JOURNAL OF MATERIALS SCIENCE **39** (2004) 2263–2266

Preliminary study on resin transfer molding of highly-toughened graphite laminates by *ex-situ* method

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As reported in one of our previous papers [1], we attempted to develop a generic concept to increase the impact damage resistance of aerospace graphite laminates by periodically interleaving solid thermoplastic thin films into the plies [2 ,3]. The concept was successfully demonstrated for laminated systems cured in autoclave. As an example, for a standard high-performance epoxy prepreg system (DGEBA/TGMDA) periodically interleaved with thermoplastic PEK-C thin films, high CAI (compression strength after a low-velocity impact) data of about 300 to 340 MPa was achieved. This was about more than 25% higher than that of the traditional toughened systems with the similar composition. Because the thermoplastic component was periodically modulated layer by layer, we defined the concept as *ex-situ* compared to the traditional overall-toughening concept where the thermoplastic component was homogenously distributed in the matrix [4].

The intention of the present study was to explore the *ex-situ* concept for resin transfer molding (RTM) rather than the autoclave process [5], because it has been difficult to toughen RTMable resin systems without sacrificing the flow ability and the overall mechanical properties.

The base resin composition for this study was a combination of standard epoxy of glycidyl ester (A) and resorcinol diglycidyl ethers (B). MHHPA acted as curing agent (C). They were mixed at a ratio of A:B:C = 50:50:100. The base composition was denoted as 3266 in this study. The unidirectional graphite fibers (Toray T700SC) were pre-wet-winded with the diluted base resin system for an area weight of about 133 g/m^2 to preform laminates for RTM process.

The thermoplastic component was an amorphous polyether ketone with phenolphthalein group, called PEK-C produced by Xuzhou Engineering Plastics Factory, China (Fig. 1). PEK-C has a glass transition temperature of about 245 °C and its properties are similar with PEEK in many aspects. For *ex-situ* RTM experiment, PEK-C powders of about 100 μm in size were applied and fixed onto one side of each ply except the top layer, with a concentration of about 18 wt%. Visually, the powder distribution was not continuous, i.e., no continuous films on the surface were built-up.

Vacuum assisted RTM manufacturing process was applied using a system of our own construction. The metallic mold was heated-up to 30 to 50 °C and evacuated under a vacuum of about 90 kPa. Then under a pressure of about 0.15 MPa, the mold was infused with the base resin to manufacture both the control samples of base composition (3266) and *ex-situ* toughened samples (3266ES). After the infusion, the samples were cured in the mold at 80 °C for 2 h, followed by a post-treatment at 150 °C for 8 h. *Ex-situ* RTM did not exhibit any processing difficulty at all.

The impact resistance was evaluated by CAI using the Boeing specification [6]. For each laminate, two samples of 150 mm long, 100 mm wide and 4 mm thick were made and tested. They were quasiisotropic with ply sequence of $[-45/0/45/90]_{4S}$. The impact energy used was 6.6 J/mm. Standard mechanical properties were also measured using unidirectional laminates reinforced with 827 carbon cloth produced by Toray Industries Inc. All the testing was conducted according to the standard methods in the aerospace industry [7].

Table I shows a comparison of CAI data of the toughened (3266ES) laminates manufactured by *ex-situ* RTM and non-toughened (3266) by standard RTM method, respectively, along with the PEK-C "overall"-toughened high-performance prepreg system (5288) manufactured by autoclave method. It is obvious that

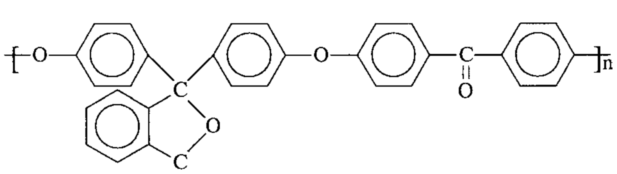

Figure 1 Molecular structure of PEK-C.

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TABLE I Comparison of the compression strength after impact (CAI) of different systems

Specimens with T700 carbon fibers	CAI (MPa)	Manufacturing method
Base epoxy resin system as control (3266)	170	Standard RTM
PEK-C "overall"-toughened high-performance prepreg system (5288)	267	Autoclave
PEK-C periodically-interleaved system with the same base composition as 3266 (3266ES)	293	*Ex-situ* RTM

the PEK-C modification improves significantly the laminate toughness either by overall toughening (5288) or by *ex-situ* periodical modulation (3266ES). However, the periodically modulated one prevails significantly in toughness compared to the overall-toughened prepregs. It is particularly interesting to note that the need of low viscosity resin systems to allow low-temperature infusion in traditional RTM process limits considerably the use of any toughening techniques associated with prepreg resins, whereas the 3266ES was just made by RTM method and it was successfully toughened.

As known, the CAI data is a measure of delamination resistance of laminated graphite/epoxy systems under low-velocity impact. The delamination can be studied by ultrasonic methods like C-scan. By using C-scan technique, reduced damage area for the *ex-situ* sample was verified compared to that of the overall-toughened one (Fig. 2).

Other important properties were also estimated and compared between the periodically-interleaved system 3266ES and the base composition as control (3266) in Table II. Though this was only a preliminary evaluation and not a systematic testing, no noticeable difference in the properties could be identified.

Fig. 3 shows the glass transition behavior of a 3266ES graphite laminate by means of DMTA. The

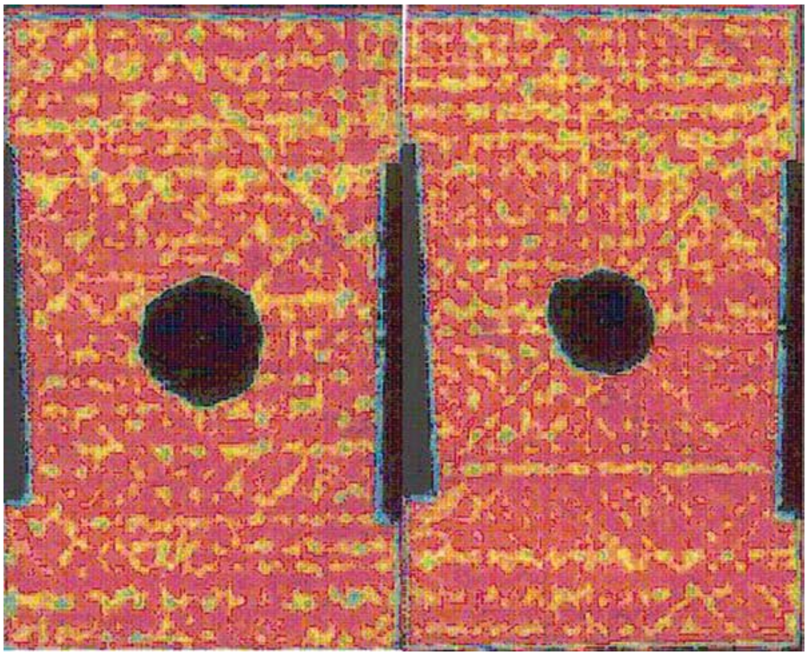

Figure 2 Comparison of damage area between the *ex-situ* (right) and control sample (left) by means of ultrasonic C-scan method.

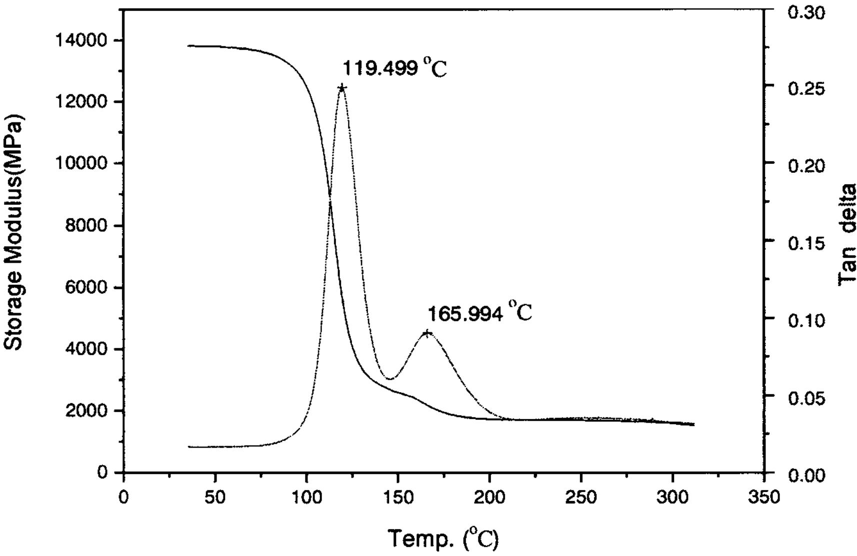

Figure 3 Glass transition behavior of 3266ES laminate made by *ex-situ* RTM.

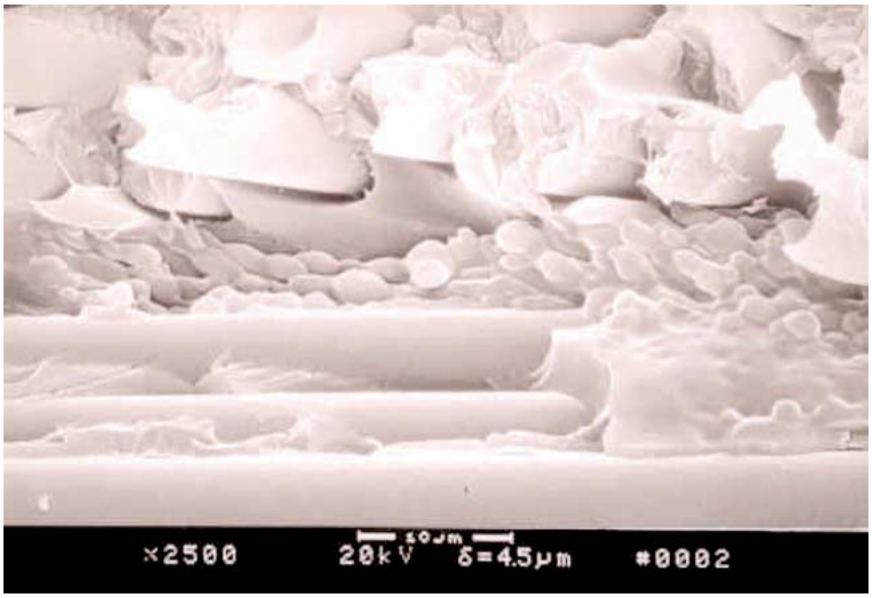

Figure 4 Interlayer morphology of quasi-isotropic graphite laminate manufactured by *ex-situ* RTM method, PEK-C was chemically etched-off. The interlaminar structure distinguishes clearly as cross-linked granules whereas within each ply there is only the base epoxy.

low-temperature peak at 119.5 °C corresponds exactly to the base resin system of 3266, whereas the high-temperature one at 166.0 °C could be ascribed to the new phase structure resulting from the interaction between 3266 base resin component and PEK-C component. The matrix in the laminate was thus typically a two-phase system.

An evidence for the new phase structure could be found in the interply layer (Fig. 4). Shown in the figure are the horizon fiber (0 °) ply and the 45 ° fiber ply of an *ex-situ* laminate. It is noteworthy that, in the interply layer, there is a characteristic granular morphology which is very similar to that often observed on the overall-toughened laminates. Because of the similarity in morphology, we believe that the granular structure results from the reaction-induced spinodal decomposition and coarsening mechanism [8].

On the other hand, the extension of the interlayer structure was very limited; the layer thickness was only about 5–8 μm. Because of the two-phase morphology, its extension and thickness, the granular interlayer structure distinguished significantly from the traditional one-phase interleaving concept [9, 10] where there is only one thick bulk thermoplastic layer in existence, usually a few tens to hundreds microns. Therefore, we believe that the structural priority associated with the thin granular interlayer morphology is responsible for the toughness improvement. And the *ex-situ* concept is applicable for RTM method which improves the laminate toughness without sacrificing the flow ability and the overall physical properties.

TABLE II Comparison of some typical properties of the two systems

	Specimens with T700 carbon fibers	
Properties	Periodically-interleaved system (3266ES)	Base composition as control (3266)
0 ° flexural strength	1513 MPa	1580 MPa
0 ° flexural modulus	110 GPa	103 GPa
Interlaminar shear strength	89.4 MPa	85.3 MPa
Fiber volume fraction (%)	55	55
PEK-C weight percentage (%)	10	0

In conclusion, there were two important aspects in this study.

1. Based on the known overall-toughening concept of reaction-induced spinodal decomposition and phase inversion where the thermoplastic and thermosetting components are co-continuously connected to each other [7], we designed a periodically interleaved system where the co-continuously connected granular structure occurs layer by layer between each ply and the interlayer was relatively very thin.
2. As demonstrated, we applied the concept to RTM process. It was evident that the impact damage resistance of laminates was significantly improved compared to the non-toughened and overall-toughened ones without noticeable reduction of other mechanical properties. The RTM processing characteristics were hardly affected.

Acknowledgments

This investigation was carried out at the National Key Laboratory of Advanced Composites (LAC/BIAM) in Beijing, financed by the National High-tech Program (863) under grant no. 2002AADF3302. The authors Long and An acknowledge also the financial support of the Laboratory Funds for this study.

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Received 3 July
and accepted 12 September 2003