JOURNAL OF MATERIALS SCIENCE 23 (1988) 4091–4096

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

Part 1 *Tensile behaviour and craze initiation*

C. X. ZHU, S. UMEMOTO*, N. OKUI, T. SAKAI
Department of Textile and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguroku, Tokyo, Japan

Mechanical behaviour of laminated films of PS and PE, especially the altered mechanical properties of PS in the laminated state, were studied as functions of PE volume fraction. It was observed that crazing in PS can be modified by laminating layers of PE to both sides. Elongation at break and hence fracture energy increased conspicuously when PE volume fraction increased. Craze yielding stress in PS layers also increased with increasing PE volume fraction because craze formations in PS layers were suppressed by the reduction of tensile stress concentration effect at craze tips. Craze initiations were always found at the free side edges of the laminated films, which can be correlated with the transverse interlaminar shear stress concentrations existing at the edges of the laminated films caused by the difference in Poisson's ratios between PS and PE.

1. Introduction

Many glassy polymers have been used as structural components over the last decade, but there is a limitation of such application because of the tendency of these materials to fail in a macroscopically brittle manner, i.e. with no large-scale plastic deformation before cracking. In the fracture mechanism of a glassy polymer, cracking is frequently preceded by a crazing phenomenon [1, 2], and these crazes with very thin planar shapes are nucleated and grow in planes normal to the direction of maximum principal stress. It has been recognized now that when uncontrolled, crazes usually fracture and cause brittle behaviour, while controlled crazing can impart to the polymer very substantial toughness [2–4].

In bulk glassy polymers, most of crazes are formed sporadically and are limited only to the thin surface layer. Such crazes will easily transform into cracks that can propagate without significant energy absorption, so that crazing in bulk glassy polymer will frequently cause a brittle fracture. Hence the study of control of crazing is of considerable technological interest.

The toughening of a glassy polymer by the incorporation of compliant heterogeneities has recently been discussed in detail [5, 6] and has been practised industrially on a large scale, whereas there is only a limited amount of published information about the effect of lamination on crazing and toughening. Here we will concentrate our attention on how crazing in a normally brittle glassy polymer can be modified by lamination with ductile polymer films to impart very substantial toughness to the glassy polymer. We will also be interested in craze initiation mechanisms in glassy polymer films in the laminated state under uniaxial tension.

Polystyrene and polyethylene were chosen in this work as they are representative brittle and ductile polymers, respectively, and have been studied extensively by other investigators.

2. Experimental details

2.1. Materials and preparation of laminated films

Polystyrene (PS) and polyethylene (PE) films used in this investigation are kindly supplied by Mitubishi-Yuka Corp. and their physical parameters are listed in Table I.

PS film was sandwiched between PE films to form a multilayer structure. Then it was wrapped in a PE film as shown in Fig. 1, in order to eliminate the environmental effect on fracture of the PS layer and also to reduce the influence of scratches on the PS layer edges that would induce flaws and decrease the strength of the laminated film. The volume fraction of PE is controlled by the number of PE films in the laminated film. The sample shown in Fig. 1 is one of a case containing three PE layers on each side, i.e. with a PE volume fraction of about 55%.

PE and PS films were bound together by a heat-pressing method in a vacuum. Because the adhesion between PE and PS layers was poor, the surfaces of such films were pretreated in an oxygen plasma to reinforce the binding strength. A heat-pressing process was carried out at 130° C for 30 min and then the heat-press was quenched with water.

PS and PE films to be tested directly were also annealed under the same conditions mentioned above.

2.2. Tensile test

Tensile tests for PS, PE and the laminated films were performed at room temperature on a conventional

---

*Author to whom all correspondence should be addressed.

0022–2461/88 $03.00 + .12

TABLE I PS and PE films and their physical parameters

Material	Commercial name	Poisson's ratio	Density ($g cm^{-3}$)	Glass transition temperature (° C)	Thickness (μm)
PS	16ERA-8	0.33	1.05	105	100
PE	FZ-70	0.45	0.95	− 110	20

tensile testing machine model UTM-II-20 (Tokyo Baldwin Corp.). The width and gauge length of the specimens were 5 and 20 mm, respectively, and a cross-head speed of 2 mm min^{-1} was selected for all tests.

Stress and hence Young's modulus were calculated using the initial cross-sectional area of the guage section that was measured for each specimen before testing.

With the aid of reflected light from crazes, the craze initiation places in both laminated and bulk films were observed directly through a lens during tension.

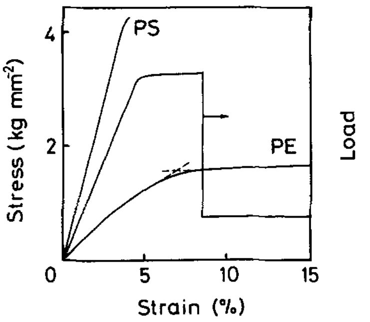

Figure 2 Stress–strain curves for PS and PE films and general form of load–strain curve for the laminated films.

3. Results and discussion

3.1. Tensile behaviour

The typical nominal stress–strain curves for PS and PE films stretched at a cross-head speed of 2 mm min^{-1} are shown in Fig. 2. The PS film possesses a high Young's modulus but exhibits only elastic behaviour followed by a brittle fracture at low elongation except for a little deviation from linearity caused by formation of extrinsic crazes on the PS surfaces just before fracture. The PE film, on the other hand, displays a prevalent plastic linear region following the elastic region and its elongation at break is extremely high (up to 500%).

Table II presents the mechanical properties of these films obtained from the stress–strain curves. The Young's moduli were calculated from the initial slopes of these curves and the yield stress was determined in a way as defined in Fig. 2 on the PE curve.

In tensile tests for the laminated films, the majority of the load–strain curves took the form shown in Fig. 2. Nominal elongation at break was determined where the load dropped abruptly because of failure of the PS layer in the laminated film.

The stress–strain curves for the laminated films strained at the same speed mentioned above are shown in Fig. 3 as a function of PE volume fractions; the parameters on the curves refer to the numbers of PE layers on each side. It is obvious that the mechanical behaviour of laminated films is very different from that of bulk PS film. Three different regions can be recognized in these curves: an elastic region, a plastic region, and a smooth transition zone between the two especially for samples with high PE volume fractions. This indicates that craze formation and propagation were allowed in the PS layer without premature fracture and a transverse crack propagation in the PS layer must have been suppressed by the adhesion force between PE and PS layers. It resulted in a very substantial increase in the toughness of the laminated films.

Young's modulus of various laminated films as a function of PE volume fraction is shown in Fig. 4, as the individual data points. It appears that Young's modulus of the laminated films decreases approximately linearly with PE volume fraction.

For a simple parallel model, the expression for Young's modulus is well known as the simple rule of mixtures

$$E = V_1 E_1 + V_2 E_2 \qquad (1)$$

where V and E are, respectively, volume fraction and Young's modulus, and subscripts 1 and 2 refer to PS and PE.

When the laminated film is stretched in the length direction, the strain difference between the PS and PE layers in the film width direction will tend to arise due to their Poisson's ratio difference. However, PS and PE layers are bonded together completely and they must have the same strains in both directions. Therefore, transverse interlaminar shear stresses and transverse pressure or stress in PS and PE layers arise.

For simplification, consider in the first place a simplified parallel model shown in Fig. 5a in which two pairs of hypothetic transverse stresses are introduced instead of the transverse interlaminar shear stresses. The two pairs of stresses act on the transverse surfaces of the edges of PS and PE layers, respectively, to keep the strains of both layers in the width direction identical. The Young's modulus of a laminated film can thus be deduced from Hooke's law and equilibrium condition.

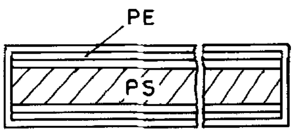

Figure 1 Cross-section of a laminated sample with a sandwiched structure wrapped in a PE film.

TABLE II Mechanical properties of PS and PE films

Material	Young's modulus ($kg mm^{-2}$)	Fracture or yield stress ($kg mm^{-2}$)	Fracture or yield strain (%)
PS	151	4.12	3.25
PE	66	1.82	7.33

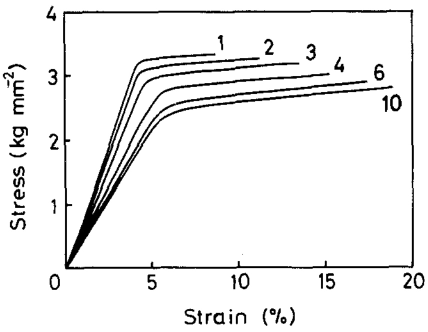

Figure 3 Stress–strain curves for various laminated films; the number on the curves are the number of PE layers on each side in the laminated films.

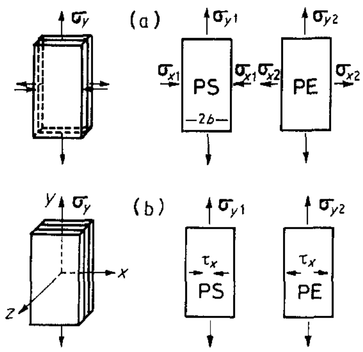

Figure 5 Parallel models. (a) Simplified parallel model, (b) normal parallel model.

$$E = \frac{(\nu_1 V_2 E_2 + \nu_2 V_1 E_1)^2 - (V_2 E_2 + V_1 E_1)^2}{\nu_2(\nu_1 V_2 E_2 + \nu_2 V_1 E_1) - (V_2 E_2 + V_1 E_1) - \nu_1(\nu_2 - \nu_1)} \qquad (2)$$

where ν is Poisson's ratio.

Young's moduli calculated from Equations 1 and 2 are shown in Fig. 4 as broken and solid line, respectively. There is a little difference between the two lines; however, Young's modulus of the laminated films appears to fit both lines although the latter appears to be somewhat more suitable.

The applicability of simple parallel model can be used to calculate approximately the stresses in PS layers from the strain–stress curves of the laminated and PE films

$$\sigma_{y1}(\varepsilon) = [\sigma_y(\varepsilon) - V_2\sigma_{y2}(\varepsilon)]/V_1 \qquad (3)$$

where σ and ε refer to stress and strain, and subscript y denotes film length direction (hereafter subscript x is used to denote film width direction).

Fig. 6 shows the calculated stress–strain curves for PS layers in various laminated films. It is very interesting that the mechanical properties of PS were altered conspicuously by lamination, i.e. crazing in PS was modified substantially by laminating PE to both sides. These curves are to be used below to examine the altered mechanical properties of PS in the laminated state.

In Fig. 7 the yield stress for laminated films and that calculated for PS layers are plotted against PE volume fraction. The circle on the left-hand axis represents the fracture stress of bulk PS film that will not yield before fracture. Examination of these data shows that the yield stress in PS layers increases with PE volume fraction although that for laminated films decreases approximatley linearly when the PE volume fraction varies from about 30% to 80%. Two effects may be the reason for the increase in yield stress in PS layers. First, it has been found that extrinsic crazes are usually observed to nucleate at the surface of the sample beneath defects and that if small samples of PS were perfectly produced from single moulding pellets, the stress required for craze initiation would increase substantially [7]. In the present work the tensile stress concentrations at PS surface defects would be lowered by the PE supporting these defects and hence these defects would be blunted especially for samples with high PE volume fractions. Most of the extrinsic craze initiations would be delayed to some extent and only the intrinsic ones resulting from heterogeneities were realized. Therefore, the stress required for a given rate of craze initiation increased with PE volume fraction. Secondly, but more importantly, it is recognized that the extension ratio in craze fibrils is far higher than the nominal one, and that craze thickening is an important feature of yielding by craze formation [8]. As craze growth in the PS layer occurs, the strain-hardening effect of PE supporting these crazes would hinder the opening of crazes due to the local large deformation around the craze tips. For this reason both their extension in the plane of the craze and their rate of thickening would be reduced under a given tensile stress. Increased thicknesses of the supporting PE on either

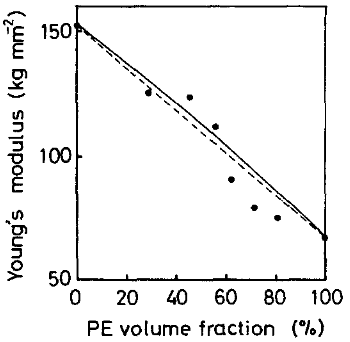

Figure 4 Relationship between Young's modulus and PE volume fraction.

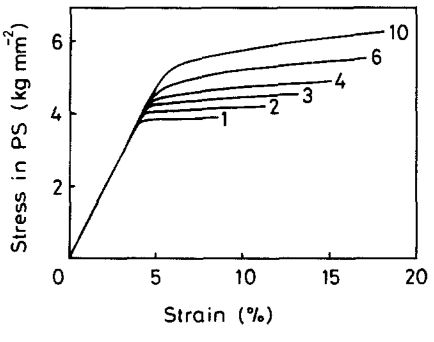

Figure 6 Calculated stress-strain curves for PS layers in various laminated films; the numbers on the curves have the same meaning as in Fig. 3.

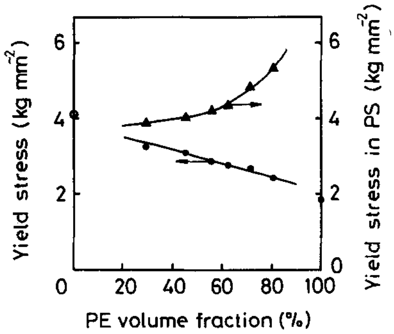

Figure 7 Yield stress for the laminated films and that calculated in PS layers plotted against PE volume fraction.

side of the film would make craze opening more difficult, so that higher stresses were needed for crazes to grow to maintain a given strain rate.

There is little difference between fracture stress and yield stress because the post-yield curves are almost linear and approximately parallel to the horizontal axis (see Figs 3 or 4). The relationship between strength and PE volume fraction can be assessed by referring to Fig. 7.

Yield strain is plotted against PE volume fraction in Fig. 8. The relationship between the yield strain and PE volume fraction is somewhat complex; however, the tendency exists that the yield strain increases with increasing PE volume fraction. This can be considered a consequence of the increase in yield stress in the PS layers.

Elongation at break, the scatter of which is quite large and becomes larger at higher PE volume fractions, is also plotted against PE volume fraction in Fig. 8; the length of the vertical marks on the curve represents the degree of scatter. As illustrated in Fig. 8, the elongation at break increases with increasing PE volume fraction but tends to saturate as PE volume fraction surpasses two thirds. The increase in the ultimate elongation during post-yield deformation can be related to the delay of crack initiation and propagation. The PE supporting the mature crazes would effectively inhibit craze rupture and blunt the propagating crack, i.e. both crack initiation and propagation would be delayed, especially for samples with thicker PE. As a result, the elongation at break increased with increasing PE volume fraction at a given strain rate.

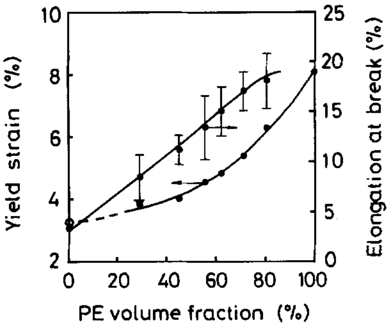

Figure 8 Yield strain and elongation at break plotted against PE volume fraction.

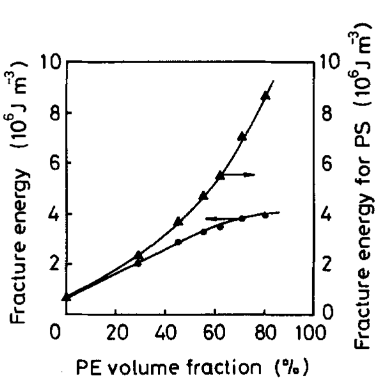

Figure 9 Fracture energies for the laminated films and for PS layers plotted against PE volume fraction.

Both fracture energies, which are calculated from the areas beneath the stress–strain curves for laminated films and those for PS layers, increase with PE volume fraction as shown in Fig. 9. The latter varies more conspicuously because not only the elongation at break but also the yield stress in the PS layers will increase when the PE volume fraction increases. These curves indicate that the tenacity of PS film can be enhanced remarkably through lamination with PE films. It is reported that the energy absorption in the craze region is far greater than that in uncrazed medium during tensile deformation [9]. In the laminated films, craze formation and propagation were allowed in the PS layer without premature fracture so that the craze density in these films increased, especially for samples with high PE volume fractions. Consequently, the fracture energies for PS and for the laminated films increased conspicuously with PE volume fraction.

Finally, there is some evidence in the literature that oxygen, or other pollutants in the air, can have an effect on crazing in stressed glassy polymers. It has been noted that crazing occurring during creep tests of PS specimens can be inhibited by testing in a water environment [10] and that craze growth under tension is reduced when the tests are carried out under vaccum [11]. Therefore, compared with that of bulk PS film, the increase in tenacity of PS in the laminated state may be partly attributed to the protection against chemical attack by oxygen or other contaminating influences in laboratory air.

3.2. Craze initiation site

During tensile tests of the laminated films, craze initiations were always found at the free side edges of the films. They then grew in a direction normal to the tensile direction. 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. In the case of bulk PS film, on the other hand, crazes were initiated randomly in the width direction, some at the edges and others at distances from the edges, and they appeared to have limited short lengths before the specimen fractured.

Although the detailed mechanisms of craze initiation are not well understood, it is widely considered that the local region of voided, oriented polymer which constitute the craze structure result from the generation, accumulation and plastic expansion cavities within the polymer [2, 12]. It has also been recognized that the negative pressure component of the stress tensor and the microshear bands caused by shear stress are important factors associated with craze initiation [13]. Many attempts have been made to formulate craze initiation criteria [7, 14–18]. Among those that most often mentioned appears to be that of Argon and Hannoosh [7, 17, 18].

$$3\sigma_0/(2Y) = -\ln(\beta_0 t) + \Delta G^*(S)/(kT) \quad (4)$$

where Y, t and T are, respectively, yield stress, time and absolute temperature, and β_0 and k refer to a constant and the Boltzmann's constant,

$$\Delta G^*(S) = 0.225\pi\mu^2 f^3/S \quad (5)$$

is the activation free energy, μ is the shear modulus, f is a microdisplacement of the order of molecular diameter, and the negative pressure, σ_0, and the deviatoric stress, S, are given by

$$\sigma_0 = (\sigma_x + \sigma_y + \sigma_z)/3 \quad (6)$$

$$S = \{[(\sigma_x - \sigma_y)^2 + (\sigma_y - \sigma_z)^2 + (\sigma_z - \sigma_x)^2]/6 + \tau_x^2 + \tau_y^2 + \tau_z^2\}^{1/2} \quad (7)$$

Substituting Equation 5 into Equation 4 yields

$$3\sigma_0/(2Y) = -\ln(\beta_0 t) + 0.0225\pi\mu^2 f^3/(kTS) \quad (8)$$

This criterion indicates that craze nucleation by a negative pressure is far easier when deviatoric stress is present.

To examine the negative pressure and deviatoric stress in the laminated films, we can, for simplification, consider a normal parallel model shown in Fig. 5b in which the transverse interlaminar shear stresses are taken into consideration while the longitudinal ones are neglected. With the similar approach made by Hayashi [19], the transverse interlaminar shear stress in the width direction, $\tau_x(x)$, can be deduced as

$$\tau_x(x) = -\frac{\lambda d_1 \sigma_{xm} \sinh(\lambda x)}{\cosh(\lambda b) - 1} \quad (9)$$

$$\lambda^2 = K(1/d_1 E_1 + 1/d_2 E_2) \quad (10)$$

where d and b are layer thickness and the half-width of the sample, K is the shear rigidity of the bonded layers, and σ_{xm} refers to the maximum of the transverse pressure in PS layer, $|\sigma_{x1}(x)|$, which can be yielded by integrating Equation 9 from $-b$ to x:

$$\sigma_{x1}(x) = -\sigma_{xm}\frac{\cosh(\lambda b) - \cosh(\lambda x)}{\cosh(\lambda b) - 1} \quad (11)$$

To a first approximation, the magnitude of σ_{xm} which is dependent on PE volume fraction, can be estimated with the simplified parallel model mentioned for calculation of Young's modulus of laminated films (Fig. 5a) in the previous section

$$\sigma_{xm} = \frac{(\nu_2 - \nu_1)E_2 V_2}{\nu_2(\nu_1 V_2 E_2 + \nu_2 V_1 E_1) - (V_2 E_2 + V_1 E_1)}\sigma_{y1} \quad (12)$$

The value increases with increasing PE volume fraction. Fig. 10 shows the stress ratio of σ_{xm}/σ_{y1} as a function of PE volume fraction. In general the maximum of the transverse pressure, σ_{xm}, is of the order of one-tenth of the longitudinal tensile stress in the PS layer, σ_{y1}, when PE volume fraction falls in the region of about 30 to 80%.

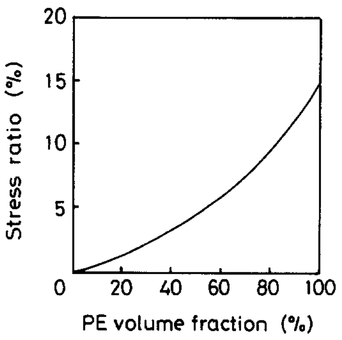

Figure 10 Stress ratio of σ_{xm}/σ_{y1} as a function of PE volume fraction.

Schematic representations of $\tau_x(x)$ and $\sigma_{x1}(x)$ along the film-width direction are shown in Fig. 11. It is interesting that there are very intensive shear stress concentrations at the free side edges of the laminated film (so-called end effect), and the transverse pressure in the PS layer, $|\sigma_{x1}(x)|$, is minimum (zero) at the edges. The maximum of $\tau_x(x)$ at the edges ($x = \pm b$) reaches about several tenths of the magnitude of tensile stress for the present work.

If σ_{xm} is, as an example, one-tenth of σ_{y1}, the negative pressure, $\sigma_0(x)$, and the deviatoric stress, $S(x)$, in the PS layers will take the form shown schematically in Fig. 11. The negative pressure is maximum at the edge, although the difference between the values at the edge and at the centre is small. The deviatoric stress, on the other hand, varies considerably from the centre to the edge. According to Equation 8 craze initiation is easier at the sample edges than at the central part for a set of given situations. This might be the reason why craze initiations are always found at the edges of the laminated films besides the common effect of scratches on PS layer edges.

In bulk PS film, on the other hand, the stress state was macroscopically uniform over the cross-section, and stress concentrators of both micro-defects on the PS surfaces and heterogeneities in PS are positioned randomly in the width direction, so that some of the craze initiations happened at the edges and others at distances from the edges.

Further studies about the craze yielding and the

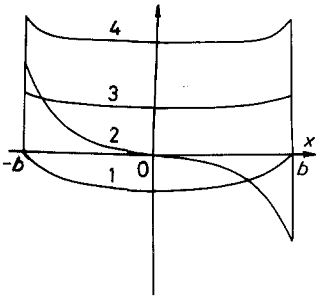

Figure 11 Distributions of (1) transverse stress $\sigma_{x1}(x)$, (2) interlaminar shear stress $\tau_x(x)$, (3) negative pressure $\sigma_0(x)$ and (4) deviatoric stress $S(x)$ in the PS layer along the film width direction.

fracture mechanism of the laminated films will be reported in the subsequent paper.

4. Conclusion

The mechanical behaviour of PE/PS/PE laminated films, especially the altered mechanical properties of PS in the laminated state, was studied as a function of PE volume fraction. Of particular interest is that crazing in PS can be modified by laminating layers of PE to both sides, which, in addition to the understanding of crazing, provided evidence that a glassy polymer can obtain very substantial toughness through controlled crazing when it is laminated with ductile polymer films.

Elongation at break of the laminated films with PE volume fraction of about 30 to 60% is three to five times as large as that of bulk PS film and hence the fracture energy also increases conspicuously.

Craze yielding stress in PS layers was found to be dependent on PE volume fraction. This might be due to the reduction of the tensile stress concentration effect at craze tips which is essential to craze growth.

Craze initiations were always observed at the edges of the laminated films. This can be elucidated with the transverse interlaminar shear stress concentrations existing at the film edges caused by the difference in Poisson's ratios between PS and PE.

The capacity of PS in the laminated state to exhibit prominent craze yielding to very high elongation appears to be an attractive property promoting its possible candidacy in the area of structural component applications.

References

1. S. RABINOWITZ and P. BEARDMORE, "Critical Reviews in Macromolecular Science", Vol. 1, edited by E. Baer (CRC Press, Cleveland, Ohio, 1972) p. 1.
2. R. P. KAMBOUR, *J. Polym. Sci. D Macromolec. Rev.* **7** (1973) 1.
3. S. RABINOWITZ and P. BEARDMORE, *Crit. Rev. Macromol. Sci.* **1** (1972) 1.
4. A. N. GENT, "The Mechanisms of Fracture", Vol. 19, edited by F. Erdogan (American Society of Mechanical Engineers, New York, 1976) p. 55.
5. C. B. BUCKNALL, "Toughened Plastics" (Applied Science, London, 1977).
6. A. S. ARGON, R. E. COHEN, O. S. GEBIZLIOGLU and C. E. SCHWIER, *Adv. Polym. Sci.* **52/53** (1983) 275.
7. A. S. ARGON and J. G. HANNOOSH, *Phil. Mag.* **36** (1977) 1195.
8. B. D. LAUTERWASSER and E. J. KRAMER, *Phil. Mag. A* **39** (1979) 469.
9. S. S. PANG, Z. D. ZHANG, S. S. CHERN and C. C. HSIAO, *J. Polym. Sci. Polym. Phys.* **23** (1985) 683.
10. C. C. HSIAO and J. A. SAUER, *J. Appl. Phys.* **21** (1950) 1071.
11. A. S. ARGON, R. E. COHEN and G. W. HAWKINS, paper presented at US–Japan Science Seminar on Crazing, Flow and Forming of Polymers, Rutgers University, May 1980.
12. A. S. ARGON, *J. Macromol. Sci. Phys. B* **8**(3–4) (1973) 573.
13. A. S. ARGON, J. IM and R. SAFOGIN, *Metall. Trans. A* **6** (1975) 825.
14. S. S. STERNSTEIN and L. ONGCHIN, *Polym. Prepr. Amer. Chem. Soc. Div. Polym. Chem.* **10** (1969) 1117.
15. P. B. BOWDEN and R. J. OXBOROUGH, *Phil. Mag.* **28** (1973) 547.
16. A. N. GENT, *J. Mater. Sci.* **5** (1970) 925.
17. A. S. ARGON, *J. Macromol. Sci. Phys. B* **8** (1973) 537.
18. *Idem, Pure Appl. Chem.* **43** (1975) 247.
19. T. HAYASHI, *Trans. Jpn Soc. Aero. Space Sci.* **8** (1973) 225.

Received 1 June
and accepted 16 December 1987