JOURNAL OF MATERIALS SCIENCE 24 (1989) 3154–3159

Plastic flow of polypropylene (PP) and PP-based blend

Part 2 *Effect of molecular mobilities on the elementary deformation mechanism*

K. PORZUCEK*, J. M. LEFEBVRE, G. COULON, B. ESCAIG
Laboratoire de Structure et Propriétés de l'Etat Solide, (Unité Associée au C.N.R.S. 234), Université des Sciences et Techniques de Lille Flandres-Artois, 59655 Villeneuve d'Ascq, France

The evolution with temperature of the deformation mechanisms responsible for yielding in polypropylene (PP) and a PP-based blend is correlated to the molecular mobilities associated to glass transitions processes occurring in these materials.

It is shown that the elementary local deformation event remains the same throughout the whole temperature range and that the onset of mobility only affects the average internal stress field $\bar{\sigma}_i$ in which this thermally activated event takes place.

1. Introduction

In Part 1 [1] we conducted a thermodynamic and kinetic analysis of the compressive yield behaviour at constant strain rate of polypropylene (PP) and of its blend with high density polyethylene and an ethylene propylene rubber (PP/HDPE/EPR).

At very low temperatures ($T < 175$ K), it could be shown that both systems obey the same elementary deformation process, i.e. both exhibit the same linear temperature variation of the Gibbs free energy of activation ($\Delta G_a = \alpha kT$ with $\alpha \simeq 14$). Also the spatial extension of the elementary activation event, namely the activation volume V_a, is identical (of the order of 6 PP monomer volumes).

As the temperature is increased, critical temperatures T_c's are evidenced for both materials which preclude a thorough determination of all activation parameters. Of particular interest is the existence at these T_c's of singularities in the temperature variation of the operational activation volume and enthalpy.

These singularities relate to the onset of glass transition phenomena in both pure PP and its blend. Complementary to the classical thermodynamic analysis of plastic flow, the present approach is an attempt to understand the role played by molecular mobilities in the elementary deformation mechanism.

In order to account for the observed behaviour, special attention is paid to identifying the influence of these mobilities on long range as well as on local stress fields.

2. General aspects of the thermally activated yielding mechanisms

2.1. Thermal activation of σ_y and V_0; "athermal" temperature

We first recall that, according to a "metallurgical" point of view, yielding in polymers is assumed to originate from the stress-aided and thermally activated propagation of shear nuclei (plasticity defects) over energy barriers ΔG_0, opposed by localized obstacles [1]. This local barrier height ΔG_0 [2] can be written

$$\Delta G_0 = \Delta G_a + (\sigma_y - \sigma_i) V_a \qquad (1)$$

The Gibbs free energy of activation ΔG_a represents the energy provided to a defect by thermal fluctuations. The quantity $(\sigma_y - \sigma_i) V_a$ reflects the "mechanical" energy supplied by the local effective stress σ^* defined by

$$\sigma^* = \sigma_y - \sigma_i \qquad (2)$$

where σ_y and σ_i are the yield stress and the internal stress respectively. The activation volume V_a stands for the critical size V_c of the activated defect. Details about the physical meaning of these parameters have been given in Part 1 [1].

We also recall that, taking as the rate equation for plastic flow

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp\left[-\Delta G_a(\sigma - \sigma_i T)/kT\right] \qquad (3)$$

the operational activation volume V_0 has been defined as the stress sensitivity of the strain rate $\dot{\varepsilon}_p$ in the form

$$V_0 = kT\left(\frac{\partial \ln \dot{\varepsilon}_p}{\partial \sigma}\right)_{T,\sigma_i} = V_a + kT\left(\frac{\partial \ln \dot{\varepsilon}_0}{\partial \sigma}\right)_{T,\sigma_i} \qquad (4)$$

According to Equation 1, Equation 3 may be rewritten as

$$\dot{\varepsilon}_p = \dot{\varepsilon}_0 \exp\left(\frac{-\Delta G_0}{kT}\right) \exp\left(\frac{(\sigma_y - \sigma_i) V_a}{kT}\right) \qquad (3')$$

This expression is, however, only valid when the effective stress $(\sigma_y - \sigma_i)$ is high enough to prevent a mobile plasticity defect from moving back to its initial position after a jump over a localized obstacle.

---

*Present address: NORSOLOR (ORKEM) Centre de Recherche Nord B-P 57 62670 Mazingarbe.

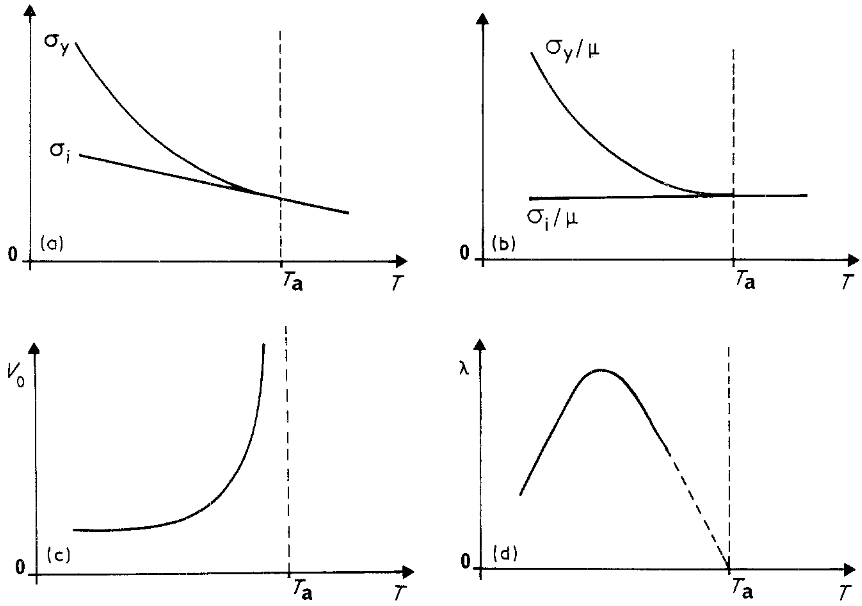

Figure 1 Identification of the "athermal temperature T_a" from the variation with temperature of (a) the yield stress σ_y, (b) the reduced yield stress σ_y/μ, (c) the operational activation volume V_0, (d) the strain-rate sensitivity of the flow stress $\lambda = kT/V_0$.

Let us suppose that ΔG_0 is temperature and stress independent. As the temperature is increased, the amount of energy $(\sigma_y - \sigma_i)V_a$ decreases so that Equation 1 is always obeyed. As derived from the early Eyring rate theory, when σ^* decreases, i.e. when σ_y comes close to the internal stress σ_i, the probability for backward jumps is no longer negligible. In this case, Expression 3′ has to be replaced by Equation 5 (see, e.g. [3])

$$\dot{\varepsilon}_p \simeq \dot{\varepsilon}_0 \exp\left(\frac{-\Delta G_0}{kT}\right) \sinh\left(\frac{(\sigma_y - \sigma_i)V_a}{kT}\right) \qquad (5)$$

For small values of $(\sigma_y - \sigma_i)$, the hyperbolic sine term can be linearized to give

$$\dot{\varepsilon}_p \simeq \frac{\dot{\varepsilon}_0(\sigma_y - \sigma_i)V_a}{kT} \exp\left(\frac{-\Delta G_0}{kT}\right) \qquad (5')$$

from which we get

$$V_0 \simeq \frac{kT}{\sigma_y - \sigma_i} \qquad (6)$$

Equation 6 indicates that V_0 becomes infinite for $\sigma_y = \sigma_i$. This occurs for a peculiar temperature T_a. According to Equation 1, at $T = T_a$, the local barrier height ΔG_0 is such that $\Delta G_0 = \Delta G_a$. The thermal energy is thus sufficient to make any local obstacle transparent to the glide process. The applied stress σ_y is then needed only to overcome the long range internal stresses acting on a plasticity defect.

As mentioned in [1], the average internal stress field $\bar{\sigma}_i$ may be written as $\bar{\sigma}_i = A\mu$ where μ is the elastic shear modulus. Consistently, $\bar{\sigma}_i$ may be viewed as arising from interface misfits left behind the shear defects. It relates to the interface energy γ, itself directly proportional to μ [4].

Equation 2 may thus be rewritten as

$$\frac{\sigma_y}{\mu} = \frac{\sigma^*}{\mu} + A \qquad (7)$$

As a consequence, above T_a, the "reduced" yield stress σ_y/μ should appear as a constant value A, i.e. it no longer depends on temperature.

The temperature T_a at which the yielding process becomes athermal, i.e. when

$$\sigma_y = \sigma_i$$
$$\Delta G_0 = \Delta G_a$$
$$V_0 \rightarrow \infty$$

is called by extension the "athermal" temperature. The behaviour of corresponding quantities is illustrated in Figs 1a, b and c.

The athermal temperature T_a appears, therefore, as an essential parameter since it determines the temperature domain within which a single thermally activated mechanism should be operative.

2.2. Experimental determination of T_a

In principle, the plot of the reduced yield stress σ_y/μ as a function of temperature should give access to T_a as shown in Fig. 1b. It is worth noting, however, that such a determination requires a knowledge of the temperature variation of the shear modulus μ at the frequency ν_{def} relevant for the deformation process. Due to the lack of proper experimental techniques, modulus measurements at this frequency are not always accessible [1]. An accurate determination of T_a derived from experimental data regarding the yield stress is thus not straightforward.

The $V_0(T)$ curve provides another mean for determining the athermal temperature T_a (Fig. 1c). The V_0 parameter is only frequency-dependent through the strain-rate $\dot{\varepsilon}$. Since our analysis has been performed at constant $\dot{\varepsilon}$, the $V_0(T)$ plot allows a determination of T_a without solving for the frequency ν_{def}. In practice, it is, however, not easy to evaluate the precise temperature at which V_0 tends to infinity. It is far more convenient to deduce the value of T_a from the temperature dependence of the strain-rate sensitivity of the flow stress, i.e.

$$\lambda = \frac{kT}{V_0} = \left(\frac{\partial \sigma}{\partial \ln \dot{\varepsilon}_p}\right)_{T,\sigma_i} \qquad (8)$$

As shown on Fig. 1d, this plot yields the value of T_a

by extrapolation down to the T axis. Note that the profile of the $\lambda(T)$ curve is easily understood from Equation 8: at low temperature, the increase of T overwhelms the slight increase of V_0 so that λ increases with temperature; at higher temperatures, the increase in V_0 overtakes, making λ smaller and smaller. A polynomial fit of degree two may be justified to account for this behaviour [5]. Such a determination of T_a has been initially applied to metals [6] and then extended to polymers [2].

This approach is compared in this paper with the observed deformation behaviour of polypropylene (PP) and the ternary PP/HDPE/EPR blend for which the usual thermodynamic analysis of plastic flow was developed in Part 1. More specifically, we shall try to elucidate the role played by molecular mobilities in the deformation process involved at yield.

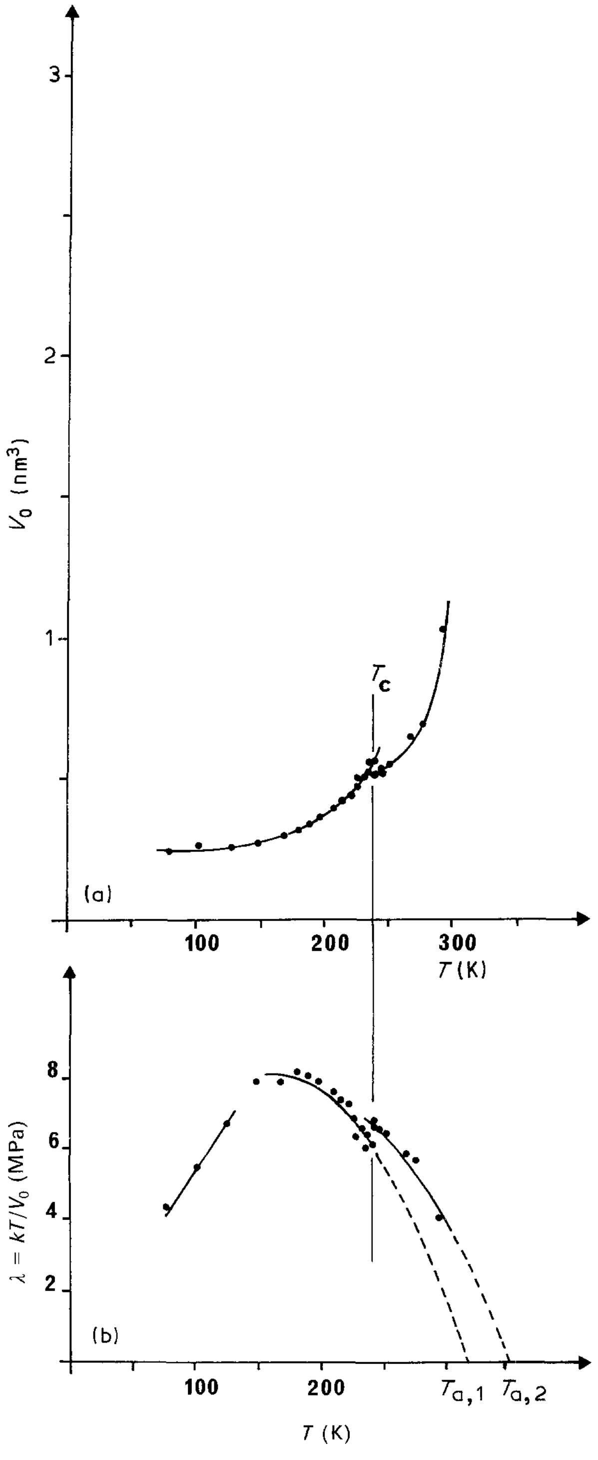

Figure 2 The temperature variation for PP of (a) the operational activation volume V_0, (b) the parameter $\lambda = kT/V_0$.

3. Experimental and results

The materials under investigation are a pure PP and a ternary polypropylene 3.5 wt % high density polyethylene 17.5 wt % random ethylene propylene copolymer blend, supplied by le Centre d'Etude, de Recherche et de Développement d'ATOCHEM, Serquigny (France). Details of moulding, annealing conditions and deformation procedure have been given in Part 1 [1].

Fig. 2a reports on the temperature variation of the operational activation volume V_0, obtained through stress-relaxation tests performed at yield for PP [1]. Fig. 2b shows the corresponding $\lambda(T)$ plot. A singularity is clearly evidenced on the two curves at $T_c \simeq 240$ K. The peculiar profile of these plots, compared to that obtained in a general case (Figs 1c and d) is indicative of the existence of two different athermal temperatures, as illustrated in Fig. 2b. As previously stated, in order to minimize the error in the determination of athermal temperatures, an analytical formulation has been given for each part of the $\lambda(T)$

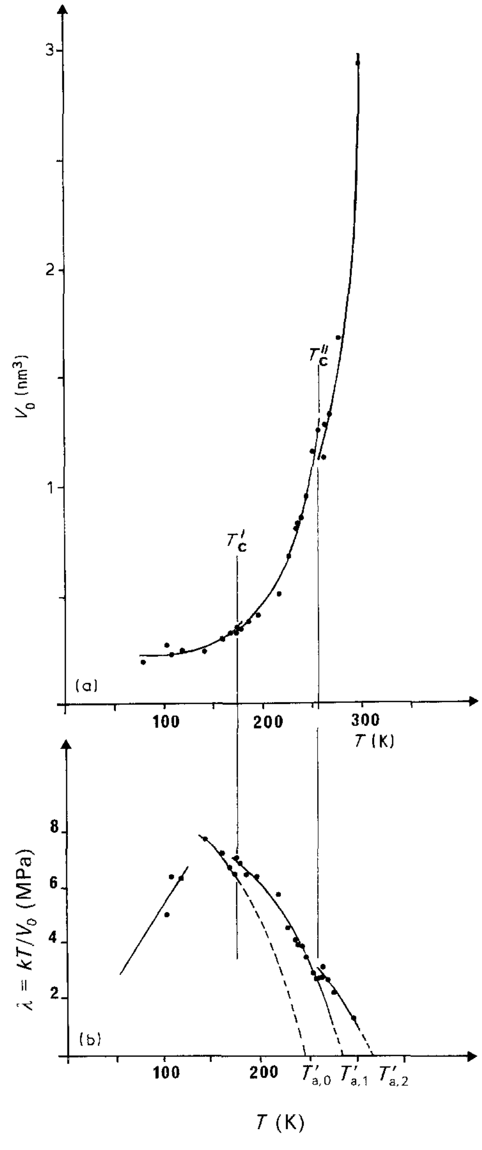

Figure 3 The temperature variation for the PP-blend of: (a) the operational activation volume V_0 and (b) the parameter $\lambda = kT/V_0$.

curve. More precisely, we have shown that on both sides of T_c this curve could be correctly described by the following expression

$$\lambda = aT^2 + bT \qquad (9)$$

Such a fit is, however, not valid at very low temperatures. Indeed, below around 150 K, V_0 is roughly constant with temperature and λ is thus directly proportional to T. A detailed derivation is given in [5].

Solving for $\lambda = 0$ in Equation 9 leads to the values of athermal temperatures $T_{a,1}$ and $T_{a,2}$ as defined in Fig. 2b

$$T_{a,1} = 318\,\text{K}$$
$$T_{a,2} = 351\,\text{K}$$

In the case of the PP-blend, the temperature variations of V_0 and λ are shown in Figs 3a and b respectively. These plots show again two singularities at $T_c' \simeq 175\,\text{K}$ and $T_c'' \cong 255\,\text{K}$. According to the same procedures as in the case of PP, three athermal temperatures may be extrapolated from the $\lambda(T)$ curve

$$T_{a',0} = 246\,\text{K}$$
$$T_{a',1} = 285\,\text{K}$$
$$T_{a',2} = 317\,\text{K}$$

4. Discussion

We shall first consider the departure of experimental $V_0(T)$ data for PP and its EPR blend from the simple behaviour discussed in the theoretical section.

Fig. 4a gives a schematic presentation of Fig. 2a. The complex situation encountered here (as compared to Fig. 1c) is such that a clear drop occurs in V_0 at temperature T_c. A tentative explanation is given below which focuses on the temperature dependence of the effective stress $\sigma_y - \sigma_i = \sigma^*$. For $T \ll T_c$, σ^* is high enough so that the strain-rate law at yield can be written according to Equation 3′. As the temperature is increased, the effective stress becomes smaller and smaller, and it becomes necessary to take into account backward jumps of the shear nuclei. In this case, the strain-rate law is better expressed as Equation 5′ with the consequence that $V_0 \simeq kT/\sigma_y - \sigma_i$ should tend to infinity at $T = T_{a,1}$. This is, however, not observed and it might be postulated that at T_c a sharp drop in $\bar{\sigma}_i$ brings the plastic behaviour back to the former case (i.e. Equation 3′), as illustrated in Fig. 4b. Along the same lines, as the temperature is increased beyond T_c, σ^* will be reduced again until one reaches $T = T_{a,2}$ when V_0 tends to infinity.

A similar argument may be developed in the case of the PP-blend: the two observed decreases in V_0 at T_c' and T_c'' respectively should be associated with drops of the internal stress field $\bar{\sigma}_i$ as schematized in Figs 5a and b.

The relevance of this interpretation may be found in the physical origin of the T_c's.

As stated in the first part of this paper, T_c's are related to the onset of molecular mobilities responsible for glass transition phenomena: T_c corresponds to the low temperature part of the T_g process of amorphous PP whereas T_c' and T_c'' in the blend relate to the glass transition process of the EPR phase and the amorphous PP respectively. As the temperature is increased, these extra molecular mobilities release stress concentrations. As a consequence, a drop in the average internal stress field $\bar{\sigma}_i$ is expected.

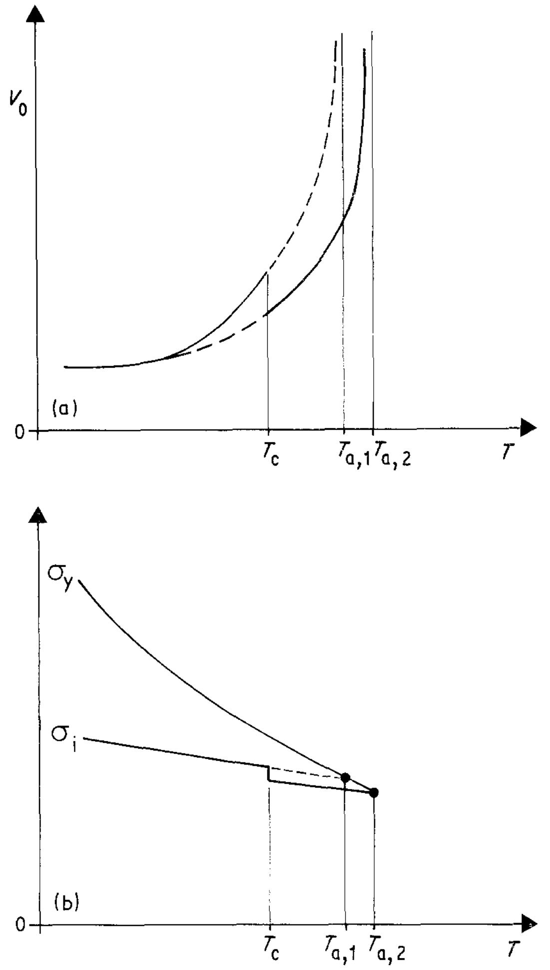

Figure 4 Schematic presentation for PP of the temperature dependence of (a) the operational activation volume V_0 and (b) the flow stress σ_y and the internal stress σ_i.

We postulate that these structural rearrangements only affect $\bar{\sigma}_i$ and that the elementary local plastic deformation mechanism characterized at low temperature [1] remains the same.

According to this scheme, we propose the following model to describe the yielding behaviour of PP and its blend with EPR:

(i) Over the entire temperature range under investigation, plastic flow is governed by the propagation in the amorphous phase of shear nuclei which are the same for both the pure PP and its blend, i.e. the local barrier height is the same for both materials.

(ii) The molecular mobilities responsible for the glass transition behaviour only affect the average internal stress field $\bar{\sigma}_i$ within which the activated glide event occurs.

In order to illustrate these assumptions, shear nuclei are viewed as quasi-dislocations or micro shear bands travelling through polymer chains [4]. These should shear crystalline regions rather easily. On the other hand, when entering the amorphous phase (i) they would trail a molecular misfit interface (or shear interface) in their wake responsible for a back stress σ_i, (ii)

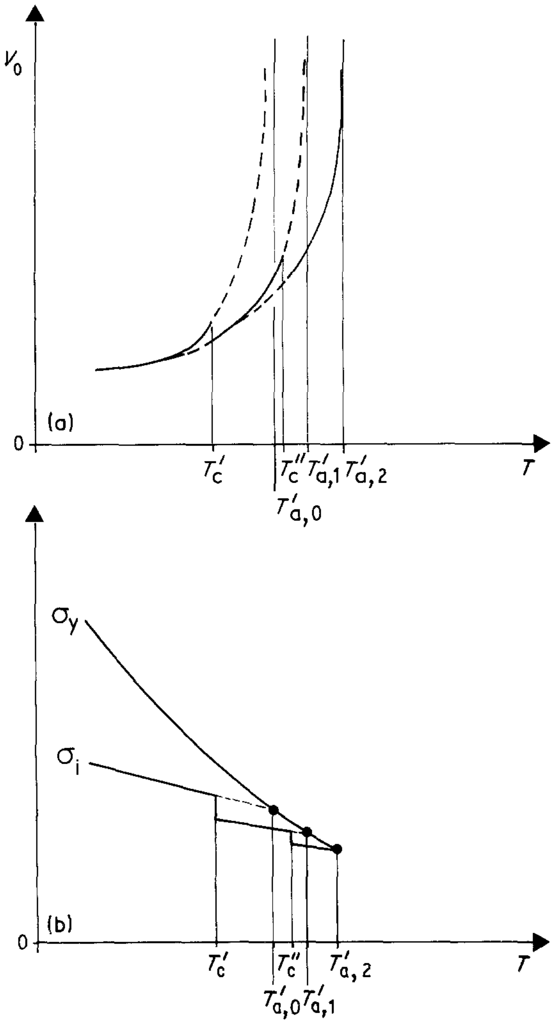

Figure 5 Schematic presentation for the PP blend of the temperature dependence of (a) the operational activation volume V_0 and (b) the flow stress σ_y and the internal stress σ_i.

they would encounter chain entanglements through their path; these are at the origin of localized obstacles of height ΔH_{00}.

The above assumptions state that entanglements are met in the PP amorphous phase in the same way whether second phase precipitates exist or not (same ΔH_{00} in both materials), and that molecular mobilities relax merely the high energy molecular stacking (or misfit interfaces) left behind dislocations (only $\bar{\sigma}_i$ is affected).

The next step in our discussion is to check the validity of this deformation model.

The local barrier which opposes the motion of a defect is characterized by its free energy ΔG_0. This quantity may be expressed as

$$\Delta G_0 = \Delta H_{00} - T\Delta S_0 \qquad (10)$$

where ΔS_0 holds for the entropic contribution.

Due to the lack of consistent experimental ΔG_a data for both materials over the whole temperature domain [1], it is difficult to draw conclusions on the energy barriers ΔG_0 as defined by Equation 1. However, a closer look may be given to the enthalpic part ΔH_{00} which may be written

$$\Delta H_{00} = \Delta H_0 + (\sigma_y - \sigma_i)V_a$$

The operational activation enthalpy ΔH_0, identified as the "true" activation enthalpy ΔH_a [1], is available over the entire temperature range and has been derived through the equation

$$\Delta H_0 = -TV_0\left(\frac{\partial \sigma_y}{\partial T}\right)_{\dot{\varepsilon}_p, \sigma_i}$$

We recall that ΔH_0 does not rely on any assumption regarding the frequency of the elementary deformation event.

Let us define the enthalpy of the barrier ΔH_{00} as the value of ΔH_0 corresponding to the athermal temperature $T_{a,1}$ identified in PP. The determination of this quantity requires extrapolating the part of the $\Delta H_0(T)$ plot located below T_c up to $T_{a,1}$, as illustrated in Fig. 6. We obtain

$$\Delta H_{00} = \Delta H_0(T_{a,1}) \simeq 4.2\,\text{eV}$$

We now assume ΔH_{00} stands for the local rate-controlling barrier enthalpy in the amorphous phase whatever the situation, i.e. (i) for pure PP as well as for the blend, (ii) on both sides of the temperatures T_c's at which $\bar{\sigma}_i$ starts relaxing.

Under these assumptions, extrapolations of the

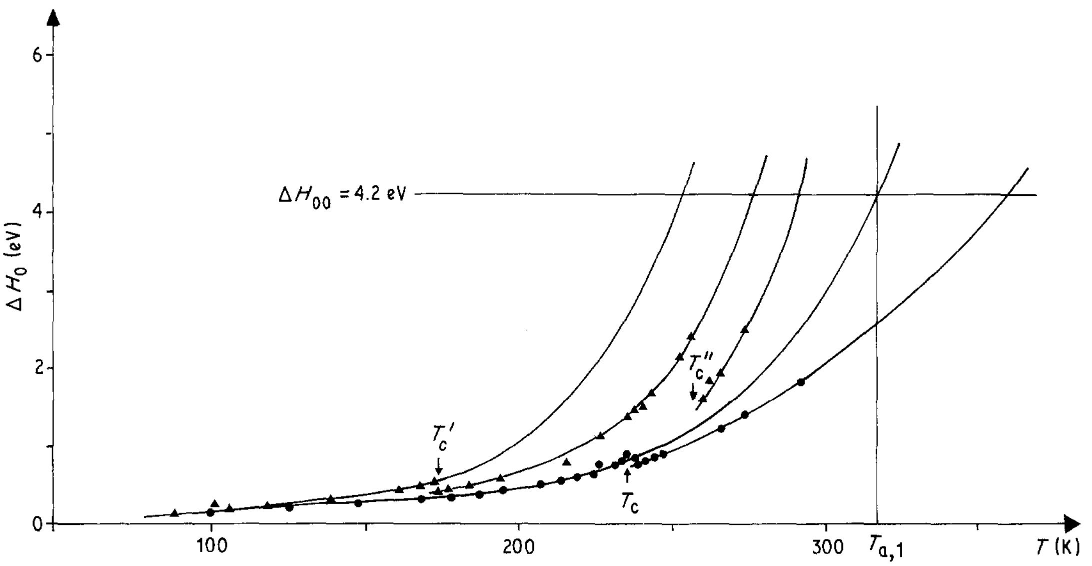

Figure 6 The temperature variation of the operational activation enthalpy ΔH_{00}, (●) PP, (▲) PP-blend.

TABLE I

	Range of data extrapolated	$T_{a,i}$ from $\Delta H_0(T_{a,i}) \cong 4.2\,\mathrm{eV}$ (K)	$T_{a,i}$ from Figs 2b and 3b (K)
PP	ΔH_0 for $T > T_c$	361	$T_{a,2} = 351$
	ΔH_0 for $T > T_c''$	292	$T_{a',2} = 317$
PP-blend	ΔH_0 for $T_c' < T < T_c''$	278	$T_{a',1} = 285$
	ΔH_0 for $T < T_c'$	255	$T_{a',0} = 246$

corresponding $\Delta H_0(T)$ plots up to $\Delta H_{00} \simeq 4.2\,\mathrm{eV}$ should yield values for the other athermal temperatures comparable to those deduced previously from Figs 2b and 3b. The extrapolation procedure may be justified beyond the range of experimental data, since it has to be consistent with the parameters of the polynomial fits used in the determination of athermal temperatures from the $\lambda = kT/V_0$ against T plots [5]. As a consequence, the uncertainty associated with the extrapolation of ΔH_0 is quite low.

The comparison of temperatures deduced from Figs 2b and 3b and from Fig. 6 is achieved in Table I. Agreement is quite satisfactory and we may thus conclude with a reasonable degree of confidence that the height of the barrier opposed by local obstacles is the same in PP and its blend over the whole temperature range under investigation.

A further implication is that the main difference in the behaviour of the EPR blend as compared to pure PP originates from entropic contributions, i.e. from the temperature dependence of the shear elastic modulus. This may be illustrated in the following way: writing $\Delta H_{00}(\mathrm{PP}) = \Delta H_{00}(\mathrm{blend})$ implies, according to Equation 10, that

$$(\Delta G_0 + T_{a,1}\Delta S_0)_{\mathrm{PP}} = (\Delta G_0 + T_{a',1}\Delta S_0)_{\mathrm{blend}} \qquad (11)$$

If we recall that $\Delta G_a(T_{a,i}) = \Delta G_0(T_{a,i})$ and $\Delta G_a = \alpha kT$ [1], Equation 11 can be expressed as

$$T_{a,1}(\alpha k + \Delta S_0)_{\mathrm{PP}} = T_{a',1}(\alpha k + \Delta S_0)_{\mathrm{blend}} \qquad (12)^*$$

As a consequence, since $T_{a,1} > T_{a',1}$, Equation 12 leads to

$$(\Delta S_0)_{\mathrm{blend}} > (\Delta S_0)_{\mathrm{PP}}.$$

In the next step, we should, therefore, aim at translating this information gained about entropic effects into terms of modifications in the dynamic mechanical response. More precisely it should enable us to predict the plastic behaviour of a blend, given that of its parent matrix and the dynamic elastic spectra of both materials.

Acknowledgements

Financial support under Contract M.I.R. 84-P-0719 is gratefully acknowledged. K. Porzucek is also indebted to ATOCHEM for a research grant during the course of this work.

References

1. K. PORZUCEK, G. COULON, J. M. LEFEBVRE and B. ESCAIG, in press, *J. Mater. Sci.*
2. B. ESCAIG, in "Plastic Deformation of Amorphous and Semi-crystalline Materials", edited by B. Escaig and C. G'Sell (Les Editions de Physique, Les Ulis, 1982) p. 187.
3. J. P. POIRIER, in "Plasticité à Haute Température des Solides Cristallins" (Editions Eyrolles, Paris, 1976) p. 91.
4. B. ESCAIG, *Helvetica Physica Acta* **56** (1983) 293.
5. K. PORZUCEK, Thèse de l'Université de Lille I (1988).
6. J. P. COTTU, J. P. PEYRADE, P. CHOMEL and P. GROH, *Acta Metall.* **19** (1971) 895.

Received 6 June
and accepted 21 October 1988

---

*Note that strictly speaking the proportionality between the Gibbs free energy of activation and temperature was shown to yield the same α value for both systems only up to T_c in pure PP and up to T_c' in the blend [1], but this should not alter the validity of the analysis.