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The effect of varying the polyethylene content and the co-polymer content on crazing in polystyrene–low-density polyethylene blends

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The effect of varying the low-density polyethylene content and the polystyrene–polyethylene block co-polymer content on the rates of craze initiation and craze growth in polystyrene/low-density polyethylene blends has been studied. It was found that the parameters in the Eyring rate coefficients for craze initiation and craze growth are not dependent on the low-density polyethylene content. However, the rates of craze initiation increased with increasing low-density polyethylene content. This is explained tentatively by a new model for craze initiation. It is argued that effective crazes are only formed within clusters of low-density polyethylene particles that have overlapping stress-concentration fields. The dependence of the rate of craze initiation on the volume-fraction of dispersed phase that follows from this cluster model is qualitatively in agreement with experimental results. PS–PE co-polymer addition gives rise to changes in the Eyring parameters of the rate coefficients of craze initiation and craze growth. This may be a consequence of changes in morphology near the interface and of the different stress state at the interface.

1. Introduction

In a previous paper [1] a model was developed that described the stress–strain behaviour of toughened polystyrene (TPS). The model was based on the observation that apart from craze growth the stress–strain behaviour of crazed TPS is well approximated by a linear elastic series of uncrazed TPS and polystyrene (PS) crazes. If the volume-fraction of PS that has been converted into craze fibrils is denoted v, then, applying the linear elastic series model, it can be shown that

$$v = \frac{\epsilon - \sigma/E_{\mathrm{TPS}}}{(f/E_{\mathrm{cr}} - 1/E_{\mathrm{TPS}})\sigma + f - 1}, \qquad (1)$$

where E_{TPS} and E_{cr} are the elastic moduli of, respectively, TPS and crazes, and f^{-1} is the PS volume-fraction with a craze. Furthermore, denoting k_{i} as the rate of craze initiation, or more precisely the rate of craze area formation normal to the stress direction per unit volume TPS, and denoting k_{g} as the rate of craze growth in the stress direction (or the rate of craze thickening), then it follows that

$$v = \frac{1}{f}\int_0^t k_{\mathrm{i}}(\tau)\int_\tau^t k_{\mathrm{g}}(\zeta)\,\mathrm{d}\zeta\,\mathrm{d}\tau. \qquad (2)$$

The combination of Equations 1 and 2 results in a general stress–strain–time equation and allows determination of k_{i} and k_{g} from analyses of stress–strain–time curves. The validity of this model has been verified experimentally for PS–low density polyethylene (ldPE) blends [2, 3]. It has been shown that for these blends the stress and temperature dependence of k_{i} and k_{g} is well described by Eyring activated flow equation

$$k_{\mathrm{i}} = A_{\mathrm{i}} \exp\left(\frac{-\Delta H_{\mathrm{i}}^*}{kT}\right) \exp\left(\frac{\gamma_{\mathrm{i}}\sigma V_{\mathrm{i}}^*}{4kT}\right) = a\mathrm{e}^{b\sigma} \qquad (3)$$

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and

$$k_g = A_g \exp\left(\frac{-\Delta H_g^*}{kT}\right) \exp\left(\frac{\gamma_g \sigma V_g^*}{4kT}\right) = c e^{d\sigma}. \quad (4)$$

In the present study the effect of varying the PS–PE co-polymer content and the ldPE content on the rates of craze initiation and growth will be considered.

2. Experimental procedure

The PS/ldPE and PS/ldPE/PS–PE co-polymer blends were prepared by melt-mixing on a Schwabenthan laboratory mill at 190° C. The blends thus obtained were compression moulded (10 min, 200° C) into sheets to avoid orientation effects. The sheets were machined into tensile specimens with dimensions according to ASTM D 636 III.

The PS used was Styron 634 from Dow Chemical Co., the ldPE was Stamylan 1500 from DSM, The Netherlands. A PS–PE block co-polymer was prepared by hydrogenating a polystyrene–polybutadiene (PS–PB) co-polymer, Solprene 1205 of Phillips Petroleum Co., consisting of the following sequences: $[\text{PS}-(\text{PS/PB})_{\text{random}}-\text{PB}] = [14000-11000-54000]$. The blend composition varied between 97/3 (wt/wt) and 85/15 (wt/wt) PS/ldPE. From earlier research it is known that blends with ldPE contents up to 15 wt% ldPE deform by crazing only apart from the elastic deformation [4, 5] (Fig. 1).

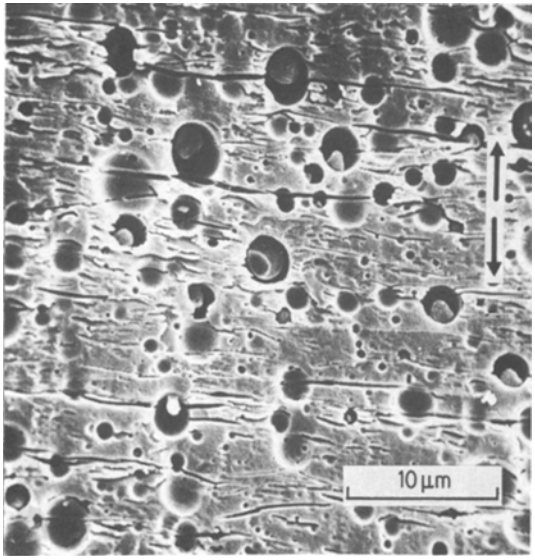

Figure 1 Microtomed and oxygen plasma-etched surface of a crazed 85/15 (wt/wt) PS/ldPE blend. Arrows indicate tensile stress direction.

Tensile tests at constant strain rate were performed on a thermostatted Zwick 1474 tensile tester. The strain was measured on the tensile specimen to avoid clamp effects. Closed loop operation made accurate constant strain rate experiments possible.

3. Results

3.1. Apparent craze modulus

In order to apply the model outlined above it is necessary to determine the apparent craze modulus, E_{cr}, for the various blends to be investigated. Applying the fast relaxation method described in [1] and assuming $f = 4$ [1] the results given in Table I were obtained.

3.2. PS/PE homopolymer blends

The stress dependence of the product $k_i k_g$ was determined for PS/ldPE blends with ldPE contents that varied between 3 and 15 wt%. The experiments were hampered by the brittleness of these blends particularly at low ldPE contents. This prevented determination of $k_i k_g$ at higher strain rates and thus narrowed the stress range in which $k_i k_g$ could be determined. Nevertheless the results, represented in Fig. 2, are consistent. For all compositions the relation between $\ln k_i k_g$ and stress is approximately linear at higher stresses, in accordance with previous results that showed that $k_i k_g$ is described by the Eyring activated flow equation [2]. Deviations from linearity at low stresses were attributed previously to the existence of a critical craze initiation stress [2]. Values for the slope (equal to $b + d$, as can be inferred from Equations 3 and 4) for the experiments at 22° C are given in Table II. The differences between the values for $b + d$ obtained from different blend compositions are small. Thus it appears that the sum of the apparent activation volumes for craze initiation and craze growth, $\gamma_i V_i^* + \gamma_g V_g^*$, is independent of the ldPE content in the ldPE concentration range studied here, and averages 9 nm^3.

The sum of the activation enthalpies of craze

TABLE I Apparent craze moduli

Blend composition PS/ldPE/co-polymer (g)	E_{cr} (MPa)
95/6/0	400
90/10/0	350
85/15/0	310
85/15/1	460
85/15/2	430

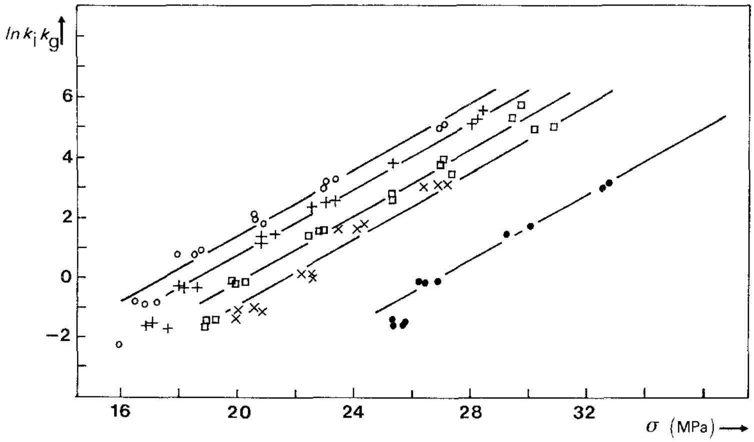

Figure 2 Dependence of $\ln k_i k_g$ on stress. Blend compositions (PS/ldPE) (wt/wt): ●, 97/3; ×, 94/6; □, 91/9; +, 88/12; ○, 85/15.

initiation and growth can be calculated by determining the temperature dependence of $k_i k_g$. The brittleness of the blends, especially at lower temperatures, prohibited determination of the temperature dependence of $k_i k_g$ in a wide temperature range. However, as shown in Fig. 3, plots of values $k_i k_g$ extrapolated to zero stress for different PS–ldPE blends against the reciprocal temperature can be fitted with a set of parallel lines. This indicates that the sum of the activation enthalpies of the craze initiation and growth process is not dependent on the ldPE content. The optimum value for $\Delta H_i^* + \Delta H_g^*$ is 150 kJ mol^{-1}.

Concluding, it appears that the ldPE content does not appreciably affect the sum of the apparent activation volumes and the sum of the activation enthalpies of the crazing processes. However, the product of the pre-exponential factors $A_i A_g$ is strongly dependent on the ldPE content. Using averaged values for the activation parameters the product $A_i A_g$ has been calculated. Results are given in Table II and represented in Fig. 4.

3.3. Blends containing PS—PE co-polymer

The stress and temperature dependence of $k_i k_g$ has been determined from two PS/ldPE/PS–PE block co-polymer blends with the compositions 85/15/1 and 85/15/2 (wt%). The relations between $\ln k_i k_g$ and stress (Figs 5 and 6) and between $\ln k_i k_g$ extrapolated to zero stress and the reciprocal temperature (Fig. 7) were approximately linear, showing that the Eyring flow equation is applicable. The sum of the activation enthalpies and of the activation volumes, and the product of the pre-exponential factors for craze initiation and craze growth as calculated for the co-polymer containing blends and the 85/15 (wt/wt) homopolymer blend are given in Table III. The addition of rather small amounts of copolymer is found to result in higher values for all Eyring parameters, while increasing the copolymer concentration produces only a small extra effect.

TABLE II

Blend composition PS/ldPE (wt/wt)	$b + d$ (MPa^{-1})	$A_i A_g$ (× 10^{21} min^{-2})
97/3	0.55	0.02
94/6	0.52	0.6
91/9	0.53	1
88/12	0.55	1.7
85/15	0.54	3.5

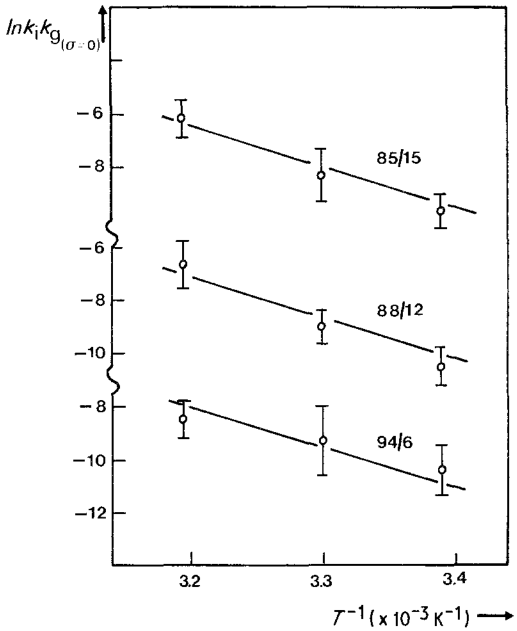

Figure 3 Values for $\ln k_i k_g$ extrapolated to zero stress plotted against the reciprocal temperature. Blend compositions as indicated (PS/ldPE).

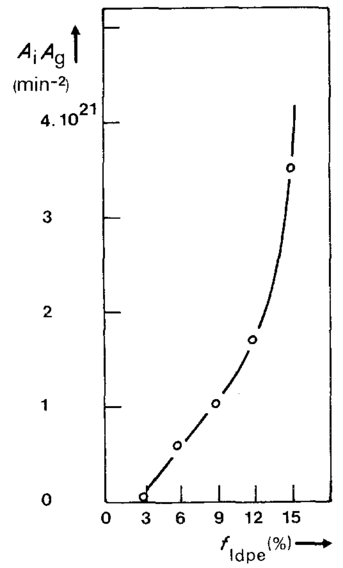

Figure 4 Dependence of the product A_iA_g on the ldPE content.

4. Discussion

4.1. Variation of the ldPE content in PS/ldPE homopolymer blends

As crazing takes place within the glassy polymer matrix the rate coefficient of craze initiation and of craze growth will be dependent on the properties of the matrix and will not be influenced by the dispersed phase content. This is in accordance with the results on PS/ldPE blends with varying ldPE content that indicate that the sum of the activation volumes and of the activation enthalpies of the craze initiation and craze growth processes is not dependent on the ldPE content. It then can be expected that the frequency factor that belongs to the Eyring rate coefficient will also not be affected by the ldPE content.

The rates of the crazing processes increase rapidly with increasing ldPE content. As the rate coefficients are unaffected by the ldPE content, the increase of these rates is apparently caused by a higher concentration of units that can participate in the craze initiation and growth process at higher ldPE contents. As the number of potential flow units that are involved in the process of fibril elongation (which essentially controls craze growth) is not likely to be affected by the ldPE content, it follows that the increase in the rates, or, the increase of the product A_iA_g, results from an increase in the area that is available for craze initiation. To explain this we propose the following tentative model for craze initiation.

4.2. Clusters

From the investigations by Matsuo *et al.* [6] on crazing in PS, it is known that at a certain stress a craze growing between rubber spheres with overlapping stress concentration fields grows faster and becomes larger normal to the stress direction than a craze that develops from an isolated sphere. It follows that crazes growing between particles with overlapping stress-concentration fields contribute more to the total craze area normal to the stress direction than crazes growing from isolated particles. Thus especially crazing between particles with overlapping stress-concentration fields contributes to the rate of craze initiation (which is defined above as the rate of craze area formation normal to a stress direction).

If a cluster is defined as a group of particles with overlapping stress-concentration fields, then it follows that craze initiation for the greater part takes place within clusters. Furthermore, as Matsuo *et al.* [6] showed that crazes in overlapping

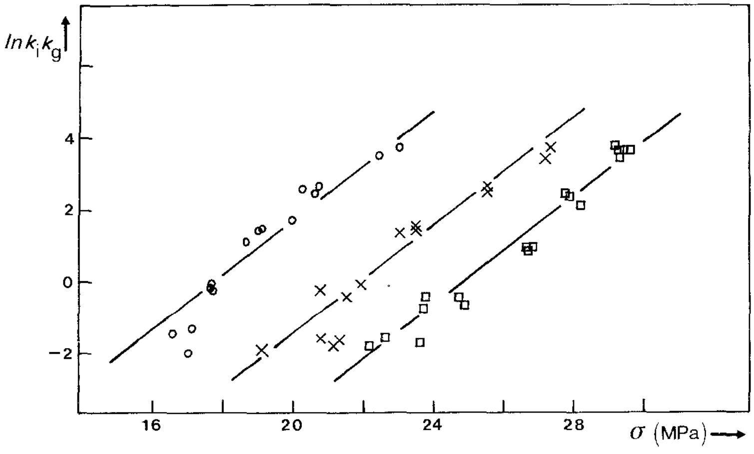

Figure 5 Dependence of ln k_ik_g of an 85/15/1 (wt/wt) PS/ldPE/co-polymer blend at temperatures: □, 295 K; ×, 303 K; ○, 313 K.

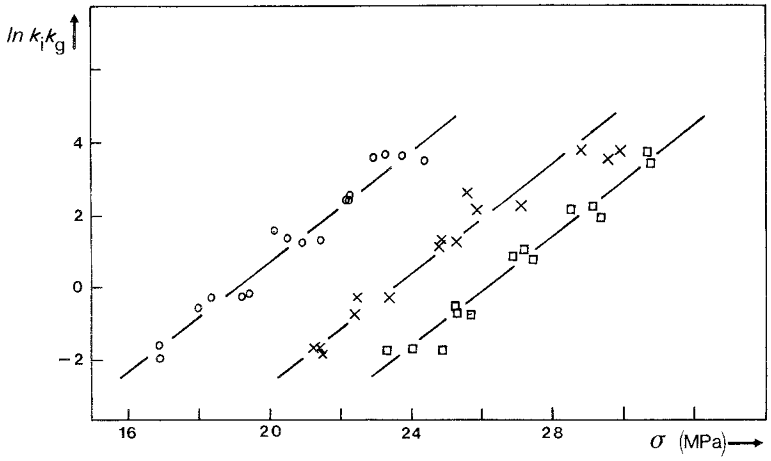

Figure 6 Dependence of ln $k_i k_g$ of an 85/15/2 (wt/wt) PS/ldPE/co-polymer blend at temperatures: □, 295 K; ×, 303 K; ○, 313 K.

stress-concentration fields grow from one rubber sphere towards the other, it can be assumed that a craze nucleated at a nucleation site within a cluster will reach a size that is approximately equal to the cluster area. Denoting the rate of the craze nucleation, that is the rate of craze formation in terms of numbers of crazes, as k_n and denoting N_T and N_{cl} as, respectively, the total number of potential craze nucleation sites and the number of potential craze nucleation sites within clusters, the effective craze nucleation rate, defined as the rate of nucleation of crazes that develop into large crazes, is given by

$$k_{n,\,eff} = \frac{N_{cl}}{N_T} k_n. \qquad (5)$$

Craze area growth is a fast process if the craze grows between spheres with overlapping stress-concentration fields. The rate of craze area formation normal to the stress direction therefore equals the effective craze nucleation rate multiplied with the average cluster area, A_{cl}, i.e.,

$$k_i = k_{n,\,eff} A_{cl} = \frac{N_{cl}}{N_T} k_n A_{cl}. \qquad (6)$$

As k_n in PS is described by the Eyring equation [7], it follows that

$$k_i = \left[A_n \exp\left(\frac{-\Delta H_n^*}{kT}\right) \times \exp\left(\frac{\gamma_n \sigma V_n^*}{4kT}\right)\right] N_T \frac{N_{cl}}{N_T} A_{cl}, \qquad (7)$$

where A_n, ΔH_n^*, V_n^* and γ_n are, respectively, the frequency factor, activation enthalpy, activation volume and stress-concentration factor belonging to the rate coefficient of craze nucleation.

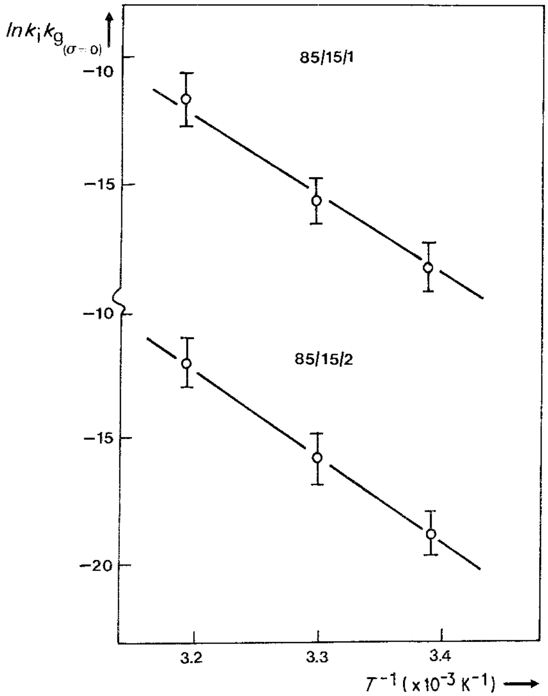

Figure 7 Values for ln $k_i k_g$ extrapolated to zero stress plotted against the reciprocal temperature. The blend compositions are as indicated (PS/ldPE/co-polymer).

TABLE III Eyring parameters of co-polymer-containing blends

Blend composition PS/PE/ co-polymer (wt/wt/wt)	$\gamma_i V_i^* + \gamma_g V_g^*$ (nm^3)	$\Delta H_i^* + \Delta H_g^*$ (kJ mol^{-1})	$A_i A_g$ (min^{-2})
85/15/0	9	150	3.5×10^{21}
85/15/1	12	280	3.5×10^{41}
85/15/2	12	300	3.5×10^{44}

It thus appears that the activation enthalpy and volume found for craze initiation are in effect connected with craze nucleation. Furthermore, the increase of the pre-exponential factor with the volume-fraction ldPE must arise from an increase of the term $N_{cl}A_{cl}$.

Values for the average cluster size cannot easily be obtained. The major difficulty is that the definition of cluster area must be rather arbitrary as there is no detailed knowledge concerning the stresses between the spheres. Nevertheless, some indication about the dependence of the term $N_{cl}A_{cl}$ on the ldPE content can be obtained from a two-dimensional computer simulation of a monodisperse system:

A two-dimensional matrix, representing a cross-section normal to the stress direction of TPS, is filled in a random fashion with squares, representing cross-sections of the ldPE spheres, until the total area has been covered to an extent that corresponds with the volume fraction ldPE. A square is said to be part of a cluster if the distance to another square is such that significant overlap of stress-concentration fields takes place. For spherical particles significant overlap takes place if the inter-particle distance is less than $(R_1 + R_2)$, where R_1 and R_2 are the radii of the particles [8]. This can be simulated by surrounding a square (of side dimension, D) with another square (of side dimension, $2D$) that represents the extent of the stress-concentration field (Fig. 8). If this stress-concentration field overlaps the stress-concentration field of another square then both squares belong to the same cluster (Fig. 8). The total area of the clusters and the number of clusters can be determined to obtain the average cluster area, A_{cl}.

As N_{cl} will be proportional to the number of squares within the clusters, the dependence of $N_{cl}A_{cl}$ (in arbitrary area units) on the volume-fraction can be determined. Results are represented in Fig. 9.

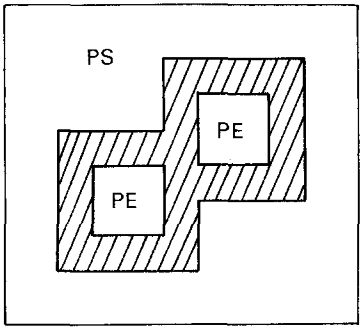

Figure 8 Shaded area is defined as cluster area.

Upon comparison of Figs 4 and 9 it is evident that the qualitative agreement is promising. The cluster model simulation predicts a more than proportional increase of the term $N_{cl}A_{cl}$, and thus of the rate of craze initiation, with the ldPE content, which is in agreement with the experimental results. However, the increase in particle size with increasing ldPE content [9] has not been taken into consideration in this simulation. The dependence of $N_{cl}A_{cl}$ on the particle dimensions can be derived as follows: N_{cl} equals the number of particles situated within clusters, M_{cl}, multiplied by the number of potential craze nuclei per particle. The number of potential craze nuclei per particle is unknown, but can be taken to be proportional to a power function of the particle radius r. Thus

$$N_{cl} \sim M_{cl}r^i. \tag{8}$$

Furthermore, M_{cl} is proportional to r^{-3} at a constant volume-fraction of the dispersed material and A_{cl} is proportional to r^2, resulting in

$$N_{cl}A_{cl} \sim r^{i-1}. \tag{9}$$

As effective crazes are nucleated at a band around the equator of the rubber particles [6] it can be assumed that the number of craze nuclei per particle is proportional to the area of this particle. Then i equals 2 and $N_{cl}A_{cl}$ is found to be proportional to the radius of the particles at a

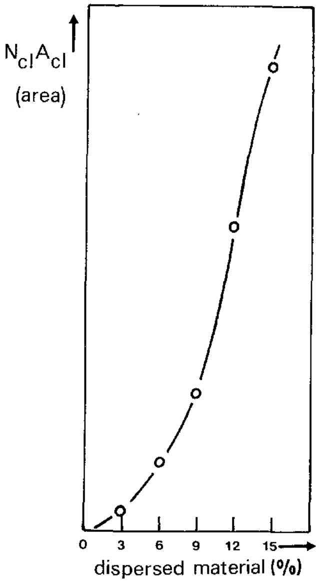

Figure 9 Dependence of the term $N_{cl}A_{cl}$ on the dispersed material content as determined by simulation.

constant volume-fraction of dispersed material. Thus it can be expected that for the actual blends the term $N_{cl}A_{cl}$ increases faster with the ldPE content than indicated in Fig. 9.

4.3. Co-polymer modified blends

It is rather difficult to pin-point the causes of the effect that co-polymer addition has on the craze rates. In general it is not likely that co-polymer addition affects the rate of the craze growing process, as the co-polymer is situated not within the PS phase but at the interface. Due to constraints caused by co-polymer induced interfacial adhesion [10] a decrease in the growth stress concentration factor, γ_g, may be possible.

Nevertheless, it is fair to assume that most of the changes in the crazing parameters that result from co-polymer addition can be ascribed to changes in the rate of craze initiation.

The decrease in particle size due to the emulsifying behaviour of the co-polymer [11] results, as argued below, in a decrease in the pre-exponential factor that belongs to the rate of craze initiation. As this factor increases upon co-polymer addition, this effect appears to be of minor importance as compared with other effects.

The presence of co-polymer near the interface causes changes in composition and in morphology. As craze nucleation takes place near the interface the rate of craze nucleation can be strongly affected by these changes, which would be reflected in the rate of craze initiation. Furthermore, co-polymer provides interfacial adhesion [10]. Upon stress application this causes a triaxial stress at the interface. In PS/ldPE homopolymer blends no adhesion exists, so in these blends the stress at the interface is bi-axial and will be tri-axial at some distance from the interface. This difference also may have consequences for the rate of craze initiation.

5. Conclusions

The activation parameters of craze initiation and craze growth are not influenced by the ldPE content (in the concentration range studied here), reflecting the fact that these activation parameters are PS material constants. The increase of the product of the pre-exponential factors, A_iA_g, with the ldPE content can be explained tentatively by a cluster model, which is essentially a refinement of the multiple crazing mechanism developed by Bucknall [12]. This cluster model has some interesting features. It inherently explains craze termination caused by a stop in craze initiation [3] as the total craze area that can be formed normal to the stress direction is limited to the cluster area. Furthermore the cluster model can explain the dependence of the rate of craze initiation on the particle size. It predicts an increase in yield stress with decreasing particle size, which is in accordance with results obtained by Fletcher *et al.* [13] on TPS. The way the craze area normal to the stress direction increases with time is explained as well by the cluster model. The area was found to increase proportional to time at constant stress [1], while a proportionality to the square of time can be expected in case of bi-directional areal growth. In the model, however, it is assumed that fast areal growth of a craze to a size equal to the cluster area takes place once the craze is nucleated. Craze nucleation is considered to be the limiting step and so the rate of nucleation gives rise to the observed time dependence of craze area growth. Although the cluster model comprises well-known features, like a maximum craze density in regions with maximum principal stress [14], craze nucleation [12] and termination [15] at rubber particles, it must be remarked that this model needs further experimental verification. Furthermore the computer simulation to determine the term $N_{cl}A_{cl}$ described above is rather crude and must be refined for more detailed analyses.

Co-polymer addition gives rise to significant changes in the rate of crazing. It is likely that the rate of craze initiation is more affected by co-polymer addition than the rate of craze growth. Differences in composition and in morphology of the material near the interface that are caused by co-polymer addition may well account for the strong increase of the activation enthalpy and the pre-exponential factor of craze initiation. Furthermore, co-polymer provides interfacial adhesion, which causes changes in the stress state at the interface. This effect may have consequences for craze initiation as well.

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