Fabrication of PEEK/carbon fibre composites by aqueous suspension prepregging*

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Poly(ether ether ketone) (PEEK) composites were made by impregnation of continuous carbon fibres with aqueous suspensions of PEEK particles made by a novel precipitation process. These particles were suspended in aqueous solutions of ammonium salts of polyamic acids which performed two essential roles: as a polymeric dispersant and as a binder at the fibre–matrix interface. The resulting composite panels had properties that were comparable in some cases to those of commercially available PEEK composites. Fracture surface analysis from unidirectional panels suggests that the miscibility of the matrix and binder affects the failure mode at the fibre–matrix interface.

(Keywords: PEEK; LaRC TPI; suspension prepregging; thermoplastic composites; polyamic acid; colloid dispersion; flexure properties; transverse tensile properties; polymer binder)

INTRODUCTION

There is increasing interest in high performance thermoplastic composites for their unique performance properties, such as good resistance to high temperature and good fracture toughness[1]. Processing advantages of thermoplastic–carbon fibre composites include indefinite prepreg shelf life, short processing time and reprocessability. Thermoplastics in a variety of forms can be combined with fibres in prepregging operations. These forms include holt melts[2], solutions [3–6], dry powders[7–11] and suspensions[4,12–15].

Melt impregnation suffers from problems of high melt viscosities, sometimes leading to fibre breakage. In addition, prepreg made by melt impregnation has poor tack properties and is stiff, which gives poor drapeability. Finally, new high performance thermoplastics with very high glass transition temperatures and/or melting temperatures may not be easily processable by melt impregnation due to thermal degradation.

Solution prepregging requires dissolving polymers in toxic, organic solvents with high boiling points which are often difficult to remove from the composite during consolidation[5,6]. While the solution viscosities are lower than melt viscosities by typically an order of magnitude or more, the disadvantages of working with organic solvents have effectively made this technique unfeasible for commercial production.

Dry powder prepregging offers several advantages, including the elimination of the solvent removal problem. In the past depositing dry powder and binding it to the fibre surface proved difficult. Recent work by Muzzy *et al.*[15] addressed the deposition problem by electrostatically charging the powder while grounding the fibre. Rapid heating was used by Edie and co-workers[8,9] to fuse the powders to the fibre. The optimum particle size for this appears to be greater than 20 μm. Another recent approach with dry powder prepregging was to dampen the carbon fibres with a fine water mist before contacting the fibres with dry powder[7]. The powder particles were then fused to the fibres in a rapid heating step.

We have chosen to investigate suspension prepregging as an alternative to dry powder prepregging for high performance thermoplastic composites. Suspension prepregging involves impregnating carbon fibres by contacting them with a suspension of polymer particles, typically in a drumwinding operation[13,14,16]. In the present work, water was chosen as the suspending fluid due to its environmental safety. Addition of a soluble polymer to the suspension serves two functions: to bind the matrix to the fibre and to disperse the particles for good processing. Water removal occurs before and during the consolidation step. The advantages of suspension prepregging are notable: (i) particle sizes in the submicrometre range can be used, circumventing the ~20 μm limit of dry powder prepregging, which is especially important for carbon fibre cloth impregnation because it cannot be spread like unidirectional carbon fibre tow to allow large particles, e.g. greater than ~50 μm, to penetrate effectively into the carbon fibre bundles; (ii) there is no polymer solubility limitation as in solution prepregging; (iii) aqueous suspensions

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typically have very low viscosities, e.g. less than 100 mPa s, thus circumventing the problem of high viscosity in melt impregnation; (iv) the aqueous suspensions can be handled easily and safely; and (v) the fibre–matrix interphase properties may be controlled by the combination of matrix and binder polymers chosen. The suspension prepregging process used in the present work is similar in some aspects to the process developed by BASF for making prepregs with a variety of powdered polymers produced chiefly by grinding. These include poly(ether ketone) (PEK), poly(ether ketone ether ketone) (PEKEK), Ultrapek, poly(ether ether ketone ketone) (PEEKK), LaRC TPI polyimide, poly(ethersulfone) (PES), poly(etherimide) (Ultem), and a fully imidized powder form[4,12] of PMR-15. While precise details of this process are not available, it is believed that the BASF suspension prepregging process uses a polymeric binder that degrades during consolidation. This contrasts with the present work where the ammonium salts of polyamic acids are used as binders; these form polyimides upon consolidation and, as will be shown, influence binder–matrix interphase properties.

There are several issues concerning suspension prepregging which are relevant to processability and composite performance, including: (i) the relative unavailability of fine powders of high performance thermoplastics; (ii) binding of the thermoplastic matrix to the fibres, i.e. the structure of the fibre–matrix interphase and interface regions; (iii) water removal from the prepreg which is essential to minimize void formation and maximize fibre–matrix adhesion; and (iv) the effect of particle size on prepregging and consolidation. The first three issues are addressed in this work while the effect of particle size on prepregging and consolidation will be addressed in a future paper.

An important problem with powder prepregging in general has been the lack of sufficiently small, high performance thermoplastic particles obtained usually by grinding or, in the case of soluble polymers, from spray drying. Grinding has been the only effective method for making powders from semicrystalline polymers whereas spray drying has some utility for mostly amorphous, soluble polymers. Although much work has been reported recently using flashing from supercritical solutions to make fine powders of a variety of materials including polymers[17], there are no known economical processes for the large-scale production of submicrometre powders of thermoplastics with relatively high glass transition temperatures, T_g. Aromatic PEKs are of considerable interest as matrix materials in carbon fibre composites. These polymers are semicrystalline and exhibit relatively high melting temperatures, T_m. The crystallinity contributes to the excellent chemical resistance, mechanical properties and extended use temperature above T_g. However, the chemical and solvent resistance of PEEK along with its high T_m make fabrication of composites from this material unfeasible by solution prepregging. A commercially available PEEK prepreg that is used widely, APC-2™ from ICI, is presumably made by melt impregnation. Thus, there is considerable interest in producing small powders of PEEK and using them to fabricate composites by powder prepregging techniques. The excellent toughness of PEEK limits the conventional cryogenic grinding method for fine powders to ~20 μm which is still large relative to the ~8 μm diameter fibre. Recently, a novel synthesis of poly(ether ether ketone) (PEEK) was developed which results in particles in the size range 0.2–30 μm that are dispersible in water[16,18,19]. This method involves synthesizing soluble, amorphous poly(ketimine) precursors to PEEK and hydrolysing them to powdered PEEK with dilute acids. Thus, no grinding is required to make fine PEEK powders.

During suspension prepregging, poor binding can result in matrix particles falling off fibres after prepregging and removal of the water. In recent work with LaRC TPI™ matrix polymers, fibre–matrix powder binding was improved with the addition of water-soluble, ammonium salts of polyamic acids to the matrix particle suspension prior to prepregging[13,14,20]. During the drying step after prepregging and prior to consolidation, the polyamic acid salts formed a dry film coating matrix particles and fibre, leading to binding. After consolidation, the polyamic acid salt thermally imidized to form a polyimide which served to bind matrix and fibre. In addition to functioning as a binder, it was shown that polyamic acid dispersed particles of LaRC TPI[14] and PEEK[21].

Thermoplastic particles in water tend to form relatively large aggregates due to attractive Van der Waals forces. In previous work with LaRC TPI matrix–carbon fibre composites, it was shown that the ammonium salt of LaRC TPI polyamic acid adsorbed onto LaRC TPI particles, leading to strong electrostatic and steric repulsive forces which inhibited particle–particle aggregation[14]. The dispersed LaRC TPI suspensions had smaller mean aggregate sizes than LaRC TPI suspensions that were not treated with polyamic acid salts. Aggregate size may be important since the smaller particles should penetrate the carbon fibre bundles and pack more tightly around fibres than would larger aggregates, possibly leading to lower void volume in the consolidated composite. The binding and dispersing functions of polyamic acid salts will be described in more detail below.

The purpose of the present study was to determine the feasibility of making carbon fibre composites by suspension prepregging with aqueous dispersions of the novel PEEK particles. Special attention was given to the effects of the dispersing polyamic acid salts on PEEK article aggregation and on fibre–matrix binding.

EXPERIMENTAL

Materials

Carbon fibre. Hercules AS-4™ carbon fibre tow was used in this work. The fibres were unsized but surface-treated. The tow consisted of ~12 000 fibres, each ~8 μm in diameter. The tow was used as received.

PEEK matrix particles. PEEK particles were synthesized by a procedure reported elsewhere[16,18,19]. PEEK particles crystallize and precipitate following the hydrolysis of a soluble poly(ketimine) precursor. The PEEK repeat structure is shown in *Figure 1*. Three samples of PEEK were used in the experiments. The molecular weight distributions of samples 1 and 3 were determined by gel permeation chromatography (g.p.c.) at 25°C with a VISKOTEK™ intrinsic viscosity detector which permitted the use of a universal calibration curve[22]. The mobile phase was anhydrous *N*-methyl pyrrolidinone (NMP) with 10 g/l LiBr added to suppress polyelectrolyte effects. The results are shown in *Table 1*.

Sample 1 was used in preliminary particle dispersion experiments. Samples 2 and 3 were used in fabricating unidirectional panels by suspension prepregging. In addition to these panels, a sample of unidirectional PEEK prepreg, APC-2™ from ICI, was evaluated to provide benchmark composite characterization data.

Binders/dispersants. Two types of polyamic acid were used in the experiments: (i) LaRC TPI polyamic acid (Lot no. 58-703) obtained from Mitsui Toatsu in the form of a dry powder; (ii) the copolymer bis-aniline-P/benzophenone tetracarboxylic dianhydride (Bis P-BTDA) synthesized at Virginia Tech and obtained as a dry powder[23]. These polyamic acids thermally imidize at temperatures above 150°C. The structure of LaRC TPI polyamic acid and the polyimide it forms, LaRC TPI, are shown in *Figure 2a*[24,25]. Corresponding structures for Bis P-BTDA polyamic acid and its resulting polyimide

Table 1 Characterization of PEEK by universal g.p.c.

Sample	M_n (kg mol^{-1})	M_w	M_z
1	6.5	22.0	33.9
2	^{a}	^{a}	^{a}
3	24.3	40.9	55.8

^{a} Approximately the same as sample 3

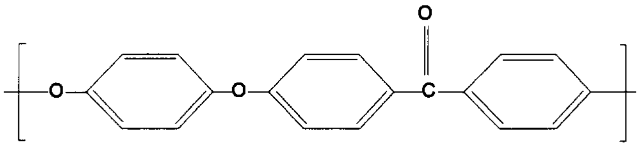

Figure 1 Repeat structure of poly(ether ether ketone) (PEEK)

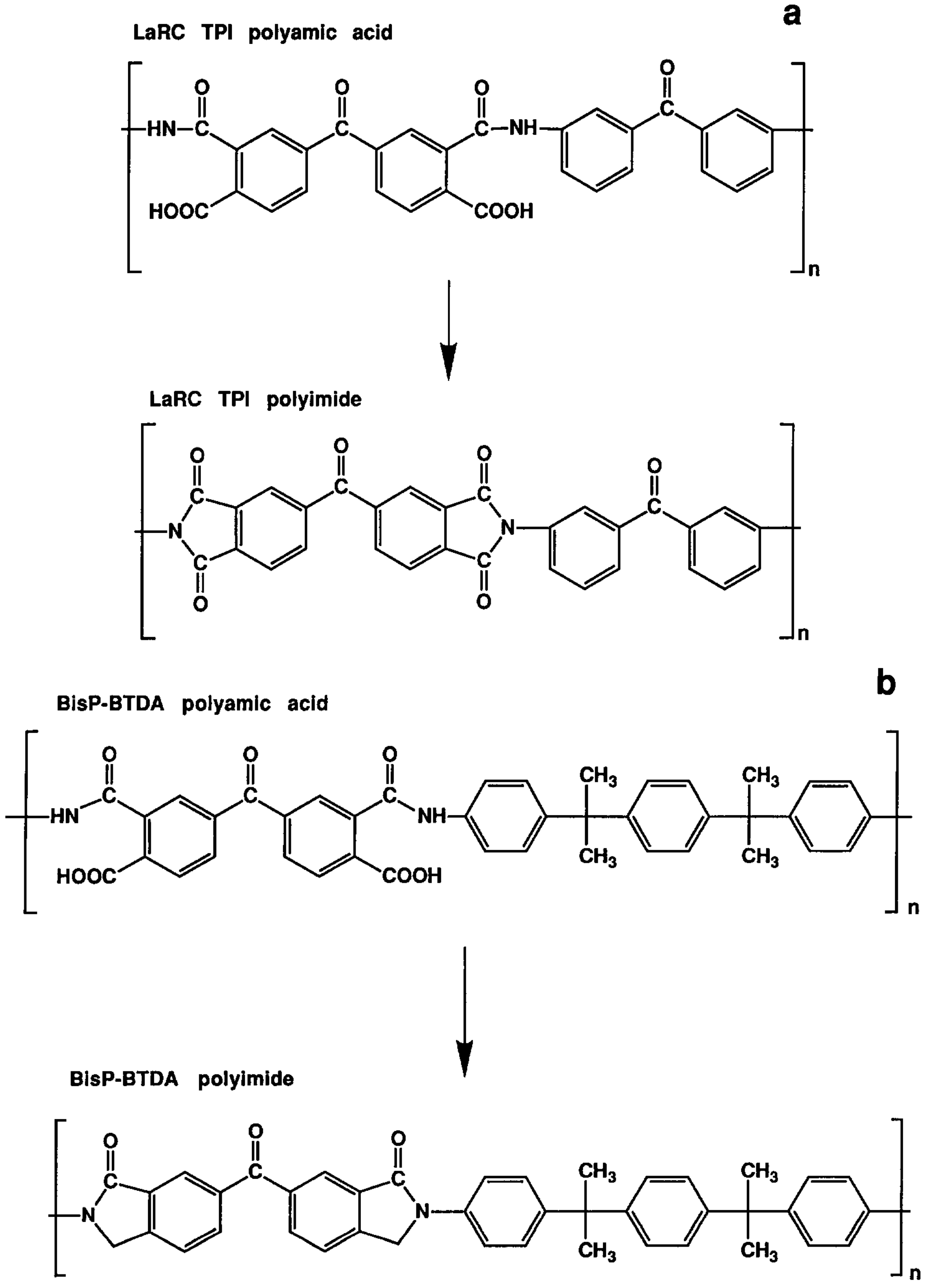

Figure 2 (a) Structure of LaRC TPI polyamic acid and LaRC TPI; (b) structure of Bis P-BTDA polyamic acid and Bis P-BTDA polyimide

are shown in *Figure 2b*. Two nominal molecular weights of this latter polyamic acid were used, 10 and 20 kg mol^{-1}, hereafter referred to as 10K and 20K, respectively. Molecular weight data on the LaRC TPI polyamic acid were not available.

In addition to the polyamic acid salts used for dispersion, three polymers and two surfactants were tested for their ability to disperse PEEK powders in an effort to understand better the particle dispersion effect, even though it was clear that these materials, unlike polyamic acid salts, were not thermally stable at the consolidation conditions. The polymers included: (i) HPC E^{TM}, a type of hydroxypropylcellulose which is a non-ionic, water-soluble cellulose derivative containing an average of 2.5 hydroxypropyl groups per backbone repeat unit and an approximate molecular weight of 60 kg mol^{-1}, provided by Hercules Inc.; and (ii) Pluronics^{TM} F-38 and F-108, triblock copolymers with a polypropylene centre block and poly(ethylene oxide) tail blocks containing roughly 80 wt% poly(ethylene oxide) with molecular weights of 4.7 and 14.6 kg mol^{-1}, respectively, provided by the BASF Corporation. The low molecular weight surfactants included: (i) DOWFAX 2A1^{TM}, an anionic diphenyl ether with one sulfonate per phenyl group with a molecular weight of 0.576 kg mol^{-1}, provided by the Dow Chemical Company; and (ii) TRITON X-100^{TM}, a non-ionic polyoxyethylene ether surfactant with a nominal molecular weight of 0.646 kg mol^{-1}, from Aldrich Chemical Company.

Water used in these experiments was deionized in a NanoPure II^{TM} unit equipped with a 0.2 μm filter and had a resistivity typically of 15 MΩ cm or higher. Analytical grade ammonium hydroxide, 13 M, was used.

Suspension preparation

The ammonium salts of the polyamic acids, hereafter referred to in general as NH_4 PAA, were used in the aqueous solutions since polyamic acids are not water soluble. Water, concentrated NH_4OH, and polyamic acid powder were placed in a beaker that was then sealed and heated to ~50°C for 10–15 min while stirring with a magnetic stirring bar. Polyamic acid dissolved rapidly in this NH_4OH solution to form clear solutions of the NH_4PAA salts. The NH_4OH concentration in these suspensions was fixed at 12.5 mol% excess based on the moles of polyamic acid following an earlier study by Towell *et al.*[13], which showed the polyamic acid's salt solubility increased with excess NH_4OH. When not used immediately, the NH_4PAA solutions were stored at 4°C and were typically used within 48 h after preparation.

PEEK powder was added to the NH_4PAA solutions and was mixed in an ordinary household blender equipped with curved blades at ~1000 rev min^{-1} for several minutes to promote intimate contact between the PEEK particles and the polymeric dispersant. In all cases, the weight ratio NH_4PAA/PEEK was fixed at 0.055 and the final PEEK concentration in the suspension prepregging experiments was in the range 9–13 wt%[20]. Additional PEEK suspensions were prepared at 300 mol% excess NH_4OH to determine the effect of pH on particle size.

Particle size measurements

PEEK particle size was determined using a Shimadzu model SA-CP3 centrifugal particle size analyser, which measures size distribution by the sedimentation method. The density of PEEK was taken to be 1.3 g cm^{-3} for these experiments. Particle sizes were measured in dilute, aqueous suspensions of PEEK as a function of polyamic acid salt concentration, NH_4OH concentration, and sonication conditions. The concentration of PEEK in the suspensions used for size analysis was less than ~0.1 wt%, which resulted in the slightly turbid suspensions required by the size analyser. Some of the suspensions were sonicated with a Tekmar model TM300 sonic disruptor at a power level of 75 W for 3 min using a microtip sonicator horn.

Differential scanning calorimetry

The miscibility of PEEK matrix with the polyimide binders LaRC TPI and Bis P-BTDA was measured, since it was recognized that the binder/matrix miscibility might influence the fibre–matrix interphase and interfacial properties. Blends of 50/50 PEEK/LaRC TPI and PEEK/Bis P-BTDA were prepared by mixing the appropriate weight of each component in benzophenone to achieve a 1 wt% homogeneous solution at about 240°C. The solution was then quenched to room temperature and extracted many times with acetone at room temperature so as to isolate the blend precipitate and to dissolve the crystalline benzophenone. Blend samples were then dried in a vacuum oven at a temperature of 260°C for the former blend and 200°C for the latter until a constant weight was achieved. The miscibility behaviour of these blends was studied by differential scanning calorimetry (d.s.c.) by investigating their glass transition and cold crystallization behaviour. In this study, we used a Perkin Elmer DSC model II operated under dry nitrogen flow at a heating rate of 5°C min^{-1} and calibrated with indium and lead standards.

Suspension prepregging

Carbon fibre tow was impregnated with a Research Tool Corporation model 30 prepregger that was modified to work with suspensions. This is shown in *Figure 3a*. A load cell monitored the tow tension, which was approximately 0.9 N in all experiments. The drum diameter was 60.9 cm and the line speed varied in the range 8.4–9.6 cm s^{-1}. A resin pot with a capacity of 250 ml, shown in *Figure 3b*, was designed to allow prepregging with suspensions having very low viscosities (< 100 mPa s). The size of the PEEK particles in *Figure 3b* is exaggerated for illustrative purposes. Guide rollers in the resin pot spread the carbon fibre tow to ~25 mm, which resulted in good matrix particle impregnation and negligible fibre breakage. A small, modified aquarium pump in the resin pot maintained the particles in suspension. The impregnated bundle was taken up on a drum on a moveable carriage so that the overlap of the towpreg from each successive revolution of the drum was 35–50%. Single layer prepregs were made in every case.

The prepreg was left on the drum to dry for 2–3 h before being removed and laid flat on a table. Layers were cut to 7.62 cm × 7.62 cm or 7.62 cm × 12.7 cm and stacked to make eight-ply unidirectional panels. Prior to consolidation, the panels were dried in a convection oven at 100°C for 1 h and then at 177°C for 2 h. This drying procedure removes over 99% of the physically bound water in the prepreg and imidizes virtually 100% of the

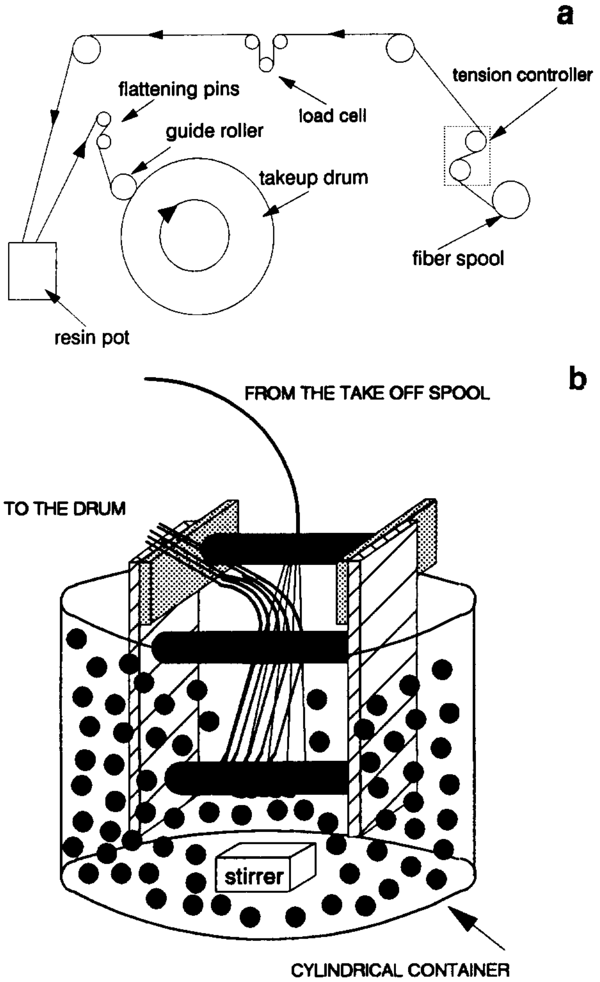

Figure 3 (a) Drumwinder used for prepregging; (b) resin pot

polyamic acid, as shown by thermal gravimetric analysis. During imidization, two molecules of water were released for each polyamic acid repeat unit[24].

Consolidation conditions

The top and bottom sides of the dry, unidirectional panels were covered with one layer of Kapton™ film before being placed in steel moulds which had four removable sides. Before placing the panels in the mould, the mould was sprayed with FREKOTE™ 34H release agent. The sides of the Kapton films in contact with the panels were also sprayed with FREKOTE before use. The panels were then consolidated in a Tetrahedron Pneumapress P-400 pneumatic hot press where the temperature and pressure were controlled and monitored continuously. In some cases, the panels were consolidated under vacuum to facilitate the removal of residual water and other volatile species. This was accomplished by enclosing the mould in a bag made of thick aluminium foil made vacuum-tight with a high temperature sealant and connected to a vacuum pump that reduced the gas pressure in the bag to 101.3 Pa during consolidation. The vacuum bag was inside the press and the vacuum was maintained throughout consolidation.

Three drumwinding experiments each were performed with PEEK samples 2 and 3. Consolidation with the P-400 press was done using various time–temperature–platen pressure (TTP) cycles with and without vacuum processing to test the effects of processing variables. The temperature and pressure were controlled and monitored continuously. Three TTP cycles were used with panels made with PEEK sample 2 and are illustrated in *Figures 4a–c*. Cycle (a) consisted of one temperature ramp from room temperature to 400°C where it was held for 40 min. The platen pressure cycle consisted of a step function increase to 200 psig* once the T_g of PEEK was reached, followed by another step function increase to 300 psig. Cycle (b) consisted of the same temperature cycle along with pressure cycled between contact pressure to 300 psig to facilitate degassing of the panel. Cycle (c) used the same TTP cycle as cycle (a) along with vacuum processing. For panels made with PEEK sample 3, a fourth TTP cycle (d) was used, shown in *Figure 4d*. This cycle used the TTP cycle in cycle (b) along with vacuum processing. A sample of APC-2 PEEK composite was also processed with cycle (d).

These time–temperature cycles are comparable to those used in previous work for consolidating AS-4 fibre/PEEK prepreg tapes (388°C for 30 min) and AS-4/PEEK commingled fabrics (399°C for 60 min), although our consolidation pressure of 300 psig was higher than the recommended[26] 200 psig. PEEK has been shown to be quite stable at temperatures as high as 415°C in an inert nitrogen atmosphere for up to 40 min[27]. Our TTP cycles are somewhat different from the recommended cycle for APC-2, which consists of a maximum temperature of 390°C, a maximum pressure of 200 psig, and a total cycle time of 30 min in air. However, we believe our cycles do not lead to appreciable thermal degradation of PEEK, particularly cycles (c) and (d). For all four cycles, the cooling rate at the end of consolidation was $\sim 5°\mathrm{C\,min^{-1}}$. This is slightly below the range of cooling rates of $10\text{–}700°\mathrm{C\,min^{-1}}$ for PEEK recommended by ICI to obtain the desired level of approximately 30% crystallinity for optimum mechanical properties[28]. The crystallinity of the PEEK in the composites was not measured.

Composite testing

After consolidation, panels were evaluated non-destructively with a modified Sperry Corporation S-80 C-scan ultrasonic scanning unit to determine the regions of good and poor consolidation. A graphic printer was connected to the C-scan apparatus to record an image of the panel. The printed image ranged in gray scale values from 0 to 20 based on an internal gray scale calibration standard. Relatively dark regions had high gray scale values corresponding to dense, well consolidated laminates, while relatively light coloured regions had low gray scale values which corresponded to poorly consolidated regions with more voids. Samples for mechanical testing were taken from the parts of each panel that had the darkest appearance or highest gray scale values. PEEK content was determined by acid digestion using procedure b of the ASTM D 3171-76 method. Panels 3–5 were evaluated with the flexure test ASTM D 790-86 and panels 6–8 were evaluated with the transverse tensile test ASTM D-3039[29]. A sample of APC-2 PEEK composite was also evaluated with the transverse tensile test. All mechanical tests were performed with dry specimens at room temperature on an Instron model 4204 instrument at a crosshead

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* 1 psig $= 6.895 \times 10^3$ Pa

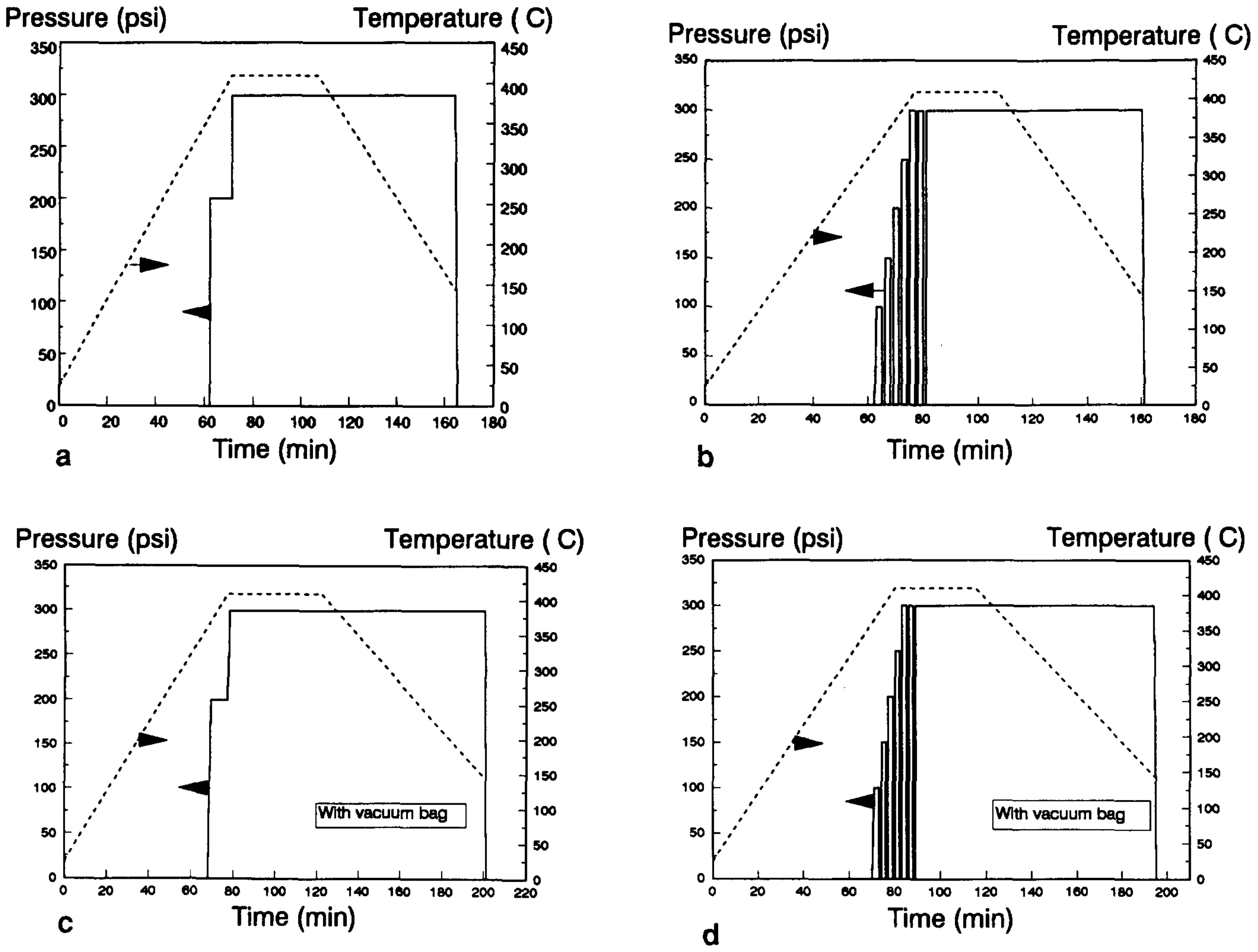

Figure 4 (a)–(d) Time–temperature–pressure cycles (a) to (d), respectively, used in consolidation

speed of 0.127 cm min^{-1}. In the flexure test, the specimen thickness ranged from 0.15 to 0.20 cm and the corresponding length ranged from 6.1 to 7.8 cm. A constant width of 1.27 cm and a span of 5.08 cm were used in all tests. For panels 6–8 and for the APC-2 panel, scanning electron micrographs of the fracture surfaces were also taken at magnifications ranging from 300 × to 1500 ×.

RESULTS AND DISCUSSION

Polyamic acid salt solutions

Dissolution of the three polyamic acids in an aqueous ammonium hydroxide solution resulted in a large decrease in the viscosity of the solutions, which was observed during mixing of the solutions. Most likely, the molecular weight of the polyamic acid salt decreased due to chain scission which occurred through the hydrolysis of the amide linkages present in the backbone of the polyamic acid. However, the lower molecular weight of the polyamic acid salts is useful for particle dispersion, since charged, water-soluble dispersants typically have molecular weights[30] in the range 2–5 kg mol^{-1}.

During the heating step in the convection oven, the polyamic acid undergoes cyclodehydration to form the polyimide. Amine and acid end-groups may undergo further reactions during heating, leading to chain extension of the polymer. Branched structures may also be present through the ketimine-forming reaction of the amine end-groups with the ketone linkages in the polymer[31]. The structure of the polyimide will be further studied by n.m.r. spectroscopy.

Particle stabilization

A suspension consisting of 20/80 (wt/wt) PEEK/water formed a highly viscous paste consisting of strongly aggregated particles due to strong, attractive Van der Waals forces. Since suspension prepregging requires suspensions with very low viscosities, it was necessary to disperse the particles. The surfactants and polymers in aqueous solutions were tested for their dispersion capabilities by adding a few drops to a small amount of paste from PEEK sample 1 until a significant decrease in viscosity was observed. The viscosities resulting after addition of the surfactants, while lower than that of the control sample of PEEK powder in deionized water, were still too high to permit suspension prepregging. Only HPC E and the ammonium salts of LaRC TPI polyamic acid and Bis P-BTDA polyamic acid dispersed the PEEK aggregates sufficiently to obtain suspensions with viscosities less than ~100 mPa s, as determined by a Brookfield viscometer equipped with a low viscosity, concentric cylinder fixture. This is not surprising, as polymeric dispersants are usually much more effective in dispersing colloidal particles than are non-polymeric surfactants. Polymeric dispersants adsorbed onto the

PEEK particles, resulting in steric and electrostatic repulsive forces between the particles which reduced aggregation and hence suspension viscosity[32]. Since it is important to maximize the fibre–matrix interfacial binding and minimize void volume in the composite, only LaRC TPI polyamic acid and Bis P-BTDA polyamic acid were used in fabricating PEEK composites due to the high temperature performance of polyimides. By comparison, HPC degrades[33] in the range 250–300°C.

The particle size distribution of the PEEK samples was measured as a function of the type of polyamic acid salt, NH_4OH concentration, and sonication conditions. Before addition of the polyamic acid salts, the PEEK aggregate size was typically greater than 100 μm and thus could not be measured by the Shimadzu SA-CP3 particle size analyser. Thus, only particle sizes of PEEK samples dispersed with polyamic acid salts are reported. Two different NH_4OH concentrations were used: 12.5 mol% excess, based on the moles of polyamic acid, and 300 mol% excess. PEEK samples 1 and 2 were dispersed with the ammonium salt of LaRC TPI polyamic acid; the results are presented in *Figures 5* and *6*, respectively.

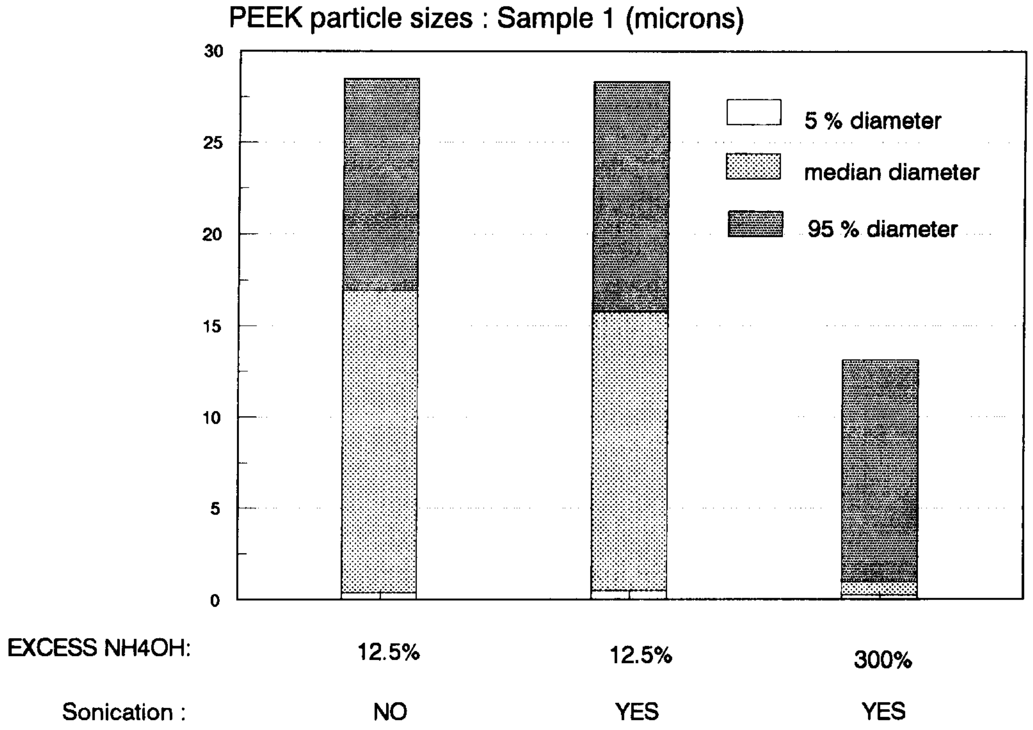

Figure 5 PEEK sample 1 particle size distribution

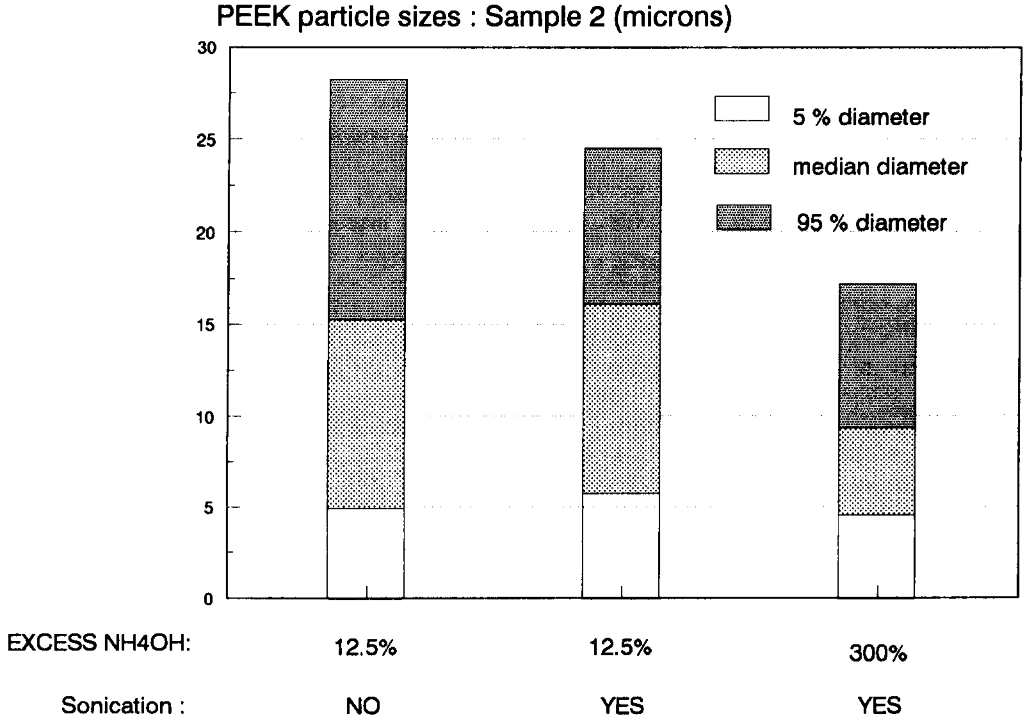

Figure 6 PEEK sample 2 particle size distribution

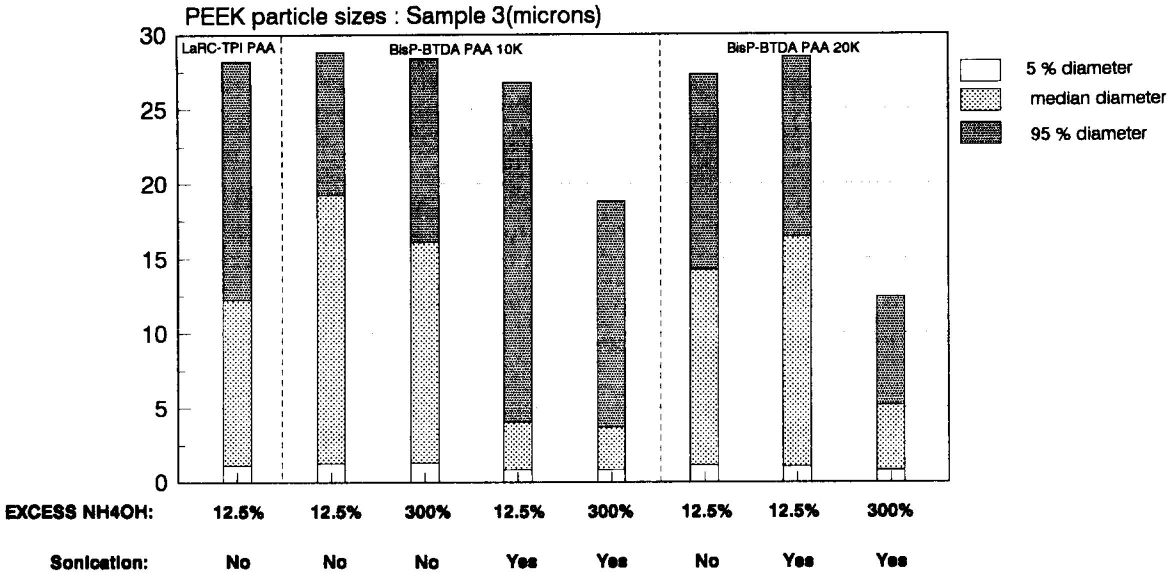

Figure 7 PEEK sample 3 particle size distribution

PEEK sample 3 was dispersed with the ammonium salts of LaRC TPI polyamic acid and the 10K and 20K Bis P-BTDA polyamic acids. The particle sizes for sample 3 are summarized in *Figure 7*.

Particle size measurements from all three samples show that excess NH_4OH reduces PEEK aggregate size, causing the median size for sample 1, for example, to drop from 15 μm to less than 1 μm when accompanied by sonication. The median aggregate size decreased with increasing NH_4OH or equivalently, increasing pH, due to an increase in the repulsive electrostatic forces between particles caused by the increasing charge of the polyamic acid salt adsorbed on the PEEK. This is characteristic of electrostatic stabilization[32].

Sonication at a power level of 75 W for 3 min at 12.5% excess NH_4OH reduced the median aggregate size somewhat for PEEK samples 1 and 2. A significant reduction in median size upon sonication was observed for sample 3 dispersed with Bis P-BTDA 10K. However, sonication of sample 3 dispersed with Bis P-BTDA 20K resulted in a slight increase in median size. This may be due to weak bridging flocculation caused by the initial, higher molecular weight of the 20K sample.

Sonication of all three PEEK samples at 300% excess NH_4OH results in a significant reduction in median aggregate sizes compared to particles measured with no sonication and no excess NH_4OH. For sample 1, the median size decreased from 17 to 1 μm; for sample 2, the median size decreased from 15 to 9 μm; for sample 3, the median size decreased from an average value of 15 to 4 μm for particles dispersed with 10K Bis P-BTDA and 5 μm for particles dispersed with 20K Bis P-BTDA. Sonication tends to break up aggregates which may reform if no dispersant is present. If sonication is done in the presence of a dispersant such as an ammonium salt of a polyamic acid, then the dispersant adsorbs onto the newly fragmented aggregates, thus inhibiting re-aggregation.

Particle binding

Suspensions of PEEK particles in water and in LaRC TPI polyamic acid solutions were mixed and used to impregnate a carbon fibre bundle. After drying at room temperature for 48 h, the PEEK particles deposited onto the fibres from deionized water showed no adhesion and fell off the fibre during handling. By contrast, the PEEK particles deposited onto the fibres from solutions of LaRC TPI polyamic acid salts adhered very well due to the film formed by the NH_4PAA that covered the fibre and PEEK particles.

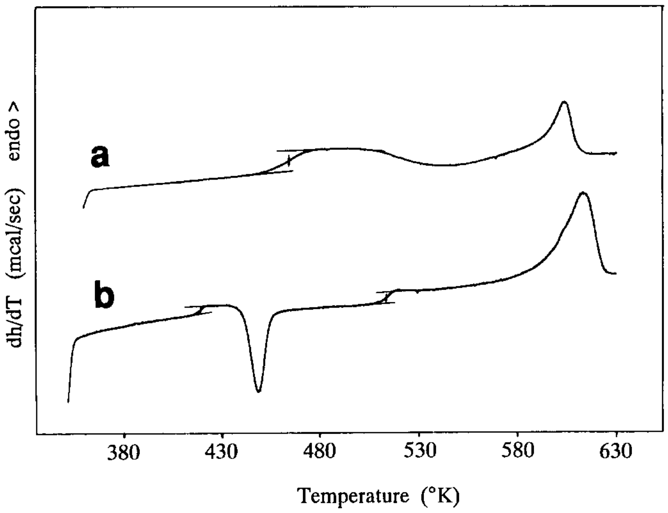

Figure 8 D.s.c. traces (5°C min^{-1}) for PEEK/polyimide blends: (a) PEEK/Bis P-BTDA 50/50 mixture; (b) PEEK/LaRC TPI 50/50 mixture

Binder/matrix miscibility

The d.s.c. studies indicate that the PEEK is miscible with Bis P-BTDA whereas it is immiscible with LaRC TPI. *Figure 8* shows the heating traces of blend samples that were first brought to the liquid state at 658 K and then quenched at the fastest possible rate to about 353 K. A numerical scale is not given on the y-axis because we only want to show the difference in miscibility, i.e. the change in T_g between the two blends. In *Figure 8a* (PEEK/Bis P-BTDA 50/50 mixture) a single T_g is observed at 463 K which is intermediate between that of PEEK ($T_g = 416$ K) and that of Bis P-BTDA ($T_g = 514$ K) and indicative of molecular level miscibility[34]. The

Table 2 Process conditions and composite characterization

Panel	PEEK sample	Binder, PAA type	Median particle size (μm)	PEEK concentration (wt%)[a]	Fibre content (vol%)	Consolidation cycle[b]
3	2	LaRC	15	13	36	(a)
4	2	LaRC	15	13	35	(b)
5	2	LaRC	15	13	36	(c)
7	3	LaRC	12	9	43	(d)
7	3	10K[c]	19	9	64	(d)
8	3	20K[c]	14	9	61	(d)

Table 3 Flexure test results

Panel	Fibre content (vol%)	Flexure strength (MPa)	Flexure modulus (GPa)
3	36	813±63	59±1.7
4	35	869±13	62±1.2
5	36	883±50	63±1.7
APC-2	61	1883[a]	121[a]

[a] Data from ref. 28

Table 4 Transverse tensile tests for composites

Panel	Polyamic acid	Fibre content (vol%)	Transverse tensile strength (MPa)
6	LaRC TPI	43	73.4±1.4
7	10K Bis P-BTDA	64	58.8[a]
8	20K Bis P-BTDA	61	73.1±1.7
APC-2	N/A	61	94.4±2.0 (measured) 80.0 (from ref. 28)

[a] From single measurement

maximum rate of cold crystallization for PEEK in this blend is shifted to higher temperature than in pure PEEK because in this temperature range the crystallization is diffusion controlled and the blend's T_g is significantly higher than that of pure PEEK. In *Figure 8b* (PEEK/LaRC TPI 50/50 mixture) two T_gs are observed, corresponding to the transition in the pure components ($T_g = 513$ K for LaRC TPI). Furthermore, the cold crystallization behaviour of PEEK in this blend is identical to that of pure PEEK. From these observations one can conclude that PEEK/LaRC TPI mixtures are not miscible at the molecular level. As additional evidence for this conclusion, d.s.c. results for 20/80 and 80/20 LaRC TPI/PEEK mixtures (not shown) also exhibit two T_gs.

Composite mechanical properties

Effect of processing parameters. Six unidirectional panels were made with PEEK samples 2 and 3. The processing conditions and panel characterization data are summarized in *Table 2*. The PAA/PEEK weight ratio was 0.055 in all cases.

Panels 3–5 were made with PEEK sample 2 with a prepregging suspension concentration of 13 wt% PEEK. The flexure test results for panels 3–5 are summarized in *Table 3*. These panels were made with the ammonium salt of LaRC TPI polyamic acid as a binder. Literature data for APC-2 PEEK composite are also shown[28].

The flexure strength and modulus values for panels 3, 4, and 5 were approximately the same, with the APC-2 values being roughly twice as high. The C-scans of these samples had typical gray scale values of ~3 (on a scale of 0–20), which indicated relatively poor consolidation overall due to relatively high void content. Thus, the TTP cycle in *Figure 4d* was developed to incorporate pressure cycling and vacuum processing, to minimize void content by promoting removal of volatile compounds and to promote homogeneous distribution of matrix around the fibres. In addition, the fibre volume percentage values for panels 3–5 were significantly lower than the target value of 61% of the APC-2 PEEK composite. As expected, the flexure strength and moduli values for panels 3–5 were significantly lower than those of APC-2.

To approximate the composition of APC-2 more closely, panels 6–8 were made at a PEEK concentration of 9 wt% in the suspension prepregging step while consolidating under vacuum processing using TTP cycle shown in *Figure 4d*. These panels were made with PEEK sample 3. In addition, the type of polyamic acid binder was varied to probe the effect of binder chemistry. C-scans of panels 6–8 showed much better consolidation than those of panels 3–5 with a typical gray scale value of ~10. This suggests that a combination of vacuum processing and pressure cycling during consolidation leads to significant improvements in composite consolidation. The transverse tensile test results for panels 6–8 are summarized in *Table 4* along with data for APC-2[28].

Effect of polyamic acid chemistry. The transverse tensile strength of panel 8, 73.1 MPa, was relatively close to that of the APC-2 panel, especially if the literature value of 80.0 MPa is used for comparison. The plies in panel 7 were not properly aligned and hence its tensile strength, 58.8 MPa, is not strictly comparable to those of the other panels. In addition, since the fibre contents of panels 6, 7 and APC-2 are not identical, the transverse tensile strengths of these panels could not be compared quantitatively. However, the panels were evaluated qualitatively by scanning electron microscopy of the fracture surfaces, shown in *Figures 9a–d*. The fracture surface of panel 6, shown in *Figure 9a*, was characterized by brittle failure at the fibre–matrix interface. The fracture surfaces of panels 7 and 8, shown in *Figures 9b* and *c*, respectively, were virtually indistinguishable from that of the APC-2 panel shown in *Figure 9d*. These latter three surfaces showed ductile failure at the interface with virtually no bare carbon fibres. The qualitative difference between the fracture surfaces of panel 6 and those of panels 7, 8 and APC-2 may be

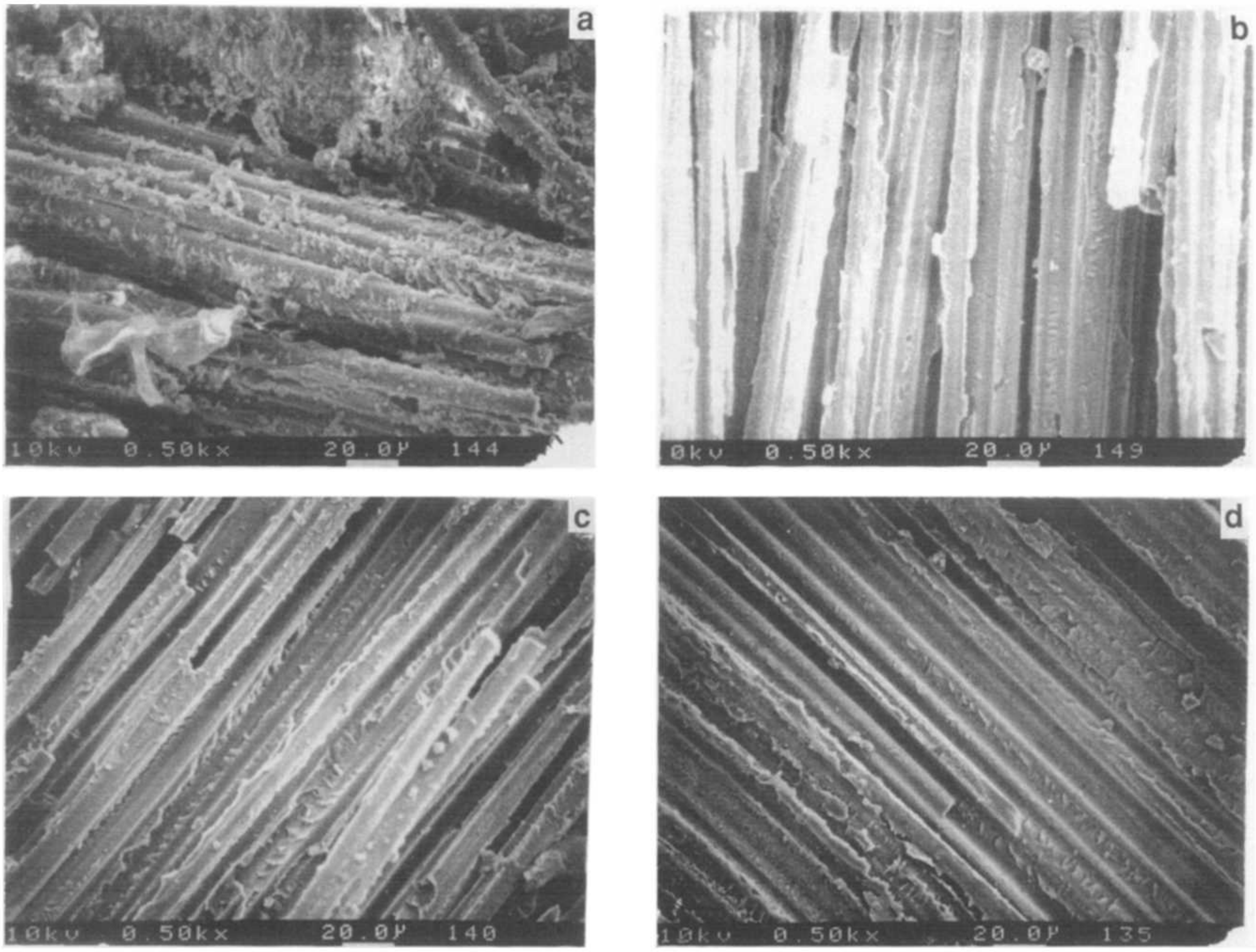

Figure 9 Fracture surface micrographs of PEEK composites made with: (a) LaRC TPI polyamic acid binder; (b) Bis P-BTDA (nominal M_n 10 kg mol^{-1}) polyamic acid binder; (c) Bis P-BTDA (nominal M_n 20 kg mol^{-1}) polyamic acid binder; (d) ICI APC-2 PEEK composite

due to the differences in miscibility of the polyimide binders and the PEEK matrix detected by the d.s.c. experiments. It is possible that the brittle failure in panel 6 occurred at the interface between PEEK-rich regions and LaRC TPI-rich regions, whereas in the case of panels 7 and 8, failure in the panel does not involve weak interphase boundaries between immiscible polymer phases. This suggests that it may be possible to control fibre–matrix interphase and interface properties by controlling the relative miscibility and the relative concentrations of the polymeric binder and matrix materials. This would have important consequences for control of composite properties. Thus, the soluble NH_4PAA, in addition to serving as a dispersant, functions as a binder in two ways: (i) binding powder particles to the fibre prior to consolidation, which is essential for handling; and (ii) binding matrix to fibre after consolidation by forming an interphase and interface region around the fibre.

CONCLUSIONS

High performance thermoplastic composites were made by impregnation of continuous carbon fibres with aqueous suspensions of PEEK particles made by a novel precipitation process. These particles were suspended in aqueous solutions of ammonium salts of polyamic acids which performed two essential roles: as a polymeric dispersant and as a binder at the fibre–matrix interface. The resulting composite panels had properties that were comparable in some cases to those of commercially available PEEK composites. Three different polyamic acid salts were used to disperse the PEEK particles, resulting in dramatic decreases in median particle diameters and suspension viscosity. Under the most dispersed conditions, the lowest median particle diameter was $\sim 1\ \mu$m. Fracture surface analysis from unidirectional panels suggests that the miscibility of the matrix and binder may control the failure mode at the fibre–matrix interface. Future work will include: (i) n.m.r. and solubility studies to determine the structure of the polyimide formed from the ammonium salts of LaRC TPI polyamic acid and Bis P-BTDA polyamic acids; (ii) further studies of the effect of dispersant/binder chemistry on the fibre–matrix interfacial properties with the aim of controlling fibre–matrix adhesion; (iii) a study of the effect of matrix particle size on processing and composite performance; and (iv) further optimization of the consolidation cycle with a study of PEEK melt rheology and further variation of the heating and cooling steps.

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