Viscosity Reduction of Polymeric Liquid by Dissolved Carbon Dioxide

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ABSTRACT: The viscosities of polydimethylsiloxane (PDMS)/CO_2 solutions were measured over the range of pressures of 1–3 MPa and at the ambient temperature. The viscosities were measured by using a specially designed falling ball viscometer (FBV). The Stokes equation was used to determine the viscosities and the Stokes force expressing the viscous drag of the sphere was corrected for the effect of the lateral cylindrical wall. The Kelley–Bueche (KB) free-volume treatment of the viscosities of polymeric solutions was modified to account for the gas solvent and applied to interpret our data on PDMS/CO_2 systems. It was shown that the theoretical equation, based on the assumption of the additivity of free volumes of the components, was capable of predicting with remarkable accuracy the concentration and pressure dependence of the viscosities of the investigated polymeric solutions. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 459–466, 1997

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INTRODUCTION

Viscosity has been regarded as an important characteristic of polymeric materials since the beginning of polymer science. The viscosity of polymer-containing solvent or plasticizer is a subject of considerable practical interest. It is important in several stages of the manufacturing and processing of polymers, e.g., in the spinning of fibers and the casting of films from solutions and in the paint and coatings industry. It is also especially of very much importance for the extrusion of polymers during form production.

In our previous article,[1] we reported the gas-plasticization effect of CO_2 for poly(ethylene glycol) (PEG)/CO_2 systems at various temperatures and pressures. Photon correlation spectroscopy (PCS) was used to determine the viscosities of PEG/CO_2 systems based on measuring diffusivities of suspended colloidal particles.

It is well known that dissolved CO_2 decreases the glass transition temperature (T_g) of a polymer. Wessling et al.[2] studied the mechanism of foaming a glassy polymer using sorbed carbon dioxide. They reported that a glass polymer supersaturated with CO_2 foams the foamlike structure at much lower temperatures, which indicates the T_g-depressing effect of CO_2. Chow[3] derived an explicit expression based on both classical and statistical thermodynamics for predicting the T_g of polymer–diluent mixtures. The result is expressed in terms of the molecular weight, size, and concentration of the diluent, the number of lattice sites, the monomer molecular weight, and the transition isobaric specific heat increment.

This article focuses on the viscosity reduction of polydimethylsiloxane (PDMS)/CO_2 systems by dissolved gas, i.e., CO_2 in this study. This phenomenon is called a gas plasticization, a process in

which plasticization is affected by dissolved gases instead of liquid solvent.[1,4] Our goal of this study was to formulate a quantitative description of the viscosity reduction of the polymer melt when a gas solvent is dissolved in the polymer. Gas plasticization is particularly useful when polymers degrade due to heating. Viscosity reduction by a gas solvent can be an alternate process to simplify heating and for reducing viscosity. Potential applications of gas plasticization are achieving longer critical length in the compounding of short glass fibers and improved fiber wetting in manufacturing polymer composites.[4]

PDMS was chosen in this work because it is liquid at ambient conditions and is the simplest silicones which consist of the basic structure of the silicones, i.e., silicon–oxygen–silicon backbone. PDMS shows the unique properties of the silicone family: low surface tension, excellent thermal stability, and shear stability. These favorable characteristic properties lead to a great deal of commercial applications. This is a model polymer melt for studying gas plasticization at ambient temperature without the experimental difficulty of exceeding the melting temperature of engineering thermoplastics.

The experimental objective of this study was to determine viscosities of solutions of PDMS with CO_2 by using an appropriate technique. The viscosities of PDMS/CO_2 systems are measured by a specially designed falling ball viscometer (FBV). The FBV is capable of measuring the viscosity at the low shear rate range.

The Kelley–Bueche (KB) theory[5] predicts the viscosities of concentrated polymer solutions based on the total available free volume in the solution. The total free volume is calculated from free volumes of pure polymer and solvent by using a simple mixing rule. We modified the KB theory to account for the polymer–gas solvent system. The modified theory explains our experimental data very well.

EXPERIMENTAL

As shown in Figure 1, a specially designed FBV in this study consists of a Plexiglas tube, an electromagnet, a dc power supply, a pressure transducer, a pressure regulator, and a digital voltmeter. The outside and inside diameters of the tube are 1.905 and 1.27 cm, respectively. The length of the tube is 17.78 cm.

A conventional FBV had to be modified so that

PDMS/CO_2 systems at elevated pressures above the atmospheric pressure can be loaded onto the FBV. For this purpose, a metal rod was magnetized by an electrical coil. The top of the tube is connected to the copper tubing by Swagelok tube fittings and the bottom of tube is closed by a cap, so that the tube can be charged easily.

All viscosity data from the FBV are measured at room temperature. The pressure is measured by the Dynisco pressure transducer whose output is read on the HP digital voltmeter. The specification of the metal spheres used in this work, their diameters and densities measured within an accuracy of $\pm 0.5\%$, are presented in Table I.

It is very important to drop the sphere at the center of the tube. A slightly off-centered fall can introduce a significant error. The sphere was moved vertically through the polymer sample by using a permanent magnet. It is then held in place by an electromagnet. The polarity of the electromagnet is changed to release and allow the sphere to free fall through the sample fluid. Then, the same sphere is used in subsequent measurements and the system is completely closed. Thus, this FBV can operate at pressures above atmospheric pressures. The apparatus was tested up to 5 MPa using N_2 gas.

There are two marked lines on the outside surface of the tube. The distance between two lines is 3.81 cm. To measure the terminal velocity, a sphere is dropped at the center of the tube and the time required for the sphere to pass the marked distance is recorded. Subsequently, the same sphere is used again as we previously mentioned.

The characteristics of the PDMS samples used in this study are listed in Table II. The PDMS sample is charged in the tube through the funnel gravimetrically. The weight of the charged sample is determined by weighing the tube with and without the sample. The loading procedure of CO_2 was reported elsewhere.[1,4]

CORRELATING EQUATIONS

Williams–Landel–Ferry (WLF) Model[6]

WLF defines a quantity a_T to represent the temperature variation of the segmental friction coefficient for any mechanical relaxation and show that it can be represented by an equation of the type

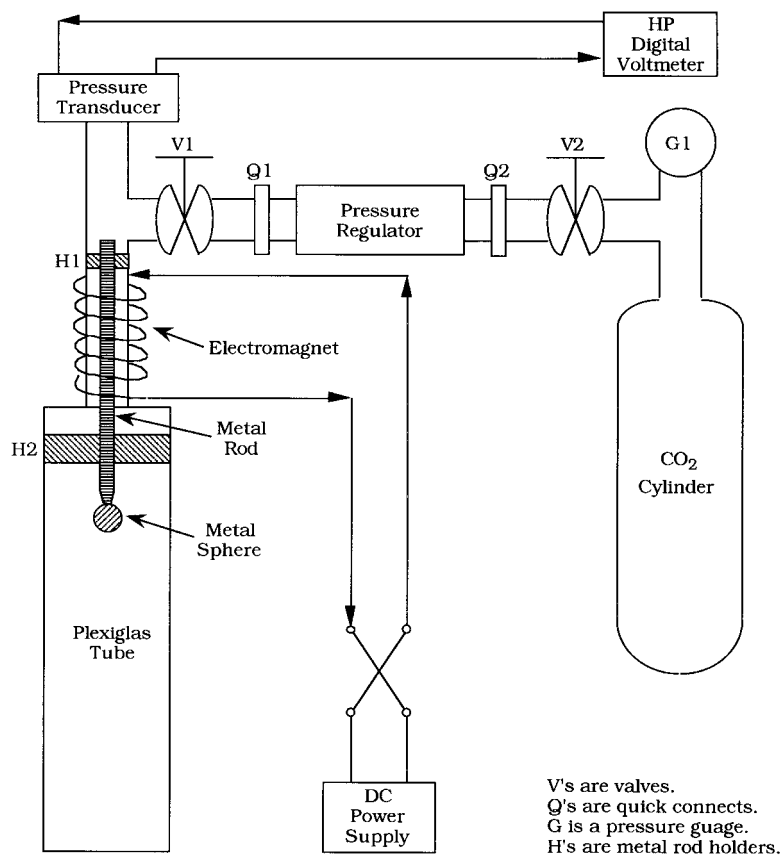$$\log a_T = \frac{-C_1(T - T_s)}{C_2 + T - T_s} \qquad (1)$$

Figure 1   Schematic diagram of falling-ball viscometer.

where C_1 and C_2 are constants and T_s is a standard temperature. They also showed that if, instead of T_s, a characteristic reference temperature for the polymer was used, e.g., the glass transition temperature T_g, with $T_s + 50 \approx T_g$, they obtained the relation

$$\log a_T = \frac{-17.44(T - T_g)}{51.6 + T - T_g} \qquad (2)$$

They claimed that eq. (1) generally represents the temperature dependence of the viscosity in the range $T_g < T < T_g + 100°C$.

The derivation provided by WLF is based on an analogy to Doolittle's equation. They started with Doolittle's equation[7]

$$\ln \eta = \ln A + B \frac{V_0}{V_F} \qquad (3)$$

where A and B depend on the nature of the liquid and V_0 and V_F are the occupied and free volumes (cm^3/g), respectively. Then, they used Fox and Flory's free-volume concept.[8,9] When the glass transition is approached, the relative free volume diminishes sharply. This is believed to be primar-

Table I   Specifications of Spheres

Ball No.	Weight (g)	Diameter (cm)	Density (g/cm^3)
1	0.253	0.395	7.863
2	0.129	0.316	7.822

Table II   Correction Factors of PDMS (B_p) and CO_2 (A_s)

MW	A_s	B_p
28,000	0.157	1.020
67,700	0.195	1.021
204,000	0.220	1.023
Avg.	0.190	1.021

ily responsible for the accompanying large viscosity increase. The existence of a universal function such as eqs. (1) and (2) implies that the nature of this volume change and its effect on the rates of molecular rearrangements are essentially the same for all supercooled systems, polymeric, nonpolymeric, and their mixtures, independent of molecular structure.

For supercooled systems, eq. (3) can be modified by noting that V_F is small and V_0 is practically equal to the specific volume $(V_0 + V_F)$, so V_F/V_0 can be replaced by the fractional free volume, $V_F/(V_0 + V_F) = f$. The constant B was found by Doolittle to be of the order of unity; for supercooled liquids, the existence of a universal a_T function implies that B must be independent of temperature, and WLF theory simply makes it unity. Then, a_T is defined as η/η_g and, approximately,

$$\log a_T = \frac{1}{2.303}\left(\frac{1}{f} - \frac{1}{f_g}\right) \qquad (4)$$

where f_g is the fractional free volume at T_g.

The dependence of fractional free volume on temperature is taken to be the thermal expansion coefficient α, i.e., $f = f_g + \alpha(T - T_g)$. Substitution of this relation into eq. (4) yields

$$\log a_T = -\frac{1}{2.303}\left(\frac{T - T_g}{f_g/\alpha + T - T_g}\right) \qquad (5)$$

This equation is identical in form to eq. (1), with the constants $\alpha = 4.8 \times 10^{-4} \deg^{-1}$ and $f_g = 0.025$. Consequently, WLF's fractional free volume can be written as

$$f = 0.025 + 4.8 \times 10^{-4}(T - T_g) \qquad (6)$$

WLF claimed that the value of f_g is reasonable for many polymer melts, but the application of their approach to mixture data requires a more specific interpretation of f. This statement supports our modification of fractional free volume for PDMS when CO_2 is dissolved in the polymer.

Kelley–Bueche (KB) Model[5]

This section introduces KB's viscosity and glass transition temperature (T_g) relations for polymer solutions. The viscosity, η, of a polymer solution is related to the segmental friction factor f_0 by

$$\eta = KM^{3.5}C_p^4 f_0, \quad M > M_{cr} \qquad (7)$$

and

$$\eta = K'MC_p f_0, \quad M < M_{cr} \qquad (8)$$

where K and K' are model constants and M and M_{cr} are the molecular weight of the sample polymer and its critical molecular weight for entanglement formation, respectively. The variation of f_0 with concentration is an additional complicating factor since it is to be expected that added diluent will cause f_0 to decrease.

A convenient way of picturing the effect of a diluent on a polymeric system is the relative increase in free volume contributed by the diluent, thereby loosening the local liquid structure. Cohen and Turnbull[10] derived an expression for the dependence of molecular transport on a critical free volume V^*, required for the displacement of a flow unit, and arrived at a modified Doolittle relationship:

$$f_0 = A'\exp\left(\frac{V^*}{V_F}\right) = A'\exp\left(\frac{1}{f}\right) \qquad (9)$$

where f is WLF's fractional free volume.

If the assumption is made that the free volume contributed by the diluent is added to that of the polymer, the fractional free volume of the solution at a volume fraction of polymer, ϕ_p, is expressed as

$$\begin{aligned} f &= \phi_p f_p + \phi_s f_s \\ &= \phi_p(0.025 + 4.8 \times 10^{-4}(T - T_g)) \\ &\quad + (1 - \phi_p)(0.025 + \alpha_s(T - T_g')) \end{aligned} \qquad (10)$$

where α_s and T_g' are the thermal expansion coefficient and glass transition temperature of the solvent, respectively. Then, by combining eqs. (7)–(10),

$$\eta = B C_p^4 \exp\left[\frac{1}{\phi_p f_p + (1 - \phi_p)f_s}\right] \qquad (11)$$

for $M > M_{cr}$, where B is a combined constant including the molecular weight.

The corresponding equation for $M < M_{cr}$ is of the same form except that the concentration dependence is to first power. Kelley and Bueche used Cohen–Turnbull's equation for the segmental

friction factor. They employed WLF's fractional free volume to predict f of the solution by a simple mixing rule. They combined these two concepts with Bueche's viscosity model of a polymer solution (which includes the concentration of a polymer) to obtain eq. (11).

Modified Kelley–Bueche (KB) Equation for Gas Solvent [1,4,11]

Our modification of the KB equation is based on the compressibility effect on the free volume of polymeric liquids. We start our derivation from the KB equation [eq. (11)].

The polymer concentration, C_p, is related to ϕ_p:

$$C_p = \rho_p \phi_p \qquad (12)$$

Combining eqs. (11) and (12) yields

$$\eta = B \rho_p^4 \phi_p^4 \exp\left[\frac{1}{\phi_p f_p + (1 - \phi_p)f_s}\right] \quad (13)$$

For pure polymer, $\phi_p = 1$,

$$\eta_p = B \rho_p^4 \exp\left(\frac{1}{f_p}\right) \qquad (14)$$

Then, taking the ratio, η/η_p, gives

$$\frac{\eta}{\eta_p} = \phi_p^4 \exp\left[\frac{1}{\phi_p f_p + (1 - \phi_p)f_s} - \frac{1}{f_p}\right] \quad (15)$$

In our application, f_s is the fractional free volume of CO_2. KB's definition of f_s for liquid solvents is not applicable. To introduce a realistic value of f_s for CO_2, we go back to WLF's definition of f. For CO_2, the assumption that $V_F \ll V_0$ does not hold any more. Instead,

$$f_s = f_{CO_2} = \frac{V_F}{V_0 + V_F} = \frac{V - V_0}{V} \qquad (16)$$

where V is total volume of CO_2. With this definition, we can calculate f_s from the experimental data of V_0 and V for CO_2. Since we modified the KB equation, we proceeded to express the viscosity expression with two model parameters, B_p and A_s, as follows:

$$\eta = \eta_p \phi_p^4 \exp\left[\frac{1}{B_p \phi_p f_p + A_s(1 - \phi_p)f_s} - \frac{1}{f_p}\right] \quad (17)$$

Both A_s and B_p can then be calculated by fitting the data.

RESULTS AND DISCUSSION

In the study of polymer solutions, it is very important to have information on the volume fraction of the polymer at each state. We measured the swollen volume of $PDMS/CO_2$ solutions by measuring the height of our sample in the FBV by using a cathetometer. Since we know the initial volume (the volume of pure PDMS), the volume of CO_2 in the $PDMS/CO_2$ solutions can be calculated, assuming ideal mixing, by subtracting the volume of pure PDMS from the swollen volume with CO_2.[4]

The fitted equations from the volume data at room temperature are as follows:

$$\phi_p = 1.0252 - 0.0149\,P, \quad MW = 28{,}000 \qquad (18)$$

$$\phi_p = 1.0202 - 0.0116\,P, \quad MW = 67{,}700 \qquad (19)$$

$$\phi_p = 1.0182 - 0.0100\,P, \quad MW = 204{,}000 \quad (20)$$

where ϕ_p is a volume fraction of the polymer and P is the pressure in MPa. From the literature review, Kamiya et al.[12] reported the volume expansion vs. pressure data for CO_2 in a PDMS liquid. Their volume fraction of PDMS in the CO_2 system at 3 MPa was 0.89. However, they did not give information about the molecular weight of the PDMS used. Garg et al.[13] discussed the solubilities of CO_2 in PDMS and correlated their data with lattice theory-based equations of state, namely, Sanchez–Lacombe and Panayiotou–Vera equations of state. They reported that the volume fraction of PDMS (MW = 308,000) in the $PDMS/CO_2$ system at 3 MPa was about 0.96. Their measurement temperature was 50°C. By comparing our result (= 0.97) with those of two other groups, there is a slight deviation that is 1–8%. It might be due to different molecular weights of PDMS samples used for each group.

There are two concerns about the viscosity measurements by using the FBV. First, the sample solutions used in the FBV measurement must be Newtonian fluids. Because the Stokes' equation is valid only for Newtonian fluids. For the FBV, the shear rate is fixed by the size of the ball used.

We must ensure that the shear rate is low enough to be in the Newtonian region. Second, the hydrodynamic motion of the sphere is in the Stokes' regime with $Re < 0.1$, where Re is the Reynolds number.

It was another reason why we chose PDMS as our sample. The silicones are well-known Newtonian fluids. Experimental data are also available elsewhere.[4]

In general, the effect of solvent on the shear rate range for the Newtonian limit is expected to extend to a higher shear rate. As the solvent (CO_2 in this study) is added and the viscosity is reduced, the rheological relaxation time for the mixture is also reduced. The onset of non-Newtonian behavior, which is governed by the dimensionless product of relaxation time and the shear rate in many models for polymer rheology,[14] should therefore occur at higher shear rates as CO_2 is added to the mixture.

We estimated the maximum shear rate of the FBV for PDMS/CO_2 systems as discussed below. For the FBV, the shear stress at the surface of the sphere (τ_R) will be

$$\tau_R = \frac{3}{2} \frac{\eta V_\infty}{R} \sin \theta \qquad (21)$$

where η and V_∞ are the viscosity of fluid and the terminal velocity of sphere, respectively. At $\theta = 90°$,

$$\tau_R = \frac{3}{2} \frac{\eta V_\infty}{R} \qquad (22)$$

But

$$\eta = \frac{\tau_R}{\dot{\gamma}} \qquad (23)$$

where $\dot{\gamma}$ is the shear rate (s^{-1}).

Combining eqs. (22) and (23) gives

$$\dot{\gamma} = \frac{3}{2} \frac{V_\infty}{R} \qquad (24)$$

All the highest shear rates for each PDMS/CO_2 solution lie in the range of the Newtonian fluid region of pure PDMS.[4] Since adding the solvent in the polymer extends the Newtonian fluid region, all PDMS/CO_2 solutions in this study are assumed to be Newtonian fluids. Another restriction of the Stokes' equation is $Re < 0.1$. All our

calculated Re's are less than 0.1.[4] We thus checked all restrictions of Stokes' equation used and verified its validity for our data.

The molecular weights of PDMS used in this study are in the range of 28,000 to 204,000. The lowest molecular weight of 28,000 is quite close to M_{cr} (M_{cr} for PDMS = 30,000).[15] So, we assumed that all molecular weights used are greater than M_{cr} and used the modified KB equation for the case $M < M_{cr}$, i.e., eq. (17). The application of eq. (17) to the results on the PDMS/CO_2 solution requires the knowledge of the fractional free volumes f_p and f_s of the polymer and solvent at each temperature and pressure. For PDMS, we used WLF's fractional free volume given by eq. (6). Since there might be a pressure effect on the polymer, we introduce a model parameter, B_p.

The value of f_s for CO_2 at each temperature and pressure is evaluated from eq. (16). The value of V_0 is 0.8798 cm^3/g (Ref. 16), and for the specific volume, V, we use the density data of CO_2 (ρ_{CO_2}) from elsewhere.[17] In this study, the experimental temperature is 25°C. For ρ_{CO_2}, the following equation is used and it is valid in the pressure range up to 5 MPa:

$$\rho_{CO_2} = 0.007 + 0.0112\,P + 0.0026\,P^2 \quad (25)$$

where ρ_{CO_2} is in g/cm^2 and P is the pressure in MPa.

Raw viscosity data in this study are corrected based on the tube wall effect. Because of the finite value of the ratio $k = r/R$ (where r and R are the radius of sphere and the radius of tube, respectively), the Stokes force expressing the viscous drag of the sphere must be corrected for the effect of the lateral cylindrical wall by introducing

$$F_s(k) = 6\pi\eta r V_\infty \lambda(k) \qquad (26)$$

The correction factor $\lambda(k)$ increases continuously from the value 1 for $k = 0$ (classical Stokes equation). As k approaches 1, $\lambda(k)$ should tend to infinity because of the increased shear stresses between the surfaces in relative motion. An additional effect, which can be expressed as a "backflow" contribution, comes from the continuity equation for the liquid. As the sphere moves downward, an equivalent amount of fluid must move upward in the restricted annulus between the sphere and the cylinder. Haberman et al.'s experimental values of $\lambda(k)$[18] was used in this study to correct our measured viscosity. Conse-
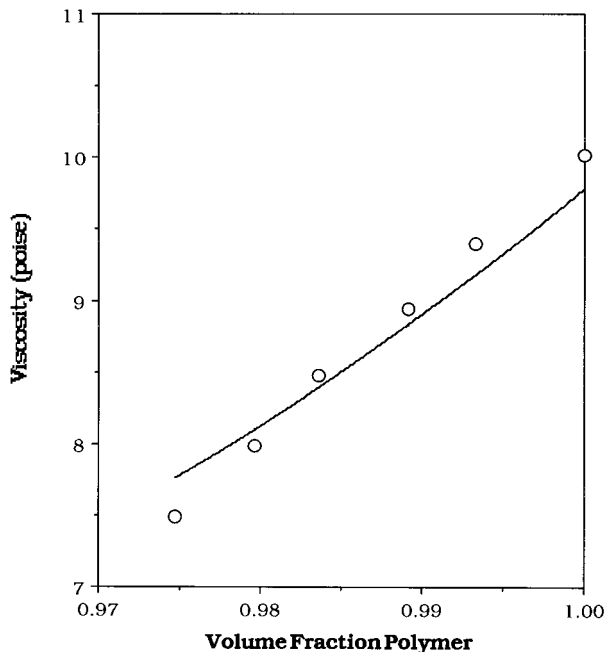
Figure 2 Plot of viscosity (η) vs. volume fraction of polymer (ϕ_p) for PDMS (MW = 28,000). Open circles are experimental data and the solid line is the modified KB theory.
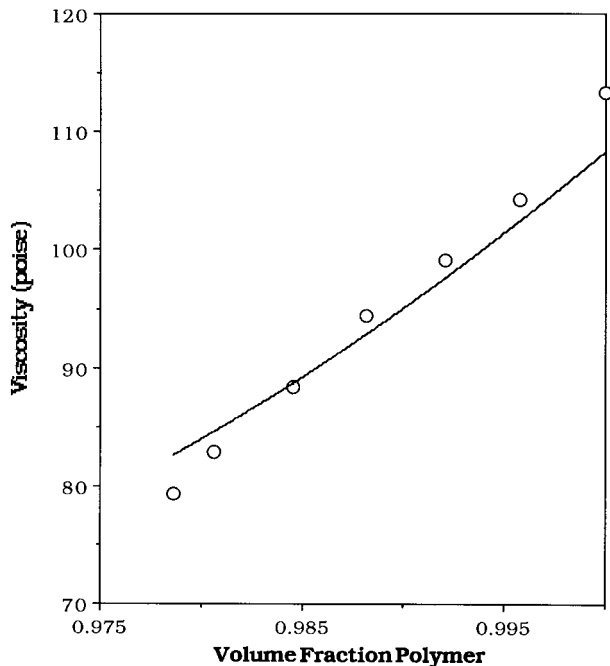

Figure 3 Plot of viscosity (η) vs. volume fraction of polymer (ϕ_p) for PDMS (MW = 67,700). Open circles are experimental data and the solid line is the modified KB theory.

quently, our final viscosity equation can be given as

$$\eta = \frac{2R^2(\rho_s - \rho)g}{9V_\infty \lambda(k)} \qquad (27)$$

where R is the radius of the sphere and ρ_s and ρ are the densities of the sphere and the fluid, respectively. The value of $\lambda(k)$ is interpolated in terms of k.

The correction factors, A_s and B_p, obtained by a nonlinear fit of the viscosity data are listed in Table II. The values of A_s for PDMS/CO$_2$ systems vary with molecular weight. If an average value of $A_s = 0.19$ is considered, it implies that f_s in the mixture is about an order of magnitude less than f_s of pure CO$_2$. On the other hand, B_p is very close to unity and does not depend on temperature or molecular weight. This indicates that f_p calculated from WLF and weighted by f_p yields the correct fractional free-volume contribution of the polymer in the mixture.

Figures 2–4 show that viscosities of PDMS/CO$_2$ systems with various molecular weights of PDMS. The results show that the theoretical viscosities of PDMS/CO$_2$ solutions from the modified KB equation are in very good agreement with
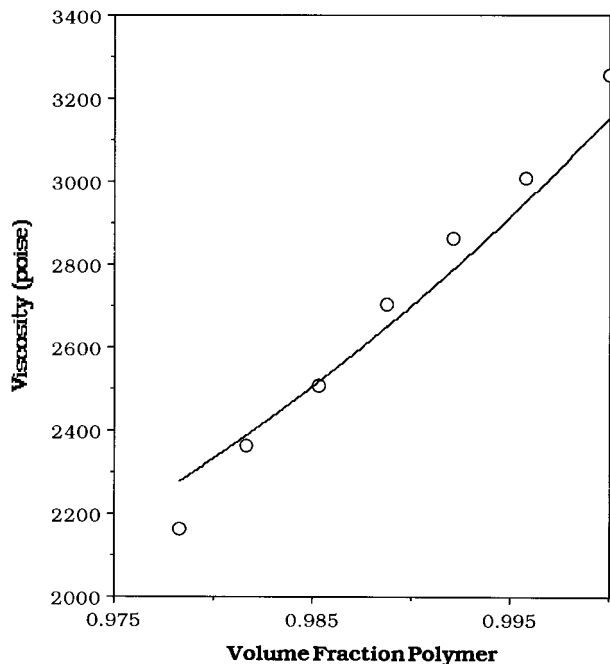

Figure 4 Plot of viscosity (η) vs. volume fraction of polymer (ϕ_p) for PDMS (MW = 204,000). Open circles are experimental data and the solid line is the modified KB theory.

those of the experimental viscosities. Since our pressure range is limited in PDMS/CO$_2$ solutions, the data do not show the transition points. However, we can predict the transition point by calculating $P_{\min}$ by setting $d\eta/dp = 0$. We calculate the minimum viscosities ($\eta_{\min}$) of each molecular weight by finding $P_{\min}$ but all $P_{\min}$'s are found around 8 MPa which are out of range in this study. The pressure range of the FBV extends to only 5 MPa; thus, the region of the theoretical viscosity minima for PDMS was not accessible.

CONCLUSION

We have studied the viscosity reduction of polymer melts by gas plasticization, a process in which a gas is dissolved in a polymer melt at elevated pressures and at the ambient temperature. A specially designed FBV was used to determine the viscosities of PDMS/CO$_2$ systems. The measurements were made as a function of concentration and pressure.

Free-volume concepts were employed to interpret our experimental results. KB theory, which predicts the viscosities of concentrated polymer solutions based on the total available free volume in the solution, was modified to account for gas solvents. Two adjustable variables, A_s and B_p, were introduced to correct a simple mixing rule for the free-volume contributions of solvent and polymer.

When the values of A_s and B_p, obtained from fitting the modified KB theory to data, were compared, B_p is very close to unity and does not depend on molecular weight. This indicates that f_p calculated from WLF and weighted by ϕ_p yields the correct fractional free-volume contribution of the polymer in the mixture. On the other hand, A_s is a weak function of molecular weight and is a strong function of polymer segment–solvent interaction. The modified KB theory presented here provides a good understanding of the study of viscosities of polymer–gas solvent systems.

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