

Diffusion of Organic Solvents into Polycarbonate Film

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ABSTRACT: Diffusion rates of organic solvents and water into polycarbonate film were measured under saturated vapor, and the diffusion coefficients were determined by combining the finite element method and the least squares method. The logarithm of the diffusion coefficients decreased linearly with the increase of the molecular volumes of organic solvents and water. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 943–949, 1997

INTRODUCTION

Polycarbonate is used under various circumstances and is sometimes exposed to the vapor of organic solvents. This polymer has strong resistance to alcohols, oils, weak acids, etc., but it is not durable to weak basic compounds, strong acids, and some kinds of organic solvents. Cracks and creases in the molded specimens may be promoted by such compounds. In our previous article¹ it was clarified that a large amount of solvent was absorbed into the test pieces of polycarbonate when the solubility parameter of the solvents was equal to that of this polymer.

We can say that the correlation of this polymer with solvents was clarified fairly well under an equilibrium state. The penetration rate of solvents into polycarbonate is important when the articles prepared from this resin are used under solvent vapor. However, only a few studies have been done on the diffusion coefficient of organic compounds,^{2,3} especially for this polymer. In this study the diffusion rate of organic solvents and water into polycarbonate film was examined in detail, and the diffusion coefficient was calculated from the experimental results. A numerical calculation technique was adopted to improve the accu-

racy by combining it with a traditional technique. The mechanism of the diffusion of organic solvents was discussed in relation to solubility pa-

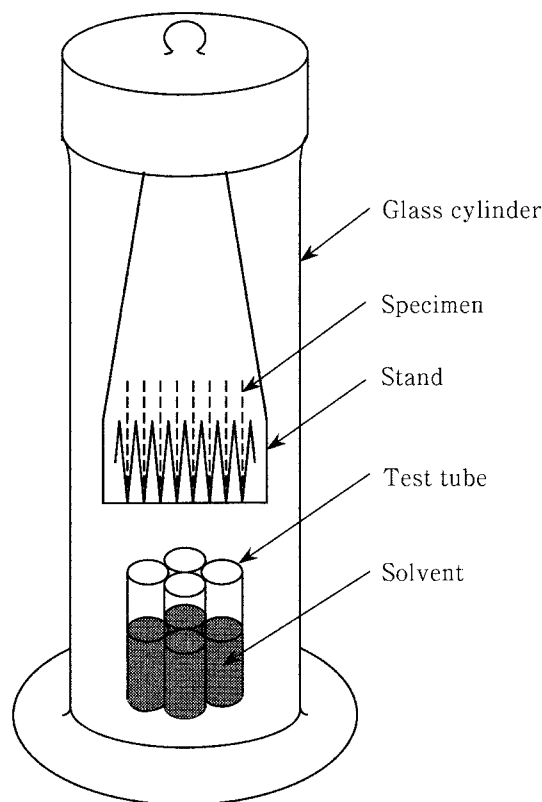


Figure 1 Experiment on vapor absorption.

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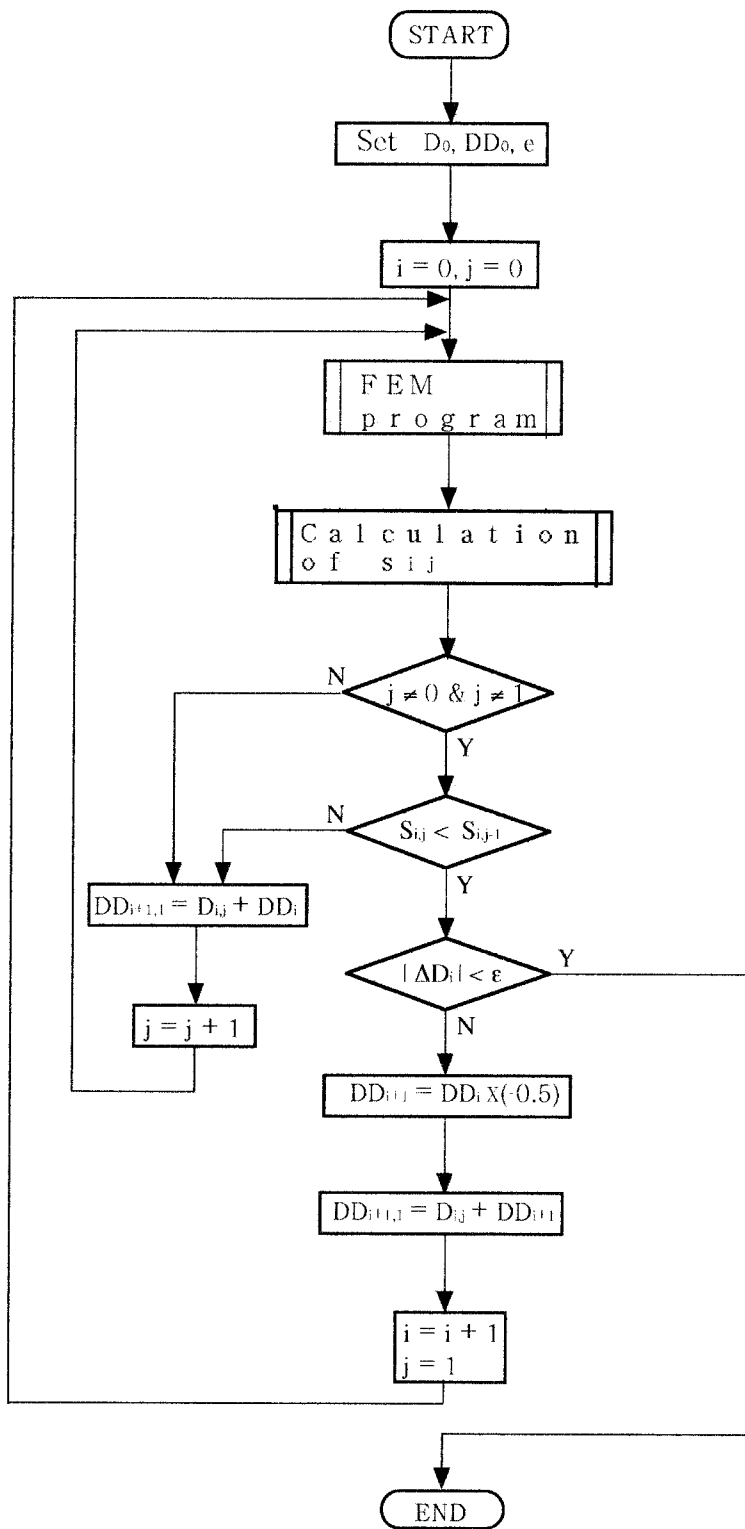


Figure 2 The flowchart of the method to determine the diffusion coefficient.

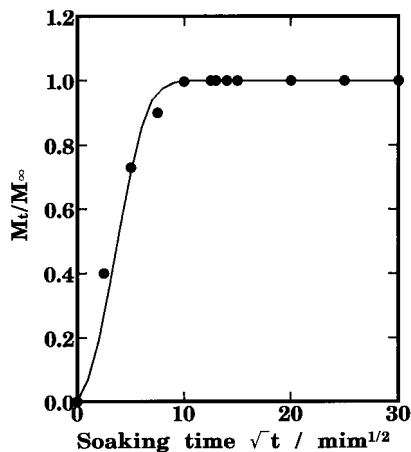


Figure 3 Absorption curve of water for nylon 6 film under 100% relative humidity at 23°C. (●) Experimental values obtained in the bottle shown in Figure 1. (—) Curve obtained by application of TGA apparatus.⁴

parameter^{2,3} and the molecular volume of the organic solvents.

EXPERIMENTAL

Materials

Polycarbonate (bisphenol A carbonate) was supplied by Bayer Japan Co. (Tokyo). Grade 2600 was used. The film was prepared by casting with chloroform and was cut off at the 30 × 20 mm size. The thickness of these pieces was in the range of 40–60 μm.

Nylon 6 film of 30-μm thickness was supplied by Ube Industries Ltd. (Japan), and the 1022B grade was used to confirm the reliability of the experimental method for diffusion, which was adopted in this study.

Molecular Volume

As the first step, the molecular volume of the organic solvents and water was calculated by molecular weight and density. These values were quoted from the literature. As the second step, the molecular volume of the organic solvents and water was calculated by using a computer program on the molecular orbital method (ANCHOR). In this program, the molecular configuration is optimized before the calculation in the molecular orbital method is conducted, and the reasonable molecular volume is expected to be obtained. This program was supplied by Fujitsu Co. Ltd. (Japan). In this method, the molecular vol-

ume was calculated to be included in the volume of the smallest rectangular prism for the molecular structure.

Diffusion Experiment

The diffusion experiment was carried out by suspending polycarbonate films in a cylinder, as shown in Figure 1. Fifteen sheets of the film were usually mounted on the stand. The total weight of the sheet was in the range of 0.3–0.5 g. An organic solvent was introduced into small test tubes placed in the cylinder, and they were left for a few days to obtain saturated vapor pressure. The diffusion experiment was started by introducing polycarbonate films in it. The weight of the polycarbonate films was measured by taking them out with a hanging cage at a given interval.

In this study, the diffusion coefficient was calculated by the method that organic solvents diffuse only from both surfaces of the film.

Two methods^{4,5} are known to obtain diffusion coefficients from a weight versus time curve. In the first method, the diffusion coefficient is obtained by using the straight line of the part in an M_t/M_∞ versus $t^{1/2}$ curve, where M_t indicates the weight of the film at the time t , M_∞ at the time infinity. In the second method, the diffusion coefficient is obtained from the time when $M_t/M_\infty = 0.5$. A straight line was required for the starting region of the M_t/M_∞ versus $t^{1/2}$ curve in the first method; but in the second method, the diffusion coefficient can be obtained without consideration of the straight line in the initial region of M_t/M_∞ versus $t^{1/2}$. However, the consideration of minimizing the error was not conducted in both methods. Therefore, the following data treatment tech-

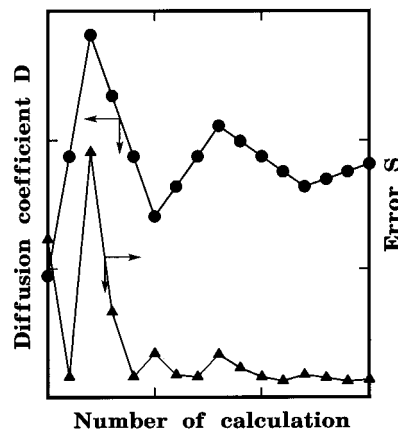


Figure 4 Schematic determination process of the diffusion coefficient by the FEM-least squares method.

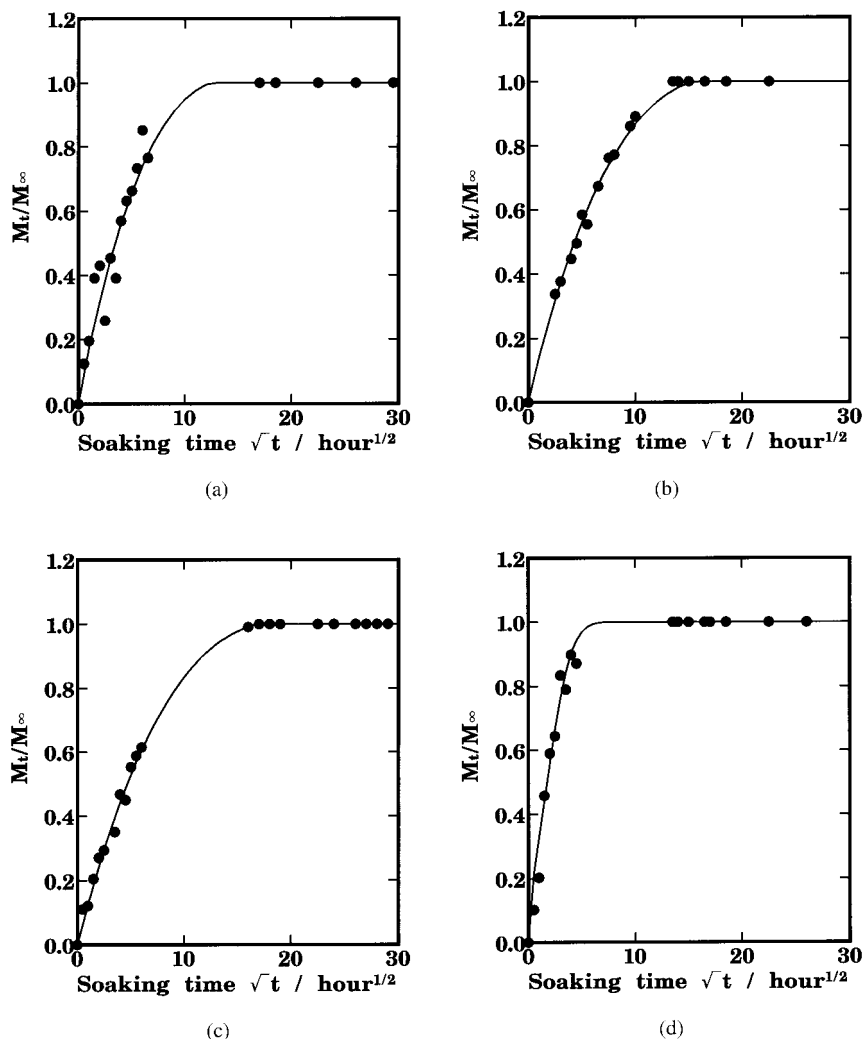


Figure 5 (a) Solvent absorbed curve for polycarbonate film under 100% *n*-pentane at 20°C. (●) Experimental values obtained with the method described in this article. (—) Curve obtained by FEM-least squares method. (b) Solvent absorbed curve for polycarbonate film under 100% isopropyl alcohol at 20°C. (●) Experimental values obtained with the method described in this article. (—) Curve obtained by FEM-least squares method. (c) Solvent absorbed curve for polycarbonate film under 100% *n*-propyl alcohol at 20°C. (●) Experimental values obtained with the method described in this article. (—) Curve obtained by FEM-least squares method. (d) Solvent absorbed curve for polycarbonate film under 100% ethyl alcohol at 20°C. (●) Experimental values obtained with the method described in this article. (—) Curve obtained by FEM-least squares method.

nique was adopted in this study. First, the conventional diffusion coefficient was obtained according to the second method given by eq. (1).

$$D = \frac{0.0491}{t_{0.5}} \cdot d^2, \quad (1)$$

where $t_{0.5}$ is the time that $M_t/M_\infty = 0.5$ and d is the thickness of the film. This equation is easily

derived from eq. (2), which indicates the diffusion equation at a short time.⁵

$$\frac{M_t}{M_\infty} = 4 \left[\frac{Dt}{\pi d^2} \right]^{1/2}. \quad (2)$$

The error in the diffusion coefficient is not minimized, because we usually obtain a larger number

Table I Comparison of Experimental Moisture Absorption and Diffusion Coefficient with Those from Literature for Nylon 6

	Maximum Moisture Absorption (wt %)	Diffusion Coefficient ($\times 10^{-8}$ cm ² /s)
Literature ⁹	10.0	5.60
TGA method ⁸	10.2	5.45
This work	9.2	5.30

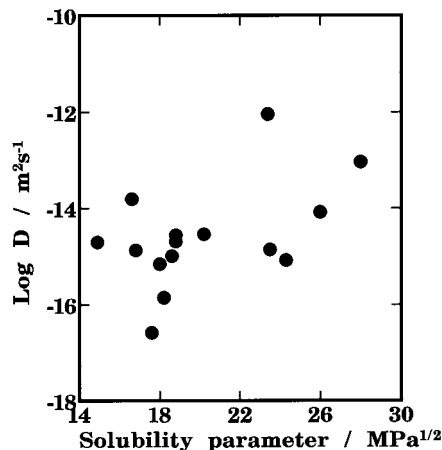
of experimental points than those used in obtaining the D value from eq. (1).

Therefore, to minimize the experimental error, the calculation was conducted by applying the program, PC-9801 Finite Element Method, Programming of Thermal Stress Analysis on Non-Steady State (Nikkan Kougyou Sinbunsha, Tokyo, Japan).⁶ Actually, the program was used after replacing the conductivity coefficient of heat by the diffusion one. In the program, the diffusion equation was solved based on the implicit finite-difference method (Crank–Nicolson method). The simulation process is the same as that reported previously.⁷

The flow chart to determine the diffusion coefficient D is shown in Figure 2. D_0 , ΔD_0 , and ε are set in advance; that is, D_0 is obtained using eq. (1) from the experimental points. The diffusion coefficient $D_{i,j}$ was changed at a given interval shown in Figure 3. The value $S_{i,j}$ was calculated for a given D_0 value. The value $S_{i,j}$ was obtained from eq. (3).

Table II Diffusion Coefficient, Molecular Volume, and Maximum Length Obtained in This Study

Solvent	Diffusion Coefficient ($\times 10^{-15}$ m ² /s)
Water	911
Methyl alcohol	92.1
Ethyl alcohol	8.27
Acetone	2.88
Benzene	2.77
Trichloroethylene	2.02
<i>n</i> -Pentane	1.96
Toluene	1.40
Isopropyl alcohol	1.38
Tetrahydrofuran	1.02
<i>n</i> -Propyl alcohol	0.826
Carbon tetrachloride	0.0263

**Figure 6** Relationship between the logarithm of the diffusion coefficient and the solubility parameter for organic solvents.

$$S_{i,j} = \sum_{k=1} (C_{\text{exp}k} - C_{\text{cal}i,j,k})^2, \quad (3)$$

where C_{exp} is the concentration of the solvent obtained from the experiment, and C_{cal} is that obtained by the finite-element method (FEM) for the same diffusion time t as that of a given experimental point. $S_{i,j}$ was compared with $S_{i,j-1}$ by this program. If $S_{i,j-1}$ was larger than $S_{i,j}$, the interval of the diffusion coefficient was not changed. If $S_{i,j}$ was larger than $S_{i,j-1}$, the interval of the assumed diffusion coefficient was changed to $\frac{1}{2}$ of the previous one. This process can be expressed by eq. (4). When the difference of the calculated two diffusion coefficients reached within a given error ε , the calculation was finished. The finally obtained diffusion coefficient D_t is expressed by eq. (5).

$$\Delta D_i = \left(-\frac{1}{2}\right)^i \cdot (D_1 - D_0), \quad (4)$$

$$D_t = D_{i-1} \pm \Delta D_{if}, \quad (5)$$

where i is a number of the change of ΔD , ΔD_i the interval of diffusion coefficient in the i th calculation, and ΔD_{if} the final ΔD_i . The method explained above is called hereafter the FEM–least squares method. The decreasing process in the error is shown in Figure 4.

RESULTS AND DISCUSSION

The diffusion experiment of water into nylon 6 was conducted in order to confirm the reliability

Table III Molecular Volumes Obtained by M/d and Molecular Orbital Method

Solvent	Volume by M/d ($\times 10^{-6}$ m ³ /mol)	Volume by Molecular Orbital Method ($\times 10^{-6}$ m ³ /mol)	Maximum Length ^a (Å)
Water	18.01	22.49	3.94
Methyl alcohol	40.40	56.94	5.25
Ethyl alcohol	59.10	74.91	6.49
Acetone	73.49	98.43	6.60
<i>n</i> -Propyl alcohol	74.70	101.61	7.39
<i>n</i> -Pentane	74.70	106.87	8.00
Isopropyl alcohol	76.48	101.93	9.24
Tetrahydrofuran	81.24	107.94	8.34
Benzene	88.91	102.02	6.71
Trichloroethylene	89.71	117.21	7.19
Carbon tetrachloride	96.32	144.07	7.18
Toluene	106.44	138.08	6.52

^a Obtained by optimization of molecular conformation in ANCHOR.

of the method. The experimental result was compared with that obtained by the method already established by us.⁸ The result agreed well with that by the previous method,⁸ as shown in Figure 3. The amount of moisture absorption and the diffusion coefficient for nylon 6 are shown in Table I together with the values appearing in the literature. The experimental and study results were in good agreement. The moisture absorption for polycarbonate was 0.47 wt % in the study, in agreement with the value found in the literature.⁹ We can believe that the method adopted in this study is reliable and is applicable to polycarbonate.

Then this method was applied to the polycarbonate–organic solvent system. The examples of M_t/M_∞ versus $t^{1/2}$ are shown in Figure 5(a–d). The curves in this figure were calculated based on the FEM–least squares method. The experimental points fall very well on the simulated curves. The experimental results are summarized in Table II. All the diffusion coefficients for organic solvents are smaller than that of water.

We reported in the previous article¹ that the mechanical properties of polycarbonate were very weak in the organic solvent having the value close to the solubility parameter of the polycarbonate. Therefore, as the first step, the relationship between the logarithm of the diffusion coefficient and the solubility parameter was examined for various organic solvents. However, no good correlation was found between them, as shown in Figure 6. As the second step, it was expected that there was some correlation between molecular

volume of the organic solvents and the diffusion coefficient.

First, the molecular volume was estimated from the molecular weight and density. The molecular volumes of the organic solvents and water are summarized in Table III. The logarithms of the diffusion coefficient were plotted against the volumes, and the result is shown in Figure 7. The relationship between the logarithm of the diffusion coefficient and the molecular volume are expressed by eq. (6).

$$\log D = -0.040 \times V - 11.60, \quad (6)$$

where V is the molecular volume multiplied by

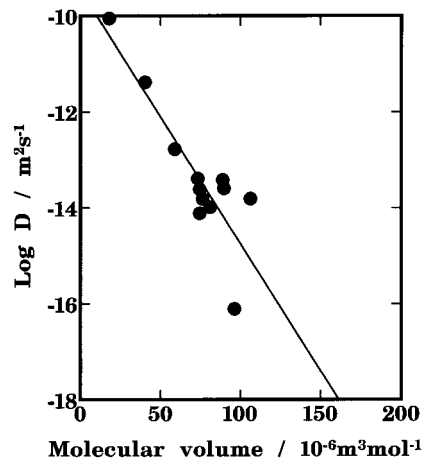


Figure 7 Relationship between the logarithm of the diffusion coefficient and the molecular volume obtained by using molecular weight and density.

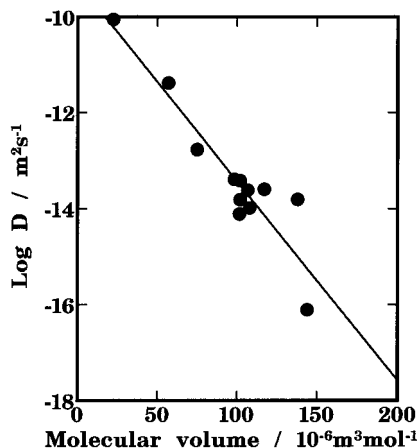


Figure 8 Relationship between the logarithm of the diffusion coefficient and the volume for the organic solvent.

$10^{-6} \text{ m}^3/\text{mol}$. The standard deviation of this plot expressed by $\{1/n \sum (Y_i^1 - Y_i^0)^2\}^{1/2}$ is 0.526, where Y_i^1 is the experimentally obtained $\log D$, Y_i^0 that of the calculated one for a given molecular volume, and n the number of experimental points. The deviations in carbon tetrachloride and toluene are particularly large. Next, the molecular volume was calculated by the molecular orbital method, where the optimum molecular configuration was taken into account. The result is summarized in Table III. As shown in Figure 8, the relationship between the logarithms of the diffusion coefficient and the molecular volume was fairly improved and the standard deviation is 0.391. This result can be expressed by the following equation.

$$\log D = -0.031 \times V - 11.47. \quad (7)$$

The latter correlation is slightly better than the former one. From this result, the smaller the molecular size becomes, the more the it diffuses easily into the polycarbonate. The relationship is the same as that for H_2 , H_2O , O_2 , etc.¹⁰ It is surprising that even the polar organic solvents like alcohols follow the linear correlation. It is known that the

polycarbonate has the free volume above a $10\text{-}\text{\AA}$ diameter.¹¹ The molecular lengths of all the organic solvents and water are smaller than $10\text{-}\text{\AA}$, as shown in Table III. Therefore, it is considered that the solvent and water molecules easily diffuse through the free volume.

CONCLUSIONS

1. The diffusion rate of organic solvents and water into polycarbonate film were measured under saturated vapor, and the diffusion coefficients were calculated from the data by applying the FEM-least squares method, which was adopted for the first time in this study.
2. The logarithm of the diffusion coefficient decreased linearly with the increase of the molecular volumes of organic solvents and water.

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