Amine-terminated poly(aryl ether ketone)–epoxy/amine resin systems as tough high performance materials

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A series of tough thermosetting resins based on the incorporation of amine-terminated poly(aryl ether ketone) oligomeric derivatives into commercial epoxy/amine resins, through a solventless process, have been evaluated. It is shown that when the amine-terminated oligomer is loaded at a level sufficient to form a material consisting of a lightly crosslinked thermoplastic continuous phase with epoxy/amine-rich inclusions, the fracture energy of the system increases by 350–750%, with either no loss or a slight increase in modulus, with respect to the unmodified commercial epoxy/amine resin, while possessing glass transition temperatures greater than the neat thermoplastic material. These tough resins are processable by conventional thermoset technology, as the system is initially a miscible low viscosity ternary melt consisting of a commercial epoxy, an amine-terminated oligomeric modifier, and an amine curing agent. Room temperature B-stage tack and drape is also maintained to allow for conventional prepreg lay-up procedures. The toughest systems combine the toughness characteristics of thermoplastic systems with the processing characteristics of thermosetting systems into a unique hybrid material. Phase separation occurs with curing and results in a lightly-crosslinked thermoplastic-rich phase and a highly-crosslinked epoxy/amine-rich phase. The thermal and mechanical properties are shown to be dependent on the morphology of the system which is determined by the loading level of oligomer for a given curing cycle. Three morphologically distinct systems are discussed. The synthesis, processing, solvent, thermal and mechanical properties of resins formulated with amine-terminated tertiary-butylhydroquinone, methylhydroquinone and bisphenol A based poly(aryl ether ketone) oligomers with various commercial epoxy resins are reported, and the properties are related to the observed phase separated morphology. The materials represent conventionally processable high performance thermosetting resins with significantly increased fracture energies and equivalent moduli, with respect to the unmodified materials.

(Keywords: reactive oligomers; poly(aryl ether ketone)s; epoxy resins; phase separation; microscopy)

INTRODUCTION

There has been increased interest in the last 20 years in the development of composite structures that can withstand environmental extremes with a minimum of damage. The motivation for this interest stems largely from the need for materials in aerospace applications. The environmental extremes encountered in these applications may include high temperature, high stress, corrosive solvents and impact. The intense effort to develop lightweight composite materials for this area has been fuelled by potential weight savings in structural applications where operation cost and performance are strong functions of unit mass. Composite materials designed to operate in these extremely rigorous environments are generally referred to as high performance composites. The properties which are desirable in a high performance composite matrix material include high fracture energy, high modulus, high glass transition temperature, good solvent resistance, good adhesion to the fibrous reinforcement and processability.

There has been a considerable effort to develop tough, processable high performance materials[1–7]. An approach has recently been taken to impart the desirable processing properties associated with thermosetting systems and the toughness of thermoplastic systems into a single material. In this approach, an end-functionalized aromatic thermoplastic oligomer is reacted into a high glass transition temperature epoxy resin system to alter its morphology. This system can be characterized by initial miscibility followed by phase separation during cure[8–14]. The end-functionalized oligomer can be loaded at a level sufficient to cause a phase inversion in the cured resin[10–12,14]. The phase inverted system consisting of a lightly crosslinked aromatic thermoplastic-rich continuous phase and highly crosslinked epoxy-rich inclusions, has been shown to exhibit toughness which approaches that of the high molecular weight aromatic thermoplastic homopolymer while maintaining a high level of processability[12].

Pioneering work in this area was carried out on phenol-terminated poly(aryl ether sulphone)[13]. Later developments, by the same researchers, involved the use of aromatic amine-terminated poly(aryl ether sulphone), a system for which no catalyst is required, and the use of higher molecular weight amine-terminated poly(aryl ether sulphone)s. A toughened epoxy network resulted from these efforts[8,9].

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Researchers at Hercules Inc. also investigated the use of amine-functionalized poly(aryl ether sulphone) oligomeric modifiers[10,11]. Amine-terminated oligomers with number average molecular weight, $M_n < 5000$ were used at up to 40 wt% in Heloxy 69 resulting in materials considerably tougher than those specified above. These materials were shown to possess a thermoplastic-rich continuous phase accounting for the system's improved toughness.

The approach taken here emphasizes amine-terminated oligomers based on several poly(aryl ether ketone)s. A limited amount of work involving the bisphenol A based material has been reported elsewhere[9]. However, this effort was based on low oligomer loading levels resulting in modest toughness increases, and some samples utilized solvent casting techniques and others resulted in macrophase separated resins.

The development of a tough matrix material that can be processed without solvents using conventional thermosetting technology is the goal of this effort. In addition to being processable, desirable room temperature tack and drape properties were also preserved to facilitate conventional prepreg lay-up techniques. An understanding of the mechanism by which these enhanced properties are achieved is also presented.

The amine-terminated oligomers investigated in this research were the tertiary-butylhydroquinone-based poly(aryl ether ketone) (tBPK), the bisphenol A-based poly(aryl ether ketone) (BPAPK), the methylhydroquinone-based poly(aryl ether ketone) (MePK) and hydroquinone-based poly(aryl ether ketone) (HDPK). The structures of the respective oligomers are shown in *Figure 1*. Because these materials are not commercially available they were synthesized in our laboratory.

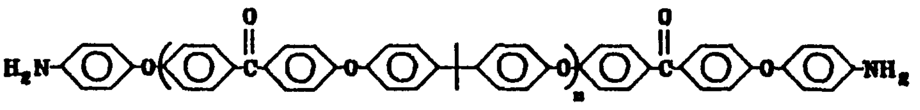
EXPERIMENTAL

Materials

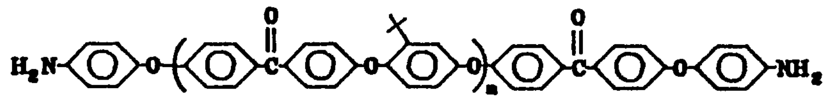
Potassium carbonate, potassium hydroxide, bisphenol A, methylhydroquinone, tertiary-butylhydroquinone, 4,4′-difluorobenzophenone, 4-aminophenol, 1,4-phenylenediamine, 4,4′-diaminodiphenylmethane (MDA) and 4,4′-diaminodiphenylsulphone (DDS) were obtained from Aldrich Chemical Company in the highest purity available. Epon 828, a diglycidyl ether of bisphenol, and Heloxy 69, a resorcinol-based diglycidyl ether were obtained from Shell, and Wilmington Chemical Company respectively. *N*-methyl-pyrrolidinone (NMP) was vacuum distilled over P_2O_5 and stored under nitrogen. Toluene was distilled over CaH_2 and stored under nitrogen.

Synthesis of amine-terminated poly(aryl ether ketone) oligomers

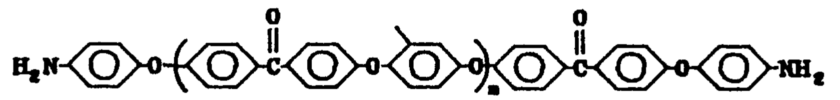
The synthesis of the amine-terminated oligomers involves a two-step process. Both the polymerization and endcapping reactions are nucleophilic aromatic substitutions and follow a technique developed elsewhere[15–18]. The molecular weight of the oligomers was controlled by applying the standard Carother's-type equations governing non-stoichiometric step reactions involving (A–A + B–B) two-component systems[19,20]. A predetermined molar excess of the 4,4′-difluorobenzophenone was used in all of the reactions. A typical reaction scheme to synthesize a 3000 g mol^{-1} amine-terminated tertiary-butylhydroquinone based poly(aryl ether ketone) oligomer is described below. A four-neck flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, Dean-Stark trap outfitted with a condenser, nitrogen outlet and



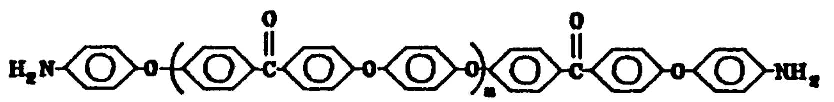
Amine–Terminated Bis Phenol A Based Poly(aryl ether ketone)



Amine–Terminated tertiary–butylhydroquinone Based Poly(aryl ether ketone)



Amine–Terminated Methylhydroquinone Based Poly(aryl ether ketone)



Amine–Terminated Hydroquinone Based Poly(aryl ether ketone)

Figure 1 Chemical structures of amine-terminated poly(aryl ether ketone) oligomers a heating mantle was charged with tertiary-butylhydroquinone (0.0300 mol, 4.9866 g), (methylhydroquinone, bisphenol A, or hydroquinone were used as the diphenol for the other oligomers shown in *Figure 1*) difluorobenzophenone (0.0337 mol, 7.3427 g), and a 40% molar excess of potassium carbonate (0.0420 mol, 5.8048 g). The flask was purged for 1 h with dry nitrogen. NMP, 100 ml, and toluene, 25 ml, were added to the flask via cannula. The reaction mixture was heated to reflux, 160°C, until all the water of reaction had been collected, 4 h. A large excess of 4,4′-difluorobenzophenone (0.005 mol, 1.0911 g) dissolved in NMP was added to the reaction to ensure fluorine endcapping and reacted for an additional hour. Toluene was quickly ($\sim$10 min) removed qualitatively through the Dean-Stark trap until the reflux temperature reached 175°C. The mixture was then cooled to 50°C, coagulated into methanol, filtered, twice washed with boiling methanol for 2 h to remove excess endcapping reagents and trapped solvent, filtered and twice washed with 80°C water for 8 h to remove trapped salts. The oligomer was filtered and dried at 110°C under vacuum for 24 h. The fluorine-terminated oligomer was then analysed by elemental analysis, using a Schoniger oxidation where the fluorine is burned in the presence of oxygen in a flask containing a platinum catalyst and water. The fluoride anion produced dissolves in the water and was measured with a fluoride ion selective electrode which had been calibrated using known standards to determine the number average molecular weight.

In the second step, the previously determined 3100 M_n fluorine-terminated oligomeric tertiary-butylhydroquinone based poly(aryl ether ketone) (0.0074 mol, 11.4662 g), and a stoichiometric amount of 4-aminophenol (0.0074 mol, 0.8076 g) were placed into a four-neck flask equipped as above. Toluene, 55 ml, and NMP, 55 ml, were added via cannula. The ratio of these two solvents was such that a stable reflux temperature of 135°C was obtained. When the reaction temperature reached 100°C a stoichiometric amount of oxygen-free potassium hydroxide (0.0074 mol, 1.75 ml of 4.2316 N) in water was added via cannula. It is important to keep the reaction temperature low and add only a stoichiometric amount of base to prevent attack of the amine at the fluorine end groups and/or at the carbonyls[21,22]. The 135°C reaction temperature was maintained until all the water of reaction had been collected, 2 h. The reaction temperature was then raised to 170°C by quantitatively removing the toluene. The mixture was then quenched to room temperature. The amine-terminated oligomer was then precipitated into methanol, washed with methanol, then resuspended in hot distilled water, washed with distilled water and dried under vacuum at 110°C for 24 h. Elemental analysis for fluorine was again carried out to estimate the amine termination efficiency and was found to be greater than 92%. An 89.6% overall yield, 11.0462 g, of fine white powder was obtained.

Resin formulation

The functionalized oligomers were slowly added to the epoxy resins at 120–150°C while mixing vigorously. A prereaction period of 0.5 h was followed by the addition of DDS or MDA, diamine curing agents. Mixing was continued for 5 min resulting in a miscible low viscosity ternary melt. At this point, upon cooling, the resin was in a B-stage, and all formulations reported had sufficient tack and drape in this B-stage at room temperature for conventional prepreg lay-up procedures. All reported resins were made at an amine to epoxide ratio of 1.0. The reaction mixture was then degassed under vacuum at 180°C and transferred to a preheated aluminium sheet mould also at 180°C. The resins were cured for 2 h at 180°C followed by 2 h at 220°C under vacuum. The sheets were then allowed to cool slowly to room temperature to minimize thermal stresses.

A typical resin formulation using 40% 3100 M_n amine-terminated tertiary-butylhydroquinone poly(aryl ether ketone) as the modifier in an Epon 828-DDS matrix resin system involved dissolving (11.3 g, 0.0036 mol) of the above oligomer in (17.00 g, 0.0452 mol) of Epon 828 at 140°C for 30 min. After the oligomer was completely dissolved in the epoxy a stoichiometric amount of the diamine curing agent, DDS (4.70 g, 0.0189 mol) was added at the 140°C mixing temperature. After 5 min the diamine was completely dissolved and the resin was degassed at 180°C for 5 min, poured into a 180°C preheated sheet mould, cured for 2 h at 180°C and then cured for 2 h at 220°C under vacuum. The cured resin was slowly cooled to room temperature and a transparent orange/yellow sheet resulted.

Thermal, mechanical and morphological property characterization

Critical stress intensity factors, K_{IC}, and fracture energy, G_{IC}, determinations were made using compact tension samples following a modified ASTM E399-83 procedure for mode one crack propagation[23–25]. Compact tension and three point bend samples were cut from these sheets using a jewellers slotting blade on a Bridgeport milling machine. Compact tension sample precracks were inserted by an above T_g insertion technique[26]. Young's modulus calculations were made in three point bend following ASTM D790M. Both determinations were carried out with an Instron testing machine at a crosshead rate of 0.05 cm min^{-1}. Dynamic mechanical measurements were made with an IMASS Dynastat in the three point bend mode. Differential scanning calorimetry (d.s.c.) measurements were made with a Perkin-Elmer d.s.c. 4. Transmission electron microscopy (TEM) samples were prepared by room temperature microtoming followed by osmium tetroxide staining for 3 h. The TEM samples were taken from bulk material away from the fracture surface, and were approximately 80 nm thick. All TEM micrographs were taken using a Jeol 100 CX transmission electron microscope at 100 kV. Scanning electron microscopy (SEM) micrographs were taken from room temperature compact tension fracture surfaces after gold sputter coating. All SEM micrographs were taken using a Jeol JSM-35CF scanning electron microscope operating at 20 kV.

RESULTS AND DISCUSSION

The solubility of the amine-terminated oligomers at workable temperatures below the homopolymerization temperature of the epoxy determines the system's ease of processability. The hydroquinone and the methylhydroquinone based amine-terminated oligomers are both semicrystalline, while the tertiary-butylhydroquinone, and the bisphenol A based amine-terminated oligomers are both amorphous. The amorphous materials were, as expected, much easier to process requiring moderate temperatures of 120–150°C. The semicrystalline hydroquinone based amine-terminated oligomer was found to be insoluble in all of the commercial epoxy resins at elevated temperatures and low molecular weights, and the methylhydroquinone based material was processed above its melt temperature of 230°C in Epon 828. Because a solventless system is one of the main objectives of this work, attempts to process these materials by solvent incorporation techniques are not reported here.

All of the resin formulations reported below had sufficient B-stage tack and drape at room temperature to be processed using conventional prepreg lay-up procedures. The amount of tack and drape, however, decreases with increasing functionalized oligomer addition.

Table 1 shows the thermal and mechanical properties at different loading levels of 7000 M_n and 21 000 M_n amine-terminated BPAPKs incorporated into different commercial epoxy/amine systems. *Table 2* summarizes the thermal and mechanical properties of amine-terminated tBPKs of 3200 M_n and 4600 M_n, incorporated into Epon 828 and Heloxy 69 resins at several loading levels. *Table 3* represents the thermal and mechanical properties of 5000 M_n amine-terminated MePK oligomers incorporated into Epon 828 at different loading levels.

The data in *Tables 1* and *2* shows that the toughness of these materials greatly increases as the weight per cent incorporation of the amine-terminated oligomers is increased. *Figure 2* is a plot of the fracture energy of 7000 M_n BPAPK incorporated into an Epon 828/DDS resin system and 4600 M_n tBPK also incorporated into the Epon 828/DDS system as a function of weight per cent oligomer. A 744% increase in the fracture energy of the 7000 M_n BPAPK/Epon 828-DDS system was achieved, and a 405% increase in the fracture energy of

Table 1 Thermal, mechanical and morphological properties of BPAPK/Epon 828 modified resins

Resin	Loading level (%)	DMA T_g[a] (°C)	Modulus (GPa)	K_{IC} (MN m$^{-3/2}$)	G_{IC} (J m^{-2})	Phase sep.[b]
7000 M_n	0	213	2.52	0.89	315	–[c]
BPAPK/	20	145	2.55	1.6	905	A
Epon 828-DDS	30	145	2.47	1.8	1390	B
	40	145	2.49	2.5	2344	B
21 000 M_n	0	185	2.33	0.81	281	–[c]
BPAPK/	10	175	2.44	1.1	517	A
Epon 828-MDA	20	160	2.36	1.5	893	–[d]
	25	160	2.42	1.8	1350	B

[a] 1 Hz loss modulus peak corresponding to largest storage modulus decrease

[b] A = Epoxy/amine-rich continuous phase with thermoplastic-rich inclusions; B = thermoplastic-rich continuous phase with epoxy/amine-rich inclusions

[c] Neat epoxy/amine system only one phase

[d] Not measured

Table 2 Thermal, mechanical and morphological properties of tBPK/epoxy-amine modified resins

Resin	Loading level (%)	DMA T_g[a] (°C)	Modulus (GPa)	K_{IC} (MN m$^{-3/2}$)	G_{IC} (J m^{-2})	Phase sep.[b]
3200 M_n tBPKPK/Epon 828-DDS	0	213	2.52	0.89	315	–[c]
	30	180	2.70	1.6	907	B
	40	160	2.74	1.6	877	B
3200 M_n tBPK/Heloxy 69-DDS	30	155	2.87	1.5	737	A
	40	150	3.17	1.9	1104	B
4600 M_n tBPK/Epon 828-DDS	30	165	2.60	1.5	883	A/B
	40	165	2.73	1.9	1277	B

[a] 1 Hz loss modulus peak corresponding to largest storage modulus decrease

[b] A = Epoxy/amine-rich continuous phase with thermoplastic-rich inclusions; B = thermoplastic-rich continuous phase with epoxy/amine-rich inclusions

[c] Neat epoxy/amine system only one phase

Table 3 Thermal, mechanical and morphological properties of MePK/epoxy-DDS modified resins

Resin	Loading level (%)	DMA T_g[a] (°C)	Modulus (GPa)	K_{IC} (MN m$^{-3/2}$)	G_{IC} (J m^{-2})	Phase sep.
5000 M_n MePK/Epon 828-DDS	0	213	2.52	0.89	315	–[b]
	10	195	2.57	0.91	319	–[c]
	20	195	2.96	1.0	359	–[c]
	30	195	2.33	0.97	403	–[c]

[a] 1 Hz loss modulus peak corresponding to largest storage modulus decrease

[b] Neat epoxy/amine system only one phase

[c] Not measured

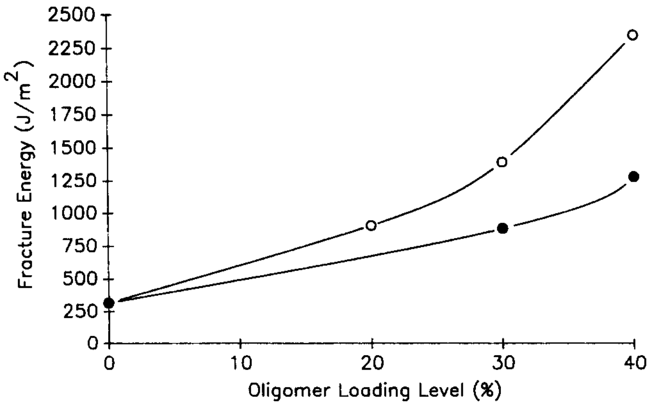


Figure 2 Fracture energy as a function of thermoplastic oligomer loading level. ○, 7000 M_n BPAPK/Epon 828-DDS; ●, 4600 M_n tBPK/Epon 828-DDS

the tBPK/Epon 828-DDS system was obtained with respect to the neat resin system. The modulus was nearly constant, 2.5–3.0 GPa, for all of the systems as a function of the oligomer loading level.

The fracture data reported may not be true K_{IC} and G_{IC} values because thin compact tension samples were used and the satisfaction of the plane strain condition assumed in the derivation of the ASTM E399 equations may not be met. Limited amounts of material were available for testing and an investigation into the effect of sample thickness on K_{IC} and G_{IC} was not performed. The fracture surfaces did not suggest plane stress conditions nor was there significant plastic deformation prior to the initiation of crack growth since P_{max}/P_Q is < 1.0, where P_{max} is the maximum load the specimen was able to sustain, and P_Q is a material failure dependent load defined by ASTM E399. While these values may not be true K_{IC} and G_{IC} parameters, they have been shown to be consistent with literature values of commercial systems, and are reproducible.

The large increase in the toughness of the system is associated with the morphology of the material as a function of the loading level of the amine-terminated oligomer. At the lower loading levels the morphology consists of a highly crosslinked epoxy-rich continuous phase with lightly crosslinked thermoplastic-rich inclusions. A TEM micrograph of a 10% 3100 M_n tBPK/Epon 828-DDS material, shown in *Figure 3*, clearly displays this morphology. (The less electron-dense epoxy/amine-rich phase is the light-coloured continuous phase while the more electron-dense thermoplastic-rich phase is the dark inclusions.) As the loading level of the oligomer is increased the morphology phase inverts and the continuous phase is now a lightly crosslinked thermoplastic (LCT) and the inclusions are epoxy-rich. This is apparent in the micrograph shown in *Figure 4* where the morphology of a 40% 3100 M_n tBPK/Epon 828-DDS material is shown. The system can also be trapped in an intermediate mixed continuous phase morphology as shown in *Figure 5* where each phase is shown with inclusions of the other for a 30% 3100 M_n tBPK/Epon 828-DDS resin. In this system it appears that the viscosity increase associated with gelation became too large before the thermodynamically driven phase separation transport could be completed. Visible evidence for phase separation was not evident in any of the cured materials. The domain sizes are sufficiently large to scatter visible light, but very little scattering is observed indicating that the refractive indices of the two phases must be very similar.

The SEM micrographs of the system as a function of the loading level of the oligomer also suggest that the materials fail by different mechanisms. *Figures 6, 7* and *8* are the fracture surfaces of a neat Epon 828/DDS

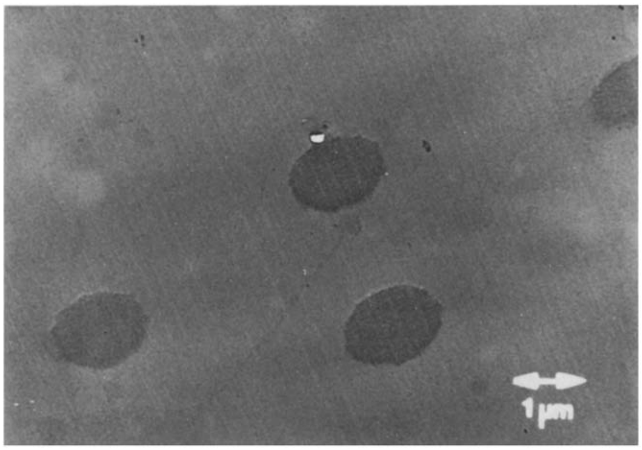


Figure 3 TEM micrograph of 10% 3100 M_n tBPK/Epon 828-DDS showing light epoxy/amine-rich continuous phase with dark thermoplastic-rich inclusions

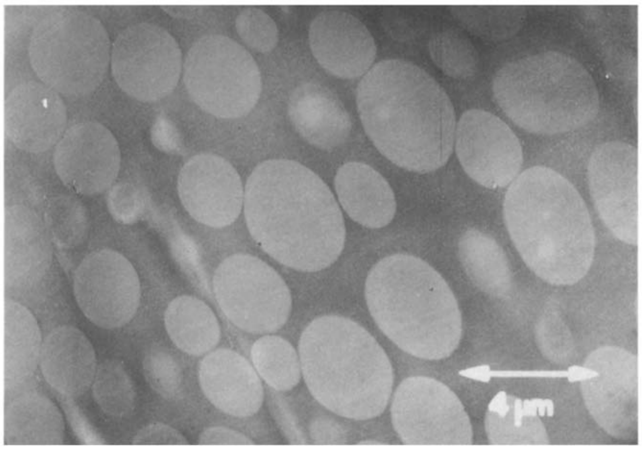


Figure 4 TEM micrograph of 40% 3100 M_n tBPK/Epon 828-DDS showing dark lightly crosslinked thermoplastic, LCT, continuous phase with light epoxy/amine-rich inclusions

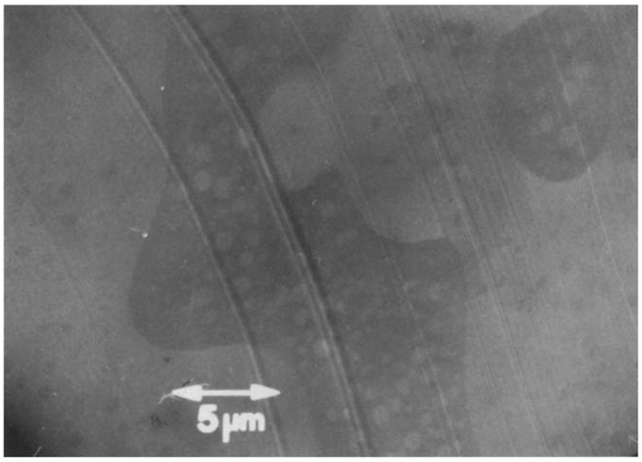


Figure 5 TEM micrograph of 30% 3100 M_n tBPK/Epon 828-DDS showing mixed continuous phases with inclusions of each phase within the other

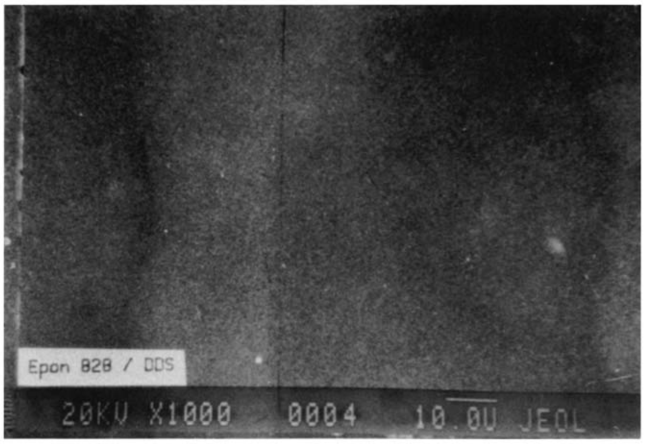


Figure 6 SEM 1000× micrograph of neat Epon 828-DDS showing a featureless fracture surface indicative of brittle failure

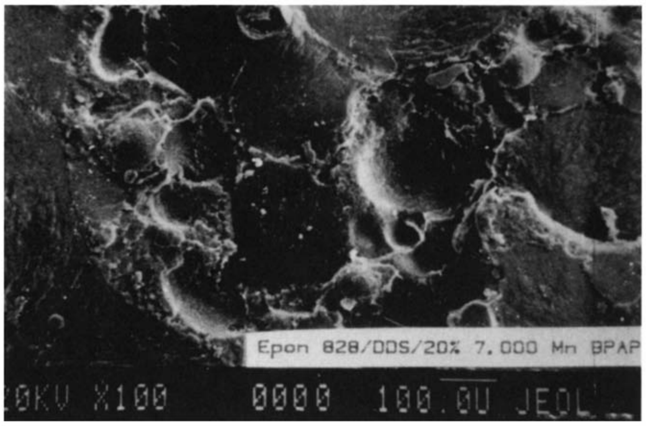


Figure 7 SEM 100× micrograph of 20% 7000 M_n BPAPK/Epon 828-DDS fracture surface showing torn areas within a featureless background

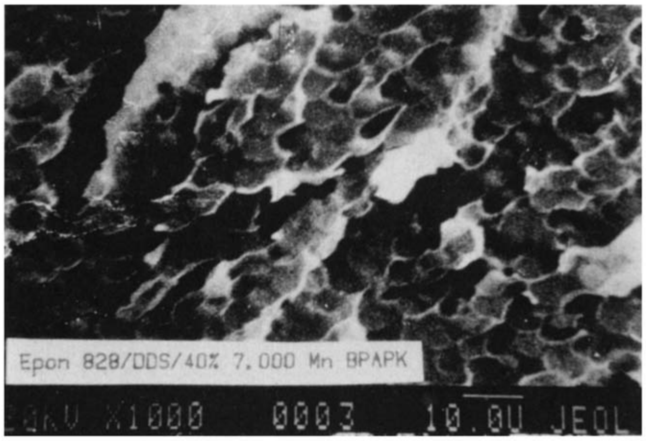


Figure 8 SEM 1000× micrograph of 40% 7000 M_n BPAPK/Epon 828-DDS fracture surface showing extensive tearing

resin, a 20% 7000 M_n BPAPK/Epon 828-DDS resin, and a 40% 7000 M_n BPAPK/Epon 828-DDS resin having fracture energies of 300 J m^{-2}, 900 J m^{-2} and 2300 J m^{-2} respectively. A correlation between G_{IC} and fracture surface topology is evident. The micrograph of the neat Epon 828-DDS resin fracture surface, *Figure 6*, at 1000× magnification is featureless, indicative of a smooth fracture surface and brittle failure. The micrograph of the 40% 7000 M_n BPAPK formulation, *Figure 8*, at the same magnification shows extensive tearing of the fracture surface. This extremely tough sample in fact exhibits significant stress whitening of the fracture surface which is visible to the naked eye. The micrograph of the 20% 7000 M_n BPAK/Epon 828-DDS resin at 100× magnification, *Figure 7*, shows what appear to be large torn rough features within an otherwise featureless background. This fracture surface did not exhibit any stress whitening. This loading level is below that at which phase inversion to a thermoplastic-rich continuous phase occurs and the rough areas may represent fracture regions around the BPAPK-rich inclusions. (Note that the size of these features is much too large to be the BPAPK-rich regions alone.)

The two phase separated regions have been consistently referred to as being either thermoplastic oligomer-rich or epoxy/amine-rich, indicating that each phase is not pure and in fact consists of a chemically bound mixture of each component. Evidence for this behaviour is shown in *Figure 9* where d.s.c. scans of a neat Epon 828/DDS system, and an Epon 828/DDS system loaded with 10, 20, 30 and 40% 3100 M_n amine-terminated tBPK oligomer and the pure tBPK material are represented. The scans show that as the loading level of the oligomer is increased the glass transition temperature (T_g) of the epoxy/amine-rich phase remains approximately constant and the T_g of the LCT phase increases slightly. This data suggests that the composition of the epoxy/amine-rich phase remains nearly constant as a function of the thermoplastic oligomer loading level, while the composition of the thermoplastic-rich phase appears to be changing. As the oligomer loading level is increased the T_g of the thermoplastic-rich phase increases and may indicate the incorporation of more epoxy/amine material into the thermoplastic-rich phase, possibly accounting for its increasing T_g.

The d.s.c. thermal data clearly indicate the T_gs of each phase but do not indicate how the bulk properties of the matrix change with temperature. The storage and loss moduli have been measured to determine the temperature range over which the system softens. Representative curves illustrating the dynamic mechanical properties, as a function of temperature, of the three morphologically distinct systems (thermoset-rich continuous phase with thermoplastic-rich inclusions; mixed thermoplastic-rich and thermoset-rich continuous phases; and thermoplastic-rich continuous phases with a thermoset-rich

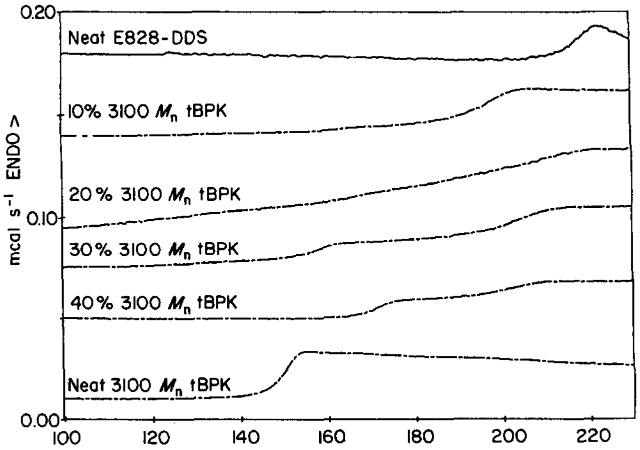


Figure 9 Normalized d.s.c. data as a function of thermoplastic oligomer loading level

included phase) at 1 Hz, for the 3100 M_n tBPK/Epon 828-DDS material are shown in *Figures 10, 11* and *12* for loading levels of 10, 30 and 40%, respectively.

The dynamic mechanical data show that the loading level of the oligomer influences the dynamic modulus of the system. The T_g of the neat Epon 828-DDS resin is 213°C. The T_g decreases to 194°C for the 10% loading level as represented in *Figure 10*. At the 30% loading level, *Figure 11*, two glass transition values are observed. An initial decrease in the storage modulus from about 2.0 to 0.5 GPa occurs, at about 164°C, followed by a further softening to a rubbery state near 202°C. The 40% loading level material, *Figure 12*, exhibits a complete drop in the storage modulus at 173°C to a rubbery material, and the final onset of segmental motion within the epoxy-rich inclusions is seen at 205°C.

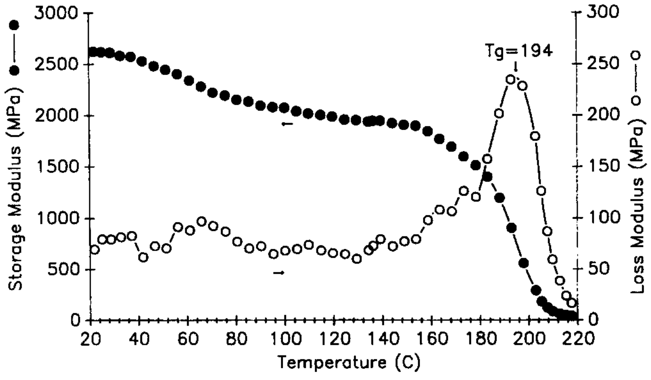


Figure 10 1 Hz dynamic mechanical data of 10% 3100 M_n tBPK/Epon 828-DDS

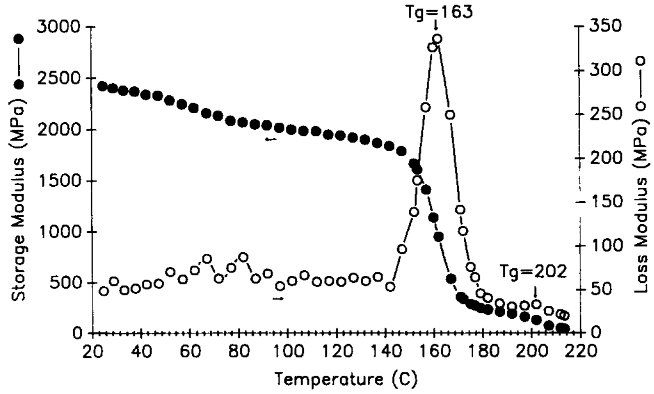


Figure 11 1 Hz dynamic mechanical data of 30% 3100 M_n tBPK/Epon 828-DDS

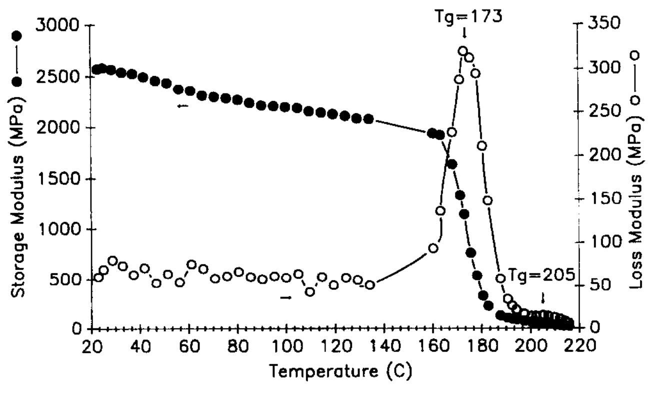


Figure 12 1 Hz dynamic mechanical data of 40% 3100 M_n tBPK/Epon 828-DDS

The dynamic mechanical behaviour of these materials is also explained by the respective morphologies of each system. The 10% loading level material consists of an epoxy/amine-rich continuous phase that goes from a glassy to a rubbery state without a significant influence from the loaded thermoplastic oligomer and exhibits behaviour similar to that of the neat epoxy/amine material. The T_gs of the thermoplastic-rich inclusions were not detectable at the 10% loading level in the dynamic three point bend testing mode. The morphology of this material is shown in *Figure 3*.

In the 30% loading level system, where the mixed continuous phases are represented in *Figure 5*, the storage modulus drops to a near rubbery state, ~0.5 GPa, which is approximately maintained until the T_g of the epoxy/amine-rich phase is passed and the material becomes a rubber. The drop in the storage modulus of this system is quite large because the thermoplastic-rich phase is partially continuous and the associated softening of this phase leaves the partially continuous epoxy/amine phase as the remaining glassy component. As a result, the storage modulus drops to much lower values than the previous cases where the epoxy/amine-rich phase was continuous.

The 40% loading level material is interesting in that its glassy modulus is slightly greater than the 30% loading level material. The morphology of this system is shown in *Figure 4* and is shown to have a LCT continuous phase. At the T_g the storage modulus drops to the rubbery state as the system now consists of a rubbery continuous phase with glassy epoxy/amine-rich inclusions. The transition of the epoxy/amine phase is detectable at 205°C. The slightly greater T_g of the thermoplastic phase of this material may be explained by the curing process of the system. Many factors, both kinetic and thermodynamic, are involved in the phase separation process. One of the influences that could account in part for the increased T_g of this system is its related melt viscosity. The higher loading level oligomer materials exhibit marginally greater viscosities and this increase may hinder phase separation and trap slightly more epoxy/amine material in the continuous phase and, therefore, increase the crosslink density and the associated T_g of the continuous LCT phase. However, this system is still significantly tougher because the increased loading level of the thermoplastic results in a tough LCT continuous phase and any possible trade-off between epoxy/amine entrapment is greatly outweighed by this morphological phase inversion.

Finally the solvent absorption characteristics of the 40% 7000 M_n BPAPK/Epon 828-DDS system are compared to the neat Epon 828-DDS material in water, deicing fluid, methylene chloride, JP5 jet fuel, and Skydol hydraulic fluid. *Figures 13, 14* and *15* show the weight per cent of absorbed water, deicing fluid, and methylene chloride respectively as a function of time for the two systems. The data in *Figure 13* represents the thermoplastic oligomer-modified system that is phase inverted, where the thermoplastic-rich phase in the continuous phase absorbs approximately half as much water after 1150 h of immersion as the corresponding neat epoxy/amine resin. Immersion in deicing fluid for the same amount of time, shown in *Figure 14*, also results in considerably less, ~40%, solvent uptake in the thermoplastic-modified material than in the unmodified system. However, the amorphous LCT continuous phase

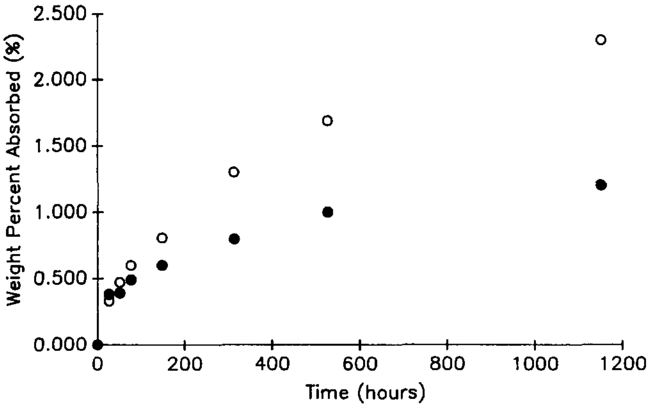


Figure 13 Water absorption as a function of time. ○, Neat Epon 828-DDS; ●, 40% 7000 M_n BPAPK/Epon 828-DDS

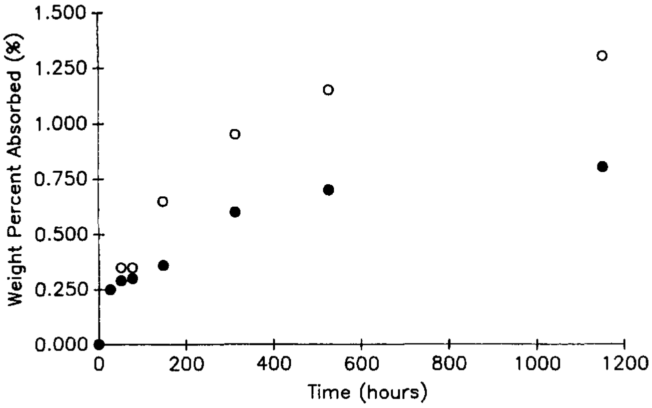


Figure 14 Deicing fluid absorption as a function of time. Symbols as for *Figure 13*

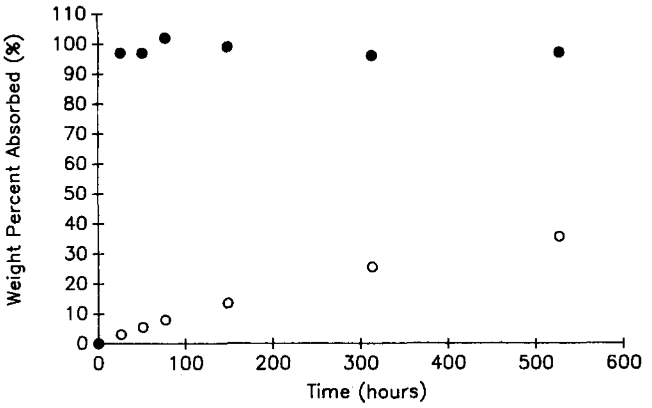


Figure 15 Methylene chloride absorption as a function of time. Symbols as for *Figure 13*

is much more sensitive to methylene chloride than the tightly crosslinked epoxy/amine network. *Figure 15* shows that the 40% 7000 M_n BPAPK/Epon 828-DDS system picks up nearly 100 wt% methylene chloride in 24 h and maintains this level over time. The neat Epon 828-DDS resin absorbs less than 5% in 24 h and absorbs 40% after 525 h of immersion. Absorption of JP5 jet fuel, and Skydol hydraulic fluid is not shown here but negligible absorption for both formulations was measured.

The phase separated morphology is again correlated to the solvent absorption data. The deleterious effect of water absorption on the bulk properties of epoxy systems is well documented, and attributed in part to the hydrophilic nature of hydroxyl groups created during an amine cure[27,28]. Non-polar thermoplastics are less sensitive to water absorption, and the system where the continuous phase is thermoplastic-rich has been shown to be substantially less water sensitive compared to the epoxy/amine system. The amorphous thermoplastic continuous phase is also shown to be more sensitive to methylene chloride. Because of its inherently higher molecular weight between crosslinks the LCT phase is not as tightly bound as the epoxy/amine system, allowing for rapid solvent diffusion through the network and an equilibrated system.

Improved solvent resistance, as well as improved material properties, could be achieved if a semicrystalline continuous phase could be created. Because both the neat BPAPK, and the neat tBPK amine-terminated oligomers are amorphous, crystallinity within the oligomer modified material cannot be achieved. However, the amine-terminated MePK oligomer is semicrystalline and attempts are being made to induce crystallinity within the modified network. Unfortunately, the MePK system is more difficult to incorporate into commercial epoxy resins.

In summary, a tough matrix material can be achieved via the incorporation of amine-terminated oligomeric poly(aryl ether ketone)s into commercial epoxy/amine resins while maintaining processability. Higher molecular weight functionalized oligomers yield higher K_{IC} and G_{IC} values. The substantial increase in resistance to fracture, while maintaining a modulus of 2.5–3.0 GPa and processing characteristics similar to conventional thermosetting systems has been achieved. It is known from the TEM data that at low thermoplastic oligomer loading levels the phase separated morphology consists of an epoxy/amine-rich matrix with thermoplastic-rich inclusions, and at high loading levels the matrix is phase inverted and consists of a LCT continuous phase with epoxy/amine-rich inclusions. It has also been shown that a mixed continuous phase exists for an intermediate loading level.

As expected, the greatest resistance to fracture is attained when the lightly crosslinked amine-terminated thermoplastic oligomer-rich phase is continuous. The phase inversion point has been shown to be near the 30 wt% oligomer loading level in two different commercial epoxy resins. The morphology of this system creates a continuous phase matrix where the average distance between the crosslinks is substantially increased and allows the chain mobility necessary for large energy absorption deformations prior to catastrophic failure. Therefore, at these high loading levels the inherent ductility of the thermoplastic material is incorporated into the bulk properties of the phase separated system and is responsible for the observed tremendous increase in fracture resistance. Deformations and ductile fracture become similar to those associated with the neat parent aromatic thermoplastic material. The phase inverted morphology leads to greater resistance to water and deicing fluid absorption but also leads to greater methylene chloride absorption.

At loading levels below the phase inversion point the thermoplastic-rich inclusions probably act as stress concentrators within the epoxy-rich matrix. These stress concentrations, however, should be small as a result of the similarity in the tensile, shear and bulk moduli of the two phases. These small stress concentrations may cause the initiation of some localized shear yielding in the matrix resulting in increased resistance to crack propagation. These inclusions also have the ability to deform in a ductile manner thereby increasing the energy required for crack propagation. Energy absorption is further facilitated by the incorporation of some thermoplastic oligomer into the epoxy/amine-rich continuous phase increasing the average molecular weight between crosslinks resulting in increased molecular mobility and ductility.

Finally, the glass transition temperature of the oligomeric thermoplastic modified Epon 828/DDS resins at the higher loading levels ranges from 145°C for the BPAPK materials to 170°C for the tBPK systems. These T_gs are sufficient for high performance applications. Initial results also indicate that K_{IC} and G_{IC} values obtained for tBPK materials are greater than those obtained for BPAPK materials at comparable number average molecular weights.

CONCLUSIONS

In conclusion, it has been shown that a series of amine-terminated poly(aryl ether ketone)s can be incorporated into a variety of commercial high performance epoxy/amine resin systems through a solventless process. The modified materials have been shown to exhibit three distinct morphological states with properties unique to each. Resins where the morphology consists of a LCT continuous phase with epoxy-rich inclusions have been shown to be the toughest materials and may be more correctly considered as processable thermosetting poly(aryl ether ketone)s rather than toughened epoxies.

The formulations in *Tables 1* and *2* represent a series of materials that possess the desirable processing characteristics of low viscosity thermosetting resins and exhibit toughness properties approaching those of thermoplastic materials while maintaining or increasing the modulus of the system, having glass transition temperatures required for high performance applications, and greatly reduced water absorption properties in comparison to the unmodified epoxy/amine systems.

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