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The influence of thermal history on the dynamic mechanical and dielectric studies of polyetheretherketone exposed to water and brine

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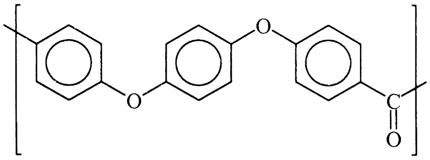
Abstract

The effects of thermal history on the absorption of distilled water and brine and their influence on the dynamic mechanical and dielectric properties of semi-crystalline polyetheretherketone (PEEK) are reported. Changes in the physical properties of the samples were monitored as a function of time of exposure using gravimetric measurement, dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC) and dielectric spectroscopy. The water and brine sorption behaviour follows a Fickian Case I process with a maximum solubility of 0.5 w/w% at 75°C. The observed sorption behaviour was independent of the salinity of the water to which the polymer was exposed. The water uptake proved to have an effect on the degree of crystallinity. It is observed that the crystallite distribution generated in the formation of the sample has a profound effect on the nature of the water uptake process and also its reversibility. During the initial stages of water uptake smaller crystallites are destroyed and these do not reform when the samples are dried. Low frequency dielectric spectroscopy exhibits a very close correlation with the gravimetric measurements and indicate that this method provides a useful non-destructive evaluation technique for the assessment of water content in filler free thermoplastics. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyetheretherketone; Water; Dielectric spectroscopy

1. Introduction

Over three decades ago, Bonner reported the first preparation of poly(aromatic ketones) using aluminium chloride catalysed acylation of diphenyl ether with aromatic diacid chlorides [1]. Since then a variety of different synthetic methodologies have been developed allowing the production of a large range of poly(aromatic ketones). Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene), more commonly known as poly(aryl-ether-ether-ketone) or polyetheretherketone, and abbreviated to PEEK, is a tough, thermally stable polymer. The basic stiffness of the PEEK structure arises from conjugation with the neighbouring aromatic ring structures with the bridging ketone group and the two ether linkages introduce limited flexibility. The end group is usually a fluorine atom [2]. The PEEK repeat unit has the following structure:



Although all the oxygen atoms lie in a single plane, phenylene rings are inclined at an angle of ±37° to each other down the backbone chain [3]. The ketone link makes an angle of 125° with the two neighbouring phenyl ring structures, which is similar in magnitude to the ether linkage which generates an angle of 120° between the neighbouring phenyl rings. As a consequence the chain follows an overall straight linear projection and neighbouring chains can easily come into close register without requiring identical sequencing. PEEK can be crystallised either by melt- or cold-crystallisation [4]. During crystallisation, PEEK crystals grow in spherulites. The morphology of these spherulites depends on the process used, the thermal history of the sample [5] and the nucleation density [2]. The most effective nucleating agents for spherulite growth are residual, not fully melted crystallites. A decrease in crystallisation kinetics has been observed after a certain time and is attributed to secondary

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crystallisation that is commonly thought to consist of imperfect crystals or regions of crystallinity containing initially hindered or rejected macromolecular segments [6].

Semi-crystalline PEEK has a melting point of 335°C and the glass transition temperature [T_g] for the amorphous polymer is 143°C and increases when the degree of crystallinity of the polymer increases [2]. This change in T_g is related to a decrease in the number of accessible chain conformations due to the loss of mobility caused by impinging spherulites on the amorphous phase of the polymer [7]. Therefore, increased crystallinity lowers the magnitude of $\tan \delta$ of the α- or T_g transition and shifts the peak value towards higher temperatures. The loss of mobility caused by increased crystallinity is also responsible for the increase of the elastic modulus [8].

The diffusion of water in neat PEEK resin follows a classical Fickian Case I diffusion process. In the temperature range of 35–95°C, the solubility of water increases from 0.44 w/w% at 35°C to 0.55 w/w% at 95°C [9]. The diffusion coefficients for absorption, desorption and reabsorption are found to be equal, suggesting that the morphology of the polymer does not change during water sorption. However, over a critical stress value of 26 MPa the equilibrium solubility of water in PEEK has been shown to increase rapidly [10].

This study is concerned with the evolution of the characteristics of the polymer during ageing in distilled water and brine as studied by dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC). Gravimetric analysis was used to follow the absorption and desorption of water by the polymers and to determine the diffusion behaviour. Low frequency dielectric spectroscopy was evaluated as a possible alternative to gravimetric measurement for the assessment of water uptake in this type of polymeric material.

2. Experimental methods

2.1. Materials

The samples of PEEK used in this study were obtained from Victrex Plc and Tronic Ltd and were the same semi-crystalline polymer, Victrex™ PEEK 450G, with a weight average molar mass of 10^5 g mol^{-1}. Victrex provided circular disks of a diameter of 115 mm and a thickness of 3.3 mm produced by injection moulding of granules and are designated [Victrex PEEK]. This polymer has a flexural modulus of 4.1 GPa at 23°C and 0.3 GPa at 250°C, a T_m of 340°C, a T_g of 143°C, a degree of crystallinity of 30 w/w% and a dielectric permittivity of 3.3. The Tronic samples were obtained by extrusion and had the form of a rod of a diameter of 20 mm and a length of 300 mm from which samples were taken and are designated [Tronic PEEK]. The extruded samples have undergone a post heat treatment in order to remove any stress crystallisation produced during the manufacturing process, whereas the Victrex discs have not undergone any post treatment and would therefore present a certain degree of stress crystallinity.

2.2. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) measurements were performed using the Polymer Laboratories DMTA MkIII. The samples used, cut from the rods and discs, were heated at a rate of 5°C/min from 25 to 300°C. The instrument was operated in a single cantilever mode with a sinusoidal displacement of 64 μm applied at a frequency of 1 Hz. The sample width, for the Tronic samples were 5 mm and 19 mm for Victrex samples. The samples cut from Victrex discs were 35 mm long, 12 mm wide and 3.3 mm thick. Those cut from Tronic rod were 15 mm long, 10 mm wide and 1 mm thick.

2.3. Differential scanning calorimetry

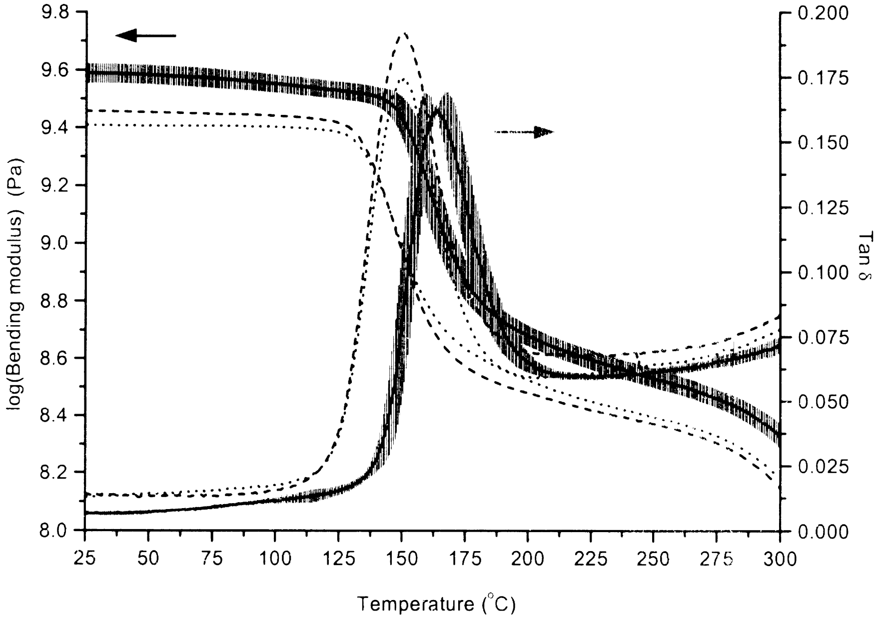
Differential scanning calorimetry (DSC) was performed between 125 and 300°C at a rate of 20°C/min using a Perkin–Elmer DSC-2 Differential Scanning Calorimeter calibrated with indium. The sensitivity of the calorimeter was set at 10 mcal/s full scale range. The enthalpy of fusion of a completely crystalline PEEK sample was taken as 130 J/g [8].

2.4. Gravimetric measurement

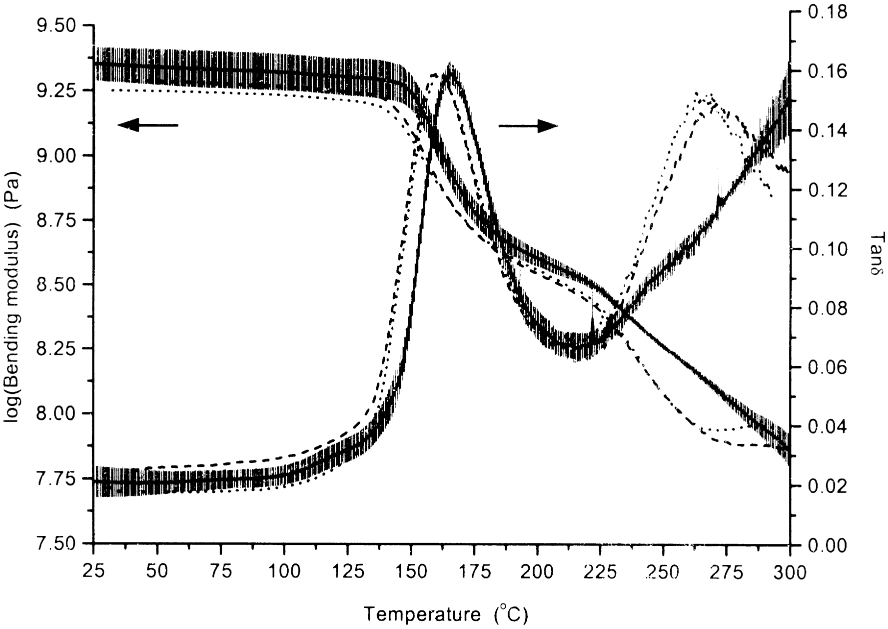
Samples cut from Victrex discs and Tronic rods had the following dimensions, respectively: 35 mm long, 12 mm wide, 3.3 mm thick and 20 mm diameter, 1 mm thick. The absorption experiment was performed by exposing samples in individual sealed tube to distilled water and to a saline solution, referred as brine, at 30 and 75°C. Brine was a sodium chloride solution with a salinity of 35‰. At fixed times, the samples were removed, rapidly blotted, and weighed using a Mettler AJ100 electronic balance. The desorption experiment was performed using an air circulated oven set at the same temperatures.

2.5. Dielectric spectroscopy

Measurements were performed using a computer controlled Frequency Response Analyser (Schlumberger 1250A) which allows direct capacitance measurements at frequencies between 1 and 6.3×10^4 Hz. The network analyser was interfaced via a charge amplifier to the sample. This configuration minimises impedance mismatch problems which usually limit the range of measurement [11]. A capacitance structure was formed by evaporation of a 100 nm thick layer of silver, on one side of the sample, to form a ground electrode and a 60 nm thick layer of metal, on the other side of the sample, to form an active electrode which was subsequently exposed to moisture. The active electrode was sufficiently thin to be permeable to water, yet thick enough to exhibit metallic conductivity. Leads



(a)



(b)

Fig. 1. DMTA of (a) Victrex PEEK and (b) Tronic PEEK after exposure to brine at 75°C for 58 and 14 days, respectively. (— unaged samples, ··· sample 1, -- sample 2).

were connected to the electrodes and covered with epoxy resin and silicone sealant to make them watertight. The whole assembly was immersed in distilled water at 30°C and the dielectric response measured at set time intervals.

3. Results and discussion

3.1. Dynamic mechanical thermal analysis

Typical DMTA results are presented in Fig. 1. The mean

Table 1
DMTA results for aged Victrex and Tronic PEEK

Ageing environment			Distilled water				Brine			
Ageing temperature			75°C		30°C		75°C		30°C	
	‘as received’									
PEEK	T_g (°C)	$\log E'$ at 25°C (Pa)	T_g (°C)	$\Delta\log E'$ at 25°C (Pa)	T_g (°C)	$\Delta\log E'$ at 25°C (Pa)	T_g (°C)	$\Delta\log E'$ at 25°C (Pa)	T_g (°C)	$\Delta\log E'$ at 25°C (Pa)
Victrex	162 ± 7	9.58 ± 0.03	146	0.06	152	0.13	150	0.13	152	0.13
				0.08		0.21		0.18		0.14
Tronic	166 ± 3	9.34 ± 0.07	161	0.01	155	0.08	161	0.06	155	0.02
				0.11				0.09		

trace represent the mean values obtained from five measurements performed on the ‘as received’ unaged samples. The standard deviation (error bars) is included to allow differentiation between the effects on the traces due to inhomogeneity and those due to the effects of exposure to the environment. Table 1 is a summary of all the results where T_g is the glass transition temperature and E' is the elastic modulus of the material at 25°C.

The relaxation processes occurring in the temperature range studied are the α-relaxation corresponding to the T_g of the polymer which is 162 ± 7°C for Victrex PEEK and 166 ± 3°C for Tronic PEEK with a second relaxation process located around 250°C. This second relaxation is related to the melting processes of the crystallites produced during the manufacturing process. The assignment of the higher temperature process to a melting of the crystallites, confirmed by DSC results, is related to the melting of a crystal population produced during the manufacturing process.

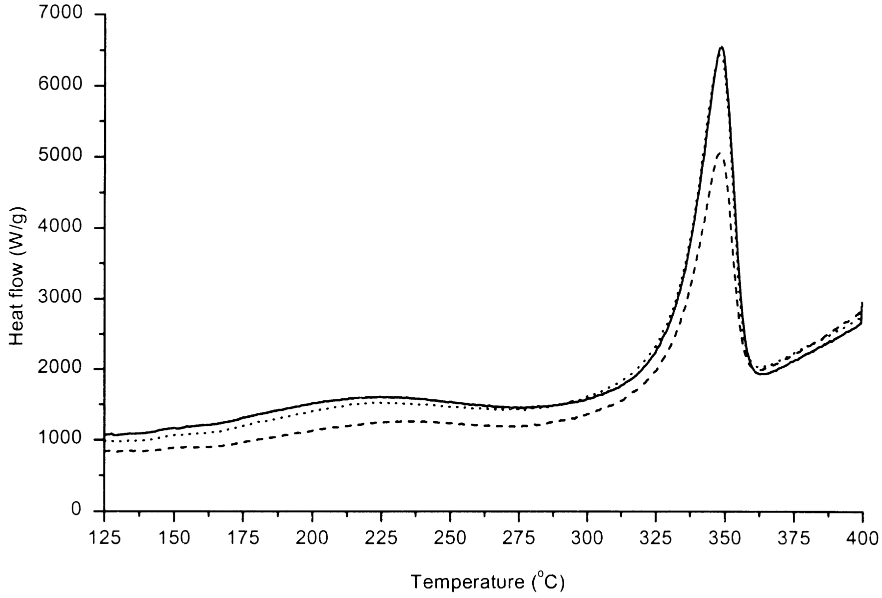
For both PEEKs and for all exposure conditions, a decrease in the bending modulus in conjunction with a decrease of the T_g were observed. Both effects are consistent with a plasticisation process caused by the penetration of the water into the polymer that weakens molecular interaction in the spherulites. The shift of the tan δ peak towards lower temperature was more significant with exposure to water at 75°C where the amplitude of the peak is also greater compared with the unaged samples.

The shift of the tan δ peak is less significant in the case of Tronic PEEK. However, the important increase in the magnitude of the second relaxation is consistent with the plasticisation of the secondary crystal population which should be of a much smaller size than the main primary population. It would therefore be more sensitive to a plasticisation effect as its thermodynamic stability and ratio volume/surface are smaller.

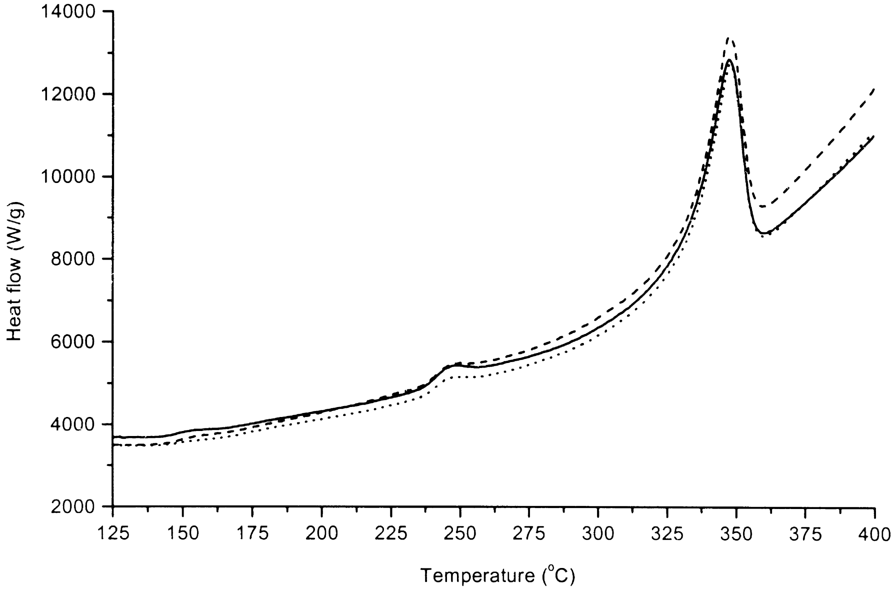
For each temperature of exposure, no significant difference were observed between the exposure to distilled water and brine implying that the presence of sodium chloride does not have any effect on the ageing behaviour of the polymer ruling out absorption by osmotic process in PEEK.

3.2. Differential scanning calorimetry

The main purpose of the DSC analysis was to investigate how the hydration process might be changing the proportion of the crystalline phase in the polymer samples. It was observed, Fig. 2, that crystalline content decreased on exposure and this can be correlated with changes in the DMTA traces. Since all the DSC traces were similar, only one typical example of the data obtained is presented. All the DSC scans presented a clear melting peak at about 350°C and a very broad peak from about 175 to 275°C for Victrex PEEK, whereas a second melting endothermic peak at about 250°C was shown during DSC scans of Tronic PEEK. As proposed in the DMTA section, this peak relates to the melting of a



(a)



(b)

Fig. 2. DSC of different samples of (a) Victrex PEEK and (b) Tronic PEEK after exposure to brine at 75°C for 58 days and 14 days, respectively. (— sample 1, ··· sample 2, – – sample 3).

secondary crystal population created during manufacturing of the PEEK rod. In the case of Tronic PEEK, the T_g can be observed around 160°C, which agrees with the T_g determined by the DMTA measurements. An annealing process necessary to eliminate the stress crystallisation generated during the extrusion of the rod will have been undertaken at about 230°C. This will also achieve the maximum rate of crystallisation. This process would lead to the production of a crystal population in the polymer that would melt at about 250°C when the polymer is reheated. Stress alignment during the injection process can also induce a higher level of crystallinity than that would have been normally

Table 2
Degree of crystallinity (w/w %) of Victrex and Tronic PEEK

Ageing environment		Distilled water			Brine		
Ageing temperature		75°C		30°C	75°C		30°
PEEK	'as received'	abs.	des.	abs.	abs.	des.	abs.
Victrex	30 ± 0.3	23	26	26	24	26	26
Tronic	24 ± 0.3	24		20	24		23

expected and this is clearly retained in the Victrex PEEK samples which have not been annealed.

A summary of the crystallinity measurements is presented in Table 2 where 'abs.' denotes the measurement performed after absorption and 'des.' denotes the measurement performed after desorption. The calculated degree of crystallinity of Victrex PEEK in its unaged state was 30 w/w%. This fell, after exposure at 75°C, to 23 w/w% for distilled water and 24 w/w% for brine, and 26 w/w% after exposure at 30°C to both waters. Since the standard deviation of the measurement is 0.3 w/w%, the difference observed during crystallinity measurement can be considered significant enough. These results are a confirmation of the occurrence of a plasticisation process due to water uptake which is responsible for a loss of crystallinity.

The degree of crystallinity of the unaged Tronic PEEK was 24 w/w%. No variation of this degree can be observed after exposure to both waters at 75°C. A slight decrease can be observed after exposure at 30°C. The lower degree of crystallinity of unaged Tronic PEEK compared with Victrex PEEK is consistent with the lower bending modulus observed in DMTA results.

Since Victrex PEEK presented the greater loss of crystallinity with the more drastic conditions being exposure at 75°C, measurements of the degree of crystallinity of Victrex PEEK after desorption of the samples were performed to identify the type of ageing occurring in PEEK during water uptake. When considering reversible physical ageing, the polymer should regain its crystallinity after desorption that is 30 w/w%. In the case of irreversible ageing it should not recover any of its original degree of crystallinity and remains 23–24 w/w%. It is proposed that there are two types of crystallites in the material; those produced by normal nucleation and those induced by stress orientation of polymer chains during the production process. The latter on swelling will not be reformed once the water is removed from the sample. The degree of crystallinity obtained after desorption for exposure to both waters is 26 w/w%. Physical ageing that is swelling of the polymer increases the sample free volume but the sample recovers after removal of the water.

3.3. Water diffusion

The purpose of this experiment was to determine the solubility of distilled water and brine in PEEK and eventually, in the case of a Fickian sorption behaviour, to calculate the coefficient of diffusion for a given environment. This allows, by using a Fickian model, determination of the amount of water present in the polymer at any time for any thickness.

The results and methodology used were similar for each exposure conditions, that is at 30 and 75°C in distilled water and brine. Therefore, only typical results that are exposure at 75°C in brine, are presented in Fig. 3 for Victrex PEEK and Fig. 4 for Tronic PEEK. However, a summary of all the results are presented in Tables 3 and 4 for exposure at 75 and 30°C, respectively. Figs. 3(a) and 4(a) show the cycle of absorption/desorption/reabsorption applied to the samples in conjunction with the desorption of the polymer 'as received'. Figs. 3(b) and 4(b) are a comparison of the desorption and reabsorption curves and absorption and desorption curves, respectively. Figs. 3(c)–(e) and 4(c)–(e) are a presentation of the results for each sorption.

Determination of the diffusion coefficient D is necessary to be able to use the following Fickian Case I model [12]:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{Dt}{l^2}\pi^2(2n+1)^2\right] \quad (1)$$

where M_t and M_∞ are the mass of water absorbed at time t and at equilibrium respectively, t the exposure time and l the sample thickness. In order to do so the data obtained during the gravimetric measurement were normalised and plotted against the square root of time divided by the sample thickness. A linear regression on the apparent initial linear part of the curve up to 60% of the equilibrium was used to determine D using Eq. (2):

$$D = \frac{\pi}{16}R^2 \quad (2)$$

where R is the slope calculated from the linear regression. After determination of the diffusion coefficient, Eq. (1) was used to compare the model to the experimental data by measuring the correlation coefficient between model and data. The smaller number of points with which a correlation coefficient has been calculated in this work is 11. With calculation based on more than 10 points, a correlation coefficient superior to 0.7 is very significant. It is highly significant when superior to 0.8 [13].

3.4. Exposure at 75°C

3.4.1. Victrex PEEK

It can be seen in Fig. 3(a) that the amount of water desorbed is greater than the amount absorbed but equals the amount reabsorbed. This is due to the presence of water in the samples when received. This is confirmed by desorption curve of the samples 'as received' which shows that the amount of water desorbed corresponds to the difference between the absorption and desorption. Consequently, the amount desorbed equals the amount of water that was

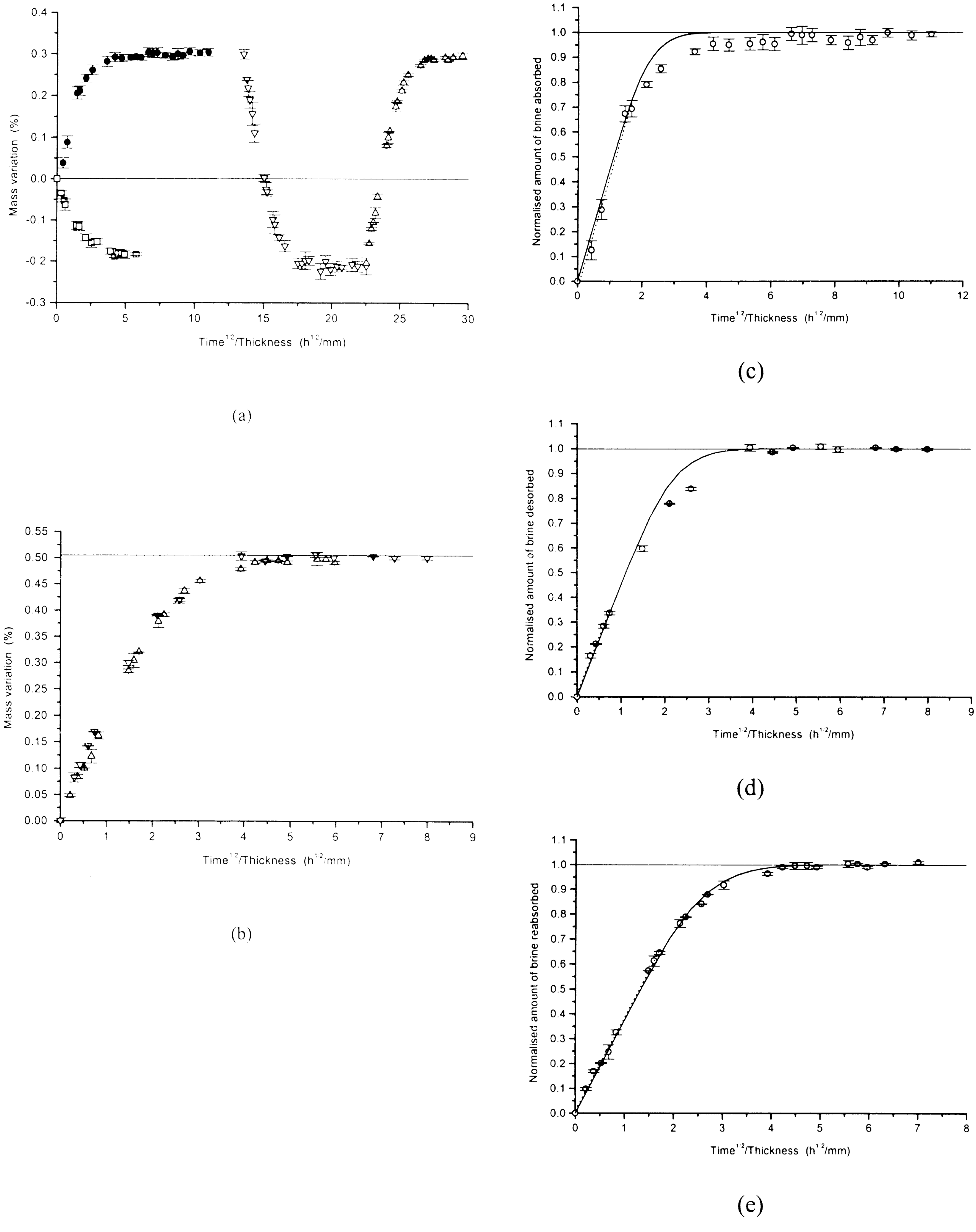
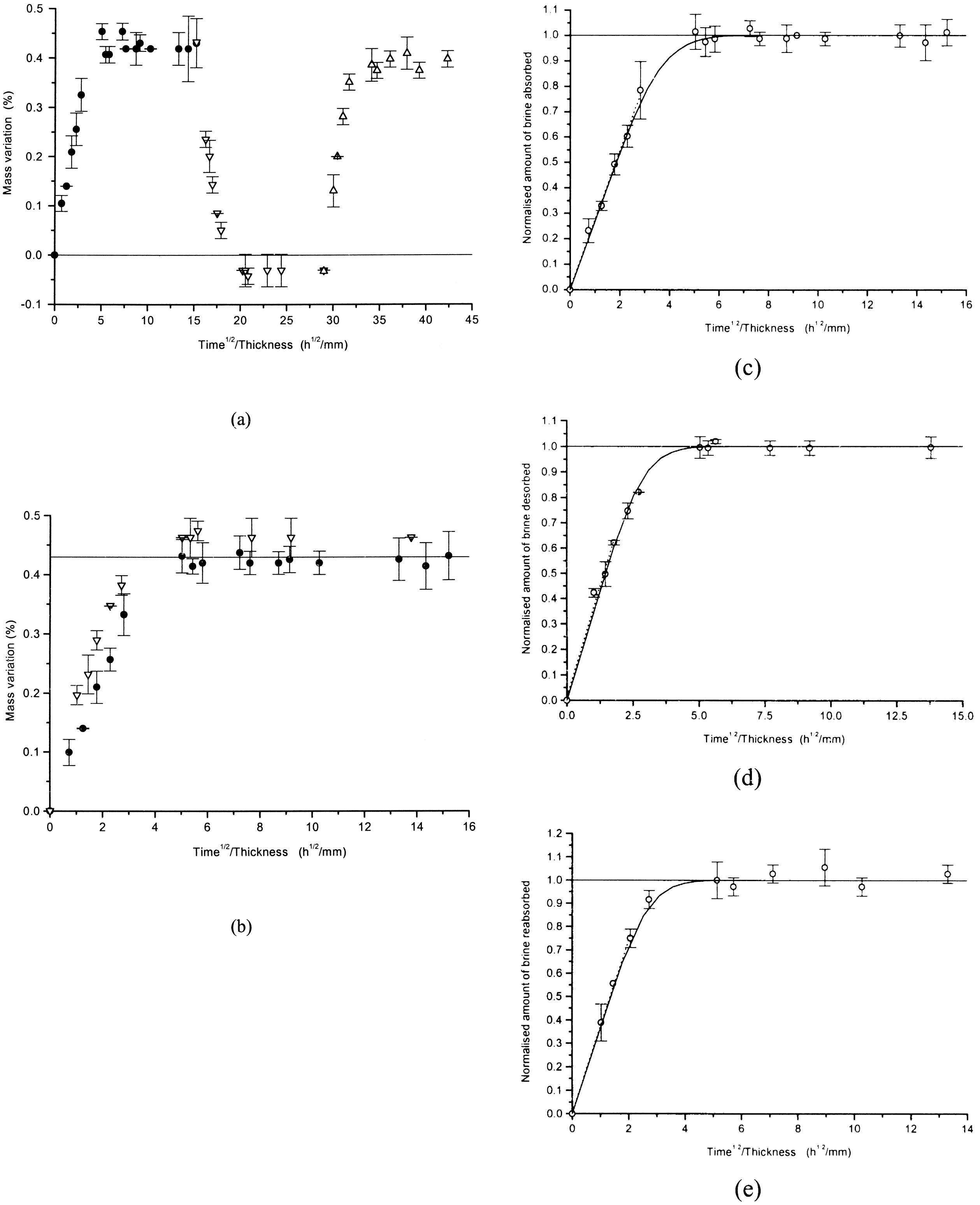


Fig. 3. Victrex PEEK exposed to brine at 75°C: (a) cycle ● absorption; ▽ desorption; △ reabsorption; and □ desorption of 'as received' samples; (b) comparison desorption – reabsorption; (c) normalised absorption; (d) normalised desorption; and (e) normalised reabsorption.



(a)

(b)

(c)

(d)

(e)

Fig. 4. Tronic PEEK exposed to brine at 75°C: (a) cycle ● absorption; ▽ desorption; △ reabsorption; (b) comparison desorption–reabsorption; (c) normalised absorption; (d) normalised desorption; and (e) normalised reabsorption.

already present in the samples plus the amount absorbed during the exposure. Fig. 3(b) shows that both desorption and reabsorption are linear at the start of the experiment and concave against the abscissa axis further on. Furthermore, the thorough matching of the desorption and reabsorption data confirms that the sorption follows a Fickian Case I process. Fig. 3 confirms the Fickian Case I sorption process as each sorption curve is linear up to 60% of the

Table 3
Summary of the results after exposure at 75°C

Diffusion coefficient (10^{-2} mm^2/h)/Solubility (w/w%) PEEK	Environment	Absorption	Desorption	Reabsorption
Victrex	Distilled water	5.21	4.26	2.61/0.5 ± 0.01
	Brine	4.01	3.98	2.75/0.5 ± 0.01
Tronic	Distilled water	1.79/0.43 ± 0.02	2.20	1.96/0.43 ± 0.02
	Brine	1.43/0.43 ± 0.02	2.34	2.66/0.43 ± 0.02

equilibrium. The solubility of the polymer in distilled water is 0.5% and agrees with the data provided by Victrex [14].

3.4.2. Tronic PEEK

Tronic PEEK samples were dried before exposure to water in order to remove all the water present in the samples when received. Fig. 4(a) shows that the amount of water desorbed is slightly greater than the amount absorbed. However, since the amount of water absorbed and the amount reabsorbed are equal in both cases this would suggest that a small amount of indigenous materials leached during exposure. The solubility is 0.43% which agrees with the value published in the literature [15]. The presence of sodium chloride does not affect the diffusion process. Figs. 4(c)–(e) present the results for each sorption experiments with a highly significant correlation coefficient between the collected data and the Fickian model. The calculated diffusion coefficient agrees with the results published in the literature [8].

3.5. Exposure at 30°C

Since the sorption process at 75°C was Fickian Case I, it was expected to be the same at 30°C. Consequently, only absorption and desorption experiments were performed at this temperature which confirmed a Fickian Case I diffusion process. The solubility of water in Victrex PEEK was the one calculated from the desorption as the material already contained some water when received. The solubility of this polymer at 30°C is identical for distilled water and brine, being, respectively, 0.34 and 0.33%. As expected it is lower than the one observed at 75°C since the temperature of exposure is much lower. The solubility of Tronic PEEK at 30°C is of the same order as the solubility of Victrex PEEK and agrees with value published in the product data sheets [14].

Table 4
Summary of the results after exposure at 30°C

Diffusion coefficient (10^{-3} mm^2/h)/Solubility (w/w %) PEEK	Environment	Absorption	Desorption
Victrex	Distilled water	3.90/0.27 ± 0.01	4.20/0.34
	Brine	3.30/0.22 ± 0.01	4.40/0.33
Tronic	Distilled water	1.95/0.33 ± 0.03	3.95/0.30
	Brine	2.15/0.36 ± 0.03	3.40/0.32

4. Discussion

The similar solubility of Victrex PEEK and Tronic PEEK at both temperatures confirms that the diffusion follows a Fickian Case I process since the diffusion is independent of the thickness exposed, Victrex PEEK samples being 3.3 mm thick whereas Tronic PEEK samples only 1 mm thick. Furthermore, the values obtained from these gravimetric measurements are in agreement with published data [9,14].

The sorption behaviour of both PEEKs is identical when exposed to distilled water or brine which means that a high concentration of sodium chloride salt does not have any significant effect on the diffusion. This also agrees well with the literature that showed that the ageing in distilled water would have the same effect or a more drastic effect than the exposure to sea water and that, in fact, only distilled water actually diffuses in the material [16].

The fact that absorption, desorption and reabsorption diffusion coefficients are not identical for a given exposure condition suggests that the morphology of the polymers changed during water ageing. This is consistent with the DMTA and DSC results.

4.1. Dielectric spectroscopy

This experiment was only performed at 30°C on Tronic PEEK exposed to distilled water for the following reasons: Victrex PEEK samples were too thick and therefore would have needed an extensive exposure time to reach equilibrium since only one face of the sample is exposed in this experiment, the temperature of 30°C was used for comparison with the gravimetric measurements and it has been shown that the sorption behaviours are identical in distilled water and brine. Furthermore, the main purpose of this experiment was to confirm the Fickian Case I sorption behaviour of the polymer using another technique and to validate this technique for water uptake measurement.

The tri-dimensional Figs. 5(a) and (b) present the evolution of the dielectric permittivity and the dielectric loss, respectively, measured as a function of the exposure time and the frequency. In order to present all the data measured, the frequency and time axis in the dielectric loss plot are reversed compared with the dielectric constant plot. This was necessary to allow observation of the decrease with time of the amplitude of the β-relaxation occurring at

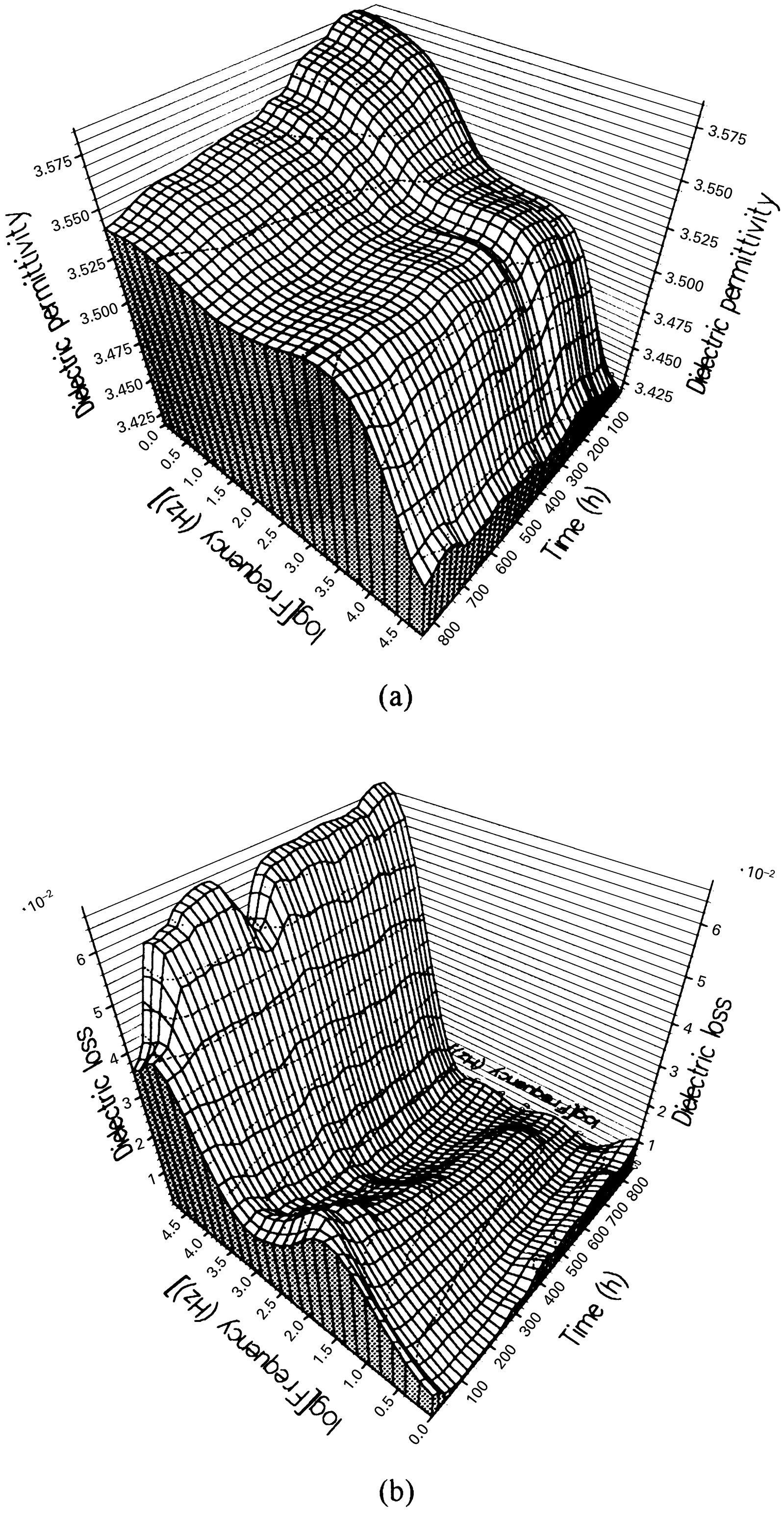


Fig. 5. Dielectric permittivity (a) and dielectric loss (b) of Tronic PEEK exposed to distilled water at 30°C.

40 Hz with water uptake. Comparison of the decrease in amplitude of the dielectric loss with the change in the permittivity increment indicates that they are coupled events. The dielectric spectrum contains processes which are associated with both polymer chain motion and the effects of water absorption. In order to be able to differentiate between fixtures due to relaxation processes of the polymer chain from these associated with water dipoles a

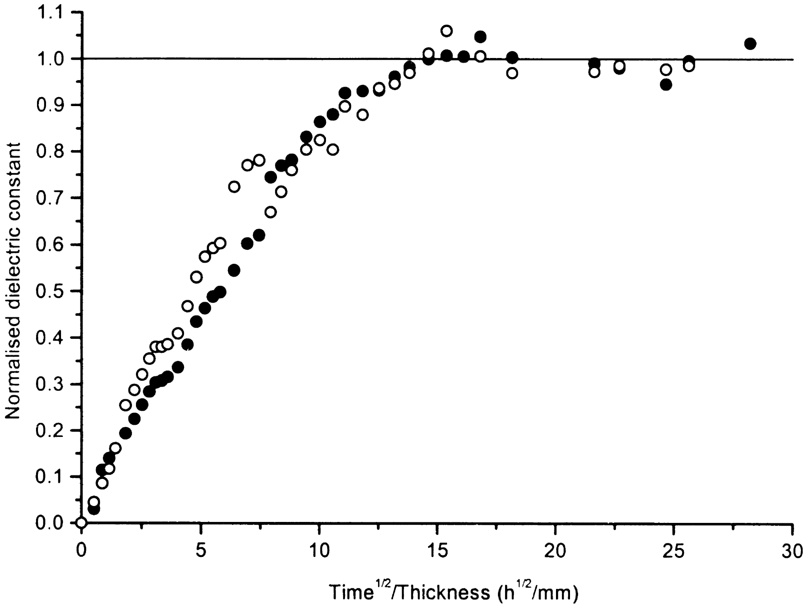


Fig. 6. Comparison of normalised dielectric constant at ○ 63 030 Hz and ● 1000 Hz: correlation coefficient = 0.98.

comparison of the normalised dielectric constant at 1 and 63 kHz was undertaken (Fig. 6). Comparison of time evolution of these data yielded a correlation coefficient of 0.98. This indicates that the relaxation centred at 40 Hz can be assumed to be independent of that at 63 kHz, the latter being associated with water uptake by the polymer matrix. The former process is associated with polymer chain relaxation which is a consequence of water uptake changing its amplitude. Such a reduction in amplitude of a relaxation process can be associated with densification of the polymer matrix. Since water uptake is considered in this study, it was decided to use the results obtained at 63 kHz rather than 1 kHz. Indeed, the higher the frequency, the less probable the results would be distributed by a relaxation of the polymer itself. It should be noticed at this point that the procedure for measuring the frequency is valid for any material. However, the operator should make sure that the range in which the frequency is chosen does not present any disturbance caused by a variation during ageing of a relaxation of the material itself.

Fig. 7 shows the results after normalisation of the dielectric constant at 63 kHz. It can be seen that the results are in

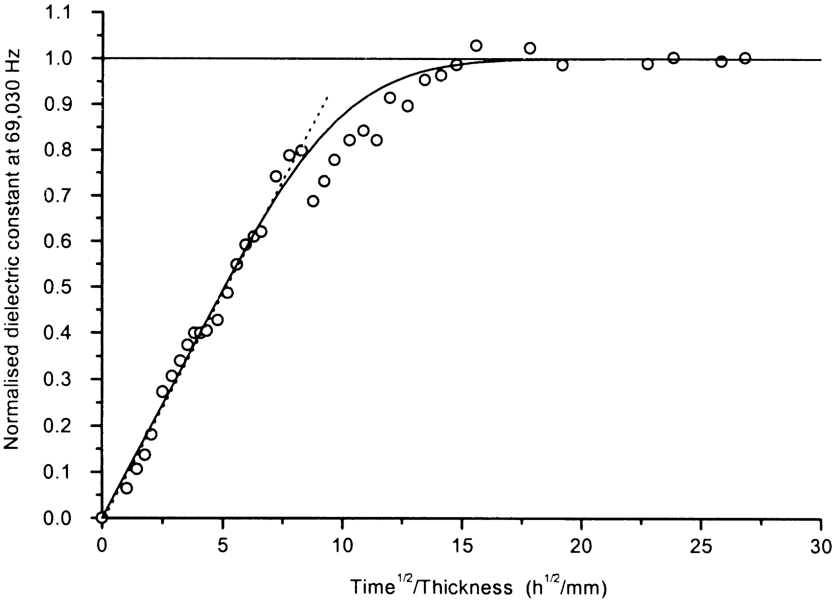
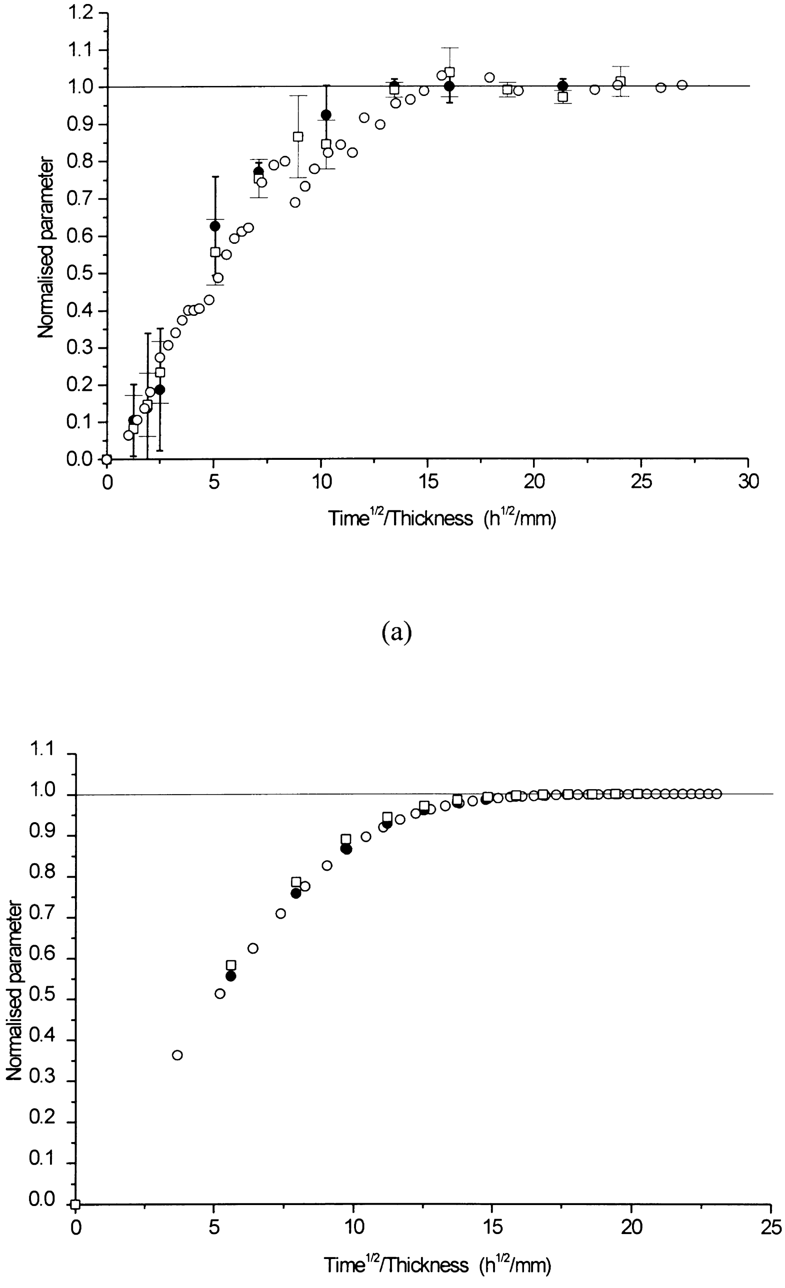


Fig. 7. Normalised dielectric constant of Tronic PEEK exposed to distilled water at 30°C: $D = 1.91\ \mathrm{mm}^2/\mathrm{h}$, correlation coefficient between normalised dielectric constant and Fickian model: 0.80.



(a)

(b)

Fig. 8. Comparison of (a) normalised data for Tronic PEEK exposed at 30°C and (b) Fickian models for exposure at 30°C: ○ dielectric constant at 63 030 Hz ($D = 1.91\mathrm{e} - 3\ \mathrm{mm}^2/\mathrm{h}$), ● distilled water uptake ($D = 1.95\mathrm{e} - 3\ \mathrm{mm}^2/\mathrm{h}$), □ brine uptake ($D = 2.15\mathrm{e} - 3\ \mathrm{mm}^2/\mathrm{h}$).

agreement with a Fickian Case I sorption behaviour (curve linear up to 60% of the equilibrium, then concave against the abscissa) and a highly satisfactory correlation coefficient of 0.80 between the dielectric data and the Fickian model was obtained.

Comparison of the normalised gravimetric and dielectric data (Fig. 8a) and of the Fickian models (Fig. 8b) show that the results of gravimetric and dielectric experience are similar and present a high correlation with the diffusion coefficient of distilled water being identical whereas calculated from the gravimetric or the dielectric measurements. Furthermore, it shows that, at 30°C, the sorption behaviour is independent of the salinity of the water since the results obtained for brine and distilled water are similar.

This experiment, therefore, validates the use of low frequency dielectric spectroscopy as a way to measure

Table 5
Summary of the results

PEEK	T_g (°C)	f_c (w/w%)	Solubility (w%)	D (mm^2/h) Absorption Reabsorption	Correlation Coefficient (data/model)
Victrex					
‘as received’	162 ± 7	30 ± 0.3			
Tronic					
‘as received’	166 ± 3	24 ± 0.3			
Exposure at 75°C					
Victrex					
Distilled water	146	23	0.5 ± 0.01	5.21×10^{-2}	0.88
				2.61×10^{-2}	0.80
Brine	150	24	0.5 ± 0.01	4.01×10^{-2}	0.82
				2.75×10^{-2}	0.74
Tronic					
Distilled water	161	24	0.43 ± 0.02	1.79×10^{-2}	0.82
				1.96×10^{-2}	0.80
Brine	161	24	0.43 ± 0.02	1.43×10^{-2}	0.86
				2.66×10^{-2}	0.81
Exposure at 30°C					
Victrex					
Distilled water	152	26	0.34 ± 0.01	3.89×10^{-3}	0.75
Brine	152	26	0.33 ± 0.01	3.30×10^{-3}	0.94
Tronic					
Distilled water	155	20	0.33 ± 0.03	1.95×10^{-3}	0.75
Brine	155	23	0.36 ± 0.03	2.15×10^{-3}	0.74

water uptake in polymeric materials, at least for filler free thermoplastics.

5. Conclusion

A summary of the results for all the experiments performed on Victrex PEEK and Tronic PEEK is presented in Table 5. In agreement with the literature [8] and the data provided by Victrex [14], the water sorption behaviour of semi-crystalline PEEK follows a Fickian Case I process with a maximum solubility of 0.5% at 75°C. This allowed use of a model based on Fick’s laws proposed in Crank’s book on the mathematics of diffusion [12]. Using this model it is possible to determine, for the same conditions of exposure, the amount of water present in a sample at any time, anywhere in its thickness. Furthermore, the sorption behaviour seems independent of the salinity of the water to which the polymer is exposed.

The water uptake proved, however, to have an effect on the characteristics of the material as shown by a decrease of its bending modulus up to 40% in the case of Victrex PEEK and a decrease of the glass transition temperature, both of which were consistent with a decrease in the crystallinity of the polymer. It is proposed that physical processes caused loss of the crystalline phase and an apparent restriction of the extend of chain motion associated with the relaxation which occurs at 40 Hz.

Finally, it is concluded that low frequency dielectric spectroscopy can provide a useful non-destructive evaluation technique to allow determination of water uptake in filler-free thermoplastics. This, however, requires a careful and considerate selection of the measuring frequency. The advantages of this technique over the gravimetric technique are that the sample is never removed from its environment and that evolution of other characteristics such as the dielectric properties of a material over a wide range of frequencies can be simultaneously observed.

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