Phase behaviour, morphology and properties of poly(ether imide)/polyarylate blends

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Poly(ether imide) (PEI)/polyarylate (PAr) blends of different compositions were obtained by melt blending followed by compression moulding. 90/10 and 80/20 blends appeared miscible by both differential scanning calorimetry and dynamic mechanical thermal analysis. The other compositions were biphasic; one phase was almost pure PAr and the other PEI with a fairly constant PAr content of roughly 25%. This phase behaviour agreed with both the observed transparency and the fracture surfaces observed by scanning electron microscopy. The mechanical properties of the blends as a function of composition showed values close to linearity or were even enhanced, with an unexpected synergism in ductility. This behaviour and that observed in other polymer blends, suggest that, assuming isotropy and constant crystallinity content, the relation between increased miscibility level and improved ductility is not a general rule. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Among polymer blends, those comprising two engineering polymers are (after rubber-toughened blends) probably those that have been paid the greatest attention. This is because blending is the main way to achieve (1) a more balanced set of mechanical properties than that provided by fibre or particle reinforcement or (2) specific polymer properties whilst maintaining the mechanical properties of the main component at a level that commodity polymers cannot offer.

Poly(ether imide) (PEI) is a high-performance thermoplastic with especially good properties for mechanical and electrical applications as well as good chemical and flame resistance; it has been also used as a matrix for fibre-reinforced composites but is fairly expensive. Polyarylate (PAr) also shows relevant mechanical and electrical properties as well as ultraviolet radiation and flame resistance, but it is less rigid and resistant than PEI.

Reports of blends of PEI are not rare in the literature. PEI was reported to be fully miscible with poly(ether ether ketone) (PEEK)[1,2] and polybenzimidazole (PBI)[3], and appeared to be immiscible both with poly(ether sulfone) (PES)[4] and in the ternary blends comprising PEI/poly(p-phenylene sulfide)/polysulfone[5]. Moreover, PEI/liquid crystal polymer[6,7] and epoxy/PEI[8] blends have been also studied.

Blends of PAr of the composition used in this work have been fairly well studied. Among the most recently reported blends, besides blends with a liquid crystal polymer[9], partial miscibility was seen in the case of blends of PAr with poly(ethylene terephthalate)[10] and

polycarbonate (PC)[11,12], full amorphous miscibility in the case of poly(butylene terephthalate)[13], PBI[14] and a copolyester of cyclohexanedimethanol, ethylene glycol and terephthalic acid (PETG)[15], and was temperature-dependent in the case of phenoxy[15]. A complete review of interchange reactions that can take place in blends of polyesters like PAr has been recently published[16].

PEI/PAr blends, with the exception of some brief information in the patent literature[17-19], have not been investigated from the point of view of either their mechanical compatibility or their phase behaviour in the solid state. Both polymers are interesting from a practical point of view, some of their features are complementary and they can be easily melt-blended. For these reasons, in this work PEI/PAr blends of different composition have been obtained by melt blending and their phase behaviour studied by differential scanning calorimetry (d.s.c.) and dynamic mechanical thermal analysis (d.m.t.a.). Moreover, the morphology observed by scanning electron microscopy (SEM) and the phase behaviour have been related to mechanical properties obtained from a tensile test.

EXPERIMENTAL

The polymers used in this work were commercial products. PEI was Ultem-1000 from General Electric. Its structural formula is:

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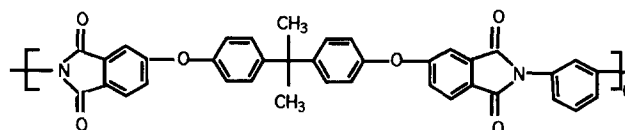
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PEI has an intrinsic viscosity $[\eta] = 0.494\,\mathrm{dl\,g^{-1}}$, as measured in chloroform at 23°C. Its molecular weights, estimated by the manufacturer, are $M_n \approx 12\,000$ and $M_w \approx 30\,000$.

PAr was Arilef U-100, from Solvay. It has the following chemical structure:

CH₃ / O
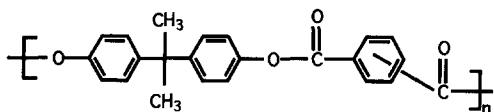
The molecular weights of PAr were measured by gel permeation chromatography in tetrahydrofuran at 30°C. They were $M_n = 21\,500$ and $M_w = 51\,400$.

Both polymers were dried *in vacuo* before mixing: the PEI at 135°C for 8 h and the PAr at 80°C for 24 h. Melt mixing was carried out in a Brabender Plasticorder at 300°C at a mixing blade speed of 30 rev min^{-1}. The mixing operation was maintained until a constant torque was obtained, at a mixing time of 12 min. For the sake of comparison, the pure blend components were subjected to the same processing conditions.

After blending, the pure polymers and the blends were compression moulded at 300°C, to obtain films with approximate thickness of 0.1 mm and sheets with approximate thickness of 1 mm. After moulding, both the films and sheets were rapidly cooled from the melt by immersing them in cold water. Specimens for tensile testing (ASTM D638, type IV) were punched out from the films with a pneumatic die. Samples for calorimetric analysis, dynamic-mechanical analysis and Vicat softening temperature measurements were obtained from the sheets.

Calorimetric analysis was carried out in a DuPont DSC cell equipped with a DuPont 2000 Thermal Analysis System at a heating rate of 20°C min^{-1} in a nitrogen atmosphere. The glass transition temperature (T_g) of the pure polymers and the blends was determined at the onset of the transition. Dynamic mechanical analysis was performed on a DMTA from Polymer Laboratories which provided the storage (E') and loss (E'') moduli and the loss tangent (tan δ). A heating rate of 4°C min^{-1} was employed at a frequency of 1 Hz. Vicat softening points were measured at 50°C h^{-1} and with a 1000 g load (ASTM D1525), stacking three layers in order to achieve the minimum thickness.

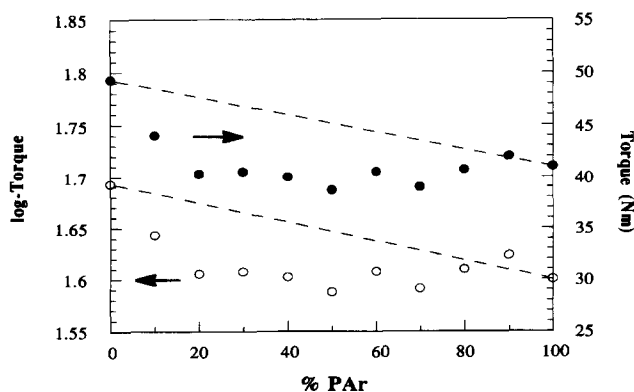Tensile tests were performed using an Instron 4301 tensile tester, at a crosshead speed of 10 mm min^{-1}. The different parameters were obtained from the force–displacement curves. A mean of at least eight specimens was tested for the determination of each datum.

The fractured surfaces of some samples were examined by SEM using a Hitachi S-2700 electron microscope operated at 15 kV. In order to remove the PAr phase, an etching treatment was carried out in a solution of potassium hydroxide and ethanol before coating the surfaces with gold.

RESULTS AND DISCUSSION

Melt behaviour

A first estimation of the blend miscibility can be obtained from transparency in the melt state. Although, in some cases, the miscibility criterion cannot be applied[20], there are many systems in which transparency and miscibility are clearly related. In PEI/PAr blends, both components and the blends with 90/10 and 80/20 compositions were transparent. Blends with compositions between 70/30 and 20/80 were opaque and finally the PEI/PAr (10/90) blend was translucent. These differences in transparency for different blend compositions were seen both in the melt and in the solid state, and agree with previously reported observations[17,19]. Thus transparency data seem to indicate that blends with high PEI contents are homogeneous, while those having PEI contents of 70% or lower are multiphasic materials.

In *Figure 1*, the log-torque of blending and the torque of blending are plotted against blend composition. The number of miscible blends with negative deviation behaviour (NDB) from log-additivity is increasing steadily[21] and, as a consequence, linear or positive deviation behaviour (PDB) is far[22] from a rule of miscible blends. Another exception to this rule takes place in these blends. This is because, in *Figure 1*, the immiscible blend composition values are those that show very little deviation from a log-linear relationship, while the log-torque of miscible compositions progressively separates from the log-linear line. Additionally, at these blending conditions, the PEI-rich blends mainly show an improved processability with respect to that of the pure components because of the low torque values measured.

Solid-state phase behaviour

The phase behaviour of PEI/PAr blends was studied by d.s.c., d.m.t.a. and Vicat softening temperature measurements. In *Figure 2*, the glass transition temperatures of the blends, measured both in the second calorimetric scan and by d.m.t.a., are shown as a function of blend composition. As can be observed from the filled circles obtained by calorimetry, two regions exist in this graph. At high PEI contents a single glass transition is found, while at PEI contents of 70% or lower, two T_gs appear. This indicates the existence of a single phase or at least second phases of less than roughly 0.01 μm in dimension[23] and consequently, for practical purposes, miscibility at 90% and 80% PEI contents in the blends. We will refer to this as 'practical miscibility'. For PEI contents between 70 and 10% the high T_g is lower than that of pure PEI and the low T_g, although a little erratic, appears somewhat higher than that of pure PAr. This overall behaviour points to the existence of partial
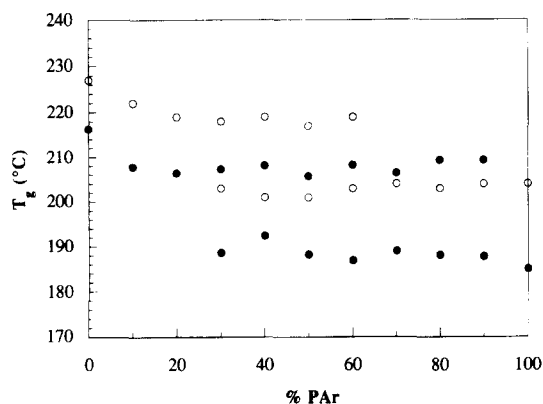

Figure 1 Torque (●) and logarithm of torque (○) as a function of PEI/PAr blend composition

Figure 2 T_g values *versus* PEI/PAr blend composition measured by d.s.c. (●) and d.m.t.a. (○)
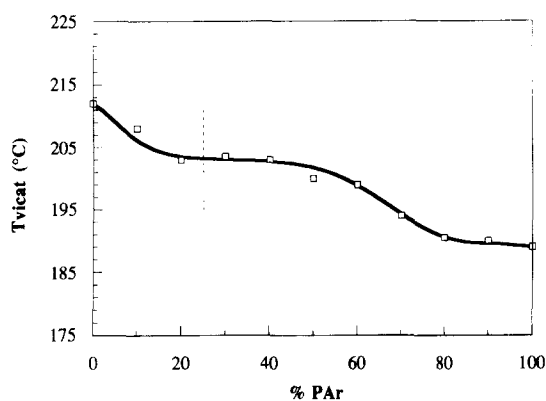

Figure 3 Vicat softening points of PEI/PAr blends as a function of composition (reprinted from ref. 25)

miscibility in this composition region. These calorimetric results agree with the transparency results, and are indicative of the existence of some affinity between the two blend components.

The results obtained by d.s.c. are corroborated by d.m.t.a. As observed from the unfilled points of *Figure 2*, and although as usual the absolute T_g values by d.m.t.a. are higher, the T_g behaviour is similar to that found by calorimetry. Blending did not change the important secondary transitions of either PEI or PAr that clearly influence the mechanical properties. There are two differences, however, between d.s.c. and d.m.t.a results. Firstly, at low PEI contents, the high-temperature transition is not observed by d.m.t.a, and only small shoulders on the main T_g peaks are observed. This is due to the weak consistency of the PAr matrix at these temperatures and to the small content of PEI-rich phase. The second difference is that the low-temperature T_gs of the biphasic blends also appear close to the T_g of PAr, but in this case are slightly below it. From both the d.s.c. and d.m.t.a results it can be concluded that the real T_g change must be fairly small. As a consequence, the low T_g phase should be almost entirely composed of only pure PAr.

The T_g values of the PEI-rich phases in the biphasic region may be used to estimate their composition. This estimation has been made by applying the Fox equation[24] to the experimental T_g data, and leads to an approximate mean PAr content of 25% in the PEI-rich phase.

Finally, this phase behaviour agrees with the Vicat softening temperature measurements of *Figure 3*. It has

been noted[25] that this parameter shows a different behaviour with respect to blend composition depending on the miscibility level. Thus, in miscible blends a continuous variation is observed, while in immiscible systems a sigma-shaped relation exists, with a 'plateau' at high content of each component and a variation at intermediate compositions. In the PEI/PAr system, the high PEI content region (up to 80% PEI composition) shows the expected behaviour for a miscible system. In the biphasic region the shape is sigmoidal, the Vicat softening temperature of the miscible PEI/PAr (80/20) system being one of the 'plateaux' and the other that of the pure PAr. These results are additional evidence of the phase behaviour of PEI/PAr blends and of the suitability of Vicat measurements for a preliminary fast determination of the phase behaviour of amorphous polymer blends.

Morphology

After both cryogenic and tensile fracture, no second phase could be observed in the fracture surface of the blends, this being similar to that of the pure polymers. This proves the full cohesive nature of the fracture and predicts remarkable values of stress and elongation at fracture. Chemical attack of the PAr revealed the presence of the two phases and gave additional support to the practical miscibility of the 90/10 and 80/20 blends that appeared monophasic by microscope observation even after harsh chemical attack.

In *Figures 4a*, *b* and *c*, the morphologies of the cryogenically fractured 60/40, 50/50 and 30/70 compositions are shown. The surfaces of the tensile fractured specimens, after chemical treatment, appeared very similar to those fractured cryogenically. As can be seen in *Figure 4a*, the PAr holes are homogeneously distributed on the matrix and take the form of elongated ellipsoids. The surface of the holes is seldom clear, and rough surfaces with hardly deformed short and thin fibrils usually appear. This proves the very high adhesion level that exists at the surface and the existence of some continuity of the matrix through the interphase.

In the case of the 30/70 blends of *Figure 4c*, that are seen at an angle of 50° from the vertical axis, elongated ellipsoids and the rough nature of the surface are clearly seen. No sign of dewetting was ever observed. The observed shape is probably due to the flow during compression moulding.

Finally, the fracture surface of the 50/50 blend composition that is seen in *Figure 4b* shows two apparent co-continuous phases. This indicates that phase inversion takes place at a composition close to 50%. Despite the fact that other factors besides the viscosity of both components influence the phase inversion composition[26], it may be calculated by the proposed relation[27]:

$$\frac{\eta_1 \phi_2}{\eta_2 \phi_1} \approx 1$$

that predicts the composition at which phase inversion takes place. Thus, if torque values are used instead of viscosity, the PEI composition that phase inversion would take place is 55%. Thus the PAr-rich phase of the 50/50 composition would be more continuous, in close agreement with the mechanical response that will be seen in most of the mechanical properties–composition plots.
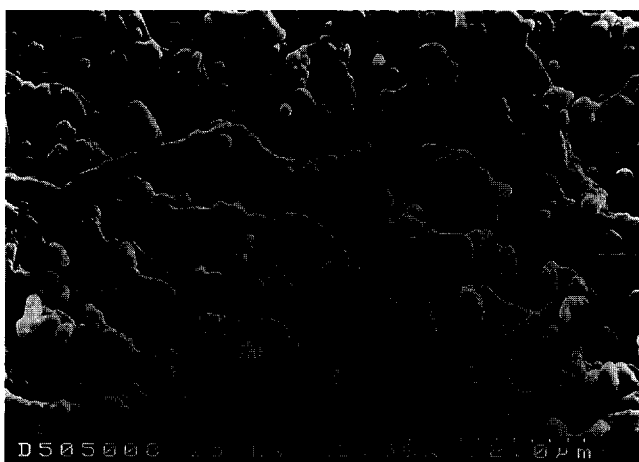
Figure 5   Modulus of elasticity *versus* blend composition for compression-moulded PEI/PAr blends

Figure 6   Yield stress *versus* blend composition for compression-moulded PEI/PAr blends

Figure 7   Break stress *versus* blend composition for compression-moulded PEI/PAr blends

Figure 4   SEM photomicrographs of cryogenically fractured PEI/PAR blends of different composition (a) 60/40; (b) 50/50; (c) 30/70

Mechanical properties

The mechanical properties of the blends are shown in *Figures 5–8*. Tensile fracture always took place in the cold drawing zone. Under the conditions of the test PEI yielded by means of clear shear bands that produced a sharp stress decrease after yielding. Shear bands in the case of PAr were more diffuse. As can be seen in *Figure 5* where the moduli of elasticity are shown, the overall behaviour is greater than the arithmetic average of the moduli of the two pure components. Mainly in the blends that are very rich in PEI, a usually small
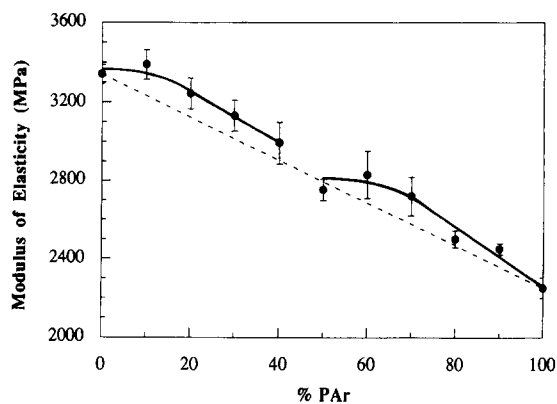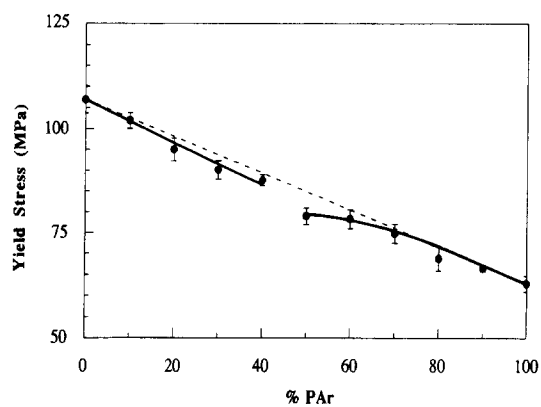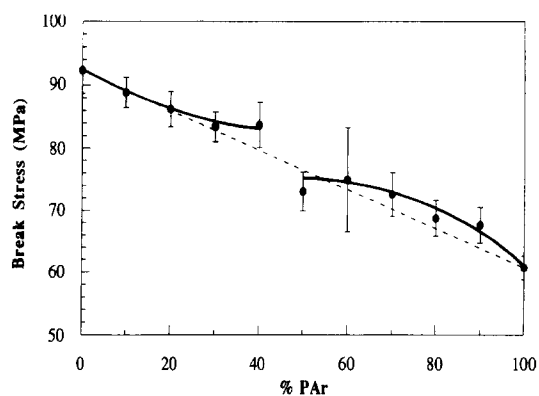
synergism appears probably due to the miscible nature of the blends at these compositions. The deviation of the 50/50 blend is probably due to phase inversion.

With respect to the synergism of the modulus of elasticity, it is known that the specific interactions that may give rise to miscibility usually produce a negative excess volume of mixing[23,28]. These volume contractions would give rise to increased moduli of elasticity[29] because of the decrease in the free volume available, although this is small[30]. Thus density increases should be associated with miscibility and synergisms in the modulus of elasticity. Hence, the specific volume of the
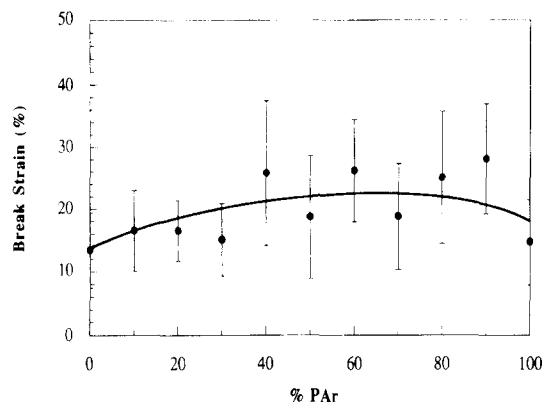
Figure 8 Break strain *versus* blend composition for compression-moulded PEI/PAr blends
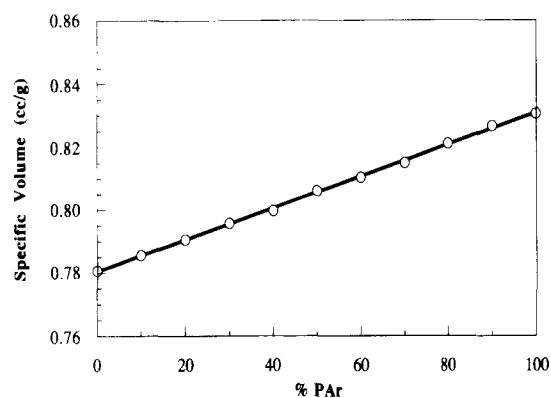

Figure 9 Specific volume of PEI/PAr blends as a function of composition

blends is shown in *Figure 9*. As can be seen the plot is really linear, and no difference can be distinguished between the miscible part corresponding to the blends very rich in PEI and the rest of the blend compositions. This indicates that the synergism in the modulus of elasticity can hardly be due to volume changes: if the latter took place they were too small to resolve, because the accuracy of the density gradient column ($\pm 2 \times 10^{-4}$ g cm^{-3}) is 12 times larger than the usual density change in miscible blends which is in the range of 0.5–0.6% (ref. 31). Thus these synergistic values are not a consequence of negative volume of mixing, but a feature observed even in fully immiscible blends[32].

The behaviour observed in *Figure 5* is corroborated by the plot of the yield stress against composition of *Figure 6*. As can be seen, the values are lower with respect to the arithmetic mean than those of the modulus of elasticity, but most of the features commented on above also appear in this property which, despite being measured at a slightly greater deformation, usually follows the tendency of the modulus of elasticity.

In *Figure 7*, the break stress of the blends is shown against blend composition. As can be seen, although a single straight line may also be plotted, the two curves plotted are an improved fit to the experimental values. *Figure 7* demonstrates that the two curves are in this case more clearly indicative than usual of the fact that it is the matrix, although modified by the presence of the minority phase, that controls fracture. In the case of co-continuous 50/50 composition it is the PAr that

mainly controls fracture because, as was seen before, this component constitutes the matrix of the blend.

In *Figure 8* the ductility of the blends is shown against blend composition. A clear synergism can be seen over all the composition range. Despite the cohesive fracture and remarkable adhesion observed by SEM, it is a surprising and particularly positive result. This is because the relation between the presence of the other component in each phase, interfacial adhesion and ductility or other fracture parameters is usually fulfilled. Thus, in summary: miscible polymer blends, despite the negative volume of mixing[33], give rise to synergisms or linear behaviour in fracture properties[34,35], partially miscible blends give values close to linearity[36] and immiscible blends give values well below linearity[32,33].

Besides miscibility level, other important factors also influence ductility. Thus the ability to crystallize may change as a result of blending, with concomitant changes of properties[37]. Moreover, it is well known that in oriented blends a certain miscibility level is not a *sine qua non* condition to reach an acceptable mechanical performance. Thus, even in the case of practical full immiscibility, the development of oriented structures may be responsible for the appearance of synergistic properties[38,39]. This is not only in the case of short-term properties, where the small strain and stress are not very demanding of adhesion, but also in the case of properties closely related to fracture, such as ductility or impact strength. However, fairly isotropic blends, with their small ratio of interphase area to dispersed component content, need an improved adhesion between phases that, although other ways to achieve this exist[40], usually comes from partial miscibility[41].

Thus increased miscibility levels should give rise to increased ductility levels. However, the counter-evidence is growing continuously. For instance, these compression-moulded PEI/PAr blends show a greater ductility level than could be expected from their miscibility level or that observed in several fully miscible blends. In addition, fully immiscible compression-moulded non-crystallized blends like PEEK/PES[42], and amorphous PC/phenoxy[43] as well as phase-separated PC/poly-(methyl methacrylate)[44], gave ductility values close to linear behaviour.

Other parameters, such as different Poisson moduli and the possible greater volume increase with deformation of the dispersed phase, could give rise to compression stresses that would help adhesion. But if this were true, the opposite should take place when the matrix polymer is the other component of the blend, and different behaviours are not seen in the ductility–composition plots of PEI/PAr blends. Thus, we must conclude that the miscibility level, as measured by the change of T_gs referred to those of the pure components, does not play a definitive role when determining the ductility behaviour in fairly isotropic morphologies.

CONCLUSIONS

PEI/PAr blends are partially miscible. The maximum PAr content miscible in PEI is, whatever the composition, roughly 25%. This gives rise to miscibility in 90/10 and 80/20 blends and to partial miscibility in the rest of compositions. Brabender mixing and compression moulding produce homogeneous blends with the

dispersed phase being elongated ellipsoids firmly bonded to the matrix. This gives rise to fracture surfaces similar to those of the homopolymers that agree with the unusually high values of tensile properties observed. The lack of a relation between miscibility and ductility levels, which also occurs for other reasonably isotropic polymer blends, indicates that it is not a general rule.

ACKNOWLEDGEMENTS

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