absorption performance increased with increasing concentration of GnPs. However, at 60J, the energy absorption performance was highest for the pristine specimens, whereas the GnP-reinforced samples exhibited the same trend as described for 20 and 40J impact energies. This anomaly may be the result of cumulative effects of many parameters including but not limited to thickness variation between tested specimens, slight variation in sample surfaces and resulting boundary conditions. At 80J, the energy absorption performance reached saturation for both pristine and 0.25 wt% GnP samples; perforation of the tested specimens by the impactor tup was observed. However, the 1.0 wt% GnP samples were able to absorb some of the impact energy, protecting the specimen from perforation.

The force-deflection histories of pristine, 0.25 wt% and 1.0 wt% GnP specimens impacted at 20, 40, 60 and 80J, respectively, are shown in **Figure 11**.



**Figure 4.11:** Force-deflection histories of pristine, 0.25 wt% and 1.0 wt% GnP specimens at 20, 40, 60 and 80J impact energies, respectively [21].

At 20, 40 and 60J of impact energy, the pristine, 0.25 wt% GnP and 1.00 wt% GnP specimens show a closed loop. This area inside the loop is the energy absorbed during impact and the area under the curve is the energy transferred from the tup to the plate and

back [30]. As anticipated, these loops were observed to increase with increasing impact energy.

Analysis of **Figures 9-11** shows that the slopes of the pristine and 0.25 wt% GnP specimens are similar at all of the energies tested. However, the 1.0 wt% GnP specimens have a different slope than the other concentrations; this effect is more pronounced at higher impact energies. As such, samples with 1.0 wt% GnP exhibited different failure modes under low-velocity impact than the pristine or 0.25 wt% GnP specimens.

Post impact testing specimens were examined under dye-penetration inspection (DPI). **Figure 12** shows the impact-side **(12a)** and back-side **(12b)** DPI images of pristine, 0.25 wt% and 1.0 wt% GnP samples tested at 20, 40, 60 and 80J, respectively. Images in **Figure 12a** and **12b** show prominent surface damage of the pristine specimens, which could have resulted from delamination, matrix cracking and/or fiber breakage. This damage increased with increasing impact energy levels. The impact-side images show a "cross" pattern, which is attributed to the fiber weave. The back-side images show a "star" pattern, which results from buckling of the panel by the impact tup. Since the 80J pristine specimen was perforated during the impact event, the back-side of the panel did not buckle much and a "cross" pattern was observed.



**Figure 4.12:** Dye-penetration inspection (DPI) images of the impact side (12a) and back side (12b) of nanocomposites with various concentrations of GnP tested at 20, 40, 60 and 80J of impact energy, respectively [21].

At each energy level, the images in **Figure 12a** show a substantial decrease in damage area and intensity with increasing GnP concentration (across a row). The backside of the panels shown in **Figure 12b** have an increased surface damage area with increasing concentration of GnP, but the fluorescence decreases and thus the surface damage intensity is decreased.

Ultrasonic c-scan images of 0, 0.25 and 1.0 wt% GnP reinforced specimens impacted at 20, 40, 60 and 80J, respectively, are shown in **Figures 13** (impact-side) and **14** (back-side).



**Figure 4.13:** C-scan images of the impact-side of nanocomposites with 0, 0.25 wt% and 1.0 wt% GnP tested at 20, 40, 60 and 80J of impact energy, respectively [21].



**Figure 4.14:** C-scan images of the back-side of nanocomposites with 0, 0.25 wt% and 1.0 wt% GnP tested at 20, 40, 60 and 80J of impact energy, respectively [21].

The UTwinTM® software privides images consisting of pixels with RGB values from 0 to 255, as shown in the color-legends adjacent to each image. During the test, the sound emanates from the transducer and meets the first water/composite interface; some of the sound is reflected back (peak 1) and some is passed through the composite. Eventually, some sound will reach the second water/composite interface and again is partly reflected

back (peak 2). The UTwinTM® software indicated that the dark red pixels represented lost signal from the first water/composite interface. These pixels represent highly damaged areas. The lighter red-to-yellow pixels represent fiber breakage, matrix cracking and/ or interfacial delamination. Finally, the more blue colored pixels represent areas with little or no damage.

Qualitatively, **Figure 13** shows that the damage delocalizes and decreases in intensity with increasing concentration of GnPs. Also noteworthy is the lack of a 'cross'-like pattern from the presence of weaved fiber tows in the GnP specimens tested at 20 and 40J. This pattern becomes clear, albeit less intense for GnP specimens at 60 and 80J, as compared to the pristine specimens. It was also observed that the 0.25 wt% specimen tested at 60J contained a relatively large region of extensive damage, which could be attributed to surface variations, thickness variations and/ or resulting boundary conditions. The images in **Figure 14** showed delocalization of the damage with increasing concentration of GnP. However, unlike the front side images, the damage intensity appears to increase with increasing concentration of GnPs.



**Figure 4.15:** Damage area (mm<sup>2</sup>) of nanocomposites with 0, 0.25 wt% and 1.0 wt% GnP tested at 20, 40, 60 and 80J of impact energy, respectively [21].

In order to quantify the c-scan results, the image files were processed with MATLAB. A histogram of pixel values with a threshold value of 250 is shown in **Figure 15a**. This histogram is from the 0.25 wt% GnP, 60J impact energy C-scan image; each histogram showed a similar distribution of pixel values and therefore a threshold of 250 was chosen. Pixels with values beyond the threshold represent severely damaged regions in the samples. Therefore, these damage regions can be quantified by converting pixel values to mm<sup>2</sup> using the appropriate conversion factor from the UTwinTM® software (1 square pixel equals 0.16 mm<sup>2</sup>). The damage area for each c-scan image is shown for each concentration at all of the energy levels tested for both the impact-side (Figure 15b) and

back-side (Figure 15c) of the laminates. This analysis shows that the impact-side damage area decreases with increasing concentration of GnPs, while the back-side damage area increases. At higher concentrations, the GnPs were better able to absorb and dissipate impact energy throughout the specimens leading to increased interfacial damage on the back-sides of the panels. This effect was most pronounced at higher impact energies (60 and 80J) and at higher concentrations of GnPs (1.0 wt%).

# 4.4 Conclusion

A novel method for the dispersion of GnPs into the interply regions of FRPs produced with vacuum assisted resin transfer molding (VARTM) has been developed. The concentration of GnPs in the resulting nanocomposites was experimentally optimized to 0.25 wt% with enhancements of 29% in flexural strength and 25% in mode-I fracture toughness. However, at higher loadings of GnPs, the improvements in flexural strength were found to be relatively minimal and the strengths were similar to the baseline samples. Conversely, drastic reductions in fracture toughness were observed at high GnP concentrations. Fractographic investigation of the mode-I tested specimens indicated that channel regions, where the warp and fill cross over, had a relatively rougher fracture surface morphology due to the addition of GnPs. Low-velocity drop-weight impact testing of the nanocomposites developed in this study revealed enhanced energy absorption performance by interlaminar incorporation of GnPs. This enhancement was observed to increase with increasing interlaminar concentration of GnPs. Post impact damage analysis by DPI and ultrasonic C-scan imaging qualitatively confirm these results. A quantitative analysis of the C-scan data showed that the impact-side damage

area *decreased* with increasing GnP concentration, while the back-side damage area *increased*. This effect was attributed to the ability of the GnPs to absorb and dissipate impact energy throughout the laminates.

REFERENCES

# REFERENCES

- U. EPA, "GHG Emission Standards for Light-Duty Vehicles: Manufacturer Performance Report for the 2012 Model Year." [Online]. Available: http://www.epa.gov/otaq/climate/ghg-report.htm. [Accessed: 16-May-2014].
- [2] B. Wetzel, P. Rosso, F. Haupert, and K. Friedrich, "Epoxy nanocomposites fracture and toughening mechanisms," *Eng. Fract. Mech.*, vol. 73, no. 16, pp. 2375–2398, Nov. 2006.
- [3] A. F. Yee and R. A. Pearson, "Toughening mechanisms in elastomer-modified epoxies," *J. Mater. Sci.*, vol. 21, no. 7, pp. 2462–2474, Jul. 1986.
- [4] S. Chatterjee, F. Nafezarefi, N. H. Tai, L. Schlagenhauf, F. A. Nüesch, and B. T. T. Chu, "Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites," *Carbon*, vol. 50, no. 15, pp. 5380–5386, Dec. 2012.
- [5] F. Yavari, M. A. Rafiee, J. Rafiee, Z.-Z. Yu, and N. Koratkar, "Dramatic Increase in Fatigue Life in Hierarchical Graphene Composites," ACS Appl. Mater. Interfaces, vol. 2, no. 10, pp. 2738–2743, Oct. 2010.
- [6] T. Ogasawara, Y. Ishida, and T. Kasai, "Mechanical properties of carbon fiber/fullerene-dispersed epoxy composites," *Compos. Sci. Technol.*, vol. 69, no. 11– 12, pp. 2002–2007, Sep. 2009.
- [7] P.-C. Ma, N. A. Siddiqui, G. Marom, and J.-K. Kim, "Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review," *Compos. Part Appl. Sci. Manuf.*, vol. 41, no. 10, pp. 1345–1367, Oct. 2010.
- [8] F. Hussain, M. Hojjati, M. Okamoto, and R. E. Gorga, "Review article: Polymermatrix Nanocomposites, Processing, Manufacturing, and Application: An Overview," *J. Compos. Mater.*, vol. 40, no. 17, pp. 1511–1575, Sep. 2006.
- [9] "Materials Science Products," Sigma-Aldrich. [Online]. Available: http://www.sigmaaldrich.com/materials-science/material-scienceproducts.html?TablePage=16376687. [Accessed: 09-Jun-2014].
- [10] J. R. Potts, D. R. Dreyer, C. W. Bielawski, and R. S. Ruoff, "Graphene-based polymer nanocomposites," *Polymer*, vol. 52, no. 1, pp. 5–25, Jan. 2011.
- [11] Y. Hernandez *et al.*, "High-yield production of graphene by liquid-phase exfoliation of graphite," *Nat. Nanotechnol.*, vol. 3, no. 9, pp. 563–568, Sep. 2008.

- [12] L. Liu, J. Zhang, J. Zhao, and F. Liu, "Mechanical properties of graphene oxides," *Nanoscale*, vol. 4, no. 19, p. 5910, 2012.
- [13] C. K. Chua and M. Pumera, "Covalent chemistry on graphene," Chem. Soc. Rev., vol. 42, no. 8, pp. 3222–3233, Mar. 2013.
- [14] T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, and J. H. Lee, "Recent advances in graphene based polymer composites," *Prog. Polym. Sci.*, vol. 35, no. 11, pp. 1350–1375, Nov. 2010.
- [15] S. Chandrasekaran, N. Sato, F. Tölle, R. Mülhaupt, B. Fiedler, and K. Schulte, "Fracture toughness and failure mechanism of graphene based epoxy composites," *Compos. Sci. Technol.*, vol. 97, pp. 90–99, Jun. 2014.
- [16] J. Li, M. L. Sham, J.-K. Kim, and G. Marom, "Morphology and properties of UV/ozone treated graphite nanoplatelet/epoxy nanocomposites," *Compos. Sci. Technol.*, vol. 67, no. 2, pp. 296–305, Feb. 2007.
- [17] I. Zaman *et al.*, "Epoxy/graphene platelets nanocomposites with two levels of interface strength," *Polymer*, vol. 52, no. 7, pp. 1603–1611, Mar. 2011.
- [18] S. Chandrasekaran, C. Seidel, and K. Schulte, "Preparation and characterization of graphite nano-platelet (GNP)/epoxy nano-composite: Mechanical, electrical and thermal properties," *Eur. Polym. J.*, vol. 49, no. 12, pp. 3878–3888, Dec. 2013.
- [19] Z. Fan, K.-T. Hsiao, and S. G. Advani, "Experimental investigation of dispersion during flow of multi-walled carbon nanotube/polymer suspension in fibrous porous media," *Carbon*, vol. 42, no. 4, pp. 871–876, 2004.
- [20] S. Movva, G. Zhou, D. Guerra, and L. J. Lee, "Effect of Carbon Nanofibers on Mold Filling in a Vacuum Assisted Resin Transfer Molding System," J. Compos. Mater., vol. 43, no. 6, pp. 611–620, Mar. 2009.
- [21] N. T. Kamar, M. M. Hossain, A. Khomenko, M. Haq, L. T. Drzal, and A. Loos, "Interlaminar reinforcement of glass fiber/epoxy composites with graphene nanoplatelets," *Compos. Part Appl. Sci. Manuf.*, vol. 70, pp. 82–92, Mar. 2015.
- [22] A. Haque, M. Shamsuzzoha, F. Hussain, and D. Dean, "S2-Glass/Epoxy Polymer Nanocomposites: Manufacturing, Structures, Thermal and Mechanical Properties," *J. Compos. Mater.*, vol. 37, no. 20, pp. 1821–1837, Oct. 2003.
- [23] A. F. Avila, M. I. Soares, and A. Silva Neto, "A study on nanostructured laminated plates behavior under low-velocity impact loadings," *Int. J. Impact Eng.*, vol. 34, no. 1, pp. 28–41, Jan. 2007.

- [24] C. H. Park and L. Woo, "Modeling void formation and unsaturated flow in liquid composite molding processes: a survey and review," *J. Reinf. Plast. Compos.*, vol. 30, no. 11, pp. 957–977, Jun. 2011.
- [25] C. B. Bucknall and I. K. Partridge, "Phase separation in epoxy resins containing polyethersulphone," *Polymer*, vol. 24, no. 5, pp. 639–644, May 1983.
- [26] J. L. Hedrick, I. Yilgör, G. L. Wilkes, and J. E. McGrath, "Chemical modification of matrix Resin networks with engineering thermoplastics," *Polym. Bull.*, vol. 13, no. 3, pp. 201–208, Mar. 1985.
- [27] J. H. Hodgkin, G. P. Simon, and R. J. Varley, "Thermoplastic toughening of epoxy resins: a critical review," *Polym. Adv. Technol.*, vol. 9, no. 1, pp. 3–10, Jan. 1998.
- [28] W. D. Bascom, J. L. Bitner, R. J. Moulton, and A. R. Siebert, "The interlaminar fracture of organic-matrix, woven reinforcement composites," *Composites*, vol. 11, no. 1, pp. 9–18, Jan. 1980.
- [29] M. V. Hosur, M. R. Karim, and S. Jeelani, "Experimental investigations on the response of stitched/unstitched woven S2-glass/SC15 epoxy composites under single and repeated low velocity impact loading," *Compos. Struct.*, vol. 61, no. 1–2, pp. 89–102, Jul. 2003.
- [30] G. Belingardi and R. Vadori, "Low velocity impact tests of laminate glass-fiberepoxy matrix composite material plates," *Int. J. Impact Eng.*, vol. 27, no. 2, pp. 213–229, Feb. 2002.

# CHAPTER 5: HYBRID GRAPHENE NANOPLATELET (GNP)/TRIBLOCK COPOLYMER MODIFIED EPOXY AND CARBON FIBER REINFORCED/EPOXY POLYMER COMPOSITES (CFRPS)

#### Abstract

This work explored the fracture behavior and toughening mechanisms of graphene nanoplatelet (GnP) and poly(styrene)-block-poly(butadiene)-blockpoly(methylmethacrylate) (SBM) modified epoxy and carbon fiber reinforced/epoxy polymer composites (CFRPs). GnPs were dispersed in diglycidyl ether of bisphenol-A (DGEBA) resin cured with m-phenylenediamine (mPDA) using sonication (son.) and three roll mill (3RM) methods. At 3 wt% GnP, 3RM and son. dispersion methods led to 70 and 90% increases in fracture toughness,  $K_0$  (MPa\*m<sup>1/2</sup>), respectively. At 3 wt% SBM, K<sub>0</sub> of epoxy was increased by 70%. Scanning electron microscopy (SEM) of compact tension specimen fracture surfaces showed that GnPs activated crack deflection toughening mechanisms, while nanocavitation of sub 100 nm spherical SBM micelles induced void growth and shear yielding of epoxy. Debonding of SBM micelles was also observed on the fracture surfaces in the fast crack growth regime. Combined SBM and GnP hybrid modified epoxy showed an additive toughening effect, but no synergy in fracture toughness. Three point flexural testing indicated that GnPs (3 wt%) increased the flexural modulus of epoxy by 13% using either 3RM or son. dispersion methods; however, GnPs reduced epoxy flexural strength. Finally, GnPs were incorporated into a sizing applied to carbon fibers (AS4-12k) used to make GnP modified CFRPs via an in house sizing tower system, prepreg, vacuum bag and autoclave manufacturing method.

At only 1 wt% in the sizing, GnPs increased CFRP mode-I fracture toughness,  $G_{Ic}$  (J/m<sup>2</sup>) by 100% with no corresponding reduction in T<sub>g</sub> and a 14% reduction in longitudinal flexural strength. SEM of mode-I double cantilever beam fracture surfaces showed that GnPs in the matrix near the fibers activated crack bifurcation and deflection toughening mechanisms to increase fracture energy. Hybrid SBM/GnP modified CFRPs gave an 80% increase in G<sub>Ic</sub> with no corresponding reduction in flexural properties and T<sub>g</sub>.

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# 5.1 Introduction

The aromatic amine cured diglycidyl ether of bisphenol-A (DGEBA) can have intermediate or high glass transition temperature ( $T_g$ ), good mechanical properties and is used as matrix material in carbon fiber reinforced/epoxy polymer composites (CFRPs). However, cross-linked epoxy polymers are brittle and are susceptible to failure initiated at a defect in the material under an applied load or impact event. Therefore, a second phase is incorporated into the epoxy to activate toughening mechanisms to increase composite fracture toughness.

One method to increase the fracture toughness of epoxy is by incorporation of a block copolymer consisting of both soft and epoxy miscible blocks [1], [2], [3] and [4]. Block copolymers consist of polymer chains of dissimilar chemical functionality bound by covalent chemical bonds [5]. Block copolymers can self assemble into mesostructures with a rich range of morphologies [6]. In amphiphilic diblock copolymers, for example, the morphology of the block copolymer depends on two competing factors, those being

the interfacial energy between two blocks of dissimilar chemistry and stretching of the polymer chains [6]. Both diblock and triblock copolymers have been used to make nanostructured thermosets to improve the fracture toughness of epoxy [1] and [4]. The triblock copolymer poly(styrene)-block-poly(butadiene)-block-poly(methylmethacrylate) (SBM) has been studied as a toughening agent in lower and intermediate T<sub>g</sub> amine cured DGEBA [7] and [8]. The toughening mechanism in SBM modified epoxy is similar to that of phase separating carboxyl-terminated butadiene-acrylonitrile (CTBN): cavitation of SBM micelles induces void growth and shear yielding of the surrounding epoxy [7] and [8]. However, SBM is a more effective toughening agent than CTBN for DGEBA cured with m-phenylenediamine (mPDA) due to an order of magnitude decrease in interparticle distance at identical loading levels [8]. Although the toughening mechanisms in block copolymer modified epoxies have been identified, their synergistic effect with rigid fillers is not well understood [9].

Hybrid modified epoxies consist of an epoxy matrix filled with a combination of both rigid and soft particles. Combinations of rigid and soft fillers in epoxy include spherical nanosilica particles with CTBN, graphene nanoplatelets with CTBN and carbon nanotubes with a block copolymer [10], [11] and [12]. For nanosilica/CTBN hybrid modified epoxies, some researchers have observed a synergy in fracture toughness, while others have not [13]. The synergy in fracture toughness of nanosilica/CTBN hybrid modified epoxy may result from a decrease in cross-link density of the epoxy network in the hybrid systems. The nanosilica particles hinder phase separation of CTBN, which lowers the cross-link density of the network and enhances the effect of rubber toughening [10] and [13].

In addition to potential synergistic effects, there are other unknowns in hybrid systems. In particular, the interactions between particles during fracture of hybrid modified epoxy are complex and therefore the toughening mechanisms have not been clearly established [10], [13] and [14]. Rio *et al.* investigated the toughening mechanisms in SBM/CNT hybrid modified DGEBA cured with piperidine [12]. Although the CNTs had an influence on the void growth of epoxy initiated by cavitation of SBM micelles, no synergy in fracture toughness between SBM and CNT modified epoxy was observed. SBM was a more effective toughening agent than CNTs. On the other hand, Yang *et al.* observed a synergy in fracture toughness between carboxylated CNTs and 50 nm diameter core shell rubber particles in epoxy [15].

Another possible hybrid modified epoxy is SBM combined with graphene nanoplatelets (GnPs). GnPs alone can toughen epoxy via crack pinning, deflection and bifurcation toughening mechanisms [16]. A combined SBM/GnP hybrid modified epoxy may show multi scale toughening and a synergy in fracture toughness. Therefore, this work investigates the fracture behavior and toughening mechanisms, as well as the mechanical and thermomechanical properties of SBM, GnP and hybrid SBM/GnP modified DGEBA cured with mPDA.

In addition to toughening epoxy, improvements in the interlaminar fracture toughness of CFRPs are also of interest. Fiber bridging, fiber nesting and fiber pullout mechanisms contribute to the fracture toughness of CFRPs [17]. Further improvements in CFRP fracture toughness can be achieved by toughening the composite matrix with phase separating rubber, core shell particles, silica nanoparticles or some combination of these additives [18]. However, there are only a small number of studies on the fracture

behavior of CFRPs modified with GnPs. Kostagiannakopoulou *et al.* manufactured CFRPs with GnP and graphite oxide (GO) modified matrices, respectively [19]. Their results showed that GnPs were a more effective toughening agent than GO, since separation of layers in GnPs may have contributed to the fracture toughness of the GnP modified CFRPs. At 0.5 wt% GnP in the matrix, the fracture toughness of the CFRP was increased by 50%. Their fractographic analysis showed that GnPs pinned and bifurcated the propagating crack, with platelet pullout and separation of layers observed as well. The influence of GnPs and GO on the composite mechanical and thermomechanical properties was not quantified in their work.

Other researchers have explored GnPs and GO as a reinforcing agent in the carbon fiber/epoxy matrix interphase. For example, Zhang *et al.* found that compared to a commercial sizing, GO (7.5 wt%) sized carbon fibers improved composite interfacial shear strength and interlaminar shear strength by 36% and 12.1%, respectively [20]. The improvements in composite interfacial properties by incorporation of GO were attributed to covalent chemical bonding between GO and the thermoset network. Qin *et al.* incorporated high surface area GnPs into the fiber/matrix interphase in CFRPs to improve transverse flexural strength and interlaminar shear strength by 52 and 19%, respectively [21]. However, the influence of the sub-micron diameter GnPs on the interlaminar fracture toughness of the CFRPs was not determined.

Researchers have explored GnPs as a toughening agent in the matrix of CFRPs. However, the influence of GnPs in the composite interphase on the fracture toughness, mechanical properties and thermomechanical properties of CFRPs has not yet been explored. Furthermore, the combination of GnP and SBM terpolymer toughening agents may show a synergy in CFRP fracture toughness. Thus, this work explores the combination of GnP and SBM additives on the mechanical, thermomechanical and fracture behavior of CFRPs.

# 5.2 Methods

# 5.2.1 Materials

The diglycidyl ether of bisphenol-A (DGEBA, n = 0.2) epoxy resin was purchased from Momentive (Epon 828). The curing agent was the aromatic diamine m-phenylenediamine (mPDA) and was purchased from Acros Organics. The SBM terpolymer was provided by Arkema under the name E21. Graphene nanoplatelets (GnPs) were supplied by XG Sciences and the AS4-12k carbon fibers used to manufacture CFRPs were supplied by Hexcel.

### 5.2.2 Raman and X-ray photoelectron spectroscopy

Raman spectroscopy of GnPs was conducted using a LabRAM Aramis Raman spectrometer with a HeNe laser (514 nm) at room temperature. The surface chemistry of the top 50-80 Å of GnPs was determined with X-Ray Photoelectron Spectroscopy (XPS). The measurements were performed using a PHI 5400 ESCA system. The base pressure of the instrument was less than 10<sup>-8</sup> Torr. The X-Ray was a non-monochromatic Mg source with a take-off angle of 45 degrees. Two types of scans were performed for each sample; a survey scan from 0-1100 eV taken with a pass energy of 187.85 eV and regional scans of each element at a pass energy of 29.35 eV. Data was fit using PHI Multipak (v8.0) software.

# 5.2.3 Production of neat, modified and hybrid modified epoxy

The neat DGEBA was blended as follows. DGEBA and mPDA were heated separately in a convection oven at 75 °C until the mPDA melted. The DGEBA and melted mPDA were blended at stoichiometry (14.5 phr) by hand for 2 min. The mixture was degassed in a vacuum oven at 75 °C under 27 mmHg for 5 min. The blend was cast into silicone molds and cured in a convection oven at 75 °C for 2 hrs followed by post cure at 125 °C for 2 hrs.

The SBM/DGEBA blend was made as follows. SBM was added to acetone and mixed on a stir plate for 24 hrs. Then, DGEBA was cast into the mixture and stirred for 1 hr. The SBM/DGEBA/acetone mixture was stirred on a hot plate at 65 °C overnight to remove the acetone. Once most of the acetone was removed, the SBM/DGEBA blend was degassed in a vacuum oven (27 inHg) at 60 °C for 4 hrs to remove any residual solvent. The SBM/epoxy blend was then mixed with metled mPDA (75 °C) for 2 min, followed by an additional degassing in a vacuum oven (27 inHg) at 60 °C for 5 min. Finally, the SBM/epoxy/mPDA blend was cast into silicone molds and cured in a convection oven under the same cure cycle described for the neat epoxy.

Both sonication and three roll milling methods were used to make GnP/DGEBA blends. The sonication (son.) dispersion method is described first. GnPs were dispersed in acetone using stirring and probe ultrasonication at 100W with a 7 second pulse for 1 hr. DGEBA was then cast into the GnP/acetone mixture followed by mixing on a stir plate for 1 hr. The GnP/DGEBA/acetone mixture was then sonicated for 1 hr at 100W with a 7 second pulse and then stirred overnight on a hot plate at 65 °C to remove the acetone. During sonication steps, the GnP mixtures were cooled with a dry ice bath. The
GnP/DGEBA mixture was then degassed in a vacuum oven (27 inHg) at 60 °C for 1 hr to remove any residual acetone. Finally, the GnP/DGEBA mixture was mixed with melted mPDA (75 °C) by hand for 2 minutes and degassed in a vacuum oven (27 inHg) at 60 °C for 5 min. The GnP/DGEBA/mPDA blend was cast into silicone molds and cured in a convection oven under the same cure cycle as described for the neat DGEBA.

The three roll mill (3RM) GnP/DGEBA blend dispersion method is identical to the sonication method, except that after sonication and solvent removal steps, the GnP/DGEBA mixture was milled using an EXAKT® three roll mill (3RM). The 3RM was operated at 250 rpm and the GnP/DGEBA blend was passed through 20, 10 and 5 µm nip gaps for 5, 5, and 10 passes, respectively.

The hybrid SBM/GnP/DGEBA blends were made using the sonication method, since fracture toughness testing revealed higher values in fracture toughness for GnP modified epoxy made using sonication dispersion only. Prior to addition of GnPs to acetone, SBM was mixed with acetone by stirring on a hot plate for 24 hrs. The sonication and casting method was identical to that described above for GnP/DGEBA blends made using the son. method.

#### 5.2.4 Characterization of epoxy

#### 5.2.4.1 Flexural testing

Three-point flexural testing was performed on a UTS screw driven load frame in accordance with ASTM D-790, "the test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials". Four samples were tested for each modified epoxy type. The thickness and width of the coupons was ~3.00 mm and

 $\sim$ 12.7 mm, respectively. A 16:1 span-to-depth ratio was used to test the coupons. The loading rate was determined for each coupon according to the the standard. The loading rate was  $\sim$ 1.30 mm/min. Values of flexural strength were determined at or below the 5% strain limit.

#### 5.2.4.2 Dynamic mechanical analysis

A TA Instruments DMA 800 was used to determine the thermomechanical properties of the neat and modified DGEBA. Single cantilever beam specimens having a length, width and thickness of 17.4 mm, 12.4 mm and 3.00 mm, respectively, were tested at an amplitude of 20  $\mu$ m and frequency of 1 Hz. The ramp rate was 3.00 °C/min and the temperature was ramped from room temperature to 250 °C. The storage modulus (G'), loss modulus (G'') and the Tan  $\delta$  were calculated from the data.

#### 5.2.4.3 Compact tension specimen testing

Compact tension specimen testing was performed in accordance with ASTM D5045, "the standard test method for plane-strain fracture toughness and strain energy release rate of plastic materials". A sharp pre-crack was generated by placing a fresh razor blade in the molded notch and dropping a stainless steel tube down a guide column onto the razor blade. The specimen thickness was 8.00 mm and the width was 32.0 mm. The specimens were tested on a Materials Test Systems (MTS) 810 servo-hydraulic load frame using clevis grips and loading pins. Care was taken to ensure the samples were level prior to testing. The fracture toughness, K<sub>Q</sub> was calculated as follows:

$$K_Q = \frac{P_Q}{BW^{1/2}} * f(x), \tag{1}$$

where  $P_Q$  is the maximum load (kN) sustained by the specimen, B is the specimen thickness (cm), W is the specimen width (cm) and f(x) is a geometric form factor for the compact tension specimen coupon described in ASTM D5045.

#### **5.2.4.4 Fractography via scanning electron microscopy**

Compact tension specimen coupons were coated with a 1-3 nm layer of tungsten using a Leica EM MID020 sputter coater, mounted onto a scanning electron microscope (SEM) stage with carbon tabe and grounded to the stage with copper tape. The stage and specimens were placed into a Carl Zeiss Auriga Dual Column FIB SEM for microscopy.

#### 5.2.5 Composite manufacturing

#### 5.2.5.1 Fiber sizing

AS4-12k carbon fiber tows were treated using an in-house, patented UV-ozone (UVO) treatment process (US 6,649,225 B2). The UVO treatment process increases the quantity of surface oxygen on the fibers and removes a weak boundary layer from the fiber surface to improve fiber tensile strength and interfacial shear strength in epoxy. After UVO treatment, the fibers were pulled through an in house, continuous fiber sizing system with drying towers set to 75 °C. Two types of fiber sizing were investigated. The first consisted of a 1 wt% solution of DGEBA + 9 phr mPDA in isopropanol. The second sizing type consisted of 1.0 wt% GnPs in isopropanol containing 1 wt% DGEBA + 9 phr mPDA.

To make the GnP modified sizing solution, 1.0 wt% GnPs were dispersed into a solution of 1.0 wt% DGEBA + 9 phr mPDA in isopropanol using a probe ultrasonication flow cell and a peristaltic pump to circulate the sizing solution from a reservoir through the sonication cell. GnPs were sonicated in the polymer solution at 100W for 1.5 hrs.

After sizing, the fibers were heated in a convection oven at 60 °C for 3 hrs to remove residual solvent.

#### 5.2.5.2 Prepreg and autoclave

Unidirectional prepreg tapes were made using a Research Tool drum winding prepregger. The resin pot, flattening pins and guide roller were set to 52.0 °C. The neat DGEBA + mPDA blend was made as previously described. The 10 phr SBM modified DGEBA + mPDA resin was made as follows. A quantity of 10 phr SBM powder was blended with DGEBA by stirring on a hot plate for 12 hrs at 150 °C. The SBM/DGEBA solution was then degassed for 1 hr at 60 °C to remove gas entrapped by the mixing process. After degassing, melted mPDA was mixed with the SBM/DGEBA blend by hand for 1 min. Finally, the SBM/DGEBA/mPDA blend was transferred to a Whipmix® bowl, pulled under vacuum and mixed with a paddle using a rotary motor for 2 minutes.

The DGEBA + mPDA resin or SBM modified resin was then poured into the resin pot and the sized fibers were pulled through the bath at 1.2 RPM to make tapes 0.30 m wide and 1.8 m long. The prepreg tapes were then cut, laid up in unidirectional configuration, vacuum bagged and autoclaved under 0.59 MPa (85 psi) at 75 °C for 2 hrs and 125 °C for 2 hrs. Vacuum (27 inHg) was applied to the vacuum bag during the first 30 min. into the first hold. 8 ply panels having dimensions (length x width x thickness) of

168

 $0.30 \ge 0.15 \ge 0.0013$  m were made for mechanical and thermomechanical testing. 18 ply panels having dimensions (length x width x thickness) of  $0.15 \ge 0.15 \ge 0.0034$  m were made for mode-I fracture toughness testing. A 60 mm long, 0.15 m wide Teflon® peel ply was placed between the middle plies of the mode-I panels at one edge to form a 50 mm pre-crack after removal of 10 mm of the plate edge with diamond bonded composite saw blade.

#### 5.2.6 Characterization of CFRPs

#### 5.2.6.1 Void volume and fiber volume fraction

Cross-sections (0°) of each panel were mounted in epoxy and polished to a 0.5 micron alumina finish. The polished surfaces were then etched using a Plasma Science  $O_2$  plasma reaction chamber to remove a small amount of the epoxy matrix to enhance microscopic observation of the carbon fibers. The mounts were examined under SEM as described above. At least two cross-sections were investigated for each panel and 8 images were taken for each cross-section. Adobe Photoshop® was used to determine the void volume, since the voids are contrast strongly from the fibers and matrix. The optical method is safer than acid digestion, which can also be difficult to perform experimentally.

The FVF was determined by the rules of mixtures using Equation (2):

$$V_f = \frac{\rho_c - \rho_m}{\rho_f - \rho_m},\tag{2}$$

where  $\rho_c$ ,  $\rho_m$  and  $\rho_f$  are the density (g/cm<sup>3</sup>) of the composite, polymer matrix and carbon fiber, respectively. The density of the matrix and CFRPs was measured according to

ASTM D792, "the standard test method for density and specific gravity (relative density) of plastics by displacement".

#### 5.2.6.2 Flexural testing

Three-point flexural testing was performed on a UTS screw-driven load frame according to ASTM D790, "the standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials". The ASTM standard indicates that larger span-to-depth ratios may be needed for accurate determination of the flexural modulus for highly orthotropic specimens. Therefore, span-to-depth ratios (L/D) of both 32:1 and 60:1 were used for each specimen type. The coupons were 1.3 mm thick and 12.7 mm wide. To ensure no more than 10% overhang was allowed for each specimen, the length of the specimens tested at L/D = 32 and 60 were 47 mm and 90 mm, respectively. The loading rates for the specimens tested at L/D = 32 and 60 were 2.54 mm/min and 9.4 mm/min, respectively. At least 5 coupons of each composite type were tested at each span-to-depth ratio for both longitudinal (0°) and transverse (90°) fiber directions. Values of flexural strength were determined at or below the 5% strain limit.

#### 5.2.6.3 Dynamic mechanical analysis

Dynamic mechanical analysis of CFRPs was performed in the same manner as for the GnP and SBM modified DGEBA. The CFRP specimens were 1.3 mm thick and 12.7 mm wide. At least 3 transverse specimens were tested for each composite type.

### 5.2.6.4 Mode-I fracture toughness testing

Mode-I fracture toughness testing was performed according to ASTM D5528, "the standard test method for the mode-I interlaminar fracture toughness of unidirectional fiber-reinforced polymer matrix composites". Double cantilever specimens were machined from the 18-ply mode-I panels such that the pre-crack was 50 mm. The specimens were nominally 3.4 mm thick and 21 mm wide. Piano hinges were mounted to the ends of the specimens using J-B Weld® adhesive and could freely rotate after bonding to the CFRPs. The hinge point was mounted along the edge of specimen for simpler attachment.

The specimens were gripped on a Materials System 810® servo hydraulic load frame and loaded at a rate of 5 mm/min. A Cannon® EOS Rebel® T4i camera was used to record the propagating crack and the load-displacement data was collected for analysis. The strain energy release rate,  $G_{Ic}$  (J/m<sup>2</sup>) was calculated using the modified beam theory method via **Equation (3)**:

$$G_{Ic} = \frac{3P\delta}{2ba},\tag{3}$$

where P is the load (N),  $\delta$  is the crack opening displacement (m), 'b' is the specimen width (m) and 'a' is the crack length (m) corresponding to a particular P and  $\delta$ . At least 5 specimens were tested for each composite type. To mitigate the influence of the starter crack in AS4-12k/DGEBA + mPDA CFRPs, the propagation values of fracture toughness were calculated for each specimen (G<sub>Ic</sub>) [22].

# 5.2.6.5 Fractography via scanning electron microscopy

CFRP mode-I cantilever beam fracture surfaces were shortened using a Felker ® saw with a diamond bonded blade. Care was taken to ensure that the cut corresponded to the end of the test and the specimens were not damaged during their preparation. The mode-I fracture surfaces were inspected along the fracture direction by electron microscopy as previously described to determine the failure mechanisms.

## 5.3 Results

# 5.3.1 Graphene nanoplatelets and SBM

Graphene is a single atomic layer of sp<sup>2</sup> hybridized carbon atoms arranged in a honeycomb lattice [23]. Graphene nanoplatelets (GnPs) consist of a few layers of graphene. According to the manufacturer's specifications, the specific surface area of the GnPs using in this work is 150 m<sup>2</sup>/g. Scanning electron microscopy (SEM) images of the GnPs are shown in **Figure 1**.



Figure 5.1: Scanning electron micrographs of graphene nanoplatelets.

The SEM images show that the GnPs have a smooth basal plane with folding observed at the platelet edges. The GnPs tend to aggregate due to their high surface area and attractive van der Waals forces between layers, which makes them difficult to disperse in a host epoxy [24].

GnPs consist mostly of sp<sup>2</sup> bonded carbon atoms on the basal plane with oxygen functional groups at the edges of the platelets [25]. Raman and X-ray photoelectron spectroscopy (XPS) were used to characterize the GnPs used to make GnP modified epoxy and CFRPs. In Raman spectroscopy of graphene, laser excitation (532 nm) gives rise to two primary peaks at 1580 cm<sup>-1</sup> (G) and 2690 cm<sup>-1</sup> (2D) [26]. A so called "disorder" (D) peak arising from defects in the sp<sup>2</sup> bonding structure is observed at 1350 cm<sup>-1</sup> [26]. The ratio of intensities of the D and G peaks (I<sub>D</sub>/I<sub>G</sub>) is an indicator of the disorder in graphene nanoplatelets [26]. The Raman spectrum of the GnPs is shown in **Figure 2**.



Figure 5.2: Raman spectrum of graphene nanoplatelets (GnPs).

The Raman spectrum of GnPs shows the G and 2D peaks at 1578.0 cm<sup>-1</sup> and 2711.8 cm<sup>-1</sup>, respectively. The D peak is found at 1353 cm<sup>-1</sup> giving rise to an  $I_D/I_G$  ratio of 0.1, which implies that the GnPs are pristine. The 2D peak for GnPs is shifted to a higher frequency compared to single layer graphene due to interactions between layers [26]. The red shift in the G peak in the layered structure is also due to interactions between layers [26].

X-ray photoelectron spectroscopy (XPS) was used to identify the chemical functional groups on the GnPs. The XPS C1s spectrum results are shown in **Table 1**.

**Table 5.1:** XPS C1s spectrum measured binding energies and corresponding functional groups.

Peak area	Binding energy (eV)	Chemical functional group
89.7	284.8	C=C
4.3	286.3	C-0
0.6	287.8	C=O
0.9	289.3	O-C=O
4.5	290.6	π=π*

The largest peak corresponds to sp<sup>2</sup> hybridized carbon atoms, with hydroxyl, ketone and carbonyl functional groups detected as well. The Raman spectrum and the XPS results indicate that the GnPs used in this work are mostly pristine with oxygen functional groups located at the platelet edges.

A solution casting method described in Section 2.3 was used to prepare SBM,

GnP and SBM/GnP hybrid modified epoxy. Films of SBM coated GnPs were cast from acetone (prior to solution casting in epoxy) and examined under SEM. The SEM images of the SBM coated GnP films (unstained) are shown in **Figure 3A1** and **A2**, respectively.



Figure 5.3: Scanning electron micrographs of GnPs coated with SBM.

The SEM images show that SBM is decorated on the surface of the platelets in the form of small, sub 100 nm spherical micelles. The Hansen solubility parameters listed in **Table 2** show that acetone is a better solvent for PMMA than for PS and PB blocks. **Table 2** also shows that PMMA is more miscible with GnPs than PS and PB blocks. Thus, the PS and PB blocks self assemble into spherical micelles surrounded by PMMA which decorate the surface of the GnPs.

Constituent	$\delta_{\rm D}({\rm MPa}^{1/2})$	$\delta_{\rm P}({\rm MPa}^{1/2})$	$\delta_{\rm H}({\rm MPa}^{1/2})$
Acetone	15.5	10.4	7.0
PS	22.28	5.75	4.30
PB	17.53	2.25	3.42
PMMA	18.6	10.5	7.5
GnPs	18.0	9.3	7.7

 Table 5.2: Hansen solubility parameters for acetone, SBM blocks and GnPs [27] and
 [28].

# 5.3.2 SBM, GnP and SBM/GnP hybrid modified epoxy

Representative micrographs of GnP modified epoxy cross sections are shown in

Figure 4.



Figure 5.4: Scanning electron micrographs of GnP modified epoxy cross-sections.

The cross sections in **Figure 4A** and **5B** show the dispersion in GnP modified epoxy made with son. and 3RM methods, respectively. It is noteworthy that both methods led to a good dispersion of GnPs. Tang et al. found that thermally reduced graphite oxide (RGO) is difficult to disperse in DGEBA, even after a combination of sonication and ball milling dispersion methods [29]. Comparison of **Figures 4A** and **4B** shows that the 3RM process breaks apart the GnPs reducing their diameter and aspect ratio. The dispersion of GnPs in the SBM/GnP hybrid modified epoxy made with the son. method (**4C**) appears similar to the GnP modified epoxy without SBM made under the same processing conditions (**4A**). The neat epoxy was transparent, while the GnP modified epoxy is black due to the carbon filler. The 3 wt% SBM modified epoxy is semi-transparent, as shown in **Figure 5**.



**Figure 5.5:** Photograph of 3 wt% SBM modified epoxy flexural coupons overlaid onto a laboratory notebook.

Previous research on SBM modified DGEBA showed that SBM in DGEBA cured with 4,4'-methylenebis-[3-chloro 2,6 diethylanaline] (MCDEA) results in a nanostructured and transparent thermoset over a wide range of SBM concentrations [4]. This is because the DGEBA + MCDEA network solubilizes the PMMA block of the terpolymer throughout the entire cure cycle to prevent macrophase separation of the block copolymer during formation of the network [4]. However, other DGEBA/amine networks, including those cured with 4,4' diaminodiphenyl sulphone (DDS), 4,4' methylene dianiline (MDA), aminoethyl-piperazine (AEP) and piperidine (PIP) lead to macrophase separation of the

SBM and opaque epoxies [3], [7] and [30]. Previous work on SBM modified DGEBA cured with mPDA showed that incorporation of SBM at 10 and 15 phr gives opaque epoxies [8]. This is because the SBM micelles flocculate in DGEBA cured with mPDA at higher concentrations. At lower concentrations of SBM in DGEBA cured with mPDA, there are less SBM micelles to flocculate leading to semi-transparent toughened epoxy. (The morphology of the SBM modified epoxy is revealed in scanning electron micrographs of the SBM modified epoxy compact tension (CT) specimen fracture surfaces shown in **Section 3.2** below.)

# **5.3.3 GnP and SBM modified epoxy: fracture, mechanical and thermomechanical properties**

The fracture toughness,  $K_Q$  (MPa\*m<sup>1/2</sup>) of the neat and modified epoxies made in this work is shown in **Figure 6**.



**Figure 5.6:** Fracture toughness,  $K_Q$  (MPa\*m<sup>1/2</sup>) of neat, SBM, GnP and SBM/GnP hybrid modified epoxy.

At 3 wt%, the SBM terpolymer increased the fracture toughness of epoxy by 70%. GnP modified epoxy made using the 3RM method increased the fracture toughness of epoxy by 70% at the same loading level. The GnP modified epoxy made with the son. method gives larger values of fracture toughness with larger scatter in the data compared to the 3RM method. The SEM images of the GnP modified epoxy cross sections in **Figure 4** show that the 3RM method breaks up the GnPs and decreases their aspect ratio. Previous research comparing pristine GnPs of different particle size as toughening agents in epoxy showed that GnPs with a larger platelet basal plane diameter (25 μm) gave larger values in fracture toughness than GnPs having a smaller basal plane diameter (5 μm) [31]. GnPs with higher aspect ratio better activate crack deflection and crack pinning toughening mechanisms [16]. Combining SBM and GnP at 3 wt% each in epoxy gave an additive toughening effect with no synergy in fracture toughness. SEM of the CT specimen fracture surfaces was used to identify the toughening mechanisms.

Scanning electron microscopy (SEM) images of the CT specimen fracture surfaces for the epoxy and GnP modified epoxies made using the son. method are shown in **Figure 7**.



Figure 5.7: Scanning electron micrographs of CT specimen fracture surfaces.

Each row (**A-D**) shows a different modified epoxy type and each column shows a higher magnification image of the same epoxy type. The neat epoxy fracture surfaces in **Figure 7** row **A** are smooth due to the brittle nature of the epoxy. The 3 wt% SBM modified epoxy (**B1**) has a rougher fracture surface compared to the neat epoxy (**A1**). Closer examination of the stress whitened zone on the SBM modified epoxy CT fracture surface shows that SBM micelles nanocavitate to induce matrix shear yielding of epoxy (see blue arrows in **B3**). The size of the dilated voids is ~100 nm.

The GnP and SBM/GnP hybrid modified epoxy fracture surfaces in **Figure 7** appear rougher than both the neat and SBM modified epoxy. The higher magnification images in **Figure 7 C2** and **C3** show good adhesion between the epoxy and the GnP edges (see white arrows). However, the basal plane of the GnPs is smooth, which is a qualitative indicator of poor adhesion between the GnP surface and the surrounding epoxy matrix. This particular fracture morphology is observed because the chemical functional groups found at the edges of the GnPs allow for better adhesion with the more polar epoxy polymer network compared to the basal plane of the GnPs, which consists mostly of sp<sup>2</sup> bonded carbon atoms.

The SBM/GnP hybrid modified epoxy fracture surfaces also appear rough. The SEM images shown in **Figure 7D2** and **D3** indicate that some of the GnPs on the fracture surface have SBM coated onto the platelets. The coating process described in **Section 2.3** results in GnPs coated with the SBM terpolymer as shown in **Figure 3**. During fracture of GnP and SBM/GnP hybrid modified epoxy, a crack may grow between a GnP/epoxy interface or through a platelet. If the crack grows through the GnP/epoxy interface in an SBM/GnP hybrid modified epoxy, then the SBM micelles coated onto the particles are

exposed on the fracture surface. This is observed in **Figure 7D3** (see orange arrows). If a crack grows through a platelet, then the exposed surface would be clean and SBM micelles would not be observed on the fracture surface. The images in **Figure 7D2** and **D3** also show that SBM micelles aggregated along the platelet edges in the hybrid GnP/SBM modified epoxy (see yellow arrows). The SBM micelles collected at the edges of the platelets cavitated resulting in ligaments of epoxy bridging the GnPs and the matrix. The epoxy ligaments appear to have stretched as a result of fracture.

The fracture surfaces of rubber toughened epoxy tested using the linear elastic fracture mechanics (LEFM) approach show regions of both fast and slow fracture [32]. The diagram shown in **Figure 8a** describes in general those regions on the fracture surface of a rubber modified epoxy CT specimen coupon.



**Figure 5.8:** Depiction of a toughened epoxy compact tension specimen fracture surface (a) and scanning electron micrographs of slow (A1 and A2) and fast (B1 and B2) fracture regions on 3 wt% SBM modified epoxy compact tension specimen fracture surfaces.

During loading of the coupons, the peak load is eventually reached and crack growth initiated from the pre-crack is fast until the rubber toughened epoxy can blunt the crack via toughening mechanisms induced by the rubber particles. These regions were difficult to identify on the fracture surfaces of the GnP modified epoxy CT specimen coupons because of the rougher nature of the surfaces induced by the crack deflection toughening mechanism. However, regions of fast and slow crack growth could be observed on the SBM modified epoxy fracture surfaces. The images in **Figure 8A1** and **A2** show progressively higher magnification images in the stress whitening zone at crack arrest, while the images in **Figure 8B1** and **B2** show the fracture morphology in the fast crack growth regime prior to crack arrest. At crack arrest, nanocavitation, void growth and

matrix shear yielding are identified as the toughening mechanisms. Contrarily, in the fast crack growth regime, the SBM micelles debond from the fracture surface to induce plastic void growth and matrix shear yielding.

The fracture surfaces of the GnP modified epoxy made via 3RM are shown in **Figure 9A1** and **A2**, along with lower magnification images of the GnP (**B**) and SBM/GnP hybrid (**C**) modified epoxy made with the son. method.



**Figure 5.9:** Scanning electron micrographs of GnP modified epoxy compact tension specimen fracture surfaces. Images A1 and A2 show GnP modified epoxy made with the 3RM method, while B and C show GnP and SBM/GnP hybrid modified epoxy made via the son. method, respectively.

Both the 3RM and son. methods give GnP modified epoxy with some regions of aggregated platelets. Both small and large platelets induced the crack deflection toughening mechanism, as shown in **Figure 9A2** and **B** via white and yellow arrows, respectively. The crack deflection toughening mechanism yields a rough fracture surface, since the crack is forced to twist and tilt around the GnPs leading to a variation in fracture height and an increase in fracture surface area [16]. On the other hand, the SBM/GnP hybrid modified epoxy shows two levels of toughening, namely micron scale crack deflection induced by the GnPs and nanoscale cavitation, void growth and shear yielding toughening mechanisms induced by SBM micelles. The combination of toughening mechanisms induced by SBM and GnPs accounts for the larger increase in fracture toughness in the hybrid modified epoxy.

The flexural strength and modulus of the neat and modified epoxies made in this work are shown in **Figure 10** and **Figure 11**, respectively.



**Figure 5.10:** Flexural strength (MPa) of neat, SBM, GnP and SBM/GnP hybrid modified epoxy.



**Figure 5.11:** Flexural modulus (GPa) of neat, SBM, GnP and SBM/GnP hybrid modified epoxy.

As previously reported, self assembling block copolymers do not significantly reduce the strength and modulus of epoxy at low concentrations [1] and [33]. However, the GnPs decreased the flexural strength of each modified epoxy type. The strength of the GnP modified epoxy was recovered somewhat by coating the GnP with SBM prior to solution casting. This may be due to better interaction between the GnP basal plane and the epoxy facilitated by the SBM micelles; however, the strength of the GnP modified epoxy was never fully recovered.

The modulus of the GnP modified epoxy made by either the son. or 3RM methods was increased by 13%. The rigid GnP filler reinforces the epoxy and increases the modulus. On the other hand, the increase in modulus by the GnPs in the SBM/GnP hybrid modified epoxy was minimized by the presence of the soft and flexible poly(butadiene) block in the terpolymer additive; thus, only a 7% increase in modulus was observed for the hybdrid modified epoxy. In contrast to the nano SBM/GnP hybrid modified epoxy investigated in this work, the modulus of CTBN modified epoxy is sometimes never fully recovered by incorporation of nanosilica particles [34].

Finally, the thermomechanical properties of the neat and the modified epoxy were investigated via dynamic mechanical analysis (DMA). Representative storage modulus (G') and Tan  $\delta$  curves as a function of temperature for each composite type are shown in **Figure 12** and **13**, respectively.



**Figure 5.12:** Storage modulus, G' (MPa) as a function of temperature (°C) of neat, SBM, GnP and SBM/GnP hybrid modified epoxy.



**Figure 5.13:** Tan  $\delta$  as a function of temperature (°C) of neat, SBM and GnP and SBM/GnP hybrid modified epoxy.

Prior to the main transition, G' is increased by incorporation of GnPs. G' is increased to the same extent for each GnP modified epoxy type. The sharp drop in storage modulus corresponds to the transition from glassy to rubbery behavior; GnPs increased the transition onset temperature. The glass transition temperature ( $T_g$ ) can be defined as the temperature corresponding to the maximum value of Tan  $\delta$ . The Tan  $\delta$ curves in **Figure 13** show that the  $T_g$  is increased more for GnP modified epoxy made with the 3RM method than for the son. method. This is because the 3RM process reduces GnP particle size and increases interfacial surface area.

An increase in  $T_g$  by incorporation of GnPs has been reported previously. Zaman *et al.* found that acid oxidized and 4,4-methylene diphenyl diisocyanate (MDI) treated, acid oxidized GnPs increased the  $T_g$  of DGEBA cured with Jeffamine® D230 ( $T_g = 94.7$ 

°C) by 7.7 and 13.9 °C, respectively [35]. The increases in Tg were attributed to interfacial interaction between GnPs and epoxy, which restricted network chain motion. The functionalized GnPs had a stronger interaction with the epoxy matrix and thus the larger increases in  $T_g$  [35]. The state of dispersion can also influence the  $T_g$  of GnP modified epoxy. Tang et al. found that the  $T_g$  of anhydride cured DGEBA ( $T_g = 146.3 \pm$ 1.7 °C) increased more by improving the dispersion of RGO in the matrix [29]. At only 0.2 wt% RGO, the "highly dispersed" RGO modified epoxy had a  $T_g$  of 157.4 °C, while that of the "poorly dispersed" RGO modified epoxy was 148.1 [29]. The RGO had a wrinkled morphology and the authors hypothesized that the wrinkling of the platelets in conjunction with the high surface area of the additive acted to restrict chain motion of the network in the vicinity of the platelets, thereby increasing the RGO modified epoxy T<sub>g</sub>. Wajid *et al.* found that the  $T_g$  of DGEBA cured with Fiberglast® 2120 curative ( $T_g =$ 110.1 °C) was increased by 9 °C by incorporation of poly(vinylpyrrolidone) (PVP) stabilized GnPs at 0.46 vol% [36]. The increase in Tg was attributed to filler/matrix interactions [36]. In this work, the increase in T<sub>g</sub> by incorporation of GnPs in epoxy can be attributed to restriction of chain motion by the GnPs.

Interestingly, the SBM terpolymer increased the  $T_g$  of DGEBA cured with mPDA. Previous research on SBM modified DGEBA has shown that SBM either decreases or has no effect on epoxy  $T_g$  [3] and [4]. Incorporation of 10 wt% SBM into DGEBA cured with MCDEA decreased  $T_g$  by 11.5 °C [4]. The decrease in  $T_g$  was attributed to plasticization of the epoxy network by the solubilized PMMA block [4]. Rebizant *et al.* found that SBM has little (-4 °C) or no influence on amine cured epoxy  $T_g$  [3]. Contrarily, the SBM modified DGEBA cured with mPDA made in this work shows

an increase in  $T_g$  by incorporation of 3 wt% SBM. The PMMA chains surrounding the micelles may not have completely macrophase separated from the cured network, which could result in a reduction of free volume and a restriction of chain motion at  $T_g$ .

# 5.3.4 GnP modified CFRPs: Summary

A summary of the CFRPs made in this work is shown in **Table 3**. The panel ID, fiber type, sizing, matrix, number of plies, fiber volume fraction (FVF) and void content (%) are listed for each CFRP panel evaluated in this work.

Table 5.3: Summary of composites in	including sizing	composition,	matrix, i	fiber vo	olume
fraction (FVF) and void content for e	each panel evalu	ated in this w	ork.		

Panel Name	Fiber	Sizing	Matrix	# of Plies	Fiber Volume Fraction (%)	Void Content (%)
UVO-S- CFRP	UVO- AS4-12k	1 wt% (Epon 828 + 9 phr mPDA)	DGEBA + 14.5 phr mPDA	8	63.8±1.0	$0.87\pm0.22$
UVO-S- CFRP	UVO- AS4-12k	1 wt% (Epon 828 + 9 phr mPDA)	DGEBA + 14.5 phr mPDA	18	66.9 ± 0.9	$0.24\pm0.05$
UVO-S- GnP-CFRP	UVO- AS4-12k	1 wt% (Epon 828 + 9 phr mPDA) + 1 wt% GnP	DGEBA + 14.5 phr mPDA	8	$64.0\pm0.5$	$0.12\pm0.05$
UVO-S- GnP-CFRP	UVO- AS4-12k	1 wt% (Epon 828 + 9 phr mPDA) + 1 wt% GnP	DGEBA + 14.5 phr mPDA	18	62.9 ± 1.4	$0.17\pm0.02$
UVO-S- GnP-SBM CFRP	UVO- AS4-12k	1 wt% (Epon 828 + 9 phr mPDA) + 1 wt% GnP	DGEBA + 10 phr SBM + 14.5 phr mPDA	8	$63.7\pm0.5$	$0.16\pm0.04$
UVO-S- GnP-SBM CFRP	UVO- AS4-12k	1 wt% (Epon 828 + 9 phr mPDA) + 1 wt% GnP	DGEBA + 10 phr SBM + 14.5 phr mPDA	18	61.9 ± 1.3	$0.08\pm0.04$

The FVF and void content is in agreement with AS4-12k/DGEBA + mPDA CFRPs made previously under similar processing conditions [22], [37], [38] and [39].

#### 5.3.5 GnP modified CFRPs: fracture, mechanical and thermomechanical properties

The fracture toughness results in **Section 3.2** showed that GnPs activate crack deflection to increase fracture surface area and fracture energy. Thus, GnPs may be an effective crack deflecting agent in the interphase of CFRPs. Therefore, GnPs were dispersed in a fugitive sizing applied to UVO-AS4-12k carbon fibers prior to manufacture of composites with neat epoxy and 10 phr SBM modified epoxy, respectively. SEM images of the GnP sized UVO-AS4-12k carbon fibers are shown in **Figure 14**.



**Figure 5.14**: Scanning electron micrographs of UVO-AS4-12k carbon fibers sized with epoxy and GnPs.

The micrographs show a thin film of epoxy sized onto the fibers along with GnPs. The sizing pickup for the UVO-S fibers was  $0.53 \pm 0.04$  wt%, while the UVO-S-GnP fibers had a sizing pickup of  $0.83 \pm 0.15$  wt%.

The interlaminar mode-I fracture toughness,  $G_{Ic}$  (J/m<sup>2</sup>) of UVO-S, UVO-S-GnP and UVO-S-GnP SBM composites is shown in **Figure 15**.



Figure 5.15: Mode-I fracture toughness,  $G_{Ic}$  (J/m<sup>2</sup>) of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs.

Fiber bridging was observed for all specimens during the mode-I test and appeared qualitatively similar for each composite type. Incorporation of GnPs via a fiber sizing increased the mode-I fracture toughness of the CFRP laminates by 100%, whereas the combination of GnP sized carbon fibers and a 10 phr SBM modified matrix increased CFRP fracture toughness by 80%. It is noteworthy that the differences in G<sub>Ic</sub> between the two composite types are not statistically significant. Thus, it can be concluded that the combination of SBM and GnP fillers in the CFRP did not show synergy in mode-I fracture toughness.

Scanning electron micrographs of the UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRP double cantilever beam fracture surfaces are shown in **Figure 16**.



**Figure 5.16:** Scanning electron micrographs of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRP mode-I fracture surfaces.

The UVO-S CFRP fracture surfaces show evidence of cusps and peeling of the matrix, as indicated by the blue and green arrows in **Figure 16 A2** and **A3**. These deformation mechanisms contribute to the fracture toughness of CFRPs [40]. The UVO-S-GnP and UVO-S-GnP SBM CFRPs show a rougher fracture surface, consistent with the larger measured values of fracture toughness. More matrix material is left on the carbon fibers

in the UVO-S-GnP and UVO-S-GnP SBM CFRPs than in the UVO-S CFRPs. This is because the GnPs diverted the crack away from the fiber/matrix interface.

The orange arrows in **Figure 16 B3** show that GnPs perpendicular to the crack plane bifurcate the propagating crack. The crack is forced around the particles, separating them from the matrix. On the other hand, the GnPs in the plane of the crack deflect the propagating crack, as shown by the white arrows in **Figure 16 B3**. These findings are consistent with a toughening model proposed for GnP modified epoxy previously [16].

Similar to SBM/GnP hybrid modified epoxy, the UVO-S-GnP SBM CFRP shows two levels of toughening. First, the GnPs activate micron scale toughening mechanisms. The orange arrows in **Figure 16 C2** and **C3** point to separation of a platelet lying perpendicular to the crack plane. Second, the SBM micelles nanocavitate to induce void growth and matrix shear yielding toughening mechanisms. The yellow arrows in **Figure 16 C3** point to voids resulting from nanocavitation of SBM micelles.

The three-point flexural test was used to evaluate the CFRP mechanical properties in the longitudinal (0°) and transverse fiber directions (90°). The 90° and 0° 3-point flexural properties normalized for FVF of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs are shown in **Figure 17** and **18**, respectively.

195



**Figure 5.17:** Transverse (90°) flexural strength (MPa) (a) and modulus (GPa) (b) of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs.



**Figure 5.18:** Longitudinal (0°) flexural strength (MPa) (a) and modulus (GPa) (b) of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs.

At a span-to-depth ratio (L/D) of 32, GnPs had no statistically significant influence on the  $90^{\circ}$  flexural strength and modulus. However, at L/D = 60, the  $90^{\circ}$  flexural strength

decreased by 14%. The 0° flexural modulus was unaffected by the GnPs, but the 0° flexural strength was decreased by 14% at both L/D = 32 and 60. The reduction in UVO-S-GnP CFRP flexural strength may be due to poor interfacial adhesion between the GnPs and epoxy matrix and/or aggregation of GnPs. Interestingly, the flexural properties of the composite are recovered after incorporation of 10 phr SBM in the matrix. Three point flexural results in **Chapter 3** showed that SBM did not have a deleterious effect on UVO-AS4-12k/epoxy composite mechanical properties. Thus, the good fiber/matrix adhesion in the SBM CFRPs may have mitigated the poorer interfacial properties of GnP modified epoxy.

Representative SEM images of the UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRP flexural failure surfaces are shown in **Figure 19**.



**Figure 5.19:** Scanning electron micrographs of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRP longitudinal flexural failure surfaces. Specimens were tested at L/D = 60.

Failure initiated on the tensile side of the coupons for UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs. Thus, the higher magnification SEM images are focused on the tensile side of the coupons. Fiber pullout was observed in each composite type investigated. The matrix near the fibers in the UVO-S CFRP is smooth, indicative of brittle failure. On the other hand, the UVO-S-GnP CFRPs show a rougher fracture surface with GnPs imbedded in the matrix near the fibers. The SEM images also show that the GnP basal plane is smooth, indicative of poor bonding with the matrix (see white arrows). A similar fracture morphology was observed in the GnP modified epoxy in **Section 3.2** above.

Qualitatively, the scanning electron micrographs show that UVO-S-GnP SBM CFRPs have better fiber/matrix adhesion than UVO-S-GnP CFRPs.

The storage modulus, G' (MPa) and Tan  $\delta$  of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs are shown in **Figure 20**.



**Figure 5.20:** Storage modulus, G' (MPa) and Tan  $\delta$  of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs.

These results indicate that incorporation of GnPs in the CFRPs had no influence on the composite storage modulus. This is because the composite modulus is fiber dominated.

The composite  $T_g$  is defined as the temperature corresponding to the maximum of Tan  $\delta$ . The average  $T_g$  for each composite type is shown in **Table 4**.

Composite Type	T <sub>g</sub> (°C)
UVO-S	$164.0 \pm 1.7$
UVO-S-GnP	$164.9 \pm 0.7$
UVO-S-GnP SBM	$165.9 \pm 0.6$

Table 5.4: Average T<sub>g</sub> of UVO-S, UVO-S-GnP and UVO-S-GnP SBM CFRPs.

The  $T_g$  of the CFRPs was unchanged by GnPs and SBM. However, the value of Tan  $\delta$  at the main transition increased by incorporation of GnPs. This phenomenon was not observed in the GnP modified epoxy and may result from poor interfacial interaction between GnPs and the matrix in fiber/matrix interphase. The UVO-S-GnP SBM CFRPs show an increase in dampening as well, but to a lesser extent.

#### 5.4 Conclusions

This work investigated the triblock copolymer SBM and GnPs as toughening agents in epoxy and CFRPs. Scanning electron microscopy (SEM) of GnP modified epoxy CT fracture surfaces showed that GnPs increased the fracture toughness of epoxy via a crack deflection mechanism, with larger GnPs being more effective crack deflectors. Hybrid SBM/GnP modified epoxy showed an additive toughening effect, with no synergy in fracture toughness observed at a 3 wt% additive concentration. Additionally, GnPs were incorporated into CFRPs via a fugitive sizing. CFRP mode-I fracture toughness was increased by 100% after incorporation of GnPs in the composite interphase. SEM of mode-I double cantilever beam fracture surfaces showed that the toughening mechanisms
observed in GnP modified epoxy were transferred to the GnP modified CFRPs. The combination of GnPs and SBM in CFRPs increased fracture toughness to a lesser extent than GnPs alone, but with no corresponding reduction in composite mechanical properties.

REFERENCES

## REFERENCES

- [1] J. (Daniel) Liu, Z. J. Thompson, H.-J. Sue, F. S. Bates, M. A. Hillmyer, M. Dettloff, G. Jacob, N. Verghese, and H. Pham, "Toughening of Epoxies with Block Copolymer Micelles of Wormlike Morphology," *Macromolecules*, vol. 43, no. 17, pp. 7238– 7243, Sep. 2010.
- [2] C. Declet-Perez, L. F. Francis, and F. S. Bates, "Deformation Processes in Block Copolymer Toughened Epoxies," *Macromolecules*, vol. 48, no. 11, pp. 3672–3684, Jun. 2015.
- [3] V. Rebizant, A.-S. Venet, F. Tournilhac, E. Girard-Reydet, C. Navarro, J.-P. Pascault, and L. Leibler, "Chemistry and Mechanical Properties of Epoxy-Based Thermosets Reinforced by Reactive and Nonreactive SBMX Block Copolymers," *Macromolecules*, vol. 37, no. 21, pp. 8017–8027, Oct. 2004.
- [4] S. Ritzenthaler, F. Court, E. Girard-Reydet, L. Leibler, and J. P. Pascault, "ABC Triblock Copolymers/Epoxy–Diamine Blends. 2. Parameters Controlling the Morphologies and Properties," *Macromolecules*, vol. 36, no. 1, pp. 118–126, Jan. 2003.
- [5] A.-V. Ruzette and L. Leibler, "Block copolymers in tomorrow's plastics," *Nat. Mater.*, vol. 4, no. 1, pp. 19–31, Jan. 2005.
- [6] Y. Mai and A. Eisenberg, "Self-assembly of block copolymers," *Chem. Soc. Rev.*, vol. 41, no. 18, pp. 5969–5985, Aug. 2012.
- [7] R. M. Hydro and R. A. Pearson, "Epoxies toughened with triblock copolymers," J. *Polym. Sci. Part B Polym. Phys.*, vol. 45, no. 12, pp. 1470–1481, Jun. 2007.
- [8] N. T. Kamar and L. T. Drzal, "Micron and nanostructured rubber toughened epoxy: A direct comparison of mechanical, thermomechanical and fracture properties," *Polymer*, vol. 92, pp. 114–124, Jun. 2016.
- [9] B. T. Marouf, Y.-W. Mai, R. Bagheri, and R. A. Pearson, "Toughening of Epoxy Nanocomposites: Nano and Hybrid Effects," *Polym. Rev.*, vol. 56, no. 1, pp. 70–112, Jan. 2016.
- [10] S. Sprenger, "Epoxy resins modified with elastomers and surface-modified silica nanoparticles," *Polymer*, vol. 54, no. 18, pp. 4790–4797, Aug. 2013.
- [11] F. Wang, L. T. Drzal, Y. Qin, and Z. Huang, "Enhancement of fracture toughness, mechanical and thermal properties of rubber/epoxy composites by incorporation of

graphene nanoplatelets," *Compos. Part Appl. Sci. Manuf.*, vol. 87, pp. 10–22, Aug. 2016.

- [12] T. Gómez-del Río, A. Salazar, R. A. Pearson, and J. Rodríguez, "Fracture behaviour of epoxy nanocomposites modified with triblock copolymers and carbon nanotubes," *Compos. Part B Eng.*, vol. 87, pp. 343–349, Feb. 2016.
- [13] T. H. Hsieh, A. J. Kinloch, K. Masania, J. S. Lee, A. C. Taylor, and S. Sprenger, "The toughness of epoxy polymers and fibre composites modified with rubber microparticles and silica nanoparticles," *J. Mater. Sci.*, vol. 45, no. 5, pp. 1193– 1210, Dec. 2009.
- [14] Y. L. Liang and R. A. Pearson, "The toughening mechanism in hybrid epoxy-silicarubber nanocomposites (HESRNs)," *Polymer*, vol. 51, no. 21, pp. 4880–4890, Oct. 2010.
- [15] L. Yang, C. Zhang, S. Pilla, and S. Gong, "Polybenzoxazine-core shell rubber– carbon nanotube nanocomposites," *Compos. Part Appl. Sci. Manuf.*, vol. 39, no. 10, pp. 1653–1659, Oct. 2008.
- [16] S. Chandrasekaran, N. Sato, F. Tölle, R. Mülhaupt, B. Fiedler, and K. Schulte, "Fracture toughness and failure mechanism of graphene based epoxy composites," *Compos. Sci. Technol.*, vol. 97, pp. 90–99, Jun. 2014.
- [17] D. L. Hunston, "Composite interlaminar fracture Effect of matrix fracture energy," *Compos. Technol. Rev.*, pp. 176–180, Jan. 1984.
- [18] S. Sprenger, "Fiber-reinforced composites based on epoxy resins modified with elastomers and surface-modified silica nanoparticles," *J. Mater. Sci.*, vol. 49, no. 6, p. 2391+, Mar. 2014.
- [19] C. Kostagiannakopoulou, T. H. Loutas, G. Sotiriadis, A. Markou, and V. Kostopoulos, "On the interlaminar fracture toughness of carbon fiber composites enhanced with graphene nano-species," *Compos. Sci. Technol.*, vol. 118, pp. 217–225, Oct. 2015.
- [20] X. Zhang, X. Fan, C. Yan, H. Li, Y. Zhu, X. Li, and L. Yu, "Interfacial Microstructure and Properties of Carbon Fiber Composites Modified with Graphene Oxide," ACS Appl. Mater. Interfaces, vol. 4, no. 3, pp. 1543–1552, Mar. 2012.
- [21] W. Qin, F. Vautard, L. T. Drzal, and J. Yu, "Mechanical and electrical properties of carbon fiber composites with incorporation of graphene nanoplatelets at the fiber– matrix interphase," *Compos. Part B Eng.*, vol. 69, pp. 335–341, Feb. 2015.
- [22] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: IV. Mode I and Mode II Fracture Toughness of

Graphite/Epoxy Composites," J. Compos. Mater., vol. 26, no. 7, pp. 936–968, Jul. 1992.

- [23] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nat. Mater.*, vol. 6, no. 3, pp. 183–191, Mar. 2007.
- [24] S. Chatterjee, J. W. Wang, W. S. Kuo, N. H. Tai, C. Salzmann, W. L. Li, R. Hollertz, F. A. Nüesch, and B. T. T. Chu, "Mechanical reinforcement and thermal conductivity in expanded graphene nanoplatelets reinforced epoxy composites," *Chem. Phys. Lett.*, vol. 531, pp. 6–10, Apr. 2012.
- [25] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide," *Carbon*, vol. 45, no. 7, pp. 1558– 1565, Jun. 2007.
- [26] R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio, and M. S. Dresselhaus, "Raman spectroscopy of graphene and carbon nanotubes," *Adv. Phys.*, vol. 60, no. 3, pp. 413–550, Jun. 2011.
- [27] C. M. Hansen, Hansen Solubility Parameters: A User's Handbook, Second Edition. CRC Press, 2007.
- [28] Y. Hernandez, M. Lotya, D. Rickard, S. D. Bergin, and J. N. Coleman, "Measurement of Multicomponent Solubility Parameters for Graphene Facilitates Solvent Discovery," *Langmuir*, vol. 26, no. 5, pp. 3208–3213, Mar. 2010.
- [29] L.-C. Tang, Y.-J. Wan, D. Yan, Y.-B. Pei, L. Zhao, Y.-B. Li, L.-B. Wu, J.-X. Jiang, and G.-Q. Lai, "The effect of graphene dispersion on the mechanical properties of graphene/epoxy composites," *Carbon*, vol. 60, pp. 16–27, Aug. 2013.
- [30] S. Ritzenthaler, F. Court, L. David, E. Girard-Reydet, L. Leibler, and J. P. Pascault, "ABC Triblock Copolymers/Epoxy–Diamine Blends. 1. Keys To Achieve Nanostructured Thermosets," *Macromolecules*, vol. 35, no. 16, pp. 6245–6254, Jul. 2002.
- [31] S. Chatterjee, F. Nafezarefi, N. H. Tai, L. Schlagenhauf, F. A. Nüesch, and B. T. T. Chu, "Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites," *Carbon*, vol. 50, no. 15, pp. 5380–5386, Dec. 2012.
- [32] A. J. Kinloch and R. J. Young, *Fracture behaviour of polymers*. London : New York: Applied Science Publishers ; Elsevier Science Publishing Co. [distributor], 1983.

- [33] J. M. Dean, R. B. Grubbs, W. Saad, R. F. Cook, and F. S. Bates, "Mechanical properties of block copolymer vesicle and micelle modified epoxies," *J. Polym. Sci. Part B Polym. Phys.*, vol. 41, no. 20, pp. 2444–2456, Oct. 2003.
- [34] A. J. Kinloch, R. D. Mohammed, A. C. Taylor, C. Eger, S. Sprenger, and D. Egan, "The effect of silica nano particles and rubber particles on the toughness of multiphase thermosetting epoxy polymers," *J. Mater. Sci.*, vol. 40, no. 18, pp. 5083– 5086, Sep. 2005.
- [35] I. Zaman, T. T. Phan, H.-C. Kuan, Q. Meng, L. T. Bao La, L. Luong, O. Youssf, and J. Ma, "Epoxy/graphene platelets nanocomposites with two levels of interface strength," *Polymer*, vol. 52, no. 7, pp. 1603–1611, Mar. 2011.
- [36] A. S. Wajid, H. S. T. Ahmed, S. Das, F. Irin, A. F. Jankowski, and M. J. Green, "High-Performance Pristine Graphene/Epoxy Composites With Enhanced Mechanical and Electrical Properties," *Macromol. Mater. Eng.*, vol. 298, no. 3, pp. 339–347, Mar. 2013.
- [37] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: I. Inplane and Interlaminar Shear Behavior of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 25, no. 8, pp. 932–957, Aug. 1991.
- [38] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties: II. Longitudinal (0°) and Transverse (90°) Tensile and Flexure Behavior of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 25, no. 8, pp. 958–991, Aug. 1991.
- [39] M. S. Madhukar and L. T. Drzal, "Fiber-Matrix Adhesion and Its Effect on Composite Mechanical Properties. III. Longitudinal (0°) Compressive Properties of Graphite/Epoxy Composites," *J. Compos. Mater.*, vol. 26, no. 3, pp. 310–333, Mar. 1992.
- [40] K. Friedrich, *Application of Fracture Mechanics to Composite Materials*. Elsevier, 2012.

## **CHAPTER 6: CONCLUSIONS AND FUTURE WORK**

## **6.1 Conclusions**

This research has investigated novel methods to improve the fracture and impact properties of fiber reinforced/epoxy polymer composites (FRPs). In particular, significant improvements in the mode-I fracture toughness of glass and carbon fiber reinforced/epoxy polymer composites (GFRPs and CFRPs) were achieved by specific incorporation of graphene nanoplatelets (GnPs) and the triblock copolymer poly(styrene)block-poly(butadiene)-block-poly(methylmethacrylate) (SBM) into FRPs. Moreover, the influence of the composite additives on the mechanical and thermomechanical properties of the modified FRPs was quantified to develop a thorough understanding of the modified composite properties. Additionally, the toughening mechanisms were identified for each composite type to develop an understanding of how the nanoparticles investigated in this work influence the composite fracture behavior. These results are summarized as follows.

SBM improves the fracture toughness,  $K_Q$  (MPa\*m<sup>1/2</sup>) of diglycidyl ether of bisphenol-A (DGEBA) cured with m-phenylenediamine (mPDA) at low (3 wt%) and high (15 phr) loading levels with no corresponding reductions in glass transition temperature (T<sub>g</sub>). At low concentrations (3 wt%), SBM increases  $K_Q$  of DGEBA + mPDA by 70% with no corresponding reductions in modified epoxy flexural strength, flexural modulus and T<sub>g</sub>. Scanning electron microscopy of SBM modified epoxy compact tension specimen fracture surfaces identified the toughening mechanisms as nanocavitation of sub 100 nm spherical micelles, concomitant void growth and matrix

207

shear yielding. As a toughening agent for DGEBA + mPDA, SBM outperforms the traditional, carboxyl-terminated butadiene-acrylonitrile (CTBN) telechelic oligomer. This is because the SBM microphase separates into nanoscale spherical micelles with an interparticle distance one order of magnitude smaller than observed in CTBN modified epoxy at the same loading level. Although the SBM micelles flocculate in the DGEBA + mPDA network, they individually cavitate ahead of the crack tip to induce void growth and matrix shear yielding toughening mechanisms leading to massive plastic deformation of epoxy and large increases in fracture energy. However, like CTBN, SBM reduces modified epoxy flexural strength and modulus at higher loading levels (10 and 15 phr) due to incorporation of the soft and flexible poly(butadiene) block.

SBM also improved the mode-I fracture toughness,  $G_{Ic}$  (J/m<sup>2</sup>) of CFRPs up to 10 phr with no corresponding reductions in composite flexural strength, flexural modulus and T<sub>g</sub>. Increasing the concentration of SBM to 15 phr in the CFRPs provided no additional increases in G<sub>Ic</sub> since the rigid carbon fibers constrain plastic deformation of the SBM modified epoxy. Comparison of SBM modified bulk epoxy and CFRP fracture toughness values at 5, 10 and 15 phr SBM showed that only about 10% of the toughness increases observed in the bulk modified epoxy are manifested in the CFRPs. Compared to the literature on toughening CFRPs with CTBN and nanosilica modified matrices, the transfer factor for SBM modified CFRPs was lower due to the tougher nature of SBM modified epoxy, particularly at 10 and 15 phr loading levels.

A new method was developed for the inclusion of GnPs into the interlaminar regions of GFRPs processed with vacuum assisted resin transfer molding (VARTM). At only 0.25 wt% GnP, GFRP flexural strength and mode-I fracture toughness were

208

improved by 29 and 25%, respectively. Additionally, low velocity drop weight impact testing of GnP modified GFRPs showed that GnPs improved the impact properties of GFRPs with increasing concentration. Non-destructive evaluation of impacted composite panels using ultrasonic C-scan and dye penetration inspection qualitatively supported the impact testing results. A new method was developed to quantify impact damage area from the C-scan data. These results showed that the impact side damage area decreased with increasing concentration of GnP, while the back side damage area increased.

GnPs were also explored as a toughening agent in DGEBA cured with mPDA. At 3 wt%, GnPs improved  $K_Q$  of DGEBA + mPDA by 70 and 90% using sonication and three-roll mill dispersion methods, respectively. SEM of GnP modified epoxy CT fracture surfaces showed that GnPs acted to deflect a propagating crack resulting in increased fracture surface area and fracture energy. The three roll mill method broke apart the GnPs, making them less effective crack deflectors and thus the lower values of fracture toughness compared to sonication alone. In addition, GnPs were coated with SBM and dispersed in DGEBA using a sonication method. Although the combination of SBM and GnP in DGEBA + mPDA had an additive toughening effect, no synergy in fracture toughness in the hybrid SBM/GnP modified DGEBA + mPDA was observed.

Finally, GnPs were sized onto UVO-AS4-12k carbon fibers to make GnP modified CFRPs. The composite G<sub>Ic</sub> was increased by 100% at only 1.0 wt% GnP in the fugitive sizing. SEM of mode-I double cantilever beam fracture surfaces showed that GnPs bifurcated or deflected a propagating crack depending on the platelet orientation relative to the crack plane. Although GnPs improved the fracture toughness of CFRPs markedly, their incorporation into the composites led to a 14% reduction in longitudinal

209

flexural strength. However, the combined SBM/GnP hybrid modified CFRPs gave an 80% increase in G<sub>Ic</sub> with no corresponding reductions in composite mechanical and thermomechanical properties. As was observed in the hybrid SBM/GnP modified epoxy, the hybrid SBM/GnP modified CFRP did not show a synergy in fracture toughness.

## **6.2 Future Work**

This work showed that pristine GnPs are an effective toughening agent in epoxy and CFRPs. However, pristine GnPs reduce the strength of epoxy and CFRPs due to poor adhesion between the basal plane and the surrounding epoxy matrix. Scanning electron microscopy images of both GnP modified epoxy and CFRP fracture surfaces support this hypothesis. The basal plane of GnPs consists of sp<sup>2</sup> hybridized carbon atoms, while the edges contain oxygen functional groups. The inert nature of the GnP basal plane gives rise to its poor interfacial interaction with epoxy. Previous research has shown that chemical functionalization of GnPs can improve both their dispersion and interfacial adhesion with epoxy. However, current methods to functionalize GnPs have low yields and are not yet scalable. Thus, a robust and scalable method to functionalize GnPs with particular chemical moieties such as amino groups should be developed. With such a development, the potential for facilitating covalent chemical bonding between GnPs and a surrounding epoxy polymer could lead to improved stress transfer between the polymer matrix and GnP filler. Under this hypothesis, GnPs could improve both strength and toughness of epoxy and CFRPs. Other chemistries on GnPs could be then explored to create multifunctional polymer composite materials at low filler concentrations.