

Plasticity of polystyrene–poly(2,6,dimethyl,1,4,phenylene oxide) blends

Costantino Creton*, Jean-Louis Halary, Lucien Monnerie

Laboratoire de Physico-Chimie Structurale et Macromoléculaire, URA C.N.R.S. 278, ESPCI, 10 Rue Vauquelin, 75231 Paris, Cedex 05, France

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Abstract

The temperature and strain-rate dependence of the plastic yield in compression of blends between polystyrene (PS) and poly(2,6,dimethyl 1,4,phenylene oxide) (PPO) are investigated. The salient result of our study is that an amount as small as 2 wt% of PPO can significantly lower the yield stress and elastic modulus of pure PS. This result is interpreted as being due to the creation of favourable nucleation sites for the onset of plastic deformation. The plastic flow stress, however, is unaffected by this small addition. When plotted at a constant $T - T_g$ our results show a nearly constant yield stress from 2% up to ca. 40 wt% PPO. At this point the yield stress starts to decrease and the activation volume increases, implying a more co-operative character of the plastic deformation mechanisms. This transition corresponds also to a change from more brittle to more ductile behaviour in tensile experiments. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Despite being the subject of ongoing investigations for more than 20 years, detailed understanding of the molecular parameters controlling the plastic deformation and the failure mechanisms of glassy structural polymers has proved an elusive goal. The experimental as well as theoretical advances in that area fall into two broad categories.

In the first category are the explanations based on the chemical structure of the monomer and of its close neighbouring units. These factors determine the local chain packing and directly determine the sub- T_g relaxations. They presumably also determine the yield behaviour in compression and in some cases have an influence on the macroscopic fracture toughness in tension.

In the second category are the explanations based on topological and chain parameters such as the molecular weight, molecular weight between entanglements or degree of branching and/or cross-linking. These parameters have an important influence on the rheological properties of polymer melts and, in glassy polymers, on the preferred fracture mechanism when a hydrostatic negative pressure is present (in a tensile test). They do not appear to be important in a compressive test.

If local segmental motion under stress indeed plays an important part in the onset of plastic deformation, it is tempting to postulate that the information needed to understand the

fracture toughness of glassy polymers in tension can be obtained from its dynamic mechanical behaviour and its behaviour in compression, where crazing is suppressed.

The experimental system which we have chosen to investigate is the miscible blend of polystyrene (PS) and poly(2,6,dimethyl-1,4,phenylene oxide) (PPO). Their deformation and fracture properties in tension have been thoroughly investigated [1–3] and the results can be summarized as follows: at high PS content, the blend deforms mainly by crazing and subsequently fails by brittle fracture, while at high and medium PPO content the polymer fails by shear yielding in a ductile manner. This transition is consistent with the gradual increase of the average molecular weight between entanglements M_e from pure PPO to pure PS, as argued by Donald and Kramer [4]. We will explore in detail in this paper the stress and temperature dependence of the yield behaviour of these blends.

2. Experimental

2.1. Materials

The PS was provided by Atochem and had an average molecular weight \bar{M}_w of 200 000 and a polydispersity of approximately 2.2. The poly(2,6,dimethyl,1,4,phenylene oxide) (PPO) was provided by General Electric and had an average estimated molecular weight \bar{M}_w of 50 000 and a polydispersity of 2.

* Corresponding author.

2.2. Compression

The samples for the compression tests were compression molded at $T_g + 70^\circ\text{C}$ and subsequently cut with a diamond saw to a parallelepipedic shape of $3 \times 3 \times 6 \text{ mm}^3$. Prior to testing, the samples were conditioned for 24 h at $T_g + 10^\circ\text{C}$ and quenched to erase any previous thermal history.

The compression tests were performed on a MTS 810 hydraulic testing machine at a constant crosshead speed. The crosshead speed could be varied in order to provide a nominal strain rate of $\dot{\epsilon} = 2 \times 10^{-5} - 2 \times 10^{-1} \text{ s}^{-1}$. All tests were performed inside an environmental chamber, the temperature of which could be regulated from $T = -100$ to 220°C with a precision of $\pm 1^\circ\text{C}$. No lubrication between the sample and the compression plates was used but the surface of the plates was treated with a non-stick coating which reduced friction.

2.3. Dynamical mechanical testing

The dynamical mechanical tests were performed on a MTS 831 viscoelasticimeter. The bars were compression molded to a size of $3 \times 15 \times 70 \text{ mm}^3$ and were tested dynamically at a frequency of 1 Hz with a fixed offset of 0.1% in compression and a dynamic amplitude (peak to peak) of 0.1% in order to remain in the linear viscoelastic regime.

2.4. Blend preparation

About 500 g of each of the 80/20, 60/40, 40/60 and 20/80 PS/PPO blends were prepared on a Haake laboratory extruder and were extruded at 300°C . (N.B. In the text, the blends are referred to as a/b where a refers to the weight fraction of PS. Since it is customary for polymer blends to use mole fractions, we give the conversions in Table 1). The resulting pellets were then compression molded into samples suitable for the dynamical mechanical tests and the compression tests. The 90/10, 95/5 and 98/2 PS/PPO blends were prepared by mixing pure PS to the 80/20

blend in a KAP Protoject laboratory injection molder, which allowed us to mix and inject 200 g of each material into small bars. These bars were then annealed at $T_g + 50^\circ\text{C}$ for 2 h to remove any residual chain orientation. The blends were characterized by DSC and all showed a single glass transition temperature.

In the glass transition region, the dynamical mechanical spectra of the blends also showed a single mechanical relaxation T_α , as determined by the maximum of the E'' peak. With the exception of the 20% PS and 40% PS, good agreement was found between the T_g values determined at the onset of DSC traces recorded at a heating rate of $10^\circ\text{C min}^{-1}$ and the T_α values, at the frequency of 1 Hz (see Table 1).

3. Results

3.1. Elastic modulus and secondary transitions

Both PS and PPO do not have any marked mechanically active sub- T_g relaxations in the temperature range investigated (-80°C to 210°C). The literature reports a small shoulder in the T_g peak of PS which is attributed to the motion of the phenyl ring. For PPO, the distribution of activation energies for the sub- T_g motions is very broad and produces a broad peak over a very large temperature range¹. These features are indeed found in our measurements of the tensile loss modulus E'' of the blends, shown in Fig. 1a.

The results for the storage modulus E' of the two polymers are shown for several blends in Fig. 1b and illustrate the monotonic increase of the low temperature storage modulus from the lowest value for the PPO to the highest value for PS. These results are in general agreement with literature values [1,2]. If the results are analysed, a function of a reduced temperature $T - T_g$, which takes into account the difference in T_g of the blends, the softening effect of PPO is much more evident, as shown in Fig. 2.

It is interesting to note at this point that, for this polymer pair, the glass transition temperature and the elastic modulus are clearly not due to the same molecular features, since the polymer with the higher T_g has the lower elastic modulus.

A possible explanation is obtained by calculating the Van der Waals volume (the volume occupied by the electron clouds) of each monomer and dividing it by its molar volume. This ratio gives an indication of the degree of compactness of the structure. Using the values of Bondi

Table 1
Glass transition temperatures of the PS/PPO blends as measured by DMA (1 Hz) and by DSC ($10^\circ\text{C min}^{-1}$)

Name	wt %PS	mol %PS	T_g DSC $10^\circ\text{C min}^{-1}$	T_α DMA 1 Hz
PPO	0	0	214	216
20/80	20	22.4	176	189
40/60	40	43.5	154	162
60/40	60	63.3	137	138
80/20	80	82.2	118	120
90/10	90	91.2	113	115
95/5	95	95.6	109	110
98/2	98	98.2	107	107
PS	100	100	105	105

¹ Given the large difference in the T_g of the blends, we feel that the composition dependence of the yield stress and of the modulus should also be analysed as a function of a variable of reduced temperature which would decouple the effect on the T_g from the effect on the yield behaviour. In this study we chose to use $T - T_g$ as a reduced temperature although T/T_g is also commonly used. In our case, however, the choice of one or the other reduced variable did not change our qualitative conclusions as illustrated by the comparison of Fig. 2a and Fig. 2b for the storage tensile modulus E' .

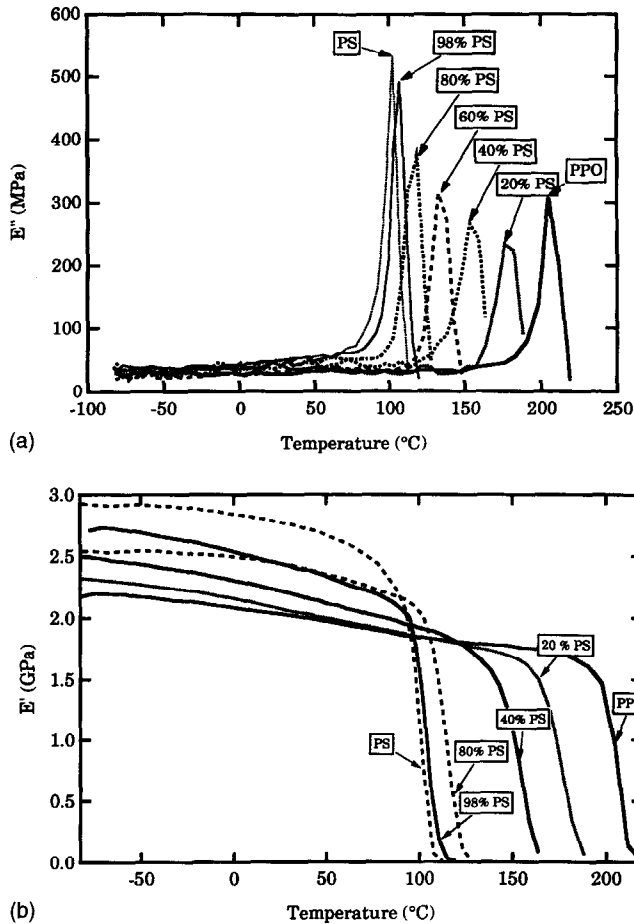


Fig. 1. Dynamic mechanical modulus of the PS/PPO blends at a frequency of 1 Hz. (a) E'' ; and (b) E' .

for the contributions of the functional groups [5], such a calculation gives a value of 0.614 for the compactness of PPO and 0.635 for PS. This difference is significant and is consistent with PPO having a less compact structure which could explain a lower elastic modulus. On the other hand, the presence of a phenyl ring in the main chain of a polymer is known to decrease the chain's mobility and therefore increase its T_g .

The elastic modulus is expected to depend on very local packing characteristics of the amorphous polymer, while the glass transition is related to the interchain and intrachain cooperative mobility of several chain repeat units and therefore depends on the main chain flexibility.

3.2. Yield stress and plastic flow stress in compression

A typical compression test of a glassy polymer exhibits first an elastic regime, where the nominal stress increases linearly with applied strain. Then a curvature is observed in a slightly viscoelastic regime and above a certain point the increase becomes strongly non-linear and the stress reaches a maximum, usually defined as the yield stress σ_y . If the polymer is strained further, the stress generally decreases

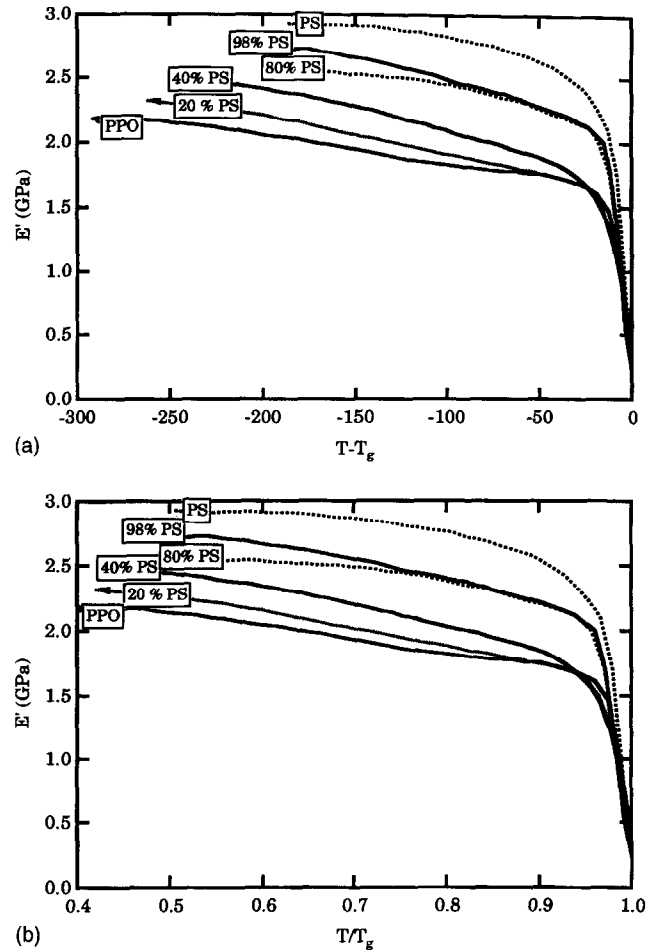


Fig. 2. Elastic moduli as a function of the reduced temperature. (a) Dynamic mechanical measurements at 1 Hz (E') as a function of $T - T_g$; (b) Dynamic mechanical measurements at 1 Hz (E') as a function of T/T_g .

and becomes constant at a lower level, generally called the drawing stress or the plastic flow stress σ_{pf} . The difference between σ_y and σ_{pf} will also be examined in this study and defined as the stress softening amplitude (SSA). An illustration of all these parameters on a typical stress-strain curve is given in Fig. 3.

3.3. Temperature dependence

The effect of changing the temperature on the yield behaviour of the PS/PPO blends is illustrated in Fig. 4 for the 80% PS blend. Both yield stress and plastic flow stress decrease with temperature.

The results for σ_y and σ_{pf} for the blend series as a function of temperature are summarized in Fig. 5. One should note from these results that for all blends investigated, σ_y and σ_{pf} decrease nearly linearly with temperature so that the SSA remains approximately constant, except near the glass transition temperature. No change in slope, which could be related to the activation of a secondary transition, is observed consistent with the dynamic mechanical spectroscopy results.

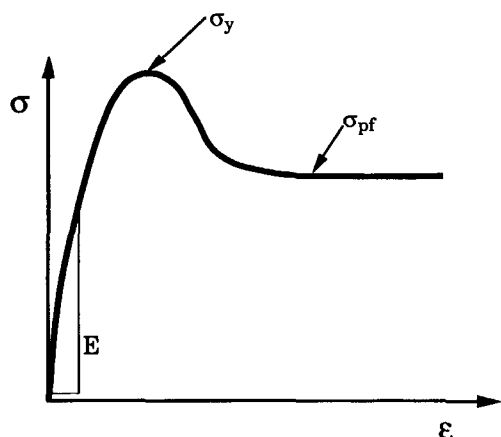


Fig. 3. Schematics of a typical stress–strain curve of a PS/PPO blend.

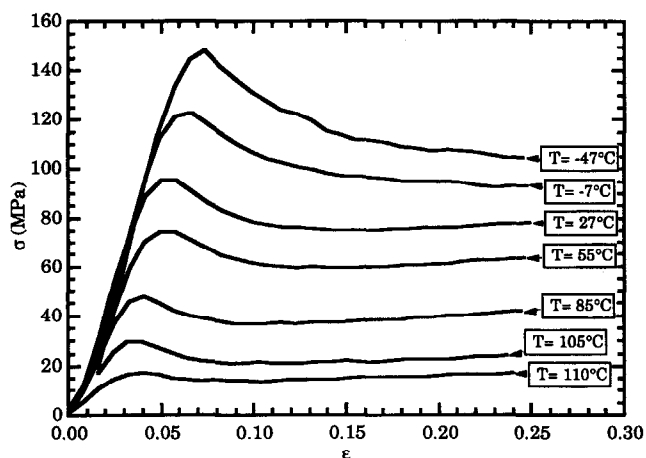


Fig. 4. σ versus ϵ for the 80/20 blend at different test temperatures.

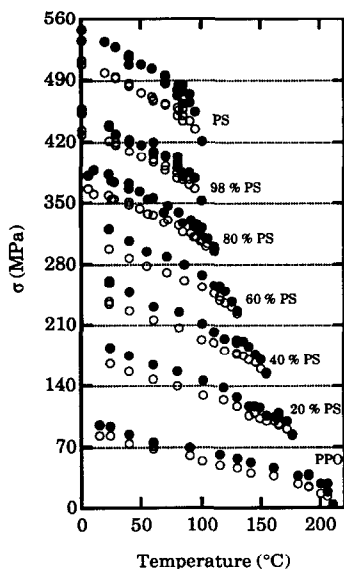


Fig. 5. σ_y (●) and σ_{pf} (○) as a function of temperature for several blends. Except for the PPO, the curves have been shifted vertically by multiples of 70 MPa for the sake of clarity.

An important feature of this experimental system is the very large difference in glass transition temperatures between PS and PPO which makes it difficult to compare the effect of the local chemical structure on the yield behaviour relative to its effect on the change in T_g . Previous results on the yield stress of PS/PPO mixtures compared at a fixed temperature, showed a maximum in yield stress at an intermediate composition between pure PS and pure PPO [2]. The occurrence of this maximum was interpreted as a sign of strong intermolecular interactions which therefore increased the yield stress.

We argue here that this observed maximum can be interpreted as the superposition of two effects: one chiefly responsible for a change in co-operative molecular mobility and therefore for the increase in T_g , and another effect more connected with local packing, which decreases monotonically (albeit not linearly) the energy barrier for yield, in going from pure PS to pure PPO.

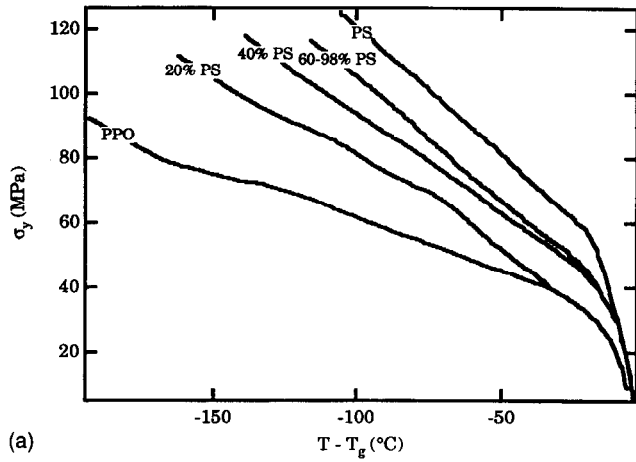
This argument becomes clear if the results are plotted as a function of the reduced temperature ($T - T_g$). This representation shown in Fig. 6 does reveal several features possibly related to molecular interactions.

Both σ_y and of σ_{pf} decrease monotonically with an increasing amount of PPO in the blend. However, near the PS side of the phase diagram, σ_y decreases markedly, even with a 2% addition of PPO and then remains nearly constant until about 40% PPO. This is not the case of σ_{pf} which remains relatively constant from pure PS to about 60% PPO. The shaded area in Fig. 6b corresponds to a regime where no clear differences or trends between the blends are apparent.

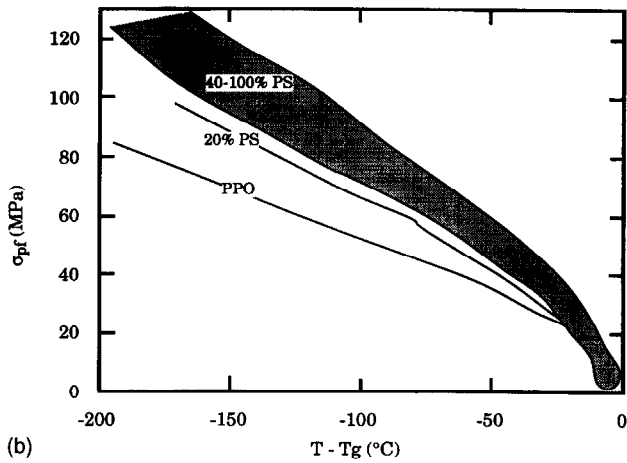
The PPO side of the curve has not been investigated in as much detail but clearly the PPO has a much lower σ_y and σ_{pf} than the blends.

The variation of the strain softening amplitude (SSA), despite a considerable scatter in the data, shows a very distinctive behaviour of pure PS and pure PPO relative to the blends, implying that a small fraction of either polymer will have important effects on the yield behaviour.

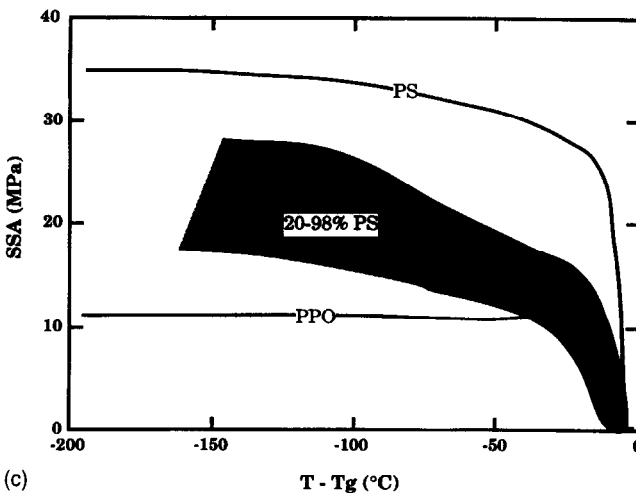
It is interesting to compare the variation in the yield parameters with composition (given here as mole %). As shown in Fig. 7a, at 25°C, after an initial decrease of σ_y and E with a small addition of PPO, both σ_y and σ_{pf} show a maximum for about 60 mol% PPO in agreement with previous studies [2,3]. The elastic storage modulus does not, however, show such a maximum in our experiments but decreases monotonically from 2% PPO to pure PPO. On the other hand, at a fixed $T - T_g$, it is apparent from Fig. 7b that the variation in yield stress closely parallels that of the storage modulus, while σ_{pf} does not show the marked decrease with a small addition of PPO but rather decreases slowly until about 60 mol% PPO. When the amount of PPO is increased beyond 60 mol% a change in slope occurs, resulting in a sharper decrease in yield and plastic flow stresses, storage modulus and SSA. It has been argued by Tordjeman et al. [6] that the SSA was related to the ductility of a given glassy polymer, a low SSA indicating a more ductile behaviour.



(a)

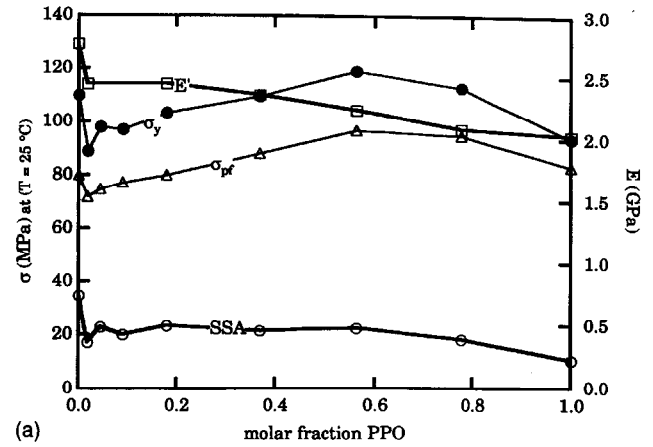


(b)

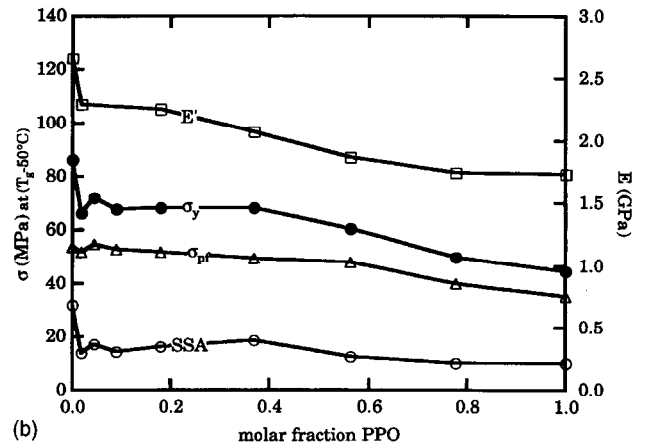


(c)

Fig. 6. (a) σ_y As a function of $T - T_g$ for several PS/PPO blends. The results for 60–98% PS are not really distinguishable within the experimental uncertainty. (b) σ_{pf} As a function of $T - T_g$ for several PS/PPO blends. (c) Stress softening amplitude ($SSA = \sigma_y - \sigma_{pf}$) as a function of $T - T_g$. The results in the shaded area (for 40–100% PS in the case of σ_{pf} and 20–98% PS for the SSA) are not really distinguishable within the experimental uncertainty.



(a)



(b)

Fig. 7. Storage modulus E' , yield stress σ_y , plastic flow stress σ_{pf} and strain softening amplitude (SSA) as a function of the molar fraction of PPO: (a) at 25°C; and (b) at $T_g - 50^\circ\text{C}$.

This trend is confirmed by our observations on the PS/PPO blends.

3.4. Strain-rate dependence

Unfortunately, probably because of the brittle nature of the polymers investigated, it was impossible to obtain a reliable value of plastic flow stress at the lower temperature (-20°C) regardless of the composition and strain rate. We present here therefore the results of the strain-rate dependence of the yield stress only.

The onset of plastic deformation in glassy polymers can be seen as a thermally and stress-activated process. In that framework, following the classical Eyring treatment one can write:

$$\dot{\epsilon} = \exp\left(\frac{-\Delta E}{kT}\right) \exp\left(\frac{V_0 \sigma}{kT}\right) \quad (1)$$

where $\dot{\epsilon}$ is the strain rate, ΔE is the activation energy and V_0 is the activation volume. One should note that for meaningful comparisons, the structure of the polymer, i.e. the amount of free volume, must be kept constant. This requirement implies that the degree of physical aging must be the

same for all materials. This is difficult to achieve in the case of blends but in our experiments we tried to use a consistent sample conditioning method, as described in the experimental section. Physically ΔE and V_0 are indicative of the temperature and stress sensitivity of a given glassy polymer. In addition, a molecular interpretation can be given to V_0 as the volume of polymer segments which must move as a whole for plastic deformation to occur, indicating therefore the degree of co-operativity involved in the plastic deformation process. In that framework the plastic deformation process in a polymer with a large activation volume would have a more co-operative character.

Experimentally we investigated the strain-rate dependence of the yield stress of nine PS/PPO blends in compression by performing a series of experiments at four different temperatures and at five different strain rates. The temperatures were: -20°C , 25°C , 80°C and $T_g - 50^\circ\text{C}$ and the nominal strain rate was varied from $\dot{\epsilon} = 2 \times 10^{-5} \text{ s}^{-1}$ to $\dot{\epsilon} = 2 \times 10^{-1} \text{ s}^{-1}$. The strain rate dependence in the Eyring framework is best illustrated in a plot of σ_y/T as a function of $\log \dot{\epsilon}$. If the activation volume remains constant over the range of strain rates investigated, one expects

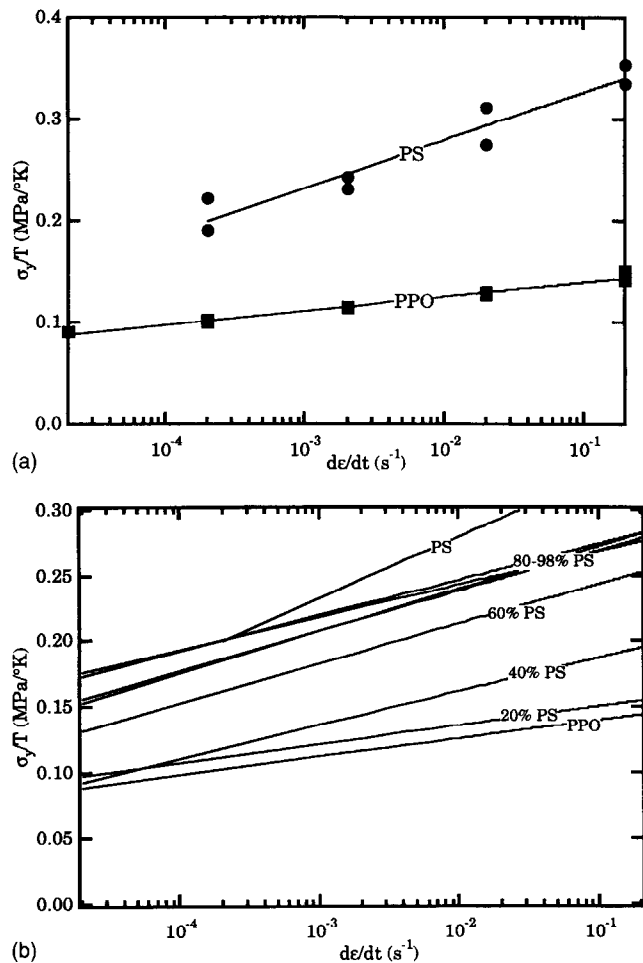


Fig. 8. σ_y/T as a function of strain rate: (a) for pure PS and pure PPO; and (b) for all blends where only the best fits to the data are shown for clarity.

the data to appear as a straight line, the slope of which gives directly k_B/V_0 , and therefore the activation volume. As an example of the two extremes, the strain-rate dependence of the yield stress σ_y of pure PS and of pure PPO at ($T_g - 50^\circ\text{C}$) are shown in Fig. 8a along with the best fit to Eq. (1). Clearly the PS is much more strain-rate sensitive than the PPO and has therefore a lower activation volume. It is interesting to examine more closely the evolution of this behaviour in the miscible blends. Fig. 8b shows the strain-rate dependence of all blend compositions at the same reduced temperature of $T_g - 50^\circ\text{C}$. For the sake of clarity, only the best fit to Eq. (1) is shown but the scatter of the data is comparable to that of Fig. 8a.

It is interesting to note that the activation volume V_0 of the blends appears to be very similar from 0 to 20% PS, then undergoes a discontinuous jump and is relatively constant from 40 to 98% PS to undergo yet another jump for pure PS.

The activation volume at $T = 25^\circ\text{C}$ and at $T_g - 50^\circ\text{C}$ are shown in Figs 9a and b for all blend compositions. While at 25°C , V_0 remains roughly constant with composition, it is no longer the case at $T_g - 50^\circ\text{C}$. In this case V_0 increases notably between 60% and 80% PPO to remain stable at 2.3 nm^3 . It should be noted that the apparent jump in V_0

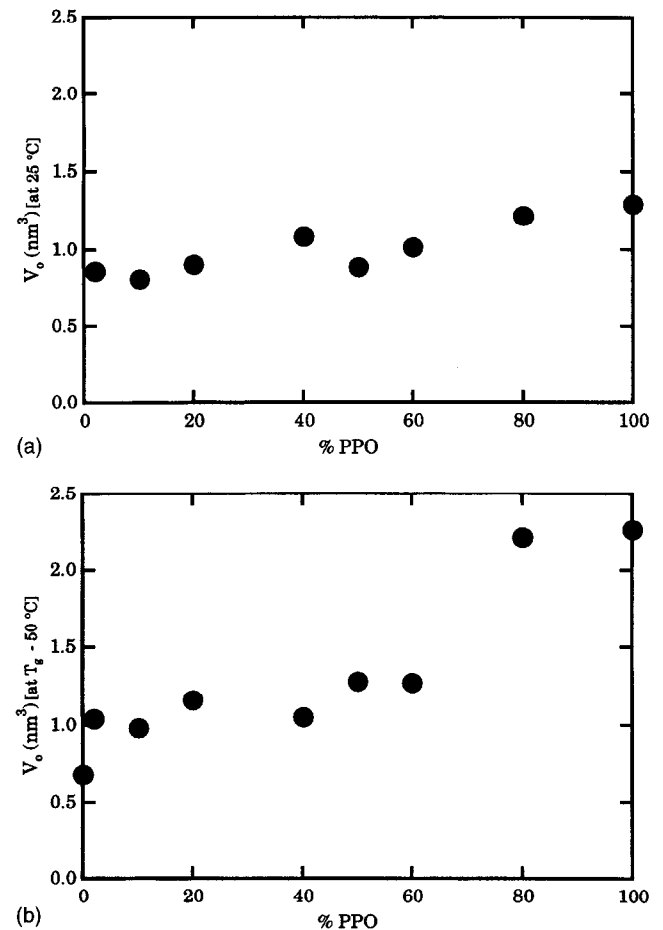


Fig. 9. Operational activation volume V_0 as a function of blend composition: (a) at 25°C ; (b) at $T_g - 50^\circ\text{C}$.

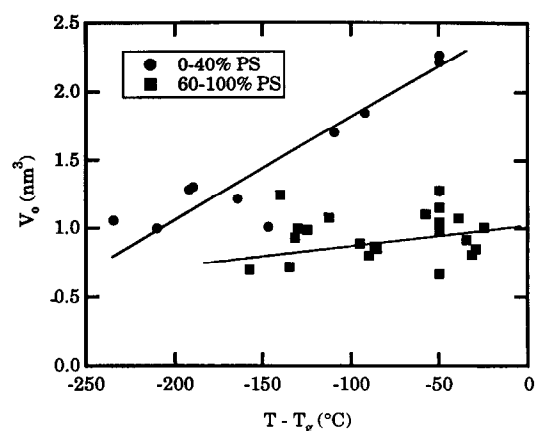


Fig. 10. Operational activation volume V_o as a function of the reduced temperature $T - T_g$.

from pure PS to 2% PPO in Fig. 9b is not significant within experimental error.

Given that a good estimate of the volume of the PS repeat unit is 0.17 nm^3 , the plastic deformation of pure PS at $T_g - 50^\circ\text{C}$ would require the deformation of 4–5 repeat units. This number increases to ca. 10–12 units for the PPO value, which is much higher than a statistical segment length but remains much lower than a typical value of M_e found in the literature of around 40–50 units. Note, however, that the activation volume of ca. 800 \AA^3 which we find in the present work for pure PS at 25°C is somewhat higher than that given by Gloaguen et al. [7] of 500 \AA^3 . The temperature dependence of V_o shown in Fig. 10, does stress the different behaviour of the PPO-rich blends, where V_o has a strong temperature dependence, with the behaviour of the PS-rich blends where V_o is nearly temperature independent in the range of temperatures investigated. Therefore, the variation of V_o with composition does only become notable near the glass transition temperature.

4. Discussion

The results of the compression tests for the series of blends broadly show three types of behaviour: that of pure PS, that of PS-rich blends which encompass compositions up to 40% PPO, and the PPO-rich blends containing 20% or less PS. The pure PS does have the highest yield stress and the highest modulus as well as the lowest activation volume. However, the addition of an amount as small as 2% of PPO has a dramatic effect on the yield stress and on the elastic modulus. This effect cannot be due to a mechanically active relaxation but is probably related to the creation of nucleation sites for the plastic deformation which clearly facilitate the motion of the PS units.

Further addition of PPO up to about 40% does not have any other effect apart from raising the T_g of the blend (σ_y , σ_{pf} , E and V_o remain nearly constant at the same $T - T_g$). Presumably a substantial number of PPO–PPO contacts are necessary to soften the blend further.

Finally, the PPO-rich blends (for 80% and more PPO) have a markedly lower yield stress and much higher activation volume, implying a clear change in the plastic deformation mechanisms.

A possible molecular interpretation is the following: even a small amount of PPO is sufficient to facilitate the initial motion of PS units from their starting position, acting therefore like a softener (we do not use the word plasticizer here because the modulus decreases markedly but the T_g is virtually unchanged). This must be a very local packing effect as the plastic flow stress and the T_g are unaffected. A further increase in PPO does affect the average co-operative chain mobility by increasing the T_g , but does not change the local energy barrier to yield.

This ceases to be true when PPO becomes clearly the majority phase, arguably when the PS–PS interactions are screened out, and the blend behaves then like pure PPO with a much higher activation volume, indicating a higher degree of cooperativity necessary for plastic flow.

These results emphasize, in our opinion, the role of local packing constraints on both the modulus and the onset of yield. In this case, a small difference in local packing as induced by the addition of 2% PPO does not affect the cooperative motions of the glass transition or of plastic flow.

A similar qualitative behaviour showing a clear effect of a small amount of PS or PPO in a matrix of PPO or PS, respectively, was also found by Bouton et al. in their FTi.r. investigation of the chain orientation properties of PS/PPO blends [8].

An important aspect of our study was the possible correlation between our results obtained in compression and the fracture mechanisms of the PS/PPO blends in tension. Unfortunately, direct comparisons with tensile and fracture toughness results are difficult because of the lack of good data as a function of temperature. In thin film experiments, Donald and Kramer [4] reported that, at room temperature, quenched films deform by shear yielding only when the weight fraction of PPO in the blend equals or exceeds 75%, consistent with our trends of change in behaviour at that weight fraction. On the other hand, the thin film results of Wellinghoff and Baer [1] do not really predict a change in fracture mechanism with composition at $T_g - 50^\circ\text{C}$.

Interestingly, and as shown in Fig. 11, plane strain fracture toughness results at room temperature [3] parallel rather well our observations showing an increase in G_{ic} with the addition of a small amount of PS followed by a decrease at intermediate compositions and a further increase for high PPO content. This general observation had already been made by Yee [3] but unfortunately, he did not investigate the very low PPO content compositions.

5. Concluding remarks

The plastic deformation of miscible blends of PS and PPO is governed by two effects which can be separated: an effect

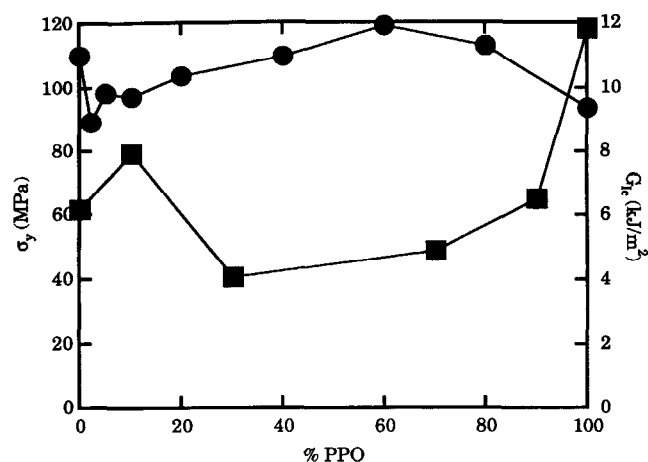


Fig. 11. ■, Fracture toughness G_{IC} of PS/PPO blends tested in a 3-point bending geometry. Data from ref. [3] ●, Yield stress σ_y of our PS/PPO blends.

of 'overall chain mobility' which is responsible for the increase in T_g in going from pure PS to pure PPO, and an effect due chiefly to intermolecular local interactions which influences the yield behaviour at constant $T - T_g$. The most remarkable result is that PPO acts as a softener of PS, sharply reducing the yield stress and the elastic modulus, even at contents of less than 2 mol%. This behaviour had not been reported so far and could be due to the creation of nucleation sites for plastic yield at a lower level of stress than for pure PS. After this initial strong softening effect in an intermediate range of 2 to 40 mole% PPO, the main effect of the presence of PPO is to raise the T_g . Only when it becomes the majority phase, above 40% does it have the additional effect of reducing further the yield and plastic flow stress of the blends, as well as increasing their activation volume.

This change in yield behaviour around 40% PPO could be related to a change in fracture mechanism from crazing to shear yielding [4] and with an increase in the macroscopic fracture toughness [3].

It has been argued that the observed change in ductility could be explained by the gradual decrease of the average molecular weight between entanglements going from PS to PPO [4]. While this is a reasonable argument to rationalize the qualitative results of thin film experiments, it is not consistent with macroscopic fracture toughness results shown in Fig. 11. A more detailed fracture toughness study of these blends as a function of temperature would be necessary to clarify the role of the thermally activated local motions on the fracture mechanisms in tension.

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