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21

Model Multilayer Toughened Thermosetting Advanced Composites

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A model multilayer toughened high-performance thermosetting matrix composite was developed and the interlaminar fracture toughness was measured in modes I and II. Processing was accomplished using two impregnation steps followed by an autoclave curing process to consolidate the final laminate. The final multilayer laminate structure contained layers of matrix resin with reinforcing carbon fibers separated by thin layers of matrix resin with modifier particles. Characterization of the processing was examined in terms of preimpregnation and final laminate morphologies. Structure–property relationships were evaluated by measuring the mode-I and -II interlaminar fracture toughness of the multilayer structure in comparison to the fracture toughness of a conventional composite with the same resin content but without the interlayer structure. The mode-II fracture toughness increased from 530 to 1135 J/m^2. No changes were observed in the mode-I fracture toughness.

INCREASED TOUGHNESS OF THERMOSETTING MATRICES IS THE KEY in the development of primary commercial aircraft structures with advanced composites. Initial efforts concentrated on toughening the entire thermosetting matrix with elastomer or thermoplastic modifications. Although large toughness improvements were observed in neat-resin samples, only a small fraction of the neat-resin toughness improvements translated into increased laminate toughness (*1*). This lack of toughness translation from neat resin to laminate

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redirected many efforts from neat-resin modifications toward examining laminate toughness from the viewpoint of the composite structure.

During impact, the major type of failure that occurs within the laminate structure is ply delamination (*2*, *3*). These delaminations create significant reductions in resulting composite mechanical properties after impact. To prevent delamination during impact, interleaving concepts have been incorporated into commercial advanced-composite systems (*2–14*). Interleaving is an engineering solution that minimizes the delamination problem by creating a multilayer composite structure with a thin layer of a tough resin matrix between each ply. The thin interlayers of resin are designed to absorb the large interlaminar stresses developed during impact, and can be employed as a homogeneous or a heterogeneous modification as shown schematically in Figure 1.

Homogeneous interleafs were the first modifications to commercial advanced-composite systems (*2–8*). In the homogeneous interleaved systems, a base-resin system that produced good composite mechanical properties was used within each ply, and a second tough homogeneous resin system was used between plies. The interlayer resin was either thermosetting or thermoplastic and created dramatic increases in the composite impact properties. The interleaf also led to reductions in the important composite compressive and hot–wet properties (*4*).

To maintain the improvements in composite toughness and prevent the reduction in composite compressive and hot–wet properties, second generation commercial interleaving systems were developed that utilize a heterogeneous resin layer between plies (*9–14*). The heterogeneous interleaved systems use the same base-resin matrix within each ply and between plies but

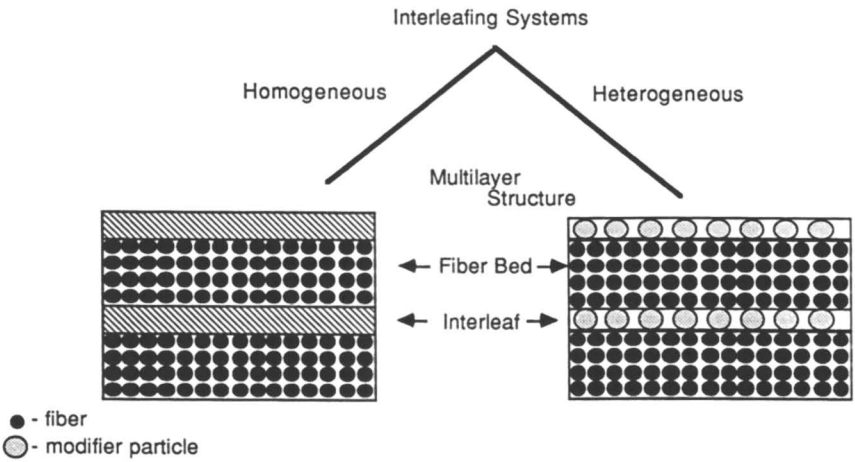

Figure 1. Two types of interleaving systems: homogeneous and heterogeneous.

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the interlayer resin is mixed with either soft or rigid modifier particles approximately 10–50 μm in diameter. Modifier particles that are used in these systems possess mechanical properties similar to those of the base-resin matrix in order to maintain the overall required composite mechanical properties. The diameter of the modifier particle must be larger than the fiber diameter so that the particles can be trapped between plies to create a heterogeneous interleaf. For the interleaved composite to have the same resin content as a conventional composite without an interlayer structure, the fibers must be packed closer together to allow for some of the resin to be used between plies. Because the same base-resin system is used both within the ply and in the interlayer region, the laminate is able to maintain adequate hot–wet properties, while the impact and damage tolerance improve because of the interleaf created by the modifier particles.

To fully understand the concept of the layered matrix structure in advanced composites, a model system has been formulated. This part of the work examined the processing and toughness improvements of the model heterogeneous interleaved-composite system over conventional thermoset-type systems. The effects of processing on the preimpregnated (prepreg) characteristics and performance as well as the final toughened composite structure and properties were examined.

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Process Modeling

There are two basic techniques for processing a multilayer composite structure that utilizes a heterogeneous interleaf. The first technique involves sprinkling modifier particles on prepreg surfaces and then processing the prepreg in an autoclave to consolidate the final laminate. The second technique involves premixing modifier particles with the base-resin matrix to create a multilayer prepreg structure, which is then processed with typical autoclave curing procedures. This second technique, which utilizes two impregnation steps, is referred to as double-pass impregnation.

In double-pass impregnation, the first impregnation step is used to impregnate the collimated fibers with only the base-resin matrix. The second impregnation step is used to apply a thin layer of particle-modified resin to the top and bottom prepreg surfaces. The resulting multilayer prepreg structure contains a matrix-resin-impregnated fiber bed, with thin layers of particle-modified matrix resin on the top and bottom surfaces. For this toughened prepreg structure to have the same resin content as conventional prepreg systems and at the same time be fully impregnated, the fiber spacing must be closer than that of conventional systems, so that some of the matrix resin may remain on the prepreg surfaces, as shown schematically in Figure 2.

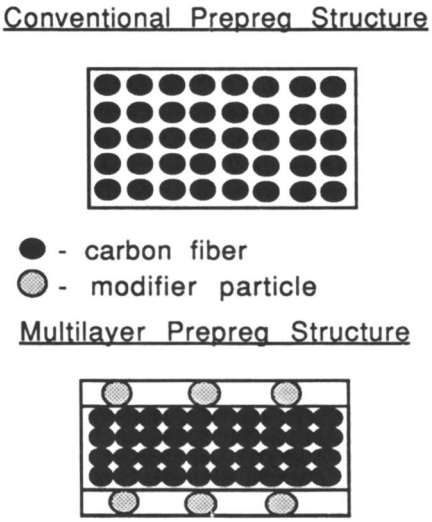

Figure 2. Comparison of a conventional prepreg structure to a multilayer prepreg structure.

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During processing, only a fraction of the desired total resin content may be applied during the first impregnation step, because more resin will be applied during the second impregnation. The amount of resin that can be applied during the first impregnation is a function of the modifier-particle diameter. Ideally, the thickness of the resin film applied during the second impregnation will be equal to the modifier-particle diameter, thereby obtaining an even monolayer distribution of particles. The amount of resin that may be applied during the first impregnation can be calculated if the diameter of the modifier particle, final desired resin content, and fiber areal weight are known:

$$w_{r1} = \frac{\left(A_f/(1 - w_r) - A_f\right) - 2D_p\rho_r}{A_f + \left(A_f/(1 - w_r) - A_f\right) - 2D_p\rho_r} \quad (1)$$

where w_{r1} is the first-pass weight fraction of resin, w_r is the final desired weight fraction of resin, A_f is the areal weight of the fibers (g/m^2), D_p is the average diameter of the modifier particles (m), and ρ_r is the density of the resin (g/m^3).

The effect of modifier-particle diameter on the first-pass resin content is shown in Figure 3 for a prepreg containing a fiber areal weight of 145 g/m^2, final resin content of 35 wt %, average modifier-particle diameter of 20 μm, and a resin density of 1.2 g/cm^3.

After processing, the resin distribution in both the final prepreg and the laminate is extremely important in the multilayer structure. The prepreg resin distribution can be viewed schematically as shown in Figure 4, where A represents the amount of resin on the prepreg surface, B represents the amount of impregnated resin, and C represents the amount of resin waste (*15*). In conventional prepreg processing, resin left on the prepreg surface is undesirable. However, in processing the multilayer prepreg structure, the amount of resin on the prepreg surfaces becomes an important design parameter. Prepreg tack and porosity characteristics are directly affected by the prepreg resin distribution (*15–18*).

Examination of the resin distribution in the final laminate structure is important to understanding the processing of the multilayer structure. The processing sequence for a multilayer composite morphology is schematically illustrated in Figure 5. Initially the prepreg contains a thin layer of particle-modified resin on the top and bottom surfaces. This resin layer thickness is equal to the modifier diameter. When the prepreg is layed-up for the

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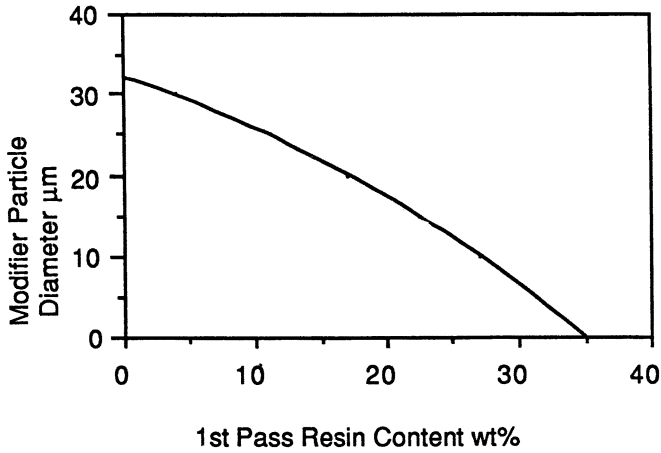

Figure 3. Effect of modifier-particle diameter on first-pass resin content.

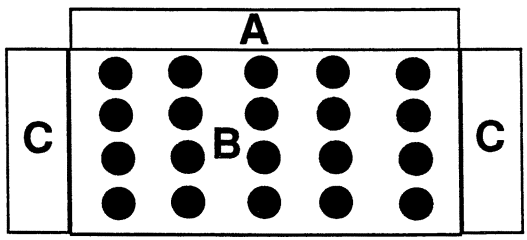

Figure 4. Schematic of prepreg resin distribution.

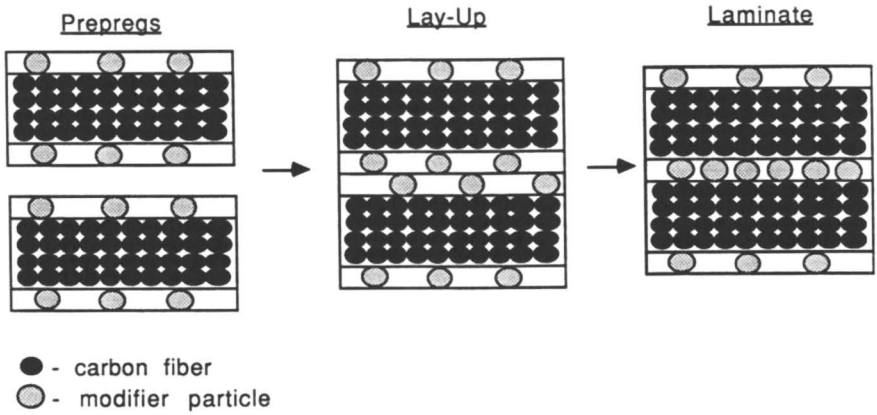

Figure 5. Changing morphology during processing of multilayer structure laminate.

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autoclave curing process, the fiber bed of each prepreg layer is separated by a particle-modified resin-layer thickness that is equal to two modifier-particle diameters. During consolidation, the resin is able to flow, which creates a heterogeneous interleaf thickness equal to one modifier-particle diameter that contains twice the modifier-particle concentration that was initially on the prepreg surfaces.

Limitations of the maximum modifier-particle diameter that can be used in processing can be calculated from volumetric and geometric arguments. If the thickness of the interlaminar region is assumed to be equal to the modifier-particle diameter, the maximum particle diameter then can be calculated and will be a function of the fiber areal weight, final resin content, and maximum fiber-packing arrangement. The calculation is based on the concept that in a void-free composite, there must be enough matrix resin to fill all the void areas surrounding the fibers and all the void areas surrounding the particles between plies. As the fibers become closer packed, smaller amounts of resin are required within each ply and more resin is available for the interlaminar region. For the assumption that the maximum fiber-packing arrangement is between a square array and a hexagonal packed structure, as shown in Figure 6, we can calculate the maximum modifier-particle diameter:

$$D_{P\max} = \frac{A_f\left(\left(1 + \left(V_r/V_f\right)\right)\pi - 2(1 + \cos\theta)\right)}{\rho_f \pi} \qquad (2)$$

where A_f is the fiber areal weight (g/m^2), $D_{P\max}$ is the maximum modifier diameter (m), V_r is the volume fraction of resin, V_f is the volume fraction of fibers, ρ_f is the fiber density (g/m^3), and θ is the shift angle as defined in Figure 6 (for maximum effect $\theta = 30°$).

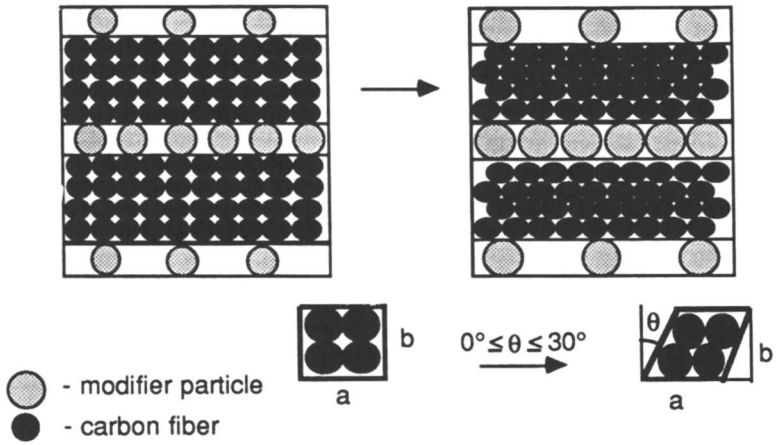

Figure 6. Maximum fiber packing arrangements.

An interesting relationship observed from this calculation is that the maximum modifier diameter is a linear function of the fiber areal weight. Therefore, the modifier diameter may be increased by increasing the prepreg fiber areal weight.

To examine the effects of the prepreg process on the prepreg resin distribution and performance, a previously developed prepreg methodology was extended (*15*). This methodology is based on the combination of the important operating parameters of temperature, pressure, and production speed into a dimensionless number known as the prepreg flow number (PFN):

$$\mathrm{PFN} = \frac{KP_e}{\mu V Y_f} \tag{3}$$

where K is the collimated fiber bed permeability (m^2), P_e is the effective pressure (Pa), μ is the viscosity of the impregnating resin (Pa · s), V is the production line speed (m/s), Y_f is the fiber bed thickness (m). The PFN represents a ratio of the impregnation residence time to the time required for full impregnation. Therefore, impregnation may be considered complete if the PFN is greater than or equal to 1. Thus analyzing the different passes with the aid of the PFN, the prepreg resin distribution may be described as a function of the prepreg operating conditions.

Experimental

The model resin system used for this study was epoxy-based with the following composition: 60% tetraglycidyldiaminodiphenylmethane (TGDDM;

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Ciba-Geigy), 40% diglycidyl ether of bisphenol A (DGEBA; Epon 828; Shell Chemical Company) 10-parts per hundred parts resin (phr) polyethersulfone (PES; Imperial Chemical Industries), and 42-phr diaminodiphenylsulfone (DDS) curing agent (Ciba-Geigy). The particles used to modify the base-resin system were semicrystalline nylon 6 (1002 D NAT; Atochem Corporation). The nylon particles were produced through a precipitation process and were approximately 20 μm in diameter. Modifier particles were mixed with the base-resin system before the second-pass impregnation. The concentration of the nylon particles was measured as phr in the base-resin mixture.

All composite samples were processed using a laboratory-scale hot-melt prepreg machine that has been described previously in detail (*19*). The reinforcing carbon fibers were 12K T-800 (Toray Industries). The prepreg that was produced had a fiber areal weight of 255 g/m^2 and a final resin content of 35 wt %. Although a fiber areal weight of 255 g/m^2 is larger than conventional areal weights of 145 or 190 g/m^2, it was used because of thin-film production limitations.

Fracture-toughness testing was done on a mechanical testing apparatus (4505 Instron). Mode-I interlaminar fracture-toughness testing was performed using double cantilever beam samples. Mode-II interlaminar fracture-toughness testing was performed using end-notch-flexure specimen configurations (*20*).

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Results and Discussion

In double-pass impregnation, the objective of the first-pass impregnation is to produce a low base-resin content prepreg. The amount of resin that can be applied is controlled by the modifier-particle diameter. In this work, the 20-μm nylon 6 particles applied to both top and bottom prepreg surfaces only allowed a first-pass resin content of 25 wt % resin. The lower resin content increased the difficulty of creating a void-free prepreg structure because more fiber compaction must be obtained than for conventional 35 wt % resin content. Because of the low resin content, large void areas were observed at the center of the prepreg under all processing conditions, but were smallest as the PFN exceeded 1. The voids were concentrated at the center of each fiber tow.

The objective of the second-pass impregnation is to apply a thin layer of particle-modified base resin on the top and bottom prepreg surfaces. The optimum second-pass processing condition represented a trade-off between prepreg porosity and prepreg tack. At a second-pass PFN of 0.001, only a small fraction of the applied resin impregnated the fiber bed, which created a prepreg with a porous structure but a high level of tack. As the second-pass PFN exceeded 1, the prepreg was fully impregnated but had a low level of tack. A decrease in the tack of the prepreg surface was because only

thermoplastic particles were present on the prepreg surface and all the thermosetting resin had impregnated the fiber bed.

After the autoclave processing, the final laminate structure contained the multilayered structure shown in Figure 7. All laminates were void-free and appeared to be independent of prepreg morphology. The thickness of the interlayer resin varied slightly across the laminate width but averaged 20–30 μm. To obtain a constant particle-bed thickness across the laminate width, an even monolayer of particles must be achieved on the prepreg surfaces. Therefore, the important prepreg characteristic of laminate morphology is the distribution of particles on the prepreg surfaces.

To evaluate the structure–property relationships, the interlaminar fracture toughnesses of multilayer composite systems were measured in modes I and II at concentrations of 0-, 10-, 20-, and 30-phr nylon 6 particles in the second-pass impregnation resin. A sample with no nylon particles was processed to represent a conventional composite structure with no interleaf. Results of the mode-I fracture-toughness testing are shown in Figure 8. The results indicate no improvement in the mode-I interlaminar fracture toughness by creating a multilayer structure. All mode-I values were approximately 300 J/m^2, including the unmodified sample. This observation can be explained by examining the fracture surface for the location of crack growth. In all samples, the crack propagated at the interface between the interleaving resin and the fiber bed or within the surface fibers of the fiber bed. Therefore, increasing the modifier concentration would not increase the fracture toughness because the crack propagation remained at the interface.

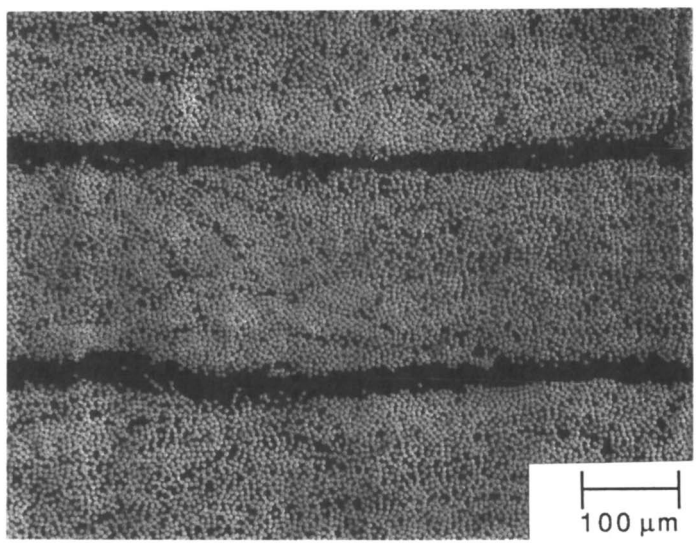

Figure 7. Model multilayer composite structure.

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Creation of the multilayer structure had a definite improvement in the mode-II fracture toughness as shown in Figure 9. The unmodified mode-II fracture toughness had a value of 530 J/m^2 and a maximum mode-II fracture toughness occurred in the 20-phr sample at 1135 J/m^2. Above a 20-phr particle concentration, a decrease in the mode-II fracture toughness was

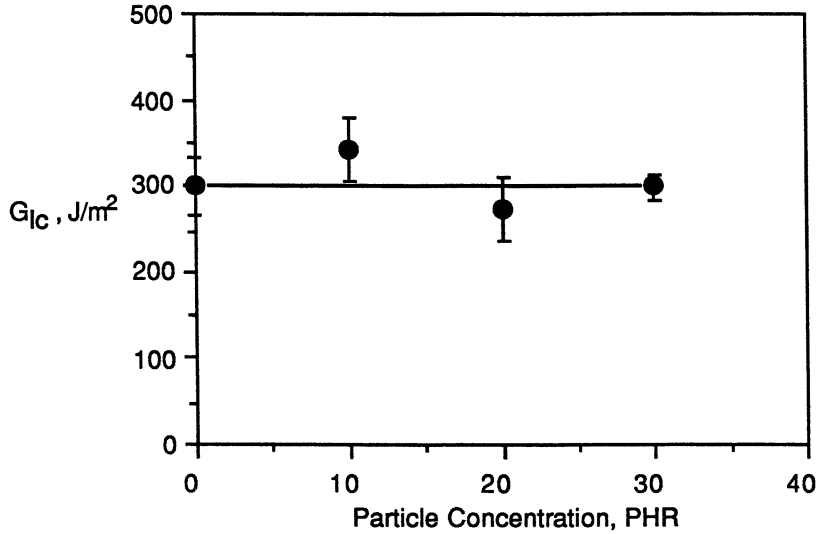

Figure 8. Mode I interlaminar fracture toughness as a function of modifier-particle concentration in second-pass impregnation resin.

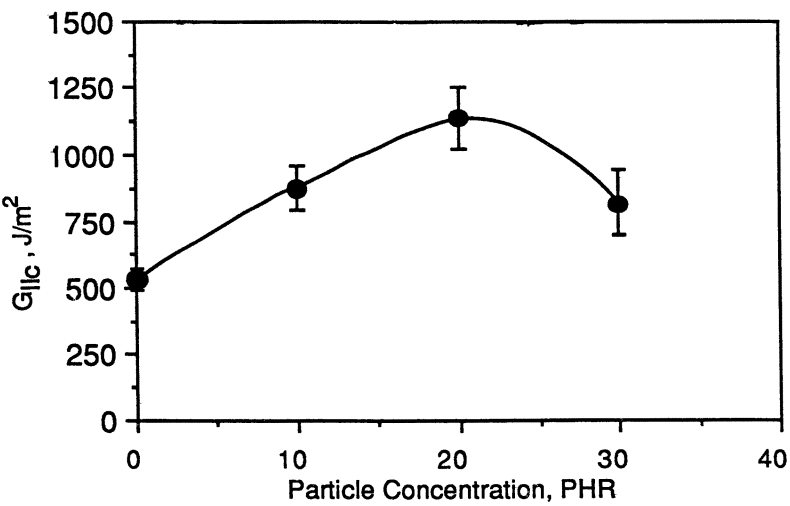

Figure 9. Mode II interlaminar fracture toughness as a function modifier-particle concentration in second-pass impregnation resin.

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observed. This decrease in fracture toughness can also be explained by examining the fracture surfaces. In the 10- and 20-phr samples the majority of crack propagation occurred in the interlaminar resin-rich region, whereas in the 30-phr sample intralaminar crack propagation occurred. Consequently, the decrease in fracture toughness of the 30-phr sample is because the crack leaves the interlaminar region and jumps into the fiber bed of intralaminar region.

Summary

A model multilayer prepreg structure has been formulated and analyzed in this work. The importance of resin distribution and fiber packing was identified and utilized to create a realistic model system. The prepreg resin distribution was found to influence porosity as well as final prepreg tack. The model prepreg was successfully produced in a double-pass impregnation, and the operating conditions during each impregnation step were used to control the resin distribution and produce a final prepreg with controlled levels of porosity and tack. Obtaining an even monolayer of modifier particles on the prepreg surfaces was found to be of importance. The particle distribution controlled the uniformity of the interleaf thickness.

Creation of the multilayer composite structure exhibited no improvement in the mode-I interlaminar fracture toughness, but showed definite improvements in the mode-II interlaminar fracture toughness. A maximum in the mode-II fracture toughness occurred at a nylon particle concentration of 20 phr in the second-pass impregnation resin. In larger nylon concentrations, the crack propagation occurred not in the interlaminar region, but within the fiber bed, thus reducing the measured fracture toughness.

Overall, this work demonstrated that a model multilayer toughened thermoset-based system can be successfully developed and used for detailed study of manufacturing as well as performance-related issues in advanced structural composites.

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