

Increasing the Resistance of Poly(ether imide) to Solvents by Blending with Poly(trimethylene terephthalate)

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ABSTRACT: We studied the sorption behavior of poly(ether imide) (PEI) upon the addition of minor amounts (10 and 30%) of miscibilized poly(trimethylene terephthalate) (PTT) under acetone and other common solvent environments. Significant solvent sorption (maximum solvent sorption = 8–12 wt %) and changes in mechanical properties were observed only in the case of acetone. The sorption of acetone was Fickian and partially irreversible. Both sorption and solubility decreased markedly upon PTT addition to PEI, most likely as a result of a blending-induced decrease in the free volume. The decreases in the

modulus were attributed to plasticization, and the mixed effects on the elongation at break were attributed to the combined effects of fast plasticization and slower swelling. The joint effects of applied stress and the presence of acetone were studied with creep tests. In these tests, a combination of a free volume increase, plasticization, and superficial cracking of PEI was proposed to occur. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 896–903, 2009

Key words: blends; diffusion; mechanical properties

INTRODUCTION

It is well known that some of the applications of polymer materials are related to their inherent resistance to a variety of chemical compounds. However, some undesirable property changes can occur upon the sorption of fluids by the solid polymer. The most important effects of sorption are related to the deterioration of fracture properties induced by chemical attack on the surface and to the plasticization of the polymer. Other negative processes, such as the deterioration of the polymer–polymer interphase in multicomponent polymeric materials, may also happen. Both of these processes obviously depend on the nature of the polymer and on the fluid in contact with it, and they are difficult to predict. This is especially true in the case of sorption, for which deviations from Fickian-like kinetics are often encountered. Moreover, the amount of fluid sorption varies significantly from system to system, and this makes the study of new polymer/chemical compound pairs necessary.

Poly(ether imide) (PEI) is a high-performance amorphous thermoplastic that exhibits great thermal resistance as well as excellent mechanical performance. As an engineering material, it can be exposed to different environments. For this reason, studies on PEI's response to the presence of water,^{1,2} dichloromethane,^{3,4} a wide spectrum of organic liquids,⁵ and some fluids used in aviation,⁶ as well as its gas sorption^{7,8} and effects on the mechanical properties,^{1,2,5–7} have been performed. Poly(trimethylene terephthalate) (PTT) is a semicrystalline thermoplastic commercialized since 1998. The available literature on solvent sorption in this matrix is scarce because only the sorption of methylene chloride⁹ and some dyes¹⁰ has been examined.

It is known that PEI/PTT blends are miscible¹¹ throughout the whole composition range; furthermore, it has been observed that blending induces a decrease in the free volume of this system.¹¹ This effect can act as a hindrance to sorption because solvent penetration and space availability for the solvent molecules are reduced. Therefore, it is expected that the addition of small amounts of PTT to PEI could improve the mechanical performance of the resulting material by reducing solvent sorption. In a preliminary study on solvent sorption by PEI, the measured sorbed amounts of carbon tetrachloride, ethanol, and isooctane were below 0.3%. In the case of water, the equilibrium content was 0.8%, and no effects on the properties of PEI were observed. In the case of acetone, both the sorbed amount and

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the effects on the mechanical properties were significant.

In this work, the sorption of acetone in PEI and in PEI/PTT blends rich in PEI is studied to determine the possibility of improving the resistance of PEI to acetone by blending it with PTT and to contribute to the knowledge of the behavior of miscible polymer blends in the presence of solvents. The effects of sorption on the mechanical properties of the blends and the pure PEI (used as a reference) are also examined. Besides the usual tensile behavior, we analyze the creep behavior of the blends and their pure components in both acetone and acetone-free environments.

EXPERIMENTAL

The PEI was Ultem 1000 (General Electric; melt flow index = 7.7 g/10 min at 337°C and with a 6.7-kg load), and the PTT was Corterra CP509200 (Shell Chemicals; $[\eta] = 0.92$ dL/g). Before processing, neat polymers and blends were dried at 150°C for 4 h in an air oven to avoid moisture-induced degradation reactions. PEI/PTT blends (90/10 and 70/30) were obtained via mixing in a corotating twin-screw extruder/mixer (ZK-25, Collin) at 290°C with a screw speed of 30 rpm. The obtained rod extrudate was cooled in a water bath and pelletized. Neat polymers and blends were injection-molded in a Battenfeld BA 230E reciprocating-screw injection-molding machine to obtain 2-mm-thick ASTM D 638 type IV tensile specimens and 3.2-mm-thick flexural-type ASTM D 790 specimens. The screw of the plasticization unit had a diameter of 18 mm, a length/diameter ratio of 17.8, a compression ratio of 4, and a helix angle of 17.8°. The barrel temperatures were 260°C for the PTT, 285°C for the 70/30 PEI/PTT blend, 320°C for the 90/10 PEI/PTT blend, and 340°C for the PEI. A mold temperature of 21°C, a screw rate of 140 rpm, an injection speed of 10 cm³/s, and an injection pressure of 2000 bar were used in the injection-molding process.

The sorption/desorption measurements were carried out on tensile specimens at 23°C and 50% relative humidity. The specimens were immersed in acetone until an almost constant weight was reached in the pure PEI, and then they were hung for desorption. Samples were periodically removed from the solvents, wiped down, and quickly weighed in a Gibertini E42S balance (accuracy = 10⁻⁴ g).

The acetone content in the samples at time t was calculated as follows:

$$\text{Acetone content at time } t = (\text{Weight at time } t - \text{Initial weight}) / \text{Initial weight}$$

Differential scanning calorimetry (DSC) analyses were performed with a PerkinElmer DSC-7 differen-

tial scanning calorimeter. The samples were heated from 15 to 270°C at a heating rate of 20°C/min. The crystalline contents were calculated from the crystallization enthalpy and melting enthalpy with a value $\Delta H_m^o = 145$ J/g for 100% crystalline PTT.¹² Dynamic mechanical analysis (DMTA) was performed in a TA Instruments Q800 DMA, which provided the loss tangent values against the temperature from -120 to 280°C at a heating rate of 4°C/min and a frequency of 1 Hz.

X-ray diffraction (XRD) patterns were recorded in a Philips PW 1729 GXR X-ray diffractometer at 45 kV and 50 mA with a Ni-filtered Cu K α radiation source. The scan speed was 0.5°/min.

Tensile tests were carried out in an Instron 4301 machine at 23°C with a crosshead speed of 10 mm/min. The yield and break stresses, Young's modulus, and break strain were obtained from the load-elongation curves of the specimens before sorption, during sorption (100 h), at equilibrium sorption, and after desorption.

Creep tests were carried out in a Rosand CRE-164 machine with a three-point bending geometry with a load of 30 MPa at 23°C. Deflection was measured with an accuracy of ± 0.001 mm. The tests were performed both in the absence and in the presence of acetone: the specimens, immersed in acetone, were packed into polyethylene bags, and were sealed after the expulsion of the air. The results were expressed as the creep compliance $J(t)$:

$$J(t) = \varepsilon(t) / \sigma_0$$

where $\varepsilon(t)$ is the flexural strain and σ_0 is the applied load. Each creep curve was calculated from the mean values of three test specimens.

RESULTS AND DISCUSSION

Sorption

In Figure 1, the amount of the solvent sorbed by PEI, PTT, and the 90/10 and 70/30 blends is plotted against the square root of time. The linear behavior shown in Figure 1 up to roughly 56 days [half-life ($t^{1/2}) = 2200$ s^{1/2}] reveals that the sorption process is Fickian for the pure polymers and for the blends. When the sorption curves are plotted as M_t/M_∞ versus $t^{1/2}$, where M_t is the amount of the sorbed solvent at time t and M_∞ is the equilibrium sorption at long times, the diffusion coefficient is found to be the same (1.1×10^{-9} cm²/s) for the neat polymers and the blends. This is because the higher slope of the curve of PEI in Figure 1 also leads to a proportionally higher equilibrium concentration, that is,

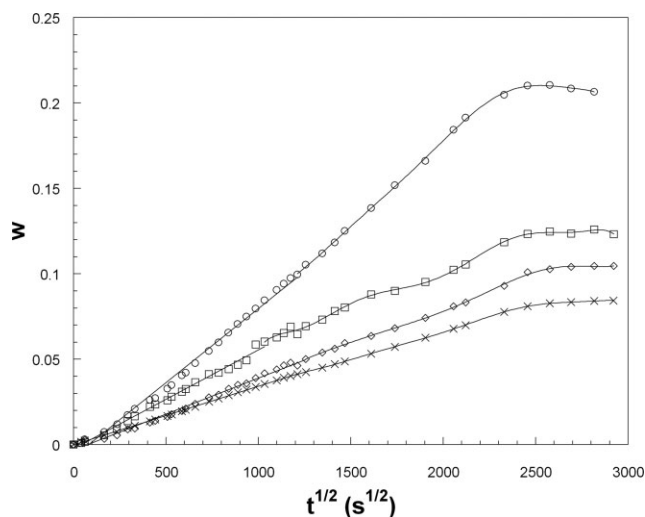


Figure 1 Acetone sorption curves of (×) PTT, (□) a 70/30 PEI/PTT blend, (◇) a 90/10 PEI/PTT blend, and (○) PEI.

solubility. However, as shown in Figure 1, both the equilibrium concentration and the amount of acetone sorbed after a fixed exposure to acetone (the slope of the sorption curve) are fairly different and smaller in the case of PTT. This is in agreement with its greater barrier performance.

Figure 1 also shows that only small amounts of PTT in the blends are necessary to reduce both the solubility and the slope of the sorption curve of acetone in PEI. The decrease is substantial and can be attributed to the fact that, as in many miscible blends, mixing PEI with PTT induces a net loss of free volume in the blends¹¹ versus that of the pure components. Besides the decrease in the free volume, other parameters, such as the size of the free volume voids with respect to the volume of the penetrant molecule and the affinity between the solvent and the matrix, can also influence the solvent sorption. The reduction in the free volume is an additional parameter that needs to be taken into account when either diffusion or solubility is discussed.

Upon a comparison of the performances of the two blends, it appears that the addition of 30% PTT to PEI leads to equilibrium sorption values and a slope of the sorption curves higher than those of the 90/10 blend. These results are unexpected because the substitution of PEI by PTT in the 70/30 blend should lead its curve to be farther from that of pure PEI than that of the 90/10 blend. This indicates that the sorption effects of PTT in the blends are due not only to the lower sorption ability induced by its presence but also to the modification of any physical characteristics of PEI. Thus, it would be interesting to test whether this enhanced sorption behavior at low PTT contents represents a minimum across the PTT composition range. It would also be interesting

to find the location of this minimum, provided that it exists. Similar anomalous behavior has been reported in previous works, including the sorption of acetone by PEI/poly(ether ether ketone) (PEEK) blends.¹³ The equilibrium sorption values observed in Figure 1 are large and indicate an affinity between the liquid and the polymer. This is supported by the similarity between the solubility parameter of acetone ($19.7 \text{ MPa}^{1/2}$)¹⁴ and that of PEI (between 20 and $23 \text{ MPa}^{1/2}$).^{5,15} Values of the solubility parameter for PTT are not reported in the literature; however, we would expect this value to lie between those of poly(ethylene terephthalate) ($21.5 \text{ MPa}^{1/2}$)¹⁵ and poly(butylene terephthalate) ($21.6 \text{ MPa}^{1/2}$)¹⁵ because the structure of PTT is intermediate between those of poly(ethylene terephthalate) and poly(butylene terephthalate). Thus, the solubility parameter of PTT should also be similar to that of acetone.

An attempt was made to study possible acetone-induced plasticization by means of DSC and DMTA. The DSC curves of the sample in the presence of acetone were not completely clear near the glass-transition temperature (T_g). The DMTA scans were performed with a relatively fast heating ramp rate ($25^\circ\text{C}/\text{min}$) and a low starting temperature to minimize the effects of acetone evaporation. The results are shown in Table I. In the case of PEI and its blends, T_g decreased to close to room temperature. This indicates that plasticization exists, but the results are not entirely reliable because the specimens were clearly swollen as a result of heating-accelerated evaporation. For this reason, the plasticization effect is also discussed in view of the changes in the mechanical properties.

Solvent-induced crystallization of PTT is an additional factor that can influence acetone sorption, and it was studied with DSC and XRD. The XRD patterns of the pure PTT reference before sorption and at equilibrium (maximum) sorption are shown in Figure 2(a,b), respectively, whereas the corresponding scans of the 70/30 blend are shown in Figure 2(c,d). The scans of the 90/10 blend were equivalent to those of Figure 2(c,d). As can be seen in the scan of the pure PTT [Fig. 2(a)], an amorphous halo appeared before sorption, indicating the absence of crystallinity. The peaks that correspond to the crystalline phase of PTT (also seen in annealed samples) develop after equilibrium sorption is reached,

TABLE I
 T_g Values of the PEI/PTT Blends and the Pure Components Before and After Sorption

Time	PEI	90/10	70/30	PTT
Before sorption	220	182	127	42
1 week	53	48	52	44
2 weeks	47	41	49	37

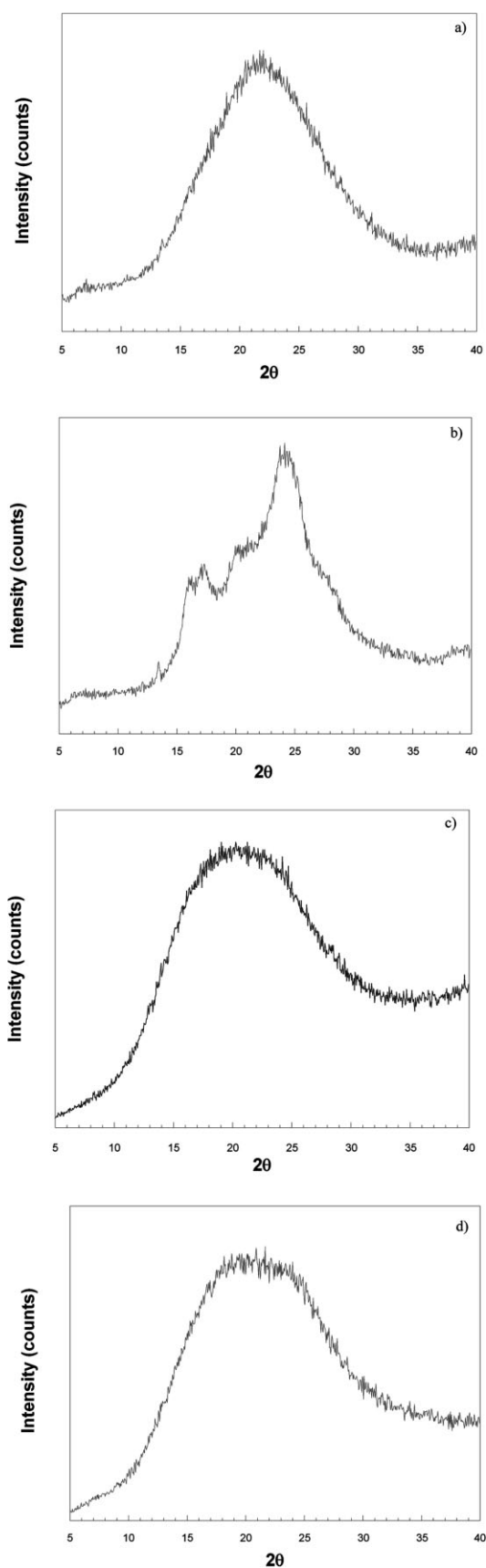


Figure 2 XRD patterns of PTT (a) before and (b) after sorption and of a 70/30 PEI/PTT blend (c) before and (d) after sorption.

indicating that the sorption of acetone induces crystallization. When the crystalline content of PTT was studied by DSC, it was found to be close to 10% before sorption. However, at equilibrium sorption, it was not easy to measure accurately because of solvent evaporation and the occurrence of crystallization/recrystallization processes, as evidenced by the presence of a wide peak, much like the case of PEEK.¹⁶ Nonetheless, the crystalline content was estimated to be 20% after sorption. Upon crystallization, solvent molecules are expected to be expelled from the solvent-induced crystals; this is a typical phenomenon of solvent-induced crystallization.^{17,18} However, no decrease in the acetone content of PTT can be seen in Figure 1. This indicates that either the additional crystallization took place at the beginning of the sorption curve, when only small amounts of the solvent could be expelled, or the process was rather slow and resulted in a distributed decrease in the slope of the sorption curve.

In the case of the 70/30 blends of Figure 2(c,d), as in the case of the 90/10 blends, no clear peak and therefore no crystalline domains were observed before or after sorption. In agreement with the XRD results, no crystallization could be observed in the 90/10 blend with DSC, and only a very low content (2%) was estimated to exist in the case of the 70/30 blend. This lack of crystalline content of PTT in the blends can be attributed to the miscibilization of PTT in PEI and to the low PTT concentration in the blends. The possibility of solvent-induced crystallization of PTT is, therefore, ruled out. The crystalline phase can be considered a barrier to both diffusion and solubility. Therefore, in these blends, the partially crystalline nature of PTT is not a parameter that can contribute to increased resistance to solvent sorption.

Desorption

The desorption curves corresponding to the materials of Figure 1 are shown in Figure 3. The slopes of the plots of Figure 3 at short times as well as the calculated diffusion coefficients ($4.5 \times 10^{-9} \text{ cm}^2/\text{s}$ for pure PTT and between 40 and $50 \times 10^{-9} \text{ cm}^2/\text{s}$ for both PEI and the blends) are clearly higher than those from the sorption curves. This has been seen in other works¹⁹ and has been attributed²⁰ to the ease of solvent evaporation from the swollen surface. At longer desorption times, the desorption rate decreases and approaches that observed during sorption. After desorption, considerable amounts of acetone remain in PEI and in the blends. Thus, acetone sorption is a partially irreversible process.

Mechanical properties

In Figure 4, stress–strain curves are used to compare the effects of sorption on PEI and on the 90/10

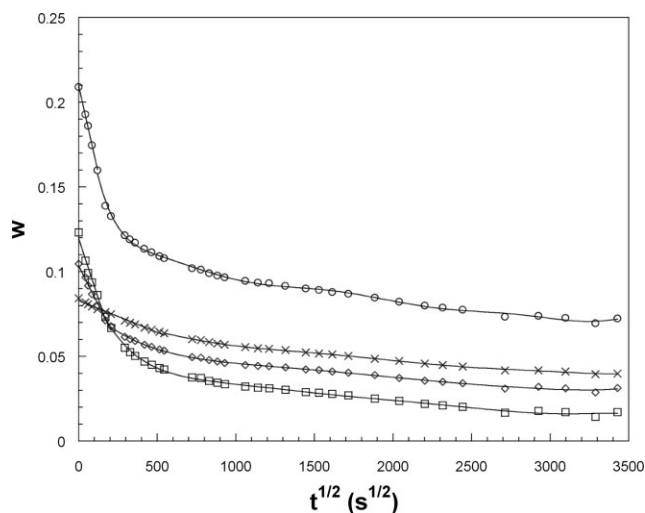


Figure 3 Acetone desorption curves of (×) PTT, (□) a 70/30 PEI/PTT blend, (◇) a 90/10 PEI/PTT blend, and (○) PEI.

blend. The modulus of elasticity and the elongation at break of the blends and the two constituent components as references (measured before sorption, after several sorption times, and at equilibrium sorption) are collected in Table II.

In agreement with previous results,¹¹ in Table II, we observe that the values of the modulus of elasticity of the blends before sorption are larger than those predicted by a direct rule of mixtures. Furthermore, despite the rather low modulus of PTT, the modulus of the 90/10 blend is slightly higher than those of the two constituent components. This agrees with a decrease in the free volume of the blends, which, as stated before, acts as a hindrance to diffusion.

As shown in Table II, the modulus of both the pure polymers and blends clearly decreases in the presence of the solvent, and this proves the strong plasticizing effect of acetone. The sorption-induced decrease in the modulus of elasticity is smaller in the blends than in the pure PEI, and this demonstrates the protective effect of PTT against solvent sorption. After 250 h of acetone sorption, the modulus decreases slightly in all materials, and this is consistent with the small solvent content.

At long sorption times, that is, at equilibrium, the decreases in the modulus of both PEI and the blends are substantial, but the modulus values are still high. That of PTT is not characteristic of a mostly amorphous material with a T_g close to room temperature, as measured by DMTA. This suggests a lack of reliability of the DMTA results for the specimens after sorption, as mentioned earlier. Additionally, the effect of the solvent on the modulus was the largest for the neat PTT, although the amount of sorbed acetone was the smallest. This is probably

due to the low T_g of PTT (47°C), which decreases upon sorption to values close to room temperature, even though the overall solvent sorption and the plasticization effect are small. A T_g close to room temperature should consequently have a strong effect on the modulus of elasticity.

After desorption, the modulus is partially recovered. An exact comparison of the modulus before the equilibrium sorption and after desorption could not be made because of the different solvent contents and modulus values of the PEI and its blends under these two conditions. This prevented us from determining whether the effects of sorption on the modulus were reversible or not. However, after desorption, the modulus increased, approaching the values measured before sorption, despite the presence of residual solvent. Moreover, we observed larger deviations from the modulus values before

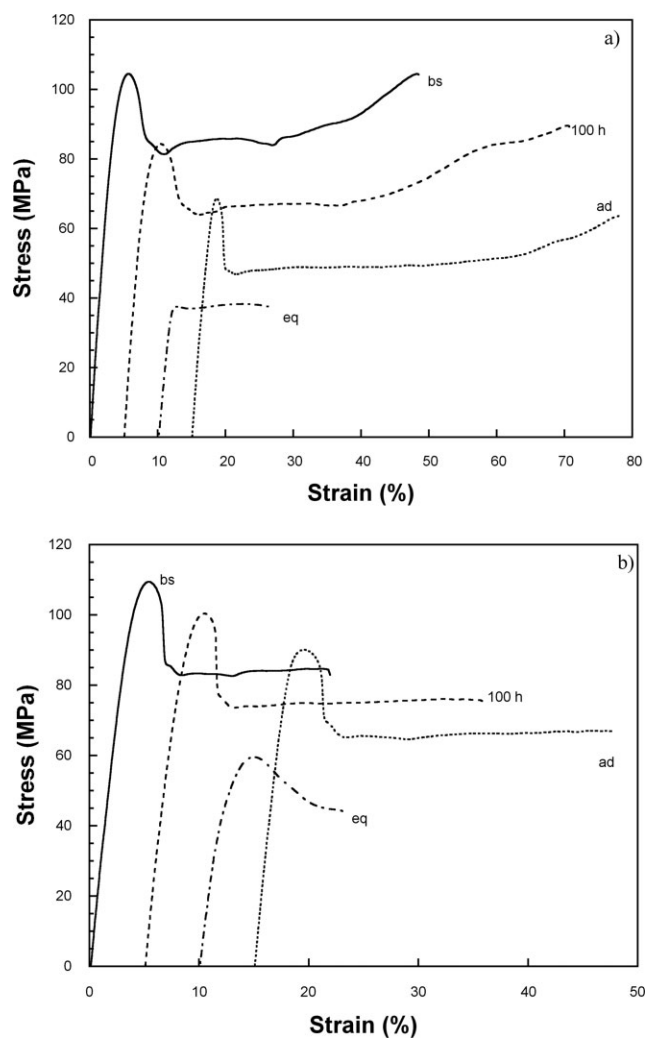


Figure 4 Tensile curves of (a) neat PEI and (b) a 90/10 PEI/PTT blend. For clarity, each curve has been slipped a unity (5% strain) toward the right (100 h = after sorption for 100 h; ad = after desorption; bs = before sorption; eq = equilibrium sorption).

TABLE II
Young's Modulus and Ductility (Measured as the Elongation at Break) of PEI, 70/30 PEI/PTT, 90/10 PEI/PTT, and PTT in Acetone

Time	Young's modulus (MPa)				Elongation at break (%)			
	PEI	90/10 PEI/PTT	70/30 PEI/PTT	PTT	PEI	90/10 PEI/PTT	70/30 PEI/PTT	PTT
Before sorption	3220	3280	3030	2000	48	22	10	251
50 h	3140	3190	2870	1790	59	24	9	244
100 h	2990	3140	2840	1680	66	29	11	203
250 h	2710	2860	2410	1330	39	17	7	213
Equilibrium	2150	2400	1890	620	15	13	2	203

The average standard deviation of the modulus was 40 MPa. The average standard deviation was 1.8% for elongation at break values below 20 and 14.2% for the rest of the values.

sorption in the samples in which the solvent content was higher after desorption. Both facts shed light on the reversibility of the sorption process with respect to the modulus. Similar results, in which partially reversible plasticization and large decreases in the modulus take place, have been observed in highly crystalline PEEK/methylene chloride²¹ and in unfilled and liquid crystal polymer (LCP) or talc-filled polypropylene of various organic solvent systems²² with solvent contents ranging from 10 to 45%. These systems did not show total reversibility because of the presence of residual solvent after desorption. The modulus after desorption might be even higher than that observed before sorption when solvent-induced crystallization is present.^{23,24}

The elongation at break of PEI and its blends (Table II) increased after 100 h of sorption. This is indicative of plasticization and agrees with the presence of the solvent and the observed decrease in the modulus of elasticity. The transparency of the specimens with acetone under tensile testing was lost when they were cold-drawn. This did not occur before sorption. As discussed earlier, crystallization is not induced by the solvent in these blends. Therefore, the fracture mechanism of PEI and its blends changed in the presence of acetone. This is in agreement with the drop in T_g induced by the presence of acetone.

At equilibrium sorption and with solvent contents between 10 and 20%, however, the elongation at break decreases markedly. In the case of PTT, the elongation at break remains practically constant, regardless of the sorption/desorption time. This is probably because the low solvent contents were enough to reduce T_g to values close to room temperature. When the test temperature is in the vicinity of the T_g , the elongation at break hardly changes. In the case of PEI and its blends, an antiplasticization effect is ruled out because their modulus values are lower. As expected, plasticization and enhanced ductility took place. Thus, the decrease in the elongation at break must be the result of another negative effect that counteracts the effect of plasticization

and that remains effective after long sorption times. The sorption process induced swelling of the specimens, among which PEI showed the largest effect; this agreed with its largest solvent sorption. This swelling led to a hydrostatic tensile stress that overshadowed the stress from the tensile test. Moreover, scanning electron microscopy (SEM) revealed the formation of superficial cracks (not seen before sorption) on the PEI specimens after 100 h of sorption (Fig. 5). This additional and detrimental effect was exclusive to the PEI sample (perhaps because the blends had lower solvent contents) and should have contributed to the behavior of the elongation at break. Thus, at short sorption times, swelling is not large enough to effectively influence the elongation at break, and the effect of plasticization is dominant. However, the degree of swelling at long sorption times increases markedly and becomes the dominant mechanism (along with superficial cracking in the case of PEI) that controls the elongation at break.

In Figure 6(a), the creep curves of PEI and its blends under the combined effects of acetone and an

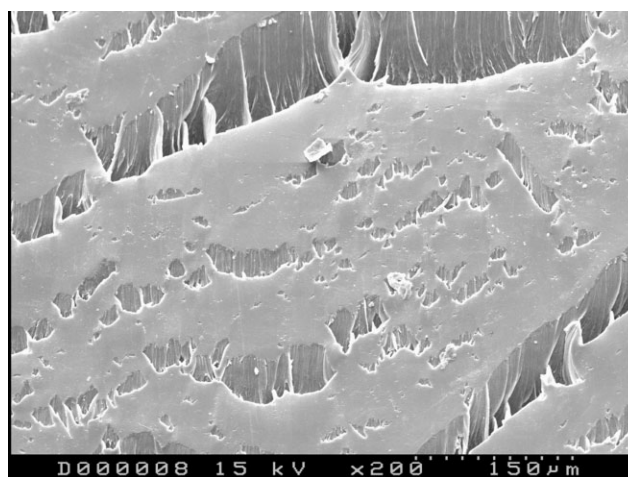


Figure 5 SEM microphotograph of a fractured tensile specimen of PEI after 100 h of sorption. The photograph was obtained by SEM at an angle of 40° from the vertical axis.

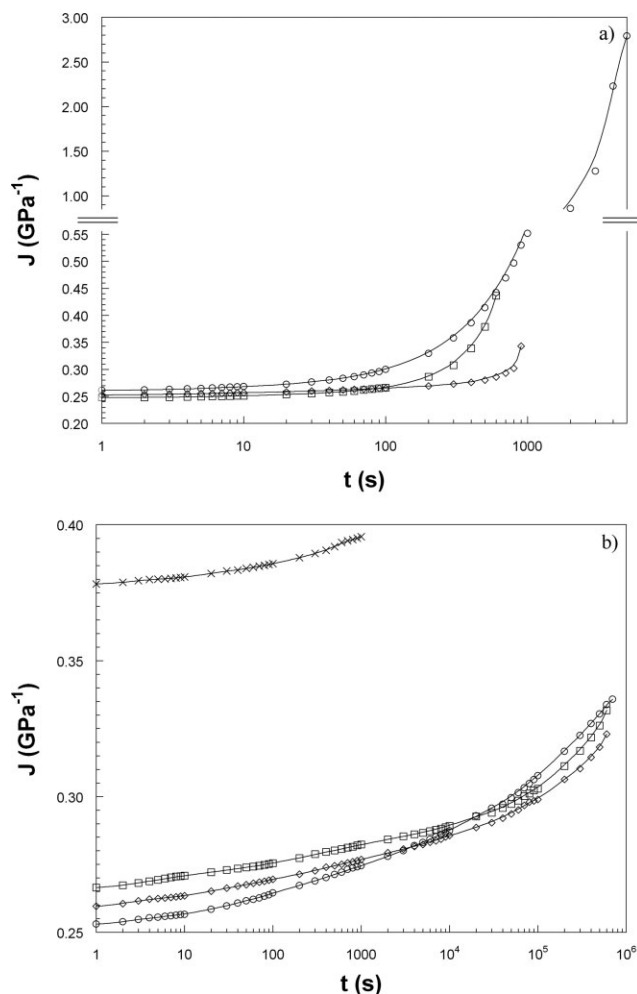


Figure 6 Creep curves of (□) a 70/30 PEI/PTT blend, (◇) a 90/10 PEI/PTT blend, (○) PEI, and (×) PTT in the (a) presence and (b) absence of acetone. The initial stress was 30 MPa.

applied constant stress at different stages of the sorption process are shown. In Figure 6(b), the corresponding creep curves in the absence of the solvent are also shown as a reference. In the PTT specimens, the creep deformation was much higher than that in PEI and its blends, regardless of the sorption time, and it is only partially shown. As can be seen in the reference curves of Figure 6(b), the creep resistance of PEI barely changed upon the addition of PTT, despite the large tendency of PTT to creep. This can be attributed to the decrease in the free volume induced by blending, which clearly restricts the long-term deformation (Fig. 4).

The creep curves of the materials tested under acetone [Fig. 6(a)] are similar to those without the solvent only at short times (100 s). Afterwards, the curves clearly differ from the behavior observed in Figure 6(b), and a sudden increase in the deformation of pure PEI and its blends occurs between 100 and 1000 s. However, the time required for creep

fracture increases with the addition of 30% PTT. The sudden creep increase in Figure 6(a) can be attributed to a plasticizing effect of the solvent because it is not present in the curves before sorption in Figure 6(b). It must be taken into account that the creep conditions and the sorption characteristics are related in three main ways: (1) the applied and constant external stress induces an increase in the free volume of the specimens because of the elastic deformation of materials with a Poisson modulus below 0.5, such as PEI and PTT; (2) the effects of the applied external stress are enhanced by the plasticization effect of the solvent, which decreases the gap between room temperature and T_g ; and (3) stress cracking may occur, leading to an increase in the surface available for sorption. Interactions between these effects may enhance them. In the case of pure PTT, large cracks that formed before fracturing were visible to the naked eye. In the case of PEI, superficial cracks, like those shown in Figure 5, also occurred, albeit to a smaller extent than in the tensile test. These cracks increased the external surface available for solvent transport, thus speeding sorption, plasticization, and creep deformation. All these effects are responsible, to different extents, for the creep behavior shown in Figure 6(a).

CONCLUSIONS

In the presence of acetone, Fickian sorption and large degrees of partially irreversible swelling and sorption were observed in both pure PEI and blends with PTT. The amount of sorbed acetone decreased with increasing PTT content. This was attributed to the lower likelihood of sorption in the presence of PTT and mainly to a blending-induced decrease in the free volume.

The decreases in the modulus of elasticity induced by sorption were smaller in the blends than in PEI, and this agreed with the lower acetone content of the blends. After short solvent exposure times, the elongation at break increased, and this indicated plasticization. However, after long sorption times, it decreased, and this was attributed to the observed swelling. The observed creep increase upon sorption was attributed to a combination of a free volume increase, plasticization, and additional superficial cracking in the case of PEI.

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