Dakai Bian¹

Department of Mechanical Engineering, Columbia University, New York, NY 10027 e-mail: db2875@columbia.edu

Bradley R. Beeksma

Department of Mechanical Engineering, Columbia University, New York, NY 10027

D. J. Shim

GE Global Research, Niskayuna, NY 12309

Marshall Jones

GE Global Research, Niskayuna, NY 12309

Y. Lawrence Yao

Department of Mechanical Engineering, Columbia University, New York, NY 10027

Interlaminar Toughening of GFRP—Part I: Bonding Improvement Through Diffusion and Precipitation

A low concentrated polystyrene (PS) additive to epoxy is used, since it is able to reduce the curing reaction rate but not at the cost of increasing viscosity and decreasing glass transition temperature of the curing epoxy. The modified epoxy is cocured with a compatible thermoplastic interleaf during the vacuum assisted resin transfer molding (VARTM) to toughen the interlaminar of the composites. Using viscometry, the solubilities of thermoplastics (TPs) polycarbonate (PC), polyetherimide (PEI), and polysulfone (PSU) are determined to predict their compatibility with epoxy. The diffusion and precipitation process between the most compatible polymer PSU and epoxy formed semi-interpenetration networks (semi-IPN). To optimize bonding adhesion, these diffusion and precipitation regions were studied via optical microscopy under curing temperatures from $25 \,^{\circ}C$ to 120°C and PS additive concentrations to epoxy of 0-5%. Uniaxial tensile tests were performed to quantify the effects of diffusion and precipitation regions on composite delamination resistance and toughness. Crack paths were observed to characterize crack propagation and arrest mechanism. Fracture surfaces were examined by scanning electron microscopy (SEM) to characterize the toughening mechanism of the thermoplastic interleaf reinforcements. The chemically etched interface between diffusion and precipitation regions showed semi-IPN morphology at different curing temperatures. Results revealed deeper diffusion and precipitation regions increase energy required to break semi-IPN for crack propagation resulting in crack arrests and improved toughness. [DOI: 10.1115/1.4036126]

Keywords: diffusion and precipitation, delamination, toughening, thermoplastic interleaf

Introduction

Glass fiber reinforced polymer (GFRP) composites have been widely used as laminated structures in automotive, marine, and aerospace industries due to unique properties such as reduced weight, high strength, and increased energy efficiency compared to traditional metal materials. However, their poor through thickness strength leads to delamination, which can cause catastrophic failure. Thus, preventing laminar from delamination always plays an important role in design and test of the GFRP.

In the past decades, many researchers have been working on finding methods for toughening laminate composites. Some of them used different thermoplastic materials as modifiers. Shetty et al. used 0-10 wt % of polycarbonate (PC) to toughen the epoxy resin [1]. Jin et al. studied the effect of polyetherketone cardo (PEK-C) thickness on the fracture toughness [2]. Xu et al. found moderate increase in the fracture toughness by using polyphthalazinone ether sulfone ketone (PPESK) [3]. Martines et al. blended polysulfone (PSU) with the epoxy under at different weight fractions and curing temperatures [4]. Blanco et al. studied the amine-ended polyethersulfone (PES) influence on the thermomechanical properties of the epoxy [5], and Heitzmann et al. studied the influence of different cure cycles of polyetherimide (PEI) [6]. Other researchers used different methods to achieve composite toughening. Tan et al. used laser to bond layer of fabric by fusing a dense glass bead [7,8]. Groleau et al. used the blends with nylon

¹Corresponding author.

particles [9]. Hillermeier and Sefeis studied the effect of modified powder/spray tackifier on the fracture toughness [10]. Li et al. toughened the composite using electrospun nanofibers [11], and Kuwata and Hogg investigated the toughness of composites by using interleaved TP veil [12]. The above results indicate that both high toughness and adhesion strength are required for the interleaved material [13]. However, most thermoplastics are not likely to be compatible with thermosetting epoxies due to the low reactivity, small surface energies, and weak polarities. Thus, adhesion failure between the interleaved material and matrix still remains.

A strong thermoplastic-thermoset interface is vital to guarantee bonding quality and improve toughness behavior, especially at drop-off regions which induce stress concentration [14]. Good adhesion can be realized if two polymers are compatible and their molecules diffuse sufficient distance to generate a gradient interphase, leading to entanglements between the long chain thermoplastics (TPs) and the crosslinked thermosets (TSs). The formation of the entangled long chain TP in crosslinked TS is known as semi-interpenetration network (semi-IPN).

A dual bonding process was introduced in the previous work [14], and the present study focused on the effect of diffusion and precipitation. The present study introduces PSU interleaved glass fiber reinforced composites cured with PS modified epoxy to overcome the limitation of polymer diffusion. Compatibility of polymers was determined experimentally by using viscometry. Diffusion and precipitation regions between the thermosets system and the inserted PSU film were examined by optical microscopy and scanning electron microscopy. Single external drop-off specimen tensile tests were performed to simulate real loading

Journal of Manufacturing Science and Engineering

Copyright © 2017 by ASME

Manuscript received November 21, 2016; final manuscript received February 14, 2017; published online March 24, 2017. Assoc. Editor: Donggang Yao.

conditions. Crack initiation and propagation was observed by microscopy. Fracture surface morphology and toughening mechanism were studied.

Background

Polymer Compatibility. Compatibility between polymers is determined by the solubility of the solute and solvent. The key factor leading to diffusion and precipitation is the ability of solvent molecules to overcome the intermolecular forces of the solute and occupy spaces within the solute molecules. Only polymers that have similar intermolecular forces are likely to be miscible. If the intermolecular forces are sufficiently different, the strongly attracted molecules will gather together and exclude the weakly attracted molecules. The Hildebrand solubility parameter is the reflection of the degree of intermolecular forces holding the polymer molecules together and is used to predict the compatibility of polymers. The limitation of Hildebrand solubility parameter is that it is not suitable for some polar polymers especially with hydrogen bonds. This solubility parameter is an important reference for choosing a proper solvent or polymer because it is a prediction of compatibility. Usually, heat of vaporization can be measured directly to determine the solubility of a polymer with low molecular weight (MW). However, due to the huge molecular interaction of TPs, it is difficult to gasify a polymer with high MW. Thus, viscometry is introduced in this study to determine the solubility parameter of polymers. The intrinsic viscosity of the solution is related with the degree of solvent's solubility: the solubility of the polymer is the same as the solubility of the solvent when the intrinsic viscosity of the solution reaches maximum value [15]

$$[\eta] = [\eta]_{\max} \cdot e^{V \cdot (\delta - \delta_p)^2} \tag{1}$$

when $[\eta] = [\eta]_{\text{max}}$ and $\delta = \delta_p$. For this equation, η is the intrinsic viscosity, V is the molar volume of the solvent, δ is the solubility parameter of the solvent, and δ_p is the solubility parameter of the polymer. Polymers sometimes cannot be dissolved in a pure solvent, so mixed solvent is used to find the proper solvent for specific polymer. The solubility parameter for the mixed solvent can be approximated by

$$\delta_{\text{mixed}} = \phi_1 \delta_1 + \phi_2 \delta_2 \tag{2}$$

where ϕ is the volume fraction of the component in the solution, and 1 and 2 stand for two different solvents. In a binary solvents system, as long as the solubility of the test polymer is within the range of the two solvents, the volume fraction of the solvents can be adjusted to make the solubility of the solution close to the solubility of the test polymer. Thus, the limitation of Eq. (2) is that the solvents should be compatible with each other, and the solubility of the test polymer should be in the range between those of the two solvents. The intrinsic viscosity is determined by the experimentally measured viscosity of the solution

$$[\eta_s] = \frac{1}{C} \sqrt{2\left(\frac{\eta_s - \eta_0}{\eta_0} - \ln\left(\frac{\eta_s}{\eta_0}\right)\right)}$$
(3)

where *C* is the concentration of the solute in the solution, η_0 is the viscosity of the solution without dissolved polymer, and η_s is the viscosity of the solution with dissolved polymer.

Diffusion Process in Thermoplastic-Rich Region. From the macroscopic perspective, a diffusion process is the thermal motion of species. It explains the net flux of species from a region of higher concentration to one of lower concentration resulting in a gradual mixing of material. However, this process is different for the epoxy system due to the spontaneous curing during the



Fig. 1 Phase diagram of nucleation growth (NG) and spinodal decomposition (SD). The system can lower its free energy by separating into two phases with an interphase between c⁻ and c⁺. Within the range of c⁻/c_S₋ and c⁺/c_S₊, phase separation is due to nucleation and growth. Within the range of c_S₋ and c_S₊, phase separation is due to spinodal decomposition.

diffusion. As the TPs begin to encounter the initial liquid phase epoxy, it becomes softened by the TS epoxy. The entangled long chain structures in the TP become swollen, which increases the free space within the TP region. Then, the curing epoxy molecules fill the free space in the TP and keep swelling the long chain structure. In the diffusion process, the elevated temperature reduces the viscosity of both the TP and TS. Under high curing temperature, the diffused TS in the TP-rich region remains as an unstable single phase solution at the early stage of curing process. With the processing of the curing reaction, low MW TSs connect with each other through branching and crosslinking, leading to a significant increase of the viscosity and reduction of solubility [16]. This system can lower its free energy by separating into two phases to maintain stability as illustrated in Fig. 1, which shows the typical free energy trends with concentration of solute. In the diffusion region, the concentration difference of solute and solvent is small, and the spinodal decomposition (SD) dominates the phase separation. During SD, large clusters form due to high concentration of the penetrating species [17,18]. When the large clusters form, the epoxy is not fully cured. The undergoing curing process generates secondary networks within and around the clusters. These networks are also an important factor that leads to improved toughness [19].

Precipitation Process in the Epoxy-Rich Region. As the epoxy begins to diffuse into the TP-rich region, the TP molecules simultaneously start to flow into the epoxy-rich region. At the initial stage of curing, the uncured small molecular weight epoxy prepolymer is compatible with the thermoplastic and has high mobility. The contact between the uncured epoxy and thermoplastic leads to swelling effect, which the amorphous entangled thermoplastic molecules start to undergo chain relaxation. The surface of the thermoplastics generates more free spaces, and the mobility of the long chain thermoplastics increases. Thus, the uncured epoxy molecules fill into these free spaces in the TP-rich region and keep swelling the TP beneath the surface, and on the other hand, the long chain TP flows in the uncured epoxy region due to the increased mobility due to the swelling effect. Due to the elevated temperature and chain relaxation of TPs, the mobility of the

071010-2 / Vol. 139, JULY 2017

TPs increases, and the swollen long chains transfer to the liquid epoxy region. With the increasing time, the liquid phase epoxy starts to cure, turning into gel and finally into cured solid phase epoxy. Since the crosslinked structures are gradually generated during the curing process, the diffusion and precipitation process is coupled with curing reaction which reduces the mobility of the species. At a certain degree of curing, the diffusion and precipitation process ceases. The long chain TP molecules entangle with the cured crosslinked TS structure along the interface between the TP and TS. In the precipitation region, the concentration difference of solute and solvent is significant due to the low mobility of long chain TP. As can be seen from Fig. 1, the nucleation growth (NG) dominates the phase separation, in which part of solute molecules separates out and clings together to form clusters. From the work of Bernard et al., morphologies in epoxy-amine/TP blends depend on the TP concentration [16]. The blends containing less than 10 wt % of TP exhibit precipitation with dispersed TP-rich particles in an epoxy-rich matrix. The blends above 20 wt % of TP exhibit diffusion with dispersed-epoxy-amine rich particles in a TP-rich matrix. The sharp interface is located between precipitation and diffusion regions where the spinodal decomposition is the dominant mechanism for the phase separation. The distance of this gradient interphase is believed as one of the major reasons for the improved toughness.

Factors Influence the Diffusion and Precipitation Process. The diffusion and precipitation process in the epoxy system is complicated because it includes both physical and chemical reactions. Both curing reaction and the diffusivity of epoxy and TP are highly dependent on the processing temperature, which is the most important factor. At low processing temperature, the high viscosity of the epoxy and TP has the minimum mobility even if the time before gelation is longer due to the reduction of curing reaction rate. Therefore, the diffusion and precipitation process is limited because the species are not able to transport enough distance with low mobility within the time period that diffusion and precipitation can occur. At high processing temperature, the time before gelation is shortened but the mobility of the system is significantly enlarged. Compared to the case at low processing temperature, the species under high processing temperature are able to transport relatively larger distance during the shortened diffusion and precipitation process. In order to achieve maximum diffusion and precipitation region, it would be better if the curing reaction rate can be reduced at high processing temperature. Thus, PS is used to modify the epoxy because PS additive can be dissolved into the epoxy but not react with it [20]. Also with the low concentration of the PS additive (<5%), the viscosity and glass transition temperature of the modified epoxy shows almost the same performance as the nonmodified epoxy [20]. However, with the PS additive, the curing reaction rate reduces significantly due to the dilute effect. Thus, the time before gelation is more than that of the nonmodified epoxy, which makes the diffusion and precipitation process take longer [20].

Crack Propagation in the Semi-Interpenetration Network. In order to study the mechanical behavior, crack propagation needs to be studied, since it directly relates to the fracture energy. The crack initiates near the interfaces under the in-plane loading conditions. After the crack initiates, it propagates essentially in the weakest region within the crack tip yield zone [21,22]. When the stress at the crack tip reaches the yield strength, it becomes large enough to break the bond and allow the crack to spread if the material is brittle. On the other hand, the stress for ductile materials will be relieved by the formation of plastic zone at the crack tip.

The main purpose of interleaving is to toughen the resin-rich region between the plies and improve the delamination resistance by absorbing more energy when a crack spreads. However, due to the dissimilar materials, the crack can still reach the interface



Fig. 2 (a) Schematic of semi-interpenetration network. Semiinterpenetration network is formed by the entanglement between the long-chain thermoplastic molecules and the crosslinked thermosets. (b) Schematic of crack propagation in the diffusion and precipitation region. When the crack propagates, it needs to break the semi-interpenetration network structure.

between the inserted TP and epoxy matrix and propagate along the interface. With the modified epoxy, as can be seen from Fig. 2(a), the diffusion and precipitation process generates semi-IPN through the interface between TP and epoxy matrix. The diffusion region is TP-rich region, which is more ductile. The precipitation region is epoxy-rich region, which is more brittle. Within these two regions, the long chain TP entangles with the crosslinked TS structure. When the crack approaches to the interface, the crack tip yield zone will shrink due to the high strength fiber and epoxy. The diffusion and precipitation region will arrest the crack within it. Thus, the crack will need to break the semi-IPN to propagate, which consumes more fracture energy, as shown in Fig. 2(b).

Experiment Materials and Procedures

The epoxy resin is purchased from EPOKOTE Resin MGS RIMR 135, of which the major component is bisphenol A diglycidyl ether (DEGBA). The hardener is EPIKURE curing agent MGS RIMH 137, which contains diamine group. The PC, PSU, and PEI are the three potential TPs tested in this study, and PSU was the only TP that used as a toughener. The detailed explanation of choosing PSU is in the Results and Discussion section. The solubility parameters of PC, PSU, and PEI are evaluated by viscometry. Methyl chloride is used to dissolve 0.2 g TP with the total volume of 25 ml, which produces a solution with approximately 1% weight concentration of tested polymers. For PC, dimethyl sulfoxide (DMSO) is chosen to mix with chloroform by a volume ratio from 1:4 to 4:1 but the total volume of the mixed solution is still 25 ml. For PEI and PSU, ethyl acetate is mixed with methyl chloride at different ratios as the solvents. Cambridge VISCOpro 2000 is the viscometer to measure the viscosity in each case.

The specimens were produced by VARTM [23], since it was able to obtain a constant high fiber volume fraction with low thickness gradient along the infusion direction. The test specimens were fabricated using Saertex 970 g/m^2 glass fiber fabric. The specimens consisted of three core plies of dimensions $11 \text{ in} \times 1 \text{ in}$, as well as one drop-off ply of dimensions 5.5 in \times 1 in. A 2 in \times 1 in polysulfone (PSU) Udel/Thermalux interleaf was inserted between the drop-off ply and the adjacent core ply [14]. As can be seen from Fig. 3, the entire infusion of epoxy process was accomplished under vacuum environment to minimize the porosity in the final specimen. The heater is used to provide constant processing temperature during the curing. The morphology of the diffusion region was examined by optical microscopy and energydispersive X-ray spectroscopy (EDX). The current study employed mechanical tests as per ASTM-D3309 on an Instron 5569a universal testing machine. The stain gauges were mounted

Journal of Manufacturing Science and Engineering



Fig. 3 Vacuum assisted resin transfer molding experiment setup. The entire process is under high vacuum, which provides the lowest porosity in the final specimen.

on the drop-off ply 0.4 in from the drop-off. The specimens were loaded at strain rate of 1 mm/min until the drop-off layer was entirely delaminated, i.e., until the strain at the strain gauge dropped to zero [14]. Scanning electron microscopy was used to examine the fracture surfaces.

Results and Discussion

Compatibility of Thermoplastics and Epoxy. In this study, the three TP materials PC, PEI, and PSU are chosen as the tested materials for potentially toughening the TS epoxy structure due to their high toughness and high glass transition temperatures.

Since the solubility parameter is generally used to determine the compatibility between polymers, it is important as a guide to choose the proper polymer. Due to the huge interaction forces between high MW polymers, traditional vaporization method is not suitable to measure the solubility parameter. Instead, viscometry was used in this study to determine the compatibility between PC, PEI, PSU, and RIMR 135 epoxy.

Figure 4 shows the experimental determined solubility parameters of PC, PSU, and PEI by using viscometry. The *x*-axis represents the ratios of the two mixed solvents. The *y*-axis represents the intrinsic viscosity of the solution calculated from Eq. (3). All three trends increased at the beginning and then leveled off at some point. The mechanism of solution viscosity of polymers is similar to that of swelling: with a good solvent, polymer was likely to interact with the solvent, the molecular chain of the polymer was able to extend, leading to a retractive force, which is similar to the process that happened during the swelling process



Fig. 4 Experimentally determined intrinsic viscosity of PSU, PEI, and PC by using Eq. (3)

071010-4 / Vol. 139, JULY 2017

[15]. Thus, the most compatible solvent is the one can swell the polymer most, making the solution of highest intrinsic viscosity. Since the solubility parameter of the dissolved polymer was equal to the solubility parameter of the solution when the intrinsic viscosity approached the maximum value, for the PSU solution the highest intrinsic viscosity is around 34. By using Eq. (2) in the Background section, the average solubility parameter for PSU was 21.800. For the PEI, the highest intrinsic viscosity is around 17, and the average solubility parameter of PEI was 23.114. For the PC, the highest intrinsic viscosity is around 46, and the solubility parameter of PC was determined as 22.465.

The major component of RIMR 135 epoxy is DGBEA, of which the solubility parameter was 20.000. Compared with the solubility parameters of PEI, PSU, and PC, it was obvious that the PSU was of the closest solubility parameter to that of the epoxy. Thus, the PSU should be the most compatible polymer of the three to the epoxy and was expected to achieve significant diffusion region with the thermoset epoxy as the toughener of the epoxy system.

Temperature and Additive Concentration-Dependent Diffusion/Precipitation Process. The PSU interleaf was cured with nonmodified epoxy and PS modified epoxy from 0% to 5%



Fig. 5 Average diffusion depths of the specimens (a) with 0% and 5% polystyrene modified epoxy cured from room temperature to 120 °C and (b) with 0–5% polystyrene modified epoxy cured at 80 °C and 120 °C

under various curing temperatures from room temperature to 120 °C. The cured samples were polished to mirror surface for optical observation.

Figure 5(a) shows the diffusion depths with various curing temperatures at 0 wt % and 5 wt % concentrations of PS. The nonmodified epoxy (0% PS) is the lower black line in the figure. It shows no observable diffusion region until the curing temperature reached to 80 °C. The diffusion depth reached to 25 μ m into PSU at 120 $^{\circ}\text{C}.$ Compared to the nonmodified epoxy, with the addition of PS, the diffusion depths into PSU were improved with the increasing concentration of PS dissolved in the epoxy. With 5% PS modified epoxy, the diffusion depths under 120 °C reached to more than 80 μ m into PSU, which were almost four times than the nonmodified epoxy. The main reason that both curves show a jump of the diffusion depths above 60 °C was that the diffusivity of the polymer was extremely small at low curing temperature but much higher at elevated curing temperature. The diffusivity of polymer is highly sensitive to the processing temperatures. Under low curing temperatures, the limited mobility and high viscosity of the TP polymers made the TS difficult to penetrate into the PSU-rich region before the diffusion process ceased due to the curing kinetics. Under high curing temperatures, the significantly reduced viscosity increased the diffusivity of the polymers and made the TS able to transport deep into the PSU region within the decreased time frame for diffusion process. With the PS additive, the curing reaction rate was lower than that without the PS additive. Thus, the curing epoxy required more time to reach gelation point at which the diffusion process would stop, and diffusion process was longer than that of nonmodified epoxy.

Figure 5(*b*) shows the diffusion depths with different concentrations of PS additives from 0 wt % to 5 wt % cured at 80 °C and 120 °C. Under 80 °C, the diffusion depths gradually increased with concentration of PS from 0 wt % to 2 wt % and leveled off from 2 wt % to 5 wt %. Under 120 °C, the diffusion depths kept increasing. This was mainly due to significant reduction of polymer viscosity and curing reaction rate at elevated temperature, which led to increasing polymer chain mobility.

Figure 5(b) also showed that with the same concentration of PS additive, the specimens had deeper diffusion depth under higher curing temperatures. The difference between the specimens with same PS concentration cured at different temperatures was small at low PS concentration and became larger as the concentration rose to 5%.



Fig. 6 PSU thermoplastic diffusion and precipitation region with 5% PS modified epoxy cured at 120 °C is measured from optical microscopy imaging of the thermoplastic (TP)-thermoset (TS) interface. The thermoset diffusion into thermoplastic is characterized by a gradient island-shaped phases, and the thermoplastic precipitation region is characterized by the dispersed PSU in the epoxy after curing.



Fig. 7 PSU thermoplastic diffusion and precipitation region with 5% PS modified epoxy cured at 80 °C is measured from optical microscopy imaging of the thermoplastic (TP)–thermoset (TS) interface

Figure 6 shows the diffusion and precipitation morphology under 5% PS modified epoxy cured at 120 °C. The bright area represents the PSU region, and the dark area represents the epoxy region. The islands-shaped gradient interphase due to the diffusion from the epoxy to the TP region can be clearly observed. The average diffusion depth in this case was 83.7 μ m. Within the gradient interphase region, the size of islands decreased with deeper diffusion depth. This decrease in size was due to the reduced concentration of epoxy with deeper diffusion. As a result, when the liquid epoxy phase started to turn to gelation, it separated out from the solution and formed smaller sizes of clusters along the diffusion direction due to the reduction of epoxy concentration. In the epoxy region, there were small bright dots. These dots were PSU-rich region in the epoxy due to the precipitation process. The precipitation depths in this case were around 32 μ m.

As a comparison, Fig. 7 shows the diffusion and precipitation morphology under 5% PS modified epoxy but cured at 80 °C. The average diffusion depth in this case was 37.1 μ m, and the average precipitation depth was 25 μ m. The reason for the reduced diffusion and precipitation depths was that the diffusivity was highly temperature-dependent. The diffusivity was expected to increase significantly with evaluated curing temperatures, even though the



Fig. 8 PSU thermoplastic diffusion and precipitation region with nonmodified epoxy cured at 120 °C is measured from optical microscopy imaging of the thermoplastic (TP)-thermoset (TS) interface

Journal of Manufacturing Science and Engineering



Fig. 9 Average precipitation depths of the specimens (*a*) with 0% and 5% polystyrene modified epoxy cured from room temperature to 120 °C and (*b*) with 0–5% polystyrene modified epoxy cured at 80 °C and 120 °C

curing reaction rate also increased. Figure 8 showed the diffusion and precipitation morphology with nonmodified epoxy under 120 °C. Compared with Fig. 6, the diffusion depth reduced to around 25 μ m and the precipitation depth to around 15 μ m. With the modified epoxy, significantly improved diffusion and precipitation region can be realized compared to the nonmodified epoxy.

Figure 9(a) shows average precipitation depths with 0% and 5% PS modified epoxy cured from room temperature to 120 °C. Figure 9(b) shows average precipitation depths with 0–5% PS modified epoxy cured at 80 °C and 120 °C. The precipitation depth was determined by the deepest observable precipitates from the interface between PSU and epoxy. Both curves increased with the elevated temperatures. Compared to Fig. 5, the precipitation depths was normally smaller than diffusion region. The reason for this phenomenon was that the mobility of the long chain TP molecules was smaller compared to the mobility of low molar weight uncrosslinked TS molecules. Figure 10 shows the EDX line scan of the specimen across the interface between the PSU and the epoxy matrix. Sulfur element was traced along the line which only existed in the PSU, and chloride element was traced to represent the existence of epoxy. From Fig. 10, it can be known that at high temperature, the low MW TS diffused much faster than the



Fig. 10 EDX line scan across TS–TP interface of the specimen (*a*) under 5% PS modified epoxy cured at 80°C and (*b*) under 5% PS modified epoxy cured at 120°C. The dashed lines indicate the diffusion and precipitation region.

high MW TP, leading to sharp reduction of sulfur element counts in Fig. 10(b) but gradual reduction of sulfur elements in Fig. 10(a). The existence of sulfur elements in the precipitation region indicated that only part of the PSU precipitated out, the rest was mixed with epoxy matrix due to the limited mobility of long chain structure after the gelation of curing epoxy.

Geometry Influence on the Diffusion and Precipitation Process. The geometry factor also influenced the diffusion and precipitation process. The PSU film was embedded between the fiber plies and cocured with the epoxy. Figure 11 shows the diffusion and precipitation region of the 5% PS modified epoxy cured at 120 °C. The arrows were used to highlight the TS diffusion and TP precipitates in the epoxy matrix, and the white line was used to distinguish the interface between the TP and the epoxy. Compared with the case under the same condition but without fiber structures, the diffusion and precipitation regions both reduced significantly. In this condition, the diffusion depth was around 45 μ m, and the precipitation depth was around 30 μ m. The reason for the reduction of diffusion and precipitation region was that the existence of the fiber bundles acted as obstacles in the direction of PSU diffusing into epoxy. The small gaps between the fibers generated great resistance for PSU to pass through and increase the length of the path that TP needs to travel, which led to the reduced precipitation region. On the other hand, since less PSU was transferred into epoxy-rich region, there were less free space in PSU-rich region, and the existence of the fiber beams reduced the amount of epoxy in the unit region that was able to swell the TP.

071010-6 / Vol. 139, JULY 2017



Fig. 11 PSU thermoplastic diffusion and precipitation region in the fiber matrix with 5% PS modified epoxy curing at 120 $^{\circ}$ C. The dashed line represents the boundary of TS–TP interface. The arrows represent the locations where there are precipitates.



Fig. 12 PSU thermoplastic diffusion and precipitation region in the fiber matrix with 5% PS modified epoxy curing at 80 $^{\circ}$ C. The dashed line represents the boundary of TS–TP interface. The arrows represent the locations where there are precipitates.

Both reasons led to significant reduced diffusion depth. Figure 12 shows the diffusion and precipitation region of 5% PS modified epoxy with fiber structure under 80 °C. The average diffusion region was 19 μ m, and the precipitation region was 10 μ m. Since the fibers were not uniformly distributed in the local area, the region with less fibers showed more diffusion and precipitation. On the other hand, the region where the fiber came into contact with PSU, almost no diffusion and precipitation was observed. Figure 13 shows the diffusion and precipitation with nonmodified epoxy curing at 120 °C. Very limited diffusion and almost no obvious precipitation can be observed under this condition. The impermeable fiber beams reduced the diffusivity of both curing epoxy and PSU with or without PS additive. The diffusion and precipitation depth decreased under all conditions but the specimen with 5% PS still showed relatively large diffusion and precipitation region.

Stress–Strain and Toughness Behavior. Uniaxial tensile tests were carried out. The drop-off specimen used in the test was to simulate the mixed mode loading conditions in reality [14]. The



Fig. 13 PSU thermoplastic diffusion and precipitation region in the fiber matrix with nonmodified epoxy curing at 120 $^{\circ}$ C. The dashed line represents the boundary of TS–TP interface.



Fig. 14 Representative strain-stress curves obtained from the strain gauge mounted on the drop-off layer in uniaxial tensile tests: reference specimen (without interleaf) and interleaved specimens with 5% PS modified epoxy cured at $80\,^{\circ}$ C and $120\,^{\circ}$ C

specimens were loaded until the drop-off region was totally delaminated by cracking through the interlaminar region and the value of the strain gauge returned to zero, which were mounted on the surface of drop-off layer 0.4 in away from the drop-off. Figure 14 shows the stress and strain curves of the drop-off layer under three conditions. The curve marked "reference" referred to the case where no interleaf was introduced. As a result, the reference specimen began to fail at a low strain (about 0.35%). The curves whose slopes were similar to the reference specimen were the specimens with 5% PS cured at 120 °C and 80 °C. As Fig. 14 shows, because of the inserted interleaf, the interlaminar layer connecting the drop-off layer to the core plies became much tougher. For the curve marked 120 °C, it did not fail until the strain reached almost 0.8% due to its increased diffusion and precipitation depth (Fig. 11).

The toughness, which represents the energy required for a crack to initiate and propagate, was calculated by integrating the area under the stress strain curve (Fig. 15). In Fig. 16, for each curing temperature, three specimens were tested to validate the data repeatability under different concentrations of PS. Each average toughness and their standard errors were represented by a symbol and an error bar. As shown in the figure, the toughness of the specimens had a gradual increase and a peak at 5% PS modified

Journal of Manufacturing Science and Engineering

JULY 2017, Vol. 139 / 071010-7



Fig. 15 Toughness of PSU interleaved specimens from 0.5% to 5% PS modified epoxy cured at 80 $^{\circ}$ C and 120 $^{\circ}$ C. The error bars represent standard errors.

epoxy cured at 120 °C. The trend resembled that of the diffusion and precipitation depths seen in Fig. 10 and provided strong evidence that deep semi-IPN of the interleaf into the matrix led to increased toughness and improved delamination resistance. At its peak, the toughness was almost three times as high as the reference specimen which had no interleaf.

Crack Propagation Location and Toughening Mechanism. Fracture surfaces of the specimens after mechanical tensile tests

were observed via scanning electron microscopy. Figure 16(a)shows the fracture surface of the reference specimen. It was clean where fewer broken fiber beams were found on the surface. Individual fiber beams were seen with very few particles on their surfaces. Clean and clear river lines between the fibers indicated there was no plastic shear deformation. The crack of this kind mainly went through the interface between epoxy and fiber, which led to adhesion failure. For the PSU interleaved specimens cured with 5% PS modified epoxy cured at $120 \degree C$ (Fig. 16(b)), more residues were observed on the fibers throughout the fracture surface. Most fibers were not clean and had a veil attached on the surface, which indicated large plastic deformation. Fig. 16(c) shows the fracture surface of fiber beam under high magnification (5 K). On the surface of the fiber beam, a spongy veil can be observed throughout the entire fracture surface. The porous residue was the diffusion and precipitation region, which matched the morphology in Fig. 10. Thus, the crack was located at the generated semi-IPN region and propagated by breaking the network, which required much more energy due to the plastic shear deformation of the diffusion and precipitation region. The results indicated that high toughness interleaf and deep diffusion and precipitation region were both the key factors to improve the toughness of the composites by avoiding the traditional adhesion failure along the interface between epoxy and fiber.

Conclusion

The effect of the interleaf deep diffusion and precipitation on the delamination resistance was investigated for the PSU interleaved GFRP. PSU was chosen due to its close solubility to the epoxy system. The diffusion and precipitation depth increased with the curing temperature and concentration of the PS additive. The improved diffusion and precipitation depth is mainly due to



Fig. 16 SEM image of the fracture surface of (*a*) the reference specimen without interleaf, (*b*) the interleaved specimen with diffusion and precipitation, and (*c*) high resolution close up of the fracture surface

071010-8 / Vol. 139, JULY 2017

the increased mobility of the molecules at high temperature and increased time for diffusion and precipitation process due to the addition of PS. As compared with the GFRP without interleaf, the fracture toughness increased by a factor of 3 with the 5% PS modified epoxy cured at 120 °C. This is mainly because the deep diffusion and precipitation zone of improved ductility confines the plastic zone ahead of the crack tip within its boundaries and thus requires more facture energy for the crack to propagate. Spongy veil covered the entire fracture surface, indicating the crack propagated through the generated semi-IPN, which was the key factor for the improved delamination resistance.

Acknowledgment

This research was supported by the National Science Foundation under a GOALI Award No. CMMI-1363328. The authors would also like to thank Ming Gao from Columbia University for providing us viscometry equipment.

References

- [1] Shetty, R. R., Pavithra, G. K., and Rai, S. K., 2013, "Studies on Mechanical and Fractographic Behavior of Polycarbonate-Toughened Epoxy-Granite Particle Hybrid Composites," Polym. Plast. Technol. Eng., 52(11), pp. 1122–1126. [2] Jin, Z., Tong, L., and Xungai, W., 2010, "Electrospun Nanofiber Toughened
- Carbon/Epoxy Composites: Effects of Polyetherketone Cardo (PEK-C) Nanofiber Diameter and Interlayer Thickness," Compos. Sci. Technol., 70(11), pp. 1660–1666
- [3] Xu, Y., Liao, G., Gu, T., Zheng, L., and Jian, X., 2008, "Mechanical and Morphological Properties of Epoxy Resins Modified by Poly(Phthalazinone Ether Sulfone Ketone)," J. Appl. Polym. Sci., 110(4), pp. 2253–2260.
- [4] Martines, I., Martin, M. D., Eceiza, A., Oyanguren, P., and Mondragon, I., 2000, "Phase Separation in Polysolfune-Modified Epoxy Mixtures. Relationships Between Curing Conditions, Morphology and Ultimate Behavior," Polymer, 41(3), pp. 1027-1035.
- [5] Blanco, I., Cicala, G., and Faro, C. L., 2003, "Improvement of Thermomechanical Properties of a DGEBS/DDS System Blended With a Novel Thermoplastic Copolymer by Realization of a Semi-IPN Network," J. Appl. Polym. Sci., 88(13), pp. 3021-3025.
- [6] Heitzmann, M. T., Hou, M., Verdt, V. M., Vandi, L., and Paton, R., 2013, "Morphology of an Interface Between Polyetherimide and Epoxy Prepreg," *Adv. Mater. Res.*, **393–395**, pp. 184–188. [7] Tan, H., and Yao, Y. L., 2013, "Laser Joining of Continuous Glass Fiber
- Composite Preforms," ASME J. Manuf. Sci. Eng., 135(1), p. 011010.

- [8] Bian, D. K., Satoh, G., and Yao, Y. L., 2015, "The Laser Interlaminar Reinforcement of Continuous Glass Fiber Composites," ASME J. Manuf. Sci. Eng., 137(6), p. 061001
- [9] Groleau, M. R., Shi, Y. B., Yee, A. F., Bertram, J. L., Sue, H. J., and Yang, P. C., 1996, "Mode II Fracture of Composites Interleafed With Nylon Particles," Compos. Sci. Technol., 56(11), pp. 1223–1240.
- Hillermeier, R. W., and Sefeis, J. C., 2001, "Interleaf Toughening of Resin Transfer Molding Composites," Composites, Part A, 32(5), pp. 721–729.
 Li, G., Li, P., Zhang, C., Liu, Y. H., Zhang, H. Y., Jia, X. L., Yang, X. P., Xue,
- Z. M., and Ryu, S. K., 2008, "Inhomogeneous Toughening of Carbon Fiber/ Epoxy Composite Using Electrospun Polysulfone Nanofibrous Membranes by In Situ Phase Separation," Compos. Sci. Technol., 68, pp. 987-994.
- [12] Kuwata, W., and Hogg, P. J., 2011, "Interlaminar Toughness of Interleaved CFRP Using Non-Woven Veils," Composites, Part A, **42**(10), pp. 1551–1570. [13] Tan, H., and Yao, Y. L., 2013, "Feasibility Analysis of Inter-Laminar
- Toughening for Improving Delamination Resistance," Manuf. Lett., 1(1), pp. 33-37.
- [14] Bian, D. K., Bucher, T., Shim, D. J., Jones, M., and Yao, Y. L., 2016, "Effect of Deep Penetration of Interleaf on Delamination Resistance in GFRP," J. Manuf. Sci. Technol., 138(7), p. 071011.
- [15] Mangaraj, D., Bhatnagar, S. K., and Rath, S. B., 1963, "Cohesive-Energy-Density of High Polymers Part III: Estimation of C.E.D by Viscosity Measurement," Macromol. Chem. Phys., 67(1), pp. 75-83.
- [16] Bernard, L., Chapel, J. P., and Gernard, J. F., 2001, "Gradient Interphase Between Reactive Epoxy and Glassy Thermoplastic From Precipitation Process, Reaction Kinetics and Phase Separation Thermodynamics," Macromolecules, 34(5), pp. 1204-1213.
- [17] Gyunn, N., Yong, Y., Won, G., and Kim, S. C., 2004, "Toughening of Epoxy Composite by Dispersing Polysulfone Particle to Form Morphology Spectrum, Polym. Bull., **52**(5), pp. 365–372. [18] Gyunn, N., Yong, Y., Won, G., and Kim, S. C., 2004, "Toughening of Carbon
- Fiber/Epoxy Composite by Inserting Polysulfone Film to Form Morphology Spectrum," Polymer, 45, pp. 6953–6958.
- Gan, W. J., Yu, Y. F., and Liu, X. Y., 2009, "Kinetics of Phase Separation at the Early Stage of Spinodal Decomposition in Epoxy Resin Modified With PEI Blends," Colloid Polym. Sci., **287**(1), pp. 23–28.
- [20] Rico, J. L., Montero, B., Diez, J., and Ramirez, C., 2009, "Polymer Blends Based on an Epoxy-Amine Thermoset and a Thermoplastic: Effect of Thermoplastic on Cure Reaction and Thermal Stability of the System," J. Therm. Anal. Calorim., 95(2), pp. 369-376.
- [21] Brewer, J. C., and Lagece, P. A., 1988, "Quadratic Stress Criterion for Initiation of Delamination," J. Compos. Mater., 22(12), pp. 1141-1155.
- [22] Aksoy, A., and Carlsson, L. A., 1991, "Crack Tip Yield Zone Estimates in Mode II Interlaminar Fracture of Interleaved Composites," Eng. Fract. Mech., 39(3), pp. 525-534.
- [23] Woods, J., Modin, A. E., Hawkins, R. D., and Hanks, D. J., 2002, "Controlled Atmospheric Pressure Infusion Process," International Patent No. WO 03/ 101708 A1.