

Toughness improvement of PMR-type polyimide and laminated graphite systems by *ex-situ* concept

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Thermosetting polyimides are high performance matrix resins with distinguished thermal oxidative stability (TOS) and excellent mechanical property retention at elevated temperatures. The PMR-type polyimides, prepared by polymerization of monomer reactants, are high temperature polymers used as matrix resins in graphite fiber-reinforced composites for a variety of aerospace applications [1–3]. PMR-15, the first generation of PMR-type polyimide developed by NASA, has played an important role in the composition structural or sub-structural components with long-term service temperature as high as 260–288 °C [4, 5]. However, PMR-type polyimides are intrinsically brittle. As a consequence, they severely tend to micro cracking in comparison to other polymer matrices of laminated graphite composites [6]. Thus, the toughness improvement of PMR-type polyimides is of great importance in the pursuit of increasing their applications.

In the aircraft industry, toughness of matrices and impact damage resistance of laminated graphite systems are characterized by compression strength after impact (CAI). For high-temperature matrices like PMR-type polyimides and the laminated graphite systems, the CAI data are typically lower than 200 MPa. A traditional method to increase the impact damage resistance of thermosetting resin-based composites is to use toughened resin systems. However, there are rarely references reporting consistent data for PMR-type polyimide matrix composites.

Recently, we developed a new concept to significantly increase the CAI properties of laminated-graphite systems by periodically interleaving solid thermoplastic thin films into the graphite plies [7–10]. This so-called *ex-situ* concept, has successfully been demonstrated in many epoxy-based laminates [7–10]. It is likely an all-purposed concept for toughening any laminate independent of the chemistry of matrix resins. Hence, it was expected that *ex-situ* concept could also be applied to PMR-type polyimide based graphite laminates.

In this paper, a thermosetting polyimide model matrix resin and laminated systems made of the polyimide were investigated. The polyimide denoted as LP-15 was an own development of the National Key Laboratory [11]. Its basic composition is very similar to that of PMR-15. The polymerization of PMR-15 monomer reactants yields an oligomer with a molecular weight of about 1500 g mol⁻¹, whereas LP-15 was prepared in two stages of three monomer reactants: 2-carbomethoxy-3-carboxy-5-norbornene (nadic ester, NE), 2,2'-bis(4-aminophenoxyphenyl)-propane (BAPP) and the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE). The molecular formulae are shown in Fig. 1.

The thermoplastic component used was an amorphous polyetherketon with a phenolphthalein side group, developed in China (Xuzhou Engineering plastics Factory) [7]. It was denoted as PEK-C in the study. Fig. 2 shows its molecular structure. PEK-C with a glass transition temperature (T_g) of about 210 °C shows a great similarity in its properties to PEEK (Polyetheretherketone) in many aspects. PEK-C was dissolvable in THF, making it suitable for manufacturing thin films and for blending with LP-15 in solution.

LP-15 and PEK-C were first mixed in solution at different ratios (Table I). To determine the mechanical properties, bars of LP-15/PEK-C blends were cast according to GB2570-81 and JB/T 3958.2-1999. It was found that both the impact toughness and flexural strength increased significantly with increasing PEK-C concentration (Table I). The impact test was carried out

TABLE I Typical data of LP-15/PEK-C blends for various PEK-C contents

	LP-15/PEK-C ratio				
	100/0	90/10	80/20	70/30	60/40
Impact toughness (kJ/m ²)	7.17	9.03	10.50	13.55	16.59
Flexural strength (MPa)	86.7	99	106	114	116
T_g (°C)	289.0	286.8	284.5	272.8	272.7

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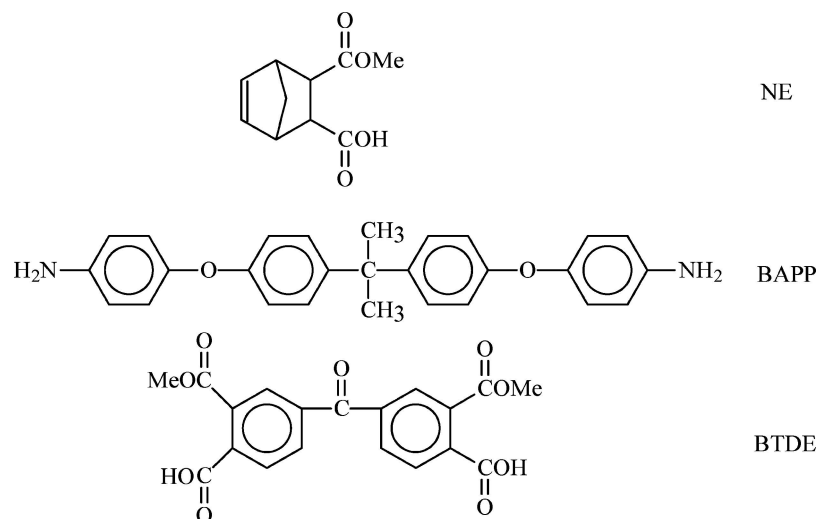


Figure 1 Molecular formulae of monomers for LP-15.

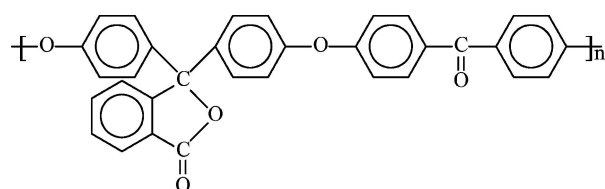


Figure 2 Molecular structure of PEK-C.

on an Izod impact test machine. Three-point bending test was performed on an Instron MTS 810.

Table I also lists T_g of the blends in dependence on the LP-15/PEK-C ratios. T_g decreases with the increase of PEK-C. T_g of LP-15/PEK-C blends were measured in the study by means of dynamic mechanical analysis (DMA). DMA was carried out on a DMA-V equipment at a heating rate of $5^\circ\text{C}/\text{min}$ from room temperature to 400°C . It was found that there was only one single glass transition for different PEK-C blending ratios, suggesting good compatibility between LP-15 and PEK-C. The decrease in T_g of the blends at higher PEK-C concentrations is obviously ascribed to the lower T_g of about 210°C for neat PEK-C.

Toray T300 graphite laminates were manufactured by conventional prepreg technique. The temperature-time cycle for curing the laminates is shown in Fig. 3. As matrix resins, there were two variants [12]: (1) Pure LP-15 as control and (2) LP-15/PEK-C blend at a constant ratio. It is worth noting that the blended matrix-based laminates correspond to the traditional toughening concept, being an overall-toughening concept.

According to *ex-situ* concept, there were two options in the application method for laminated systems [12]: The graphite prepreps wet-impregnated with pure LP-15 were additionally interleaved with PEK-C thin films or spay-coated with PEK-C powders on the one side. The thickness of interleaving film was about $16\ \mu\text{m}$ in average and the powder concentration was comparable with the film in order to compare the toughening effect for different application methods. It is apparent that *ex-situ* concept corresponds to the selective-toughening concept.

The impact damage and impact resistance was evaluated by using C-scan and QMW CAI specimens [12],

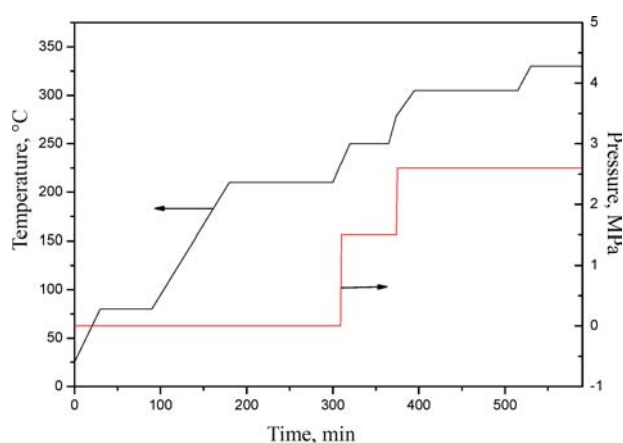


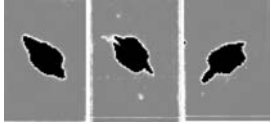
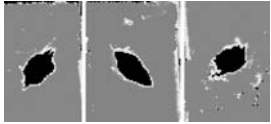
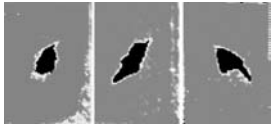
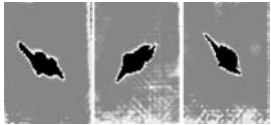
Figure 3 Curing cycle for the composite laminates.

respectively. The specimen were quasi-isotropic laminates with the plies of $[-45/0/45/90]_{2S}$, $89 \times 55\ \text{mm}$ in size. The impact energy used was $2\ \text{J}/\text{mm}$. CAI results of the laminates are compared in Table II. Each datum was an average of three specimens and C_V (%) stands for the deviation. C-scan results are also attached.

The control shows a CAI of about $212\ \text{MPa}$, whereas for the blended matrix specimens CAI was increased to about $276\ \text{MPa}$. The toughness improvement is remarkable for the overall-toughening concept. However, the toughness improvement resulting from the *ex-situ* concept was much more significant: by interleaving or coating the same quantity of PEK-C as in the blended matrix, both the specimens exhibit CAI data that exceed $300\ \text{MPa}$. Particularly, the powder-coated laminates show the highest impact resistance among all specimens studied. The C-scan results show the impact damage. It is obvious that the damage area reduces with increased CAI.

Fig. 4 shows representatively the interlaminar morphology of the laminated system made according to *ex-situ* concept. It is, at the first glance, nothing new except for the phase-inversed fine granular structure usually observed for the reaction-induced phase decomposition reaction. It is believed that it would be the granular structure located greatly in the interply regions responsible for the toughness improvement of

TABLE II CAI test results of T300 reinforced laminates

Specimen	CAI (MPa)	C_V (%)	C-scan results
LP-15 pure (control)	212	2.50	
LP-15/PEK-C blend (overall-toughening concept)	276	0.14	
LP-15/ PEK-C interleaved (<i>ex-situ</i> concept)	309	3.15	
LP-15/ PEK-C powder coated (<i>ex-situ</i> concept)	327	5.91	

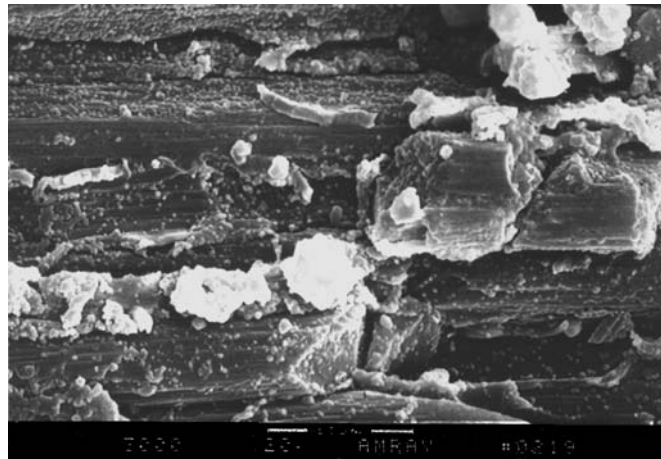


Figure 4 Fine granular phase-inversion structure of PEK-C modified polyimide in the interlaminar region.

polyimide laminates [9]. However, because this was just a preliminary investigation, we do not know how the application methods and the resulting structures affect the impact resistance for the same composition. Further study is going on.

In conclusion, the thermosetting polyimide LP-15 and thermoplastic toughening agent PEK-C are compatible to form polymeric blend for a wide range of composition ratios. The impact toughness of the blends increases with PEK-C loading. In terms of compression after impact (CAI) behavior the *ex-situ* toughening concept has successfully been demonstrated for LP-15/PEK-C laminated graphite systems. It is evident that the impact resistance of the graphite laminates can be enhanced in both cases: by incorporating a thermoplastic component into the resin to form a toughened matrix, corresponding to the overall-toughening concept, or by interleaving or spray-coating the same quantity of PEK-C component in the form of films or powders into each plies according to *ex-situ* concept.

Compared with the overall method, the *ex-situ* concept is apparently more effective in CAI properties because it directly improves the interlaminar toughness. It is also certain that, for periodically toughened laminates, the toughness improvement obtained by powder coating is superior to that by film interleaving and in far distance to the *overall* concept.

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