Interlaminar crack growth in third-generation thermoset prepreg systems*

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The growth of interlaminar cracks from pre-existing defects under static and cyclic loading is of major concern in the application of advanced composites in primary structures. To overcome this problem, within the last few years many toughened graphite composites have been introduced by materials suppliers. Based on fundamental studies about the influence of the constituent properties, a third generation of toughened epoxy and bismaleimide prepreg systems with a well balanced property profile have been developed. Key factors influencing interlaminar fracture toughness and damage tolerance were identified in the frame of the development. Different toughening concepts of the matrix, rubber toughening as well as the incorporation of thermoplastics, have been studied in the neat resin as well as in the composite in combination with different fibre types. The multifaceted aspects of the relationship between the chemical structure of the matrix, the geometrical restrictions due to microstructure and the corresponding properties of the composite will be discussed.

(Keywords: thermoset prepreg systems; interleaf; toughening; fracture energy; hackling)

INTRODUCTION

Delamination has been termed 'the most prevalent life-limiting failure mode in advanced composite structures'[1]. The growth of interlaminar cracks from pre-existing defects under static and cyclic loading is thus of major concern for advanced composites used in primary structures. To overcome this problem, a third generation of supertough thermoset prepreg systems have been introduced by the materials suppliers in the last few years. The multifaceted aspects of the relationship between the chemical structure of the matrix, the geometrical restrictions due to microstructure and the corresponding properties of the composite will be discussed.

TOUGHENING HISTORY OF COMPOSITES

The first generation of thermoset composites achieved high strength and service temperature using homogeneous high-functional resins and a homogeneous fibre/resin distribution (*Figure 1*).

Second-generation thermoset composites were toughened by modification with rubbers or engineering thermoplastics. Rubber toughening was first employed to overcome the inherent brittleness. However, this method is restricted by the loss in modulus of the modified matrix, even at low rubber concentrations, which affects the high-temperature performance. Further, significant improvements can only be achieved when the crosslink density of the thermoset resin is low enough[2].

In the last few years, a variety of approaches in which brittle high-temperature thermosets are blended with tough thermoplastics have been developed. Investigations concentrated especially on the phase behaviour of the thermoset–thermoplastic blends, and the optimization of special morphologies to optimize toughness[3–5].

Adhesive film interleaving, the technique of inserting a tough material into the composite laminate as extra interlaminar layers, has been used in several studies to enhance the damage tolerance of thermoset resin composites[6]. The resulting loss of the full specific weight-saving potential and the fact that there is no absolute certainty that the interlaminar layers are applied at the most critical places of a structural part led to the development of a third generation of thermoset prepreg systems, known as 'interleaf prepreg' systems[7].

Interleaf systems are characterized by an integrated interleaf, which allows a conventional fibre volume content of 60% to be used. Resin-rich layers are developed by concentrating a specific amount of resin within the interlaminar zone during the standard autoclave consolidation process[8,9]. For structural applications, this assures that the interleaf is always present between the individual prepreg plies.

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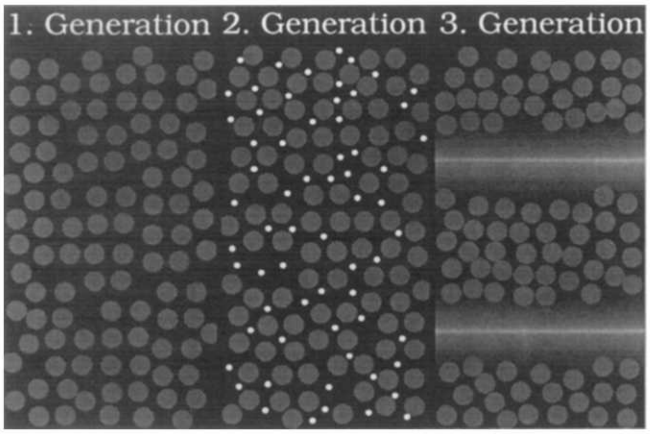

Figure 1 Morphology of various generations of thermoset composites. First-generation: single-phase matrix; homogeneous resin/fibre distribution. Second-generation: multiphase matrix; homogeneous resin/fibre distribution. Third-generation: heterogeneous matrix; inhomogeneous resin/fibre distribution.

UNDERSTANDING THE FRACTURE MECHANICS

From a fracture mechanics standpoint, composite toughening is understood to be the suppression of crack initiation and the hindrance of crack propagation by increasing the fracture energy, G_c. Unfortunately, the risk of delaminations in laminated composites is not only dependent on the opening tensile stresses (mode I), but mode II, mode III, mixed mode loading and rate effects also have to be taken into account[10].

It is generally accepted that a higher mode I fracture energy in the neat resin will transform into higher mode I fracture energy of the corresponding composite[11]. This correlation of neat resin G_{Ic} *versus* laminate G_{Ic} is valid for different toughening methods. The slope of this correlation decreases with increasing neat resin fracture energy. Thus, a considerable increase in the neat resin fracture energy is required to achieve any improvement in the composite[12]. This lack of proportionality is a result of the constriction of the plastic deformation zone in the matrix between the reinforcement (*Figure 2a*). Tougher resins have a more extensive deformation zone ahead of the crack tip than brittle resins. During crack propagation, the deformation zone is limited to the geometrical spacing between the fibres. For a conventional composite with 60% fibre volume content, the average distance between two carbon fibres is 5–8 μm. With an interleaf prepreg system, the interlaminar spacing is significantly increased to 15–20 μm, which allows for a larger plastic zone size. The interleaf concept inherently creates an inhomogeneous resin matrix. The resin composition in the fibre-rich zone is significantly different from the composition in the interply zone (*Figure 2b*). The increased concentration of the toughening modifier and the larger spacing in the interply zone account for the improved mode I fracture energy. Neither resembles the homogeneous 'neat resin matrix' tested with neat resin G_{Ic} CT specimens. Consequently, the neat resin G_{Ic} test is meaningless with this toughening technology.

Mode II interlaminar fracture energy correlates linearly with the composite compression strength after impact[7,12]. This means that increasing the mode II fracture energy without sacrificing mode I interlaminar fracture energy should be a major goal for improving composite damage tolerance. Thus, it is important to know how the chemical structure and the morphology of the matrix resin affect the mode II fracture energy of the corresponding composite.

The correlation between interlaminar mode II fracture energy and neat resin mode I fracture energy at various test temperatures was investigated for epoxy resins with different functionality (tetrafunctional tetraglycidyldiaminodiphenylmethane / diaminodiphenylsulphone, TGDDM/DDS, difunctional diglycidyl ether of bisphenol A/diaminodiphenylsulphone, DGEBA/DDS) unmodified and toughened with rubber and thermoplastics (*Figure 3*)*. The tetrafunctional TGDDM/DDS resin shows the lowest neat resin and interlaminar fracture energy and almost no temperature dependence. In contrast, at room temperature, the difunctional DGEBA/DDS and the thermoplastic-modified epoxy resin exhibit very high interlaminar mode II fracture energies, while the neat resin fracture toughness is only moderate. Surprisingly, at higher temperatures the interlaminar mode II fracture energy decreases, and the neat resin fracture energy is increased. The decrease in the mode II fracture energy is more pronounced with the thermoplastic-modified epoxy resin than with the rubber-modified epoxy resin, which has only a moderate mode

* Details as to materials, specimen preparation and test procedure are described elsewhere[11–13]

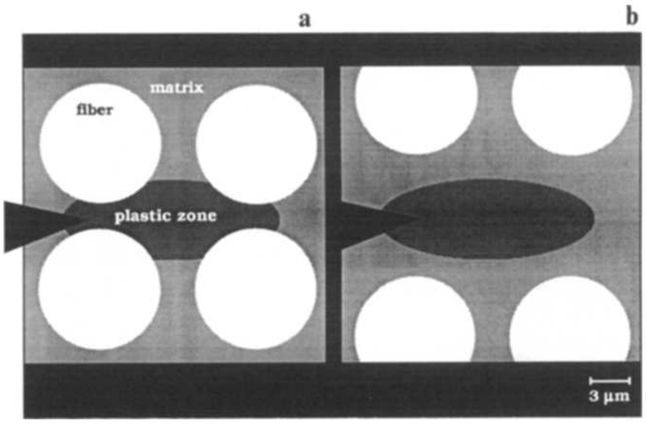

Figure 2 Geometrical restrictions of the plastic zone in front of a crack tip: (a) standard thermoset composite; (b) interleaf-type thermoset composite

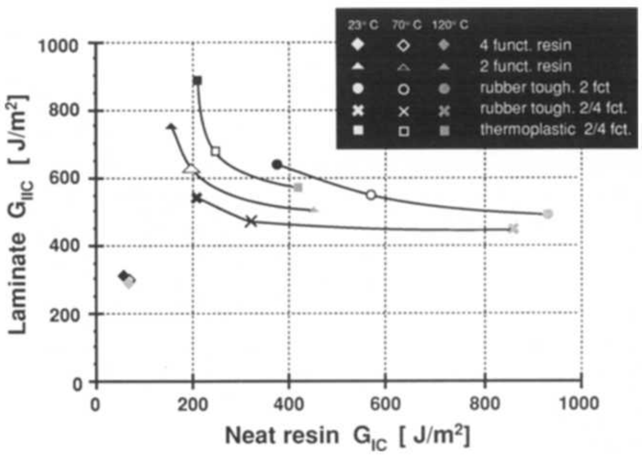

Figure 3 Correlation between interlaminar mode II fracture energy and neat resin mode I fracture energy

II fracture energy at room temperature. The poor correlation in *Figure 3* clearly shows that the interlaminar mode II fracture energy is not adequately characterized by the neat resin mode I fracture energy. The lack of an adequate neat resin mode II fracture toughness test makes the mode II fracture energy, as characterized by the end notch flexure test, a valuable tool. The microscopic characteristics of interlaminar mode II crack propagation were identified by microscopic inspection of the fracture surfaces generated under shear loading of an end-notch-flexure test specimen. The fracture surface under mode II revealed numerous inclined platelets (hackles) characteristic of cohesive resin fracture. The hackles tend to be oriented at approximately 40–60° to the plane of applied shear. The growth of the primary cracks results from the coalescence of these cracks (*Figure 4a*). On a microscopic scale, the hackle formation can be explained by the fact that, under shear loading, crack propagation occurs in a tensile stress state (mode I) at the crack tip[13,14].

The amount of hackling increases drastically with increasing mode II fracture toughness. Both the increased surface area and the rougher path of crack growth resulting from the sigmoidal shape of the microcracks seem to be responsible for the observed increase in mode II fracture energy. Thus, high-energy hackling is the dominant mode by which the mode II fracture toughness of thermoset composites can be increased. At room temperature the results in *Figure 3* show that tetrafunctional resins like TGDDM/DDS have a low mode II fracture energy and therefore only a very low tendency to hackle, while the difunctional DGEBA/DDS and the thermoplastic-modified system show a high mode II fracture energy combined with a high hackle tendency. At higher test temperatures, the hackle tendency decreases with increasing neat resin fracture energy.

The drastic improvement in the mode II fracture energy of third-generation interleaf prepreg systems can also be explained by a geometrical effect. As the interlaminar spacing increases during crack propagation, the surface area also increases greatly, resulting in a correspondingly higher fracture energy (*Figure 4b*). Thus, matrix hackling and increased interlaminar spacing are responsible for the increased mode II fracture energy and damage tolerance of interleaf-type systems.

New prepreg resins for commercial aircraft applications require significantly improved toughness, without sacrificing hot/wet properties. The third-generation epoxy and bismaleimide prepreg systems provide this combination of toughness and exceptional mechanical properties (*Table 1*). This, combined with their flexible processing, warrants their consideration for any composite application[7,15].

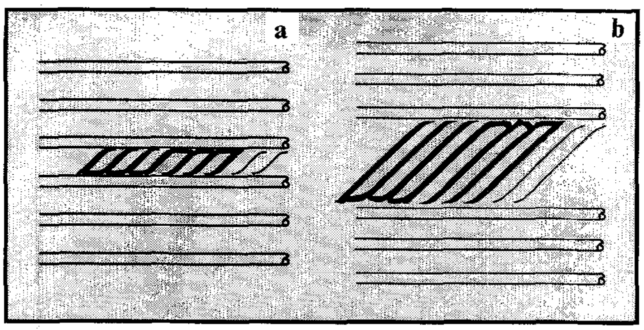

Figure 4 Geometrical restrictions for crack propagation under mode II: (a) standard thermoset composite; (b) interleaf-type thermoset composite

Table 1 Mechanical property profile of third-generation bismaleimide and epoxy resin prepreg systems

	Third-generation epoxy X5276/G40-800	Third-generation BMI R5260/G40-800
CAI (Dynatup 6.7 J mm^{-1})	330 MPa	310 MPa
Mode I G_{Ic} (DCB test)	541 J m^{-2}	464 J m^{-2}
Mode II G_{IIc} (ENF test)	1520 J m^{-2}	1350 J m^{-2}
0° compression (Sacma SRM 1-88)	1100 MPa (82°C/wet)	1240 MPa (150°C/wet)
T_g dry (DuPont DMA)	190°C	265°C
T_g wet (DuPont DMA)	145°C	195°C

SUMMARY

Based on fundamental studies a new generation of thermoset resin systems has been developed to overcome microstructural limitations found with the first- and second-generation systems. Use of an integrated interleaf makes it possible to increase mode I and mode II fracture energy and damage tolerance significantly above the level of conventional systems, without sacrificing the full specific weight-saving potential. The interlaminar spacing, and especially the tendency of a matrix resin to hackle, are important factors governing the fracture toughness under shear loading.

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