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The effects of solvent sorption on the properties of poly(ether ether ketone)

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A study has been carried out on the sorption of ortho-dichlorobenzene, *N,N*-dimethylformamide and water by poly(ether ether ketone) (PEEK). Two types of PEEK samples have been analysed; the first in the amorphous state and the second with a high crystallinity level. The sorption and desorption curves have been determined and the effect of the solvent presence on the mechanical properties has been analysed by means of the tensile test. PEEK is affected to a different extent by the solvents studied and also by the crystallinity of the polymer. Sorption takes place only in the case of amorphous PEEK. Its effect on the mechanical properties of PEEK is explained on the basis of the two concomitant processes that are the consequence of sorption, these are: plasticization and induced crystallization.

1. Introduction

Among the polymers used as a matrix of composite materials, some temperature-resistant engineering thermoplastic polymers compete with thermosets. This is due to their improved toughness and ductility and easier processing but they are usually less resistant to attack from solvents. However, it has been reported [1] that the crystalline poly(ether ether ketone) (PEEK), widely used as a matrix of polymer composites, has a remarkable resistance to the action of solvents, but different chlorinated solvents that are used in paints as well as tetrahidrofuran are sorbed by the polymer to different extents [2–8]. The most important effect has been observed in the case of methylene chloride, due to the high degree of solvent sorbed and also to the induced crystallization that usually seems to take place. For this reason, in another paper [9] we studied the sorption of methylene chloride by PEEK. The sorption and desorption curves indicated that a great interaction exists between the solvent and the polymer. Density measurements and WAXS analysis showed the existence of induced crystallization in the case of initially amorphous PEEK; for the crystallized material this process was practically negligible. The effects of methylene chloride sorption on the mechanical properties of PEEK were studied and analysed as a consequence of plasticization and solvent-induced crystallization.

Furthermore, although most of the work on solvent sorption by PEEK has been carried out with methylene chloride, other solvents may also be sorbed and may affect its mechanical properties. For this reason in this paper we have tested the possible sorption by PEEK of several solvents. Among the tested solvents, cyclohexane, ortho-xylene and ethanol were not sorbed in a significant amount; however, ortho-dichlorobenzene (*o*-DCB) and *N,N*-dimethylformamide (DMFA) were sorbed. A very small amount of water was sorbed in relation to these two solvents, however, due to its relevant practical importance, the possible effect of sorption on the mechanical properties has also been tested. The effect of PEEK crystallinity on the polymer–solvent interaction and the possible induced crystallization have also been analysed. Finally, we have determined the effect of the presence of solvents on the mechanical properties of the polymer by means of the tensile test. Explanations are given for the different behaviours observed.

2. Experimental procedure

The PEEK used in this work was Victrex 450 G supplied by ICI Materials, Wilton, Middlesborough, UK. Its melt flow index determined at 370 °C and with a 3800 g load, is 5.0 g/10 min. Its molecular weight $M_w \simeq 40\,000$.

PEEK films with an approximate thickness of 0.1 mm were obtained by compression moulding after drying the pellets. A Schwabenthan Polystat 200-T press was used and the processing temperature was 390 °C. Amorphous (A) films were obtained by immersing them in cold water immediately after compression moulding. Crystalline (C) films were obtained by slow cooling under pressure in the compression press.

The density of the PEEK samples was determined at 23 °C using a density gradient column with sodium nitrate solution. The crystallinities of PEEK were determined using $\rho_a = 1.2626$ g cm^{-3} and $\rho_c = 1.4006$ g cm^{-3} as the densities of totally amorphous and

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totally crystalline PEEK, respectively [1]. The crystallinity values obtained for A-PEEK and C-PEEK samples were 0% and 34%, respectively.

Sorption measurements were carried out at 20 °C, using the following procedure: samples with a surface area of 1 mm^2 were immersed in the solvent for periods of up to 10 days. After the immersion period, the samples were blotted with filter paper to remove the surface liquid and weighted.

After sorption up to equilibrium, desorption measurements were performed at room temperature and atmospheric pressure. In both sorption and desorption measurements the solvent content in the samples at time t was calculated as

$$\% \text{ solvent} = ((\text{weight at time } t - \text{initial weight}) / \text{initial weight}) \times 100 \qquad (1)$$

The densities of the samples after sorption or desorption were measured by means of the procedure explained above. After desorption, WAXS analysis was also carried out with 0.154 nm (CuK_α) radiation using a Phillips PW1729 generator, with a PW1820 vertical goniometer and a graphite monocromator.

Specimens for the tensile tests were punched out from the films. The tensile tests were performed at 23 °C using an Instron 4301 tensile tester. The different mechanical properties (Young's modulus, E; nominal yield stress, σ_y; nominal break stress, σ_b, and ductility as measured from the nominal deformation at break, ε_b) were determined from the force–displacement curves.

3. Results and discussion

3.1. Solvent sorption and desorption

Figs 1 and 2 show the sorption curves obtained for A-PEEK and C-PEEK with *o*-DCB and DMFA as the solvents used, respectively. The sorption data for water are not represented because the weight per cent of sorbed water was practically zero, irrespective of the sorption time.

The results reported in Figs 1 and 2 with respect to the sorption of *o*-DCB and DMFA show that in the case of C-PEEK, no weight-gain in these solvents exists. On the contrary, high sorptions of both solvents by A-PEEK are observed. The equilibrium sorptions are approximately 39% and 27% for *o*-DCB and DMFA, respectively. These results indicate that the crystallinity of PEEK has a great effect on the sorption behaviour of the polymer, and also that the crystallized material is unaffected by these solvents. This behaviour differs from that obtained in the case of methylene chloride, which is sorbed by C-PEEK with an equilibrium weight gain of 13% [9]. This different sorption behaviour seems to be related to the molar volume of the solvents. Thus, the small (molar volume 64 $cm^3\ mol^{-1}$) methylene chloride molecules are easily sorbed by crystalline PEEK; however, the very large (molar volume 112 $cm^3\ mol^{-1}$) *o*-DCB ones are not.

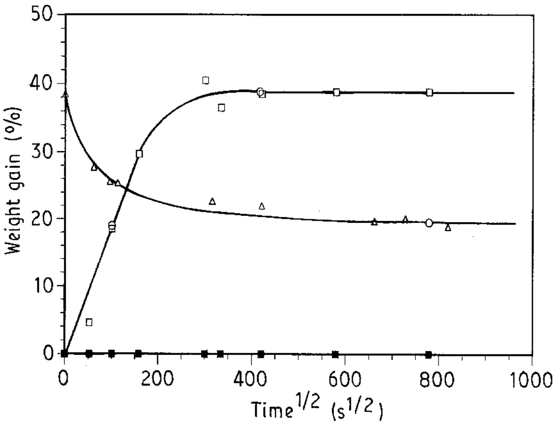

Figure 1 (□, ■) Sorption and (△) desorption curves of (□, △) A-PEEK and (■) C-PEEK with *o*-DCB. (○) Points at which the mechanical properties were measured.

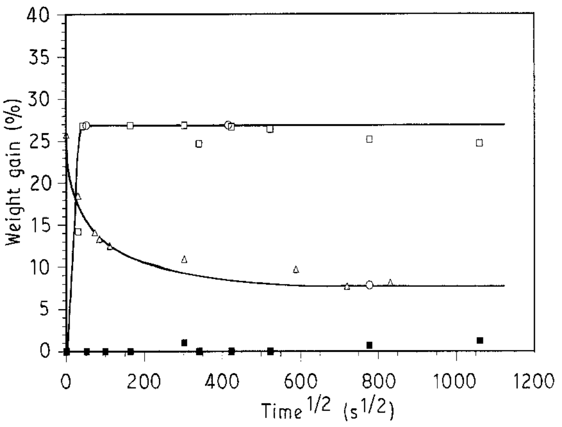

Figure 2 (□, ■) Sorption and (△) desorption curves of (□, △) A-PEEK and (■) C-PEEK with DMFA. (○) Points at which the mechanical properties were measured.

Figs 1 and 2 also show the desorption curves obtained at room temperature and atmospheric pressure for PEEK with *o*-DCB and DMFA. As can be observed, desorption takes place in a similar way in both cases. In the first stage, a rapid desorption occurs, and following that, the desorption rate decreases. Similar desorption curves have been obtained previously in the case of other PEEK/solvent systems. The residual weight-gains after 1 week are, respectively, 20% and 7% for A-PEEK/*o*-DCB and A-PEEK/DMFA. These residual weight-gains seem to be related to the boiling point of the solvents which is higher in the case of *o*-DCB (180 °C) than in the case of DMFA (153 °C).

The shape of the desorption curves is in alignment with the accepted desorption mechanism for other solvents such as methylene chloride [3]. Such a mechanism supposes that, during desorption, an initial rapid solvent loss from the superficial regions takes place, followed by a long and slow desorption from the core of the material.

3.2. Induced crystallization

Different studies have shown that induced crystallization of initially amorphous PEEK takes place during sorption of methylene chloride. In an attempt to analyse the possible induced crystallization in our PEEK/solvent systems, density and WAXS studies have been carried out after desorption. From the experimental density values, the apparent densities of PEEK were determined by means of the equation [2]

$$\rho_p = (\rho - \rho_f V_f)/V_p \qquad (2)$$

where ρ is the measured density, ρ_f and V_f the density and the volume fraction of the solvent, respectively, and ρ_p and V_p the density and the volume fraction of the polymer.

In the next stage, the apparent crystallinity values of PEEK were determined as explained in the experimental section. Table I shows the density values after desorption for the PEEK/solvent systems studied in this work, in addition to the corresponding density and crystallinity values calculated for PEEK. As can be seen, the density of A-PEEK (1.2626 g cm^{-3}) clearly increases as a consequence of solvent exposure. This indicates that great crystallinity level increases (from 0% to roughly 35%) will take place if it is supposed that density increases are only due to crystallization.

Fig. 3 shows the WAXS diffraction patterns obtained for A-PEEK before and after solvent treatment. As can be observed, A-PEEK before treatment only shows an amorphous halo. However, the WAXS diagrams obtained for A-PEEK/*o*-DCB and A-PEEK/DMFA after desorption, which are also represented in Fig. 3, show several small peaks and shoulders over the amorphous halo and at angular positions which coincide approximately with those found previously for crystalline PEEK [6, 10].

These results indicate that in agreement with some of the results reported in the literature [2, 6, 8], solvent treatment gives rise to an induced crystallization of PEEK. However, from the WAXS diagrams, it appears that this induced crystallization takes place at a fairly low level (roughly 5%), much lower than that suggested by density results (roughly 35%).

This difference in crystallinity between the two methods is attributed to the compression of the solvent by the swollen PEEK which has after desorption 20% *o*-DCB and 7% DMFA. This compression will clearly increase the density value of the solvent that is used in Equation 2. This is in accordance with the proposal forwarded by Grayson and Wolf [4] and with that experimentally observed in our laboratory [9] in the case of PEEK/methylene chloride systems. It also corroborates the fact that when solvents are sorbed by PEEK, the compressive forces of the swollen PEEK on the solvent are large enough to increase the density of the sorbed solvent. This would modify the crystallinity values obtained by means of Equation 2 if the uncompressed density values of the solvents were used.

TABLE I Apparent density and crystallinity data for PEEK after desorption

PEEK/solvent system	Density after desorption (g cm^{-3})	Apparent density of PEEK (g cm^{-3})	Apparent crystallinity (%)
A-PEEK/*o*-DCB	1.308	1.3168	39.3
A-PEEK/DMFA	1.274	1.3077	32.7

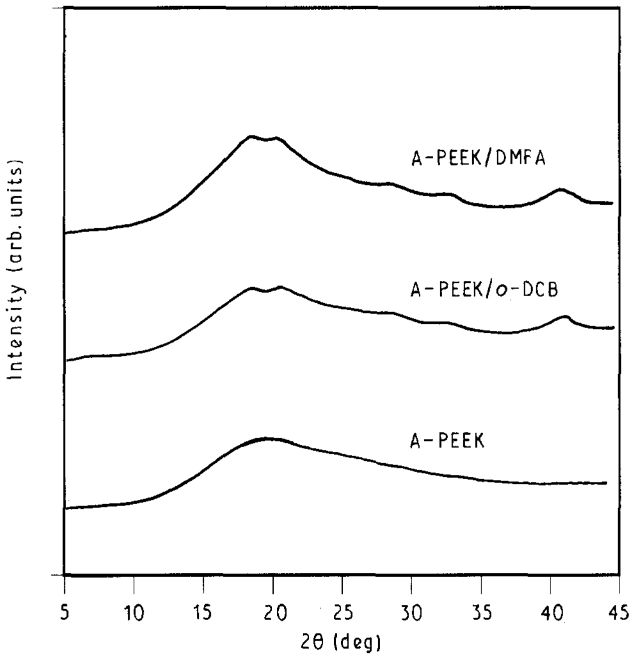

Figure 3 WAXS diffraction patterns of A-PEEK before and after desorption for a week.

Thus, the observed density increase of the solvent-sorbed PEEK with respect to that of the pure PEEK is due only in a small degree to the crystallinity increase of PEEK. The density increase of the solvent produced by the swollen, thus highly deformed PEEK, will be the main reason for the observed density increase. A decrease in the free volume of the solvents-sorbed PEEK concomitant with the two processes and due to the presence of solvent and to the involved high pressure cannot be rejected.

3.3. Mechanical properties

The mechanical properties of the solvents-sorbed A-PEEK were measured in materials corresponding to points on the sorption curves (Figs 1 and 2) and to materials after desorption for a week. The points on the sorption curves were, in the case of *o*-DCB, after middle sorption (170 min) and at the onset of equilibrium sorption (48 h), and in the case of DMFA at the onset of equilibrium sorption (45 min) and at long exposure times (48 h) longer than that of equilibrium.

The tensile curves of *o*-DCB sorbed A-PEEK and those of pure amorphous and crystalline PEEK as a reference are plotted in Fig. 4. The curves for DMFA were similar to those for *o*-DCB and are not plotted. Table II shows the effect of solvent sorption and desorption on the tensile mechanical properties of PEEK compared with those of the untreated PEEK. It can be observed in Table II that water does not have any overall effect on the mechanical properties of C-PEEK; in the case of A-PEEK, a slight rigidification giving rise to an increase in Young modulus and in yield stress seems to be observed, but it is close to the level of experimental error. The fact that the properties were almost constant after exposure of PEEK to water, was expected taking into account that this solvent is practically not sorbed by PEEK.

TABLE II Effect of water, o-DCB and DMFA on the mechanical properties of PEEK

PEEK/solvent system	Young's modulus (MPa)	Yield stress (MPa)	Break stress (MPa)	Ductility (%)
Untreated PEEK				
A-PEEK	2790 ± 260	52.7 ± 1.7	69.8 ± 8.9	86 ± 17
C-PEEK	4380 ± 120	99.3 ± 4.6	87.7 ± 4.9	5.5 ± 1.3
Water				
A-PEEK (25 h)	3010 ± 120	56.5 ± 1.8	68.8 ± 6.4	81 ± 13
C-PEEK (3 days)	4310 ± 230	89.8 ± 13.8	89.6 ± 3.6	6 ± 2.7
o-DCB				
A-PEEK/sorption 170 min	1800 ± 160	37.4 ± 4.1	50.9 ± 6.6	76 ± 24
A-PEEK/sorption 48 h	920 ± 130	–	32.5 ± 3.7	71 ± 23
A-PEEK/desorption (7 days)	2880 ± 120	44.9 ± 1.5	40.1 ± 1.3	31 ± 11
C-PEEK/sorption 3 days	4375 ± 230	88.4 ± 13.3	80.2 ± 12.1	6 ± 1.7
DMFA				
A-PEEK/sorption 45 min	1630 ± 170	24.2 ± 1.7 (3/8) *	31.5 ± 3.9	58 ± 24
A-PEEK/sorption 48 h	1560 ± 170	–	29.7 ± 3.9	47 ± 30
A-PEEK/desorption (7 days)	2750 ± 260	45.9 ± 5.9	40.2 ± 2.7	15 ± 6.6
C-PEEK/sorption 3 days	4250 ± 370	89.1 ± 11.9	80.9 ± 9.4	5.5 ± 3.6

* Number of specimens that yield/total number of specimens.

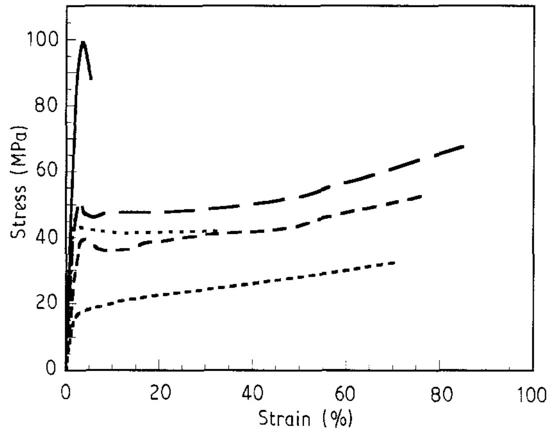

Figure 4 Tensile curves of o-DCB-sorbed A-PEEK: (— — —) middle sorption; (– – –) equilibrium; (· · ·) desorption. The tensile curve of (——), crystalline PEEK (C-PEEK), and that of neat amorphous PEEK (A-PEEK) (— —) are also plotted as a reference.

With respect to the effect of sorption and desorption of o-DCB and DMFA on the properties of the crystallized C-PEEK ($X_c = 34\%$), the effect, if any, is very small, as expected from the practically zero sorption of these solvents by C-PEEK.

Referring to the mechanical behaviour of A-PEEK, the solvent presence may give rise to two concomitant effects. These effects, which have been seen in the case of other solvents [2, 4–9, 11], are plasticization of PEEK due to the presence of the small solvent molecules and induced crystallization of PEEK due to the decrease in T_g produced by the solvent presence. It must be taken into account that these two effects have an overall opposite effect on properties and that, moreover, while plasticization due to solvent presence in PEEK will probably be a rather reversible process, induced crystallization is not.

If we look at the properties of the A-PEEK/DMFA after 45 min, when the equilibrium is reached, and after 48 h we realize that they do not change with time. Given the fact that the solvent content has not changed, this lack of change of properties with time indicates that crystallization does not practically progress with time once equilibrium sorption is reached. Thus, crystallization is a rather fast process, faster than solvent sorption because it has mostly taken part at times less than those of equilibrium.

If we look at the stress-related properties (those reported in Table II except ductility) of the A-PEEK/o-DCB and A-PEEK/DMFA systems, we realize that the plasticization effect of the solvents is very clear. This is because all these properties decrease with sorption time and in the case of yield stress it even disappears, giving rise to a rubber-like behaviour similar to that observed by Hay and Kemmish using chloroform and other solvents [8]. This effect of the presence of the solvents may be even higher than that observed in Table II because, concomitant with it, crystallization and its opposite effect on properties, may take place. After the long desorption times, however, crystallization and solvent loss have taken place; as a result both of them will give rise to an increase in these stress-related properties.

As can be seen, the properties after desorption are rather similar to those of A-PEEK, with the exception of the low break stress that is a consequence of the small ductility. Thus, the increased deformation ability caused by the residual plasticization is counteracted by the rigidification proper to crystallization. Finally, despite the fact that the solvent content after desorption is different, the mechanical properties related to stress of both PEEK/DMFA and PEEK/o-DCB after desorption are very similar. This indicates that, although the nature of the solvents is not the same, at constant crystallinity levels, different solvent contents have no significant influence on the stress-related mechanical behaviour of the crystallized PEEK.

The above discussion of the balance of the two effects, i.e. plasticization and crystallization, is supported by the ductility behaviour. Thus, during sorption the usually greater effect of crystallization on ductility than on stress-related properties gives rise to a decrease in ductility. After desorption, the negative effect on ductility of the two processes, i.e. loss of solvent and crystallization gives rise to the lowest value of ductility observed in both PEEK/solvent systems.

4. Conclusion

The results obtained in this work show that *o*-DCB and DMFA are sorbed to an important extent by amorphous PEEK, whereas no effect of the solvents on crystalline PEEK is observed. Both *o*-DCB and DMFA sorption by amorphous PEEK give rise to plasticization and solvent-induced crystallization. However, the amount of originally amorphous PEEK crystallized by sorption is less than the amount that could be calculated from density values, due to the increase in density of the solvent. Sorption of solvents has an important effect on the mechanical properties of the amorphous polymer. These effects are a consequence of the concomitant processes of plasticization by the solvents and solvent-induced crystallization.

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