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Craze yielding and fracture mechanism in PE/PS/PE laminated films

Part 2 *Post-yielding, craze advance and fracture*

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The change in polystyrene (PS) layer thickness, which has been simultaneously determined during post-yield deformation, shows that crazing is the basic mechanism of toughening in all laminated films, and that shear deformation supplements the contribution of crazing especially for samples with high polyethylene (PE) volume fractions. Crazes formed in PS layers in the laminated films are slender and regular compared with the short and lenticular crazes formed in bulk PS film. When PE volume fraction increased, craze advance speed decreased because of the reduction of the stress concentration effect at craze tips. The life-time of the first mature craze to be formed at a given strain rate increased with PE volume fraction because the PE supporting the mature crazes could effectively inhibit craze rupture and blunt out the propagating crack by absorbing the stored elastic energy in the PS layer that would have been dissipated as fracture surface energy.

1. Introduction

In our previous paper [1] the mechanical behaviour of laminated films, especially the altered mechanical properties of polystyrene (PS) in the laminated state, as functions of polyethylene (PE) volume fraction was discussed. It was observed that crazing in PS can be modified by laminating layers of PE to both sides, and that the tenacity of PS or that of the laminated films increased conspicuously with PE volume fraction.

As reported in the previous paper, the elongation at break of the laminated films is three to five times larger than that of bulk PS film. The question arises as to whether craze formation was sufficient to account for the observed plastic strain or, in other words, whether only craze yielding was involved in the post-yield deformation of the laminated films.

The situation of craze growth, unlike that regarding craze nucleation, now seems quite clear. It has been shown that craze kinetics in PS (unlike craze nucleation kinetics) are only sensitive to the magnitude of the maximum principal stress [2]. It has been recognized that the craze tips advance by the mechanism of meniscus instability [3–6], and that crazes thicken by continued drawing of new polymer from the craze interfaces into fibrils maintaining the extension ratio of the fibrils almost constant for a given stress on the craze surfaces [7, 8].

It is also observed that once a few neighbouring fibrils have broken down, a large void is formed in the craze [9, 10]. The cause of such breakdown has been found to result from particulate impurities trapped in the polymer during manufacturing [11, 12]. These voids may grow slowly by slow fibril breakdown at void edges until a critical size has formed within the craze. The crack then propagates rapidly, breaking craze fibrils as it grows [13].

In this paper we will concentrate our attention on the yielding mechanism of PS in the laminated films. We will also be interested in the advance and fracture of crazes in PS in the laminated state under axial tension on the basis of the considerations mentioned above.

2. Experimental procedure

2.1. Samples and tensile testing

Materials, preparation of the laminated films and tensile tests were the same as described in Part 1 [1] except that some of the samples used in measurements for change of thickness during tension and for craze tip advance speed had widths of 10 mm, and some of the tensile tests were performed at a cross-head speed of 10 mm min^{-1} rather than 2 mm min^{-1}.

2.2. Measurement of change of sample thickness during post-yield deformation

An immersion ultrasonic technique was used because of the ease with which the change of thickness of the specimen caused by tension could be rapidly measured. The principle of this method is illustrated in Fig. 1. A high-frequency (30 MHz) sound pulse from the emitter travels with normal incidence to a specimen under tension. Part of the energy penetrates through the specimen and propagates to the receiver. The change of time required for the pulse to travel from the emitter to the receiver during post-yield deformation was measured with a digital storage oscilloscope 6041 (Hitachi). The shape of the pulse was slightly distorted due to craze formation in the specimen, and the major part of the pulse that corresponded to the change of

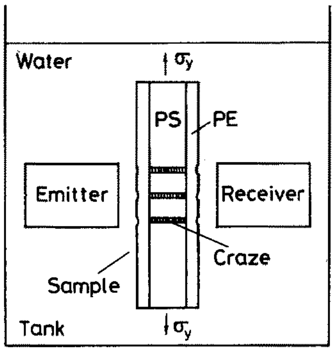

Figure 1 Illustration of ultrasonic measurements for change of sample thickness during post-yielding deformation.

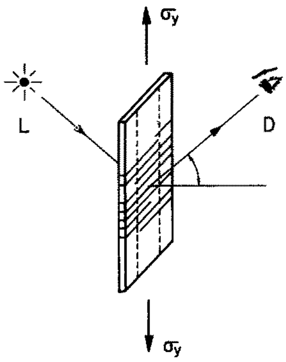

Figure 2 Measurement for craze tip advance speed. $\dot{\varepsilon} = 0.1\ \text{min}^{-1}$.

thickness of uncrazed parts was made use of for the measurement.

It has been reported [14] that sound velocity in a polymer in the thickness direction is hardly influenced by tension. Neglecting changes of sound velocities in PS and PE layers and assuming the strain before yielding to be completely elastic, the change of time required for the pulse to travel through the sample during post-yield deformation can approximately be expressed as follows

$$\begin{aligned} \Delta t &= t - t^{y} \\ &= (d_1^{y} - d_1)(1/v_w - 1/v_1) \qquad (1) \\ &\quad + (d_2^{y} - d_2)(1/v_w - 1/v_2) \\ d_1^{y} &= d_1^{o}(1 - \nu_1 \varepsilon^{y}) \qquad (2) \\ d_2^{y} &= d_2^{o}(1 - \nu_2 \varepsilon^{y}) \qquad (3) \end{aligned}$$

where t, d, v, ε and ν are, respectively, time, thickness, sound velocity, longitudinal strain and Poisson's ratio, the subscripts 1, 2 and w refer to PS, PE and water, and the superscripts o and y denote original value and the value at yield point.

For accuracy several laminated films were positioned in parallel as one sample in the measurement. When the PE volume fractions surpassed two-thirds the calculated values for PS layer would be less credible and hence were left out.

2.3. Optical microscope observation and determination of craze density

The aspects of crazes and cracks developed during tensile testing for the laminated films and bulk PS film were observed through an optical microscope Model BHSP (Olinpas). After the PE layers on both sides of stretched laminated films had been stripped off, the surfaces of the PS layers were examined and compared with those of stretched bulk PS film. The fracture cross-sections of both PS layers and bulk PS film were also investigated.

Because most of mature crazes formed in the laminated films penetrated through the PS layer thickness and spread completely across the specimens from one edge to the other (see Fig. 6b), ultimate craze density was estimated with the number of crazes per unit length. It was measured through a multipurpose projector Model 1 (Nikon). In general, the density of craze varied along the gauge length and the mean craze density for each sample was determined by averaging the values at five places along the gauge length.

2.4. Measurement of craze tip advance speed

With the aid of reflected light from the craze tip, the craze advance speed in the PS layer was qualitatively measured directly during tension as a function of distance from the film edge as illustrated in Fig. 2.

The average craze tip advance speed in the middle region of various samples with different PE volume fractions was determined using the following procedure. The middle half region of the specimens had been demarcated previously by two longitudinal lines marked on the surfaces. The time required for the craze to advance through the middle region under tension was measured with a stopwatch. The average craze advance speed was determined from the time divided by the half-width of the sample (5 mm).

3. Results and discussion

3.1. Yielding mechanism

In general, the total elongational strain of PS, ε, can be assumed to have contributions from elasticity, ε_e, crazing, ε_c, and shear deformation, ε_s [15, 16].

$$\varepsilon = \varepsilon_e + \varepsilon_c + \varepsilon_s \qquad (4)$$

The adhesion between PS and PE layers may be considered sufficient before the fracture of the PS layer so that the elongational strains in PE supporting crazed and uncrazed parts could be supposed identical with those in PS.

To a first approximation, ε_e may be considered constant during post-yield deformation, and hence the increment of strain would be contributed from crazing and shear deformation.

$$\Delta\varepsilon = \varepsilon - \varepsilon^{y} = \varepsilon_c + \varepsilon_s \qquad (5)$$

It has already been reported [17] that crazing includes void formation and does not contribute to lateral strain (its contraction ratio $\nu_c = 0$), and that shearing, on the contrary, does not change the volume ($\nu_s = 0.5$). For uncrazed parts where $\varepsilon_c = 0$, both the volume of PS and that of PE supporting these uncrazed parts could be considered unchanged. The shear strain and crazing strain during post-yield deformation can thus be deduced from the lateral shear strain, ε_{ds}, which can be calculated from the change of time required for a pulse to travel through the uncrazed parts. From

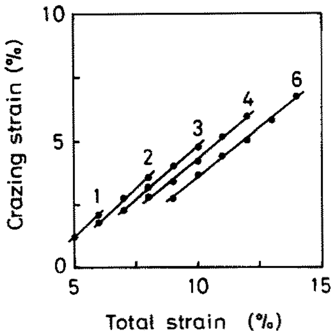

Figure 3 Crazing strain plotted against longitudinal strain.

Equations 1 and 5

$$\varepsilon_{ds} = \frac{d_1 - d_1^y}{d_1^y} = \frac{d_2 - d_2^y}{d_2^y}$$

$$= -\frac{\Delta t}{d_1^y(1/v_w - 1/v_1) + d_2^y(1/v_w - 1/v_2)} \quad (6)$$

$$\varepsilon_s = 1/(1 + \varepsilon_{ds})^2 - 1 \quad (7)$$

$$\varepsilon_c = \Delta\varepsilon - \varepsilon_s = \varepsilon - \varepsilon^y - \varepsilon_s \quad (8)$$

The crazing strain so obtained is plotted against logitudinal strain in Fig. 3; the parameters denote the numbers of PE layers on each side in the laminated films (in the calculation, $\nu_1 = 0.33$, $\nu_2 = 0.45$, $v_1 = 2.2\,\mathrm{km\,sec^{-1}}$, $v_2 = 2.1\,\mathrm{km\,sec^{-1}}$, $v_w = 1.5\,\mathrm{km\,sec^{-1}}$ were used). It appears that there exists a linear relationship between the crazing strain and the total strain in all cases while the gradient becomes less steep in cases with higher PE volume fractions (hereafter V_2 is used to represent the volume fraction of supporting PE).

The relative contribution of crazing during post-yield deformation is of particular interest. If we define the yielding mode factor, α, as the relative contribution of crazing

$$\alpha = \varepsilon_c/\Delta\varepsilon \quad (9)$$

then α can take values between 0 (complete shear yielding mode) and 1 (complete craze yielding mode).

In Fig. 4 the yielding mode factor that was obtained from the slopes of the curves in Fig. 3 is plotted against V_2. The value is larger than 0.7 in all cases (the actual value might be larger still because the experimental error here would tend to cause an underestimation of the value) although it decreases with increasing V_2.

As has already been related in Part 1 [1], the craze initiation and propagation in the PS layer were suppressed by the supporting PE and the yield stress in the PS layer increased with V_2. In other words, the tensile stress during post-yield deformation would monotonically approach the general yielding stress of PS when V_2 increased. As a result, the shear yield contribution would also increase with V_2 although it was only a minor part of the total elongational strain in all cases.

The results outlined above can be summarized into two features: crazing is the basic mechanism of toughening in all laminated films, and shear deformation supplements the contribution of crazing especially in cases with high V_2. It seems that there exists a co-operative interaction between crazing and shear deformation: greater toughness is achieved when both mechanisms are present, as in the laminated film with higher V_2, than when crazing is acting almost alone, as in the case with low V_2.

3.2. Effect of strain rate

Fig. 5 shows an example of strain rate effect on craze yielding behaviour of a laminated film containing three PE layers on each side strain at 0.1 and $0.5\,\mathrm{min^{-1}}$, respectively. Some features can be distinguished from the figure. When tested at a higher strain rate, the specimen displayed a sharper transition between elastic and plastic deformations. The specimen exhibited higher stress at all stages of deformation but a lower elongation at break at the higher strain rate (curve b).

From the experimental results, it is recognized that not only stress but also the time characteristic of the stress is essential to craze formation in the PS layer in the laminated state. First, for PS itself, the time scale dominating the deformation process at high strain rate likely hindered fibril formation and consequently craze development became difficult. In other words, if the characteristic time of deformation was shorter, fewer sites of heterogeneity would be realized and higher stress would be needed for craze formation at the higher strain rate. Secondly, when the strain rate increased, the PE supporting the craze tips would be deformed at a higher local strain rate and hence both the advance in the plane of the craze and their rate of thickening would become more difficult because of the viscous nature of PE. As a result, higher stress would be needed to match the higher strain rate. Once mature crazes spread completely across the specimen, these craze materials were less stable to support the high stress and the transformation of craze into crack

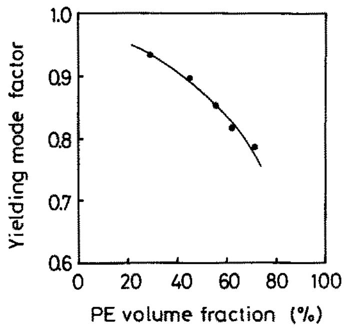

Figure 4 Yielding mode factor, α, plotted against PE volume fraction. $\dot{\varepsilon} = 0.1\,\mathrm{min^{-1}}$.

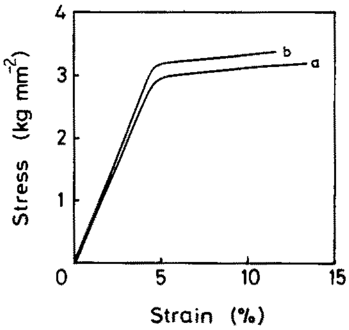

Figure 5 Effect of strain rate on craze yielding behaviour. (a) Strained at $0.1\,\mathrm{min^{-1}}$, (b) strained at $0.5\,\mathrm{min^{-1}}$.

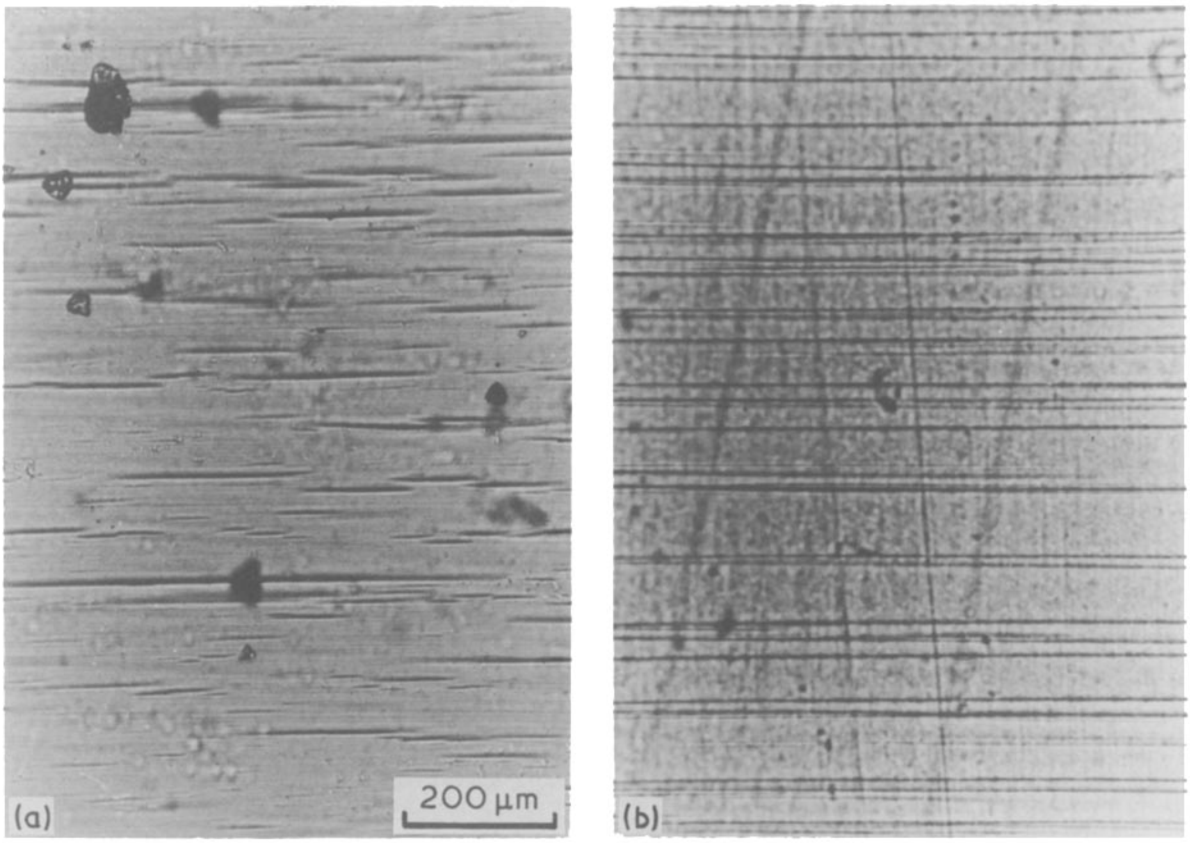

Figure 6 Optical micrographs of PS surfaces. (a) Surface of bulk PS film stretched to 3%, (b) surface of PS layer with original PE volume fraction of about 29% stretched to 5%.

would be relatively easy under the high stress, accompanied by the low elongation at break.

3.3. Comparison of morphologies of crazes and fractured cross-sections

Fig. 6 shows optical micrographs of surfaces of a bulk PS film stretched to 3% and a PS layer with an original PE volume fraction of about 29% (i.e. with one PE layer on each side) stretched to 5%. Comparing the two morphologies it can be seen that there are conspicuous differences between the two. Crazes in the PS layer are slender and linear compared to the short, wide and lenticular crazes in the bulk PS film. The crazes in the PS layer are distributed homogeneously over the whole surface, while the crazes in the bulk PS film are formed sporadically and unevenly and impingement of the crazes has occurred.

In general it can be assumed that stress concentrators of both the micro defects (scratches) on the PS surfaces and the heterogeneities in PS were distributed randomly in the width direction. In the tensile test for the bulk PS film, most of the crazes were nucleated at these randomly positioned stress concentrators, so that some of the craze initiations happened at the edges and others at distances from the edges. These crazes will easily transform into cracks that can propagate without significant energy absorption so that they appear to have a limited short length before fracture of the specimen occurs.

In the laminated films, as reported in our previous paper [1], the tensile stress concentrations at the micro defects were reduced by the supporting PE while the transverse interlaminar shear stresses concentrated at the film edges, resulting in increases both negative pressure and deviatoric stress at the edges. Therefore, craze initiations in the laminated films always happened at the edges. These crazes then grew in the film width direction without premature fracture by virtue of the supporting PE layers (the life-time of the craze will be discussed in a later section), so that most of the mature crazes that played a leading role in craze yielding penetrated through the PS layer thickness and spread completely across the specimen from one edge to the other.

The mature crazes formed in the PS layers with various original PE volume fractions have approximately the same order of thickness (0.2 to 0.8 µm from SEM), although in general the crazes formed in the case with higher PE volume fraction were found to be somewhat thicker than in other cases.

The average ultimate craze density for various laminated films is plotted against PE volume fraction in Fig. 7. It appears that there exists a linear relationship between the average craze density and PE volume fraction. This coincides with the conclusion that crazing is the basic mechanism of toughening in all laminated films.

The average craze initiation rate during post-yield deformation that is determined from the ultimate craze density divided by the duration time for each laminated film is also plotted against V_2 in Fig. 7. The value decreases slightly with V_2, which can be considered as a result of the decrease in yielding mode factor.

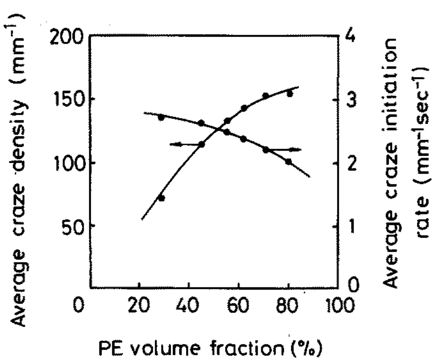

Figure 7 Average craze density and average craze initiation rate plotted against PE volume fraction. $\dot{\varepsilon} = 0.1\,\text{min}^{-1}$.

The fracture cross-sections of PS layers and bulk PS film differed mainly in the fact that the laminated films exhibited craze yielding and, therefore, exhibited the associated fracture morphology. A crack nucleated in a mature craze preformed in the laminated film that had penetrated through the PS layer thickness and spread in the width direction completely across the specimen. It then propagated through the preformed mature craze to give a fracture cross-section with macroscopically almost an entirely mirror-like surface. In the case of bulk PS film, on the other hand, a crack nucleated in a craze that was superficial and had only a limited short length, and it then spread into the bulk PS. As the crack tip happened to approach another short craze, it grew into the craze and spread forward in this manner repeatedly. Therefore the mirror regions in the fracture surface were discontinuous and were followed by distinct hackle regions.

3.4. Craze tip advance speed

Because the craze initiations were always found at the edges of the laminated films, the qualitative craze advance speed is schematically plotted in Fig. 8 as a function of the distance from the film edges. At the first stage of craze formation, the craze advance speed is somewhat higher. Then it enters a plateau for quite a wide range. As the craze tip spreads near the opposite edge, the speed decreases notably. When V_2 increases, the shape of the curve is similar to that for sample with low V_2 but the speed is lower at all stages of craze propagation.

The sequence of events leading to the change of craze advance speed may be described in the following way. At the first stage of craze formation the craze material just formed in the craze and the PE supporting the just-formed craze were not stable enough to support the applied stress so that the craze propagated rapidly until an equilibrial stress redistribution was attained. Then the craze spread under the quasi-equilibrial stress with almost a constant speed. As the spreading craze advanced, however, the craze traction stress would monotonically approach the applied stress (tensile stress in the PS layer during post-yield deformation), which would result in a considerable decrease in the driving force at the craze tip when the craze reached a certain length. Furthermore, the reduction of stress concentration effect, which was caused by the strain hardening of supporting PE due to local large deformation along the craze, would increase with the craze length. For these reasons the speed of advance of the spreading craze decreased notably in the last stage of craze propagation.

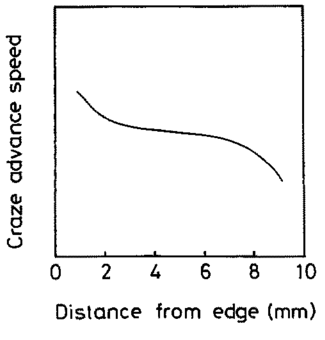

Figure 8 Schematic plot of craze advance speed as a function of the distance from the sample edges. $\dot{\varepsilon} = 0.1\,\text{min}^{-1}$.

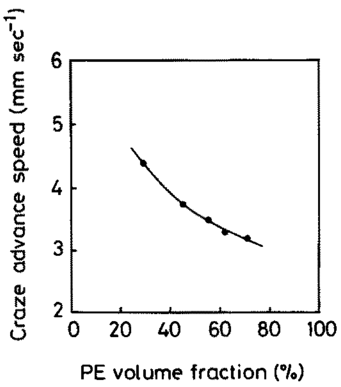

Figure 9 Average craze advance speed plotted against PE volume fraction. $\dot{\varepsilon} = 0.1\,\text{min}^{-1}$.

The average craze advance speed in the middle region of various laminated films with different PE volume fractions is plotted in Fig. 9 against V_2. It can be seen that the speed will decrease when V_2 increases.

From the meniscus instability models of Taylor [3, 4] and Argon [5, 6], Kramer [18] has recently deduced the steady state craze tip advance speed, v_0, with fewer parameters

$$v_0 = C((\sigma_0)_m - 2\Gamma/h)^{2n} \qquad (10)$$

where C, Γ, h and n are material constants, and $(\sigma_0)_m$ refers to the hydrostatic tension midway between two craze void fingers. The $(\sigma_0)_m$ is taken to be proportional to the average tensile stress at craze tip, σ_t.

$$(\sigma_0)_m = \beta\sigma_t \qquad (11)$$

As reported in the previous paper [1], the transverse pressure in the PS layer caused by the difference between Poisson's ratios of PS and PE would increase with V_2. Thus the effect of increase in yield stress on the hydrostatic tension will be counteracted partly by the increase in transverse pressure. Furthermore, increasing the thickness of the supporting PE on both sides of the film will reduce further the stress concentration effect at the craze tip. Consequently, the average tensile stress at the craze tip and thereby the hydrostatic tension midway between two void fingers will decrease with V_2 despite a little increase in the yield stress. As a result, the steady state craze advance speed will decrease when V_2 increases.

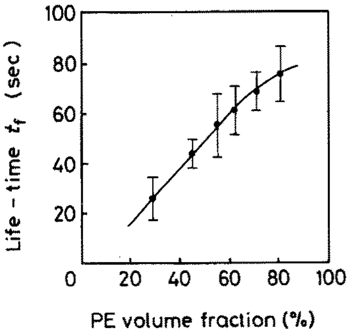

Figure 10 Average life-time of the mature craze first formed plotted against PE volume fraction. $\dot{\varepsilon} = 0.1\,\text{min}^{-1}$.

3.5. Life-time of craze matter

The mature craze matter formed first is subjected to full craze traction which after its penetration must increase to the level of the tensile stress in the PS layer, σ_{yl}, for the entire duration of post-yield deformation. We now define the life-time of the mature craze first formed, t_f, as the entire duration from the beginning of yielding to the fracture at a given strain rate. In general, the lifetime of a craze can be considered as a sum of the times of completion of two stages: crack initiation and crack propagation.

$$t_f = t_i + t_p \tag{12}$$

At first glance it seems that the craze first formed in the laminated film with higher V_2 might have a shorter life-time because the yield stress in the PS layer is higher than in other cases. The actual average life-time, t_f, on the contrary, will increase with V_2 as shown in Fig. 10.

Because the PE supporting the mature craze will tend to inhibit craze rupture, it seems reasonable to consider that the time for crack initiation might increase to a certain extent, and at least would not decrease, with V_2.

It is reported that the life-time is controlled essentially by a slow cracking region and that very slow subcritical crack growth can be characterized approximately by an empirical law of the form [19]

$$v = AK_I^c \tag{13}$$

$$K_I = \sigma_{yl}(\pi a)^{1/2} \tag{14}$$

where v, K_I, a and σ_{yl} are, respectively, crack velocity, stress intensity factor of the crack (the subscript I refers to the crack opening mode), crack length and tensile stress in the PS layer, and A and c denote a constant and an exponent (as large as 25 for PS). This law indicates that the crack velocity and thereby the life-time are very sensitive to the stress intensity factor.

In the laminated films the PE supporting the subcritical crack will produce a negative stress intensity factor, K_I', due to the strain hardening effect of PE. Because the local excess cohesive forces in the PE supporting the crack can be considered proportional to PE volume fraction and to the stress difference between the parts of PE supporting crazed and uncrazed parts of PS, $\Delta\sigma_2$, the negative stress intensity factor caused by supporting PE, K_I', can be written as

$$K_I' = -C'\Delta\sigma_2(V_2/V_1)(\pi a)^{1/2} \tag{15}$$

The total stress intensity factor of the crack then becomes

$$K_I = (\sigma_{yl} - C'\Delta\sigma_2 V_2/V_1)(\pi a)^{1/2} \tag{16}$$

In the present work the value in the first parentheses will decrease with V_2, i.e. the increased thickness of PE supporting the subcritical crack will make the total stress intensity factor of the crack decrease despite a small increase in the yield stress in the PS layers.

The increase in the life-time of the mature craze first formed can be illustrated more directly in terms of the modified Griffith theory. The local large deformation of PE supporting the subcritical crack can effectively inhibit craze rupture and blunt out the propagating crack by absorbing the stored elastic strain energy in the PS layer that would have been dissipated as fracture surface energy. Increased thickness of the supporting PE is able to absorb a greater amount of elastic strain energy stored in the PS layer so that it will become more difficult for the subcritical crack to grow, resulting in increases in the times required for crack initiation and propagation. Therefore, the life-time of the craze increases considerably with V_2.

It seems that there may be another reason for the increase in the life-time of the mature craze first formed. It has been found that in a small region near the symmetry plane of the craze (the mid-rib) the extension ratio is especially large [7]. It has also been observed that the mid-rib expands in thickness and breaks down as a crack tip approaches [20, 21]. In the laminated films, as reported previously, the craze tip advance speed decreased with V_2. This phenomenon implies that the actual drawing stress at the craze tips and hence the fibril draw ratio in the mid-rib decreased with V_2, resulting in an increase in the fibril diameter in the region. For this reason the crazes formed in the laminated film with higher V_2 would have a higher load-bearing capacity and, therefore, longer life-time.

The increase in life-time of the mature craze first formed and thereby the increase in life-time of the laminated films appears to be the essential effect on the craze yielding and fracture behaviour of the laminated films.

Further studies on the microstructure of crazes formed in various laminated films will be reported elsewhere.

4. Conclusion

Crazing is the basic mechanism of toughening in all laminated films, and shear deformation supplements the contribution of crazing especially in cases with high PE volume fractions.

Higher yield stresses and lower elongations at break were observed when the laminated films were tested at a higher strain rate.

Crazes formed in the laminated films are slender and regular compared with those short and lenticular crazes formed in bulk PS. Most of the mature crazes in the PS layer spread in the width direction completely across the specimen without premature fracture. Crack nucleated in and propagated through a weak mature craze in the laminated films and gave a fracture cross-section with macroscopically an almost entirely mirror-like region.

In the first stage of craze propagation, the craze advance speed is somewhat higher. Then it enters a plateau for quite a wide range. When the craze tip spreads near to the opposite edge, the speed decreases notably. When the PE volume fraction increases, the craze advance speed decreases, due to the reduction of stress concentration effect at the craze tip caused by the strain hardening of the PE supporting the craze.

As subcritical crack growth occurs, the local large deformation of PE supporting the crack effectively inhibits craze rupture and blunts out the propagating crack by absorbing the stored elastic energy in the PS layer that would have been dissipated as fracture surface energy. Therefore, the life-time of the mature craze formed first and thereby the life-time of the laminated films increased with PE volume fraction. This is the essential effect of the toughening of PS by laminating layers of PE to both sides of the film.

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