Fracture toughness of polyimide films

J. A. Hinkley
NASA Langley Research Center, Hampton, VA 23665-5225, USA

and S. L. Mings
AS&M Inc. Hampton, VA 23666, USA
(Received 9 February 1989; revised 13 April 1989; accepted 15 April 1989)

Two aromatic polyimides and an aromatic polyamide-imide were tested in single-edge-notched tension. Fracture toughnesses, K_c, normalized to 25 μm film thickness ranged from 1.65 to 5.4 MPa m$^{1/2}$. LARC-TPI, a thermoplastic polyimide, showed evidence of crazing ahead of a growing crack whereas the other materials formed a shear yielded zone.

(Keywords: polyimides; films; fracture toughness; crazing; crack growth)

INTRODUCTION

Aromatic polyimides are used as dielectric coatings, as adhesives, and also as self-supporting films. In the latter application, resistance to cracking is an important property, which does not seem to have been widely studied. Tensile properties[1] and failure processes[2–4] of a few materials have been reported, and the plane strain fracture toughness is known for two thermoplastic polyimides[5,6]. Recently, Theocaris examined crack tip plasticity in partially cured polyimide films[7].

In the present study, the single-edge-notched (SEN) tensile geometry was used to evaluate the resistance to crack growth from sharp notches in thin films of three different materials. Several different modes of deformation were documented.

EXPERIMENTAL

LARC-TPI[8], the polyimide from 3,3′-diaminobenzophenone and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) was obtained from Mitsui Toatsu in the form of the amide-acid precursor (inherent viscosity 0.66 dl g^{-1} in dimethylacetamide, DMAc, at 30°C). Films were prepared by spreading the stock diglyme solution or one diluted slightly with DMAc onto glass plates and curing for 1 h each at 100, 200, and 300°C in an air-circulating oven. The resulting 20–50 μm films were removed from the glass plates by soaking the plates in water.

Casting procedures were similar for the polyamide-imide prepared in this laboratory[9] from 4,4′-diaminobenzanilide and BTDA and imidized on a glass plate for 1 h each at 100, 200, and 250°C.

Kapton film (DuPont) was used as received. Cracks were run perpendicular to the machine direction (e.g. to the length of the roll) in this oriented material.

Tensile strips 1.3 cm wide were cut from each material with a razor blade. Each strip was supported on lightweight cardboard and cut with a slicing motion to create the edge notch. This procedure gave a crack which appeared sharp under the microscope. In contrast, early attempts to press a blade into the edge of a stretched film always led to visible crack blunting and deformation ahead of the crack tip. (Considerable tension had been needed to hold the film straight in this method.)

Films were tested to failure in a miniature tensile frame constructed on the stage of an optical microscope. The gauge length was 5 cm and the crosshead was driven by a d.c. gear motor at 0.185 cm min^{-1}. Load was recorded continuously via a miniature 100 N capacity load link. The crack tip region was observed at 200 × and the onset of crack propagation was noted and marked on the chart record. This visual determination could be done with an acceptable degree of consistency, as evidenced by the scatter in the data (*Figure 1*).

Because antiplane buckling is a possibility in these thin films, a few experiments were conducted using close-fitting glass guides above and below the film plane to prevent buckling. No differences in initiation loads were seen between these tests and similar ones done with unconstrained films.

RESULTS AND DISCUSSION

Initiation of crack growth

The razor notching procedure produced a sharp crack which could be seen to open as the specimen was loaded. Further increases in load led to slight crack blunting until, quite suddenly, crack propagation began, apparently simultaneously with the development of a necked-down crack tip deformation zone. This zone will be described in more detail in the following section.

The load at which propagation began depended strongly on the initial crack length. A typical set of data is shown in *Figure 1*, in which a is the crack length and W is the specimen width. Over the range of crack lengths studied, all the data are consistent with a critical stress intensity criterion for initiation of crack growth. That is, the initiation stresses σ_c, satisfy

$$K_c = \sigma_c(\pi a F)^{1/2} \quad (1)$$

where F is a geometric factor appropriate to the SEN geometry[10] and K is the stress intensity factor.

Ferguson and Williams[11] found that initiation data on poly(ethylene terephthalate) films were better described

0032-3861/90/010075-03$03.00

by a model which included a plasticity correction, particularly for short cracks. This proved unnecessary for any of the polyimide films. In fact, when a Dugdale model is applied to initiation in the present case, large values of the effective yield stress are needed to fit the data. In effect the model is reduced to the case of small-scale yielding and a single-parameter description (in terms of K_c) is recovered.

Table 1 shows the K_c values for the various materials, obtained by least-squares fits to equation (1). Also reported are critical strain-energy release rates G_c. The first observation to be made from *Table 1* is that all of these materials are reasonably tough (comparable to PET[11]). The LARC-TPI is noticeably tougher than the commercial Kapton film. It appears from the data on the two different thicknesses of TPI that the plane stress G_c is approximately proportional to the film thickness.

The polyamide-imide, which is very stiff and strong[9], is also extremely tough. Its G_c would be predicted to be over four times that of Kapton at an equal thickness and about equal to that of polycarbonate[12].

Failure processes

As discussed by Ferguson and Williams[11], ultimate failure in ductile films is usually preceded by extensive slow crack growth, so a linear elastic fracture mechanics prediction of failure load from the initial crack length would not be expected to hold. During the period of slow crack growth the load rises by an amount which depends on the material and on the sample geometry. For the polyimides in the present study, the failure loads were typically 150–230% of the initiation load (*Figure 2*).

Slow growth was accompanied by progressive development of a yielded zone ahead of the crack tip. This zone, which was considerably wider than the film thickness, differed in appearance among the materials studied. *Figures 3–5* are photomicrographs obtained by stopping the crosshead during the slow growth period after the deformation zone was well-developed but before rapid fracture ensued.

LARC-TPI (*Figure 3*) exhibits a complex zone consisting of a thin necked region bordered by a ridge of dense lines which are presumably crazes. The overall appearance of the zone is virtually identical to that seen in polycarbonate[13]. Short cracks (crazes) also appear perpendicular to the tensile direction at considerable distances from the primary crack. Because some polyimides are known to be susceptible to environmental crazing[14], the possible influence of contamination by finger oils must be considered. This does not seem to have been a major factor however, since identical crazes were seen in all TPI samples, even those subjected to a minimum of handling.

In the other polymers (*Figures 4* and *5*) no crazing was observed, and the deformation zone is not well defined. A necked region ahead of the crack has yielded, and exhibits coloured bands when viewed with white light between crossed polarizers. The birefringence persists after the load is removed. The width of the birefringent zone, or wake, left by the crack was measured after fracture and was found to extend 80 μm on either side of the crack plane in the polyamide-imide and 220 μm in the Kapton. The unexpected differences between TPI and the other polymers might be rationalized in terms of the suppression of crazing by intermolecular entanglements[15]. The LARC-TPI backbone is apparently flexible enough to decrease the entanglement density relative to the other polyimides and allow crazing.

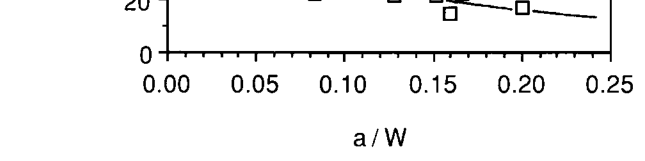

Figure 1 Load at initiation of crack growth vs. normalized crack length. LARC-TPI film, 25 μm thick. □, Experimental; ——, least-squares fit to equation (1)

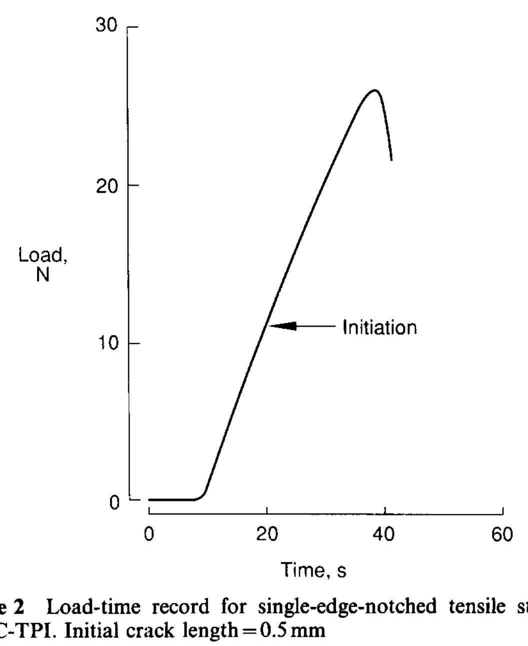

Figure 2 Load-time record for single-edge-notched tensile strip of LARC-TPI. Initial crack length = 0.5 mm

Table 1 Fracture toughness of polyimide materials

Material	Thickness (μm)	Number of tests	K_c (MPa m$^{1/2}$)	Tensile modulus, E (GPa)	$G_c = K^2/E$ (kJ m^{-2})
LARC-TPI	25	12	1.98 ± 0.37	3.52	1.1
LARC-TPI	45	16	2.79 ± 0.37	3.52	2.2
Polyamide-imide	16	16	4.28 ± 0.26	7.08	2.8
Kapton	25	37	1.65 ± 0.14	2.99	0.92

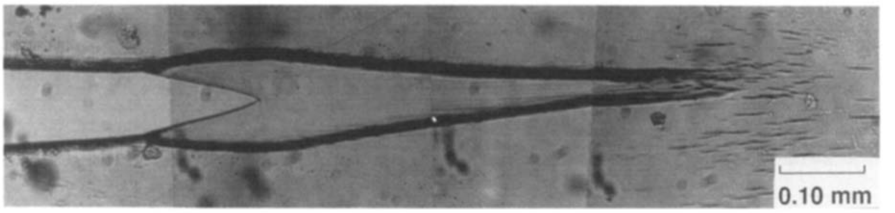

Figure 3 Photomicrograph of fully developed deformation zone in notched LARC-TPI film

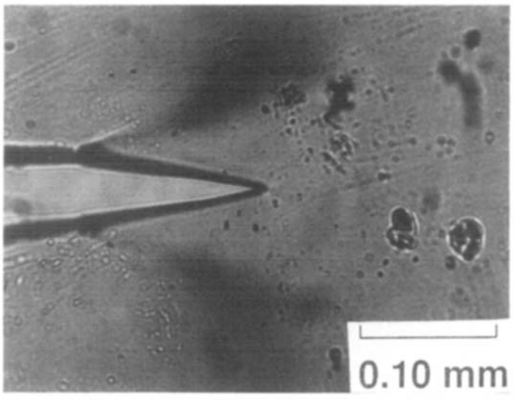

Figure 4 Photomicrograph of crack tip region in polyamide-imide film

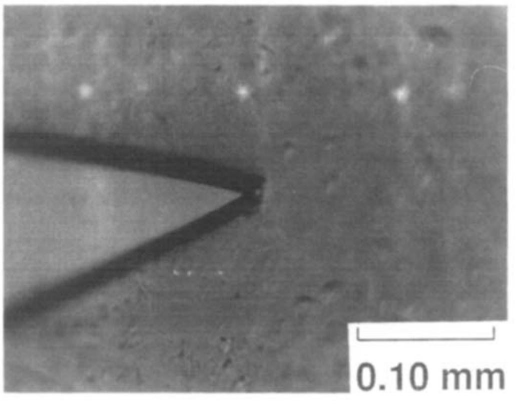

Figure 5 Photomicrograph of crack tip region in Kapton polyimide film

The final failure stress of a notched film might, in principle at least, be predicted by applying the Dugdale model to the growing crack[11]. In practice, this is not a simple matter[12,13] and it will not be attempted here. In a few cases, the SEN experiments were interrupted however, in order to measure the plastic zone lengths. The apparent stress in the yield zones could then be calculated by iterative solution of the approximate closed-form expressions

$$K^* = \sigma_y\left[\frac{8a}{\pi}\ln\sec\left(\frac{\pi\sigma}{2\sigma_y}\right)F\left(\frac{a^*}{W}\right)\right]^{1/2} \tag{2}$$

$$\frac{a^*}{W} = (a + R\rho)/W \tag{3}$$

where R is a constant and ρ, the plastic zone length, is a function of σ/σ_y (ref. 10). For LARC-TPI, the stress σ_y worked out to 175–240 MPa, a figure much larger than the conventional (offset) yield stress. This anomaly is probably due to the fact that the plastic zone has not reached its equilibrium length in the time of the experiment[16]. Ferguson *et al.*[17] showed with a similar calculation that the craze stress at a crack tip in rubber-modified polystyrene was much larger than the yield stress initially, but was asymptotic to the bulk yield stress as the test proceeded.

CONCLUSIONS

A critical stress intensity factor was calculated from the onset of crack growth in notched polyimide films. Fracture toughness depended both on film thickness and on the chemical nature of the polymer, with an aromatic polyamide-imide showing unusual toughness.

The thermoplastic polyimide exhibited extensive crazing, but its toughness was comparable to that of a material (Kapton) which did not craze.

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