

New Rheological Method to Measure Diffusion Coefficient of Volatile Liquids: Application to Butylmethacrylate in Molten Polyethylene Matrix

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ABSTRACT: A rheological method to assess the diffusion behavior of liquids in molten polymers above their boiling point is presented in this article. The evaporation of the liquid and the evolution of the blends complex modulus are followed by rheological measurement. Identification of the Fick's diffusion coefficient and the rate of evaporation of butylmethacrylate in low density polyethylene is done. The values of the diffusion coefficient are in agreement with those obtained

by classical methods. The method developed here appears as complementary to the existent ones. It allows the measurement of diffusion coefficient of liquid/polymer system at high temperatures even for volatiles liquids. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 759–763, 2010

Key words: diffusion; solvent; high temperature; rheology; polymer melt

INTRODUCTION

The study of the diffusion of organics liquids in polymers above their glass transition is of great importance to control some processing operations, which involve monomer or solvent transport and in some case even volatilization. For instance, creation of new polymer based materials by reactive extrusion^{1–10} often needed the addition of unsaturated monomers or solvent to ensure the chemical modification of the matrix or elaboration of a homogeneous polymer blend. One of the characteristics of these systems is that the diffusion process competes with the reaction kinetics. The understanding of such reactions^{8–10} and the control of the characteristic sizes of the dispersed phase requires the study of the diffusion behavior of the monomer in melt polymer.

Rheological^{11,12} and weight loss¹³ methods already exist to study the diffusion of liquid solvents, but they cannot be used if the temperature is above the boiling point of the liquids. Indeed, most of the diffusion experiments are done by mass gain of a solid sample immersed in the diffusing liquid. At high temperature or especially when the sample is molten, this method is hard to perform for many reasons.^{14–18} The dissolution of the molten sample in

the solvent can occur, the weigh-in of the sample has to be done at high temperature to avoid phase separation and it is difficult to limit the solvent evaporation during this stage. Consequently, the diffusion behavior in the molten state of some polymeric systems cannot be studied yet. To solve this problem, we have developed a new rheological method, which appears as complementary to the existing ones. For instance, the method developed by Joubert et al.,¹¹ cannot be applied for the present system. Indeed, the liquid is layered at the polymer surface and then sheared. The experimental conditions do not allow the control of the evaporation of the liquid.

The article is structured as follows: we first describe the materials, the sample preparation and the analysis device. In the second part, we expose the theory needed for the method. Finally, we present the experimental results and discuss the validity.

EXPERIMENTAL

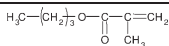
Materials

The low density polyethylene (LDPE) used in this study is supplied by Exxon [Escorene ref LD605BA, melting point 111°C, density 0.924 g cm⁻³, melt index 6.5 g (10 min)⁻¹]. The Butylmethacrylate (BMA) monomer and antioxidant used are purchased from Aldrich. Details are listed in Table I.

The method requires the miscibility of the polymer and the liquid. The miscibility of the LDPE and

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TABLE I
Characteristics of the BMA Monomer Used

Name	Code	Structure	Boiling point (°C)
Butyl methacrylate	BMA		165

the BMA have been studied by mixing the two component in a HAAKE Rheomix 600. Observation and characterization of the polymer/monomer blend by TEM, DSC, and DMA have proved their miscibility. The samples exhibit only one phase on the TEM pictures and a unique glass transition was observed by DMA and DSC.

Sample preparation

LDPE pellets were introduced into a HAAKE Rheomix 600 equipped with a sealed chamber and roller blade. The molten LDPE was mixed at 32-rpm rotation speed during 5 min at 160°C. A different amount of BMA monomers have been injected slowly, step by step, to well incorporate the BMA in the LDPE matrix and avoid the creation of BMA layer on the chamber wall which limits the mixing of the two components. The whole blend was mixed for 15 min. The monomer content is calculated as $\text{weight}_{\text{BMA}} \cdot 100 / (\text{weight}_{\text{BMA}} + \text{weight}_{\text{LDPE}})$. To avoid the monomer polymerization or the LDPE degradation, 0.3 wt % of 1,2-Benzenediol was added as inhibitor. Torque data was recorded during the mixing.

Rheological measurements

The linear viscoelastic properties were obtained using dynamic oscillatory mode and parallel plates geometry (Rheometrics® ARES device). The molten mixture is directly transferred between the two plates of the rheometer. The time evolution of the complex modulus was measured at 160°C for 1 rad/s. The partial pressure in BMA in the oven is kept null by using a heated pulsated air. Concentration range of BMA from 4.3 to 35% have been studied. The BMA content has been checked after each mixing by TGA experiments.

THEORY

In this section, the model is described. We assume that the weight loss of a sample is described by the same law of the weight gain and that the diffusion coefficient is isotropic. The drying problem described by Alsoy and Duda¹³ is similar in mathematical structure as the monomer diffusion of a solvent in polymer.

The rheological method is based on the fact that the rheological properties of a polymer solution depend strongly on the solvent concentration. As the

local rheological behavior is linked to the local solvent concentration, the complex modulus of a sample is very sensitive to the concentration gradient. Indeed, this is the sum of the local rheological behaviors which gives the global properties. This gradient is the consequence of the solvent diffusion in the sample (Fig. 1). Then the measurement of the time evolution of the complex modulus is a way to access to the concentration profile in the sample.

For our system, the boundary conditions and the initial conditions are better defined. The initial concentration Φ_0 in the sample is well known during the preparation of the homogeneous blends of LDPE and BMA. The sample is then placed in the oven of the rheometer which is heated by pulsed air. This air flow continuously renews the chamber atmosphere, which allows us to consider in the hypothesis that the concentration of BMA at the exterior of the sample is equal to zero. These two conditions enable us to simplify the experimental and mathematical treatment of the method.

The geometry of the device in the rheometer oven imposes that the diffusion of the BMA is radial. Vertical flow is inhibited by the two plates. The complex modulus G^* is then only a function of r , the distance to the rotation axis in the radial direction, and the time (as the concentration of BMA changes in time). The expression for the local complex modulus $G^*(t,r)$

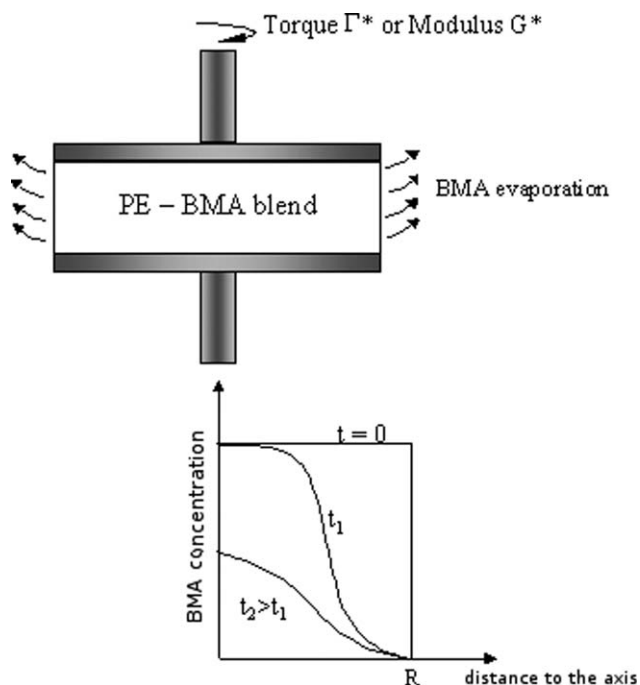


Figure 1 Sketch of the device used. The sample is sheared between two plates. The lower plate applies the strain whereas the upper one measures the torque. The graph below is a schematic representation of the variation of BMA concentration in the sample versus time and distance to the axis.

of a volume of sample at the position r and at time t is then given by the classic scaling law for polymer solutions:

$$G^*(t, r) = G_0^* [\Phi_{\text{pol}}(t, r)]^\beta = G_0^* [1 - \Phi_{\text{BMA}}(t, r)]^\beta, \quad (1)$$

where G_0^* is the modulus of pure polymer, Φ_{pol} is volume fraction of the polymer in the sample, Φ_{BMA} is the BMA volume fraction and β is an exponent depending on the interaction polymer/solvent and the nature of polymer.

The torque Γ^* developed by an inhomogeneous material is given by the sum of the contributions of all the volume elements with different rheological properties:

$$\Gamma^*(t) = 2 \frac{\pi \gamma^*}{R} \int_0^R G^*(t, r) r^3 dr, \quad (2)$$

γ^* is the maximum complex strain applied to the sample (for $r = R$) and R is the radius of the plates. On the other hand, the torque measured by the rheometer is expressed using the apparent mean complex shear modulus of the sample. For parallel plates geometry, the relation between the measured torque and the mean complex shear modulus is only link to the geometry and is given by:

$$\Gamma^*(t) = \frac{\pi \gamma^*}{2} R^3 G^*(t), \quad (3)$$

where $G^*(t)$ is the apparent modulus assuming that the sample is homogeneous.

The same torque is expressed by eqs. (2) and (3). It is thus possible to express the apparent complex shear modulus $G^*(t)$ as a function of the local rheological properties $G^*(t, r)$. Using eqs. (2) and (3) leads to the mixing law for the complex shear modulus G^* :

$$G^*(t) = \frac{4}{R^4} \int_0^R G^*(t, r) r^3 dr. \quad (4)$$

Replacing $G^*(t, r)$ by its expression in function of the concentration, one obtains the time evolution of the complex shear modulus:

$$G^*(t) = \frac{4G_0^*}{R^4} \int_0^R (1 - \Phi_{\text{BMA}}(t, r))^\beta r^3 dr. \quad (5)$$

Equation 5 shows that the complex modulus (or other dynamic rheological parameter) depends on the BMA concentration profile. This profile is driven by the diffusion laws and consequently is a function

of the diffusion coefficient. Using radial diffusion of the solvent considerably simplifies the establishment of a link between the complex shear modulus and the concentration profile in the sample. Previous studies¹¹ preferred using samples where the solvent was sandwiched between two layers of polymer. The diffusion was then in the vertical direction that leads to more complicated solutions for $G^*(t)$, which can be obtained by means of some assumptions.

The local volume fraction $\Phi_{\text{BMA}}(t, r)$ can be expressed as an analytical solution of the second Fick's law:

$$\text{div} \left(\overrightarrow{D \text{ grad } \Phi_{\text{BMA}}} \right) = - \frac{\partial \Phi_{\text{BMA}}}{\partial t}, \quad (6)$$

where D is the diffusion coefficient.

According to the free volume theory,^{19,20} the diffusion coefficient is a function of the solvent concentration. This increases the difficulty to solve the diffusion equation,^{21,22} [eq. (6)]. In the case of polyethylene matrix, Vrentas et al.¹⁹ showed a significantly different diffusivity-concentration relationship compared to most of the polymer-solvent systems. Diffusion coefficient is less dependent on the solvent concentration. For instance, typical results with *o*-xylene-polyethylene system at 150°C show variation of the mutual diffusion coefficient from 1.14 to 1.5 $10^{-9} \text{ m}^2 \text{ s}^{-1}$ when the concentration varies from 10 to 40%. This is small change compared to toluene-polystyrene systems where D increases more than three decades for the same range of concentration. According the free volume theory,²⁰ the large gap between measurement temperature and T_g of polyethylene ($\sim -100^\circ\text{C}$ for LDPE) explains such a typical behavior. Thus, for the present system, in first approximation, one can assume that the concentration dependence of the diffusion coefficient must be negligible for diffusion temperatures far away from T_g . This hypothesis will be checked in the next section. The diffusion equation is then considerably simplified. As the diffusion coefficient does not depend on the volume fraction of the solvent, eq. (6) can be cast into the form:

$$D \Delta \Phi_{\text{BMA}} = - \frac{\partial \Phi_{\text{BMA}}}{\partial t}. \quad (7)$$

The following initials and boundaries conditions have been used:

$$\Phi(0, r) = \Phi_0, \quad (8)$$

$$-D \frac{\partial \Phi}{\partial r} = \alpha(\Phi - \Phi_e). \quad (9)$$

The second condition take into account the evaporation of the BMA at the free surface of the sample ($r = R$). Φ_e is the BMA concentration required to

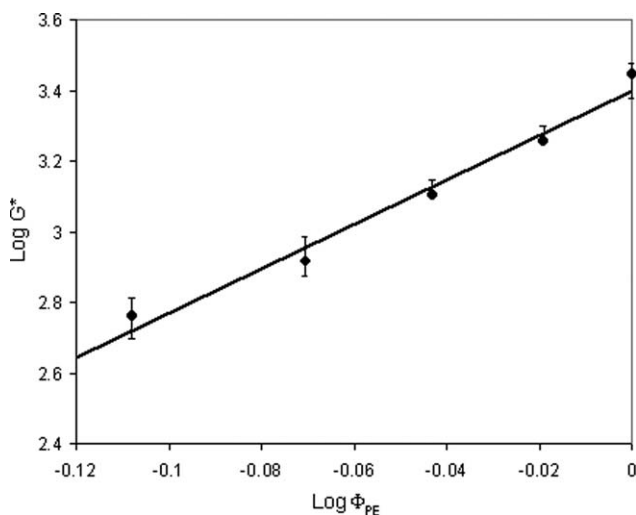


Figure 2 Scaling of the complex shear modulus of LDPE BMA blend versus the BMA volume fraction.

maintain equilibrium with the surrounding atmosphere. As the partial pressure of BMA in the oven is kept null by using a heated pulsated air, this concentration Φ_e is taken as null. α is the rate of evaporation.

Equation 7 has an analytical solution which can be expressed using Bessel functions:

$$\Phi_{\text{BMA}}(t, r) = 2 \sum_{n=1}^{\infty} \frac{Z \cdot J_0(r\theta_n/R)}{(\theta_n^2 + Z^2)J_0(\theta_n)} \exp\left(-\theta_n^2 D \frac{t}{R^2}\right), \quad (10)$$

where θ_n is the n th root of $\theta J_1(\theta) - Z \times J_0(\theta) = 0$. J_0 and J_1 are the Bessel function of respectively order 0 and 1. Z is defined as follow:

$$Z = \frac{R\alpha}{D} \quad (11)$$

Finally, eqs. (5) and (10) are used to describe the changes in the complex shear modulus induced by the diffusion of the BMA in the bulk and its evaporation at the free external surface of the sample.

EXPERIMENTAL RESULTS

The model requires the measurement of the β parameter to allow the identification of the values of α (the rate of evaporation) and D (the diffusion coefficient). The β parameter is involved in the scaling law describing the variations of the complex shear modulus of the system LDPE/BMA versus the polymer concentration. This corresponds to the variation of the initial value of the complex shear modulus before evaporation of the BMA. However, this value cannot be measured due to the temperature inertia in the oven. It is shown in Figure 3 that no experimental data are collected up to around 200 s, which is the classical time to establish constant temperature

condition for our device. The solution to get the exponent of the scaling law is to use the torque values during the mixing of the sample in the internal mixer. It has been shown that the torque developed in the chamber of the internal mixer is correlated to the stress created by the sample.²³ The same identification has been done for the rotation speed and the shear rate. As there is no evaporation in the chamber of the internal mixer, the measurement of the torque gives the value of the shear viscosity of the LDPE/BMA mixtures without loss of BMA. The complex shear modulus for 1 rad/s is then obtained by applying the Cox-Merx rule. Plotting the G^* value versus the polymer volume fraction in log scale (Fig. 2) leads to a straight line, where β is the slope. We found a value of β equal to 6.3.

This value cannot be compared to the classical value observed for linear polymers. The exponent 2–2.25 generally observed is found for the variations of the plateau modulus.²⁴ For frequency closer to the terminal zone, the exponent usually varies from 3 to 5 for linear molecules depending on the molecular weight distribution. Our measured value is out of the usual range but LDPE contains almost branched molecules and the scaling law is completely different in this case. Some recent works on LDPE²⁵ suggest that in the case of dilute polyethylene the exponent can be greater than 5. However, it is very difficult to evaluate the value theoretically from the structural parameters of the system and its composition.

Figure 3 shows an example of the evolution of the complex shear modulus during 2 h at 160°C in the oven of the rheometer for five samples with different concentrations. The increase of G^* is the consequence of the evaporation of the BMA out of the sample. The shape of the curve is linked to the distribution of

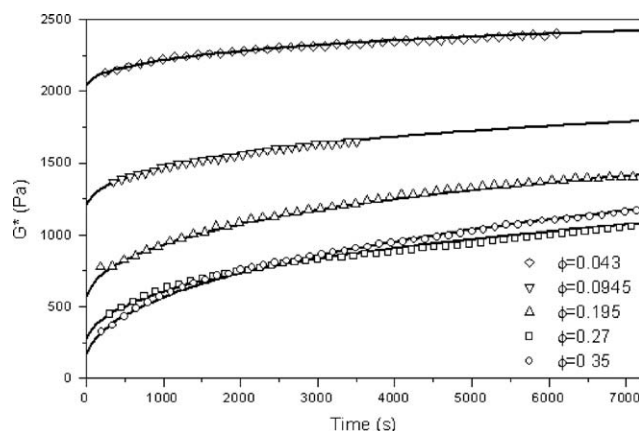


Figure 3 Experimental (symbols) and theoretical (solid lines) variations of the complex shear modulus of a LDPE/BMA blend at 160°C for various BMA content. The increase of the modulus is due to the evaporation of the BMA at the free surface of the sample and its diffusion in the bulk creating a concentration profile.

BMA in the sample during its diffusion toward the exterior of the sample. Equation (5) describes the time evolution of the sample modulus for a given initial BMA content. The diffusion coefficient D and the rate of evaporation α are then determined by fitting the experimental data. Fortunately, the two parameters are not correlated and can be adjusted separately. Actually there are the only fitted parameters. The initial BMA concentration is measured by TGA experiment. The value of the complex shear modulus of the pure polymer is easily obtained by dynamic rheological measurement. As it is shown in Figure 3 the superposition of the theoretical curves and the experimental data is excellent with a unique set of parameters. The two parameters are:

$$D = (4 \pm 0.3)10^{-9} \text{ m}^2/\text{s},$$

$$\alpha = 0.019 \pm 0.0005 \text{ m/s}.$$

Whatever the BMA concentration is diffusion coefficient appears to be the same. Actually, considering the results of Ventras et al.,¹⁹ for high temperatures greater than T_g , variations of the diffusion coefficient are included in the uncertainties of the present method. For this system, the hypothesis concerning the effect of the solvent on the free volume is then justified and may be used to simplify the theoretical treatment of the diffusion equation. It is worth to note that the order of magnitude of the value obtained by this method is the same as for other systems with polyolefin matrix.

It is not surprising to find that the rate of evaporation is independent of the BMA concentration. However, this coefficient depends on the temperature and its interaction with the diffusion coefficient will be studied in further work.

The method is simple and roughly self-consistent but it is necessary to work with evaporable solvent. The limit of the present procedure lies in the simplification of the diffusion equation considering that the diffusion coefficient is constant. In the case of matrix with higher glass temperature (close to the experiment temperature), eq. (7) does not hold and the simple analytical solution cannot be used. Then solving the diffusion equation would be trickier and needed more parameters. However, we showed that the method can be performed easily and could be an accurate tool to measure diffusion coefficient at high temperature: the sample geometry is simple and the link between the modulus and the solvent concentration profile is simple and accurate too.

CONCLUSION

The diffusion behavior of BMA in the LDPE matrix has been estimated at 160°C. Rheology proved to be

a very sensitive tool for experimental following of diffusion. Calculation developed from a rheological inversion method represents the experimental data with a very good agreement. It was shown that in the case of LDPE for which the glass transition is very low, using a simple model of Fickian diffusion enables to obtain a good estimation of the diffusion coefficient of the solvent in the polymer matrix at high temperature. The free volume theory of diffusion is simplified when the gap between experimental temperature and T_g is large. In this case, the variations of the diffusion coefficient are included in the uncertainties of the rheological method. The value of the diffusion coefficient that have been identified for the couple LDPE/BMA is thus $(4 \pm 0.3)10^{-9} \text{ m}^2/\text{s}$. The identified value for the rate of evaporation of BMA has been found at $0.019 \pm 0.0005 \text{ m/s}$. This work is a key issue in the determination of diffusion behavior of volatile liquids in melt polymers. Further works will focus on polymers with higher glass transition near the measurement temperature to check the method with more complicated diffusion equations.

References

1. Ganzeveld, K. J.; Janssen, L. P. B. M. *Polym Eng Sci* 1992, 32, 467.
2. Chen, L. F.; Wong, B.; Baker, W. E. *Polym Eng Sci* 1996, 36, 1594.
3. Ghosh, P.; Chattopadhyay, B.; Sen, A. *Polymer* 1998, 39, 193.
4. Liu, N. C.; Xie, H. Q.; Baker, W. E. *Polymer* 1993, 34, 4680.
5. Pesneau, I.; Champagne, M. F.; Huneault, M. A. *J App Polym Sci* 2004, 91, 3180.
6. Raval, H.; Singh, Y. P. *Polymer* 1991, 32, 493.
7. Yeh, J. T.; Fan-Chiang, C. C. *J App Polym Sci* 1997, 66, 2517.
8. Moad, G. *Prog Polym Sci* 1999, 24, 81.
9. Scott, H. G. U.S. Pat. 3,646,155 (1972).
10. Swarbrick, P.; Green, W. J.; Maillifer, C. U.S. Pat. 4,117,195 (1978).
11. Joubert, C.; Cassagnau, P.; Choplin, L.; Michel, A. *J Rheol* 2002, 46, 629.
12. Bousmina, M.; Qiu, H.; Grmela, M.; Klemberg-Sapieha, J. E. *Macromolecules* 1998, 31, 8273.
13. Alsoy, S.; Duda, J. L. *AIChE J* 1998, 44, 582.
14. Pickup, S.; Blum, F. *Macromolecules* 1989, 22, 3961.
15. Zielinski, J. M.; Duda, J. L. *AIChE J* 1992, 38, 405.
16. Hong, S. U. *Ind Eng Chem Res* 1995, 34, 2536.
17. Vrentas, J. S.; Vrentas, C. M. *Eur Polym J* 1998, 34, 797.
18. Tongue, M. P.; Gilbert, R. G. *Polymer* 2001, 42, 1393.
19. Ventras, J. S.; Duda, J. L.; Lau, M. K. *J Appl Polym Sci* 1982, 27, 3987.
20. Cohen, M. H.; Turnbull, D. *J Chem Phys* 1959, 31, 1164.
21. Ponsard-Fillette, M.; Barres, C.; Cassagnau, P. *Polymer* 2005, 46, 10256.
22. Bella, R.; Cassagnau, P.; Fenouillot, F.; Falk, L.; Lacoste, C. *Polymer* 2006, 47, 5080.
23. Brouillet-Fourmann, S.; Carrot, C.; Mignard, N.; Prochazka, F. *Appl Rheol* 2002, 12, 192.
24. Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W.; Fetters, L. J. *Macromolecules* 1981, 19, 1668.
25. Stanescu, P.; Majeste, J. C.; Carrot, C. *J Polym Sci B: Polym Phys* 2005, 43, 1973.