

Influence of Elastomer Distribution on the Cryogenic Microcracking of Carbon Fiber/Epoxy Composites

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ABSTRACT: Carbon fiber/epoxy laminates containing three different types of rubber modifiers, separately and in combination, were developed for testing in a cryogenic environment. Preformed rubber particles, core shell rubber, and solid carboxyl-functionalized rubber were chosen as additives to a model prepreg matrix to control the placement of the rubber within the resulting laminates. Cryogenic microcracking and mode I and II fracture toughness and interlaminar shear strength experiments were performed. Scanning electron microscopy was used to observe fracture surfaces of the rubber-modified laminates. Fracture toughness

properties were improved while the ILSS decreased because of the presence of these rubber modifiers. It was observed that the presence of these modifiers significantly reduced the microcrack density of the laminates exposed to cryogenic cycling, and in the case of one, even eliminated microcracking entirely. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2268–2275, 2003

Key words: composites; rubber; carbon fiber; particle reinforcement; microcracking; fracture toughness

INTRODUCTION

The need for high-strength and lightweight materials has made polymeric composites ideal for use in aerospace applications, which often require the storage and transportation of cryogenic liquids.^{1–5} When a composite material is exposed to cryogenic temperatures, internal stresses are generated because of cure shrinkage, Poisson's effects, and mismatches in the coefficients of thermal expansion between the fibers and the matrix as well as the ply groups, which can result in microcracking.^{1,6} Previous work has shown that exposure to low temperatures, especially in a cyclical fashion, induces degradation of composite materials. Typical damage resulting from thermal cycling at low temperatures includes delamination, pitting, and microcracking.⁷ Differences in cryogenic cycling behavior have been noted for laminates cured at a range of temperatures and those manufactured with various types of fibers.^{8,9} An earlier study has also shown that the molecular structure of the polymeric matrix in these systems can be engineered to improve the fracture toughness of epoxies at cryogenic temperature.¹⁰

Liquid rubber tougheners were found to improve the resistance of carbon fiber/epoxy composites to cryogenic microcracking.¹¹ During cure, these liquid rubbers phase separate and form an evenly distributed second phase which is locked into the matrix upon gelation.^{12,13} The phase separation process is thus significantly affected by the resin components, the cure cycle,¹⁴ and the viscosity of the resin system prior to cure initiation.¹⁵ Changes in these variables may drastically affect the microcracking response of the composite. These variables may be eliminated through the selection of toughening materials that are incorporated as preformed particles and remain as distinct particles.

Core-shell rubbers (CSR) enhance the toughness of epoxy resins similar to the use of liquid rubber materials^{16,17}; however, no decrease in glass transition temperature of the epoxy network was observed when the core-shell particles were used.¹⁶ Extensive work has been carried out to understand toughening mechanisms in rubber-modified epoxies and composites by using CSR particles. The major toughening mechanism in the core-shell-modified epoxy systems was found to be cavitation of the rubber particles followed by shear yielding of the matrix.^{17–21} Yang and coworkers came to the same conclusions by using rubber-toughened cyanate ester composites.²² CSR rubbers typically have an average diameter of 0.2 to 1 μm .

One way to toughen carbon fiber reinforced polymers is through the modification of the interlayer of the composite by using preformed particles.^{23,24} This toughening method has been shown to reduce delami-

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nation, which is one of the greatest causes of composite failure.^{25,26} A significant amount of work has been done to investigate interlayer-toughened prepreg systems. While most work has focused on prepreps with epoxy matrices, this engineering approach has also been applied to cyanate ester and bismaleimide systems.²⁷⁻²⁹ Materials used for interlayer modifiers have traditionally been preformed thermoplastic or rubber particles. The most widely used thermoplastics are polyamides³⁰ but other materials such as polyether-sulfones²⁹ and polyimides³¹ have been used. Preformed rubber particles are frequently based on crosslinked butadiene-acrylonitrile, but they sometimes include styrene to increase particle rigidity and glass transition temperatures.³² The size of these preformed rubber particles is typically found to be between 20 and 50 μm .³³ Hayes et al. provided a review of work that has been done on the use of preformed rubber or thermoplastic particles in high-performance thermosetting resins and composite materials.³⁴

Other common materials used for the modification of epoxy resins are solid rubbers based on butadiene-acrylonitrile.^{35,36} These elastomers require dissolution in a suitable solvent, such as acetone, for incorporation into the epoxy resin. The solvent can be subsequently removed with heat or under vacuum for hot-melt processing. Nevertheless, due to their high molecular weight and inherent elasticity, the percentage of a dissolved solid rubber in a formulation is usually small. Hayes and coworkers showed that higher quantities of solid carboxyl-functionalized rubber could be incorporated in a hot-melt epoxy-based resin if the epoxy/carboxyl esterification is delayed until after the prepreg is developed.³⁷

In this study, the effects of rubber placement in the polymeric matrix of composites were analyzed in relation to the microcracking response during cryogenic cycling. Composite modification consisted of interlayer toughening using 50- μm average preformed rubber particles, a dispersion of 0.3 μm core shell rubber throughout the entire matrix, and the addition of a rubber interpenetrating network (IPN) to the continuous phase of the matrix. Cross-ply laminates were developed for cryogenic cycling experiments and the microcracking density was quantified for each laminate. Experiments were also performed to determine the effect of these modifiers on the mode I and II fracture toughness and interlaminar shear strength of the laminates.

EXPERIMENTAL

Resin formulation

The resin used in this study consisted of a combination of epoxy resins resulting in a high-temperature aerospace-grade model resin. To this base resin, fumed

TABLE I
Resins Developed for Composite Matrices

Resin	DP 5045	DP 5031	Nipol 1472
Control	—	—	—
DP5045	6 phr ^a	—	—
DP5031	—	6 phr	—
Nipol 1472	—	—	6 phr
DP5045/DP5031	6 phr	6 phr	—
DP5045/Nipol 1472	6 phr	—	6 phr
DP5031/Nipol 1472	—	6 phr	6 phr
3 rubbers	6 phr	6 phr	6 phr

^a Parts per hundred resin.

silica CAB-O-SIL[®]TS-720 (Cabot Co.) was added to control flow. Chromium (2%) naphthenate (OMG Americas Inc.) was used as an epoxy/carboxyl esterification catalyst. Preformed rubber particles, core shell rubber, and solid carboxyl functional rubber were used to modify the base resin. The various formulations consisted of combining the three rubber additives separately and in all possible combinations to form a total of eight different resins, as shown in Table I. The carboxyl-functionalized modifiers (Zeon Chemicals Inc.) were Duomod[®] DP 5045, Duomod[®] DP 5031, and Nipol 1472, a preformed rubber particle with an average diameter of 50 μm , a CSR particle with an average diameter of 0.3 μm , and a solid crumb rubber, respectively. In each formulation, 6 parts per hundred resin (phr) of the rubber material was added to the base resin, so the system with all three modifiers had a total of 18 phr of rubber additives.

The different rubbers were added to the base resin and mixed in an oil bath at 130°C for 1 h. When the solid carboxyl-functionalized rubber was used, it was necessary to alter the procedure slightly. It consisted of combining a portion of the epoxy resins with the acetone rubber solution. After adequate mixing, the resin/rubber solution was placed in a crystallization dish and the acetone was removed under vacuum at 130°C. This rubber-epoxy combination was then transferred to a mixing apparatus with the remaining epoxy. A stoichiometric amount of 4,4'-diaminodiphenylsulfone (DDS), HT976 (Ciba-Geigy), was used to cure the systems. The DDS was melted, added to the resin mixture at 130°C, and mixed for 5 min before prepregging.

Prepreg development

The unidirectional prepreps developed in this study consisted of standard modulus carbon fibers (Toray T300 12K epoxy-sized fibers) and the previously described epoxy resins. The fibers were impregnated with the epoxy resin using a commercial scale hot-melt prepreg machine.³⁸ The fiber areal weight was set to 145 g/m² and the nominal resin content was 35 \pm 3 wt % for all the experiments. Resin filming was per-

formed at 62.8°C and the impregnation temperature was 93.3°C. Two 7.62-cm-diameter impregnation rollers were used to apply pressure, with the first set at 69 kPa and the second set at 276 kPa. The line speed was 0.91 m/min for all experiments.

The resin content of the prepregs was determined by weighing a 5.08×5.08 cm² square of prepreg, dissolving the resin with acetone, and weighing the dry fibers. This technique is in accordance with ASTM D 3171-99³⁹ and Boeing Support Standard 7336.⁴⁰ Five samples from each batch of prepreg were used in the determination of resin content.

Laminate fabrication

Both cross-ply and unidirectional laminates were laid up by using the model prepregs. The 12-ply cross-ply laminates consisted of 15×15 cm prepreg plies in a $[0_3/90_3]_S$ configuration. After every third ply, the prepreg was precompacted under vacuum pressure for 2 min during the lay-up before additional plies were positioned. The unidirectional laminates were 20 plies thick, 33 cm long, and had a 5.08-cm fluorinated ethylene propylene (FEP) copolymer film layer placed in the mid-plane of the sample to act as a crack starter. Specimens were cut to a width of 1.27 cm for fracture and short beam shear testing. For this second set of laminates, after every two plies, the prepreg was precompacted under vacuum pressure for 2 min before another ply was positioned.

The cure cycle for all the laminates consisted of a 2.8°C/min ramp to 177°C followed by a 2-h hold at 177°C and a ramp down to 27°C at a rate of 2.8°C/min. The laminates were manufactured by using a total consolidation pressure of 310 kPa and the vacuum bag was vented to the atmosphere when the autoclave pressure reached 103.5 kPa. Once cured, the cross-ply laminates were cut into $3.50 \times 1.27 \times 0.16$ cm (length \times width \times thickness) samples for cryogenic cycling studies. The edges of the samples were polished prior to cycling to view microcracks by using optical microscopy.

Analysis

Dynamic mechanical analysis (DMA) experiments were performed on the cross-ply laminates using a TA Instruments 2980 DMA controlled by Thermal Solutions 1.2-J software. A heating rate of 5°C/min to 300°C with a frequency of 1 Hz and amplitude of 0.10 mm was utilized in a nitrogen atmosphere. The glass transition temperature of the materials was reported as the peak in loss modulus.

Interlaminar shear strength (ILSS) of the composite materials was tested according to ASTM D 2344-00,⁴¹ short beam shear (SBS). All mechanical testing was performed with an Instron 4505 screw-testing frame

controlled by Instron Series IX software. The span-to-thickness ratio was set to 4 for all experiments and the loading rate was set to 1.27 mm/min. Five samples were tested for each reported value. Standard deviations were calculated and are shown as error bars.

Mode I interlaminar fracture toughness was measured by using the double-cantilever beam (DCB) method⁴² according to ASTM D 5528-94a.⁴³ Each specimen was precracked in the mechanical testing apparatus to provide a sharp crack tip before testing. The fracture specimens were pulled apart in tension at 2.54 cm/min until a displacement of 6.35 cm was reached, at which point the crack extension was marked. Five samples were tested and averaged for each reported G_{IC} value. Standard deviations were calculated and are shown as error bars. Scanning electron microscopy was used to examine the fracture morphology. The samples were gold sputtered and an accelerating voltage of 15 kV was used with a working distance of 48 mm.

Mode II interlaminar fracture toughness was measured by using the end notch flexure (ENF) test.^{42,44} A three-point bend apparatus with stationary posts set 10.16 cm apart was used to create shear fracture of the specimen down the mid-plane. The crack front was set 2.54 cm from the stationary post and the loading point was set 5.08 cm from the post. All specimens were precracked in the mechanical testing apparatus to provide a sharp crack tip before testing. A displacement rate of 0.254 cm/min was used to load the specimen in flexure until the crack propagated. The crack front was then located with an optical microscope fixture and moved back to 2.54 cm from the stationary post. This was repeated until the sample was cracked down its entire length. Six G_{IIC} values were obtained for each specimen and averaged for the reported G_{IIC} value. Standard deviations were calculated and are shown as error bars.

Three cut and polished cross-ply laminates were placed in a liquid nitrogen bath (-195.8°C) for 10 min during each cycle. After exposure to liquid nitrogen, the samples were placed in a desiccator and allowed to return to room temperature. Optical microscopy was used to observe and report the response of the samples to cryogenic exposure. Each sample was examined prior to exposure to ensure that there were no initial cracks or defects on the surface. After letting the samples come to thermal equilibrium in the desiccator, they were examined at $\times 100$ and $\times 200$ magnification by using an optical microscope. Photomicrographs were taken and the number of microcracks on the polished surface was counted. Each cross-ply laminate was cycled to cryogenic temperatures five times, or until optical microscopy revealed no further microcracking. To quantify the extent of microcracking in each material, the crack density was found by dividing the total number of microcracks on the sample face by the face area.

RESULTS AND DISCUSSION

In previous work, carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber was used as a modifier in the laminates with variations in concentration and acrylonitrile content.¹¹ The presence and concentration of liquid rubber in the first phase played a significant role in the decrease in microcrack density but it was not clear to what extent the matrix morphology influenced the microcrack response of the laminates. In this work, three different rubber modifiers were used to toughen the composite laminates (i.e., preformed rubber, core shell particles, and solid carboxyl-functionalized rubber). These three modifiers were preferred to other additives because different toughening conditions could be achieved. This study focused on the influence of the toughener types on the microcracking response to cryogenic cycling of the composite laminates.

Laminate mechanical properties

The base resin formulation was designed to provide an adequate microcrack response when subjected to cryogenic cycling. The glass transition temperature (T_g) of the unmodified laminate was found to be 204°C, 27°C greater than the cure temperature, which is generally a characteristic of highly crosslinked systems, susceptible to cryogenic microcracking.⁴⁵ The T_g of the other specimens was approximately the same as the control laminate except for the system made with the resin containing the three different rubbers. It is not surprising that the T_g of this highly modified system fell to 194°C given the extensive level of rubber modifier (18 phr).

The interlaminar shear strength of the unmodified laminate was significantly greater than all the modi-

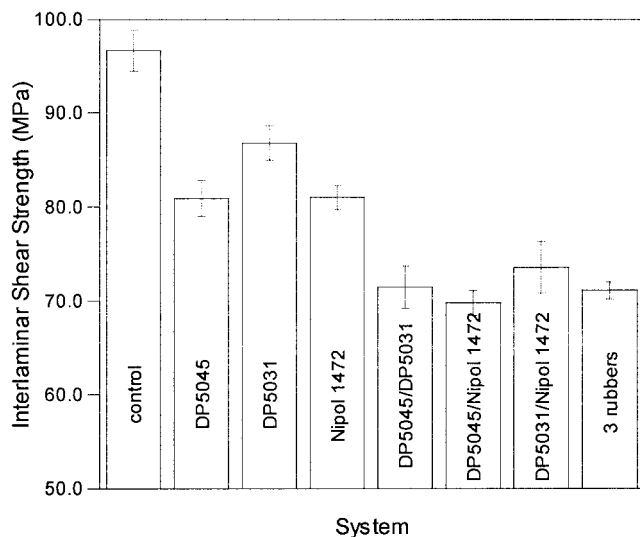


Figure 1 Interlaminar shear strength of the laminates.

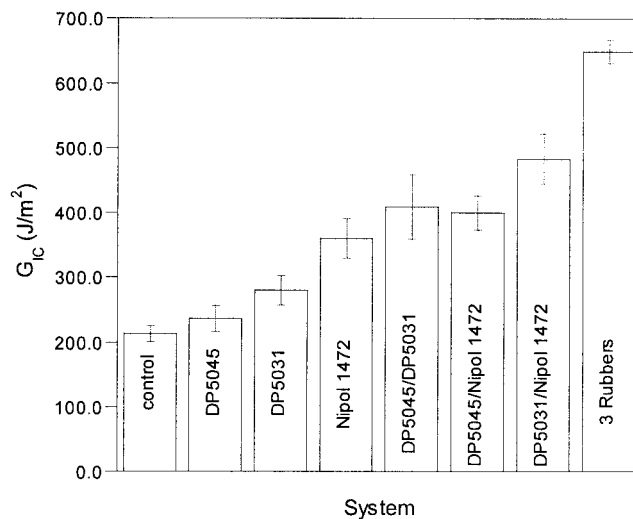


Figure 2 Mode I interlaminar fracture toughness values of the laminates as measured by G_{IC} .

fied laminates, as shown in Figure 1. When the matrices were modified with one type of rubber, the ILSS decreased by about 15% and when two or three rubber additives were used, the decrease of the ILSS values reached 30%. Interlayer particle toughening or rubber modifying the matrix continuous phase played an equivalent role in depressing the ILSS, while the ILSS of the laminate modified with the dispersed core shell particles was not decreased as significantly. Regardless of the type of modification, the rubber materials decreased the ILSS value of the laminate, most likely by lowering the modulus of the matrix.⁴⁶

The effect of rubber modifications and concentration on the mode I interlaminar fracture toughness, as measured by G_{IC} , is shown in Figure 2. The G_{IC} values of all the toughened laminates were greater than the control. The most significant increase in G_{IC} was obtained for the laminate modified with the three rubbers, in which case the G_{IC} was three times higher than that of the control. When just one rubber additive was present, the Nipol 1472 modified laminate displayed the largest increase in G_{IC} (~75%). The modification of matrix continuous phase with the solid carboxyl-functionalized rubber may have been responsible for such an increase in the fracture energy. The larger G_{IC} values obtained for the dispersed core shell particles modified laminate as compared to the interlayer toughener DP 5045 modified sample can be explained by the smaller size of the core-shell rubber particles. With a decreased particle size, a more homogeneous laminate structure was obtained and there was more contact between the crack and the fibers, which resulted in fiber influences, increasing the G_{IC} values. If the DP 5045 or the DP 5031 particles were the only modification to the matrix, there was only a slight increase of the mode I interlaminar fracture toughness

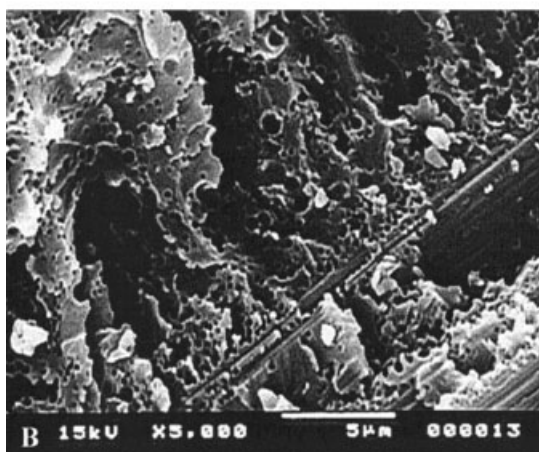
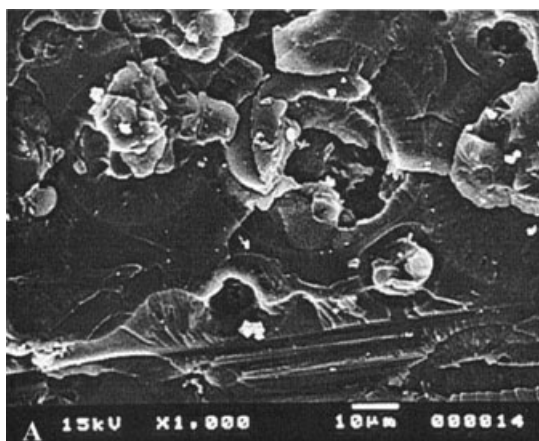


Figure 3 Scanning electron micrographs of mode I fracture surfaces of laminates modified with (A) DP 5045 ($\times 1000$), (B) DP 5031 ($\times 5000$).

of the modified laminate. When the preformed rubber particles and the core-shell rubber were used together, a significant increase was observed, probably due to the greater concentration of rubber in the crack path, absorbing more energy. Figure 2 also shows a clear correlation between the toughness of the material and the amount of rubber present in the matrix. When more rubber additive was used to modify the base resin formulation, a higher G_{IC} value was achieved for the considered laminate.

Scanning electron microscopy was used to characterize the fracture surfaces of the laminates. Figure 3 shows mode I fracture surfaces for two of the rubber-modified laminates. As seen in Figure 3(A), the particles, DP 5045, were torn and/or disbonded during fracture, which increased the energy absorption, leaving sections of some of the particles exposed on the surface. Hollow centers of torn particles on the surface can also be observed on Figure 3(A). A higher magni-

fication ($\times 5000$) was used in Figure 3(B) because of the average size of the core-shell particles ($0.3 \mu\text{m}$). It shows a well-dispersed phase caused by these particles. Cavitation was most likely the main energy absorbing mechanism explaining the increase in G_{IC} over the unmodified laminate.²¹

Figure 4 shows the mode II interlaminar fracture toughness performance of the laminates as measured by G_{IIC} , the critical strain energy release rate. The toughened laminates showed an increased value of G_{IIC} over the control of approximately 30% on average. It appeared that the preformed rubber particles (DP 5045) enhanced the mode II interlaminar fracture toughness of the laminates most effectively. However, statistically there was very little variation between the rubber-modified samples.

Cryogenic cycling analysis

Figure 5 shows optical photomicrographs that illustrate examples of the microcrack morphology developed as a result of cryogenic cycling. Microcracks propagated normal to the fibers when viewed along their length through the polymeric matrix beginning at the outer edge of the laminates and ending at the $0^\circ/90^\circ$ ply interface. The microcrack morphology did not appear to change with the additive type or amount. It must be noted that even though the microcracks appear narrower in the control laminate as shown in Figure 5(A), the spacing between microcracks was much smaller than in the rubber-modified laminates. It was also observed that more microcracks formed on the bag side of the composite part. This phenomena has been noted in previous work and may be due to the roughness of the bag side, which might

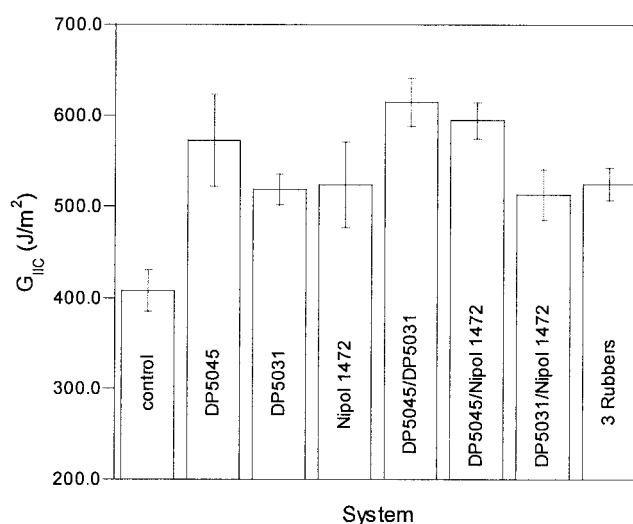


Figure 4 Mode II interlaminar fracture toughness of rubber-modified laminates as measured by G_{IIC} .

have provided more crack initiation sites than the tool side.⁴⁷

The effect of the rubber type on the response of the laminates to cryogenic cycling is displayed in Figure 6. This figure demonstrates that microcracking resistance of composites can be greatly improved by including rubber modifiers. Interlayer toughening slightly improved the microcrack resistance of the laminate where the dispersed core shell particles re-



Figure 5 Reflected optical micrographs of cryogenically cycled laminates. (A) control, (B) DP 5031, (C) DP5045/Nipol 1472 ($\times 100$ magnification).

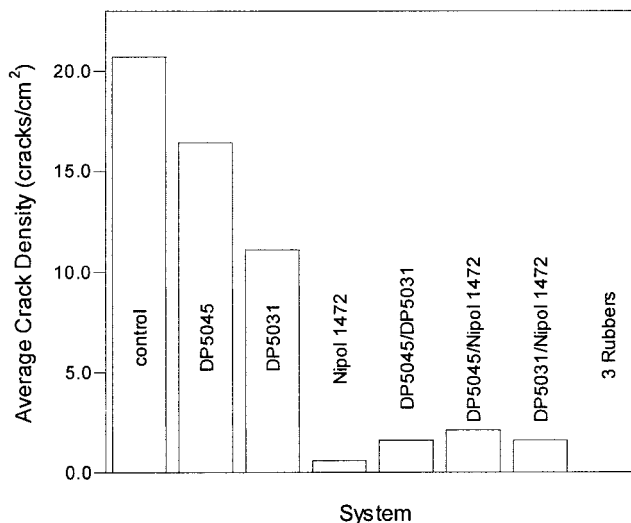


Figure 6 Average crack density of the various systems.

duced the crack density by 50%. The addition of only the dissolved solid carboxyl-functionalized rubber to the matrix resulted in a dramatic reduction in the crack density of the laminate. The presence of Nipol 1472 most likely improved the thermal shock resistance of the laminates, which decreased the level of thermal stresses generated and resulting average crack density. Because the rubber is present homogeneously in the continuous epoxy phase, it might explain the more effective resistance to microcracking when compared to the rubber particle modified laminates where dispersion is more localized or even just present as an interlayer. When the DP 5045 and DP 5031 rubber particles were combined to modify the laminate, a significant drop in the microcrack density was observed. Interestingly, when one of the two Duo-mod[®] particle additives was replaced with the Nipol 1472 in the two additive systems, there was no statistical change in the number of microcracks. It seems that at this point, the concentration of rubber additive is a more important factor than the type. The laminate modified with the combined preformed rubber particles, core-shell rubber, and solid carboxyl functionalized rubber did not display microcracks as a response to thermal cycling. This was most likely due to the high concentration of rubber in the matrix.

CONCLUSION

Model carbon fiber/epoxy composite systems toughened with preformed rubber particles, core-shell rubber, and solid carboxyl-functional rubber were developed to investigate how these additives affect the microcracking response when exposed to cryogenic cycling. A total of eight systems was developed, which included a control, each rubber separately, and every combination. Cross-ply laminates were exposed to

cryogenic cycling and most of the laminate formed microcracks in response to the thermal stresses generated by cryogenic cycling. Interlayer toughening did not significantly reduce the crack density but the dispersed core-shell particles reduced the crack density by 50%. The dissolved solid carboxyl-functionalized rubber, providing an interpenetrating network, was shown to be the most efficient modifier at reducing the transverse cracking of polymeric composite materials when exposed to cryogenic cycling. The three systems containing pairs of rubber additives resulted in a statistically similar level of microcracks that was dramatically lower than in the control laminate. The combination of modifiers did not matter as much as the amount of rubber for these laminates. A higher rubber concentration reduced the microcracking. Collectively, this work showed that the addition of different types of rubber additives reduced the level of microcracking substantially and totally in some cases. The microcrack density was also shown to be dependent on the various distributions of rubber obtained in the composites.

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