A Predictive Approach Based on the Simha–Somcynsky Free-Volume Theory for the Effect of Dissolved Gas on Viscosity and Glass Transition Temperature of Polymeric Mixtures

ERNESTO DI MAIO,[1] SALVATORE IANNACE,[2] GIUSEPPE MENSITIERI,[1] LUIGI NICOLAIS[1]

[1]Department of Materials and Production Engineering, Faculty of Engineering, University of Naples Federico II, P.le Tecchio 80, I-80125 Naples, Italy

[2]Institute of Composite and Biomedical Materials, National Research Council of Italy, P.le E. Fermi 1, I-80055 Portici (Na), Italy

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ABSTRACT: The gas concentration and pressure effects on the shear viscosity of molten polymers were modeled by using a unified approach based on a free volume theory. A concentration and pressure dependent "shift factor," which accounts for free volume changes associated with polymer-gas mixing and with variation of absolute pressure as well as for dilution effects, has been herein used to scale the pure polymer viscosity, as evaluated at the same temperature and atmospheric pressure. The expression of the free volume of the polymer/gas mixture was obtained by using the Simha and Somcynsky equation of state for multicomponent fluids. Experimental shear viscosity data, obtained for poly(ε-caprolactone) with nitrogen and carbon dioxide were successfully predicted by using this approach. Good agreement with predictions was also found in the case of viscosity data reported in the literature for polystyrene and poly(dimethylsiloxane) with carbon dioxide. Free volume arguments have also been used to predict the T_g depression for polystyrene/carbon dioxide and for poly(methyl methacrylate)/carbon dioxide mixtures, based on calculations performed, again, with the Simha and Somcynsky theory. ©2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 1863–1873, 2006
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INTRODUCTION

The measurement, modeling, and prediction of the rheological properties of polymers plasticized with gaseous or volatile compounds is crucial in the optimization and design of several industrial processes including gas-assisted injection molding, extrusion, foaming, blending, and synthesis. In recent years, rheological data of plasticized polymers became available to the scientific community from a number of research groups. Han and coworkers[1–3] first performed rheological experiments by using an extrusion slit die rheometer on low-density polyethylene (LDPE), high-density PE (HDPE), and polystyrene (PS) with several fluorocarbons and chemical blowing agents. Several important experimental issues arose in these types of measurement, in particular, the need for a homogeneous fluid in the rheometer. This has to be obtained by promoting complete dissolution of the plasticizer before the molten matter enters the capillary/slit die and by avoiding premature phase separation as the mixture approaches the die exit.

Correspondence to: E. Di Maio (E-mail: edimaio@unina.it)
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Elkovitch et al.[4] and Lee et al.[5] measured the melt viscosities of polymethylmethacrylate (PMMA)/CO_2 and PS/CO_2 solutions, respectively, with a foaming extruder equipped with a capillary rheometer. Areerat et al.[6] used similar equipment to investigate the effects of CO_2 on LDPE. The main advantages of this technique are the versatility (in fact it can be applied to the neat polymer as well as to polymer solutions with a dissolved gaseous component and volatile compound, in a very wide range of flow rates, pressures, and pressure drops) and the continuity, while disadvantages reside in the pressure-driven nature of the flow, which involves the use of several approximations for the quantitative analysis (see, for instance refs. 7 and 8). Gerhardt et al.[9] and Kwag et al.[10] measured the melt viscosity of polydimethylsiloxane (PDMS) and PS plasticized with CO_2 by using a high pressure capillary rheometer (plunger type capillary rheometer) with back pressure control to maintain the pressure above the critical pressure for bubble nucleation at the die exit. More recently, Royer et al.[11] developed a rheometer based on a magnetically levitated sphere, which allowed viscosity measurements at low shear rates of PDMS plasticized with CO_2 at constant pressure. This technique allowed the decoupling of the effects of plasticizer concentration and pressure.

Initial attempts to model the viscosity reduction of a polymer due to a dissolved gas or a volatile compound were based on diluent effect and enhancement of chain mobility, related, as proposed by Doolittle and Doolittle,[12] to a free volume increase. Great efforts have been devoted to rationalize numerous physical, chemical, and transport properties of liquid and amorphous solid phases by using free volume calculations. The role of free volume concept in several physical phenomena has been extensively reviewed in numerous publications, which highlight free volume evaluation and its applications in the field of viscosity of pure polymers (*e.g.*, Doolittle[13,14] and Williams et al.[15]), in the field of mass transport (*e.g.*, Cohen and Turnbull[16] and Duda et al.[17]), of glass transition temperature (*e.g.*, Chow[18] and Williams et al.[15]), and in the study of the equilibrium and nonequilibrium volumetric and thermal properties of pure polymer and polymeric mixtures (*e.g.*, Simha and Carri,[19] Utracki[20] and Curro and Lagasse[21]).

In the present context, it is of interest to analyze the various approaches adopted by different investigators to evaluate the viscosity reduction of plasticized polymers by using the free volume concept. Gerhardt et al.[22] presented an approach that utilizes a lattice fluid equation of state to predict the equilibrium free volume of a plasticized melt coupling it with a modified Kelley and Bueche[23] equation that relates free volume and viscosity. Their model, which is not based on a rigorously defined free volume, does not account for the effect of pressure and has to be optimized for each equation of state used. Lee et al.[5] fitted experimental data with an eight-parameter model, which cannot be considered predictive. Royer et al.[24] predicted the viscoelastic scaling of plasticized polymers by combining a theoretical prediction for the glass transition temperature depression of a polymer by a diluent, with a traditional equilibrium free-volume model for viscoelastic scaling. This model can be considered predictive, once several material's properties, which may not readily available, are known. Another relevant effect related to gas dissolution in a polymer phase is the associated depression of the glass transition temperature. A depression as large as 70 °C has been reported, for example, on PMMA and PS plasticized with CO_2.[25–28] Thermodynamic analyses of the glass transition generally make use of order parameters. Single order parameter models have proved to accurately describe most of the experimental observations of the thermodynamic behavior of glass forming materials.[29] Quach and Simha[30] and Wissinger and Paulaitis,[25] among others, identified the order parameter with the free volume and characterized the glassy state by "freezing in" the fraction of the vacant site in the adopted lattice models. However, Quach and Simha only analyzed the effect of pressure and not of gas concentration, while Wissinger and Paulaitis correlated the calculated hole fraction at glass transition and the experimental glass transition, without obtaining a completely predictive model.

The present article shows how the shear viscosity and the glass transition temperature of polymer/gas mixtures can be predicted by using a simple free-volume model. The Simha and Somcynsky equation of state (SS-EOS) is used to describe and predict both the volumetric properties and free volume of the polymer/diluent mixtures assuming a quasi-equilibrium state. In particular, the equilibrium free volume fraction has been simply assumed to correspond to the vacant site fraction or hole fraction, h,[31,32] defined in the context of the SS-EOS theory: this assumption is supported by several papers,[20,33,34] which made use of SS-EOS to relate the conventional free volume to h as well as by several pieces of experimental

evidence, including those obtained in the present investigation.

EXPERIMENTAL

Poly(ε-caprolactone) (PCL) was supplied by Solvay Interox Ltd. (PCL CAPA® 6800). Commercial purity grade CO_2 and N_2 were used as plasticizers. For the in-line measurement of viscosity, the extrusion line utilized for foaming[35] (Haake CTW100 - Rheocord 9000) was equipped with a heat exchanger, a capillary, and a downstream valve. The functions of these devices are, respectively, to enhance the solubilization of the foaming agent, to measure the pressure drop and to maintain the polymer/gas solution at sufficiently high pressure. A mass flow controller (Brooks Instr. 5850S) was used to meter the physical foaming agents into the barrel, while venting screws, designed to induce the formation of the so-called dynamic seals, were used to avoid loss of the foaming agent from the hopper. Pressures were evaluated by pressure transducers from GEFRAN (mod. WD2-5-H-B35D). The pressure sensors were located on 20 mm diameter channels mounted upstream and downstream of the capillaries. They are not positioned directly against the side of the channels but connected to the channels via "pressure holes."[36] Capillaries with a radius of 1 mm and different lengths (10, 20, and 30 mm) were used. This allowed the construction of the Bagley plot and to subtract the entry and exit losses, ΔP^{e}, from the measured pressure drop, ΔP^{tot} to obtain the pressure drop along the capillary, $\Delta P^{cap} = \Delta P^{tot} - \Delta P^{e}$. This procedure was performed on the pure polymer only. To evaluate the ΔP^{cap} in the case of polymeric mixtures, a scaling was applied based on the results obtained by using Bagley corrections for pure polymer. In fact, for mixtures, only measurements with the 30 mm capillary were performed and ΔP^{cap} was evaluated through the following expression:

$$\Delta P_{m}^{cap}(T,\dot{\gamma}) = \Delta P_{m}^{tot}(T,\dot{\gamma})\frac{\Delta P_{p}^{cap}(T,\dot{\gamma})}{\Delta P_{p}^{tot}(T,\dot{\gamma})} \qquad (1)$$

where subscripts m and p stand, respectively, for the mixture and for the pure polymer. The Rabinowitsch correction was used to account for deviation in non-Newtonian behavior of the melt. Viscosity measurements were also performed (only in the case of the pure polymer) with a capillary rheometer (Rheograph 2002 Goettfert) to validate the experimental in-line procedure, using capillary dies of 1 mm radius and three different lengths (10, 20, and 30 mm).

In analyzing the experimental raw data for evaluating the viscosity, the effects of pressure nonuniformity in the capillary, of normal stress differences (on the evaluation of pressure), of the possible slip at wall, of dissipative heating, and of compressibility of the fluids were ignored.[7] In particular, it is worth of note that, to determine the quantitative values of viscosity from capillary flow experiments, we assumed that viscosity was not affected by pressure change along the capillary in each experimental test. In fact, in the experimental range of temperature, pressure, and shear rate, the Bagley plots were rather linear and, hence, did not supply the necessary experimental information to account for pressure effect in the evaluation of viscosity by using the rather complex procedures for data treatment available in the relevant literature (see Laun[37] and Penwell and Porter[38]).

Theoretical Background

A common feature of the experimental data on the viscosity of molten polymers plasticized with gaseous or volatile compounds is that the observed concentration-dependent viscosity curves of these systems are similar in shape. Hence, classical viscoelastic scaling methods (*e.g.*, WLF theory) have been used by several authors.[1–6] This scaling has been performed by defining a concentration dependent viscosity reduction factor, a_c, as the ratio of the viscosity of the molten polymer/plasticizer mixture and of the neat molten polymer. On the basis of the experimental observations, it was established that a_c was very weakly dependent upon shear rate and temperature and, consequently, that the following simple relation can be used[2,3]:

$$\eta(\dot{\gamma},c,T) = a_c\eta^0(\dot{\gamma},T), \qquad (2)$$

where $\eta(\dot{\gamma},c,T)$ is the viscosity of the polymer/plasticizer solution at shear rate $\dot{\gamma}$, temperature T, and polymer concentration c, $\eta^0(\dot{\gamma},T)$ is the viscosity of the pure polymer at the same temperature and shear rate and a_c is the concentration-dependent shift factor. It is worth noting that the effects of pressure were not explicitly taken into account by these authors, since the experiments at different c were performed at similar pressures, which were assumed to be the average pressure in the capillary/slit die.

Several attempts have been made to model those experimental observations to predict the viscosity of molten polymer/plasticizer solutions (namely, the value of a_c), dating back to the early works of Kelly and Bueche[23] and Berry and Fox,[39] which related the effect of the diluent to the relative increase in free volume. More recently, Richards and Prud'homme[40] described the concentration dependence of the Newtonian viscosity of the solution in the limit of zero shear rate, η_0, by the following relationship, valid for high molecular weight polymers:

$$\eta_0 = Kc^n \bar{M}_w^{3.4} \zeta(c, T) \tag{3}$$

where K is a constant for a given polymer, n is the concentration exponent, $\bar{M}_w$ is the weight average molecular weight of the polymer and ζ is the segmental friction fraction. For ζ, the Doolittle experimental expression, based on free volume, has been proposed[12]:

$$\zeta = \zeta_0 \ \exp(\lambda/f) \tag{4}$$

in which, ζ_0 and λ are constants and f is the fractional free volume, defined as the ratio of the free volume to the occupied volume.

The shifting parameter, $a_{c,0}$, for scaling the viscosity of the pure polymer to that of the polymer/diluent mixtures, both in the limit of zero shear rate, can be obtained from eqs 2–4 once the concentration exponent, n, and the free volume fraction, f, are known:

$$a_{c,0} = \frac{\eta_0(c, T)}{\eta_0^0(T)} = c^n \ \exp\left(\frac{1}{f_m} - \frac{1}{f_p}\right) \tag{5}$$

where f_p and f_m are the fractional free volumes of the pure polymer and of the polymer/plasticizer mixture, respectively.

A further development of this approach was described by Gerhardt el al.[9] and Kwag et al.,[10,41] which used the following expression for a_c, for the case of a generic $\dot{\gamma}$ value:

$$a_c = \frac{\eta(c, \dot{\gamma}, T)}{\eta^0(\dot{\gamma}/a_c, T)} = (1 - \omega_c)^n \left(\frac{V_p}{V_m}\right)^n \exp\left(\frac{1}{f_m} - \frac{1}{f_p}\right) \tag{6}$$

where ω_c is the weight fraction of the plasticizer and V_p and V_m are the specific volumes of the pure polymer and of the polymer/plasticizer mixture, respectively. It is worth noting that they used the same shift factor also to scale the shear rate, to account for the wider range of Newtonian behavior of the polymeric solution as compared to the pure polymer.

To model and to predict the viscosity of polymer/plasticizer solutions by this scaling approach, one needs to evaluate:

i. ω_c: the processing variable that is often imposed by the experimental conditions. In fact, it is determined by solubility of the plasticizer in batch experiments or by the polymer/gas mass flux ratio in continuous (in-line extrusion) experiments.
ii. n: from experimental, theoretical, and semi empirical analyses,[39,40,42] it was observed that the exponent of the concentration term ranges from 3 to 4 in several polymer/diluent systems.
iii. V_p: experimental *PVT* data are available on a wide number of polymers and can be interpolated using proper EOS (*e.g.*, Tait,[43] Sanchez and Lacombe (SL),[44] and SS -EOS)[31]
iv. V_m: *PVT* data on polymeric solutions, mainly for polymer/gas mixtures, are not widely available, hence the specific volume of the mixture has to be evaluated using thermodynamic models. Statistical thermodynamic EOS of multicomponent fluid, such as the SL[45] and the SS[32] allow the evaluation of V_m by knowing some characteristic parameters of the pure components and by adopting proper mixing rules. For example, Gerhadt et al.[22] and Royer et al.[46] used the SL-EOS. We have to point out, however, that the scarcity of experimental data on the swelling of molten polymers plasticized with gaseous or volatile compounds have not allowed an experimental validation of the V_m evaluation through the mentioned EOS.
v. f_p and f_m: the different approaches to evaluate their values determine the predictive capability of the model. Gerhardt et al.,[22] for example, based on the concept of "occupied volume" (*i.e.*, the portion of the total specific volume inaccessible to the chain motion), defined f_p and f_m as follows:

$$f_p = \frac{V_p - V_{0,p}}{V_p}, \quad f_m = \frac{V_m - V_{0,m}}{V_m} \tag{7}$$

where $V_{0,p}$ and $V_{0,m}$ are the specific occupied volumes; $V_{0,m}$ was calculated from the occupied volumes of the pure components and using a linear mixing rule. The authors used extrapolated crystalline densities by Bondi[47] for carbon dioxide, while they evaluated the occupied volume of the polymer, $V_{0,p}$, by fitting viscosity data

obtained at different temperatures on the pure polymer[22] using eq 6. In this way, they defined a free volume targeted to the rheological measurements. However, some ambiguity with respect to the classical thermodynamic definition of free volume remains. This procedure seems difficult to apply and moreover, it does not account for the pressure effects. Royer et al.[46] described the effect of the gas concentration on free volume by T_g shifts, allowing the gas concentration and pressure to be manipulated in a similar manner to temperature with respect to viscoelastic effects. This approach allowed the authors to simply relate the pressure effect on the free volume and, hence, on the viscosity by using the Ferry and Stratton description.[48]

Development of Simple Free-Volume Based Models

Model for Viscosity Prediction of Polymer/Gas Mixtures

The starting point of the proposed approach is eq 6 in which f_p, f_m, and V_m have been calculated using the equilibrium SS-EOS for the pure components and the mixtures.

There are two main concerns in using this approach. The first is that one uses the equilibrium SS-EOS in nonequilibrium conditions. In fact, nonequilibrium extensions of the SS equilibrium theory, which should actually be used in the modeling of dynamic, rheological properties have been proposed in the literature[49]: however, in view of the complexity of these approaches and of their uncertain reliability, we hypothesize here that the perturbation due to the nonequilibrium state on dynamic values of the free volume is negligible, and, consequently, we adopt the equilibrium, quiescent values in the calculations. The second concern is related to the fact that, in the presence of flow, the hydrostatic pressure cannot be set as equal to the thermodynamic pressure, due to the compressibility of the fluid. Here we assume incompressibility of the solutions and identify the thermodynamic and mechanical values of pressure.

In the context of the SS model, an important parameter is h, the fraction of unoccupied sites ($h = 1-y$, where y is the fraction of occupied sites): the relevant assumption is made here that f_p and f_m are, respectively, equal to h_p and h_m, the empty site fractions of the pure polymer and of the mixture. h can be directly calculated both for pure polymer and for polymeric mixtures. For pure polymers, the SS-theory allows the evaluation of Helmoltz molar free energy function, F, as follows[31]:

$$F = F[V, T, h(V, T)] \tag{8}$$

The free-volume fraction, h, is obtained by minimizing the molar free energy at specified volume and temperature[31]:

$$\left(\frac{\partial F}{\partial h}\right)_{V,T} = 0 \tag{9}$$

which yields the relation[31]

$$\frac{s}{3\chi}[(s-1)/s + y^{-1}\ \ln(1-y)] = (\mathrm{H} - 1/3)(1-\mathrm{H})^{-1} + (y/6\tilde{T})(y\tilde{V})^{-2}[2.409 - 3.033(y\tilde{V})^{-2}] \tag{10}$$

where $\mathrm{H} = 2^{-1/6}y(y\tilde{V})^{-1/3}$, $\tilde{T} = T/T^*$, and $\tilde{V} = V/V*$ are the reduced temperatures and specific volumes, respectively, and V^* and T^* are characteristic parameters of the pure polymer defined as[31]

$$\begin{aligned} T* &= qz\varepsilon*/\chi k \\ V* &= Nsv* \end{aligned} \tag{11}$$

in which $qz = s(z-2) + 2$ represents the number of intermolecular contacts in the lattice with coordination number z, k the Boltzmann constant, ε^* is the maximum segmental-pair attraction energy, V^* is the total volume occupied by N s-mer macromolecules, M_0 is the molecular weight of a segment of the component, v^* is the repulsive volume of a segment, s and χ, respectively, the geometric (number of lattice sites occupied by a macromolecule), and dynamic parameters describing the chain character of the component.

The pressure, P, is obtained from[31]:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{12}$$

which yields the scaled equation of state (SS-EOS) of a single component[31]

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = (1 - \mathrm{H}^{-1}) + \left(\frac{2y}{\tilde{T}}\right)(y\tilde{V})^{-2}(1.011(y\tilde{V})^{-2} - 1.2045) \tag{13}$$

with $\tilde{P} = P/P^*$, where $P^* = qz\varepsilon^*/sv^*$.

Generalization of eqs 10, 11, and 13 to a binary random mixture maintains their form, provided the parameters are redefined as a function of composition (*i.e.*, s and χ become number averages and M_0 a weight average), while averages of the scaling parameters (P_m^*, V_m^*, and T_m^*) involve mean values $\langle\varepsilon^*\rangle$ and $\langle v^*\rangle$ according to the following relations[32]:

$$\begin{aligned}\langle\varepsilon^*\rangle\langle v^*\rangle^2 &= X_1^2\varepsilon_{11}^* v_{11}^{*2} + 2X_1X_2\varepsilon_{12}^* v_{12}^{*2} + X_2^2\varepsilon_{22}^* v_{22}^{*2}\\ \langle\varepsilon^*\rangle\langle v^*\rangle^4 &= X_1^2\varepsilon_{11}^* v_{11}^{*4} + 2X_1X_2\varepsilon_{12}^* v_{12}^{*4} + X_2^2\varepsilon_{22}^* v_{22}^{*4}\end{aligned} \quad (14)$$

where X_i are the site fractions corresponding to the mole fractions.

The shift factor (a_c) can be predicted by using the calculated specific volumes ($V_m = \tilde{V} \cdot V_m^*$) and free volume fractions ($f_p = h_p$ and $f_m = h_m$) in eq 6. Use of eq 6 with the parameters evaluated through the SS-EOS accounts at the same time for the effect on free volume of both pressure and dissolved gas concentration. Equation 6 can be, therefore, generalized by simply using, in place of a_c (which, in the original work refers to "concentration dependent shift factor"), a global shift factor, a, and by using, in place of V_p, V_m, f_p, and f_m, the specific volumes V_1 and V_2 and empty site fractions h_1 and h_2, where subscripts 1 and 2 refer to two generic different conditions in terms of pressure and dissolved gas concentration:

$$\begin{aligned}a &= \frac{\eta(c_2, \dot{\gamma}, T, P_2)}{\eta(c_1, \dot{\gamma}/a, T, P_1)}\\ &= \frac{(1-\omega_{c,2})^n}{(1-\omega_{c,1})^n}\left(\frac{V_1}{V_2}\right)^n \exp\left(\frac{1}{h_2} - \frac{1}{h_1}\right)\end{aligned} \quad (15)$$

In the following, n is fixed to be equal to 3.5. In view of the variable range reported for n in the literature,[37,38,40] and of the prevailing importance of exponential term in eq 15, this assumption has been considered reasonable.

Model for T_g Depression Prediction

A further application of this simple approach is the prediction of the T_g depression brought about by the addition of a gaseous component to a molten polymer. In fact, if one assumes that T_g is an isofractional free volume state,[50] the T_g depression can be evaluated by using also in this case the hypothesis that the empty site fraction (h in the SS-EOS) could be used in place of the free volume fraction. As already discussed, h is known for the pure polymer and for each polymer/blowing agent composition at experimental pressure and temperature. Therefore, isofractional free volume temperatures can be obtained as function of c and P and, consequently, T_g of a mixture can be evaluated as the temperature at which the mixture has the same fractional free volume (same h) of the pure polymer at T_g (at atmospheric pressure).

Comparison with Experimental Results

Prediction of Shear Viscosity

Theoretical predictions will be compared in the following with experimental results available in the literature or results obtained in our laboratories on viscosities of polymer/gas mixtures. Where available, model predictions are compared to "flow curves," otherwise a_c and a_p data are used.

Experimental results on pure PCL have been obtained by us using in-line shear viscosity measurements. These results are consistent with those performed with standard capillary rheometry, as reported in Figure 1a. In Figure 1b, the results of in-line shear viscosity measurements on pure PCL are compared with those obtained on PCL/CO_2 and PCL/N_2 solutions. The concentrations of the two solutions (PCL + 2.3 wt % CO_2 and PCL + 1.5 wt % N_2) were chosen to obtain homogeneous solutions in the extruder and to compare the plasticizing effect of the two gases at equal molar concentration.

As expected, the rheological curves of both the mixture containing 2.3% of CO_2 and the mixture containing 1.5% of N_2 are shifted to lower values with respect to pure PCL, maintaining a similar dependence on shear rate. To use eq 15 to predict these experimental data, the following parameters were used

- for the pure PCL
  - $T = 100$ °C, $\overline{P} = 40$bar, $V_1 = 0.9609$ cm^3/g, from experimental data (T is set in the capillary zone of the extrusion line, $\overline{P}$ is the mean pressure inside of the capillary, V_1 is measured by *PVT* tests[51])
  - $h_1 = 0.1049$, obtained from the experimental *PVT* data and eq 10, $h = 1-y$
- for the mixture with $\omega_c = 2.3$ wt % of CO_2
  - $T = 100$ °C, $\overline{P} = 80$ bar, from experimental, extrusion data
  - $V_2 = 0.9585$; $h_2 = 0.1092$, obtained theoretically using the SS-EOS

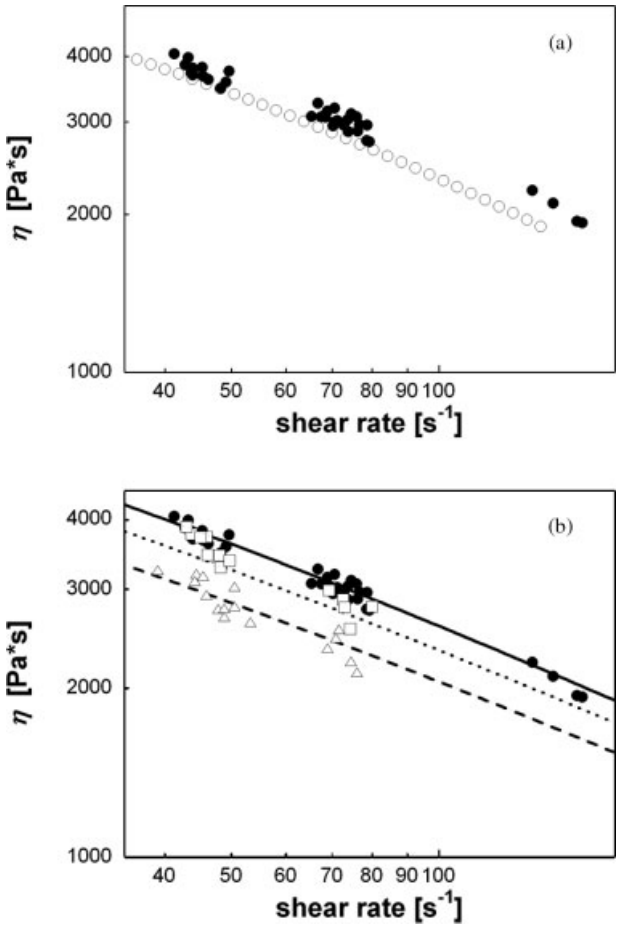

Figure 1. Effect of dissolved gases on PCL in-line rheometry: a) pure PCL in-line rheometry (●) and capillary rheometry measurements (○) and b) in-line measurements on pure PCL (●), PCL + 2.3 wt % CO_2 (△), and PCL + 1.5 wt % N_2 (□). Power-law fits of pure PCL data, continuous line; model prediction for the PCL/CO_2 solution, dashed line; and model prediction for the PCL/N_2 solution, dotted line.

- For the mixture with $\omega_c = 1.5$ wt % of N_2
  - ○ $T = 100$ °C, $\overline{P} = 120$ bar, from experimental, extrusion data
  - ○ $V_2 = 0.9647$; $h_2 = 0.1064$, obtained theoretically using the SS-EOS

In the SS-EOS calculations performed to determine values of V_2, h_1, and h_2, the characteristic parameters for pure compounds are those reported in Table 1. Using eq 15, the shift factor, a, at aforementioned experimental conditions was calculated and found to be equal to 0.64 and 0.82, respectively, for the PCL/CO_2 solution and for the PCL/N_2 solution.

To predict the rheological curves for PCL-based mixtures, fitting of in-line data for pure PCL has been performed by using a power-law model[7] (see continuous line in Fig. 1b). The shift factors (calculated as described above) have then been used to shift this model curve for pure PCL obtaining the theoretical prediction of the rheological curves for the PCL/N_2 and PCL/CO_2 mixtures (see Fig. 1b). These predictions are in a good agreement with the experimental rheological results.

Figure 2 reports the experimental a_c data for the system PDMS/CO_2, obtained by Royer et al.[11] with the magnetically levitated sphere rheometer. The authors also reported the experimental pressures, allowing us to compare our predictions with the experimental results. Although calculated results are usually reported as continuous lines, in our case calculated values are reported as discrete points, since each experimental point was obtained at a different pressure and gas concentration. In Table 2 are reported the experimental conditions along with the experimental and predicted shift factors for this system. A very good agreement between predicted and experimental data was found (see Fig. 2). The magnetically levitated sphere rheometer designed by the authors allowed the separation of the pressure contribution, by fixing the gas concentration and changing the pressure. The reported pressure dependent shift factor, a_p, (evaluated for pure PDMS) was compared with the values pre-

Table 1. Characteristic Parameters of the SS-EOS for the Different Materials Used in This Study

Material	M_w	ρ^* (cm^3/g)	T^* (K)	P^* (MPa)	Reference
CO_2	44.01	1.605	3,043	922.7	52
N_2	28.01	0.843	2,372	593.8	This work
PCL	80,000	1.111	10,059	1,038.7	51
PDMS	308,000	1.043	7,825	497.3	53
PS	132,000	1.040	12,680	737.7	53
PMMA	250,000	1.196	11,800	923.5	53

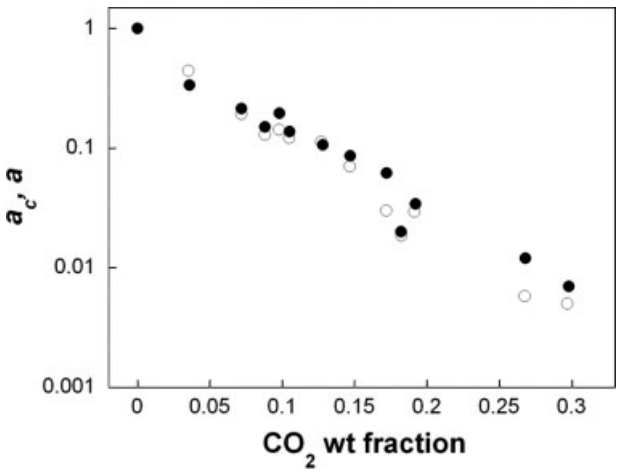

Figure 2. Comparison of model prediction of the effect of CO_2 concentration on scaling factors, a, of PDMS/CO_2 solutions (open symbols) with data from Royer et al.,[11] a_c (closed symbols).

dicted using eq 15 (see Fig. 3). The predicted shift factors are in reasonable agreement with the experimental results, although an overestimation of the experimental pressure effect is evident.

The experimental a_c data for the system PS/CO_2, obtained by Royer et al.[46] with in-line extrusion rheometer at three different temperatures (250, 225, and 200 °C) are reported in Figure 4. Our prediction obtained by using eq 15 is reported in the same figure. A deviation from experimental data is detectable; however, the model is able to estimate the extent of variation of the shift factor. Finally, in Figure 5 is reported the effect of pressure on the viscosity of molten PS as measured by Kadijk et al.[56] Fitting of data at 200 bar has been performed by using the Cross[7] model (see continuous line in Fig. 5).

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\tau\dot{\gamma})^l} \tag{16}$$

η_∞ being the infinite-shear-rate viscosity, τ a time constant, and l a power-law index.

Calculated shift factors have been used to shift the Cross model curve for PS at 200 bar obtaining the theoretical prediction of the rheological curves for PS at 500 and 1000 bar. Also in this case, the model prediction overestimates the pressure effect.

Possible further improvement of the predictive capability of the proposed approach could be based on selecting EOS models that predict a smaller depression of free volume with pressure.

Prediction of T_g Depression

For the PMMA/CO_2 system, data from Chiou et al.[27] and from Wissinger[55] are available for T_g depression. To verify the predictive capability of the model, we calculated h_1, *i.e.*, the empty site fraction of the pure polymer, at T_g and at atmospheric pressure ($T_g = 105$ °C). Then, we evaluated the T_g of each PMMA/CO_2 mixture as the temperature at which the empty site fraction of the mixture, h_2, is equal to h_1. It is important to note that, since no information is supplied on the pressure at which measurements were performed, we assumed that the experimental pressure was the CO_2 pressure, which would be in equilibrium with the

Table 2. Experimental Data on PDMS/CO_2 Viscosity Scaling Factors, 30 °C, Data from Royer et al.[11]; Specific Volumes, Empty Site Fraction as Calculated Through the SS-EOS, and Predicted Shift Factors as Calculated by eq 15

Experimental CO_2 Wt. Fraction	Experimental a_c	Experimental Pressure (MPa)	Calculated V (cm^3/g) (eq 13)	Calculated h (eq. 10)	Calculated a (eq 10)
0	1	0.1	1.0369	0.1159	
0.036	0.336	6.9	1.0384	0.1260	0.4455
0.072	0.214	6.9	1.0455	0.1373	0.1931
0.088	0.15	6.9	1.0496	0.1434	0.1297
0.098	0.196	13.8	1.0432	0.1419	0.1427
0.105	0.137	13.8	1.0449	0.1444	0.1215
0.128	0.106	20.7	1.0392	0.1463	0.1129
0.147	0.086	20.7	1.0438	0.1534	0.0703
0.172	0.062	13.8	1.0620	0.1694	0.0300
0.182	0.02	6.9	1.0760	0.1798	0.0186
0.192	0.034	20.7	1.0544	0.1695	0.0294
0.268	0.012	13.8	1.0900	0.2069	0.0058
0.298	0.007	20.7	1.0826	0.2095	0.0050

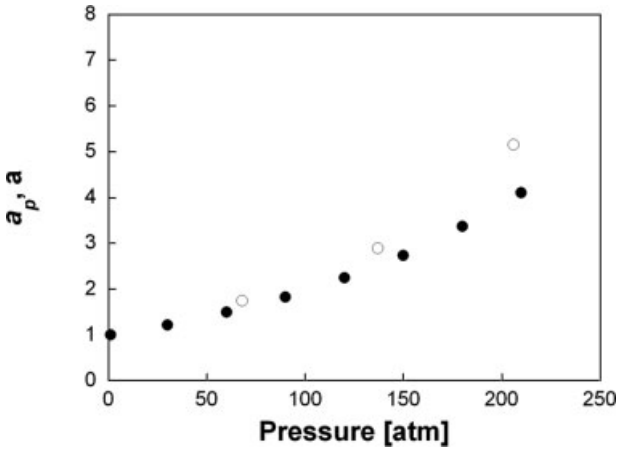

Figure 3. Comparison of model prediction of the effect of pressure on scaling factors, a (open symbols) with data from Royer et al.,[11] a_p (closed symbols), for pure PDMS. $T = 30$ °C.

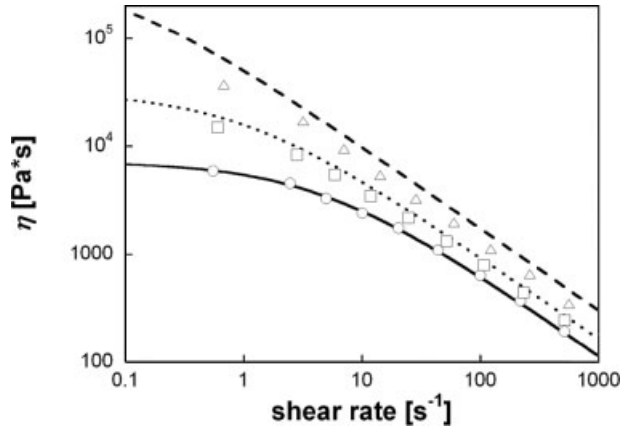

Figure 5. Effect of pressure on PS at 202 °C, data from Kadijk et al.[56] 200 bar (○), 500 bar (□), and 1000 bar (△). Cross model fits of PS at 200 bar, continuous line; model prediction for PS at 500 bar, dotted line; model prediction for or PS at 1000 bar, dashed line.

reported CO_2 concentration values. Model predictions along with literature data are reported in Figure 6: a slight overestimation of T_g depression is predicted.

Data on T_g depression for PS/CO_2 system are available from the paper of Condo et al.[56] Comparison of experimental values with model predictions (see Fig. 7) reveals, in this case, a very good agreement.

CONCLUSIONS

A simple free-volume approach based on the Simha and Somcynsky EOS for multicomponent systems has been used to predict the rheological properties of polymer/gas mixtures. The empty site fraction, which can be calculated using this theory as a function of mixture composition and pressure, was assumed to represent the free volume fraction in the classical free-volume theory for viscosity shift factor. The assumption has been made that free-volume fraction in dynamic, steady state conditions, can be taken as equal to that evaluated at equilibrium. This approach allowed a direct calculation of the effects of gas concentration and pressure on free volume in the form of a shift factor and, in turn, a simple evaluation of the viscosities of polymer/gas mixtures by shifting those of the

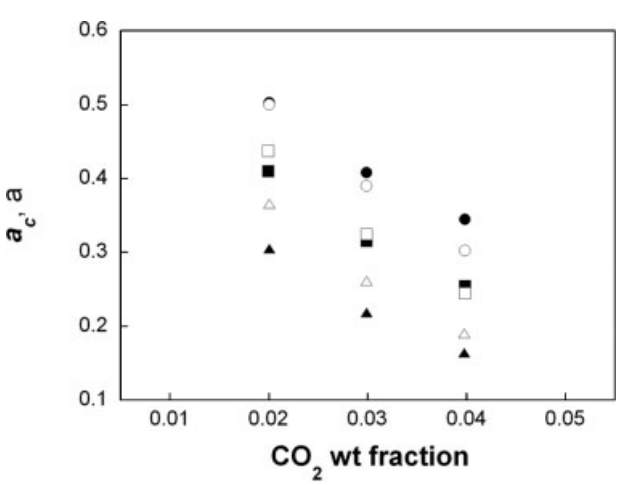

Figure 4. Comparison of model prediction of the effect of CO_2 concentration on scaling factors, a, of PS/CO_2 solutions (open symbols) with data from Royer et al.,[46] a_c (closed symbols); 250 (●, ○), 225 (■, □) and 200 °C (▲, △).

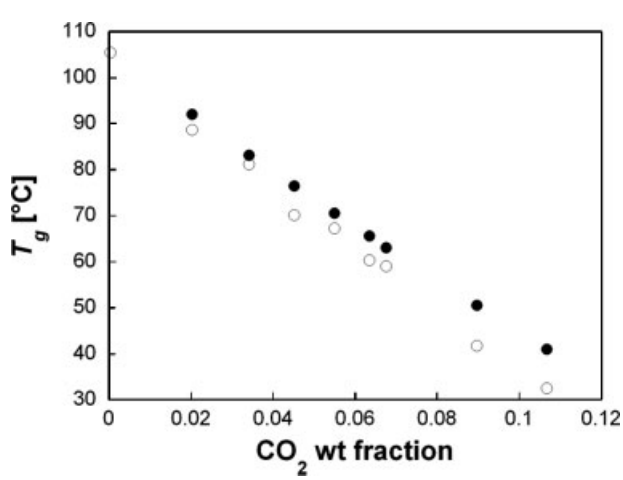

Figure 6. Effect of the CO_2 concentration on the T_g of PMMA/CO_2 system; experimental data from Chiou et al.[27] and from Wissinger[55] (closed symbols) and model prediction (open symbols).

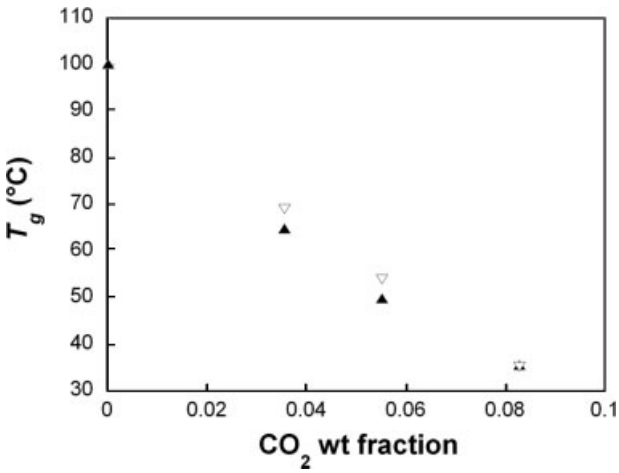

Figure 7. Effect of the CO_2 concentration on the T_g of PS/CO_2 system; experimental data from Condo et al.[56] (closed symbols) and model prediction (open symbols).

pure polymer. New experimental data obtained in this study on PCL/CO_2 and of PCL/N_2 as well as literature data on $PDMS/CO_2$ and on PS/CO_2 were satisfactory predicted by using this approach.

The same free volume approach was also used to predict the glass transition depression caused by the presence of gas in a molten polymer by assuming an isofree volume state at T_g. The cases of $PMMA/CO_2$ and PS/CO_2 systems have been considered, showing a satisfactory agreement of the model with experimental data available in the literature.

LIST OF SYMBOLS

a	Viscosity shift factor
a_c	Concentration dependent viscosity shift factor
$a_{c,0}$	Concentration dependent viscosity shift factor in the limit of zero shear rate
a_p	Pressure dependent viscosity shift factor
C	Concentration of the gas in the polymeric matrix
F	Helmoltz molar free energy
f	Fractional free volume
h, h_1, and h_2	vacant site fraction or hole fraction in the SS-EOS
K	Constant in eq (3)
k	Boltzmann constant
l	Power-law index in eq (16)
M_0	Molecular weight of a segment of a component
$\overline{M}_w$	Weight average molecular weight of the polymer
n	Concentration exponent in eq (3)
P	Pressure
P^*, P^*_m	Characteristic pressures of the pure polymer and polymer/gas mixture
$\tilde{P}$	Reduced pressure
$\overline{P}$	Mean pressure inside the capillary/slit die
ΔP^{tot}	Measured pressure drop
ΔP^{cap}	Pressure drop along the capillary
ΔP^{e}	Entry and exit pressure losses
qz	Number of intermolecular contacts in the lattice
s	Number of lattice sites occupied by a macromolecule
T	Temperature
T^*, T_m	Characteristic temperatures of the pure polymer and polymer/gas mixture
$\tilde{T}$	Reduced temperature
T_g	Glass transition temperature of the pure polymer
$T_{g,mix}$	Glass transition temperature of the polymer/gas mixture
v^*	Repulsive volume of a segment
V, V_1, and V_2	Specific volumes
V_0	Specific occupied volume
V^*,V^*,V^*_m	Characteristic specific volume of the pure polymer and polymer/gas mixture
$\tilde{V}$	Reduced specific volume
y	Occupied site fraction
X_i	Site fractions corresponding to the mole fractions

GREEK SYMBOLS

χ	Dynamic parameter describing the chain character of a component
ε^*	Maximum segmental-pair attraction energy
λ	Constant in eq (4)
$\dot{\gamma}$	Shear rate
η	Shear viscosity of the polymer/gas solution
η^0	Shear viscosity of the pure polymer
η_0	Newtonian shear viscosity of the polymer/gas solution (limit of zero shear rate)
η^0_0	Newtonian shear viscosity of the pure polymer (limit of zero shear rate)
η_∞	Infinite-shear-rate viscosity in eq (16)
τ	Time constant in eq (16)

ω_c Weight fraction of gas in the polymer/gas mixture
ζ Segmental friction fraction
ζ_0 Constant in eq (4)

SUBSCRIPTS

p Pure polymer
m Polymer/penetrant mixture

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