JOURNAL OF MATERIALS SCIENCE 27 (1992) 2335–2339

Study of the fracture toughness and fracture morphology of polybenzimidazole

J. F. GROVES*, C. M. AGRAWAL, G. W. PEARSALL
Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27706, USA

Polybenzimidazole (PBI) is a relatively new polymeric material exhibiting unusual properties that are attributable to its aromatic–heterocyclic monomer structure. Owing to its high strength, stiffness and excellent stability in hostile chemical and thermal environments, PBI is being used increasingly in critical applications. As a result, understanding the failure mechanisms of the material is vital. This paper presents the results of a study of the fracture toughness and fracture morphology of polybenzimidazole. The standard compact tension specimen was used as the basic experimental specimen in this study. The fracture tests were performed in an Instron tensile testing machine. The effects of varying the loading rate, and the ratio of the initial crack length, *a*, to the ligament length, *W*, were investigated. The fracture surface morphology was examined using optical and scanning electron microscopy. The results of this study indicate that the precracking technique significantly affects the measured fracture toughness. Also, an increase in the loading rate causes a significant decrease in fracture toughness. Examination of the fracture morphology reveals that PBI fracture surfaces exhibit many of the characteristics expected of a tough engineering plastic.

1. Introduction

Polybenzimidazole (PBI), a fully aromatic–heterocyclic polymer, was originally formulated in the early 1960s during an attempt to identify high molecular weight materials (PBI has a weight-average molecular weight of 54 000) with such exceptional properties as elevated temperature stability, retention of stiffness, and toughness [1].

The presence of three benzene rings with side groups in the repeating unit of the PBI molecular chain directly contributes to the polymer's superior properties. The benzene rings cause a high degree of rigidity in the polymer chain, and this rigidity leads to a high glass transition temperature, T_g, which helps the polymer resist normal thermoplastic behaviour at elevated temperatures. The stiff ring structure also results in a fairly low density of 1 g cm^{-3} making the material ideal for low-weight structural applications [2].

Among the polymer's outstanding properties are exceptional resilience under repeated compression, deformation, and recovery cycles; a relatively low coefficient of friction, low abrasion characteristics, and excellent high-temperature dimensional stability. For instance, PBI has a compressive strength of 393 MPa, a tensile strength of 158 MPa, and an elastic modulus of 5.86 GPa [2]. PBI is particularly well suited to hostile-environment applications because of its "pseudothermoplastic" nature. Although formed as a thermoplastic by a sintering technique, PBI possesses thermal and mechanical properties more akin to a thermoset, including no observable melting point [3].

Since its initial synthesis, PBI has been formed into fibres, films, membranes, low-to-medium-density foams, and moulded stock shapes. Important products include thermal-protective clothing, valves, washers, O-rings in corrosive environments, missile leading edges and control components, rocket nozzles, and ablative surfaces [2, 4]. The use of PBI in critical commercial and military aerospace applications makes an understanding of its failure characteristics extremely important.

Three primary factors control the susceptibility of a structure to brittle fracture once a crack is present: (1) material toughness, the ability of a material to carry a load or to deform; (2) crack size; and (3) stress level. To predict whether a product is going to fail, engineers must be able to determine quantitative values for these three factors reliably. To the authors' knowledge, until now, no literature pertaining to the fracture toughness or fracture morphology of PBI has been available. It is the intent of the present work to describe the determination of the fracture toughness of PBI according to the American Society for Testing and Materials' standard E399-83 [5], and its new standard D5045 for plastics [6]. Both of these Standards outline the procedures for determining the fracture toughness of materials by calculating K_{Ic}, the critical-stress-intensity factor. K_{Ic} has been used to characterize the resistance of materials to crack propagation because its

* *Present address*: Department of Mechanical and Aerospace Engineering, Thornton Hall, University of Virginia, Charlottesville, VA, USA.

0022–2461

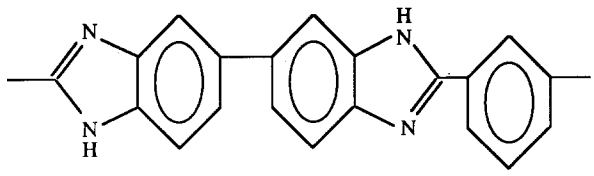

Figure 1 Repeat unit of polybenzimidazole molecular chain showing the three benzene rings.

plane-strain geometry represents a lower limiting value of fracture toughness.

The present study focuses on the determination of fracture toughness values for PBI for different a/W (initial crack length/ligament length) ratios and loading rates, and on characterizing the resulting fracture surface morphology.

2. Experimental procedure

The glassy polymer studied in this report was sintered, unfilled Celazole® polybenzimidazole, grade name U-60. The polybenzimidazole was supplied as discs 63.5 mm diameter and 12.7 mm nominal thickness.

All tests for this study were performed on compact tension (CT) specimens at room temperature. The sides of the CT specimens were machined using a milling machine. The notch in each specimen was introduced with the same milling machine. The loading-pin holes were machined using a drill press. The final step in the sample preparation procedure involved introducing a sharp "precrack" into the specimen. This was accomplished by first using a jeweller's saw to extend the initial notch to a point just short of the desired crack length, a. Second, a razor blade was used with a sawing motion to introduce a final sharp crack at the tip of the saw cut. The precracking technique used in this study can be termed "dry", because no liquid agent, e.g. ethanol, was used to induce crazing.

Both ASTM standard E399-83 [5] and the new ASTM plastics standard D5045 [6] specify that specimens should be prepared such that $2 \leqslant W/B \leqslant 4$ where B is the specimen thickness. This range has been specified to ensure a plane-strain condition. The PBI specimens in this study had nominal W/B ratios of 2.8.

Because the PBI discs were manufactured by a sintering process which should not have introduced any significant directionality, the specimens were machined without regard to orientation. During specimen preparation it was unclear whether the razor-cutting process successfully introduced a precrack in the extremely hard PBI. Nearly half of the specimens were tested without razor cuts to see if the fracture toughness values of these specimens varied appreciably from the values obtained for specimens which had razor-induced precracks.

The fracture toughness tests were performed in an Instron tensile testing machine using a load cell with a range of 0–453.6 kgf (1 kgf = 9.8067N). The machine's chart recorder produced load–displacement plots from which fracture toughness values could be determined, according to the procedures outlined in both ASTM E399-83 [5] and ASTM D5045 [6].

The fracture tests in this study can be divided into two sections. In the first, the a/W ratio of the specimens was varied to study the effects on the measured fracture toughness. Both ASTM standards recommend that a/W ratios lie between 0.45 and 0.55. In this study, a/W was varied between nominal values of 0.40 and 0.60 to investigate the effects of varying the a/W ratio beyond the specified limits. For these a/W ratios, PBI was investigated at a machine crosshead speed of 50.8 mm min^{-1}. In the second set of fracture tests, the machine crosshead speed was varied in the range 25.4–254.0 mm min^{-1} for a nominal a/W ratio of 0.50 to explore the effects of loading rate upon fracture toughness. After fracture, the length of the precrack was determined using vernier calipers and the calibrated stage of an optical microscope.

The fracture surfaces were studied using a stereo microscope ($\times 6.6$–$\times 40$), and a reflected/transmitted light microscope ($\times 50$–$\times 600$). Selected surfaces were vacuum sputter-coated with gold–paladium, and then examined and photographed using a scanning electron microscope.

3. Results

The test records satisfied the ASTM requirement that P_{max}/P_Q be less than 1.1. P_{max} is the maximum load the specimen was able to sustain. P_Q is the load at which the experimentally determined load, P, versus displacement, V, curve intersects the line with slope $0.95\,PV^{-1}$ which is the slope of the tangent to the initial linear portion of the experimental P versus V curve. The P_{max}/P_Q calculations indicate that the fracture toughness tests were valid. This conclusion was reinforced through optical microscope observations which showed no evidence of plastic deformation resulting from testing.

The results of varying a/W between 0.40 and 0.60 for a fixed machine crosshead speed of 50.8 mm min^{-1} revealed significant changes in the measured fracture toughness value as shown in Fig. 2. For the case of specimens without razor-induced precracks, the fracture toughness increases as a/W increases from 0.40 to 0.50. The fracture toughness values at a/W ratios of 0.40 are significantly lower than those at 0.45 or 0.50. For specimens with razor precracks the measured fracture toughness shows a slight decrease as a/W increases from 0.50 to 0.60. The results shown in Fig. 2 indicate an average fracture toughness of 3.74 $\pm$ 0.72 MPa m$^{1/2}$ for the specimens tested without razor cuts and 2.97 $\pm$ 0.21 MPa m$^{1/2}$ for the specimens with razor-induced precracks.

The effects of loading rates corresponding to machine crosshead speeds of 25.4, 50.8, 127.0, and 254.0 mm min^{-1} were determined using specimens with nominal a/W ratios of 0.5. As illustrated in Fig. 3 the fracture toughness values for both crosshead speeds of 25.4 and 50.8 mm min^{-1} do not exhibit significant variation. However, for crosshead speeds of 127.0 and 254.0 mm min^{-1}, the fracture toughness decreases significantly. In all cases the fracture toughness values measured using the razor-cut specimens are below those measured using non-razor-cut speci-

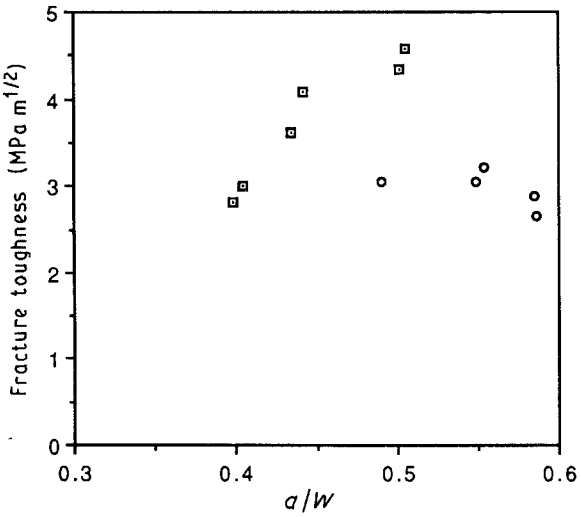

Figure 2 Variation of measured fracture toughness with a/W ratio. Machine crosshead speed = 50.8 mm min^{-1}. (⊡) No razor cut, (○) razor-induced precrack.

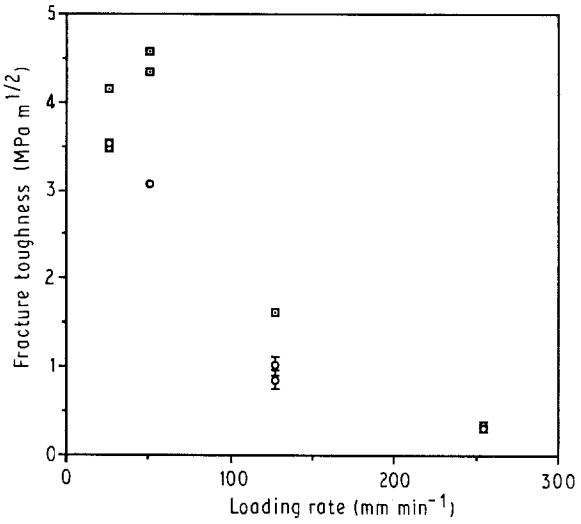

Figure 3 Variation of fracture toughness with machine crosshead speed for specimens with nominal a/W ratios of 0.5. (⊡) No razor cut, (○) razor-induced precrack.

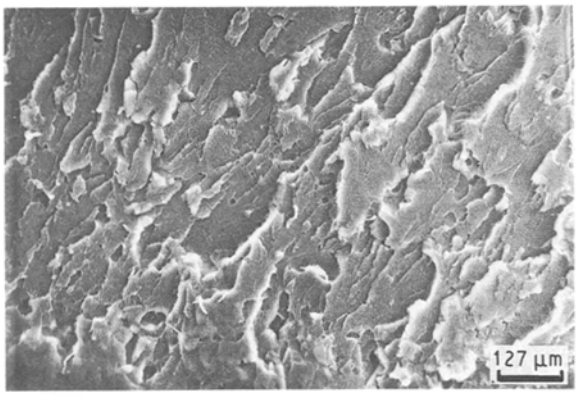

Figure 4 Fracture morphology of PBI: the initiation region. The direction of crack travel is from lower left to upper right.

mens. The razor-induced precrack appears to have decreased the resulting fracture toughness values by roughly 25%.

Initial examination of the specimen surfaces with the naked eye revealed a fairly unremarkable black,

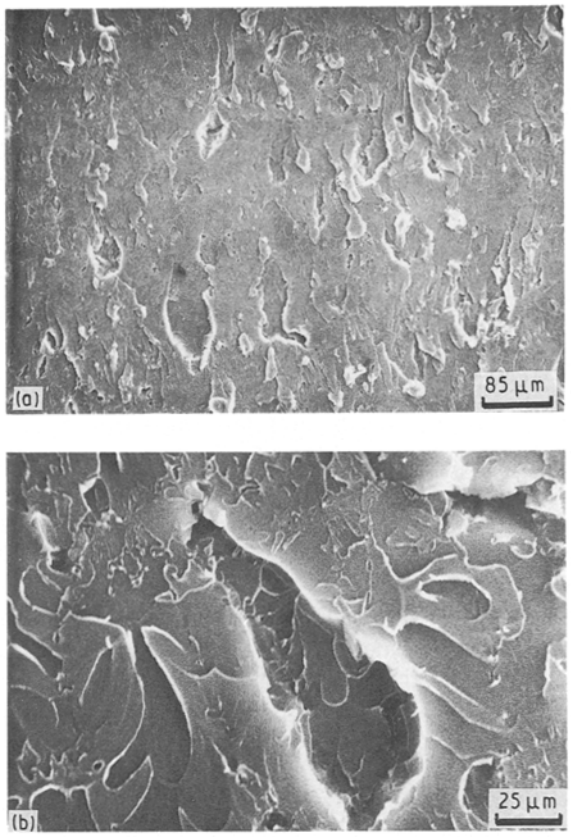

Figure 5 (a, b) Typical appearance of the majority of the fracture surface of PBI. In both cases the direction of crack travel is from bottom to top.

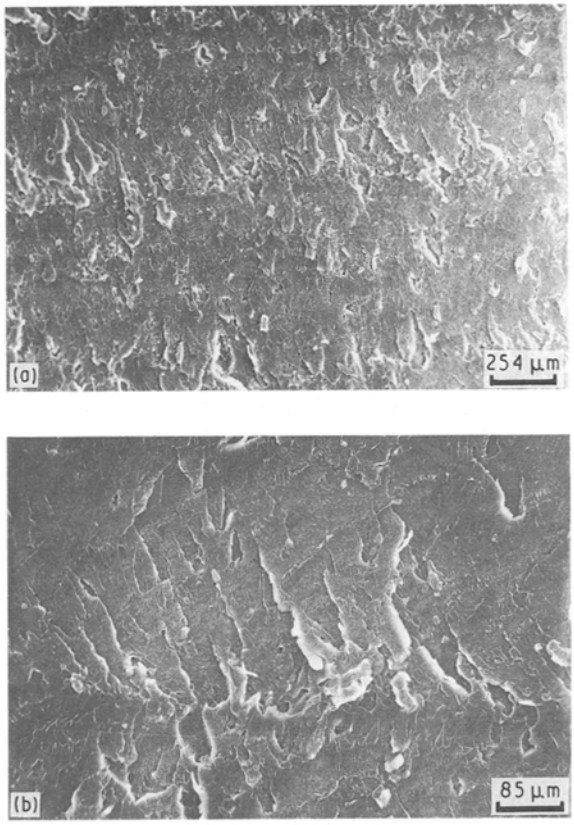

Figure 6 Fracture morphology of PBI. (a) The end band region, (b) close-up of a band. In both cases the direction of crack travel is from bottom to top.

slightly rough surface. Closer inspection with a stereo microscope revealed a clear initiation region, and a region of bands in the last quarter of the fracture surface on some specimens. Fig. 4 shows the typical initiation region. Fig. 5a and b show the appearance of the majority of the surface. The banded structure found on certain samples is shown in Fig. 6a and b. Fig. 6b is a micrograph of a specimen tested at a machine crosshead speed of 50.8 mm min^{-1}. The measured a/W ratio was 0.586, and the fracture toughness value was 2.650 MPa m$^{1/2}$. All other micrographs are of a representative specimen tested at a machine crosshead speed of 254.0 mm min^{-1}. The measured a/W ratio was 0.480, and the calculated fracture toughness value was 0.304 MPa m$^{1/2}$.

In the micrographs of the initiation region (Fig. 4) a patch morphology is apparent. This island structure results from the separation of crazed material. Although similar patch morphology can be found across much of the specimen, it is most prevalent in the initiation region and on (not between) the bands found in the last quarter of the fracture surface of some specimens.

4. Discussion

The average fracture toughness value of 2.97 MPa m$^{1/2}$ for specimens with a razor-induced precrack is considered to be a fairly accurate value for polybenzimidazole. More research is probably necessary before the fracture toughness of this material can be stated with more certainty. However, its high fracture toughness values, higher than those of polycarbonate, a tough engineering plastic, seem reasonable considering the material's high compressive and tensile strengths and high elastic modulus. Despite a lack of available comparative data, several points can be made about this high-performance polymer.

First, the graphs presented earlier show that the introduction of a razor-induced precrack into the hard material has a significant effect upon the resulting fracture toughness. The average of 3.74 MPa m$^{1/2}$ given above for non-razor-cut specimens is 25% higher than the comparative value of 2.97 MPa m$^{1/2}$ for razor-cut specimens. When the specimens were being prepared initially, it was difficult to detect any effect of the razor blade because the specimens were opaque black. However, the resulting difference in the measured fracture toughness values reinforces the ASTM requirement of using a razor blade to introduce a sharp precrack – even in tough materials like PBI. Also, for the specimens with razor-induced precracks the slight decrease in the fracture toughness values for a/W ratios greater than 0.55 supports the ASTM requirement that the a/W ratio should lie between 0.45 and 0.55. The measured fracture toughness of PBI shows a decrease when the loading rate is increased from 50.8 to 127.0 mm min^{-1}. These results are in accordance with those obtained for other glassy polymers, e.g. polycarbonate, polystyrene, and polymethyl methacrylate [7, 8].

Many of the PBI fracture surfaces show a rather rough region between the initiation and banded regions as opposed to the mirror region found on the fracture surfaces of other polymers, e.g. polymethyl methacrylate. The lack of a mirror region may be the result of PBI's microstructure. The three benzene rings in each repeat unit of the polymer may not allow easy sliding of molecular chains past one another and thus inhibit crazing and deformation during fast crack propagation. In other polymers, a generally rough surface has been associated more frequently with the mist and hackle regions [9]. However, there appears to be no obvious predictor of where a uniform rough region will appear upon a PBI fracture surface. Some specimens are covered from initiation to termination of the fracture with a uniformly rough surface, while others have distinct initiation, rough, and band regions.

Attempts to predict the appearance of an initiation region or well-defined banded region based upon a particular a/W ratio or machine crosshead speed did not reveal any correlation between testing parameters and surface features. The bands along the last quarter or so of the fracture surface may be the result of a stick–slip phenomenon. This behaviour would explain the sound heard when the fracture reached this region – a sound reminiscent of that made by the individual tinging of a metal comb's teeth one after another as they are dragged over a sharp edge.

5. Conclusions

Fracture toughness tests were conducted on the glassy polymer polybenzimidazole using the compact tension specimen geometry. The effects of varying particular geometric and testing parameters were studied, and the fracture morphology was examined. The following conclusions were drawn.

1. Polybenzimidazole's fracture toughness decreases significantly with increasing loading rates. This decrease is more evident for machine crosshead speeds greater than 50.8–127.0 mm min^{-1}.
2. Introduction of a razor cut as a part of the precracking technique significantly decreases the measured fracture toughness of PBI.
3. Variation of the a/W ratio appears to have a significant effect upon fracture toughness values for specimens without razor cuts. For these specimens the measured fracture toughness increases as a/W varies from 0.40–0.50. Specimens with razor-induced precracks exhibit a slight decrease in the fracture toughness as a/W ratio increases from 0.55 to 0.60.
4. Examination of the fracture morphology reveals three distinct regions – an initiation region, a nondescript rough region, and a band region. Although all three regions are found on many specimens, it is equally likely to find only a uniformly rough fracture surface.

References

1. H. VOGEL and C. S. MARVEL, *J. Polym. Sci.* **50** (1961) 511.
2. B. C. WARD, *SAMPE J* **25** (1989) 21.
3. B. C. WARD, L. P. DISANO and E. ALVAREZ, "Engineering Plastics", Engineered Materials Handbook, Vol. 2 (ASM International, Metals Park, OH, 1988) p. 147.

4. L. P. DISANO, in "Modern Plastics Encyclopedia" edited by B. Juran (McGraw-Hill, NY 1990) p. 41.
5. "Standard Test Method for Plane-Strain Fracture Toughness of Metallic Materials", ASTM Standard E399-83-91, edited by S. P. Canning et. al., (American Society for Testing and Materials, Philadelphia, 1991).
6. "Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials", ASTM Standard D5045-91, edited by S. P. Canning et. al., (American Society for Testing and Materials, Philadelphia, 1991).
7. C. M. AGRAWAL, Dissertation, Duke University (1989).
8. R. D. GOOLSBY and C. LIN, in "Instrumented Impact Testing of Plastics and Composites", ASTM STP 936, edited by S. L. Kessler, G. C. Adams, S. B. Driscoll and D. R. Ireland, (American Society for Testing and Materials, Philadelphia, 1987) p. 351.
9 E. H. ANDREWS, "Fracture in Polymers" (Oliver and Boyd, London, 1968) p. 177.

Received 7 November 1990
and accepted 10 April 1991