

Analysis of Butyl Acrylate Diffusion in a Glassy Polystyrene Matrix to Predict Gradient Structure

CARLOS F. JASSO,¹ J. VALDÉZ,¹ J. H. PÉREZ,¹ O. LAGUNA²

¹ Depto. de Ing. Química (Div. Ing., CUCEI), Universidad de Guadalajara, Guadalajara, México

² Instituto de Ciencia y Tecnología de Polímeros, (CSIC), Madrid, España

Received 12 March 1999; accepted 22 November 1999

ABSTRACT: To be able to control composition structure in gradient polymers prepared by sequential polymerization, diffusion phenomena has to be considered, particularly for the first 100% weight increment in a glassy polymer matrix. With that purpose, an analytical model to predict diffusion in that region has been developed for amorphous polymers. The inclusion of a relaxation time to estimate surface concentration changes during sorption led to diffusion coefficients one order of magnitude higher than Fickian coefficients. However, adding a volume increment term to account for polymer swelling, diffusion coefficients went up to 48 times the Fickian values. Experimentally, butyl acrylate with a small amount of photosensitizer was diffused into a slightly crosslinked polystyrene slab matrix at different temperatures in the glassy region. After fixing the gradient composition by photopolymerization, chemical structures throughout the slab were determined by FTIR. The proposed model was confronted with experimental sorption showing a close fit at the different temperatures in the region of interest. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1343–1348, 2001

Key words: gradient; IPN; diffusion; swelling; model

INTRODUCTION

The interest in the formation of stable two-phase polymer systems has increased in the last decades.¹ Its importance relies in the advantage of combining different structures to cover a wide range of chemical and/or physical properties. For that reason, diverse formation methods have been proposed to obtain materials with synergistic behavior.

Among those materials, interpenetrating polymer networks (IPNs) obtained by sequential polymerization are of high technological concern at the present time.² An unusual type

of IPN, where a continuous change in the composition structure offers a continuous change in individual properties,³ has been studied for some systems.^{4–7} Such special materials, which have been called gradient polymers, can acquire different profiles, depending on the diffusion conditions.^{4,5,7} From there, it the need arises to examine diffusion phenomena when trying to form this type of polymers with controlled composition. With that purpose, a model to predict monomer sorption in an amorphous glassy polymer matrix is presented in this work. The diffusion coefficients were evaluated at several temperatures; the values were compared with those obtained with Fick's eq. (8), and another model that as the main feature, takes into consideration a relaxation time to estimate surface concentration changes.^{9,10}

Correspondence to: C. F. Jasso.

Journal of Applied Polymer Science, Vol. 80, 1343–1348 (2001)
© 2001 John Wiley & Sons, Inc.

Theory

It is well known that for polymers above their glass transition temperature, a Fickian diffusion is practically expected (8). However, diffusion in glassy polymers notably deviates from such behavior. Several types of non-Fickian behavior have been identified, depending on the type of time exponential pattern of mass uptake.¹¹ Nevertheless, the "anomalous" effects for diffusion in polymers below the glass transition temperature were reported decades ago.^{9,12} Frisch presented a list of recommendations on possible directions for theoretical efforts on the different cases of non-Fickian diffusion, interrelating those patterns as a direct consequence of the glass transition.¹³ A while ago, to deal with a sharp concentration front that varies with time, a relaxation function was proposed.¹⁰ Such a type of function is applied in a model for this work with specific boundary conditions. However, to account for polymer swelling, an additional term is proposed here as part of a more realistic model to quantify mass sorption.

For the first model (including only a relaxation time), the diffusion in a semiinfinite slab as a function of time (t) is:

$$\frac{\partial w_a}{\partial t} = D_a \frac{\partial^2 w_a}{\partial x^2} \quad 0 < x < l \quad (1)$$

$$t > 0$$

As monomer mass diffusion is initially zero, boundary conditions are given by:

$$w_a(x, 0) = 0 \quad 0 < x < l \quad (2)$$

$$w_a(0, t) = w_a^\infty(1 - e^{-\alpha t^\beta}) \equiv F(t) \quad t > 0 \quad (3)$$

where w_a is mass fraction for component a of thickness x ; w_a^i is the instantaneous surface mass fraction, and α and β are constants to be determined. The mass increase at the slab surface, which influences behavior of mass transfer, is determined by the equation that considers material relaxation due to monomer entrance (9):

$$w_a(l, t) = w_a^\infty - (w_a^\infty - w_a^i)e^{-t/\tau} \equiv G(t) \quad t > 0 \quad (4)$$

where τ stands for relaxation time. To solve the differential equation, it is proposed that:

$$w_a(x, t) = w(x, t) + F(t) + \frac{x}{l} [G(t) - F(t)] \quad (5)$$

With those boundary conditions, the solution of the equation allows the obtention of the internal concentration profile. Integrating with respect to volume, an expression is developed for the amount of diffusant (M_t) taken up by the slab in a certain time, referred to that theoretically attained at infinite time (M_∞):

$$\frac{M_t}{M_\infty} = \frac{1}{2w_a^\infty} \left\{ w_a^\infty(1 - e^{-\alpha t^\beta}) + [w_a^\infty - (w_a^\infty - w_a^i)e^{-t/\tau}] \right. \\ \left. - \frac{8}{\pi^2} \sum_{k=1}^{\infty} \frac{e^{-[(2k-1)\pi/l]^2 D_a t}}{(2k-1)^2} \right. \\ \left. \times \left[(w_a^\infty - w_a^i) \frac{\{e^{[(2k-1)\pi/l]^2 D_a t} - (1/\tau)t - 1\}}{\left[\frac{(2k-1)\pi}{l}\right]^2 D_a t - 1} \right. \right. \\ \left. \left. + \alpha \beta w_a^\infty \int_0^t t^{\beta-1} e^{[(2k-1)\pi^2 t/l^2] \alpha t^\beta} dt + w_a^i \right] \right\} \quad (6)$$

To propose a mass transfer model that contains the swelling effect, a mass balance at the microscopic level has to be made, including mass transfer by the concentration difference within the slab. In addition, free volume "created" by the chains (which can be occupied by diffusant) as the sample swells due to monomer entrance, has to be considered. So, taking differentials for time and volume, a variation of Fick's second law is achieved:

$$\frac{\partial w_a}{\partial t} = D_a \left(\frac{\partial^2 w_a}{\partial x^2} \right) + \frac{w_a}{V_0} \left(\frac{\partial V}{\partial t} \right) \quad (7)$$

where V_0 is the volume before swelling. Because for low weight uptake (100% >), the diffusion is approximately linear,¹¹ a simplification of eq. (7) can be made. Also, the change in composition through time depends on the change in composition throughout the slab position along with the excess of monomer entrance due to the volume rate change:

$$\frac{\partial w_a}{\partial t} = D_a \left(\frac{\partial^2 w_a}{\partial x^2} \right) + m w_a \quad \begin{matrix} 0 < x < l \\ t > 0 \end{matrix} \quad (8)$$

Here, m is the slope of the line obtained by plotting the ratio of volume increase to initial volume vs. time. The initial and boundary conditions are

similar to the former model, with the exception of the boundary condition at the center of the slab. There, it is considered a minimum for a change in composition:

$$\frac{\partial w_a(0, t)}{\partial x} = 0 \quad t > 0 \tag{9}$$

Applying eqs. (2) and (4) also in this model, it is proposed that

$$w_a(x, t) = w(x, t) + G(t) \tag{10}$$

with

$$\alpha = \frac{D_a(2n - 1)^2 \pi^2}{4l^2} - m \tag{11}$$

It follows:

$$M_t = Vw_a^\infty \left\{ 1 - \left(1 - \frac{w_a^i}{w_a^\infty} \right) e^{-t/\tau} - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n - 1)^2} \right. \\ \times \left[\frac{w_a^i}{w_a^\infty} + \frac{\left(\frac{1}{\tau} + m \right) \left(1 - \frac{w_a^i}{w_a^\infty} \right)}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2} + \frac{1}{\tau}} \right. \\ \left. - \frac{m}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2}} \right] e^{\{m - [D_a(2n - 1)^2 \pi^2 / 4l^2]\}t} \\ - \frac{\left(\frac{1}{\tau} + m \right) \left(1 - \frac{w_a^i}{w_a^\infty} \right) e^{-t/\tau}}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2} + \frac{1}{\tau}} \\ \left. + \frac{m}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2}} \right\} \tag{12}$$

Finally, relating M_t with mass sorption at infinite time, the proposed model is obtained:

$$\frac{M_t}{M_\infty} = \left\{ 1 - \left(1 - \frac{w_a^i}{w_a^\infty} \right) e^{-t/\tau} - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n - 1)^2} \right. \\ \times \left[\frac{w_a^i}{w_a^\infty} + \frac{\left(\frac{1}{\tau} + m \right) \left(1 - \frac{w_a^i}{w_a^\infty} \right)}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2} + \frac{1}{\tau}} \right. \\ \left. - \frac{m}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2}} \right] e^{\{m - [D_a(2n - 1)^2 \pi^2 / 4l^2]\}t} \\ - \frac{\left(\frac{1}{\tau} + m \right) \left(1 - \frac{w_a^i}{w_a^\infty} \right) e^{-t/\tau}}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2} + \frac{1}{\tau}} \\ \left. + \frac{m}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2}} \right\} \frac{1}{\kappa} \tag{13}$$

where

$$\kappa = 1 - \frac{8}{\pi^2} m \sum_{n=1}^{\infty} \left\{ \frac{1}{m - \frac{D_a(2n - 1)^2 \pi^2}{4l^2}} \right\} \\ \times \frac{1}{(2n - 1)^2} \tag{14}$$

EXPERIMENTAL

Industrial grade styrene and *n*-butyl acrylate monomers were purified by vacuum distillation before use. Crosslinking agent (divinyl benzene) and photosensitizer (benzoin isobutyl ether) were both purchased from Aldrich Chemical Company. Such compounds were mixed (0.70 mol % of each one) with styrene to prepare a polystyrene matrix sheet by photopolymerization at room temperature. Polymer I thus obtained was slightly crosslinked to allow liquid sorption but not dissolution. The polymer samples in sheet form (12 × 18 × 0.24 cm³) were stored in a vacuum oven at 50°C for several days until constant weight was attained (remaining monomers were removed in that way). The crosslinked polymer in sheet form

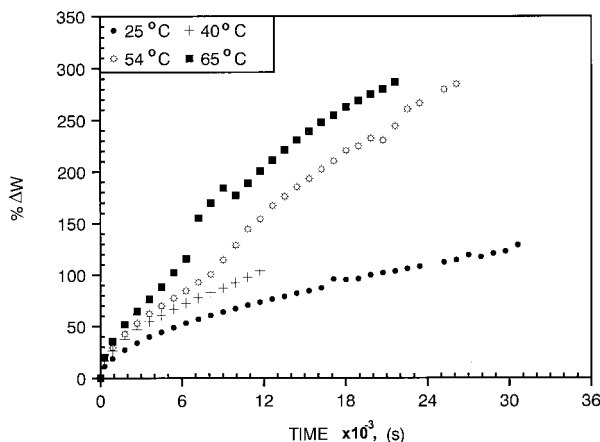


Figure 1 Experimental sorption curve for butyl acrylate in polystyrene at several temperatures.

was then ready for immersion in *n*-butyl acrylate monomer containing the same proportions of crosslinking agent and sensitizer as above. The second monomer mixture was allowed to diffuse into polymer I at several temperatures (25, 40, 54, and 65°C), following weight and volume increase as a function of time. Diffusion temperature was controlled by means of a Haake E8 model circulator (with an accuracy of $0.1 \pm 0.02^\circ\text{C}$) in a constant temperature bath where the samples for sorption were allocated. In another series of samples, after a certain immersion period, the correspondent polymer sheet was removed from the bath, quickly surface dried, and then photopolymerized for 2 days forming polymer II. The poly-(butyl acrylate) concentration profile throughout the samples was determined by IR spectroscopy in a Shimadzu IR 425 apparatus. The ca. 4 mm-

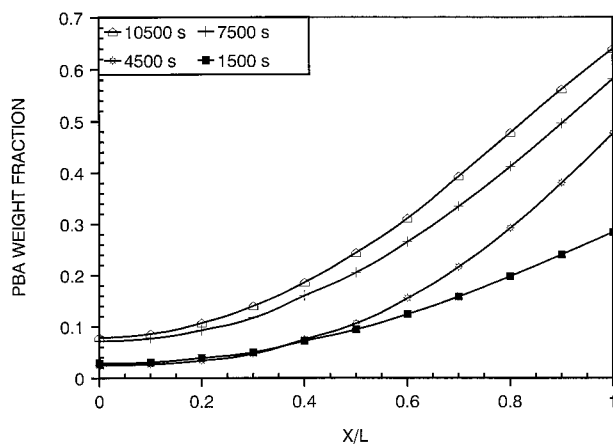


Figure 2 Composition profiles calculated with eq. (13) at 54°C for several time periods.

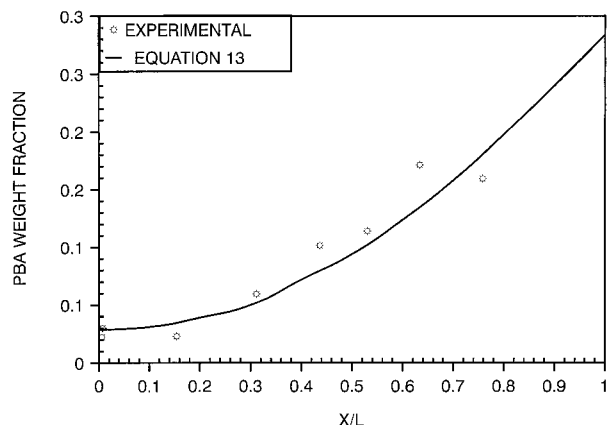


Figure 3 Composition profiles of poly(butyl acrylate) in polystyrene after 1500 s of monomer-polymer diffusion at 54°C.

thick slabs were machined off layer by layer. After grinding a specific sample, a KBr disk for each layer was prepared with a press, to be observed in the infrared region. A PS-PBA composition calibration curve was built using the C=O absorbance acrylate peak at about 1700 cm^{-1} and the aromatic absorbance peak for polystyrene at 1600 cm^{-1} .⁷

RESULTS AND DISCUSSION

To be able to apply the proposed equation for sorption predictions, experimental equilibrium values of weight uptake for PS prepared samples were determined for diffusion of the second monomer mixture. An average value of 301% increase

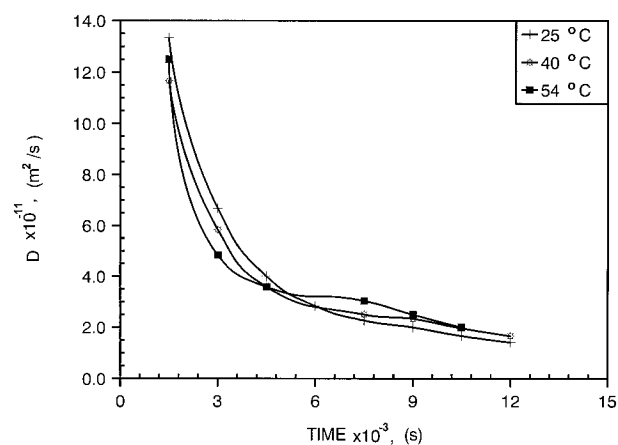


Figure 4 Diffusion coefficient behavior of butyl acrylate in polystyrene as a function of time.

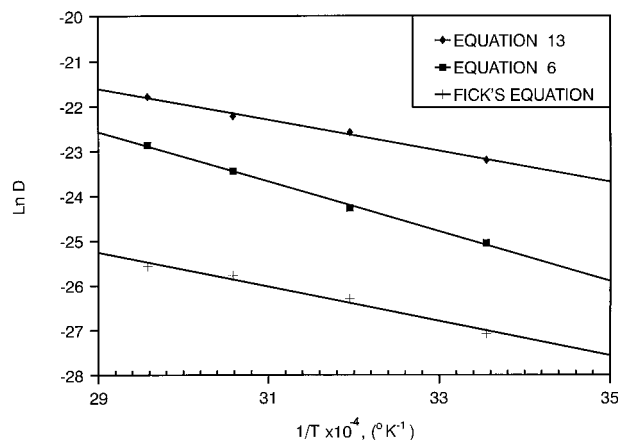


Figure 5 Diffusion coefficient behavior of butyl acrylate in polystyrene as a function of temperature.

was found. In Figure 1, the experimental sorption with time at several temperatures denotes the non-Fickian behavior. At around 100% weight increment even a sigmoidal change can be observed. Nevertheless, because the technological importance of gradient polymers is well below that value (if different properties are to be combined with gradient profile), a model to control the gradient composition by diffusion in glassy polymers does not have to fit to such high value. Using the typical equation to delimit non-Fickian diffusion,⁸ the exponent n was between 0.5 and 1.0 for all tested temperatures, showing then an anomalous behavior.

Applying eq. (13) at different time values, Figure 2 exemplifies the estimation of the gradient composition profile at 54 °C. There, it can be observed that the model is able to predict the increment of diffusant at both the center and surface of the polymer sample. In Figure 3, the experimental values of composition profile are confronted with the model at 54 °C. A diffusion time of 1500 s was chosen to present a weight increase (40%), which can still be of interest when preparing gradient polymers. It can clearly be seen that eq. (13)

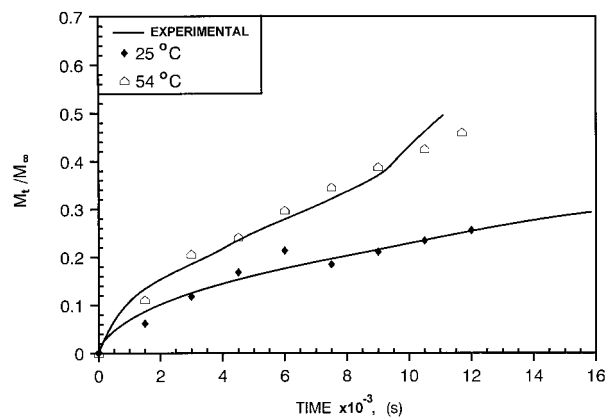


Figure 6 Comparison of eq. (13) with experimental sorption of butyl acrylate in polystyrene. Transferred mass is related to mass at equilibrium.

fits reasonably well with experimental points, even at the center of the slab.

Initial diffusion coefficients (weight increment < 100%) values that justify experimental composition trajectory can be seen in Figure 4. Such behavior, which implies an Arrhenius type function, is in agreement with literature reports.^{14,15} That type of variation can also be observed in Figure 5 for experimental values applying Fick's model as well as eqs. (6) and (13). Nevertheless, the different position and slope of the lines, denote different activation energies. In Table I, diffusion coefficients are presented for the three models using the rapid calculus¹⁶ for Fickian behavior. One order of magnitude difference can be appreciated between Fick's model and eq. (6). Furthermore, the ratio when comparing Fick's values with the ones obtained with eq. (13) increases up to 48, showing how distant can glassy plastics be from Fickian behavior.

The predicted weight uptake of the volume increment model can be observed in Figures 6 and 7 where the experimental M_t/M_∞ values are also shown for the different diffusion temperatures. A very good correlation is observed for fractions un-

Table I Diffusion Coefficient Values for Tested Models

Temperature (K)	$D \times 10^{12}$ (Fickian) (m ² /s)	$D \times 10^{11}$ [Based on Eq. (6)] (m ² /s)	$D \times 10^{11}$ [Based on Eq. (13)] (m ² /s)
298	1.740	1.131	8.386
313	3.766	2.875	15.638
327	6.283	6.533	22.416
338	7.800	11.683	34.491

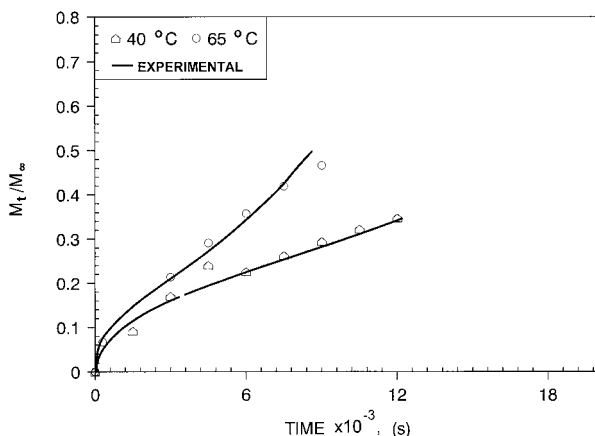


Figure 7 Comparison of eq. (13) with experimental sorption of butyl acrylate in polystyrene. Transferred mass is related to mass at equilibrium.

der 0.4 of the equilibrium value in all cases. That fraction value is beyond the range of technological importance when preparing gradient polymers, showing for that reason the validity of the model to control different gradient composition profiles.

Even though the relaxation model improves Fick's model to follow the weight uptake and composition profile, the model proposed here follows the experimental behavior more closely. That has been possible by considering a volume increment of the sample in addition to the change in its surface concentration, which is the main attribute of the relaxation model. One more advantage of the volume increment model over the relaxation model is represented by the smaller number of parameters that have to be evaluated to apply the modeling equation for sorption prediction.

In this work, it has also been found that at high sorptions (>120%), even the volume increment model deviates from experimental data. The high amount of diffusant may produce a transition (glassy to rubbery) in behavior.⁹ To be able to predict diffusion up to equilibrium, the diffusion coefficient should have to be considered as a variable, and the model would have to be solved by numerical methods. Here, an analytical solution has been presented to estimate diffusion when trying to prepare gradient blends with synergistic properties.^{4-7,17}

CONCLUSIONS

The model here, developed to predict profile concentration of monomer II diffusion in the glassy region of technological interest, is able to predict the gradient composition in polymer blends accomplished by sequential polymerization. Even though the gradient composition can be attained at either 25 or 65°C for the PS-PBA system, the higher the diffusion temperature used within that range, the faster the desired composition can be reached. That also helps in reducing the opportunity to flatten the gradient in concentration (throughout the slab), due to the high surface monomer II concentration.

REFERENCES

1. Utracki, L. A. *Two Phase Polymer Systems*; Hanser Publishers: Munich, 1991.
2. Klemmner, D.; Sperling, L. H.; Utracki, L. A., Eds. *Interpenetrating Polymer Networks*; ACS Series 239; American Chemical Society: Washington, DC, 1994.
3. Shen, M.; Bever, M. B. *J Mater Sci* 1972, 7, 741.
4. Akovali, G.; Biliyar, K.; Shen, M. *J Appl Polym Sci* 1976, 20, 2419.
5. Jasso, C. F.; Hong, S. D.; Shen, M. *Am Chem Soc Adv Chem Sci Multiphase Polym* 1979, 443.
6. Martin, G. C.; Enssani, E.; Shen, M. *J Appl Polym Sci* 1981, 26, 1465.
7. Jasso, C. F.; Martínez, J. J.; Mendizábal, E.; Laguna, O. *J Appl Polym Sci* 1995, 58, 2207.
8. Crank, J.; Park, G. S., Eds. *Diffusion in Polymers*; Academic Press Inc.: New York, 1968.
9. Frisch, H. L. *J Chem Phys* 1964, 41, 3679.
10. Frisch, H. L. *J Polym Sci Part C* 1965, 10, 11.
11. Neogi, P., Ed. *Diffusion in Polymers*; Marcel Dekker Inc.: New York, 1996.
12. Alfrey, T.; Gurnee, E. F.; Lloyd, W. G. *J Polym Sci Part C* 1966, 12, 249.
13. Frisch, H. L. *Polym Eng Sci* 1980, 20, 1, 2.
14. Frensdorf, H. K. *J Polym Sci* 1964, 2, 341.
15. Huang, R. Y. M.; Rhim, J. *J Appl Polym Sci* 1990, 41, 535.
16. Mirkin, M. A. *Polym Sci USSR* 1989, 31, 447.
17. Jasso, J. F. In *Polymeric Materials Encyclopedia*; CRC Press: Boca Raton, FL, 1996, p. 2849, vol. 4.