The solvent-induced swelling of poly(ether ether ketone) by 1,1,2,2-tetrachloroethane

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Exposure of amorphous poly(ether ether ketone) (PEEK) to the organic solvent 1,1,2,2-tetrachloroethane (TCE) was found to have considerable effects on the physical and spectral properties of PEEK. TCE causes significant bulk swelling, as well as inducing polymer chain crystallization. Lewis acid–base interactions between the polymer and the solvent are the likely explanation for this enhanced solvent compatibility.

(Keywords: infra-red spectroscopy; Raman spectroscopy; poly(ether ether ketone))

Introduction

There has been recent interest in the effects of organic solvents on the properties of the thermoplastic poly(ether ether ketone) (PEEK). One particularly important property of PEEK has been its apparent chemical inertness[1]. However, certain solvents, such as methylene chloride, chloroform, toluene and chlorophenol, are absorbed by PEEK, causing plasticization and inducing crystallization in the polymer[2–6]. This plasticization causes a serious deterioration in mechanical properties, which affects the usage of PEEK in engineering applications. Thus, an understanding of the solvent absorption mechanism and the ability to predict solvent–polymer behaviour is obviously important.

Vibrational spectroscopy has been applied in a number of other physicochemical studies of PEEK. I.r. spectroscopy was used to examine the crystallization and melting behaviour of PEEK[7–10]. Fourier transform (*FT*) Raman spectroscopy has also been used in recent studies of PEEK[11–14], including an investigation of the thermal and solvent-induced plasticization of PEEK[11]. Our investigation of the interaction of various organic solvents with PEEK[15] has revealed that 1,1,2,2-tetrachloroethane (TCE) is absorbed by the polymer to an extraordinary degree not formerly reported in studies of other organic solvents. In this paper we present the preliminary results of a study into the effect of TCE on PEEK using *FT*i.r. and *FT* Raman spectroscopy, as well as solvent swelling experiments.

Experimental

Polymer samples were supplied by ICI Materials, Wilton, UK. To produce amorphous PEEK, samples were heated to 400–420°C then quenched in liquid nitrogen before use. Samples of amorphous PEEK for spectroscopic study were exposed to TCE (Aldrich) in sealed containers at room temperature for 24 h prior to examination.

All the *FT* Raman spectra were recorded using a Bomen Ramspec 152 equipped with an indium gallium arsenide (InGaAs) photodiode detector, and using 1.05 W of 1064 nm radiation from a Quantronix Series 100 Nd: YAG laser. For each spectrum, 100 scans were co-added, apodized with a cosine function and Fourier transformed to give a resolution of $4\ \mathrm{cm}^{-1}$. The spectral contribution of TCE was removed by subtraction of the Raman spectrum of the pure solvent. The relative intensities of the bands in each spectrum were calculated with respect to the intensity of the band at $1595\ \mathrm{cm}^{-1}$. This mode was chosen as a reference because it has been shown to be relatively insensitive to changes in environment[11].

All the i.r. spectra were recorded using a Bomem Ramspec 152 spectrometer equipped with a deuterated triglycine sulfate detector. A Spectratech Contact Sampler attenuated total reflectance (a.t.r.) cell with a ZnSe crystal of angle 45° was used. For each spectrum, 200 scans over the frequency range $5000–400\ \mathrm{cm}^{-1}$ were co-added, apodized with a cosine function and Fourier transformed to give a resolution of $4\ \mathrm{cm}^{-1}$. The spectral contribution of TCE was removed by subtraction of the i.r. spectrum of the pure solvent.

The absorption experiments were carried out by immersing the polymer samples (dimensions $\sim 10\ \mathrm{mm} \times 30\ \mathrm{mm}$; thickness 0.25 mm) in TCE in sealed containers maintained at room temperature. After the appropriate time interval the samples were removed from the containers, blotted dry and weighed on an analytical balance. After weighing, the samples were immediately returned to the containers.

Results and discussion

Diffusion studies. *Figure 1* shows the mass uptake of TCE by amorphous PEEK as a function of time. This plot shows that there is a rapid solvent uptake within the initial 5 min of the experiment, after which the mass uptake remains at a relatively constant value, consistent with a Fickian diffusion process[16]. Absorption of TCE resulted in a 165% increase in the PEEK sample mass,

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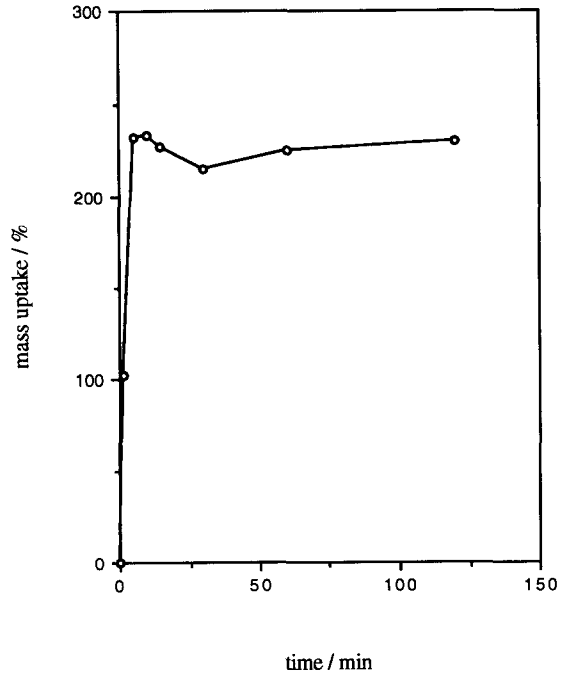

Figure 1 The mass uptake of TCE by amorphous PEEK as a function of time

Table 1 The effect of TCE on the Raman modes of amorphous PEEK

Sample	C=O stretching frequency (cm^{-1})	Symmetric C–O–C stretching intensity[a]
Amorphous	1651	1.51
Crystalline	1644	1.35
Tetrachloroethane-treated	1644	1.65

[a] Standard deviation for intensity values, ±0.03

a level three times higher than reported for any other solvent. In addition, it was observed that following immersion in TCE, the clear amorphous PEEK became opaque, as normally observed for crystalline PEEK.

Raman studies. The *FT* Raman bands of PEEK have been assigned in recent studies and are discussed in detail elsewhere[11,13,14]. The *FT* Raman spectrum of amorphous PEEK was recorded both before and after exposure to TCE. A shift in frequency is observed for the C=O stretching mode after exposure to the solvent (*Table 1*). While the C=O stretching mode appears at 1651 cm^{-1} in the untreated amorphous spectrum, after exposure to TCE it shifts to 1644 cm^{-1}, the frequency observed for the crystalline material. *Table 1* also shows the relative intensities of the symmetric C–O–C stretching mode of amorphous PEEK before and after exposure to TCE. The presence of the solvent causes a notable increase in the intensity of this mode, and this spectral change may be interpreted by comparison with spectral studies of PEEK at elevated temperatures (above the glass transition temperature, T_g). The increasing intensity of the C–O–C mode reflects enhanced polymer chain mobility for PEEK with increasing temperature above the T_g[15,17]. The TCE-swollen materials exhibit spectral characteristics equivalent to the unsolvated polymer at 225–240°C.

Infra-red studies. The a.t.r. spectra of amorphous PEEK before and after immersion in TCE were recorded. A number of vibrational modes were perturbed by the presence of the solvent. The doublet with component bands at around 952 and 965 cm^{-1}, due to asymmetric C–O–C stretching and in-plane C–H stretching modes, respectively, was shown by Chalmers *et al.*[7] to be dependent on the crystallinity of the sample. The intensity ratio of the 952 and 965 cm^{-1} bands is affected by the presence of TCE, and these ratios are summarized in *Table 2*. As the intensity ratio of the 965/952 cm^{-1} bands increases with the increasing percentage crystallinity of the PEEK sample, it is clear that TCE induces crystallization in PEEK.

Another useful mode in the i.r. spectrum is the carbonyl band, as was observed in the Raman study. *Figure 2* shows the C=O stretching mode of crystalline and amorphous PEEK, as well as that of amorphous PEEK after treatment with TCE. The carbonyl band is broad, consisting of several overlapping component bands. Both the amorphous and crystalline polymer show components centred at 1645, 1650, 1657 and 1666 cm^{-1}. The relative amounts of the components at 1645 and 1650 cm^{-1} vary according to crystallinity. For amorphous PEEK the most intense component is observed at 1650 cm^{-1}, while in the crystalline material the band at 1645 cm^{-1} is more intense. The i.r. carbonyl band is affected by the presence of TCE, as the component at 1645 cm^{-1} has increased in intensity and the ratio of the 1650 and 1645 cm^{-1} components appears very similar to that of the crystalline carbonyl band. The shoulders that appear at 1657 and 1666 cm^{-1} are also sensitive to crystallinity and are much weaker for the crystalline polymer. Notably, after PEEK is exposed to TCE these components are weaker than observed for the crystalline material, suggesting some additional effect on the C=O mode due to the presence of the solvent. Further quantitative analysis of this mode should provide a clearer picture of the nature of the polymer–solvent interaction.

Discussion

The spectral data and diffusion results have shown that TCE causes dramatic swelling of PEEK, to a degree not previously observed for any other solvent. The enhanced effect that this solvent has on PEEK may be explained by Lewis acid–base interactions between the polymer and solvent. Fowkes and Tischler[18] have previously reported the formation of weak acid–base complexes between poly(methyl methacrylate) and various acidic species in solution. They argued that these weak interactions can be important in many physicochemical processes involving polymer–solvent interactions, especially those of an interfacial nature. It is likely that these same thermodynamic driving forces account for the enhanced compatibility between PEEK and TCE, compared to most other solvents. In the current

Table 2 The effect of TCE on the i.r. ratio 965/952 cm^{-1}

Sample	I_{965}/I_{952}[a]
Amorphous	0.40
Crystalline	0.69
Tetrachloroethane-treated	0.81

[a] Standard deviation, ±0.03

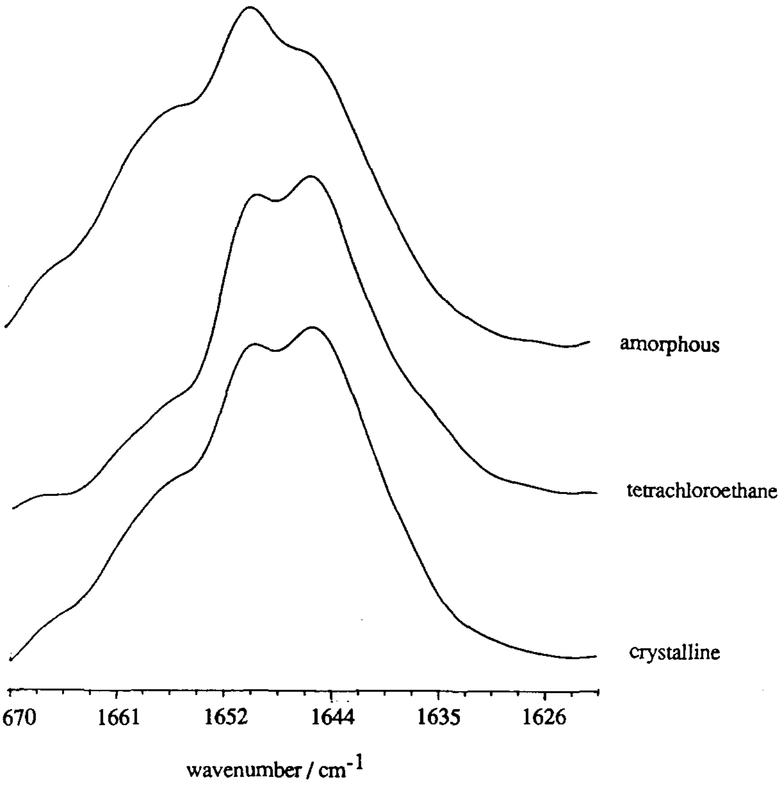

Figure 2 The carbonyl region of i.r. spectra of amorphous and crystalline PEEK, and amorphous PEEK exposed to TCE

study, PEEK acts as a soft organic base owing to the presence of the C=O, C–O–C and aromatic groups in the structure, all of which may act as electron donors. Like chloroform, TCE acts as an electron acceptor owing to the electron-deficient H atoms which are activated by the strong electron-withdrawing influence of the chlorine groups. TCE is expected to exhibit enhanced activity compared to chloroform, as it has two acidic sites per molecule. Ongoing spectroscopic studies in our laboratories are directed at clarifying the acid–base contribution to this enhanced activity.

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