# Miscible Blends of Poly(aryl Ether Ketone)s and Polyetherimides

J. E. HARRIS and L. M. ROBESON\* AMOCO Performance Products, Inc., Bound Brook, New Jersey

## Synopsis

A new class of high performance engineering resins, poly(aryl ether ketone)s, has emerged with a property balance not offered by existing polymeric materials. Blends of poly(aryl ether ketone)s with other polymers have not been described in the open literature, although several patents have revealed interesting and important properties of certain blend combinations. Ultern polyetherimide has been found to be miscible over the entire composition range and as a consequence is a very effective heat distortion temperature builder, particularly if the poly(aryl ether ketone) is allowed to crystallize. Crystallization kinetics and mechanical properties were studied as a function of blend composition and poly(aryl ether ketone) melting point. The blends exhibited a maximum in toughness at intermediate compositions along with an accompanying maximum in poly(aryl ether ketone) crystallinity. The chemical resistance of the polyetherimide is significantly improved with the addition of a poly(aryl ether ketone). In organic chemicals, the improvement was expected when tensile stress was plotted vs. log time to rupture. However, in aqueous bases, the resistance of the blends was much greater than anticipated. This property profile suggests that these blends will be useful as thermoplastic composite matrix resins.

## **INTRODUCTION**

A new class of engineering polymers [poly(aryl ether ketone)s (PAEKs)] has emerged with a property balance not offered by existing polymeric materials. Some of the earliest work on poly(aryl ether ketone)s was described by Bonner<sup>1</sup> and involved the electrophilic aromatic substitution (e.g., Friedel–Crafts catalyzed) reaction of aromatic diacylhalides with unsubstituted aromatic compounds such as diphenyl ether. The evolution of this class into a much broader range of polymers was achieved by Johnson and co-workers,<sup>2</sup> who first produced poly(aryl ether ketone)s by nucleophilic displacement. More recent references to the interesting properties of this class of polymeric materials include.<sup>3-5</sup>

Blends of poly(aryl ether ketone)s with other polymers have not been mentioned in the open literature, although several patents have revealed interesting and important properties of certain combinations.<sup>6-9</sup> Poly(aryl ether ketone) miscibility with polyetherimides was noted in a recent European patent application<sup>7</sup> and will be the subject of this paper.

The poly(aryl ether ketone)s utilized in this paper are crystalline materials with excellent hydrolytic, thermal, acid, base, and chemical resistance. These attributes are combined with excellent mechanical properties and a very high potential use temperature due to a high crystalline melting point. Poly-

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<sup>\*</sup>Present address: Air Products Corp., Trexlertown, Pennsylvania.

etherimides are amorphous materials with high glass transition temperatures. They, however, offer poor resistance to aqueous bases, fair solvent resistance, and cannot be utilized above the glass transition temperature. The combination of poly(aryl ether ketone)s and Ultern polyetherimide offers an interesting balance of properties as they exhibit miscibility in the amorphous state.

## **EXPERIMENTAL**

The poly(aryl ether ketone)s used in this study had the following structures:



PAEK-I was prepared from hydroquinone and 4,4'-difluorobenzophenone using a process similar to that described in Ref. 10. The reduced viscosity as measured in concentrated sulfuric acid at 23°C and 1 wt % was 1.05 dL/g. PAEK-II was prepared from *p*-phenoxybenzoyl chloride in hydrogen fluoride using BF<sub>3</sub> as a catalyst. The reduced viscosity measured under the same conditions as above was 1.9 dL/g. One percent by weight  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was added to PAEK-II as a thermal stabilizer as suggested by Ref. 11.

The polyetherimide had the following structure:



PEI had an RV of 0.5 dL/g as measured at 0.2 wt % and 25°C in chloroform and was obtained from the General Electric Company as ULTEM 1000.

Blends of PEI and PAEK-I were made via extrusion at 360–380°C followed by sample fabrication which involved compression molding at 360–380°C or injection molding at 370–390°C. Blends containing PAEK-II were made in a Brabender at 360–400°C and compression-molded at 380–400°C. These latter blends were not extruded or injection-molded because of the limited quantity of material available.

Mechanical properties were obtained as per the relevant ASTM tests (tensile properties: ASTM D-638; tensile impact strength: ASTM D-1822; notched Izod impact strength: ASTM D-256; heat distortion temperature: ASTM D-648). Crystalline melting points and glass transition temperatures were determined using a DuPont 1090 thermal analyzer equipped with a DSC dual sample cell. To determine the observed melting points  $T_m$  as a function of composition, the blends were cooled to 300°C from 400°C at 160°C/min and isothermally crystallized. They were then heated at 10°C/min and the  $T_m$  was determined as the maximum in the resultant endotherm. The glass transition temperatures  $T_g$  of the blends were determined by DSC using the following procedure. Samples were placed in DSC pans and heated to 400°C

for 1 min in the barrel of a Tinius–Olsen melt index cell. The samples were then removed and quenched immediately into liquid nitrogen. The resultant amorphous samples were heated at  $10^{\circ}$ C/min, and the  $T_g$  was determined as the onset of the change in heat capacity.

Crystallization studies were performed using a Perkin-Elmer DSC-2 calorimeter equipped with an external cooling unit. Samples were prepared by cooling from 400°C to room temperature at 30°C/min after pressing into a thin (ca. 5 mil) film. Portions of these films were placed in the DSC and heated at 160°C/min to 400°C for 1 min prior to any isothermal crystallizations. As the equilibrium melting point for PAEK-I,  $T_m^0$  is reported to be between 395 and 400°C,<sup>3</sup> this pretreatment was conducted in an attempt to remove any effects of thermal history. The samples were then cooled at 160°C/min to the desired isothermal crystallization temperature  $T_r$ . The time at  $T_x$  required to reach the maximum in crystallization rate was recorded as  $t_c$ . When  $T_x$  was below the temperature of maximum rate of crystallization, the samples would, in some cases, crystallize before the baseline stabilized. In these instances,  $t_c$  could sometimes be measured by quenching the sample as noted above for  $T_g$  determination and then heating at 160°C/min to  $T_x$ . Nevertheless, there existed a range of  $T_x$ 's for which  $t_c$ 's could not be determined.

Dynamic mechanical properties were determined on compression molded samples utilizing a torsion pendulum similar to the design of Nielsen<sup>12</sup> and as described in ASTM D-4065.

## EXPERIMENTAL RESULTS

#### **Thermal Characteristics**

The observed melting points and glass transition temperatures for the PAEK-I/PEI blends are given in Table I as a function of composition. At all compositions, a single, sharp glass transition temperature was observed indicating the miscibility. The single, sharp  $T_g$ 's for the blends were also observed on samples tested using mechanical methods to determine  $T_g$  values (e.g., resilience measurements<sup>13</sup> and torsional pendulum methods). Within experi-

0		-	,		
Composition (wt % PAEK-I)	$\begin{array}{ccc} T_x & T_m^{a} \\ (^{\circ}C) & (^{\circ}C) \end{array}$		$\frac{\Delta H_f/w_1}{(\text{cal/g})}$	T <sup>b</sup> <sub>g</sub> (°C)	
100	300	343	9.7	142	
80	300	340	9.6	155	
70	300	340	11.1	161	
60	300	340	11.3	168	
50	300	340	10.4	176	
40	300	340	9.8	183	
0	_	—	—	215	

TABLE I Melting Points and Glass Transition Temperatures for PAEK-I/PEI Blends

<sup>a</sup>Observed melting point after crystallizing at  $T_x$ .

 ${}^{\rm b}T_{\rm g}$  on amorphous samples quenched from 400°C.

mental error, the variation of  $T_g$  with composition obeys the Fox equation,

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \tag{1}$$

where  $w_i$  is the weight fraction of the component exhibiting  $T_{gi}$ .

For blends isothermally crystallized at 300°C, little variation of melting point with composition was observed. Also shown in Table I are the relative degrees of crystallinity  $(\Delta H_{f1}/w_1)$  for the blends. These quantities are useful in comparing the degree of PAEK-I crystallinity as a function of blend composition. As all compositions were crystallized at 300°C, any effect of temperature on the degree of crystallinity, which is well known and described in Ref. 14, is eliminated. Interestingly, the degree of crystallinity goes through a maximum at 30–40 wt % PEI concentration. This has also been observed for blends of poly(butylene terephthalate) and the polyhydroxyether of bisphenol  $A^{15}$  as well as poly(ethylene oxide) blends with the polyhydroxyether of bisphenol A.<sup>16</sup> This appears to be a common attribute of miscible blends containing one crystallizable component, and the most likely explanation is the increased mobility to be found in the interlamellar regions due to the presence of a noncrystallizing diluent. Additionally, an increased volume is present prior to the onset of spherulitic impingement.<sup>5</sup>

Blends containing equal proportions of PAEK-II and PEI were also found to be miscible with one  $T_g$  as indicated in Table II. The  $T_g$ 's were determined by DSC on amorphous films quenched from the melt, and the melting points were determined on samples crystallized by cooling from 410 to 27°C at 10°C/min. Note the effect of thermal history on the observed melting point by comparing the values given in Table I to those given in Table II. Also

Composition	$T_g (^{\circ}C)^{a}$	$T_m (^{\circ}C)^{b}$		
PEI	215			
50% PEI, 50% PAEK-I	176	332		
50% PEI, 50% PAEK-II	181	360		
50% PEI, 25% PAEK-I, 25% PAEK-II	176	351		
PAEK-I	142	337		
PAEK-II	152	361		
50% PAEK-I, 50% PAEK-II	144	360		

TABLE II Melting Points and Glass Transition Temperatures of Various PAEK-PEI Blends

 ${}^{*}T_{g}$ 's determined by DSC on amorphous samples quenched from 400-410°C.

<sup>b</sup>Melting points determined on samples crystallized by cooling at  $10^{\circ}$ C/min from  $410^{\circ}$ C to room temperature.

shown in Table II are the  $T_g$  and  $T_m$  for a PAEK-I/PAEK-II/PEI blend. As blends of PAEK-I and PAEK-II are known to be isomorphic,<sup>5</sup> it is not surprising that the ternary blend exhibits a single melting point and  $T_g$ . A 50/50 blend of PAEK-I and PAEK-II has a melting point and melting range nearly identical to PAEK-II itself.<sup>5</sup> However, the PAEK-I/PAEK-II/PEI 25/25/50 blend has a melting point of 351°C, and a much broader melting range indicating that significantly more PAEK-I units are present in the lamella. The reason for this observed change is probably kinetic. In the former case kinetics are fast with respect to the cooling rate during crystallization. Crystallization takes place at high temperatures and kinetics favor PAEK-II. In the latter case kinetics are slow with respect to the cooling rate due to the presence of the PEI. Crystallization takes place at a much higher degree of supercooling where neither PAEK-I nor PAEK-II is favored. As a result, both enter the lamella at comparable rates resulting in a crystalline phase composition similar to that of the overall blend.

An attempt was made to fit the crystallization kinetics of several of the blends to the Avrami equation<sup>17</sup>:

$$X/X^{\infty} = 1 - \exp(-Kt^n) \tag{2}$$

where t is the time at  $T_x$  (X = 0 at t = 0), X is the fraction crystallinity at time t,  $X^{\infty}$  is the ultimate fraction crystallinity, and n and K are constants. The ratio  $X/X^{\infty}$  was determined by integrating the area under the crystallization exotherm of the isothermal DSC trace obtained when determining  $t_c$ . A typical plot of  $\log_{10}[-\ln(1 - X/X^{\infty})]$  vs.  $\log_{10}t$  is shown in Figure 1. Plots



Fig. 1. Avrami plot for PAEK-I at 300°C.

were typically linear up to about  $X/X^{\infty} = 0.5$ , where the increase in  $T_{\mu}$ , due to crystallization and spherulitic impingement, caused a dramatic decrease in rate. This, of course, is typical of semicrystalline polymers. The slope of the plots between  $X/X^{\infty} = 0$  and  $X/X^{\infty} = 0.5$  (i.e., n) varied between 3 and 5 with no apparent correlation with crystallization temperature or composition. Qualitatively our results agree with those of Velisaris and Seferis<sup>18</sup>; however, the initial value of n they report for PAEK-I is 2.4. Variations in duplicate runs lead us to conclude that the cause was uncertainties in the experimental technique. Binsbergen and DeLange<sup>19</sup> have shown that n, K, and  $t_0$  (the start of crystallization process) are highly correlated. In our case samples were first heated to 410°C and then either cooled to  $T_x$  at 160°C/min, or quenched and then heated from 27°C to  $T_x$  at 160°C/min. In either case the transition to  $T_x$  took on the order of 40 s. Upon reaching  $T_x$ , the DSC temperature light immediately came on, indicating the average cell temperature was  $T_x$ . This instant was taken as  $t_0$ ; i.e., t = 0, although some crystallization may have occurred during the transition to  $T_x$ . It took several more seconds for the baseline to stabilize which, in some instances, could possibly have obscured the start of the crystallization exotherm. This uncertainty in  $t_0$  and  $X/X^{\infty}$  at short times probably accounted for our inability to accurately determine n. The isothermal crystallization times  $t_c$  did not suffer from this uncertainty and were much more reproducible. However, there was the aforementioned inability to determine  $t_c$  at intermediate temperatures where the individual rates were at their maximum. Values of  $t_c$  vs.  $T_x$  are shown in Figure 2 for



Fig. 2. Isothermal crystallization half times  $t_c$  vs. crystallization temperatures for PEI-PAEK-I blends: (**v**) PAEK-I; (**n**) PAEK-II; (**o**) 50/50 PAEK-I/PAEK-II; (**a**) 50/50 PAEK-I/PEI; ( $\bigcirc$ ) 25/25/50 PAEK-I/PAEK-II/PEI; +, 50/50 PAEK-I/PEI; ( $\longrightarrow$ ) best fit of experimental data to eq. (3).

several different compositions. In order to extrapolate the data, they were fit to the following form:

$$\left(\frac{n-1}{n}\right)^{1/n} \frac{1}{t_c} = A \exp\left[\frac{B}{T_g - 51.6 - T_x} - \frac{CT_m^{0^2}}{T_x^2(T_m^0 - T_x)}\right]$$
(3)

where we will treat A, B, and C as empirical constants. The quantity  $T_m^0$  as mentioned previously is the equilibrium melting point for lamellae of infinite dimensions. Equation (3) was derived by assuming the following form for eq.  $(2)^{17}$ :

$$X/X^{\infty} = 1 - \exp\left[-K(Gt)^{n}\right]$$
<sup>(4)</sup>

where G is the linear growth rate as defined by Hoffman et al.<sup>20</sup> for regime 1 kinetics:

$$G = A \exp\left(\frac{B}{T_g - 51.6 - T_x}\right) \exp\left[\frac{-CT_m^{0^2}}{T_x^2(T_m^0 - T_x)}\right]$$
(5)

Since  $t_c$  is the maximum in the crystallization exotherm, it can be obtained by taking the second derivative of eq. (4) and setting it equal to zero. After substitution of the above expression for G, the result is eq. (3). A value of 4 was employed for n regardless of composition, as this was a crude average of the values obtained. As for the quantity  $T_m^0$ , Blundell and Osborn<sup>4</sup> have determined a value of 395°C for PAEK-I. This compares well with the value of 400  $\pm$  5°C determined by the authors using Hoffman–Weeks extrapolation of the observed melting point. A value for PAEK-II could not be determined with any precision by this latter method because of the higher crystallization temperatures involved combined with the poorer melt stability of this polymer. A value of 430°C was assumed. Average values of  $T_m^0$  were used for blends of PAEK-I and PAEK-II. Finally, in the case of the blends the melting point depression that always accompanies miscibility was ignored.

The solid lines in Figure 2 represent the best fit of eq. (3) to the data. PAEK-I and II exhibit a maximum in crystallization rate between 230 and 240°C with  $t_c$ 's estimated at 2.5 s. PAEK-I crystallizes slightly faster at low temperatures due to its lower  $T_g$ , while PAEK-II has faster kinetics at higher temperatures because of its higher melting point. The 50/50 PAEK-I/PAEK-II blend has kinetics similar to PAEK-II, which is not surprising if the assumption is correct that the higher melting constituent predominates the crystals.<sup>5</sup> The maximum rate of about 100 s for a 50/50 PAEK-I/PEI blend occurs at 250°C. Substituting PAEK-II for PAEK-I produces little change in  $T_g$  but a significant increase in crystallization rate presumably due to the higher melting point.

As it was shown previously that the crystallization behavior of a (50/50) PAEK-I/PAEK-II blend is similar to pure PAEK-II, one might expect a (25/25/50) PAEK-I/PAEK-II/PEI blend to have kinetics similar to a (50/50) PAEK-II/PEI blend, and this appears to be the case. The former is slightly slower presumably because of the PAEK-I taking part in the crystallization,

which is exemplified by the slightly lower melting point. Both of these blends have minimum crystallization times at  $250^{\circ}$ C on the order of 20-30 s.

# DYNAMIC MECHANICAL RESULTS

Dynamic mechanical results (tan  $\delta$  and G' vs. temperature) were obtained using a torsion pendulum. The PAEK-I sample and the 50/50 by weight PEI/PAEK-I samples were run quenched, as molded, and annealed at 200°C for 2 h. The glass transition data on the various samples are listed below and the values for quenched specimens are in good agreement with the values determined for amorphous samples by DSC.

Material	$T_{g}$ (°C)
PEI	212
PAEK-I (quenched)	137
PAEK-I (annealed)	142
50/50 PAEK-I/PEI (quenched)	176
50/50 PAEK-I/PEI (annealed)	185

The tan  $\delta$  and shear modulus (G') data vs. temperature for PAEK-I (annealed), PEI, and a 50/50 by weight PAEK-I/PEI blend (annealed) are illustrated, respectively, in Figures 3(a-c). Samples were run dry and after equilibration in water at 23°C. PAEK-I exhibits a broad  $\beta$  transition over a wide temperature range centered at  $-60^{\circ}$ C when dry. The origin of this transition is presumably a restricted motion around the arylether bond similar to that seen in polysulfone. In polysulfone this transition has been shown by NMR studies to involve 180° flips of the phenyl rings.<sup>21</sup> With water present, a distinct  $\gamma$  transition appears at  $-100^{\circ}$ C superimposed over the existing  $\beta$ transition. PEI exhibits a broad  $\beta$  transition at 70°C when dry and in addition a rather large  $\gamma$  transition appears at  $-105^{\circ}$ C with water present. The  $\gamma$  transition in polyimides is well known and seen only in the presence of absorbed moisture.<sup>22</sup> It most likely involves a concerted motion involving sorbed water and small parts of the polyimide chain. A  $\gamma$  transition in polysulfone is observed at -100 °C, and it has been postulated to be due to an oscillation of a complex of water and the  $SO_2$  linkage.<sup>23</sup> The  $\gamma$  transition seen in PAEK-I probably has a similar origin. A likely explanation is that the  $\gamma$ transition in both PAEK-I and PEI is due to a concerted motion between absorbed water and the carbonyl groups. The  $\beta$  transition in polyimides is also well documented<sup>22</sup> and attributed to complex oscillations propagated along the chain involving the aromatic and benzimide rings. Not surprisingly, the PAEK/PEI blend also exhibits a  $\beta$  transition (at 40° both dry and wet) and a  $\gamma$  transition (at -100°C wet only). The single  $\beta$  transition of the blend is between the respective values for PAEK-I and PEI, although it is skewed toward PEI. This shows that the  $\beta$  transition is not solely dependent upon the structure of the polymer backbone but is also influenced by the intermolecular environment experienced by a backbone segment as has been noted in other polymer blends.<sup>24</sup>



Fig. 3. Dynamic shear modulus (G') and  $\tan \delta$  obtained by torsion pendulum for PAEK-I (a), PEI (b), and their 50/50 blend (c): (-----) dry and (---) wet.



Fig. 3. (Continued from the previous page.)

## **MECHANICAL PROPERTIES**

Blends of PAEK-I and PEI were injection-molded into ASTM test specimens using a stock temperature of 380°C and a mold temperature of 140°C. Compositions containing 30% or more of PEI were amorphous as molded under these conditions, but could be crystallized by annealing at 250°C for several minutes. To accomplish this, dry test specimens were placed in a cavity mold of the same depth as their thickness (3 mm). The mold was placed between the platens of a hydraulic press which was heated to 250°C. After 30 min the press was allowed to cool and the specimens removed. The mechanical properties at 23°C of both the as-molded and annealed specimens are given in Table III. As expected, the annealed and crystallized blends exhibit a significant increase in strength and modulus accompanied by a decrease in ultimate elongation as compared with the as-molded specimens. Tensile impact strength goes through a maximum of over 400 kJ/m<sup>2</sup> at 60 wt % PAEK-I for the as-molded test specimens. This is understandable because PAEK-I is substantially crystalline as molded under the above conditions, while blends containing 40% PEI are completely amorphous. The development of crystallinity is usually associated with a decrease in toughness, and thus it could be argued that a maximum would not be observed if compositions were compared at an equivalent level of PAEK crystallinity. However, the annealed specimens also exhibit a maximum in tensile impact strength, although when normalized for PAEK content they also exhibit a maximum in the level of crystallinity (see Table I). This synergistic behavior is quite interesting and is being investigated further.

	l Izod n)	Annealed	76	74	69	69	64	69	64	59
	Notchec (J/n	As molded	84	106	85	80	80	80	64	59
	Tensile impact strength (kJ/m <sup>2</sup> )	Annealed	170	254	248	233	224	195	189	147
TABLE III Mechanical Properties of Injection-Molded PAEK-1/PEI Blends		As molded	279	327	369	414	376	344	262	168
	Ultimate elongation (%)	Annealed	42	53	50	29	42	ŝ	22	99
		As molded	103	115	129	114	107	80	97	<b>6</b> 8
	Tensile modulus (GPa)	Annealed	3.63	3.57	3.51	3.48	3.45	3.30	3.35	3.18
		As molded	3.56	2.85	2.81	2.84	2.91	2.92	2.98	3.19
	Tensile strength (MPa) As molded Annealed	Annealed	93.7	102.7	105.4	106.8	106.1	105.4	104.0	113
		As molded	88.9	80.6	89.6	86.1	87.5	91.6	93.7	104.0
	Composition	(wt % PAEK-I)	100	80	20	<b>09</b>	50	40	30	0

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WEIGHT % PEI

Fig. 4. Heat deflection temperature (ASTM D-648) at 1.8 MPa (264 psi) vs. composition for as-molded and annealed (crystallized) PAEK-I/PEI blends.

Elongation at break increases with PAEK content up to a PAEK/PEI ratio of 70/30 in the as-molded specimens. It probably begins to drop above this level due to the crystallinity which begins to develop. Annealed specimens exhibit a tensile strength of about 105 MPa over a broad composition range.

Figure 4 shows the dependence of the heat distortion temperature at 1.8 MPa on composition. The as-molded specimens show a negative deviation from linearity. This is expected as the  $T_g$ 's obey the Fox equation; however, the deviation is exaggerated by the fact that only PAEK-I is substantially crystalline as molded. After annealing, however, the blends show a positive deviation from linearity. There are probably several reasons for this. All compositions show an increase in heat distortion temperature which is due to (1) crystallization of the PAEK-I which produces an effect similar to crosslinking and (2) densification and relaxation of molded in stresses upon annealing. The blends show incremental increases in heat distortion temperature for two additional reasons. First, as the PAEK-I crystallizes, the amorphous phase becomes enriched in PEI, thus raising the blend  $T_g$ . Second the PAEK crystallizes to a higher fraction in the blends than in the unblended state as was discussed previously.

#### ENVIRONMENTAL RESISTANCE

Figures 5(a) and 5(b) compare the environmental stress crack resistance of several PAEK-I/PEI compositions. Blends were compression molded in a 20-mil cavity mold at 400°C. The moldings were cooled to  $250^{\circ}$ C and held there before cooling to room temperature for 30 min to fully crystallize the PAEK component. Test strips of 3 mm width were shear cut from the moldings, placed under tension, and surrounded with cotton patches. The cotton patch was saturated with solvent and the time to rupture was measured. The cotton patch was surrounded with aluminum foil to inhibit solvent



Fig. 5. Environmental stress crack resistance (ESCR) of PAEK-I/PEI blends in toluene (a) and trichloroethylene (b) at 23°C. Plots are of applied tensile stress vs. time to rupture.

evaporation. Two solvents were used: toluene representing aromatic hydrocarbons and trichloroethylene representing chlorinated aliphatic hydrocarbons. The effectiveness of PAEK-I in improving the environmental stress rupture resistance of PEI in each of these solvents is clearly demonstrated even at the addition level of 30 wt %. At a 70% addition level, in some cases, failure was judged to occur by creep elongation rather than by rupture. In these instances, the solvent plasticized the blend to the point that it could deform without breaking until the stops on the stress jig were encountered. At this point, the strain was approximately 50% and failure was arbitrarily assumed to have occurred.

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Temperature (°C)	Time (h)	Weight loss (10% NaOH)			
		PEI	50% PEI, 50% PAEK-I		
40	3552	10.7%	-0.63% (gain)		
60	2520	82.6%	-0.64% (gain)		
80	259	16.2%	-0.58% (gain)		
80	594	74.1%	-0.48% (gain)		
80	1104	100%	-1.02% (gain)		

TABLE IV Weight Loss Data on PEI and a 50/50 PEI/PAEK-I Blend

As with other polyimides, PEI exhibits very poor resistance to aqueous bases. PEI exhibits a weight loss rate in hot caustic similar to polycarbonate. It was noticed that PAEK-I/PEI blends exhibit marked superiority in basic environments over PEI. We observed even greater resistance than expected from the averaged weight loss rates of the constituents. The result are shown in Table IV. Only the sample of PEI/PAEK-I 50/50 at 80°C exhibited any sign of surface erosion after 1000 h exposure, long past the point where PEI was totally disintegrated. Apparently the miscible character of this blend allows for a protective layer of PAEK to inhibit base-induced hydrolysis.

## CONCLUSIONS

Ultem polyetherimide is miscible with poly(arylether ketone)s of significantly different ether/ketone content. The reason for this observed miscibility will be an interesting subject for future work. However, the structural window of miscibility appears to be very wide. As a consequence, Ultem is a very effective heat distortion temperature builder for PAEKs. Blends of equal proportions of both constituents have amorphous  $T_g$ 's above 170°C, and, after the development of crystallinity,  $T_g$ 's approaching 190°C are observed. The effect on the crystallization kinetics of the PAEK is significant as expected from the large increase in  $T_g$ . However, blends containing as little as 30% by weight PAEK are crystallizable, and the rate is very sensitive to the melting point of the PAEK. A 30°C increase in PAEK melting point increases the crystallization rate by a factor of 4-5.

Because of the complete miscibility, the blends are necessarily mechanically compatible; however, they exhibit the unusual behavior of showing a maximum in toughness (as judged by tensile impact strength) at intermediate compositions. Solvent resistance of PEIs, as expected, is significantly improved with the addition of a PAEK. In organic solvents the improvement is as expected when tensile stress is plotted vs. log time to rupture. However, in caustic environments the resistance of the blend is much greater than what is expected from the weight-averaged values of the constituents.

This briefly outlined property profile suggests numerous applications for the blends such as in antiwear and abrasion devices, fibers and filaments, chemical process equipment, and thermoplastic composites. In many applications the ESCR required is greater than that offered by PEIs, but considerably less than PAEKs. Conversely, the blends may be preferred over PAEKs because they maintain rigidity at higher temperatures due to their higher  $T_g$ 's. Thus the blends could extend the use of PAEKs in thermoplastic composites to higher temperatures approaching 200°C, not to mention the possible advantage in toughness.

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