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Fragility in amorphous blends of linear polymers

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Abstract
By analysing the specific heats and the mechanical characteristics of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) amorphous single-state blends in the glass transition region, it has been found that increasing PVDF content causes a small reduction of the fragility of these systems. The degree of fragility has been evaluated from $\Delta C_p / C_{p,l}$, the normalized change of the heat capacity at T_g, and by modelling the mechanical α_a-relaxation. The observed behaviour has been ascribed to a more coherent structure of the blends due to strong specific interactions between PMMA and PVDF polymeric chains.

1. Introduction

According to a wealth of experimental evidence currently available (e.g., [1, 2]), the dynamics of molecular motion in glass-forming substances is controlled by the relative distance to the glass transition temperature T_g as represented by a corresponding reduced (dimensionless) temperature T/T_g. It is generally assumed [2] that in the course of a continuous cooling from the high-temperature domain ($T/T_g \gg 1$) through the intermediate-temperature domain ($T/T_g \geqslant 1$), an initially homogeneous liquid tessellates into regions characterized by basically different mobilities of relevant kinetic units. In this context the concept of fragility was introduced by Angell [3] in order to classify glass-forming liquids according to their structural behaviour through the glass transition region, quantified by the transport properties. According to this classification, strong liquids, characterized mainly by covalent bonds, exhibit an Arrhenius dependence of the viscosity over broad ranges of temperature, while 'fragile' liquids display pronounced deviations from that behaviour. The latter are substances with non-directional interatomic or intermolecular bonds whose structures undergo the phase change at

T_g showing relevant variations in the molecular aggregation. From a thermodynamic point of view, strong liquids (such as SiO_2) show small differences in heat capacity, ΔC_p, between liquid and glass at T_g, contrasting with the large changes exhibited by fragile systems. Besides the consideration of the temperature dependence of the viscosity and the change in heat capacity at T_g as a manifestation of fragility, the link between different measures of fragility obtained by various spectroscopies operating in a linear response regime has been explored [4]. It has been found that, within a very general context including a wide number of inorganic and organic glass-forming liquids, the values of fragility given by different techniques appear to agree with each other. More recently, Colucci and McKenna [5] revealed a dependence of the fragility values on the experimental probe in some polymers: using the ratios of the liquid to the glassy heat capacities $C_{p,l}/C_{p,g}$, polyvinylchloride (PVC) proved to be more fragile than polycarbonate (PC), while viscosity and thermal expansion data set PC as more fragile than PVC. On the other hand, using the changes ΔC_p in the heat capacities at T_g normalized by the molecular weight M_0 as a measure of the fragility, an overall agreement between the results obtained by the various techniques was found. These contrasting evaluations of fragility in the same polymer certainly reflect differences in the coupling between the various experimental probes and the internal degrees of freedom driving the structural rearrangements of large molecular groups. The discrepancies revealed in the fragility determinations indicate that the description of cooperative relaxations in polymers within the fragility framework needs to be more deeply explored before discussing the relaxation dynamics of polymers within a more general context including inorganic glass-forming liquids. Clarification of this question requires extensive wide-ranging studies of polymer systems. Since amorphous blends of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) show homogeneous single-state structures characterized by locally heterogeneous relaxation and vibrational dynamics [6], they were chosen for investigation to provide further insight into the link between fragility and the structural rearrangements of large molecular groups. The fragility has been quantified by analysing behaviours obtained by two different experimental techniques, differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). In the former case the fragilities have been determined from the magnitudes of the normalized heat capacity jumps at T_g and in the latter by modelling the mechanical α_a-relaxation. Both the experimental approaches indicate a fragility which decreases with increasing PVDF content. Furthermore, it has been found that the observed trend parallels a corresponding small increase of the low-temperature excess specific heat, apparently in accord with the hypothesis of a correlation between fragility and the additional low-energy vibrations.

2. Experimental details

The neat polymers, PMMA ($\langle M_n \rangle = 500$ kg mol^{-1}, $\langle M_z \rangle / \langle M_n \rangle = 1.59$) and PVDF ($\langle M_n \rangle = 550$ kg mol^{-1}, $\langle M_z \rangle / \langle M_n \rangle = 2.92$), and the binary blends with PMMA/PVDF weight ratios of 80/20 and 60/40 were the same as those used in our previous studies [7, 8]. The specific heat capacities in the temperature region around the glass transition, previously determined by two different calorimetry instruments [6], were again measured by a more sensitive Perkin-Elmer PYRIS1 differential scanning calorimeter (temperature interval: 280–450 K; heating rate: 10 K min^{-1}). Small pieces of each polymer, of mass approximately 15 mg, were encapsulated in aluminium pans and subjected to the same thermal cycles in the calorimeter. Temperature scale calibrations using indium were performed daily. In the overlapping temperature intervals, the data from all instruments agreed to within 5%. Specific heat capacities C_p in the interval 2–40 K were measured (maximum error below 2%) in steps of 0.2–0.4 K with an automated adiabatic calorimeter [9].

Table 1. Physical characteristics of PMMA/PVDF blends.

Sample	ρ (kg m^{-3})	T_g (K)	$\Delta C_p/C_{p,l}$	m	β	B (K)	T_0 (K)	v_D (m s^{-1})	θ_D (K)	(C_D/T^3) (μJ g^{-1} K^{-4})
PMMA	1190	362	0.207	145[a]				1719	244	20.07
PMMA/PVDF = 80/20	1304	352	0.199	136	0.48	3394	234	1706	244	18.74
PMMA/PVDF = 60/40	1410	337	0.187	126	0.40	3027	219	1695	254	17.83

[a] Value taken from [4].

The velocities of longitudinal (v_l) and transverse (v_t) sound waves at room temperature were measured at a frequency of 2 MHz by a custom-made acoustic spectrometer.

The real and imaginary parts of the complex mechanical modulus, $E^* = E' + iE''$, were determined in the 120–400 K temperature range and at selected frequencies between 0.3 and 30 Hz by using a dynamic mechanical thermal analyser (DMTA) from Polymer Laboratories. The samples were tested in a configuration of double cantilever driven in bending mode with a fixed displacement (±16 μm). A heating rate of 2 K min^{-1} was employed over the whole temperature range.

In order to avoid undesired effects arising from different conditions of physical ageing on the intensities of the observed mechanical relaxations, all the samples were aged for two days at about 10 K below their T_g and then cooled and stored at room temperature.

3. Results and discussion

The specific heat capacities, obtained from DSC traces between 250 and 450 K for pure PMMA and PMMA/PVDF = 80/20 (the C_p-data for the PMMA/PVDF = 60/40 blend were omitted for the sake of clarity), are reported in figure 1(a). They show the usual sigmoidal change characterizing the transition from a glassy to a liquid-like phase. The specific heat capacities in the glassy ($C_{p,g}$) and liquid ($C_{p,l}$) regions, and also the heat capacity jumps ΔC_p ($=C_{p,l} - C_{p,g}$), were evaluated by horizontal extrapolations of the glassy and liquid asymptotes. The values of the dimensionless ratio $\Delta C_p/C_{p,l}$ for the polymers investigated (included in table 1) show a moderate but well-defined trend to decrease with increasing PVDF content and are indicative of a decreasing fragility of the blends. Following Angell's indications and the results of extensive studies [3, 10, 11], in fact, the change in heat capacity ΔC_p at the glass transition is related to the strong/fragile character of a glass-former, the strongest system displaying the smallest value of ΔC_p (with very few exceptions ascribed to particular kinds of structural reorganizations at T_g [4]).

Besides the change in heat capacity ΔC_p, an alternative measure of the degree of fragility in these polymers can be obtained from the temperature behaviours of the dynamic complex modulus in the region of the glass transition.

The temperature dependence of E'' for the PMMA/PVDF blend with a 80/20 ratio at selected frequencies is reported in figure 1(b). With temperature increasing from 120 K, E'' shows three relaxation peaks, which shift to higher temperatures with increasing driving frequency. The effect of increasing PVDF content on the characteristics of the observed relaxations is illustrated in figure 1(c). The relaxation peak, located at about 191 K (at a frequency of 3 Hz) for both blends, exhibits a linearly decreasing strength with decreasing PVDF content and arises from the contributions of the γ-relaxation within the PVDF amorphous chains [6]. The relaxation peak, located at about 285 K (at a frequency of 3 Hz) for
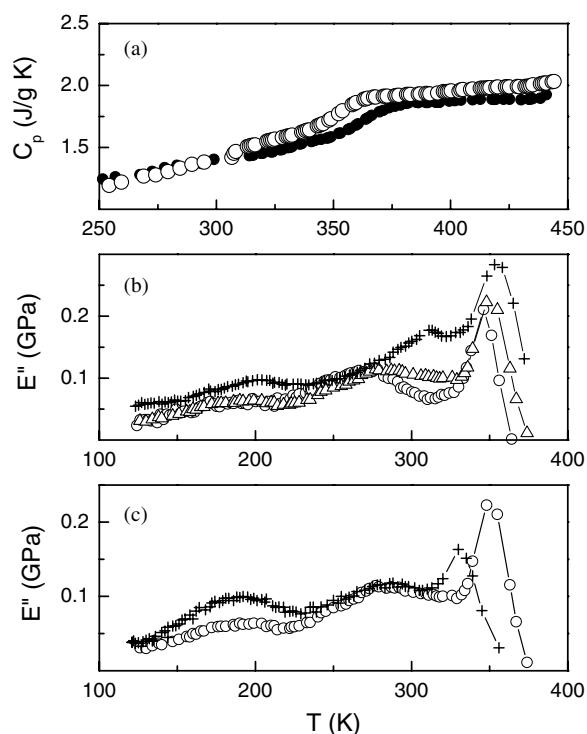
Figure 1. (a) Specific heat capacities of PMMA (●) and PMMA/PVDF = 80/20 (○) in the glass transition region; (b) the effect of a driving frequency (○: 0.3 Hz; △: 3 Hz; +: 30 Hz) on the temperature dependence of the imaginary part E'' of the complex mechanical modulus in 80/20 PMMA/PVDF blend; (c) comparison of $E''(T)$ of PMMA/PVDF blends at a frequency of 3 Hz: PMMA/PVDF = 80/20 (○); PMMA/PVDF = 60/40 (+). The continuous curves are only guides for the eyes.

both samples, exhibits a strength suffering a 'β-suppression' effect with decreasing PMMA content [6]. It arises from the contributions of the β-relaxation within the PMMA chains and is associated to the local motion of –OCOCH$_3$ side groups. The peaks of E'' at the highest temperatures are associated with the main transition (α_a-relaxation or the mechanical T_g); the occurrence of a single glass transition in both blends is consistent with our earlier claim for their single-phase state. The mechanical T_g decreases with decreasing PMMA content (the component with the highest T_g), as a consequence of the dilution effect due to the PVDF (the component with the lowest T_g) addition which softens the constraints on the overall long-range segmental motion.

Small inflections followed by well-defined non-linear drops (in both blends by about two decades) in the Young modulus E' are observed in the regions of temperatures where E'' exhibits the secondary and primary relaxation peaks; figure 2(a). The drops move to higher temperatures with increasing frequency as a consequence of the inherent dispersion.

Now the temperature dependence of E' has been used to determine the parameter β which accounts for the non-exponentiality of the α_a-relaxation. The product $(\omega\tau)_M$ of the angular frequency ω and the relaxation time τ has been estimated by the values of β at the temperature at which E'' has its maximum value. This procedure is necessary because $(\omega\tau)_M$ is equal to 1 only for a Debye or single-relaxation-time process [12]. Considering the curves of $E''(T)$ at
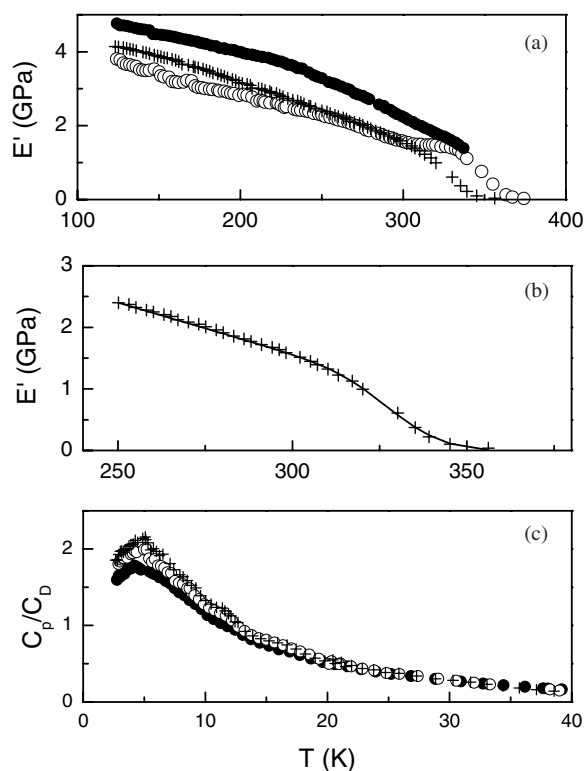
Figure 2. (a) Temperature dependences of the dynamic modulus E' at a driving frequency of 3 Hz in PMMA/PVDF blends: PMMA (●); PMMA/PVDF = 80/20 (○); PMMA/PVDF = 60/40 (+); (b) the theoretical fit (solid curve) by equation (2) of the temperature behaviour of E' for the 60/40 PMMA/PVDF blend, where the mechanical frequency is 3 Hz; (c) temperature dependences of C_p/C_D for PMMA (●), PMMA/PVDF = 80/20 (○) and PMMA/PVDF = 60/40 (+).

different frequencies, the behaviour of the average relaxation time $\langle\tau\rangle$ in a temperature range above T_g is derived and the fragility m can be calculated using the relation [4]

$$m = \frac{\mathrm{d}\log\langle\tau\rangle}{\mathrm{d}(T_g/T)}\bigg|_{T=T_g}. \tag{1}$$

To reproduce $E'(T)$ in the region of the α_a-relaxation we use the same approach as described elsewhere [13], where $E'(\omega, T)$ is given by the relation

$$E'(\omega, T) = [E'_{T'_0} - b'(T - T'_0)]_{anh} + \left[E'_\infty + \delta E' \int \frac{\mathrm{d}\phi(t)}{\mathrm{d}t}\cos(\omega t)\,\mathrm{d}t\right]_{rel}. \tag{2}$$

The first term in the right-hand side of equation (2) represents the temperature dependence of the Young modulus due to the vibrational anharmonicity. $E'_{T'_0}$ is the value of E' at the lowest temperature T'_0 in the experiment and the parameter b' is mainly determined by the Grüneisen coefficients which account for the anharmonic interactions between the vibrational modes.

The relaxational term of equation (2) is used to describe the α_a-relaxation, whose marked non-exponentiality is evaluated by the 'stretched exponential function' of Kolrausch, Williams and Watts (KWW), $\phi(t) = \exp(-(t/\tau)^\beta)$, where β is the stretching parameter ranging in the interval $0 < \beta < 1$. $\delta E' = (E'_\infty - E'_0)$ is the relaxation modulus and E'_∞ and E'_0 are the high- and low-frequency limits for the modulus, respectively. The structural relaxation time

τ has been assumed to follow a Vogel–Tammann–Fulcher (VTF) temperature dependence, $\tau = \tau_0 \exp(B/T - T_0)$, where τ_0, B and T_0 are empirical constants. The behaviours of $E'(T)$ at different driving frequencies have been analysed using equation (2), in a least-squares fit using a minimum search program with $\delta E'$, β, B and T_0 as free parameters. To reduce the number of fitting parameters, a fixed value of 3.1×10^{-14} s has been used for τ_0, this value setting the short-time limit of the structural relaxation time in Angell's plot for polymers [14]. Furthermore, the anharmonicity parameter b' was directly evaluated through the slope of $E'(T)$ in the glassy region, where the dispersion due to the secondary relaxations does not affect the linear trend of the modulus. The parameters resulting from this analysis are given in table 1. The good quality of the data fit can be assessed from figure 2(b). As a consequence of the restricted temperature range above T_g, the average relaxation time $\langle \tau \rangle$ follows an Arrhenius behaviour: the fragility can be calculated using the relation $m = E_A/(RT_g \ln 10) = -\log\langle \tau_A \rangle + \log\langle \tau_g \rangle$, where E_A is the apparent activation energy of the process, $\langle \tau_A \rangle$ is the prefactor of the Arrhenius expression and $\langle \tau_g \rangle = \tau(T_g)$ is usually taken as equal to 100 s [4].

It turns out that, in agreement with the behaviour of $\Delta C_p/C_{p,l}$, the fragility tends to decrease in PMMA/PVDF blends (see table 1) as the PVDF content becomes higher.

Since pure PMMA and PMMA/PVDF blends with a ratio equal to or higher than 1.5 are wholly amorphous, it is expected that the m-trend should parallel a corresponding increase of the low-temperature C_p scaled to the Debye contributions C_D. In fact the dynamics of a glass-former at the glass transition is expected to influence the low-energy vibrational aspect of the glass [15], the strongest glass-former showing the highest excess of low-temperature specific heat over that provided by the Debye theory.

The experimental results obtained for the specific heat, plotted as C_p/C_D, for pure PMMA and PMMA/PVDF binary blends between 2 and 40 K are shown in figure 2(c). The low-temperature specific heats deviate markedly from a cubic temperature dependence and reveal an excess specific heat having the shape of a well-defined peak with a maximum at about $T_b = 4.4$ K in both PMMA and the blends. Unlike C_p, which does not depend on the composition in the temperature range explored [6], the ratio C_p/C_D shows a slight increase with increasing PVDF content. The values of C_D have been obtained from the elastic Debye temperatures θ_D (see table 1), evaluated from the average Debye sound velocities ($v_D^{-3} = (v_l^{-3} + 2v_t^{-3})/3$, also reported in table 1) extrapolated to 0 K by using the room temperature values of v_l and v_t and the same temperature coefficients of PMMA [6]. Of course, a more accurate evaluation of C_p/C_D would require the use of the sound velocities measured at temperatures close to 0 K, but it is believed that the values obtained by extrapolation should be not significantly different from them for the following reasons:

(i) the room temperature is well below the glass transition region of these blends where large variations of the sound velocity are usually observed;

(ii) the secondary relaxations below 300 K do not appear to cause relevant deviations from a nearly linear temperature behaviour of the Young modulus; furthermore, the temperature coefficient is only slightly affected by blending—see figure 2(a).

A confirmation of the previous considerations is given by the values of v_l and v_t experimentally measured at 4.2 K for pure PMMA ($v_l = 3150$ m s^{-1} and $v_t = 1570$ m s^{-1} [16]) which are quite close to those obtained by a linear extrapolation [6].

The slight increase of C_p/C_D parallels the moderate reduction of m, the strongest polymer among those examined (PMMA/PVDF = 60/40) showing the largest value of C_p/C_D. Within the uncertainty due the approximate evaluation of C_D, these results seem to be consistent with the prediction [15] which ascribes a growing excess of soft vibrations causing the excess low-temperature specific heat to increasingly stronger systems.

The decrease of m in PMMA/PVDF blends can be explained within the fragility framework: the term 'fragility', in fact, describes the inability of glass-former liquids to preserve the short- and medium-range order against the thermal degradation. It is believed that the revealed trend reflects the decreasing number of internal degrees of freedom characterizing the mechanisms driving the structural rearrangements of large molecular groups in blends, as compared to pure PMMA. The system resulting on blending, as a whole, tends to assume a more coherent structure whose resistance to the thermal degradation is gradually increased with increasing PVDF content, as a consequence of strong specific interactions between PMMA and PVDF. These interactions have been assumed to be responsible for the apparently single-phase state (Flory–Huggins parameter $\chi < 0$) and for the positive excess volume of mixing of the blends for PMMA/PVDF ratios above 50/50 [17].

4. Conclusions

Summarizing, we have presented specific heat capacity and mechanical data for PMMA/PVDF amorphous blends in order to study their fragility. Single calorimetric and mechanical glass transitions are observed in the blends, indicating an affinity between PMMA and PVDF and also a large-scale structural homogeneity. Increasing the amount of PVDF relative to that of PMMA leads to a small but well-defined decrease of the fragility as measured both by ΔC_p at T_g and by the parameter m, determined using mechanical modulus measurements in bending mode. The specific interactions between PMMA and PVDF chains, which give rise to the single-phase state of these blends, have been assumed as responsible for their decreasingly fragile character. Finally, it has been revealed that the decreasing fragility parallels a small increase of the low-temperature excess specific heat C_p/C_D of the blends.

Acknowledgment

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