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Solvent mixtures sorption in amorphous peek

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Dedicated to Prof. Dragutin Fleš on the occasion of his 70th birthday

SUMMARY

The sorption kinetics and equilibrium isotherms of methylene chloride, n-heptane and of methylene chloride/n-heptane mixtures in glassy amorphous Poly(aryl-ether-ether-ketone) (PEEK) have been investigated. Ideal Fickian diffusion , anomalous non-ideal Fickian diffusion, "Case II" sorption mechanism and diffusion controlled swelling were observed depending on temperature, on solvent type and on external solvent activity. Gas-chromatographic analysis performed on PEEK samples contacted with methylene chloride/n-heptane mixtures indicated that the presence of methylene chloride enhances n-heptane mobility and equilibrium sorbed amount .

INTRODUCTION

Solvent sorption in glassy polymers exhibits a wide variety of effects depending on the polymer-penetrant affinity, on temperature and on penetrant activity.The behaviour ranges from ideal Fickian diffusion to relaxation controlled limiting "Case II" (HOPFENBERG and FRISCH 1969, BERENS 1977, BERENS 1978, SARTI and APICELLA 1980, SARTI et al. 1984).

Poly(aryl-ether-ether-ketone) (PEEK) is a thermoplastic polymer with attractive high performances as matrix for polymer based composite materials. It is a tough aromatic polymer having a glass transition temperature at about 145 C while the melting point of semicrystalline material is about 335 C. Its resistance to the action of solvents which it could contact is of primary importance. Some organic solvents show strong interactions with PEEK (STOBER et al. 1984, STOBER et al. 1988): In particular methylene chloride plasticizes the amorphous matrix inducing the crystallization of initially amorphous samples (MENSITIERI et al. 1989). On the basis of solubility parameter and hydrogen bonding capability n-heptane is expected to be sorbed only slightly in PEEK.

EXPERIMENTAL

Materials

Amorphous PEEK films 50 and 250 μm thick produced by ICI were used as received. Measurements performed on the virgin samples by means of a density gradient coloumn showed a density value of 1.266 g/cm^3 that is close to the value attributed to a totally amorphous sample. All the penetrant used in vapour sorption experiments were previously degassed by multiple freeze-thaw cycles.

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Apparatus and procedures

Vapour sorption experiments. The vapour sorption kinetics and equilibria were monitored using a gravimetric technique by means of a quartz spring having a sensitivity of 5 mg/cm. The spring is placed in a water jacket glass cell with service lines to a solvent reservoir and to a pressure transducer.

Liquid sorption experiments. The polymer 3x5 cm^2 samples were immersed in 100 cm^3 test tubes containing the solvent and kept at controlled temperature in a water thermostated bath (± 0.1 C accuracy). At fixed times the samples were removed, rapidly blotted, and weighed using an electronic balance (Mettler AE 100) with an accuracy of 10^{-4} grams.

Gas-chromatographic (GC) analysis. Gas-chromatographic (GC) analyses were performed to determine the methylene chloride and n-heptane sorption equilibrium uptakes and kinetics in the case of 50 µm thick PEEK films contacted with pure liquid n-heptane and methylene chloride/n-heptane liquid mixtures with low methylene chloride content at T = 36 C. The samples were removed from the solvent containers at different times, blotted, placed in analysis vials and then sealed by means of Teflon caps. The vials were then kept in oven at 125 C in order to extract the sorbed solvents. The vial content was hence analyzed by means of a Carlo Erba Strumentazione HRGC 5300 gas-chromatograph. The analysis procedure was repeated several times on each sample in order to insure the complete removal of the sorbed solvents.

RESULTS AND DISCUSSION

Pure solvents sorption

n-heptane sorption. Because of its weak interaction with polymer macromolecules, n-heptane is expected to be sorbed in small amount. Figure 1 reports the results of tests performed at 36 C and at 98 C on a 50 µm thick film. In the investigated experimental times (3 months) the system does not seem to have reached the equilibrium in both cases. The weight gain is linear with the square root of time. In fact n-heptane sorption is a very slow phenomenon: Due to its big van der Waals diameter the n-heptane has a small mobility in the glassy PEEK.

Methylene chloride sorption. Pure liquid methylene chloride sorption at temperatures ranging from -32 to 36 C and methylene chloride vapour sorption at different activities at T = 36 C have been performed.

The sorption uptakes of liquid methylene chloride in 250 µm thick films at T = -32 C and T = 36 C are reported in figure 2. At -32 C the kinetic curve showes an upward concavity indicating that the weight gain increases linearly with time. This behaviour is tipically reported as "Case II" sorption.Conversely at 36 C, although a sharp penetration front is still present as documented by optical microscopy (MENSITIERI et al. 1989), the sorption uptake increases linearly with the square root of time: The diffusive resistance in the swollen shell becomes the penetration rate controlling step.

The strong plasticizing action due to methylene chloride that leads to "Case II" sorption brings about a solvent induced crystallization at all the investigated temperatures for the samples contacted with pure liquid methylene chloride.

Methylene chloride vapour sorption kinetics have been investigated on 50 µm thick films at 36 C and at low solvent activity in order to characterize the PEEK sorption behaviour in the glassy state (figure 3). The sorption behaviour is approximately Fickian at the lowest investigated activities (a = 0.08 and a = 0.18); conversely at a = 0.34 the Fickian diffusion is coupled with a slow polymer matrix relaxation. At these activity levels no solvent induced crystallization was detected.

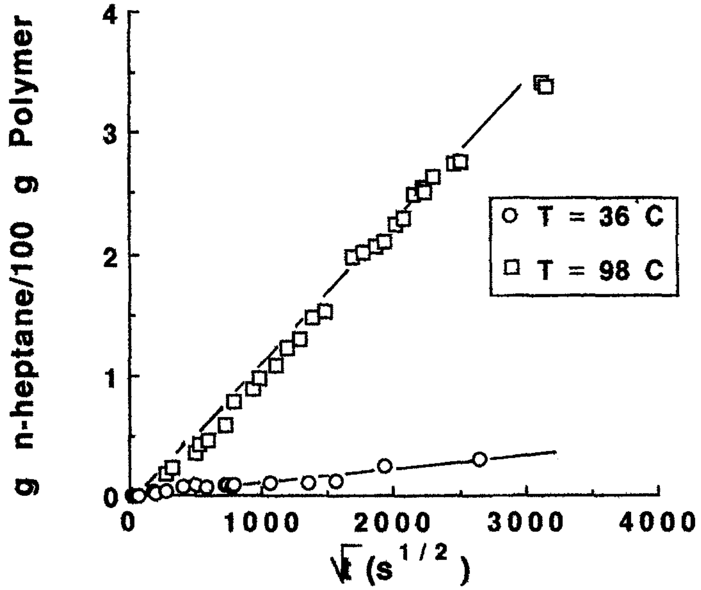

Figure 1. liquid n-heptane sorption kinetic in amorphous PEEK (50 µm); T = 36 C and 98 C

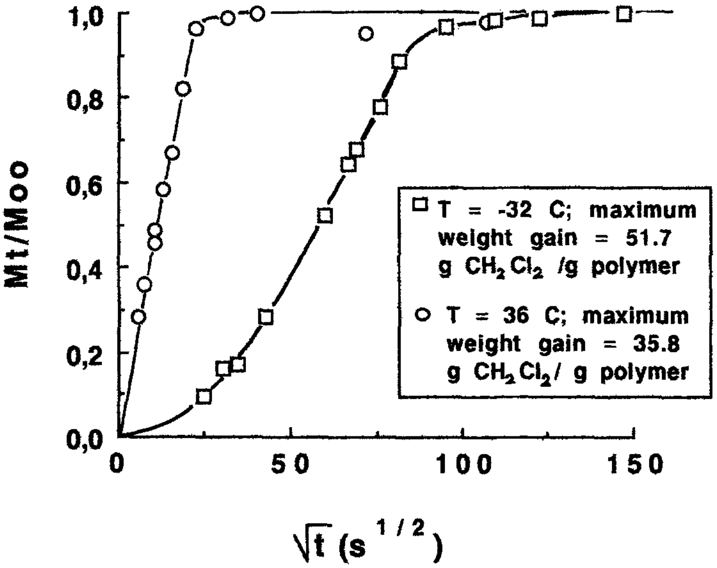

Figure 2. Liquid methylene chloride sorption kinetics at different temperatures in amorphous PEEK (250 µm)

The interpretation of equilibrium sorption data is not easy to be performed because of solvent induced plasticization and crystallization at high activities: The polymer-solvent pair interaction parameter has been approximatively evaluated relating the maximum solvent uptake detected in the case of pure liquid methylene chloride sorption to the effective amorphous fraction of the solvent crystallized sample. The value of the Flory interaction parameter (χ) calculated in this way is about 0.97.

Methylene chloride/n-heptane mixtures sorption

Sorption tests were performed at 36 C in methylene chloride/n-heptane mixtures of different methylene chloride molar fraction. The corresponding methylene chloride activity of each mixture as calculated by means of a contribution group method (KOJIMA and TOCHIGI 1979). In order to optimize the experimental times, the experiments were made on 250 µm thick amorphous PEEK films for mixture in the range of methylene chloride activity 0.375-0.95, and on 50 µm thick films in the range 0.076-0.34.

In the case of 250 µm thick films the experimental behaviour passes from a relaxation controlled diffusion (concave upward curves) to a diffusion controlled relaxation (sharp penetration front moving linearly with the square root of time) as the methylene chloride activity increases. After the attainment of the maximum solvent uptake a slow decrease in the weight gain was observed. Wide angle X-ray scattering measurements (MENSITIERI et al. 1989, MENSITIERI et al. 1990) performed after desorption on samples equilibrated in the different mixtures showed an increasing percentage of solvent induced crystallization. Only the samples contacted with the low activity mixture (a = 0.37) remained in the glassy amorphous state.

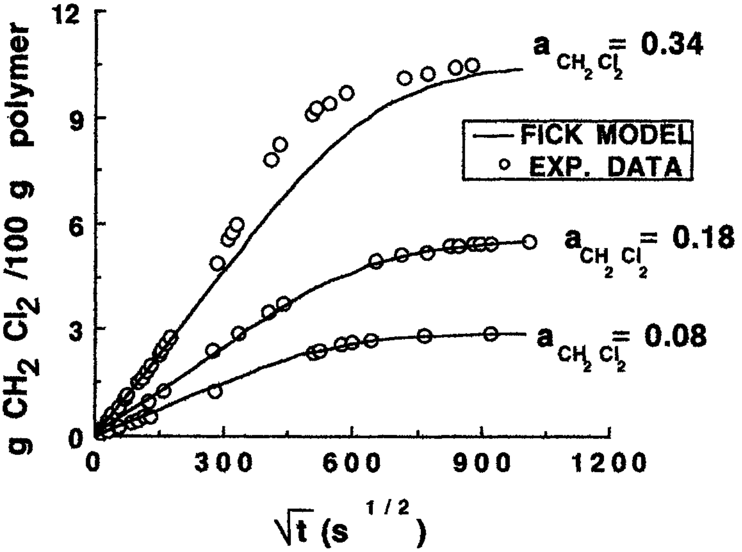

Figure 3. Vapour phase methylene chloride sorption kinetics in amorphous PEEK (50 µm) at T = 36 C for different solvent activities (quartz spring)

In the case of the low activities range (a = 0.076, a = 0.12 and a = 0.34) the tests performed on 50 µm thick films by means of electronic balance measurements, revealed a Fickian behaviour at low activities (0.076 and 0.12) while at the activity level equal to 0.34 a relaxation accompanies the solvents diffusion. The sorption behaviour is hence qualitatively similar to that reported in the case of pure methylene chloride vapour sorption (figure 3) at the same activity values. In these low methylene chloride activity tests no solvent induced crystallization was detected. Thermal analisys (Differential scanning calorimetry) performed (MENSITIERI et al. 1989) both on 50 µm and 250 µm thick films equilibrated in different composition mixtures revealed the strong plasticization effect proportional to the methylene chloride activity of the mixture.

In order to investigate the sorption behaviour of each solvent composing the low methylene chloride activity mixtures a gas-chromatographic technique was adopted using 50 µm thick films at T = 36 C.

The analysis was performed only in the case of low activity levels in order to avoid complications due to the crystallization phenomenon. The whole kinetic has been detected in the case of mixtures with a methylene chloride activity equal to 0.19 and 0.34 and in the case of pure liquid n-heptane sorption. Only long times data (about 3 months) were collected in the case of mixtures with methylene chloride activities equal to 0.076 and 0.12.

The consistency of gaschromatographic and gravimetric techniques was proved comparing the total amount of sorbed solvent evaluated by means of the two methods.

The mutual influence of the two concurrently penetrating solvents was investigated examining the solvents sorption kinetics separately. N-heptane does not seem to affect very much the behaviour of the contemporaneously diffusing methylene chloride. The methylene chloride sorption kinetic curves at methylene chloride activities equal to 0.19 and 0.34 show for the former value an approximately Fickian behaviour while for the latter the occurence of a relaxation phenomenon is evident.

The comparison between the methylene chloride sorption kinetic tests performed in the pure solvent vapour phase and the tests performed in the liquid mixture phase at the same methylene chloride activities did not show significant differences in the attained equilibrium uptake as well as in the kinetic behaviour. The only detectable difference consists of a slightly faster relaxation rate in the case of liquid mixture sorption at a methylene chloride activity equal to 0.34 compared to the case of pure methylene chloride vapour sorption at the same activity.

Because of its big van der Waals volume the n-heptane is characterized by a small diffusion constant into glassy state polymers. As consequence the equilibrium uptake can be attained only for very long experimental times at T = 36 C even in 50 µm thick film. For the adopted experimental times (3 months) the n-heptane equilibrium sorbed amount was attained only in the case of the sorption of liquid mixture with a methylene chloride activity equal to 0.34 (figure 4). In the case of pure n-heptane a sorbed amount of about 0.3% was detected after 3 months: As we will discuss later the expected equilibrium value should be 2.2%. As can be deduced from the reported n-heptane sorption kinetics the methylene chloride enhances the n-heptane mobility of several orders of magnitude: This effect is related to the plasticizing action of methylene chloride that increases the total free volume of the system.

Table 1 reports the sorbed amounts for each solvent detected after an immersion period of 3 months.

The n-heptane weight gain kinetic curve for the sorption of the mixture with a methylene chloride activity equal to 0.34 shows an evident departure from Fickian behaviour due to polymer relaxation phenomena. Figure 5 compares the methylene chloride and n-heptane sorption kinetic curves relative to this mixture.

It can be summarized that the examination of the sorption kinetic data for the concurrent penetration of the two solvents leads to the conclusion that there is a mutual influence of the penetrants. Methylene chloride improves very much the n-heptane penetration rate while the presence of n-heptane slightly enhances the speed of polymer relaxation at least in the case of the maximum methylene chloride activity mixture (a=0.34) investigated by means of gas-chromatographic technique.

TABLE 1

Methylene chloride and n-heptane percent uptake (percent weight gain relative to the polymer amount) for a 50 μm amorphous PEEK film contacted for 3 months with methylene chloride/n-heptane mixtures having different methylene chloride activity.

Calculated methylene chloride activity	methylene chlor. uptake	n-heptane uptake
0	0 %	0.30 %
0.076	3.0 % *	0.42 %
0.12	4.3 % *	0.62 %
0.19	5.6 % *	0.96 %
0.34	10.2 % *	2.42 % *

* = equilibrium value

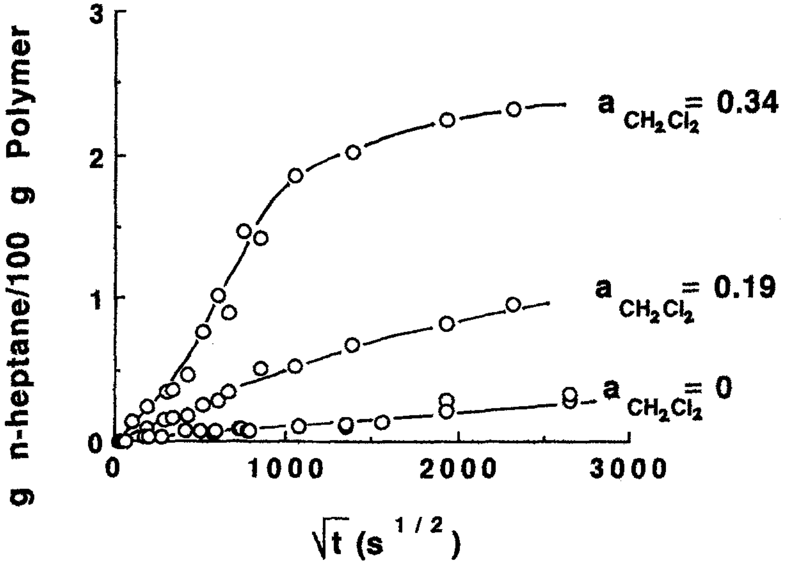

Figure 4. N-heptane weight gain kinetics for liquid methylene chloride/n-heptane mixtures sorption at two different methylene chloride activities (a = 0.34 and a = 0.19)and for pure liquid n-heptane sorpttion (methylene chloride activity = 0)at T=36C (gaschromatograph)

The equilibrium analysis of the data obtained by gaschromatographic measurements of this biphasic three-component system is difficult to be carried out for several reasons: The test temperature (36 C) is below the glass transition temperature of the system, the sorption of methylene chloride in the case of high activity mixtures induces polymer crystallization and overshoot phenomena, the pure n-heptane sorption is very slow even in the case of 50 µm thick films (the smallest available) hence the n-heptane equilibrium sorption cannot be attained in reasonable experimental times.

Even though these limitations do not allow quantitative comments, some qualitative conclusions can be drawn using the polymer multicomponent solution Flory theory (FLORY 1953). In order to use the Flory theory the mutual interaction parameters of the three components must be known. As rough approximation the interaction parameter between methylene chloride and PEEK can be assumed to be equal to 0.97, as has been previously discussed.

The solvent pair interaction parameter has been evaluated using the results of the group contribution method adopted to calculate the mixtures methylene chloride activities. The estimated value of n-heptane/methylene chloride interaction parameter is 1.63.

Because of the very long requested experimental times we have not the pure n-heptane/PEEK interaction parameter available: We used the three components Flory theory to obtain this value. The five equations system has been numerically solved by trials to comply with the only n-heptane equilirium value available: The n-heptane uptake relative to the 0.34 methylene chloride activity mixture. The involved mathematical system is composed of three equations stating the equality of each component chemical potential in the two phases(polymer rich phase and dilute phase) and two equations stating the material balance constraints (FLORY 1953, YILMAZ and MCHUGH 1986). We estimated a n-heptane/PEEK interaction parameter equal to 2.5.

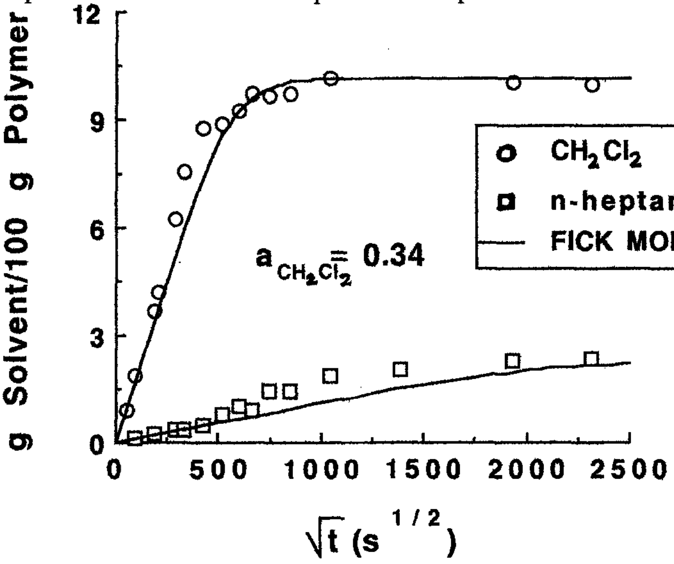

Figure 5. N-heptane and methylene chloride weight gain kinetics for liquid methylene chloride/n-heptane mixture sorption in amorphous PEEK (50µm) at a methylene chloride activity equal to 0.34; T = 36 C (gas-chromatograph).

In the foregoing discussion we assumed that the interaction parameters do not depend on the system composition; furthermore the n-heptane sorption in PEEK has been supposed to follow the Flory theory (no adsorption in microcavities or on interaction sites).

On the basis of all the aforementioned assumptions ,the application of the three components Flory theory qualitatively predict an enhancement of the n-heptane equilibrium sorption if compared to the case of pure n-heptane sorption. The n-heptane sorption curve predicted on the basis of the three components Flory theory has a concave downward curvature and even shows a maximum at a n-heptane activity lower than 1. This calculation predicts a pure n-heptane sorbed amount of about 2.2%. Sorption tests are now in progress to attain long time data in the case of the lowest activity mixtures sorption.

The theory and the experimental results show that there is practically no influence of the n-heptane presence on methylene chloride sorbed equilibrium amounts at least for mixtures with methylene chloride activity smaller than 0.4: at the same activities the equilibrium solvent uptake in case of mixture sorption is the same value detected for pure vapour solvent tests).

CONCLUSION

Exposure of amorphous PEEK films of different thicknesses to liquid and vapour phase penetrant at several temperatures and activities exhibited a broad range of sorption behaviours .Solvent induced crystallization has also been detected.

The analysis of methylene chloride/n-heptane mixtures sorption in PEEK has pointed out the mutual influence of the contemporaneously penetrating solvents.Methylene chloride enhances both the n-heptane mobility and equilibrium uptake, while n-heptane affects slightly the methylene chloride uptake rate.

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