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Toughness, fracture markings, and losses in bisphenol-A polycarbonate at high strain-rate

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As-received and heat-treated specimens of bisphenol-A polycarbonate were impacted at temperatures ranging from −196 to +100°C. The critical stress intensity has been calculated for the as-received case from the impact energy data by making a strain-rate correction. To make this correction, the time–temperature superposition principle has been applied to existing dynamic mechanical measurements of the storage modulus and loss modulus (tan δ). Critical stress intensity values of 2.2 to 3.9 MPa $m^{\frac{1}{2}}$ were found to be comparable with those obtained from instrumented impact and low strain-rate test techniques. Resulting fracture surfaces of the specimens were studied with the scanning electron microscope. Specifically, the morphology of the regions in which sharp striations were present was investigated and the width of the striations have been reported as a function of testing temperature for both as-received and heat-treated cases. There appears to be a direct correlation between the strain-energy release rate, the stress intensity, the striation spacing and the loss curve (tan δ) for the as-received case.

1. Introduction

Correlations between mechanical properties and dynamic losses have recently become a main object of research in glassy polymers. Some studies done in the past [1, 2] and recently [3-5] correlate toughness and loss processes by use of the energy absorbed in impact tests. Others done recently [6-8] suggest a correlation between toughness and loss processes by results obtained with instrumented impact testing. Also, correlations between mechanical properties and dynamic losses are suggested by fracture toughness results obtained at low strain rate [7].

Another way to investigate correlations between toughness and losses is by microfractographic means. Although the morphology of the fracture surface of samples broken under impact have been investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and optical techniques [10-12], none of these investigations have reported correlations between fracture surface markings and losses in glassy polymers.

Therefore, it appeared that additional work was desirable in two areas: (1) correlation between fracture toughness and dynamic losses with standard impact test equipment, and (2) correlation between fracture surface markings and dynamic losses with electron microscopy. To carry out the investigation in these two areas, the linear thermoplastic bisphenol-A polycarbonate was chosen because of its toughness properties which many authors [2, 13] relate to the broad peak present in the loss curve.

A testing programme was set up so that (1) fracture toughness could be obtained at different testing temperatures and related to existing data for dynamic loss (tan δ), and (2) fracture surface markings could be studied by the use of a Cambridge Stereoscan (SEM). The results obtained in this investigation have been analysed applying the theory of errors in the attempt to give more meaning to the comparison of magnitudes between physical quantities.

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2. General background

In this investigation, values of fracture toughness, K_{IC}, have been calculated from impact energy data by applying the WLF (Williams-Landel-Ferry) equation for strain-rate corrections. The stress intensity factor is calculated imposing that fracture instability occurs in the plane strain condition when

$$K_{\mathrm{IC}} = [2(1 + \nu)G\zeta/(1 - \nu^2)]^{\frac{1}{2}} . \qquad (1)$$

ζ is the elastic strain-energy release rate (equivalent to the work per unit fracture area) and is given by

$$\zeta = C_{\mathrm{I}}/A \qquad (2)$$

where C_{I} is the energy absorbed by the precracked specimens in the impact test and A is the fracture area. The modulus of elasticity in shear, G, is the complex number $G = G' + iG''$, where G' is the storage modulus and G'' the loss modulus. The ratio G''/G' is defined as $\tan \delta$ and is used to characterize the mechanical losses in the material.

Many authors [14, 15] have measured G' and G'' at different temperatures (using a torsional pendulum), but few [16] have done so at frequencies other than 1 Hz. Consequently, at high frequencies, which is equivalent to high strain-rate testing conditions, accurate data concerning G' and G'' are missing. It is possible, however, to have an estimate of G' and G'' knowing the strain-rate at which the tests were performed and applying the time-temperature superposition principle.

The equation expressing the strain-rate, $\dot{\epsilon}$, has been approximated by applying the Irwin-Williams criteria for the infinite plate, giving

$$K = \sigma(\pi a)^{\frac{1}{2}} \qquad (3)$$

where σ is the applied stress and a is the half-crack length. Differentiating with respect to time yields

$$\dot{K} = \dot{\sigma}(\pi a)^{\frac{1}{2}} + (\sigma\pi\dot{a})/2(\pi a)^{\frac{1}{2}} \qquad (4)$$

where $\dot{a}$ is the crack velocity, $\dot{\sigma} \approx \Delta\sigma/\Delta t$ where $\Delta\sigma$ is the stress at fracture and Δt is the time-to-fracture [7].

Assuming that the crack propagates by elementary discrete increments, λ, then for one increment, $\Delta a = \lambda$. The elastic strain distribution in this increment would have an $r^{-\frac{1}{2}}$ singularity. If λ is a quantity independent of time, differentiation of the strain distribution gives

$$\dot{\epsilon} = \dot{K}/E(\pi\lambda)^{\frac{1}{2}} . \qquad (5)$$

Substitution of Equation 4 into Equation 5 yields

$$\dot{\epsilon} = [\dot{\sigma}(\pi a)^{\frac{1}{2}} + \sigma\pi\dot{a}/2(\pi a)^{\frac{1}{2}}]/E(\pi\lambda)^{\frac{1}{2}} . \qquad (6)$$

This equation gives an order of magnitude estimate of the strain-rate at the crack tip and, therefore, the "frequency" at which the tests have been performed.

Once $\dot{\epsilon}$ is known, an estimate of the temperature shift factor, a_{T}, can be calculated at different strain-rates by the WLF equation [17]:

$$\log a_{\mathrm{T}} = - 17.44(T - T_{\mathrm{g}})/51.6 + (T - T_{\mathrm{g}}) \; (7)$$

where T_{g}, the glass-transition temperature, has been chosen as the reference temperature.

The results obtained in this investigation have been evaluated applying the theory of errors. A certain amount of data scatter is inevitable in any precracked impact testing. This is due, in part, to the experimental procedure (e.g. precracking procedure) and in part to the instrument errors. The mean value and the standard deviation of an experimental physical quantity have been calculated for a set of data every time it was possible. To calculate the error of quantities like ζ or K_{IC}, which were not obtained directly by test, the principle of superposition of errors [18] has been applied. Similar procedures have been applied, where possible, for the determination of quantities such as the width of a striation evaluated at a certain magnification by the SEM.

3. Materials and procedure

The material used in the tests was bisphenol-A polycarbonate in the form of a ¼ in. thick sheet under the commercial name Lexan 101. All specimens were cut longitudinally from the sheets and Charpy type specimens were machined to 2.165 in. × 0.394 in. × 0.25 in. (5 cm × 1 cm × 0.635 cm) dimensions. After machining, some of the specimens were heat-treated at 120°C for 12 h and allowed to cool slowly at room temperature. These specimens were then kept in a dessicator until the tests were performed.

Both heat-treated and as-received specimens were precracked at room temperature with a razor blade just before being tested at different temperatures. It was observed that after the precracking procedure, the crack tip was not always evenly distributed along the notch root; specimens with uneven precracks were discarded.

The Izod impact tests were performed on a 25 in. lb Tinius Olsen plastic impact tester. The specimens were held in a fixed vice jaw at the level of the notch. The hammer striking edge hit the specimens 0.866 ± 0.002 in. (22.0 ± 0.005 mm) from the plane of the jaw in conformity with ASTM standards [19].

The testing of the specimens at different temperatures was possible by the use of an environmental chamber, which allowed a range of testing temperatures between −150 and +100° C. The degree of accuracy in maintaining a constant temperature in the chamber was ± 2°C at −150°C (±0.25°C at 0°C). The chamber was kept near the impact tester so that the specimens could be put in place and hit by the hammer in less than 6 sec. The temperature of the specimen began to vary in a time above ~ 10 sec. Specimens tested at −196° C were kept in liquid nitrogen since such a temperature could not be reached in the chamber. It should be noted that using liquid nitrogen, as has been done for one datum point, could affect the mechanical properties of the polymer. Parrish and Brown [20] have found that nitrogen and liquid air at liquid nitrogen temperature are crazing agents for PC. For this reason, all the tests at other temperatures were carried out in an argon atmosphere.

The fracture surfaces of the specimens tested were then examined in the scanning electron microscope. Since glassy polymers are not good conductors of electrons, it was necessary to prepare the fracture surfaces. Two thin, uniform layers of carbon and gold-palladium were deposited by evaporation under vacuum.

4. Experimental results and observations

4.1. Izod impact test results

The strain-energy release rate, ζ, for the as-received and heat-treated cases has been calculated from Equation 2 using an average fracture area of 6.87×10^{-2} in.^{2} $\pm$ 0.625×10^{-2} in.^{2} (44.3 mm^2). The results have been plotted in Fig. 1. ζ for the as-received case has a sharp peak at −40° C and a minimum at 26° C, while it has approximately the same values at −196 and +100° C. The behaviour of the strain-energy release rate for the heat-treated case is about the same as that for the as-received specimens. A broad and lower in magnitude peak of maximum ζ is presented at −70° C and a minimum occurs at +26° C. At all other temperatures, ζ has about the same value. Each point on the graphs is the mean value of a set of data representing at least three experimental results. The largest error possible in the evaluation of ζ for both cases, as-received and heat-treated, varied from 11.86% to 13.76% of the value of ζ.

The stress intensity, K_{IC}, for the as-received case, calculated from Equation 1, and corrected with the WLF equation, has been plotted for different temperatures in Fig. 2, along with the loss curve of the actual experimental condition. The calculation of K_{IC} at $\dot{\epsilon} \simeq 5.2 \times 10^3$ sec^{-1} (the calculated strain-rate of the impact test) was facilitated by shifting the storage modulus by the same interval of temperature that the loss curve had been shifted ($\simeq$ 25° C). A transition occurs for K_{IC} in the temperature interval −40 to +26° C. The largest error possible in the evaluation of K_{IC} varied from 10.16% at −150° C to 12.43% at +26° C.

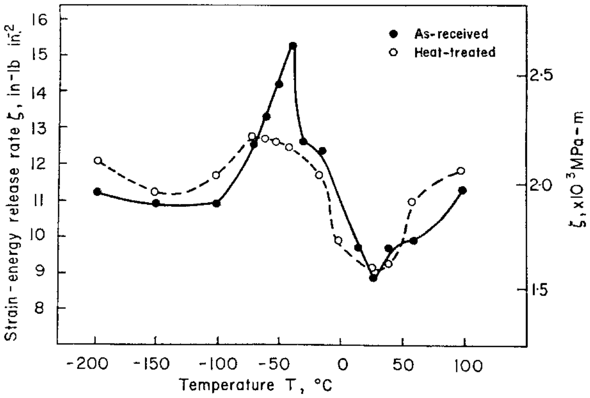

Figure 1 Strain-energy release rate versus testing temperature for as-received and heat-treated PC.

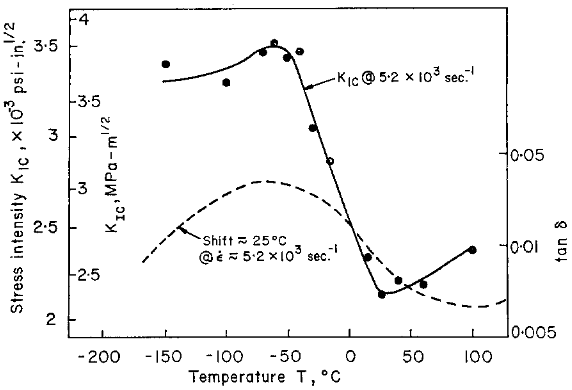

Figure 2 Stress intensity and loss curve at the calculated strain-rate versus testing temperature.

4.2. Fracture surface observations

Following the notation of Hull and Owen [10], the microscopic fracture surface of polycarbonate specimens broken under impact conditions can be divided into four regions: the initiation region, the banded and patch region, the hyperbola region, and the sharp striation region. Although the initiation region is important for crack initiation studies, it cannot be considered a region in which the markings characterize crack propagation. The microscopic structure of the patch region, the hyperbola region, and the sharp striation region have been shown in detail [10]. It has been observed in the present investigation, that at temperatures above 50° C, the hyperbola region disappears, and the sharp striation region is a continuation of the patch region. Furthermore, it has been observed that at strain-rates smaller than that of the impact tests, the sharp striations were missing; only a patch region was present (Fig. 3a to d). This indicates that the sharp striations characterize the impact test more than other surface markings. Therefore, a more complete investigation of this region was undertaken.

The spacing, λ, between two hills of a striation in this region, for both as-received and heat-treated cases, has been studied with respect to the temperatures which are significant for tan δ. Initially, 36 tests were evaluated from −196 to 120° C on as-received PC, the results being shown in Fig. 4a. These tests indicated a peak or at least a levelling out of the striation spacing near 0° C. However, owing to the considerable scatter, this was not considered statistically significant. Part of the problem was that different hammer heights had been used and specimens had been taken from different sheets of PC. Furthermore, little data had been run between 0 and −196° C to verify the location of any peak. Therefore, it was deemed essential to run additional tests, particularly in the vicinity of the β-loss peak. The results are plotted in Fig. 4b with error bars representing the largest and smallest values of the spacing, λ, that have been found. A peak in striation spacing is present for both as-received and heat-treated cases. This is documented by SEM observations of striations at different temperatures in Fig. 5 for the as-received case. The curve for λ in the as-received

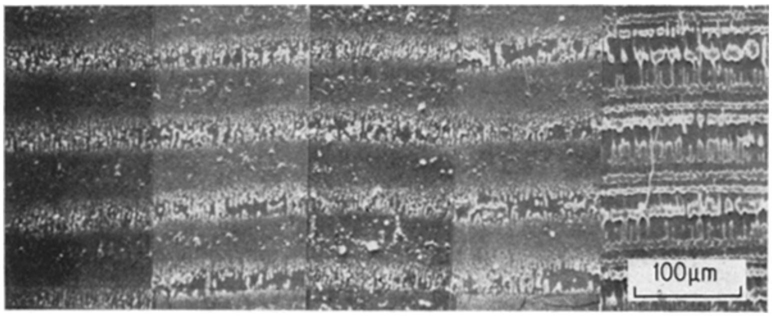

Figure 3 Patch regions for different strain-rates at room temperatures: (a) 0.04 sec^{-1}, (b) 4.0 sec^{-1}, (c) 120 sec^{-1}, (d) 320 sec^{-1}, and (e) 5.2 × 10^3 sec^{-1}.

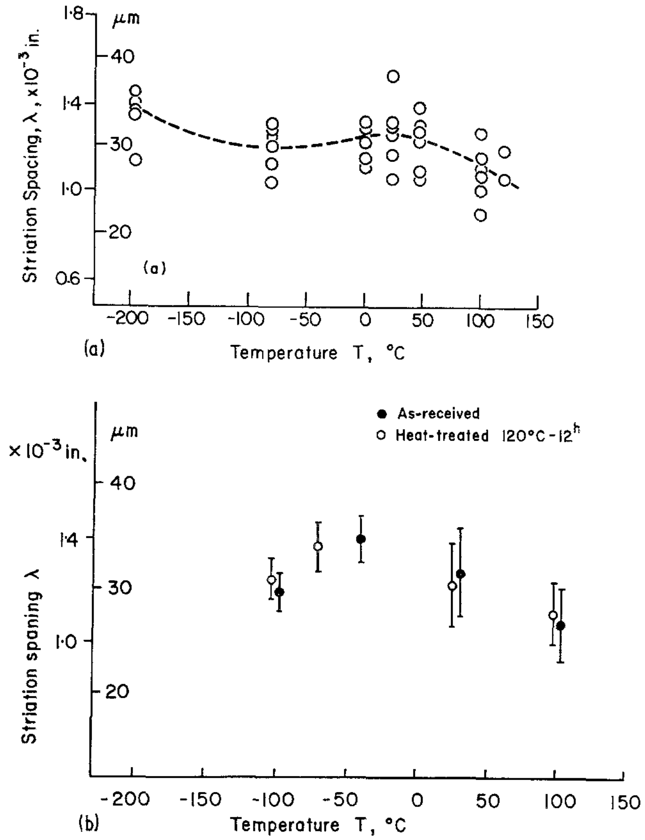

Figure 4 Striation spacing versus testing temperature for as-received and heat-treated PC: (a) initial tests; (b) tests in the vicinity of the β-loss peak.

case follows the loss curve as can be seen by superimposing tan δ from Fig. 2. In both cases, the peak is found at the temperature at which the peak for the strain-energy release rate was found.

5. Discussion

5.1. Strain-energy release rate, fracture toughness, losses

The localization of the loss peak and of the strain-energy release rate peak at about the same temperature substantiates the fact that the change in impact behaviour is caused by a change in molecular or segmental mobility, and not by structural defects or by other factors which do not affect molecular motion. Therefore, the change in impact behaviour is connected with the intimate molecular structure of polycarbonate, PC.

The behaviour of the toughness of PC in this investigation is different than that found by some investigators [4, 21]. This is due to two factors. First, in their investigations, a different type of material was used, i.e. the specimens were

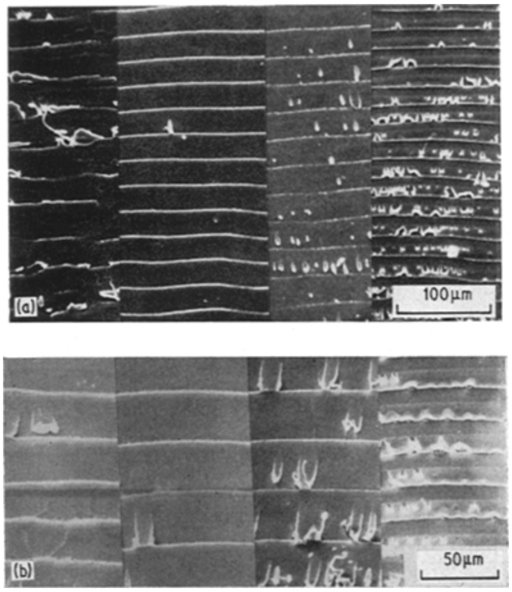

Figure 5 SEM microphotographs showing the variation of the striation spacing with testing temperature for as-received PC (from left to right: (a) −196° C, 0° C, 55° C, 100° C; (b) −100° C, −40° C, 26° C, 100° C.)

injection moulded (90° C) and shaped into discs. This processing could give specimen properties different from those found in this investigation. Secondly, they used specimens that were not precracked. Thus, their results did not give the true energy involved in the crack extension process because the notch absorbed most of it.

The peak for the strain-energy release rate has been found to be at $-40°$ C for the as-received case. Turley [22] found a peak near $-50°$ C for the impact strength in the dart drop test. The temperature position of the peak of ζ in the present work has been localized in a range of $\pm 5°$ C, and the largest possible error in its magnitude is 11.86%. Although the values of ζ have a known accuracy, tan δ values are perhaps inaccurate since dynamic mechanical measurements at the appropriate frequency were not made. Nevertheless, the values and trend of tan δ with temperature are probably a reasonable representation of the losses. Thus, coincidence of the tan δ and ζ peaks is indicated.

The accuracy achieved in K_{IC} determinations (10.6% at $-50°$C and 12.43% at $+26°$C) allows the establishment of a transition in fracture toughness between -50 and $+26°$ C. The results obtained for the fracture toughness have some connection with previous work done by Key *et al.* [9] and by Glover *et al.* [7]. As is seen in Fig. 6, the average magnitude of K_{IC} agrees very well with other magnitudes of K_{IC} obtained in previous work [7, 9]. However, the trend in the curve expressing K_{IC} deviates considerably. This is understandable because the results obtained by Key *et al.* [9] were obtained for dK/dt roughly equal to 3000 psi in.$^{\frac{1}{2}}$ sec^{-1} (3.3 MPa m$^{\frac{1}{2}}$ sec^{-1}), which translates into a strain-rate of about 0.087 sec^{-1}. This strain-rate is lower than the one involved in this investigation by a factor of 10^5. Therefore, the curve obtained by Key *et al.* should be shifted toward the right by the time-temperature superposition principle, bringing the curve closer to that obtained in the present work.

The other curve for K_{IC} obtained by Glover *et al.* [7] is in reasonably good agreement for temperatures above room temperature, but not at temperatures near the β transition. However, as Glover *et al.* have noted, a more complicated behaviour in the β-relaxation regime could cause unexpected changes in fracture toughness. The fact that the disagreement occurs at low temperatures, where the broad loss peak is localized, support that observation. It also may be significant that Glover *et al.* [7] used the instrumented impact test procedure and calculated the values of K_{IC} using the K-calibration formula of Brown and Srawley [23], while the present work applies Equation 1 for the calculation of K_{IC}. Nevertheless, the transition for K_{IC} occurs at the same temperature the transition for tan δ occurs in both sets of data. This supports the contention that the toughness properties of PC are associated with the broad peak in tan δ.

A correlation of the strain-energy release rate with the loss curve was not possible in the heat-treated case because data for tan δ in the heat-treated condition were not available. Calculation of K_{IC} was not possible since tensile moduli were not available. However, from the behaviour of the strain-energy release rate with temperature, K_{IC} data from heat-treated samples should be similar to the as-received K_{IC}. Because of the cut-off in the peak for ζ in the heat-treated case, the maximum obtainable K_{IC} should be lower in this case than in the as-received case.

5.2. Microscopic fractography

Comparison of the striation spacing for the as-received case (Fig. 4) with the loss modulus

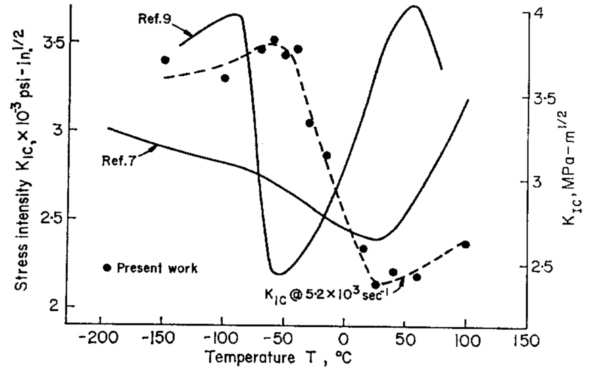

Figure 6 Stress intensity from previous present work versus testing temperature ([7] instrumented impact, [9] low strain-rate).

curve (in Fig. 2) points out that the peak for λ is localized at about the same temperature at which the peak for $\tan\delta$ is found. Furthermore, the overall behaviour of λ follows closely the behaviour of $\tan\delta$. Also, a comparison of the striation spacing behaviour with the behaviour of K_{IC} shows that the peak for λ is localized at the same temperature at which the largest value for K_{IC} was obtained. The curve for K_{IC} drops more quickly in the transition region than that for λ, but on an overall basis is almost linearly related to K_{IC}. The similar behaviour of λ and ζ for both heat-treated and as-received cases indicates that K_{IC} for the heat-treated case would approximate the as-received K_{IC}.

Fig. 7 shows the fracture surface of the region in which the striation spacing was calculated for testing temperature between 50 and 100° C. It is possible to observe a two-band region in a striation of width λ: the first region, a, has marks with irregular lips around a ball-like centre of pulled material. This material is oriented in different directions and starts in different places of the band. The second region, b, has no marks, but a granular structure. This granular structure, may have origin in the molecular structure of the polymer. The different orientation of two parabolic marks present in the region, band a, suggests that fracture starts over this band; that is, the locus of fracture involves not just a line, but the entire band. The different structure of the two bands suggests that two different fracture processes are involved in the formation of a striation: a ductile fracture occurring in the peeling region (region a) and a brittle fracture occurring in the granular region (region b). Consequently, region a is a region of "slow" crack growth and region b is a region of fast crack growth.

The slip-stick process [24] associated with the formation of these bands is not the only process involved in the formation of a striation. In fact, sharp striations have not been found on the fracture surface of single edge-notch (SEN) specimens broken at different strain-rates in tensile tests. This means that another fracture process is active at high strain-rate. This process is probably connected with the dilational stress wave which distinguishes the impact testing condition from other testing conditions. Nevertheless, a certain type of striation is present on the fracture surface of SEN specimens (Fig. 3a to d). These diffuse striations have been found in a small region (1/20 of the fracture surface) after the precracking zone, and are similar to those obtained in the patch region at the start of fracture for samples broken under impact (Fig. 3e). A comparison of the photomicrographs in Fig. 3 would indicate that one of the fracture mechanisms (the slip-stick process) involved at high strain-rate is also present at low strain-rate.

6. Summary and conclusions

Correlation between fracture toughness, fracture surface markings and losses at high strain-rate in bisphenol-A polycarbonate have been obtained. As-received and heat-treated (120° C, 12 h) polycarbonate have similar trends of toughness

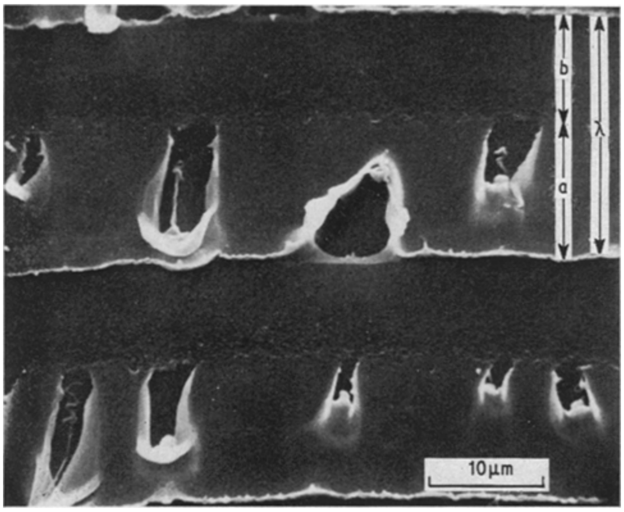

Figure 7 Morphology of the fracture surface between striations for testing temperatures above +50° C.

with test temperature except at peak toughness where the values are 15.3 and 12.7 in. lb in.$^{-2}$ (2.65×10^{-3} and 2.2×10^{-3} MPa m), respectively. Microfractographic investigations indicate a two-step striation region which most characterizes the impact fracture condition. The width of the striations and the character of the stick-slip region vary as a function of testing temperature.

The following conclusions have been reached for the as-received case:

(1) peaks in the strain-energy release rate, in stress intensity, in striation spacing, and in the loss curve (tan δ) are found to coincide at -40° C;

(2) minimum values in strain-energy release rate and in stress intensity have been localized at $+26$° C;

(3) strain-energy release rate, stress intensity and striation spacing have been found to follow closely the behaviour of the loss curve;

and for the heat-treated case:

(1) peaks in strain-energy release rate and striation spacing have been localized at -70° C;

(2) strain-energy release rate and striation spacing exhibit a behaviour similar to that of the as-received case.

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