Case II Swelling of Poly(ethylene Terephthalate) in Organic Solvents

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Synopsis

The swelling kinetics of crystalline PET films in chloroform–n-hexane mixtures were examined as a function of chloroform concentration. With increasing concentration, the swelling mechanism varied from Fickian to Case II behavior. The dependence of the swelling mechanism on the equilibrium uptake and activation energy for swelling were thoroughly compatible with those presented by other workers. From a viewpoint of superposition of Fickian and Case II swelling, the intermediate swelling between the above two limiting cases was analyzed by Kwei's equation. The magnitude of the diffusion coefficient obtained was remarkably smaller than that presented for the swollen amorphous polymer. The magnitude of the penetration velocity is also discussed in comparison with the data for amorphous polymer.

INTRODUCTION

Anomalous swelling in which the solvent uptake increases linearly with time is often observed for amorphous, glassy polymers such as polystyrene,[1-8] cross-linked epoxy resins,[9,10] and poly(methyl methacrylate).[11] This has been designated by Alfrey et al.[12] as Case II swelling and was clearly distinguished from Fickian behavior in which the uptake increases linearly with the square root of time. Another important feature of Case II swelling is that a solvent penetrates into the polymer with a sharp boundary which separates the inner unswollen glassy core from the outer swollen rubbery shell.[12]

Thermodynamic considerations of Case II swelling were taken into account by Frisch et al.[10] and Sarti.[13] Peterlin[14-16] and Kwei et al.[17,18] separately presented theories to explain the swelling process in which Fickian and Case II mechanisms were operative independently and simultaneously. Michaels et al.[1] exhibited that the rate-controlling step of the Case II swelling process is a polymer relaxation at the boundary front induced by the swelling pressure. Hopfenberg et al.[3] studied in detail the parameters affecting the polymer relaxation such as the temperature and the solvent activity in connection with Case II behavior.

The author previously studied the swelling kinetics of the crystalline PET fibers in various interactive liquid solvents and found that the uptake is proportional to time during most of the swelling process under properly chosen conditions.[19]

In this work, the swelling kinetics of the crystalline PET films in chloroform–n-hexane mixtures are studied as a function of chloroform concentration. At higher concentrations, the data indicate again that solvent uptake increases linearly with time. Based on this result, the additional data on the swelling of PET are compared with those of Case II swelling reported for amorphous polymers.

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Another object of this work is to analyze the intermediate swelling between Fickian and Case II behavior from a viewpoint of superposition of the above two limiting cases, and also to calculate the diffusion coefficient and the penetration velocity of the solvent in crystalline PET.

EXPERIMENTAL

Materials

Commercial, biaxially oriented films of crystallinity 58.7% and thickness 16 μ were used unless otherwise indicated. The solvents used were reagent grade.

Crystallinity Measurements

The crystallinity X of PET was calculated by eq. (1):

$$\frac{1}{d} = \frac{X}{d_c} + \frac{1-X}{d_a} \tag{1}$$

where d, d_c, and d_a are the densities for a given sample, and of the crystalline and amorphous phases, respectively. The values of d_c and d_a are taken to be 1.455 g/cm^3 and 1.335 g/cm^3, respectively.[20]

Swelling Procedures and Measurements

After samples were put in the liquid solvent for a specified length of time at 30°C, they were taken out of the liquid and were blotted with the filter paper to remove excess liquid from the surface. The solvent uptake Q_t was calculated by the following equation:

$$Q_t = \frac{d_1(w_2 - w_1)}{d_2 w_1} \times 100 \tag{2}$$

where w_1 and w_2 are the weights of PET before and after the swelling, and d_1 and d_2 are the densities of PET and the solvent at 30°C, respectively. The value of Q_t expressed in the form of eq. (2) implies the apparent increase in the volume for PET accompanied by the sorption. The values readily available when solvents used are of the different densities.[19]

RESULTS AND DISCUSSION

Swelling of PET Films in Chloroform–*n*-Hexane Mixtures

PET has a strong specific interaction with chloroform, but not with *n*-hexane. It could be assumed that *n*-hexane hardly penetrates into the polymer from the mixture of these solvents. Other workers have suggested that a poorly interactive solvent acts only as a diluent of a highly interactive solvent for a sorption system of the type referred to above.[21] Direct measurement for the solvent extracted from the swollen PET shows that little *n*-hexane penetrated into PET.

The Q_t/Q_∞ (where Q_∞ is the equilibrium value of Q_t) vs. time t plot for several
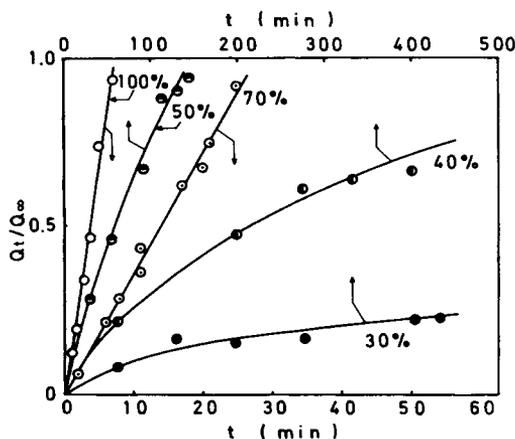
Fig. 1. Swelling kinetics of PET films in chloroform–n-hexane mixtures at 30°C. Percentage indicated represents chloroform concentration in the mixture.

chloroform concentrations is shown in Figure 1. It is observed that the plot is linear at concentrations of 70 and 100%, while it is concave against the t-axis at concentrations of 50% or less than 50%. Especially at a concentration of 30%, the plot of Q_t/Q_∞ against $t^{1/2}$ is found to be linear.

The apparent activation energy was evaluated by fitting the Arrhenius equation to the slope of the linear plot of Q_t/Q_∞ against t for concentrations of 70 and 100%, and to that of Q_t/Q_∞ against $t^{1/2}$ for a concentration of 30%. For concentrations of 40 and 50%, a rate parameter Q_t/tQ_∞ was evaluated at every Q_t/Q_∞. The Arrhenius plot of this parameter reveals that the apparent activation energy is constant during the whole swelling process for each concentration. Q_∞ is independent of the temperature within the experimental error.

As shown in Table I, Q_∞ and the apparent activation energy for swelling increase with increasing chloroform concentration. Also, a definite change in mechanism from Fickian to Case II swelling, judging from the uptake–time relationship, appears with increasing chloroform concentration. The intermediate swelling between Fickian and Case II behaviors, which takes place at concentrations of 40 and 50%, is discussed in detail in the next section.

Hopfenberg et al.[3] reported for the n-hydrocarbon–polystyrene system that the sorption equilibrium and apparent activation energy for sorption increase with the solvent activity. They also noted that a definite change in mechanism from Fickian to Case II swelling takes place with increasing solvent activity. Their results suggested that the Case II process is step-controlled by the

TABLE I
Swelling Characteristics of PET Films in Chloroform–n-Hexane Mixtures at 30°C

Concentration of chloroform, %	Swelling mechanism	Activation energy, kcal/mol	Equilibrium swelling, %
30	Fickian	11.5	7.8
40	Fickian + Case II	12.4	8.6
50	Fickian + Case II	—	10.5
70	Case II	19.0	12.2
100	Case II	23.8	12.8

larger-scale polymer relaxation which takes place at the boundary separating the swollen and unswollen parts.

In the present experiment, the exact chloroform activity is not known. However, since it is certain that the chloroform activity increases with increasing concentration, the results obtained in this work are in qualitatively good agreement with the data of Hopfenberg et al.

It is well recognized that liquid solvents penetrate as a distinct front into the amorphous PET and that those sorption kinetics obey Fickian mechanism.[22] The solvent advancing front related to the Case II process for the crystalline PET could not be observed directly under a microscope. However, one can expect the presence of this front from analogy with that for the amorphous PET.

Analysis of Intermediate Swelling and Calculation of Diffusion Coefficient and Penetration Velocity

The equation representing a superposition of Fickian and Case II swelling is given by[10,14,15,17]

$$M_t = K_1 t^{1/2} + K_2 t \tag{3}$$

where M_t is the solvent uptake per unit area crossing the polymer surface from $t = 0$ to $t = t$, and K_1 and K_2 are constants. In terms of the plot of $Q_t/t^{1/2}$ against $t^{1/2}$, one can examine whether the swelling obeys a superposition or not.

The plot of $Q_t/t^{1/2}$ against $t^{1/2}$ for the swelling at chloroform concentrations of 40 and 50% is shown in Figure 2. A superposition is clearly set up during the most part of each swelling process.

Wang et al.[17] proposed a one-dimensional expression of eq. (4). This is given by

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) - BSc \tag{4}$$
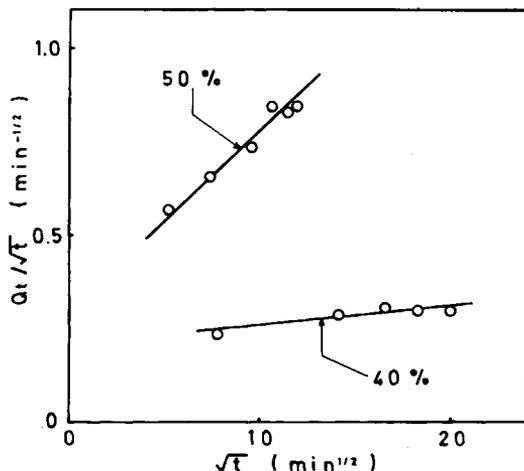
Fig. 2. Analysis of swelling kinetics of PET films in chloroform–n-hexane mixtures based upon a combination of Fickian and Case II swelling mechanisms. Percentage indicated represents chloroform concentration in the mixture.

where D is the diffusion coefficient of the solvent, B is the mobility of the solvent, and S is a dimensionless proportionality factor between the partial stress and the total uptake of the solvent in the polymer; c and x are the concentration and position of the solvent in the polymer, respectively.

Equation (5) was derived from eq. (4), under the assumption that the diffusion takes place for a semiinfinite body and that D and $v = BS$ (where v is the penetration velocity) are constants[17]:

$$M_t = C_\infty \left\{ \frac{D}{v} \, \text{erf} \left[\frac{v}{2} \left(\frac{t}{D} \right)^{1/2} \right] + \frac{vt}{2} \, \text{erfc} \left[-\frac{v}{2} \left(\frac{t}{D} \right)^{1/2} \right] + \left(\frac{Dt}{\pi} \right)^{1/2} \exp \left(-\frac{v^2 t}{4D} \right) \right\} \quad (5)$$

where C_∞ is the equilibrium solvent uptake. In this derivation,[17] $c = 0$, $x > 0$, $t = 0$ and $c = C_\infty$, $x = 0$, $t > 0$ were taken as the initial and boundary conditions, respectively.

Equation (5) satisfies eq. (3), regardless of the length of t. Peterlin[14,15] derived an alternative theory explaining eq. (3) under the assumption that a Fickian wave precedes the advancing front. Peterlin's theory can, however, apply only for small t. Successful application of eq. (5) to the present results suggested that the swelling kinetics for the PET-solvent system would be described in terms of the general diffusion equation, eq. (4).

On this basis, D and v were calculated by eq. (5), where M_t/C_∞ and v were taken as $lQ_t/2Q_\infty$ (where l is the thickness of the film) and K_2/Q_∞, respectively. The results obtained were

$$D = 3.62 \times 10^{-10} \text{ cm}^2/\text{min}$$
$$v = 5.02 \times 10^{-7} \text{ cm/min}$$

for the swelling at a chloroform concentration of 40%, and

$$D = 1.10 \times 10^{-9} \text{ cm}^2/\text{min}$$
$$v = 3.70 \times 10^{-6} \text{ cm/min}$$

for that of 50%. Also, for 70 and 100%, v was directly calculated from the slope of the plot of Q_t/Q_∞ against t. The results were 2.96×10^{-5} and 9.84×10^{-5} cm/min, respectively. In these calculations, it was reasonably assumed that only chloroform could penetrate into PET.

One can find that a superposition of two limiting mechanisms takes place at a chloroform concentration of 100%, when the PET film is annealed under properly chosen conditions. As shown in Figure 3, the superposition appears except at the initial stage of swelling for the annealed film. The film examined here was annealed at 235°C for 1 h under a fixed state in vacuo. Immediately after the annealing, the film was taken out of the oven and allowed to stand at room temperature for cooling. The cooling rate through the glass transition temperature is about 10°C/min. This annealed film has a higher crystallinity of 62.8%.

A structural change would also occur with respect to the amorphous part through the annealing. The structure which induces Fickian swelling at a chloroform concentration of 100% would be developed in the amorphous part for the annealed film. The author has exhibited separately, by dynamic viscoelastic measurement, that the amorphous chain related to Case II behavior had a more elastic character than that related to Fickian behavior.[23] It has also been shown that Cast II swelling is essentially independent of crystallinity.[23]
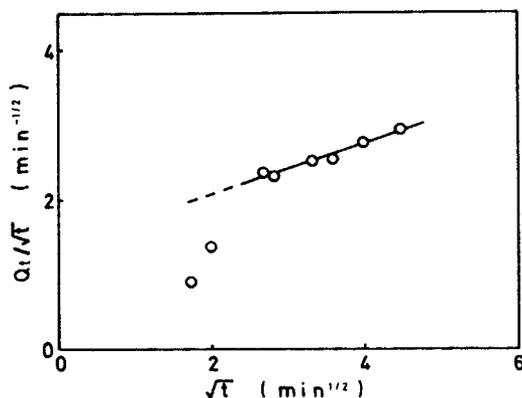
Fig. 3. Analysis of swelling kinetics of PET film in chloroform based upon a combination of Fickian and Case II swelling mechanisms. PET film used was annealed at 235°C under fixed state for 1 h.

One possible reason for the deviation from the linear relationship at small t may be that the boundary condition representing a constant surface concentration of the polymer is not fulfilled in the time interval used for the PET. The deviation would result from the fact that the mobility of the amorphous chain seems to decrease together with increase in crystallinity. The amorphous chain may have so long a relaxation time that the molecular arrangement corresponding the equilibrium concentration C_∞ could not be instantaneously established in the polymer surface.

From the additional analysis of the linear plot demonstrated in Figure 3 by use of eq. (5), the following results were obtained:

$$D = 1.07 \times 10^{-8} \ cm^2/min$$
$$v = 2.03 \times 10^{-5} \ cm/min$$

A value of $1.16 \times 10^{-4} \ cm^2/min$ was estimated for methylene chloride at room temperature in the swollen epoxy resin.[10] The magnitude of D obtained in this work seems remarkably smaller than that for the swollen amorphous polymer.

It has been recognized that the diffusion coefficient of the penetrant for a crystalline polymer such as PET depends very much upon the fine structure.[24] The mobility of the amorphous chain responsible for diffusion may be restrained by the fixation of its ends in the adjacent crystallites. Also, the unpenetrable crystalline domain has an additional, blocking effect on diffusion and can remarkably decrease the diffusion coefficient.[24]

It was reported that the value of v for the n-hydrocarbon–polystyrene system appeared around 10^{-5} cm/min at the same temperature as that of this work.[3] The magnitude of v obtained in this work is rather closer to that presented for amorphous polymer. Consequently, v seems not to be so much influenced by the crystalline domain in contrast to the case of D.

It is certain that the crystalline domain has a blocking effect on v characteristic of the Case II swelling rate in a similar manner as on D. However, there may be an alternative, enhancing effect of the crystalline domain on the Case II swelling rate. Frisch et al.[10] proposed that the driving force for Case II swelling is the partial stress gradient of the penetrant within the polymer. The amor-

phous chain for the crystalline PET would undergo stress due to the fixation of the chain ends in the crystallites, and the resulting stress seems to enhance the Case II swelling rate. Hopfenberg et al.[4] accepted the presence of the enhancing effect of the orientation stress on the Case II swelling rate for the oriented amorphous polystyrene.

It can be concluded that the above-mentioned conflicting effects of the presence of the crystalline domain on v compensate each other in the case of crystalline PET.

CONCLUSIONS

The swelling kinetics of the crystalline PET films in chloroform–n-hexane mixtures were examined. The kinetics observed at higher chloroform concentrations fitted the Case II features revealed by other workers. It was possible to demonstrate both Case II and Fickian swelling in the same PET, varying the chloroform concentration in the mixtures. The intermediate swelling between Fickian and Case II behavior was found to satisfy a superposition of the two limiting cases.

The swelling kinetics were analyzed using Kwei's equation. The magnitude of the diffusion coefficient obtained for PET was remarkably smaller than that reported for the swollen amorphous polymer. In contrast, the value of the penetration velocity was rather closer to that for amorphous polymer. The effects of the crystalline domain on the magnitude of these rate parameters were briefly discussed.

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