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Estimation of the compositional gradient in a PVC/PMMA graded blend prepared by the dissolution–diffusion method

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Abstract

We reported a new preparation method in the previous paper, by which an excellent graded polymer blend was simply prepared. In this report, we propose a new model for the dissolution–diffusion process. The model was derived by obeying Fick's second law for diffusion and by assuming that the evaporation of the solvent in PMMA solution during the diffusion could be neglected. We then proved that this model was applicable to the graded structure of a PVC/PMMA graded blend. Further, it was confirmed that the dissolution rate of PVC into PMMA solution remained constant during preparation. Thus, our model was found to be reliable. However, while the apparent diffusion coefficients (D_{AB}s) of PVC in 0.183 and 0.274 ml/cm^2 of the initial solution volumes were equal to each other, they were larger than the D_{AB} in 0.091 ml/cm^2 of the initial solution volume. Thus, the effects of PVC concentration dependency of D_{AB} and changing of PMMA concentration in the solution on D_{AB} were discussed, because all of the D_{AB}s should be equal to each other. Then, our model was modified as follows. We considered that PVC finished diffusing below a PMMA concentration of 0.18 g/ml, because the diffusion coefficient of PVC immediately increased at a higher PMMA concentration. Then, the solution layer was shrunk to about 1/6, in order to form a blend film. Thus, it was found that the D_{AB} in each of the initial solution volumes was $4.2 \pm 0.25 \times 10^{-8}$ cm^2/s. Further, the D_{AB}s estimated by diffusion thickness method, were from 1.5 to 3.5 times larger than those estimated by our model. Therefore, it was proved that our modified model was applicable to the experimental data.

Keywords: Functionally graded materials; Blend; Diffusion

1. Introduction

Many reports [1] have been published on functionally graded materials made of metals and ceramics where the concentration ratio of the pair materials in the composite changes continuously from one side to the other side of the surfaces, and each of the surfaces is made of one of the pair materials. These functionally graded materials have characteristically improved optical properties and strength against thermal stress and are used for space plane applications. However, there have been a few reports [2–4,8–18] on functionally graded polymeric materials, although numerous reports on preparations and properties of homogeneous films of blends have been published [5–7]. Few of those papers treated widely gradient films of miscible blends, although some discussion was given to a two-layer system having a gradient concentration at a very thin interface layer [8–15]. The widely graded films of miscible blends are considered to be laminate films completely lacking an interface; the absence of the interface is expected to improve several types of properties (strength against thermal stress, optical transparency property, etc.) of the blend.

The preparation of graded structures has been performed by interdiffusion [8–15] of polymers in a molten state or polymerization [2,16–18] after diffusing of monomers into another type of polymer. However, in the interdiffusion method, the interdiffusion coefficient in a molten state is sufficiently small, and thus it takes a long time for preparing a sample with a widely graded structure. In the other method,

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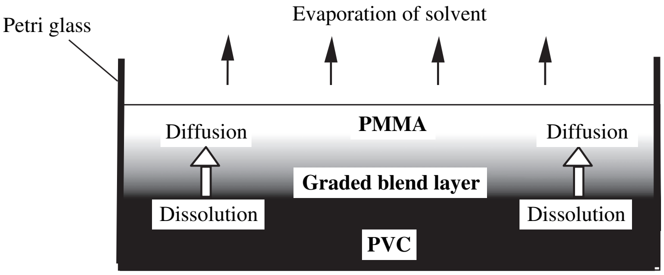

Fig. 1. Schematic model of formation of the graded structure.

the monomer is easy to maintain in a prepared graded structure, because of incomplete polymerization. The graded structure may be limited to a thin layer by using a photopolymerization process.

Thus, in a previous report [19], we prepared several types of graded films of PVC/PMMA blends by a dissolution–diffusion method as illustrated in Fig. 1, and confirmed the compositional gradient of these films by DSC and FTIR-ATR methods. In the dissolution–diffusion method, the diffusion rate is expected to be larger than that in the interdiffusion method because of diffusion in solution. The estimations of dissolution rate and diffusion coefficient are significantly important in understanding the formation of a compositional gradient prepared by the dissolution–diffusion method. However, it is considered that this preparation process is complicated because it is affected not only by diffusion but also by dissolution and evaporation processes. There have been no reports of that estimation, while some reports have been published on the diffusion of polymers in solution.

The diffusion of polymers in semidilute and concentrated solutions has been and still is under extensive experimental and theoretical investigations [20–27]. For example, the diffusion coefficient of polystyrene in *trans*-decalin was reported [21] to decrease in the range from 0.4 to 1.0×10^{-7} cm^2/s at 20 °C with the changing of the polystyrene concentration from 0 to 0.35 g/g. There have been a few reports published concerning diffusion of a polymer in another polymer solution [26,27]. The diffusion of polystyrene in a concentrated solution of poly(vinyl methyl ether) index-matched with the solvent (*o*-fluorotoluene) has been investigated by quasielastic light scattering. The diffusion coefficient of polystyrene in poly(vinyl methyl ether) solution decreased exponentially with increasing concentration of poly(vinyl methyl ether) in a range larger than about 0.2 g/ml.

In this paper, we propose a new model for the dissolution–diffusion process. We then will discuss the applicability of the proposed model to several types of graded structures of polyvinyl chloride (PVC)/polymethyl methacrylate (PMMA) graded blends and estimate the apparent diffusion coefficient and the dissolution rate coefficient of PVC. It was considered that the apparent diffusion rate was affected, not only, by the concentration change of PVC and PMMA, but also, by their molecular weights.

We could not obtain PVC with narrow distribution range in that molecular weight. Also, it could not have been known for us how the molecular weight of PVC and its distribution effect on the diffusion rate of PVC in 2-butanone. Thus, we would not discuss those effects of molecular weight of PVC and PMMA.

However, it is expected that the obtained apparent diffusion rate is useful, not only, for understanding the mechanism of formation of the graded structure, but also, for estimating that graded structure by using several conditions, although the effect of molecular weight of PVC and PMMA is not clear.

Some reports have discussed the blend of PVC/PMMA [28–32] which was reported to be a miscible blend over all blend ratios under LCST.

2. Experimental

2.1. Material and sample preparation

Atactic PVC and PMMA were supplied by Shin-Etsu Chemical Co. Ltd. and by Mitsubishi Rayon Co. Ltd., respectively. Their average molecular weights were determined by GPC analysis relative to a polystyrene standard using tetrahydrofuran (THF) as a solvent. The molecular weights of PMMA were 88,300 (M_w) and 43,700 (M_n). Those of PVC were 86,000 (M_w) and 36,800 (M_n).

PVC (30 g) or PMMA (30 g) was purified by precipitation by pouring the THF solution into methanol (1000 ml); the precipitate was then dried under vacuum for 4 h.

Sample films were prepared by the following method (Fig. 1): PVC (1 g) was dissolved in 2-butanone (4.2 wt%). Casting was done on a glass Petri dish at room temperature. PMMA solutions containing different concentrations were then poured on the cast PVC film (about 80 μm) in the dish at room temperature. The weight of PMMA was equal to that of PVC. PVC became dissolved and diffused in the PMMA solution, was kept until all the solvent was evaporated. Thus, PVC/PMMA blend films (about 160 μm) with several types of compositional gradient structures in the thickness direction were obtained.

A completely miscible blend film was also prepared by casting, after PVC and PMMA were stirred in 2-butanone for 3 h.

2.2. Measurement

Measurement of solvent evaporation was performed using a balance (Shimadzu balance LIBROR EB32000).

Fourier transform infrared spectroscopy (FTIR) of the blended films was performed with a JEOL FTIR spectrometer JIR-AQS20 attached to an attenuated total reflection (ATR) apparatus, using a KRS5 prism with an incident angle of 45°. The PVC content was then estimated from the ratios of absorbance intensities at 1728 cm^{-1} (stretching of the carbonyl group in PMMA) and 615 cm^{-1} (stretching of the C–Cl bond in PVC). The calibration curve for estimating the PVC content was constructed by using the FTIR-ATR spectra of the completely miscible blend at each PVC content. The change in the PVC content in a direction was estimated by measuring FTIR-ATR spectra of the surface of the blended film by gradually cutting off the surface of the film.

Microscopic Raman spectroscopy (MRS) of the blended films was performed with a RENISHOW spectrometer WIRE1000. The light source was a He–Ne laser. The PVC content was then estimated from the ratios of scattering intensities at 814 cm^{-1} (methoxyl group in PMMA) and 635 cm^{-1} (the C–Cl bond in PVC). The calibration curve for estimating the PVC content was constructed by using the MRS spectra of the completely miscible blend at each PVC content. The change in the PVC content in a direction was estimated by measuring MRS spectra at the focus point that was gradually shifted in the direction of the film thickness.

3. Mechanism

After the PMMA solution is poured on the PVC film (about 80 μm) in a glass Petri dish, the PVC begins to dissolve and diffuse in the direction of the airside of the solution, but the diffusion is interrupted by quick evaporation of the solvent. Thus, the blended film produced has a wide compositional gradient of PMMA (or PVC) in the thickness direction (Fig. 1).

It is considered that the process is determined by three factors: the dissolution and diffusion rates of PVC in PMMA solution, and the interruption time of the diffusion by quick evaporation of the solvent. Those factors are then considered to be controlled by the following conditions: (1) evaporation rate of the solvent, (2) casting temperature, (3) molecular weight of PVC and PMMA, (4) amount of PMMA solution.

We considered that the formation of the graded structure occurred as follows. If the dissolution rate of PVC is sufficiently larger than the diffusion rate of PVC, PVC concentration in an interface layer near the PVC film becomes close to saturated, as indicated in Fig. 2. Thus, it is expected that the dissolution rate is kept constant because the difference of PVC concentrations across the surface of the PVC film is almost kept constant. Therefore, it was considered that the thickness (d) of PVC film decreased linearly with the passed time (t) of the diffusion process, as shown in Eq. (1).

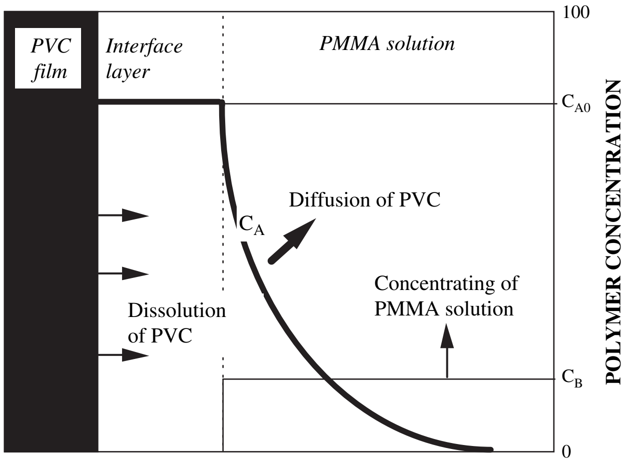

Fig. 2. Schematic model for dissolution and diffusion processes (C_A: PVC concentration, C_{A0}: saturated concentration of PVC, and C_B: concentration of PMMA.

$$d = d_0 - St \tag{1}$$

where, d_0 = the thickness of PVC film prepared at the 1st step and S = dissolution rate coefficient of PVC. Thus, the thickness of the PVC film when the solvent was completely evaporated can be estimated by substituting t_e into t in Eq. (1).

Further, the solvent diffuses in the airside direction of the PMMA solution, in order to support its evaporation. The diffusion rate of the solvent must be significantly higher than the rates of PVC and PMMA in the solution. Thus, it was considered that the concentration of PMMA was almost constant at any point in the PMMA solution.

Therefore, until the PVC completely dissolves or reaches the surface of the PMMA solution, the diffusion of PVC in the PMMA solution is considered to obey Fick's second law (Eq. (2)).

$$\frac{\partial C_A}{\partial t} = D_{AB}\left(\frac{\partial^2 C_A}{\partial x^2}\right) \tag{2}$$

where, C_A is the concentration of PVC, x is the distance from the surface of the PVC film, and D_{AB} is a diffusion coefficient of PVC.

The boundary conditions of this system are defined by the following expression: C_A is kept at 1, when $x = 0$. C_A is 0 at all points in the PMMA solution, when $t = 0$.

Eq. (3) is obtained by rearranging Eq. (2) using the Laplace transformation method.

$$C_A = \operatorname{erfc}\frac{x}{2\sqrt{D_{AB}t}} \tag{3}$$

where, erfc(x) is the Gaussian error function defined by Eq. (4).

$$\operatorname{erfc}(x) = \left(\frac{2}{\sqrt{\pi}}\right)\int_0^\infty \exp\left(-\xi^2\right)\mathrm{d}\xi \tag{4}$$

Therefore, the gradient profile in the blend at t can be estimated by Eq. (3).

D_{AB} can be estimated from Eq. (3), by two methods. In one method, the distance from the position at 1 of C_A to the one at 0 of C_A in the direction of the film thickness is obtained as a diffusion thickness (L), and then D_{AB} is estimated by substituting L into Eq. (5) [33,34] or (6) [35].

$$D_{AB} = \frac{L^2}{6t_e} \tag{5}$$

$$D_{AB} = \frac{L^2}{8t_e} \tag{6}$$

where t_e is the end time of the diffusion process and is considered as the time for total evaporation of the solvent.

The other is the curb fitting method, where Eq. (3) is used after rearranging to Eq. (7), as follows. The position of the PVC interface (i.e. $x = 0$) shifted to the Petri glass, while PVC dissolves and diffuses in the PMMA solution. Then, X

is defined as the distance from the surface of PVC film in the Petri glass side, that is, the surface of the formed graded blend in PVC rich side. And d is defined as the thickness of the PVC residue. Thus, x is replaced by $(X - d)$, and Eq. (3) is rearranged to Eq. (7).

$$C_A = \operatorname{erfc}\frac{X - d}{2\sqrt{D_{AB}t_e}} \tag{7}$$

Here d decreases with dissolution of PVC, as shown in Eq. (1). Eq. (7) then shows the graded profile, if $d = 0$ at the time when the PVC layer completely finishes dissolving.

It appeared that D_{AB} is affected not only by changing the PVC concentration, but also by the PMMA concentration in the solution.

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x}\left\{D_{AB}(C_A)\frac{\partial C_A}{\partial x}\right\} \tag{8}$$

A non-Fickian diffusion process occurs when the diffusion rate of a gas and liquid becomes higher in the higher concentrated area in polymeric materials, if the polymer material can swell in the gas and liquid.

Then, Eq. (2) is rearranged to Eq. (8), in the case of considering the effect of PVC concentration. It is known that $D_{AB}(C_A)$ is represented as Eq. (9) [33], if it depends on the concentration of PVC.

$$D_{AB}(C_A) = D_{AB0}\exp(\beta(C_A - 1)) \tag{9}$$

where D_{AB0} is the limit diffusion rate, and β is a constant relating to the degree of the effect of PVC concentration on D_{AB}. Thus, $\beta = 0$, when D_{AB} does not depend on PVC concentration at all, then, D_{AB} becomes D_{AB0}.

Further, u is defined as $(-\beta(1 - C_A))$. And a reduced time (y) is defined as the following:

$$y = \frac{x}{2\sqrt{D_{AB0}t}} \tag{10}$$

Then, Eq. (8) is rearranged into Eq. (11).

$$\frac{\partial^2 u}{\partial y^2} = -\left(\frac{2y}{u}\right)\left(\frac{\partial u}{\partial y}\right) \tag{11}$$

The differential equation of Eq. (11) is solved by Boltzmann conversion method, then, Eq. (12) is obtained.

$$u = 1 + y\left|\frac{\partial u}{\partial y}\right|_{y=0} + 2\left(\int_0^y\int_0^y \ln u\,\partial y\,\partial y - \int_0^y y\ln u\,\partial y\right) \tag{12}$$

where the effect of PVC concentration appears in the term $|\partial u/\partial y|_{y=0}$ in Eq. (12). Then, PVC concentration profiles against the thickness of the film in the case of considering the PVC concentration effect were estimated by assuming several types of values in $|\partial u/\partial y|_{y=0}$.

Thus, we did not consider the dependency of D_{AB} on molecular weight of PVC and PMMA.

The concentrating of the PMMA solution proceeds in step with the solvent evaporation. If the evaporating rate of the solvent is kept constant, the volume of the solution (V_s) can be represented against passed time (t), as Eq. (9) by using the initial solution volume (V_{s0}) and t_e.

$$V_s = V_{s0}\left[1 - \frac{t}{t_e}\right] \tag{13}$$

It means that the evaporating rate $(\mathrm{d}V_s/\mathrm{d}t)$ of the solvent is kept constant (V_{s0}/t_e). Then Eq. (14) was derived from Eq. (13).

$$C_B = \frac{C_{B0}}{1 - \frac{t}{t_e}} \tag{14}$$

where, C_B (g/ml) is the concentration of PMMA and C_{B0} is the initial concentration of PMMA. Eq. (14) means that C_B does not change significantly until t/t_e (the degree of the evaporation progress) becomes very large, if C_{B0} is significantly small.

4. Results and discussion

4.1. Evaporation rate of solvent

The evaporation of the solvent in the formation of the graded structure was measured using a balance. Fig. 3 shows the change in solvent weight during the evaporation process vs. passed time (t). The weight of the solvent decreased linearly with increasing t until it became more than 95%. Thus, the evaporation rate of the solvent was kept constant in the preparation of a graded structure. Also it was confirmed that Eq. (13) was applicable to the experimental data. The end time was considered to correspond to the end time of the diffusion process. The end times (t_e) of the evaporation processes were estimated by the cross points in the lines of the linear relation and 0% line of solvent weight, as shown in Fig. 3. The data for t_e in several initial volumes of the solutions lay on a straight line passing through 0, as indicated in Fig. 4. Thus, the evaporating rates (V_{s0}/t_e) obtained by Eq. (13) in all of the initial solution volumes were found to be equal to

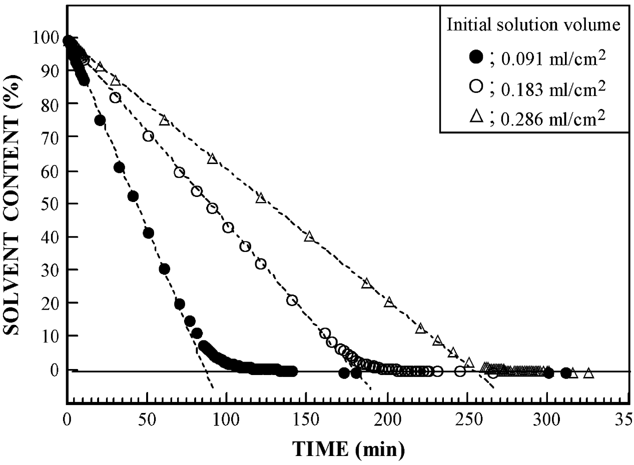

Fig. 3. The changes in solvent contents at various times.

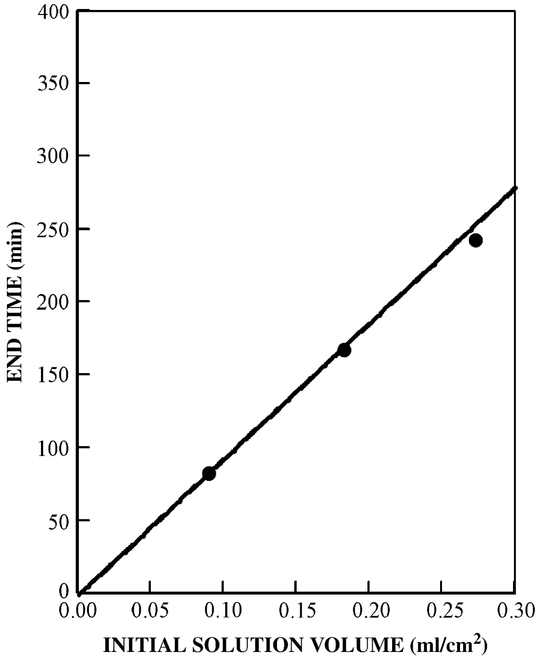

Fig. 4. End times of evaporation of the solvent at various types of initial solution volumes.

each other. This result means that the time of the diffusion process can be controlled by changing the initial volume of PMMA solution, resulting in the formation of the graded structures of the PVC/PMMA blends.

C_Bs in various types of the initial solution volumes were plotted against the degree of the evaporation progress (t/t_e), as shown in Fig. 5. The C_Bs in 0.183 and 0.274 ml/cm^2 were almost kept constant until t/t_e became about 80–90%. However, in the case of 0.091 ml/cm^2, C_B increased immediately over about 70% of t/t_e.

Further, it was reported [26] that the diffusion coefficient of polystyrene in poly(vinyl methyl ether) solution did not change much in low concentration of PMMA, but then decreased exponentially in a concentration range (larger than about 0.2 g/ml) with increasing poly(vinyl methyl ether).

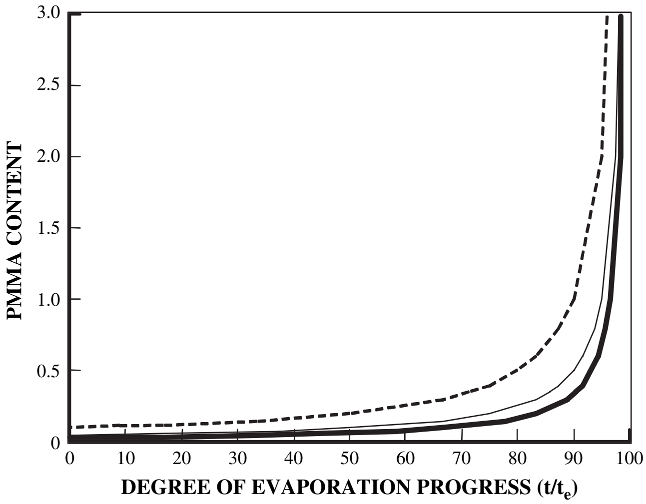

Fig. 5. The change of PMMA content in solution during evaporation of the solvent (initial solution volume: ----------, 0.091 ml/cm^2; ————, 0.183 ml/cm^2; ▬▬, 0.274 ml/cm^2).

Thus, D_{AB} might start to decrease immediately because of the immediate increase of C_B in a higher range of t/t_e. Then, the diffusion process might already be completed at a significantly earlier time compared to the complete finish time of solvent evaporation. Further, it was considered that the t/t_es at the finishing diffusion time for 0.183 and 0.274 ml/cm^2 were significantly larger than the t/t_e for 0.091 ml/cm^2. Then, D_{AB} for 0.091 ml/cm^2 may appear as lower than the D_{AB} data for 0.183 and 0.274 ml/cm^2.

4.2. Applicability of our new model to the experimental data on the graded profiles of PVC/PMMA graded blends

The profiles of PVC content in the direction of thickness in 0.091, 0.183 and 0.274 ml/cm^2 of initial volumes of PMMA solutions were measured by FTIR-ATR and microscopic Raman spectroscopy (MRS) methods, and are shown in Figs. 6, 7 and 8, respectively. The PVC contents were equal to about 1 in the range from 0 to about 50–70 μm (near the Petri glass) in all the initial solution volumes. We then concluded that the PVC had not yet finished dissolving. The range of gradient profiles of PVC contents, measured by the MRS method, became wider with increasing initial solution volumes. The numerical data measured by the FTIR-ATR method were significantly less than those measured by MRS method. However, the data measured by the FTIR-ATR method almost agreed with those measured by the MRS method in all of the initial solution volumes. Thus, the data measured by the MRS method could be confirmed to be reliable.

Then, whether Eq. (7) was applicable to the data, measured by MRS method, was examined for all of the initial solution volumes. The correlation coefficients were estimated by fitting to the master curve in the method of indirect least squares. All of the correlation coefficients were equal to about 1, as shown in Table 1. Thus, it was proved that the gradient profiles in the

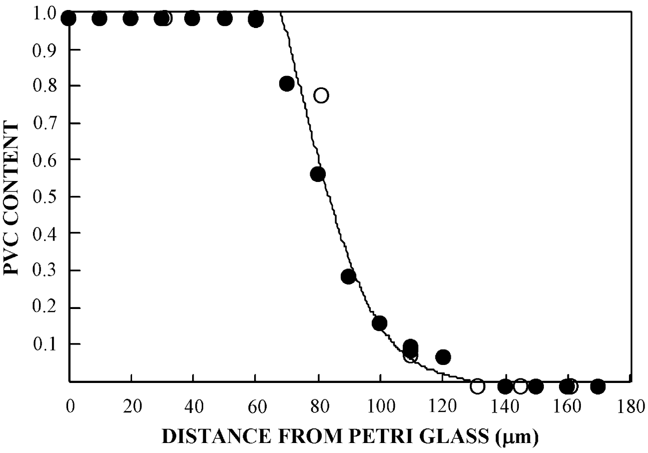

Fig. 6. PVC contents of PVC/PMMA graded blends at various distances from the Petri glass (——, predicted values; ● and ○, experimental data measured by microscopic Raman spectroscopy and FTIR-ATR methods, respectively; initial solution volume, 0.091 ml/cm^2).

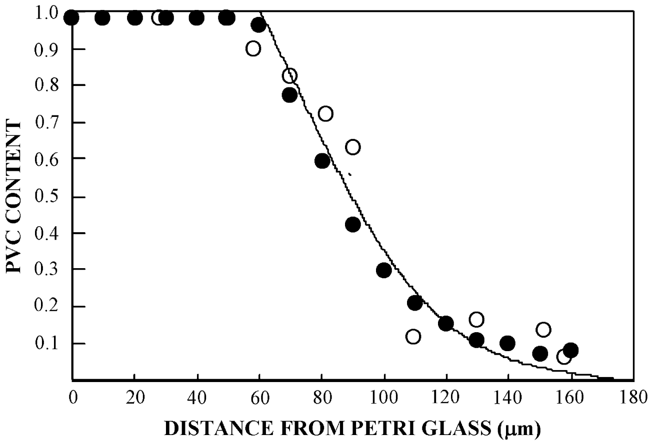

Fig. 7. PVC contents of PVC/PMMA graded blends at various distances from the Petri glass (——, predicted values; ● and ○, experimental data measured by microscopic Raman spectroscopy and FTIR-ATR methods, respectively; initial solution volume, 0.183 ml/cm^2).

blends prepared by the dissolution–diffusion method could be predicted by Eq. (7).

Further the thickness of the PVC residue and the D_{AB} (apparent diffusion coefficient) are shown in Table 1. The D_{AB}s in 0.183 and 0.274 ml/cm^2 of the initial volumes of the solutions were equal to each other, but they were larger than the D_{AB} in 0.091 ml/cm^2 of the initial solution volume. It might occur because of the effects of PVC concentration dependency of D_{AB}, and of concentration of PMMA in solution. Those effects will be discussed later in this paper.

The D_{AB} in 0.274 ml/cm^2 means that 100 μm of thickness of the graded structure can be made after about 255 min by the dissolution–diffusion method. On the other hand, it took 16 days for a 160 μm thickness to be made by the method of interdiffusion in the melt state of PVC and poly(ε-caprolactone), although the blend had a gentle compositional gradient [12]. Thus, it is confirmed that the dissolution–diffusion method is superior to the interdiffusion method for rapid preparation and for preventing oxidation of the polymer.

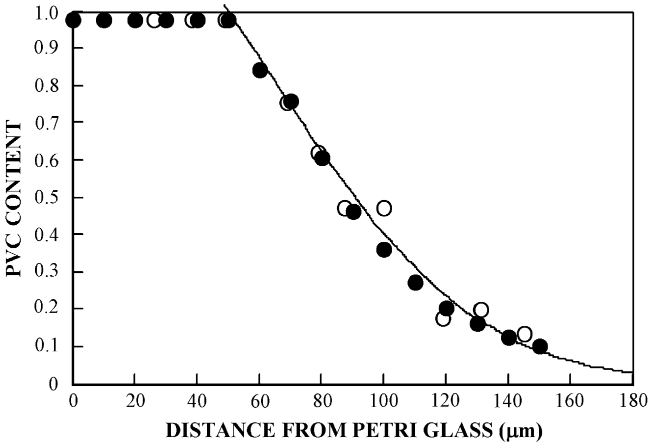

Fig. 8. PVC contents of PVC/PMMA graded blends at various distances from the Petri glass (——, predicted values; ● and ○, experimental data measured by microscopic Raman spectroscopy and FTIR-ATR methods, respectively; initial solution volume, 0.274 ml/cm^2).

Table 1
Applicability of Eq. (7) to experimental data of graded structures of PVC/PMMA blends

Initial solution volume (ml/cm^2)	End time of evaporation (min)	Thickness of PVC residue (μm)	Apparent D_{AB} (cm^2/s)	Correlation coefficient
0.091	85	68	4.8×10^{-10}	0.996
0.183	170	62	8.8×10^{-10}	0.990
0.274	255	56	8.8×10^{-10}	0.995

The diffusion thickness (L) in all of the initial solution volumes was estimated as follows. At first, a straight line was obtained by using 3 or 4 points of the data near 0 or 1 of C_A in Figs. 6, 7 or 8. The cross point of the obtained straight line near 0 or 1 of C_A with the line of C_A = 0 or C_A = 1, was obtained in each of the initial solution volumes, respectively. Then, the distance of those cross points on the lines ($C_A = 0$ and $C_A = 1$) was determined as L. Further, the D_{AB}s were estimated by substituting the obtained L into Eqs. (5) and (6), as indicated in Table 2. Those were 2–4 times larger than the D_{AB}s obtained by using Eq. (7). It might be considered that the difference in our model and diffusion thickness method was affected by the deviation of the data in FTIR and Raman measurements. However, it was confirmed that Eqs. (5) and (6) were useful for rough design of the gradient profiles in the blends prepared by the dissolution–diffusion method.

The thickness of the PVC residues was estimated using Eq. (7) in all of the initial solution volumes as indicated in Table 1, and then was plotted against the end time (t_e) of the evaporating process, as shown in Fig. 4. The experimental data lay on a straight line. It meant that Eq. (1) was applicable to the experimental data. Here $d_0 = 76.1$ μm which was almost the same as the thickness (76.8 μm) of PVC prepared in the 1st step, the dissolution rate coefficient $(S) = 1.4 \times 10^{-7}$ cm/s, and the correlation coefficient was 0.989. This phenomenon was similar to that reported by Ribar et al. [36]. Thus, it was proved that PVC was dissolved at a constant rate in the preparation. This was considered to occur because of the following. The S was sufficiently higher than the diffusion rate. The PVC concentration in the interface layer as described in Fig. 2, was then always kept constant near the saturation concentration during preparation. Therefore, the dissolution rate is essentially kept constant.

Further, Eq. (1) is useful for predicting the time of disappearance of the PVC layer, in order to design an excellently graded structure. In this system, 15 h were required for

Table 2
Applicability of Eqs. (5) and (6) to experimental data of graded structures of PVC/PMMA blends

Initial solution volume (ml/cm^2)	End time of evaporation (min)	Thickness of PVC residue (μm)	L^{a} (μm)	Apparent D_{AB}	
				Using Eq. (5) (cm^2/s)	Using Eq. (6) (cm^2/s)
0.091	85	64	72.6	1.7×10^{-9}	1.3×10^{-9}
0.183	170	59	130.0	2.8×10^{-9}	2.1×10^{-9}
0.274	255	51	133.4	1.9×10^{-9}	1.4×10^{-9}

[a] Diffusion thickness (thickness of graded structure).

disappearance of all of the PVC layers, i.e., for obtaining the graded blend with the widest compositional gradient. Thus, it may be necessary for the preparation to be performed using a lower molecular weight of PVC and at a higher temperature in order to obtain the best-graded blend in a short time (1–2 h).

4.2.1. *Dependency of D_{AB} on PVC concentration*

A non-Fickian diffusion process occurs when the diffusion rate of a gas or liquid becomes higher in the higher concentrated area in a polymeric material, if the polymer material can swell in the gas or the liquid. Then, we considered that the diffusion rate of PVC might change with increasing PVC concentration in the solution during diffusion.

Whether Eq. (8) was applicable to the experimental data of the content profiles of PVC in the direction of thickness in 0.274 ml/cm^2 of the initial solution volume was examined. PVC residue and D_{AB} were optimized for obtaining the best correlation coefficient, by assuming various types of initial concentration dependencies, i.e., $(du/dy)_{y=0}$, as shown in Fig. 9 and Table 3. Here, u = diffusion rate and $y = x/(2(D_{AB}t)^{1/2})$.

The correlation coefficient obtained in the assumption that $(du/dy)_{y=0} = 0$, was largest in all of the assumptions. This assumption meant that $\beta = 0$ in Eq. (8). Then, Eq. (8) is the same as Eq. (7), if $\beta = 0$. Thus, the values predicted by Eq. (7) were best fitted to the experimental data. It was found that the diffusion of PVC was independent of changing PVC concentration. This result was considered to occur because PVC concentration was limited to a saturated state, and was not so concentrated as to affect the diffusion process.

4.2.2. *Effect of PMMA concentration in solution on D_{AB}*

It was reported [26] that the diffusion coefficient of polystyrene in poly(vinyl methyl ether) solution did not change markedly in low concentrations of poly(vinyl methyl ether), but decreased exponentially in a concentration range higher than about 0.2 g/ml, with increasing the concentration of poly(vinyl methyl ether). Thus, the diffusion of PVC may be effected by PMMA concentrations (C_B) ranging higher than about 0.2 g/ml.

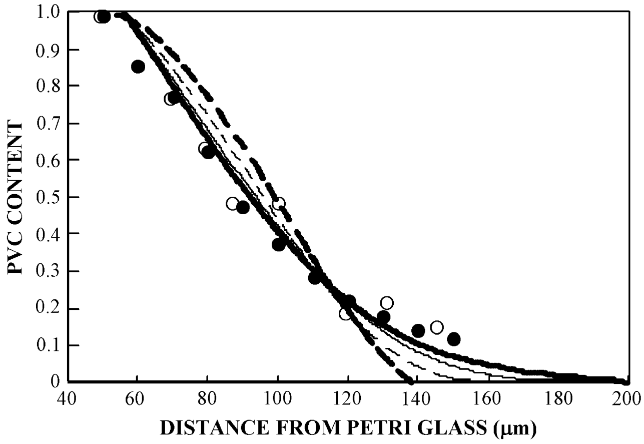

Fig. 9. PVC contents of PVC/PMMA graded blends at various distances from the Petri glass (▬▬▬, ———, ------- and ▬▬ ▬▬ are the predicted values $(du/dy)_{y=0} = 0$, −0.5, −1.0 and −1.5, respectively. ● and ○, experimental data obtained by microscopic Raman spectroscopy and FTIR-ATR methods, respectively; initial solution volume, 0.274 ml/cm^2).

Table 3
Applicability of Eq. (8) to experimental data of graded structures of PVC/PMMA blend

$(du/dy)_{y=0}$	Thickness of PVC residue (μm)	D_{AB0} (cm^2/s)	β	Correlation coefficient
0	68	8.8×10^{-10}	0	0.995
−0.5	62	1.1×10^{-9}	0.43	0.992
−1.0	56	1.3×10^{-9}	1.11	0.982
−1.5	52	1.8×10^{-9}	0.88	0.955

C_Bs in 0.183 and 0.274 ml/cm^2 of initial solution volumes were at first almost kept constant. Then they became to increase immediately in passing through 0.2 g/ml around 80% of the degree of the evaporation progress (t/t_e), as shown in Fig. 5. On the other hand, for 0.091 ml/cm^2, C_B became higher than about 0.2 g/ml around 50% of t/t_e. Thus, we considered that the diffusion of PVC might be strongly affected by PMMA concentration in the solution.

However, we assumed in our model that D_{AB} was not affected by the change in C_B. Thus, D_{AB} for 0.091 ml/cm^2 was estimated as 4.8×10^{-10} cm^2/s, while those for 0.183 and 0.274 ml/cm^2 was estimated as 8.8×10^{-10} cm^2/s. Thus, those for 0.183 and 0.274 ml/cm^2 almost equal to each other. D_{AB} for 0.091 ml/cm^2 was smaller than that in each of the other two concentrations. We considered that the difference of those D_{AB} arose because PVC had already finished diffusing before all the solvent evaporated. The PVC finished diffusing when PMMA concentration reached a special value (C_{BR}).

Therefore, the assumption in our model was modified as follows. The end time of the diffusion of PVC was changed from the end time of the evaporation of the solvent to the time (t_B), at which PMMA concentration reaches C_{BR}. It was considered that the relation of C_A with $(X - d)$ in Eq. (7) was the same in all concentrations of PMMA. Thus, it was clear that $(D_{AB}t_e)$ was kept as a constant. Therefore, t_e was calculated by using Eq. (14). Then, D_{AB} was estimated by the relation of the constant of $(D_{AB}t_e)$. We reasoned that D_{AB} was expected to increase exponentially with decreasing of C_{BR}. Thus, D_{AB} was estimated using Eq. (7) again in each case of the initial solution volumes by assuming several types of C_{BR}s, as shown in Fig. 10.

Those D_{AB}s were similar to each other, around 0.2 of C_{BR}. If $C_{BR} = 0.18$ g/ml, the difference of maximum and minimum in D_{AB}s obtained in all the initial solution volumes became smallest. That was when all of the D_{AB}s became almost equal to each other ($D_{AB} = 1.16 \pm 0.07 \times 10^{-9}$ cm^2/s). Thus, we considered that the diffusion of PVC almost finished when PMMA content reached 0.18 g/ml, because it was considered that D_{AB} should not be changed in the initial volume contents. C_{BR} (=0.18 g/ml) agreed closely with the solution concentration of poly(vinyl methyl ether), over which the diffusion coefficient of polystyrene was reported [26] to decrease exponentially. Furthermore, D_{AB}s were estimated by Eqs. (5) and (6), using t_B, as shown as $D_{AB}(1)$ in Table 4. The obtained

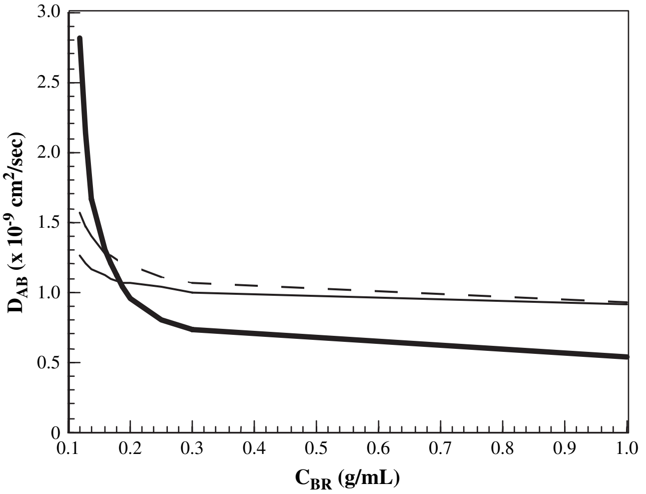

Fig. 10. Diffusion coefficient of PVC in the assumption of various types of C_{BR} (initial solution volume: ▬▬, 0.091 ml/cm^2; ——, 0.183 ml/cm^2; -------, 0.274 ml/cm^2).

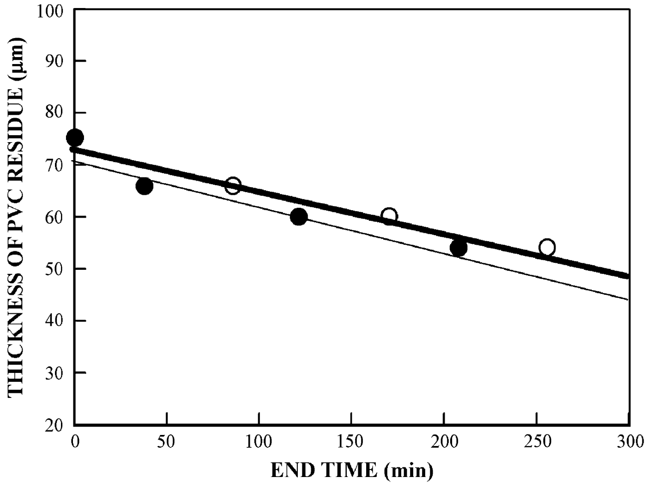

Fig. 11. Thickness of PVC residue at various end times of diffusion (○, data in using end time of the evaporation; ●, data in using arrival time at 0.18 g/ml of PMMA concentration).

D_{AB}s were from 1.5 to 3.5 times larger than those estimated by our model. The difference was smaller by considering the change of PMMA concentration.

Then, the dissolution rate coefficient of PVC and PVC residue was estimated again by using t_B. The obtained values of PVC residue are shown in Fig. 11 as open circles. The experimental data lay on a straight line. Thus, it was proved by the linear relation that Eq. (1) was applicable to the experimental data. Here, d_0 was 74.2 μm, which was almost the same as the thickness (76.8 μm) of PVC prepared in the 1st step, $S = 1.6 \times 10^{-7}$ cm/s, and the correlation coefficient was 0.927.

Further, the layer of the solution at t_B ($C_B = 0.18$ g/ml) shrunk to about 1/6, after complete evaporations of the solvent, to form a blended film. We considered that the shrink occurred only in the direction of the layer thickness. The thickness of the layer of the solution was about 6 times as large as that of the obtained film. Then, the D_{AB} might be estimated by Eq. (7) as 36 times smaller values than a real diffusion coefficient in the solution. Thus, the D_{AB}s should be estimated as $4.2 \pm 0.25 \times 10^{-8}$ cm^2/s by considering the shrink effect, and existed in the same order as the reported data, i.e., the diffusion coefficient [21] of polystyrene in *trans*-decalin at 20 °C.

Similarly, $D_{AB}(1)$s shown in Table 4 were multiplied by 16 in order to consider the shrink effect, and then existed in the same order ($D_{AB}(2)$ in Table 4).

Therefore, it was considered as follows. The formation of graded structure in dissolution–diffusion process was complicated because the process was effected by many factors: initial concentration and diffusion coefficient of PVC and PMMA and their concentration changes, their molecular weights, etc. Thus, in this report, we discussed applicability of our model and diffusion thickness method in focusing the effect of the concentration change of PVC and PMMA. However, the mechanism of the formation could be explained by our model and diffusion thickness method. Although it was not almost affected by the concentration change of PVC, it was strongly affected by that of PVC.

However, we did not discuss the effect of molecular weight. Then, the obtained diffusion coefficients were considered as apparent values.

5. Conclusions

We proposed a new model for the dissolution–diffusion process. This model was derived based on the following assumptions. Until PVC completely dissolves or reaches the surface of the PMMA solution, the diffusion of PVC in the PMMA solution is considered to obey Fick's second law, by assuming that the effect of the evaporation of the solvent in the PMMA solution during the diffusion could be neglected. Then, the model was derived by considering that the position

Table 4
Applicability of Eqs. (5) and (6) to experimental data of graded structures of PVC/PMMA blends after considering the effect of PMMA concentration

Initial solution volume (ml/cm^2)	End time of evaporation (min)	$D_{AB}(1)$		$D_{AB}(2)$	
		Using Eq. (5) (cm^2/s)	Using Eq. (6) (cm^2/s)	Using Eq. (5) (cm^2/s)	Using Eq. (6) (cm^2/s)
0.091	35	4.1×10^{-9}	3.1×10^{-9}	1.5×10^{-7}	1.1×10^{-7}
0.183	122	3.9×10^{-9}	2.9×10^{-9}	1.4×10^{-7}	1.0×10^{-7}
0.274	208	2.3×10^{-9}	1.7×10^{-9}	8.3×10^{-8}	6.1×10^{-8}

of the PVC interface was shifted to the Petri glass. Thus, Eq. (7) could be obtained from the model for estimating the graded profile of the graded blend, which was prepared by the dissolution−diffusion process.

We then examined whether Eq. (7) was applicable to the graded structure of the PVC/PMMA blend. The values predicted by Eq. (7) nearly agreed with the experimental data for the graded blends, which were prepared in several initial volumes of PMMA solution. However, the D_{AB}s in 0.183 and 0.274 ml/cm^2 of the initial solution volumes were equal to each other, while they were larger than the D_{AB} in 0.091 ml/cm^2 of the initial solution volume. Thus, the effects of PVC concentration dependency of D_{AB}, and of PMMA concentration in the solution on D_{AB} were discussed. We found that the diffusion of PVC was independent of changing PVC concentration. We reasoned that PVC concentration was limited to a saturated state during diffusion of PVC, and was not so concentrated as to affect the diffusion process.

C_Bs in 0.183 and 0.274 ml/cm^2 of initial solution volumes increased immediately over about 80% of t/t_e, passing through 0.2 g/ml, while for 0.091 ml/cm^2, C_B became higher than about 0.2 g/ml over about 50% of t/t_e. Thus, we considered that the diffusion of PVC might be strongly affected by PMMA concentration in the solution.

Then, the end time of the diffusion of PVC in our model was changed from the end time of the evaporation of the solvent to the time (t_B) at which the diffusion of PVC was almost caused to stop by the arrival of PMMA concentration at a special value (C_{BR}). On the basis of this assumption, D_{AB} was estimated again in all of initial solution volumes, by assuming several types of C_{BR}s. If $C_{BR} = 0.18$ g/ml, all of the D_{AB}s became almost equal to each other ($D_{AB} = 1.16 \pm 0.07 \times 10^{-9}$ cm^2/s).

Further, the real D_{AB} in the solution layer was estimated as $4.2 \pm 0.25 \times 10^{-8}$ cm^2/s, by considering the effect of the shrink of the solution layer at t_B ($C_B = 0.18$ g/ml), to form a blended film. Then, the obtained D_{AB} existed in the same order as the reported data for the diffusion coefficient of polystyrene in *trans*-decalin at 20 °C.

The dissolution rate of PVC into PMMA was kept constant during the preparation. Thus, the applicability of Eq. (7) was confirmed. Further, the D_{AB}s estimated by diffusion thickness method, were from 1.5 to 3.5 times larger than those estimated by our model.

Therefore, we proved that our model was applicable to the experimental data by considering the effects of PMMA concentration in the solution and of the shrink of the solution layer.

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