Polymer Vol. 37 No. 14, pp. 3011–3017, 1996

0032-3861/96/$15.00+0.00

Gas plasticization effect of carbon dioxide for polymeric liquid

Young Chan Bae
Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul, 133-791 Korea
(Received 12 July 1995)

The low-shear-rate viscosities of poly(ethylene glycol)(PEG)/CO_2 solutions were measured over a range of pressures (1–8 MPa) and temperatures (30–60°C). Photon correlation spectroscopy (PCS) was used to determine the viscosities based on measuring diffusivities of suspended colloidal particles. Assuming spherical particles and knowing the size of particles, the Stokes–Einstein relation was employed to find the medium viscosity. The interesting results were observed as follows: in the high range of the volume fraction of polymer ϕ_p, the plasticization effect is stronger than that of the compressibility, the solution viscosity decreases as more CO_2 dissolves in the polymer, while at the low range of ϕ_p the viscosity reduction reverses and the viscosity of solution increases due to the compressibility effect. The Kelley–Bueche (KB) free volume treatment of the viscosities of polymer solutions was modified to account for gas solvent and applied to interpret our data on PEG/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 excellent accuracy the concentration, temperature, and pressure dependence of the viscosities of the investigated polymeric solutions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: gas plasticization; modified Kelley–Bueche theory; photon correlation spectroscopy)

INTRODUCTION

The design of manufacturing and processing equipment requires considerable knowledge of the properties of the processed materials and related compounds. This knowledge is also essential for the application and final use of these materials[1].

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 paints and coatings industry.

This paper focuses on gas plasticization, a process in which plasticization is affected by dissolved gases instead of liquid solvent. Our goal of this study is to formulate a quantitative description of viscosity reduction of the polymer melt when a gas solvent is dissolved in the polymer at temperatures and pressures in the vicinity of the critical point of the gas solvent. Gas plasticization is particularly useful when polymers degrade due to heating. Viscosity reduction by a gas solvent can be an alternate process to simply heating and reducing viscosity. Potential applications of gas plasticization are achieving longer critical length in the compounding of short-glass fibres and improved fibre wetting in manufacturing polymer composites[2].

PEG was chosen in this work because it is liquid at ambient conditions. This is a model polymer melt for studying gas plasticization near ambient temperatures with experimental difficulty of exceeding the melting temperature of engineering thermoplastics. PEGs are completely soluble in water, very low in toxicity, quite inert and non-irritating, and possess wide compatibility, etc. This unusual combination of properties has enabled them to find a very wide range of commercial applications in fields such as pharmaceutical salves and suppositories; paper-coating lubricants; etc.

The experimental objective of this study is to determine viscosities of solutions of PEG with CO_2 by using the appropriate technique. Dynamic light scattering (DLS) from probe particles is used in this study. The method for determining viscosity of PEG/CO_2 systems at elevated pressures and temperatures is based on measuring diffusivities of colloidal particles by using photon correlation spectroscopy (PCS). Knowing the size of the probe, the Stokes–Einstein relation is employed to calculate the medium viscosity. This is an ideally suitable technique for determining fluid viscosities under non-ambient conditions. KB theory[3] 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 KB theory to account for polymer–gas solvent system. The modified theory explains our experimental data very well and also predicts the observed upturn of viscosity reduction at high pressures.

EXPERIMENTAL

In general terms most light scattering experiments contain the same components. *Figure 1* shows the

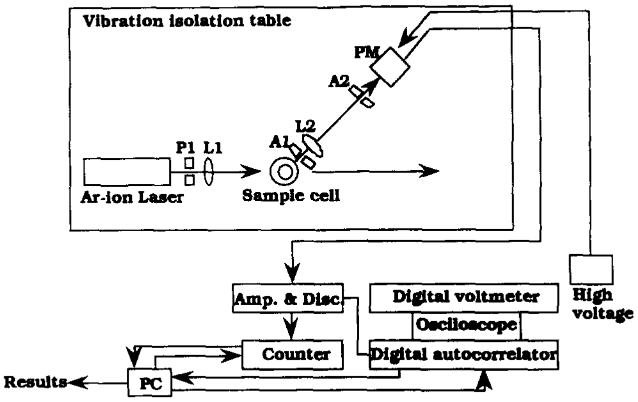

Figure 1 Schematic of light scattering spectrometer

schematic of light scattering spectrometer used in this study.

PEG were obtained from the Aldrich Chemical Company and have average molecular weights of 200, 400 and 600. CO_2 as a solvent in this work was supplied by Cryogenic Gases, Inc. and was used as received.

The sample cell, machined out of stainless steel, is fitted with flanged, 1.25 cm thick quartz windows and tested up to 20 MPa. The optical path-length of the cell is 7 cm. An anodized tube is inserted into the cell to absorb the reflected light. The sample cell is wrapped in a thermofoil heater and is insulated by Insul-Sheet Flat Sheets which are specially compounded flexible, elastomeric, thermal insulation. The temperature of sample cell is stabilized to $\pm 0.005°C$. The sample temperature is measured by a thermistor embedded in the cell block and the pressure is monitored by a Kistler 4045A pressure transducer.

CO_2 is introduced gravimetrically from high-pressure sample cylinders equipped with quick-connect type fittings. The sample cell is first charged with PEG which is filtered through 0.22 μm filter for removal of dust type impurities from sample materials. Then CO_2 is introduced into the cell from a sample cylinder until the desired loading level is achieved and the cell is closed off. In order to remove dust from CO_2 we used an inline filter which removes contamination as small as 0.5 μm. CO_2 in the loading line is determined from the difference in the weight of the sample cylinder before and after loading.

FREE VOLUME THEORIES RELEVANT TO THE VISCOSITY OF POLYMERIC LIQUIDS

A number of theories have been developed which make use of the concept of 'free volume' to describe the properties of polymeric solutions. Some of the existing free volume models are reviewed in this section.

A. Definitions of free volume

The definitions of the several different concepts of free volume are given by many researchers[4-6]. We summarize them below.

(1) Empty volume

$$V_E = V_T - V_W \tag{1}$$

where V_T is the observed volume ($cm^3\,mol^{-1}$) at temperature T, and V_W is the volume per mole of the substance as calculated from van der Waals dimensions obtained by X-ray diffraction methods or from gas kinetic collision cross-sections. Thus, according to this definition the argon atom would be regarded as a sphere, and V_E is the total volume outside the van der Waals radius of the spheres.

(2) Expansion volume

$$V_F = V_T - V_o \tag{2}$$

where V_o is the volume occupied by the molecules at 0 K in a close-packed crystalline state. V_F and V_T are the free volume and total volume, respectively. Thus, expansion volume is extra free space generated by thermal motion.

(3) Fluctuation volume

$$V_f = N_A V_Q \tag{3}$$

where V_Q is the volume swept out by the centre of gravity of a molecule as the result of its thermal motion, and N_A is the Avogadro number.

We use the concept of expansion volume since the KB free volume theory for the viscosity of polymeric liquids, which we have modified, is based on Doolittle's free volume equation. Doolittle adhered to established concepts concerning the occupied volumes of liquids and based his definitions of free volume on the expansion volume.

B. Doolittle's free volume equation

Doolittle set out to propose a suitable form for the relation between viscosity and free volume[7]. As we mentioned in the previous section, his definitions of free volume fraction is based on the expansion volume

$$\frac{V_T - V_o}{V_o} = \frac{V_F}{V_o} \tag{4}$$

He proposed the relation;

$$\eta = A\exp\left(B\frac{V_F}{V_o}\right) \tag{5}$$

where A and B depend on the nature of the liquid.

Cohen and Turnbull proceeded to show the theoretical basis for Doolittle's free volume equation[8]. Their derivation is based on the concept that statistical redistribution of the free volume opens up voids large enough for diffusive displacement. The contribution of a molecule to diffusion $D(V)$ is given by

$$D(V) = ga(V)u \tag{6}$$

where g is a geometric factor, u the molecular velocity, and $a(V)$ is roughly the diameter of the cage. They proposed that $D(V)$ will be zero unless V exceeds a critical V^* just large enough to permit another molecule to jump in. Therefore, V^* provides the lower limit in defining a volume average diffusion coefficient.

$$D = \int_{V^*}^{\infty} D(V)p(V)\,dV \tag{7}$$

where $p(V)$ is the probability of finding a free volume between V and $V + dV$. Maximizing the number of ways of distributing free volume leads to the equation $p(V^*) = \exp(-\gamma V^*/VF)$. $p(V)$ is the probability of finding a hole of volume exceeding V^*, γ is a numerical factor introduced to correct for overlap of free volume and V^* is shown to be near to the molecular volume. Finally, the equation for diffusion coefficient becomes

$$D = ga^* u \exp\left(-\frac{\gamma V^*}{V_F}\right) \tag{8}$$

This is close to the equation of Doolittle with the exception that the coefficient of the exponential term contains u which changes with $T^{1/2}$. It must be noted that V^* and V_o are values of some minimum volume. If we substitute $V^* = V_o$ in equation (8) and simply let γ equal to unity, this definition of free volume becomes the same as that of Doolittle.

C. Williams–Landel–Ferry (WLF) model[9]

WLF define 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:

$$\log a_T = \frac{-C_1(T - T_s)}{C_2 + T - T_s} \tag{9}$$

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 a relation

$$\log a_T = \frac{-17.44(T - T_g)}{51.6 + T - T_g} \tag{10}$$

They claim equation (9) generally represents the temperature dependence of viscosity in the range $T_g < T < T_g + 100°\mathrm{C}$.

The derivation provided by WLF is based on an analogy to Doolittle's equation. They start with Doolittle's equation

$$\ln \eta = \ln A + B\frac{V_o}{V_F} \tag{11}$$

where A and B depend on the nature of the liquid, and V_o and V_F are the occupied and free volume ($\mathrm{cm^3\,g^{-1}}$), respectively. Then, they use Fox and Flory's free volume concept[10,11]. When the glass transition is approached the relative free volume diminishes sharply. This is believed to be primarily responsible for the accompanying large viscosity increase. The existence of a universal function such as equations (9) and (10) implies that the nature of this volume changes and its effect on the rates of molecular rearrangements are essentially the same for all supercooled systems, polymeric, non-polymeric and their mixtures, independent of molecular structure.

For supercooled systems, equation (11) can be modified by noting that V_F is small and V_o is practically equal to the specific volume ($V_o + V_F$), so V_F/V_o can be replaced by the fractional free volume, $V_F/(V_o + V_F) = f$. The constant B is 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,

$$\log a_T = \frac{1}{2.303}\left(\frac{1}{f} - \frac{1}{f_g}\right) \tag{12}$$

where f_g is the fractional free volume at T_g.

The dependence of fractional free volume on temperature is taken to be thermal expansion coefficient α, i.e. $f = f_g + \alpha(T - T_g)$. Substitution of this relation into equation (12) yields

$$\log a_T = -\frac{1}{2.303}\left(\frac{T - T_g}{\frac{f_g}{\alpha} + T - T_g}\right) \tag{13}$$

This equation is identical in form to equation (9), and with the constants $\alpha = 4.8 \times 10^{-4}\,\mathrm{deg}^{-1}$, and $f_g = 0.025$. Consequently, WLF's fractional free volume can be written as

$$f = 0.025 + 4.8 \times 10^{-4}(T - T_g) \tag{14}$$

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

D. Kelley–Bueche model

This section introduces Kelley–Bueche'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_o by

$$\eta = KM^{3.5}C_p^4 f_o, \quad M > M_{cr} \tag{15}$$

and

$$\eta = K'MC_p f_o, \quad M < M_{cr} \tag{16}$$

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_o with concentration is an additional complicating factor since it is to be expected that added diluent will cause f_o to decrease.

A convenient way of picturing the effect of 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 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

$$f_o = A' \exp\left(\frac{v^*}{V_F}\right) = A' \exp\left(\frac{1}{f}\right) \tag{17}$$

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

$$\begin{aligned} f &= \phi_p f_p + \phi_s f_s \\ &= \phi_p(0.025 + 4.8 \times 10^{-4}(T - T_g)) \\ &\quad + (1 - \phi_p)(0.025 + \alpha_s(T - T_g')) \end{aligned} \tag{18}$$

where α_s and T_g' are the thermal expansion coefficient and glass transition temperature of the solvent, respectively. Then, by combining equations (15–18),

$$\eta = BC_p^4 \exp\left(\frac{1}{\phi_p f_p + (1 - \phi_p) f_s}\right) \tag{19}$$

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 use Cohen–Turnbull's equation for segmental friction factor. They employ WLF's fractional free volume to predict f of the solution by a simple mixing rule. They combine these two concepts with Bueche's viscosity model of a polymer solution (which includes the concentration of a polymer) to obtain equation (19).

E. Modification of Kelley–Bueche equation for gas solvent[2]

Our modification of KB equation is based on the compressibility effect on the free volume of polymeric liquids. We start our derivation from KB equation [equation (19)].

$$\eta = BC_p^4 \exp\left(\frac{1}{f}\right), \quad M > M_{cr} \qquad (19)$$

where

$$f = \phi_p f_p + \phi_s f_s$$

The polymer concentration, C_p, is related to f_p,

$$C_p = \rho_p \phi_p \qquad (20)$$

Combining equations (19) and (20) yields

$$\eta = B\rho_p^4 \phi_p^4 \exp\left(\frac{1}{\phi_p f_p + (1 - \phi_p) f_s}\right) \qquad (21)$$

For pure polymer, $\phi_p = 1$,

$$\eta_p = B\rho_p^4 \exp\left(\frac{1}{f_p}\right) \qquad (22)$$

Then, taking the ratio, η/η_p, gives

$$\frac{\eta}{\eta_p} = \phi_p^4 \exp\left(\frac{1}{\phi_p f_p + (1 - \phi_p) f_s} - \frac{1}{f_p}\right) \qquad (23)$$

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. In order 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 $V_F \ll V_o$ does not hold. Instead,

$$f_s = f_{CO_2} = \frac{V_F}{V_o + V_F} = \frac{V - V_o}{V} \qquad (24)$$

where V is total volume of CO_2. With this definition, we can calculate f_s from experimental data of V_o 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:

$$\eta = \eta_p \phi_p^4 \exp\left(\frac{1}{B_p \phi_p f_p + A_s (1 - \phi_p) f_s} - \frac{1}{f_p}\right) \qquad (25)$$

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

DATA ANALYSIS

When colloidal-sized particles are suspended in a binary mixture, there are two possible sources of optical fluctuations which contribute to the scattered intensity. One source is concentration fluctuations in the binary mixture, and the second contribution comes from the number fluctuations of the colloidal particles due to their Brownian motion. Both the concentration and the number fluctuations are exponentially decaying functions in time. The decay rate of the concentration fluctuation is proportional to D_{AB}, the binary mutual diffusion coefficient, while that of the number fluctuations is proportional to D_p a particle diffusion coefficient which is related to the viscosity of the suspending medium by Stokes–Einstein relation[12]:

$$D_p = \frac{k_b T}{6\pi\eta r_h} \qquad (26)$$

where r_h is the hydrodynamic size of the particle.

In PCS, the time dependence of the fluctuations is quantitatively determined from the measurements of the time autocorrelation function of the scattered light. Under the appropriate conditions, the correlation function of the scattered electric field is a superposition of the two exponentials and has the following form:

$$g^{(1)}(q, t) = C_1 \exp(-D_{AB} q^2 t) + C_2 \exp(-D_p q^2 t) \qquad (27)$$

where $q = (4\pi n/\lambda)\sin(\theta/2)$, n is the refractive index, λ is the wavelength of the incident light under vacuum, and θ is the scattering angle. C_1 is affected by the variation of the refractive index with the concentration of the binary mixture and the magnitude of the concentration fluctuations. C_2 is related to the number of colloidal particles and their scattering power. Thus, a simultaneous determination of D_{AB} and D_p becomes possible from analysis of correlation function profiles.

The binary diffusion coefficient for CO_2 in PEG can be estimated from solubility of CO_2 in PEG. The D_{AB} value in the temperature and pressure range of our experiments was estimated to be about $1.5 \times 10^{-4}\,cm^2\,s^{-1}$. The value of D_p for $0.1\,\mu m$ diameter latex sphere in PEG/CO_2 solution at 30°C and 1 MPa is $6.3 \times 10^{-10}\,cm^2\,s^{-1}$. Essentially, the binary diffusion coefficient is orders of magnitude faster than the particle diffusivity and the characteristic times of the two exponential decays in equation (27) are vastly different. Therefore, in our measurements of D_p, contribution of the fast exponential decay is not observed. We have checked the concentration fluctuations of PEG/CO_2 solutions without particles, but the signal does not show any autocorrelation function in the time scale of D_p measurements. Therefore, we consider only the particle diffusion term in equation (27) in our data analysis.

The refractive index of medium was corrected and used to calculate the normalized experimental diffusivity ($D_{exp,nor}$) by

$$D_{exp,nor} = D_{exp}\left(\frac{n_p}{n}\right)^2 \qquad (28)$$

where n_p and n are the refractive index of the polymer and the refractive index of the polymer solution, respectively.

RESULTS AND DISCUSSION

The reliability of the viscosities obtained from the measured diffusion coefficients of colloidal-sized latex spheres depends on the assumption that the particles have known and uniform sizes[13]. We have checked for any variations in the sizes of latex spheres with pressure

Table 1 Model parameters of CO_2, A_s

	M.W. of PEG			
T (°C)	200	400	600	Avg
30	0.092	0.099	0.102	0.097 (±6%)
40	0.099	0.107	0.110	0.105 (±5%)
50	0.106	0.117	0.119	0.114 (±7%)
60	0.112	0.129	0.144	0.128 (±13%)
Avg	0.102 (±11%)	0.113 (±13%)	0.119 (±14%)	0.111 (±29%)

Table 2 Model parameters of PEG, B_p

	M.W. of PEG			
T (°C)	200	400	600	Avg
30	0.998	0.998	0.999	0.998
40	0.999	1.002	1.002	1.001
50	0.998	1.000	1.001	1.000
60	0.998	1.001	0.998	0.999
Avg	0.998	1.000	1.000	0.999 (±0.3%)

and temperature to confirm the validity of our latex spheres as uniform-sized particles. Our test measurements showed that the measured sizes were consistent with both pressure and temperature.

The molecular weights of PEG samples used in this study are less than M_{cr} (M_{cr}, PEG = 3400)[1], so we use the modified KB equation for the case $M < M_{cr}$, i.e. equation (25). The application of equation (25) to the results on PEG/CO_2 solutions requires the knowledge of the fractional free volumes f_p and f_s of polymer and solvent at each temperature and pressure. For PEG we use WLF's fractional free volume given by equation (14). 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 equation (24). We need to know V_o and V for CO_2 to use equation (24). The value of V_o is $0.8798\,cm^3\,g^{-1}$ (ref. 14) and for the specific volume, V, we use the density data of CO_2 (ρ_{CO_2}) from ref. 15. For convenience, we fitted ρ_{CO_2} at each temperature as a function of pressure to polynomial equations. These equations are valid in the range of pressure up to 8 MPa. Since $V = 1/\rho_{CO_2}$, equation (24) becomes

$$f_s = \frac{V - V_o}{V} = 1 - V_o\rho_{CO_2} \qquad (24')$$

The polymer volume fractions are also available as a function of pressure from equations (29a)–(29d) (see ref. 2):

$$\phi_p = 1.0068 - 0.0675P, \quad \text{at } T = 30°\text{C} \qquad (29a)$$

$$\phi_p = 1.0126 - 0.0525P, \quad \text{at } T = 40°\text{C} \qquad (29b)$$

$$\phi_p = 1.0072 - 0.0378P, \quad \text{at } T = 50°\text{C} \qquad (29c)$$

$$\phi_p = 1.0023 - 0.0228P, \quad \text{at } T = 60°\text{C} \qquad (29d)$$

The calculation of fractional free volume of the solution is based on a simple mixing rule with the contribution of each component weighted by its volume fraction [equation (18)]. We do not expect the contribution of PEG and CO_2 to be additive in such a simple way. Therefore, we introduced the model parameters, A_s and B_p, which correct the free volume contributions of solvent and polymer, respectively.

Viscosity data exist as a function of pressure along isotherms (T = 30, 40, 50 and 60°C) for three PEG samples (M.W. = 200, 400 and 600). Each data set (viscosity as a function of P along an isotherm) was fitted to equation (25) using a Levenberg–Marquardt algorithm to obtain values of two arbitrary constants A_s and B_p. Values of A_s and B_p obtained from these fits are listed in *Tables 1* and *2*.

As shown in *Table 2*, 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. On the other hand, A_s is a weak function of both temperature and molecular weight. A_s appears to increase slightly with temperature and molecular weight. If an average value of $A_s = 0.111$ is considered, it implies that f_s in the mixture is about an order of magnitude less than f_s of pure CO_2.

The experimental data are compared to the theoretical viscosity vs ϕ_p curves in *Figures 2–4*. For all polymers at different temperatures, the modified KB theory predicts

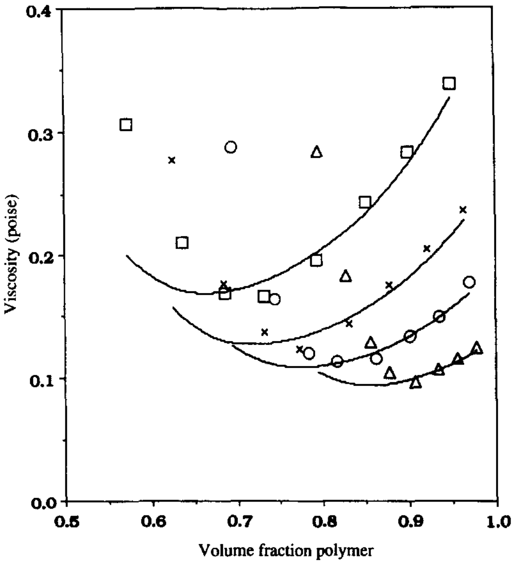

Figure 2 Viscosity *versus* volume fraction polymer for PEG, M.W. = 200 at various temperatures. Squares are at 30°C and crosses are at 40°C. Circles are at 50°C and triangles are at 60°C. (——) are predictions of the modified KB theory

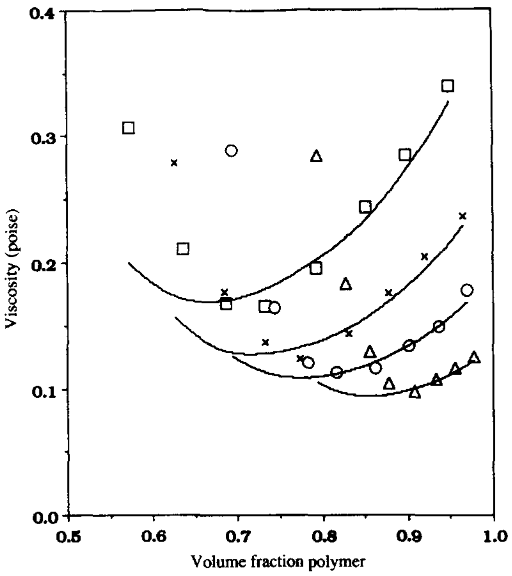

Figure 3 Viscosity *versus* volume fraction polymer for PEG, M.W. = 400 at various temperatures. Squares are at 30°C and crosses are at 40°C. Circles are at 50°C and triangles are at 60°C. (——) are predictions of the modified KB theory

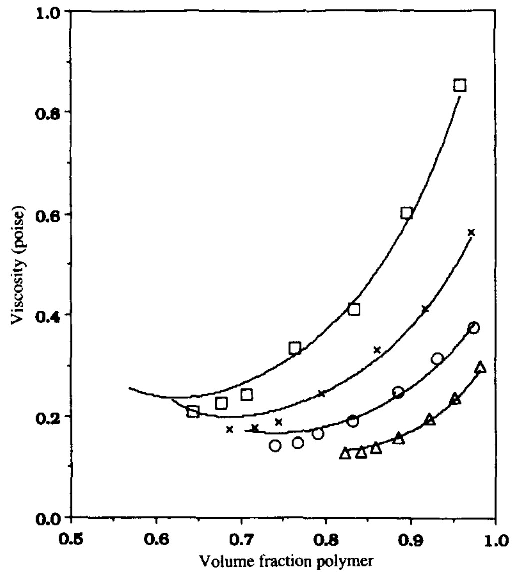

Figure 4 Viscosity *versus* volume fraction polymer for PEG, M.W. = 600 at various temperatures. Squares are at 30°C and crosses are at 40°C. Circles are at 50°C and triangles are at 60°C. (——) are predictions of the modified KB theory

the experimental data closely in the high range of ϕ_p, while for the low range of ϕ_p there is a notable discrepancy between the theoretical curves and the experimental data.

For PEG having a molecular weight of 600, all experimental data fit very well with the theory and do not show any indication of deviation. This is because ϕ_p did not reach the viscosity reversal region. The molecular weight dependence is not as significant as the temperature dependence. This is again because the range of molecular weight of PEG is narrow in our case.

A remarkable observation is noticed in this study. The modified KB theory predicts the upturn of viscosity. This is obvious if we examine equations (24) and (25). In equation (25), f_p is constant at each temperature and f_s is

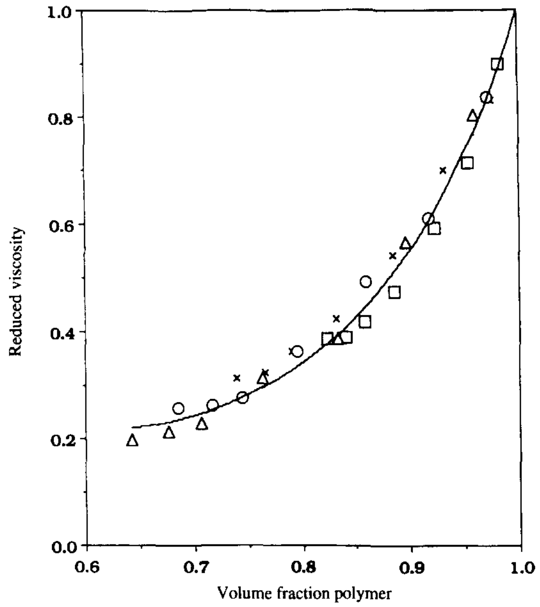

Figure 5 Master curve for PEG (M.W. = 600)/CO_2. Squares are at 30°C and crosses are at 40°C. Circles are at 50°C and triangles are at 60°C. (——) are predictions of the modified KB theory

the only factor which varies with pressure. In the exponential part of equation (25), the first term is less than the second term until the pressure increases f_s to be f_p/A_s (assuming $B_p = 1$). After that point, the exponential term is greater than unity. In fact, since f_s and f_P are available as a function of pressure, it is possible to calculate numerically the pressure where viscosity reaches its minimum value along an isotherm. Physically we can identify two competing effects which govern the viscosity behaviour: at low pressure, the plasticization effect of dissolved CO_2 reduces viscosity. At high pressure, the free volume is reduced due to pressure and the viscosity starts increasing. *Figure 5* is the master curve generated by plotting η/η_p vs ϕ_p for molecular weight 600. The whole range of data is well described by the theoretical expression. Clearly, all temperatures conveniently collapse to form a master curve.

We discuss briefly the effect of particles on the viscosity of our sample materials. In general, this effect is called the rigid filler effect. In our case, we assume the PEG/CO_2 solutions are in the Newtonian region since the rate of shear is nearly zero. From this assumption, we employ Einstein's equation of the effect of fillers on the viscosity of a Newtonian fluid[16,17]. His equation is

$$\eta = \eta_1(1 + k_E\phi_2) \tag{30}$$

where η and η_1 are the viscosities of the solution and that of suspending solution, respectively, and ϕ_2 and k_E are the volume fraction of filler (particles) and the Einstein coefficient, respectively. For particles of spherical shape, which is our case, k_E is 2.5. Therefore, for $\phi_2 = 7 \times 10^{-7}$ in our systems, $\eta \approx \eta_1$. Consequently, we can neglect this effect.

Finally, we must mention multiple scattering since the detection of any light which has been scattered more than once in the sample can cause distortion of the time dependence of the measured correlation functions. For small particles, the intensity of multiple scattering relative to that of single scattering is proportional to $\langle C \rangle a^6$ (C is particle number density and a is particle radius). Brown *et al.*[18] reported multiple scattering was small for $\langle C \rangle \approx 1.7 \times 10^9\,\mathrm{cm}^{-3}$ and $a \approx 500\,\mathrm{Å}$, our value $\langle C \rangle a^6$ is much smaller than that of Brown's. Therefore, multiple scattering in this study is also negligible.

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 temperatures. Dynamic light scattering technique from probe particles was able to successfully measure the viscosities of PEG/CO_2 solutions as a function of concentration, temperature and pressure.

Free volume concept was 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 constants, A_s and B_p, were introduced to correct a simple mixing rule for free volume contributions of solvent and polymer. When values of A_s and B_p, obtained from fitting the modified KB theory to data, were compared, the following observations were made: 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 ϕ_p yields the correct fractional free volume contribution of the polymer in the mixture. A_s is a weak increasing function of both temperature and molecular weight.

The mixture viscosity as a function of ϕ_p or pressure along an isotherm is governed by two competing effects. At low pressure, the plasticization effect of dissolved CO_2 reduces the viscosity. At high pressure, the free volume is reduced due to pressure and the viscosity starts increasing.

REFERENCES

1 van Krevelen, D. W. 'Properties of Polymers', 3rd Edn, Elsevier, NY, 1990
2 Bae, Y. C., Ph.D. dissertation, Wayne State Univ., Detroit, 1989
3 Kelley, F. N. and Bueche, F. *J. Polym. Sci.* 1961, **50**, 549
4 Bondi, A. *J. Phys. Chem.* 1954, **58**, 929
5 Haward, R. N. *J. Macromol. Sci.-Rev. Macromol. Chem.* 1970, **C4**, 191
6 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci.: Part B: Polym. Phys. Edn* 1977, **15**, 403
7 Doolittle, A. K. *J. Appl. Phys.* 1951, **22**, 1471
8 Cohen, M. H. and Turnbull, D. *J. Chem. Phys.* 1959, **31**, 1164
9 Williams, M. L., Landel, R. F. and Ferry, J. D. *J. Am. Chem. Soc.* 1955, **77**, 3701
10 Fox, T. G. and Flory, P. J. *J. Phys. Chem.* 1948, **70**, 2384
11 Fox, T. G. and Flory, P. J. *J. Phys. Chem.* 1950, **21**, 581
12 Mountains, R. D. and Deutch, J. M. *J. Chem. Phys.* 1969, **50**, 1103
13 Saad, H., Bae, Y. C. and Gulari, Es. *Langmuir* 1988, **4**, 63
14 Kumar, S. K., Suter, U. W. and Reid, R. C. *Ind. Eng. Chem. Res.* 1987, **26**, 2532
15 Vukalovich, M. P. and Altunin, V. V. 'Thermophysical Properties of Carbon Dioxide', Collet's, London, 1968
16 Einstein, A. *Ann. Physik* 1906, **19**, 289
17 Einstein, A. *Ann. Physik* 1911, **34**, 289
18 Brown, J. C., Pusey, P. N. and Ottewill, R. H. *J. Phys. A: Math. Gen.* 1975, **8**, 664