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High pressure dynamics of polymer/plasticizer mixtures

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Plasticizers are usually added to polymers to give them the desired flexibility and processability by changing the dynamical properties of the polymer chains. It is therefore important to give a quantitative description about how the dynamic behavior of a given polymer is modified by the incorporation of a second component. We analyze in this work, by means of dielectric spectroscopy, the dynamics of poly(vinyl acetate)/diethyl phthalate mixtures, at different concentrations, over a broad range of frequency, pressure, and temperature. The dynamics of these particular mixtures show only one main relaxation process contrarily to what is observed in athermal miscible polymer mixtures. From the dielectric spectra the maximum relaxation time as a function of pressure and temperature was obtained and analyzed. We studied the pressure dependence of the glass transition temperature as well as the fragility of both the neat components and the mixtures at different concentrations (on the rich polymer range). Finally, the experimental data were rationalized within the framework of an Adam–Gibbs (AG) based approach recently developed [G. A. Schwartz *et al.*, J. Chem. Phys. **127**, 154907 (2007)]. The model, originally developed for athermal blends, is here modified to take into account the non-negligible interaction between polymer and plasticizer. We found that the temperature-pressure dependence of the α-relaxation time is very well described by this AG extended model. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3187938]

I. INTRODUCTION

Plasticizers are commonly used in industry to give plastics the appropriated processability and final product properties. Plasticizers work by embedding themselves among polymer chains, increasing its free volume by spacing them apart and thus significantly lowering the glass transition temperature making the polymer softer enough to improve its processability and mechanical properties. The flexibility and durability of the final product are often improved with certain plasticizers. In particular, phthalate based plasticizers are among the most common and are typically used when good resistance to water and oils is required. Despite the technological as well as scientific relevance of the dynamics of polymer/plasticizer binary mixtures, there is a limited number of such studies in the scientific literature. A systematic research about the pressure-temperature dependence of the dynamics of these binary mixtures will help to improve technological developments as well as to increase the understanding of fundamental physics of the glass transition and associated relaxation processes.

Polymer/plasticizer mixtures are subjected to high pressures and temperatures during extruding, molding, and curing processes, and it is therefore important to know how plasticizers modify the polymer dynamics under these conditions. Although there is still no appropriate framework to

account for the pressure-temperature dynamics of the mixtures from the knowledge of the dynamics of the neat components, some attempts have been recently done to describe the dynamics of polymer blends under different conditions. Lodge *et al.*[1,2] have introduced some years ago the concept of self-concentration to explain the so-called dynamical heterogeneity in athermal miscible polymer blends at atmospheric pressure. On the other hand, Casalini and Roland[3] have recently developed an approach based on a density scaling [$(\log(\tau) \propto f(TV^\gamma)$, being γ a material constant] which superposed into a single master curve the experimental data measured at different pressures and temperatures for a given system; this approach has also shown to give a good phenomenological description of the component segmental dynamics in miscible polymer blends.[4,5] In recent works[6–8] we have proposed a new model which combines the Adam–Gibbs (AG) theory with the self-concentration concept to account for the component segmental dynamics in noninteracting miscible polymer blends starting from the knowledge of the dynamics of the neat components (see the Appendix for a more detailed explanation of the different AG extended models). This approach has also shown to give an excellent description of the component segmental dynamics in concentrated polymer/solvent athermal mixtures at atmospheric pressure.[7] However, none of these models account for the interactions that usually takes place between polymers and plasticizers; moreover, only the last two approaches take into account the pressure dependence of blends dynamics. Thus,

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the lack of systematic studies and the absence of an appropriate theoretical framework make difficult a quantitative analysis of the dynamics of polymer/plasticizer binary mixtures.

The aim of this work is to present a detailed study about the pressure-temperature dependence of the dynamics of a polymer/plasticizer system by means of dielectric spectroscopy. We analyzed the pressure and/or composition dependence of fragility, glass transition temperature, and activation volume. Additionally, we explored the ability of an AG extended model to describe the polymer/plasticizer dynamics at different pressures, temperatures, and compositions. This approach has been modified to take into account the effect of the polymer/plasticizer interactions giving an excellent fitting of the experimental α-relaxation times of poly(vinyl acetate)/diethyl phthalate (PVAc/DEP) mixtures over a broad range of pressure and temperature.

II. EXPERIMENT

In this study we have investigated the dynamics of miscible mixtures of PVAc $[-CH_2-CH(OCOCH_3)-]_n$ with DEP $[C_6H_4(COOC_2H_5)_2]$. PVAc was supplied by Aldrich Chemie and have an average molecular weight M_w of 83 kg/mol. DEP was supplied by Merck and has purity higher than 99%. Prior to sample preparation, PVAc was kept at 450 K in vacuum for at least 24 h to remove any moisture or solvent content. Possible water content in DEP was eliminated by means of molecular sieves.

A. Samples preparation

Mixtures of PVAC and DEP were prepared at nominal weight/weight concentration of 90/10 and 75/25, respectively. The appropriated amount of each component was put in bottles with toluene to get a 5% dilution and mixed at room temperature overnight. The samples for dielectric measurements were prepared by dropping the solutions over gold-plated electrodes, 20 mm diameter, with a spacer of 0.1 mm thickness. The toluene was later evaporated, first at room conditions for 24 h and later in a nitrogen atmosphere following the protocol described below. Finally, the upper electrode was put over the sample and the set was slightly pressed, above the mixture's glass transition temperature, to ensure good electrical contact.

The main problem concerning the sample preparation was to determine an appropriated protocol to eliminate the toluene from the solution without removing the DEP. To do that we performed thermogravimetric analysis (TGA). The measurements were performed on a TA Instruments Q500 TGA under nitrogen atmosphere at a heating rate of 5 K/min. Figure 1 shows the weight percentage and derivative weight percentage for a PVAc/DEP (75/25) sample dried at room temperature. We observe in this figure three peaks that correspond to the evaporation of toluene (weak peak around 50 °C) and DEP (broad peak around 180 °C), at relative low temperatures, and to polymer degradation at high temperatures. From this analysis we can determine that by drying the sample under nitrogen atmosphere at around 50 °C for 1 h, we should completely remove the toluene with a minimum
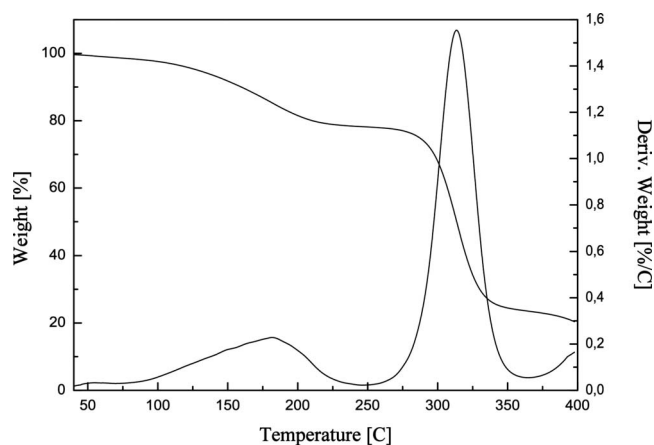

FIG. 1. Weight percentage and derivative weight percentage vs temperature for a PVAc/DEP (75/25) sample. The small lowest temperature peak in the derivative signal corresponds to toluene evaporation. The second peak, centered around 180 °C, corresponds to DEP evaporation whereas the tall high temperature peak represents the polymer degradation.

lost of DEP. For the PVAc/DEP (90/10) sample a similar analysis gave a drying temperature of 80 °C. We dried the samples following this protocol and we determined the exact composition of each sample by repeating the TGA analysis on the same samples after the dielectric measurements. The actual compositions for the nominal PVAc/DEP (90/10) and PVAc/DEP (75/25) were 89/11 and 75.5/24.5, respectively.

B. Samples characterization

Differential scanning calorimetry (DSC). Calorimetric measurements were performed on a Q2000 TA Instruments DSC in the modulated mode, with amplitude of 0.5 K, a period of 100 s, and underlying cooling rate of 0.25 K/min. Figure 2 shows the reversible heat capacity as a function of the temperature for the neat components as well as for PVAc/DEP (75/25) sample. Only one glass transition, intermediate between those of neat DEP and PVAc, is observed for the mixture. Although the glass transition for the mixture is broader than those of its components, it is rather narrow if
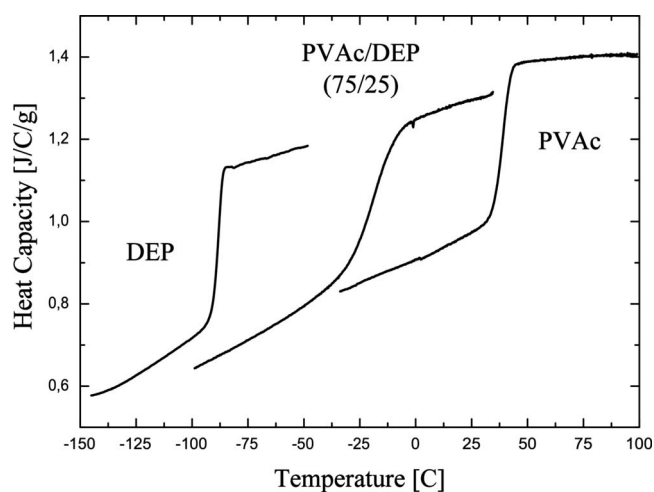

FIG. 2. Heat capacity vs temperature for neat DEP, PVAc/DEP (75/25), and neat PVAc.
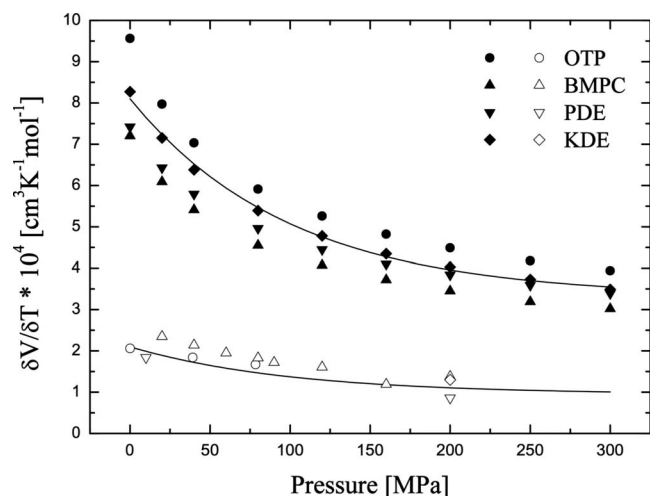
FIG. 3. Thermal expansion as a function of the pressure for melt (filled symbols) and glassy (open symbols) state of several molecular glass formers. The circles represent OTP data from Ref. 10, up triangles correspond to BMPC 11, down triangles are PDE 12, and diamonds are KDE 13.

compared it with what is usually observed for athermal polymer blends.[9]

Pressure-volume-temperature (PVT). Due to the lack of PVT data for DEP in the literature, we analyzed *PVT* data for similar glass formers and we then estimated from this study the *PVT* behavior of DEP. Figure 3 shows thermal expansion of melt and glassy state for several glass formers: *o*-terphenyl (OTP) (T_g=244 K), from Ref. 10, 1,1′-bis-(*p*-methoxyphenyl)cyclohexane (BMPC) (T_g=241 K),[11] phenylphthalein-dimethylether (PDE) (T_g=295 K),[12] and cresolphthalein-dimethylether (KDE) (T_g=313 K).[13] These molecular glass formers were selected because the availability of *PVT* data and its similar molecular structure with DEP. As shown in Fig. 3 the *PVT* behavior for these four glass formers is not too different, especially in the glassy state. We therefore calculated an average behavior for the melt and glassy state (filled lines in Fig. 3) and estimated from there the pressure dependence of $\Delta(\partial V/\partial T)_P$ according to the Appendix [see also Eq. (4) in Ref. 14]. For PVAc this pressure dependence was taken from a previous work.[14] The corresponding parameters for both components are listed in Table I.

C. Dielectric measurements

Dielectric measurements at atmospheric pressure were performed using a broadband dielectric spectrometer (Alpha analyzer Novocontrol GmbH) in the frequency range of 10^{-2}–10^{7} Hz and a Novocontrol Quatro cryosystem for temperature control with a precision better than 0.1 K. At higher pressures, dielectric measurements were carried out in a pressure cell (0–300MPa) supplied by Novocontrol GmbH. The measurements were performed by frequency sweeps (10^{-2}–10^{6} Hz) at constant temperature, after stabilizing the temperature of the cell for about 2 h, with stability better than ± 0.1K, and constant pressure, with stability better than ± 2MPa. For more details about the experimental setup see Refs. 8 and 14–16. Figure 4 shows typical spectra, i.e., dielectric loss as a function of the frequency, at constant pressure as well as at constant temperature for the two compositions here analyzed. Solid lines in these figures represent the best fit of the experimental data by means of a power law, to account for conductivity contribution plus the imaginary part of the Havriliak–Negami function,
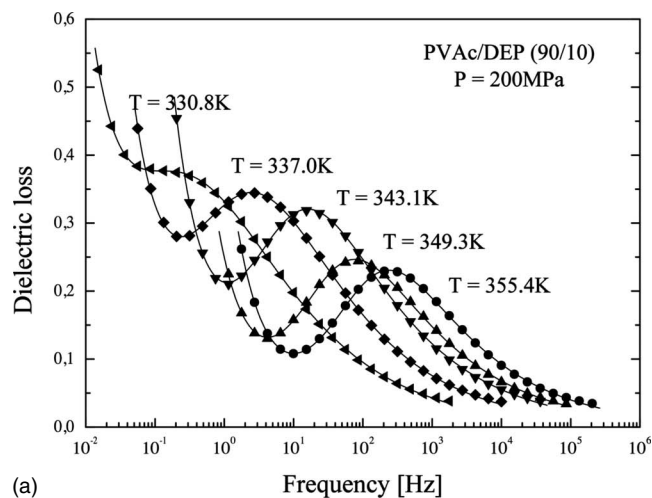
$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{[1+(i\omega\tau_{\mathrm{HN}})^{\alpha}]^{\gamma}}, \tag{1}$$

where $\Delta\varepsilon=\varepsilon_o-\varepsilon_{\infty}$, being ε_o and ε_{∞} the unrelaxed and relaxed values of the dielectric constant, τ_{HN} is the relaxation time, ω ($2\pi f$) is the angular frequency, and α and γ are shape parameters.
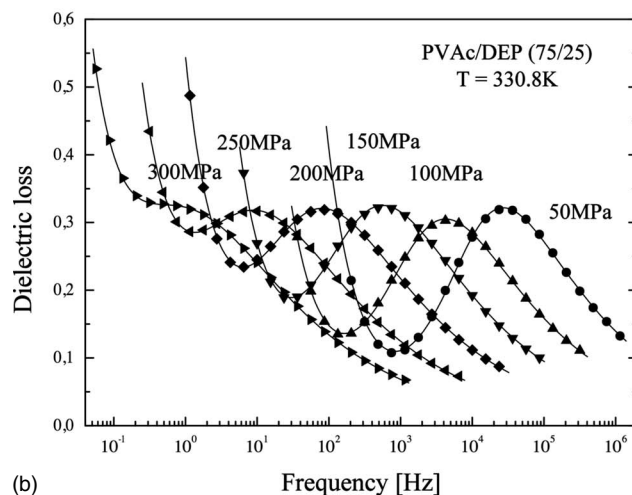
III. RESULTS AND DISCUSSION

A. Dynamics of neat components

Full DSC and *PVT* behavior of PVAc as well as the pressure-temperature dependence of the segmental relaxation time were carefully analyzed in previous works.[14,15] Details of this analysis are given in the Appendix and the corresponding parameters, according to Eq. (A5), are listed in Table I. Concerning to DEP, Fig. 5 shows the temperature dependence of the maximum relaxation times at room and high pressure. Solid lines in Fig. 5 represent the best fit of the experimental data with Eq. (A5). The corresponding fitting parameters are listed in Table I.

TABLE I. Relevant parameters for the pure components of the here studied blends. See the Appendix for the corresponding equations. Errors are about ± 1 of the least significant digit unless specified.

Polymer	Thermodynamics parameters		PVT parameters			Structural parameters	
	B (J/K mol)	m_T (J/K^2 mol)	$D(\partial V/\partial T)_{P=0}\times 10^2$ (cm^3/K mol)	$A\times 10^2$ (cm^3/K mol)	P_o (MPa)	l_K (Å)	L_P (Å)
PVAc	104	0.21	3.35 ± 0.02	2.15 ± 0.04	129 ± 5	17	3.7
DEP	54.2	0.08	4.6 ± 0.3	3.0 ± 0.3	100 ± 12	⋯	⋯

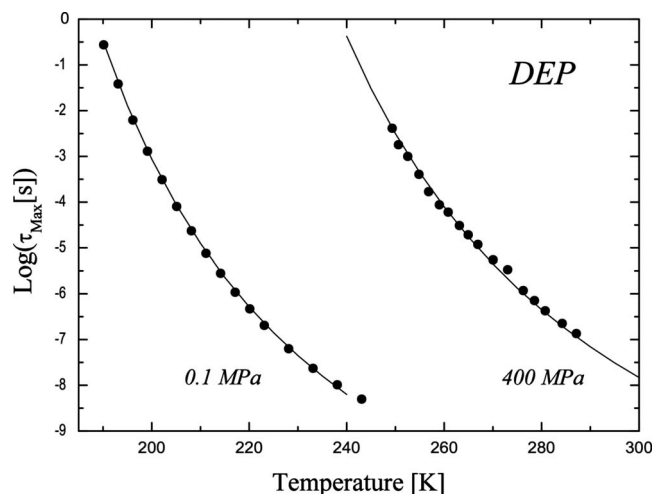| Polymer	Dynamics parameters					
	$\log(\tau_o)$ (s)	C/g_T (kJ/mol)	T_K (K)	g_P/g_T	T_g (K)	α (Å J$^{1/3}$ mol$^{-1/3}$ K$^{-1/3}$)
PVAc	-14.1	99.1	256	1.05 ± 0.05	310	17 ± 0.5
DEP	-15.2	83.5	139	$1.14+(T-T_g)\,1.85\times 10^{-3}$	183	⋯

FIG. 5. Maximum relaxation time vs temperature for pure DEP at room pressure and 400 MPa. The solid lines represent the best fit of the experimental data by means of Eq. (A5).

FIG. 4. Dielectric loss as a function of the frequency for (a) PVAc/DEP (90/10) at several temperatures and constant pressure and (b) PVAc/DEP (75/25) at different pressures and constant temperatures. The solid lines represent the best fit of the experimental data by means of a superposition of a power law for conductivity and the imaginary part of a Havriliak–Negami function for the α-relaxation process.

B. PVAc/DEP mixtures

Dynamics of the plasticized polymer. Raw data of dielectric loss (ε'') as a function of the frequency at constant pressure as well as at constant temperature are shown in Fig. 4. The main feature in these spectra is the presence of a single α-relaxation peak. It is important to remark here that both components are dielectrically active having comparable dipolar moments. Therefore, the presence of a single peak reveals the fact that both components are relaxing with very similar (or even the same) relaxation time. The observed behavior is typical of interacting blends where both components are dielectrically active,[17–19] even if the dynamic contrast (difference between the T_g of the two components) is large like in this case. For noninteracting mixtures, with similar large dynamic contrast, two different dynamics are usually observed[2,4,8,20,21] showing the so-called dynamical heterogeneity.

From the fitting of the relaxation spectra measured at different temperatures and pressures, the maximum relaxation time was determined for each composition. The maxi-

mum relaxation time is a model independent characteristic of the dynamics and is therefore less sensitive to the choice of particular fitting function used. Figure 6 shows the maximum relaxation time as a function of the temperature, at different pressures, for PVAc/DEP (90/10) and PVAc/DEP (75/25).

Activation volume. The presence of interactions between both components can be also observed through the composition dependence of the activation volume. We estimated the apparent activation volume according to[22]

$$\Delta V \approx RT \left(\frac{\partial \log(\tau)}{\partial P} \right)_T. \qquad (2)$$

Figure 7 shows the apparent activation volume as a function of the PVAc content at the glass transition temperature for the highest pressure in each case (300 MPa except for DEP that is 400 MPa). We have found in previous works[6–8] that the excess entropy (S_{ex}) or the C parameter in the AG expression (related with the energy barriers) can be expressed, for athermal mixtures, as a linear combination of the corresponding quantities for the neat components (see the Appendix). Based on these facts we assume that the activation volume for athermal mixture would also be a linear function of the composition. The dotted line in Fig. 7 represents the apparent activation volume that would correspond to an ideal athermal mixture. The calculated activation volume in the mixtures is smaller than the corresponding to an ideal noninteracting mixture confirming an attractive interaction between PVAc and DEP.

Fragility and glass transition temperature. Two important quantities for any glass forming system are the glass transition temperature T_g and the steepness of the temperature dependence of the relaxation time at T_g, i.e., the so-called fragility index defined as $m = d \log(\tau)/d(T_g/T)|_{T=T_g}$. Of special interest is their pressure dependence for both neat components and mixtures. Table II shows dielectric T_g (temperature at which τ is 100 s) and fragility index values for neat DEP and PVAc as well as for the two mixtures here analyzed at different pressures. For neat DEP T_g increases with pressure, as expected, with an average rate of dT_g/dP
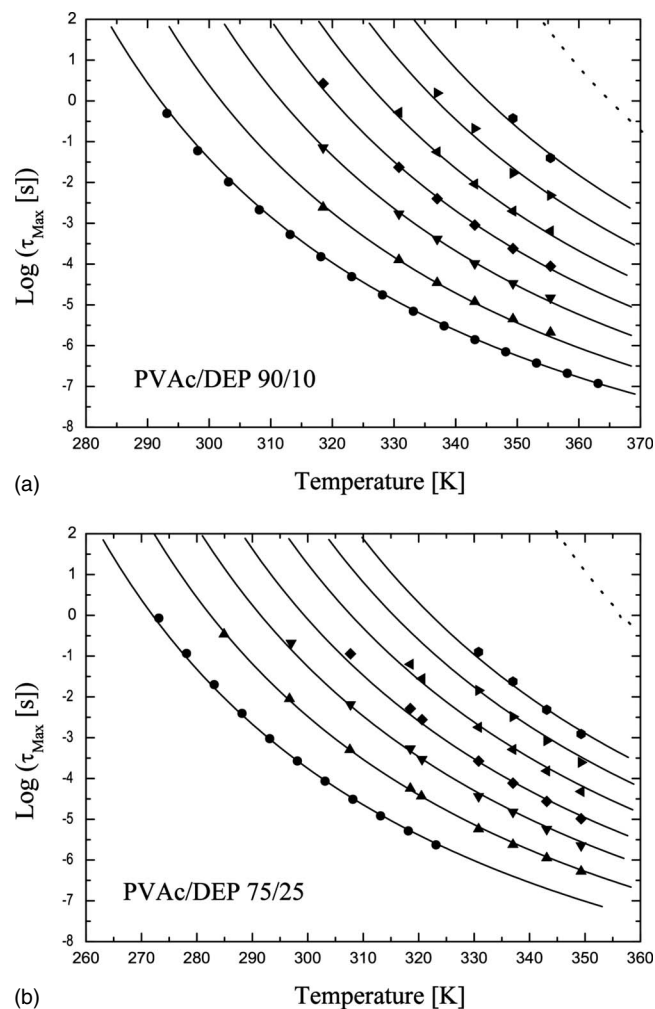
FIG. 6. Maximum relaxation time vs temperature for (a) PVAc/DEP (90/10) and (b) PVAc/DEP (75/25) at several pressures (from bottom to top: P_{atm} =0.1, 50, 100, 150, 200, 250, and 300 MPa). The solid lines represent the best fit of the experimental data through the here proposed AG extended model (see text). The dotted lines represent the fit of the highest pressure data at each composition with $\kappa=0$ and the same value of α than for solid lines.
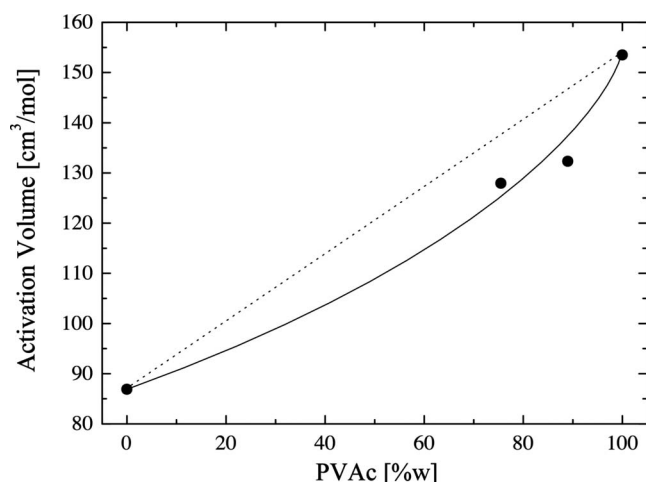

FIG. 7. Apparent activation volume vs PVAc composition at the glass transition temperature for the highest pressure. The solid line is a guide to the eye. The dotted line corresponds to the apparent activation volume for an ideal noninteracting mixture.

TABLE II. Dielectric T_g and fragility for both neat components and blends at different pressures. The pressure values in parentheses correspond only to neat DEP data. Values in square brackets correspond to extrapolation using the here proposed model (see text). Errors are about ± 1 of the least significant digit.

P (MPa)	PVAc	PVAc/DEP (90/10)	PVAc/DEP (75/25)	DEP
Dielectric T_g (K); T ($\tau=100$ s)				
0.1	310	283	263	183
50	321	293	272	[192]
100	330	302	281	[199]
150	338	310	288	[205]
200	347	317	296	[210]
250(300)	354	325	303	[221]
300(400)	361	333	309	232
m				
0.1	89	75	62	73
50	87	74	61	[77]
100	⋯	72	60	[77]
150	86	70	59	[78]
200	74	68	56	[78]
250(300)	71	67	56	[78]
300(400)	73	65	55	77

=123 K GPa^{-1}. This value is in close agreement with the previously published one (121 K GPa^{-1}).[23] Concerning to the pressure dependence of DEP fragility we observe in Table II that, beside the value at atmospheric pressure, no pressure dependence is observed and we can therefore assume that $dm/dP \cong 0$. This behavior is rather similar to that observed for similar glass formers.[24] With respect to neat PVAc, we recently reported[14] a value of $dT_g/dP|_{P=0}$ =224 K GPa^{-1} which is in close agreement with previously reported values.[25,26] Regarding to fragility in PVAc we found a small but non-negligible pressure dependence (dm/dP =−0.065 MPa^{-1}), that is, slightly higher than that previously published by Huang *et al.*[26] This difference could be most likely attributed to differences in the molecular weight (or molecular weight distribution), which could drastically affects the pressure dependence of the fragility as recently shown for polystyrene.[16] The corresponding values of T_g and fragility (m) for the two mixtures here analyzed are also listed in Table II. Figure 8 shows the pressure derivative of both T_g and fragility (m) as a function of PVAc content. Although we have measured only two compositions it is clear in Fig. 8 that most of the variation of both T_g and m pressure dependences occurs as the plasticizer content vanishes. Predicting this behavior would be quite important in industry for optimizing polymer processability.

C. Describing the dynamics of PVAc/DEP mixtures

In order to explore the ability of the AG extended model (see the Appendix) to describe the dynamics of PVAc/DEP mixtures, it is first necessary to perform a full characterization of the pressure-temperature dependence of the dynamics of the neat components of the blend.

As already mentioned, according to the Appendix [Eqs. (A3)–(A5)], we conducted DSC and *PVT* measurements on each of the neat components to calculate b and m_T on the one
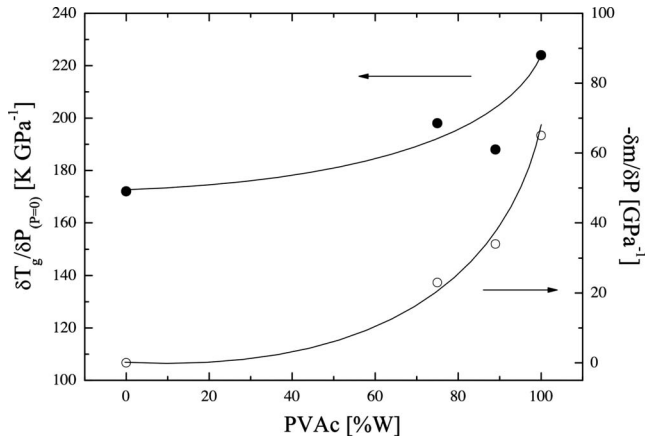
FIG. 8. Pressure derivative of T_g (filled circles) and fragility (open circles) as a function of PVAc content. The solid lines are guides to the eye.

hand, and $\Delta(\partial V/\partial T)_{P=0}$, A and P_o, on the other hand. Then, from the temperature dependence of the α-relaxation time at atmospheric pressure $\log(\tau_o[s])$, C/g_T and T_K were obtained through Eq. (A3). Finally, the only unknown parameter in Eq. (A5), i.e., the ratio g_P/g_T, was estimated by minimizing the mean square deviation between the experimental data and the α-relaxation time given by Eq. (A5). This procedure gives the full temperature-pressure dependence of the α-relaxation time for each component of the mixture. A summary of the parameters is listed in Table I.

Including the effects of the interactions. From the chemical structure of PVAc and DEP we do not expect hydrogen bonding interaction between both components, but a weaker interaction, most likely due to van der Waals forces. The influence of hydrogen bonding on the relaxation dynamics of polymer blends have been systematically studied by Painter and co-workers;[19,27,28] however, the effects due to weaker interactions have not been analyzed for this kind of system to the best of our knowledge. We observe in our mixtures that the plasticized polymer presents a dynamics that is markedly faster than that of the neat polymer. This behavior has been often rationalized as due to the larger free volume in the mixture, which should speed up the polymer dynamics. In the particular case of PVAc/DEP mixtures it is worth to note that DEP molecule is rather big compared with a PVAc monomer, and this could actually result in a worse packing of PVAc chains increasing the available free volume.

In the particular case of athermal miscible mixtures, the AG extended model (as described in the Appendix), first developed for athermal miscible polymer blends, gives an excellent description of the polymer dynamics (at high polymer concentrations) as shown in previous works.[7,20] However this AG extended model is not able, in its present form, to account for the plasticized polymer dynamics of interacting mixtures as shown in Figs. 6(a) and 6(b) (see dotted curves). The observed dynamics is much faster than that predicted by this AG based approach. By exploring Eq. (A6a), it is clear that the faster plasticized polymer dynamics could be indicative of a value of $S_{ex}^{A/blend}$ higher than that obtained from the previous approach [Eq. (A6b)]. In fact, according with previous generalizations of the AG equation to account for the effect of density changes [see Eq. (A4)], an increasing of the

excess entropy would be expected from any additional density reduction (free volume increasing). As aforementioned, the relative high volume of the DEP molecule could induce in this case a poorer packing of the polymer chains and therefore an increment of the free volume could be expected. This would result in an increasing mobility of the polymer segments with respect to the athermal case, consistent with a lower activation volume as we found above. Based on these ideas, we can add a new term to the excess entropy to account for the effect of the interaction between PVAc and DEP. Thus, our approach to the problem consists in the addition of a first order correction term to the expression of the entropy in the generalized AG equation [see Eq. (A6a) in the Appendix],

$$\tau^{A/blend}(T,P) = \tau_o \exp\left[\frac{C'^{A/blend}(T,P)}{T S_{ex}^{A/blend}(T,P)}\right]. \tag{3}$$

Hence, we can write the excess entropy of the polymer in the mixture [Eq. (A6b) in the Appendix] as

$$S_{ex}^{A/blend}(T,P) = \phi_{eff}^A S_{ex}^A(T,P) + (1-\phi_{eff}^A)S_{ex}^B(T,P) + \kappa\phi_{eff}^A(1-\phi_{eff}^A), \tag{4}$$

where κ is a parameter which accounts for the effects of the interaction and has to be determined from the fitting of the experimental data. It is interesting to note that once $S_{ex}^{A/blend}(T,P)$ is multiplied by temperature [as in Eq. (3)], the term related to the interaction is formally equivalent to that corresponding to the interaction energy of mixing in the Flory–Huggins theory[29] given by

$$\Delta\bar{U}_{mix} = \chi\phi(1-\phi)k_B T, \tag{5}$$

being k_B the Boltzmann constant, ϕ the volume concentration, and χ the Flory interaction parameter. However, whereas the later refers to an actual energy interaction term the former would reflect the difference in the entropy arising from the interaction of the mixture in the disordered form (melt) with respect to the same mixture in the glassy state.

We will see below that this simple modification of the AG extended model recently developed to account for the component dynamics of athermal mixtures is enough, at least for the here studied mixtures, to give an excellent description of the pressure-temperature dependence of the dynamics of interacting miscible polymer/plasticizer mixtures. However, it should be pointed out that this simple approach might likely fail as soon as the plasticizer concentration increases and the polymer is not longer the very major component.

Fitting the experimental relaxation times. Once the pressure-temperature dependence of the dynamics of the neat components is completely characterized, we can use the AG extended model to fit the experimental relaxation times of the mixtures. We have to solve the system of equations, Eqs. (A6a)–(A6d), with Eq. (4) replacing the corresponding Eq. (A6b), being α and κ the only fitting parameters. Based on previous works[7,8] we expect that the parameter α decreases with increasing pressure and slightly depends on composition. Parameter κ, accounting for the effects of the interaction between both components, is expected to be hardly dependent on composition (at least for the polymer rich side
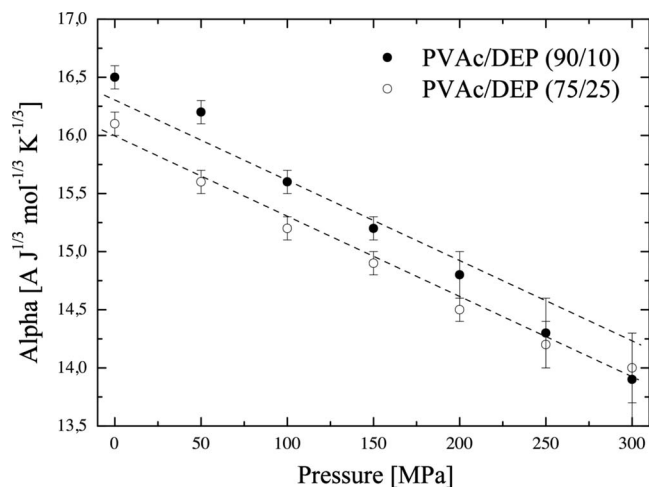
FIG. 9. Pressure dependence of the α parameter for both compositions. The lines are guides to the eye.

here analyzed). Thus, we have set the same value of κ when fitting the two mixtures. Under this assumption we have solved the system of equations by finding the values of α and κ that minimize the square difference between the experimental data and the calculated values.

Solid lines in Fig. 6 show the excellent fitting of the experimental relaxation times obtained with the here proposed AG extended model. The best fit was obtained with $\kappa = 60$ J mol^{-1} K^{-1} for both compositions; the values of the α parameter as a function of the pressure for both compositions are shown in Fig. 9. The values of α at atmospheric pressure are in close agreement with those recently published[20] for PVAc under several different environments ($\alpha = 17.0 \pm 0.5$ J$^{1/3}$ mol$^{-1/3}$ K$^{-1/3}$). As previously mentioned the parameter α decreases almost linearly with increasing pressure, within the experimental uncertainties, as already reported for other systems.[8]

It is worth mentioning that the parameters κ, when expressed in moles of macromolecules of PVAc per 100 Å^3 (as the value of χ is usually given in the literature[29]), the obtained value is around 6.24×10^{-3}. As expected, this value is much smaller than those tabulated for χ since the excess entropy contribution would represent just the (small) difference between the mixture thermodynamics in the melt and that in the glassy state at the same temperature/pressure. Finally, just mention that it would be really useful to be able to obtain the parameter κ from an independent experiment. This would help in obtaining a predictable model for the dynamics of plasticized polymers. Nevertheless according to our results once κ is determined from one polymer plasticized mixture, it could be used for obtaining the polymer dynamics in mixtures of the same components having different concentrations.

Size of the cooperative rearrangement regions (CRRs). An interesting result of the AG theory is that it relates the size of the CRR with the configurational entropy through the parameter α, i.e., $r_c = \alpha S_{ex}^{-1/3}$. Unfortunately, the AG theory itself does not give any procedure to calculate the proportionality constant (α). However, we have recently proposed a
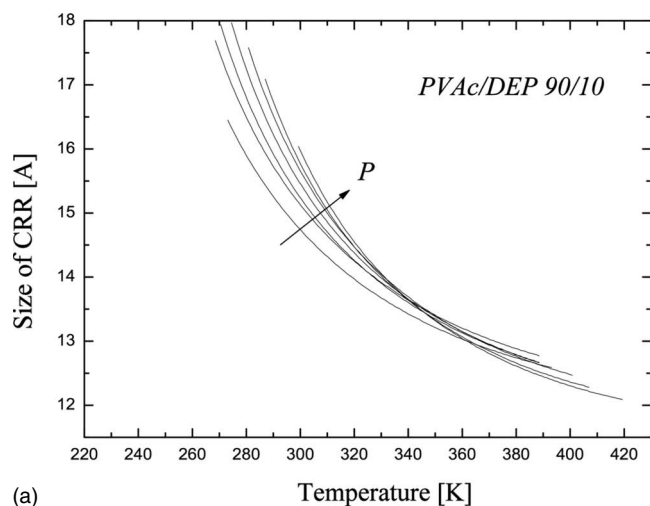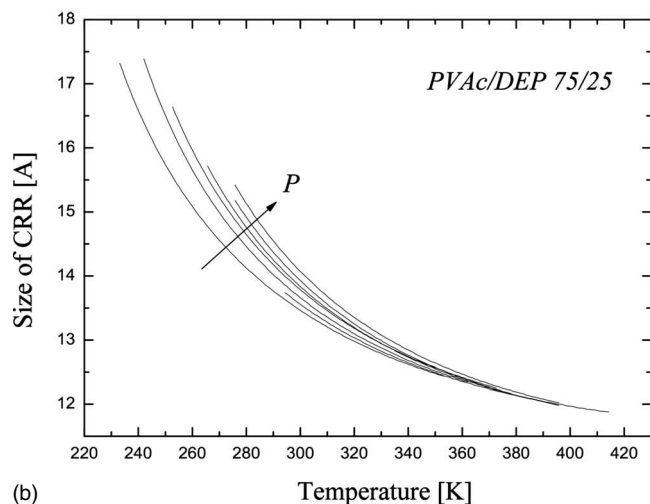
FIG. 10. Size of the CRRs as a function of the temperature at different pressures for (a) PVAc/DEP (90/10) and (b) PVAc/DEP (75/25). Pressure increases from bottom to top.

route to calculate the length scale for the glass transition in pure polymers from this AG extended model for blends.[7,20] For the plasticized polymer, once the parameter α is calculated by fitting the experimental data by means of the here proposed model, the size of the CRR ($2r_c$) can be estimated at any pressure, temperature, and composition. Figures 10(a) and 10(b) show the temperature dependence of the resulting size of the CRR for the two mixtures here analyzed at different pressures. The sizes of CRR so obtained are between 1.2 and 1.8 nm in agreement with those values obtained for PVAc in different environments[20] and for similar glass formers by means of mechanical[30,31] and calorimetric methods.[32,33] The increasing length upon temperature reduction imposed by the AG theory is clearly observed in Figs. 10(a) and 10(b). These figures also show that the effect of temperature on the size of the CRR is significantly more pronounced than that of the pressure. Increasing pressure slightly but systematically increases the temperature dependence of the size of the CRR as previously observed for similar polymers.[8] Finally, it is important to remark that the additional interaction term in the expression of the excess

entropy slightly affects the size of the CRR for interacting mixtures with respect to athermal ones. This difference in the size of the CRR is proportional to $(S_{ex}^{athermal}/S_{ex}^{interacting})^{1/3}$ and depends on temperature. For the temperature range here studied the variation of the size of the CRR is lower than 15% of the corresponding value for athermal mixtures.

IV. CONCLUSIONS

We have reported in this work a systematic study of the dynamics of polymer/plasticizer binary mixtures at different pressures, temperatures, and compositions. We have also analyzed the pressure dependence of the glass transition temperature and fragility for both neat components and mixtures. Moreover, the composition dependences of T_g, m, and ΔV were also analyzed in the present work. Additionally, we have also explored the possibility of modifying the previously developed AG extended model for athermal miscible polymer blends to describe the dynamics of interacting polymer/plasticizer mixtures. We have seen that by adding a single term that accounts for the polymer/plasticizer interactions in the expression for the excess entropy is enough to obtain an excellent description of the experimental relaxation time for the two mixtures here analyzed. The model has only two fitting parameters; the parameter κ and the pressure dependence parameter α. This latter parameter is characteristic of each component and it is expected, as in the case of atmospheric pressure, to be obtained from independent experiments. Finally, as a consequence of using the AG extended model we were able to estimate the pressure-temperature dependence of the size of the relevant length scale (CRR) where the relaxation process takes place.

APPENDIX: THEORETICAL BACKGROUND

We will summarize here the theoretical background concerning to the previously developed[8] AG extended model to

describe the dynamics of athermal miscible polymer blends at different pressures, temperatures, and compositions.

The AG theory relates the increase in structural relaxation time τ to the reduction in configurational entropy S_c by[34]

$$\tau = \tau_o \exp\left(\frac{C}{TS_c}\right), \tag{A1}$$

where τ_o is the value of τ at very high temperature and C is a material constant. Since S_c is not experimentally accessible, it is usually identified with the excess entropy ($S_c \propto S_{ex} = S_{melt} - S_{crystal}$) (this assumption is still under debate[35–37] and is discussed more in details in Ref. 8 and references therein). Thus S_c, at atmospheric pressure, can be estimated as

$$S_C(T) = g_T S_{ex}(T) = g_T \int_{T_K}^{T} \frac{\Delta C_P(T')}{T'} dT', \tag{A2}$$

where $\Delta C_P = C_P^{melt} - C_P^{crystal}$ is the excess heat capacity at atmospheric pressure and T_K is the Kauzmann temperature. If a linear dependence of the type $\Delta C_P = b - m_T T$ is assumed for the temperature dependence of the excess heat capacity, then by integrating Eq. (A2) and replacing in Eq. (A1) we obtain the following temperature dependence for the segmental relaxation time at atmospheric pressure,

$$\tau(T, P \cong 0) = \tau_o \exp\left[\frac{C/g_r}{T(b \operatorname{In}(T/T_K) - m_T(T - T_K))}\right]. \tag{A3}$$

Pressure extension of the AG theory for neat components. Casalini and Roland[3] have included the pressure as an additional experimental variable in the AG theory by adding a new term to the expression of the configurational entropy; thus,

$$S_C(T, P) = g_T \int_{T_K}^{T} \frac{\Delta C_P(T')}{T'} dT' - g_P(T) \int_0^P \Delta\left(\frac{\partial V}{\partial T}\right)_{P'} dP', \tag{A4}$$

where $\Delta(\partial V/\partial T)_P = (\partial V/\partial T)_P^{melt} - (\partial V/\partial T)_P^{crystal}$ is the difference of the thermal expansivity of the melt and the crystal. Additionally, the pressure dependence of $\Delta(\partial V/\partial T)_P$ has been empirically described according to[14] $\Delta(\partial V/\partial T)_P = \Delta(\partial V/\partial T)_{P=0} - A[1 - \exp(-P/P_o)]$ Thus, by replacing this expression in Eq. (A4) and integrating we obtain the pressure-temperature dependence of the segmental relaxation time for neat components,

$$\tau(T, P) = \tau_o \exp\left[\frac{C/g_T}{T\left\{\left[b \ln\left(\frac{T}{T_K}\right) - m_T(T - T_K)\right] - \frac{g_P(T)}{g_T}\left[\Delta\left(\frac{\partial V}{\partial T}\right)_{P=0} P - A\left[P - P_o\left(1 - \exp\left(-\frac{P}{P_o}\right)\right)\right]\right]\right\}}\right]. \tag{A5}$$

Note that most parameters of Eq. (A5) can be obtained from independent experiments: By DSC (b and m_T), by PVT [$\Delta(\partial V/\partial T)_{P=0}$, A and P_o], and by the temperature dependence of the relaxation times at atmospheric pressure [$\log(\tau_o[s])$, C/g_T, and T_K] through Eq. (A3). In this way the only fitting parameter in Eq. (A5) is the ratio $g_P(T)/g_T$ which is obtained from the measurements of the relaxation time at high pressures. This pressure extension of the AG theory has shown to be very accurate and useful to describe the pressure-temperature dependence of the segmental relaxation time in several polymers.[14–16,38,39]

AG in miscible polymer blends. We will summarize here the basic hypothesis of the model we have recently proposed to describe the segmental component dynamics in athermal miscible polymer blends. For a full detailed discussion, see Refs. 6–8. Starting from the AG equation [Eq. (A1)] we assume that for a given component in a miscible polymer blend we can write the temperature dependence of the segmental relaxation time as

$$\tau^{A/\mathrm{blend}}(T,P) = \tau_o \exp\left[\frac{C'^{A/\mathrm{blend}}(T,P)}{TS_{\mathrm{ex}}^{A/\mathrm{blend}}(T,P)}\right], \tag{A6a}$$

Where $\tau^{A/\mathrm{blend}}(T,P)$ is the segmental relaxation time of component A in the blend and τ_o is the same as defined in Eq. (A1) for the same component; $C'^{A/\mathrm{blend}}(T,P)$ and $S_{\mathrm{ex}}^{A/\mathrm{blend}}(T,P)$ refer to regions centered around a segment of polymer A (Ref. 6) and are calculated as

$$S_{\mathrm{ex}}^{A/\mathrm{blend}}(T,P) = \phi_{\mathrm{eff}}^{A} S_{\mathrm{ex}}^{A}(T,P) + (1 - \phi_{\mathrm{eff}}^{A}) S_{\mathrm{ex}}^{B}(T,P),$$

$$C'^{A/\mathrm{blend}}(T,P) = \phi_{\mathrm{eff}}^{A} C'^{A} + (1 - \phi_{\mathrm{eff}}^{A}) C'^{B}, \tag{A6b}$$

with ϕ_{eff} given by $\phi_{\mathrm{eff}} = \phi_s + (1 + \phi_s)\phi$, where ϕ is the macroscopic concentration of the component under consideration and ϕ_s is the self-concentration of the same component which can be calculated as

$$\phi_s = \frac{3 l_k l_p}{2\pi[\alpha(P)]^2}[S_{\mathrm{ex}}^{A/\mathrm{blend}}(T,P)]^{2/3}, \tag{A6c}$$

where l_p and l_k are the packing and Kuhn length, respectively, and α is a proportionality constant between r_c and excess entropy[6] according to

$$r_c(T,P) = \alpha(P)[S_{\mathrm{ex}}^{A/\mathrm{blend}}(T,P)]^{-1/3}. \tag{A6d}$$

This set of equations (A6a)–(A6d) can be exactly solved being α the only unknown fitting parameter. This model has shown to be very accurate to describe the single component dynamics in athermal miscible polymer blends at atmospheric[6,40] as well as at high pressures.[8] See Ref. 8 for more details about the AG extended model.

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