Fracture Energy Release Rate in Nylon Fibers

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ABSTRACT: The effect of relative humidity on the fracture energy release rate, G_{Ic}, for single nylon 6,6 fibers has been determined previously. In this article, it is shown that G_{Ic} is independent of relative humidity for moisture contents of $> 2.3\%$ once the plastic zone correction is made. G_{Ic} is compared with various proposed mechanisms to account for fracture energy. It is shown that the energy required to disrupt or "melt" the crystals in the plastic zone accounts for the majority of the energy required to break the specimen, and should be considered explicitly in future analyses of fracture in semicrystalline polymers. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1541–1544, 1998

Key words: nylon; fracture; plastic zone; fracture energy

INTRODUCTION

As industry tries to replace metals with plastics, it has become increasingly important to improve our understanding of the fracture process in plastics. Already, the use of fracture mechanics, borrowed from the metals industry and adapted to plastics, has found its way into the design process. A critical property in this regard is the fracture energy release rate, G, the energy released per unit area of crack (or flaw) growth. The fracture energy release rate under plane strain loading conditions is given as G_I. Above its critical value, G_{Ic}, the energy released as the crack grows is greater than that required to create additional crack area, and the crack grows rapidly to complete fracture. Due to the importance of G_{Ic} or equivalently, K_{Ic}, the critical stress intensity factor, to the design of parts, there have been many attempts to determine what physical features of the material control G_{Ic}, starting with the pioneering work of Griffith.[1] He identified G_{Ic} with the energy required to create new surface (i.e.,

the surface free energy). Although this described the case he studied well, additional dissipation through a "plastic deformation zone" around the crack tip has been identified to account for the fact that G_{Ic} measured experimentally is typically much larger than that obtained through only surface energy considerations.

In two previous articles, Michielsen[2,3] described the failure of high-strength nylon 6,6 monofilaments using fracture mechanics. These articles showed that the fracture energy release rate, G_{Ic}, depended on both moisture and orientation. G_{Ic} was some eight times larger for a transverse break in the highly oriented fibers than for unoriented nylon plaques, whereas the initial Young's modulus only increased ~ 2.2 times. In addition, it was shown that G_{Ic} was some 10 times larger for a transverse break than for axial splitting of the fibers, confirming the long-held belief that the increase in strength along an oriented fiber is accompanied by a loss in strength transverse to the fiber axis.

It was also shown that, as the relative humidity (RH) increased from 0.2 to 50%, G_{Ic} decreased by a factor of 2. At still higher RH, the G_{Ic} decreased only slightly. However, Table I, reproduced in

Table I   RH Dependence of G_{Ic}, Intercept, Plastic Zone Size, and Corrected G_{pz}

Water (%)	G_{Ic} (kJ m^{-2})	Intercept (MJ m^{-3})[a]	Plastic Zone (μm)	G_{pz} (kJ m^{-2})
0.2	31.3	−15.2	—	—
0.9	27.7	−11.2	—	—
2.5	18.8	2.6	39	25.4
3.8	17.0	2.5	57	24.7
8.0	15.6	9.2	54	25.8
Average			50	25.3

[a] Note, in ref. 3, the units for the intercept were incorrectly reported as mJ m^{-3}.

part here from ref. 3, indicates a significant problem with this analysis, namely, that the intercept of the strain energy density *versus* $1/(aY^2)$ is nonzero. Y is the geometric correction factor, and a is the crack length. This has the physically unacceptable implication that substantial energy is needed to either keep the *broken* ends in contact when the intercept is negative or, likewise, to pull them apart when the intercept is positive. This article attempts to correct for the positive intercepts and then interpret the fracture energy in molecular terms.

RESULTS AND DISCUSSION

Figure 1 is a graph of the intercept *versus* moisture content of the fibers from Table I, where per-
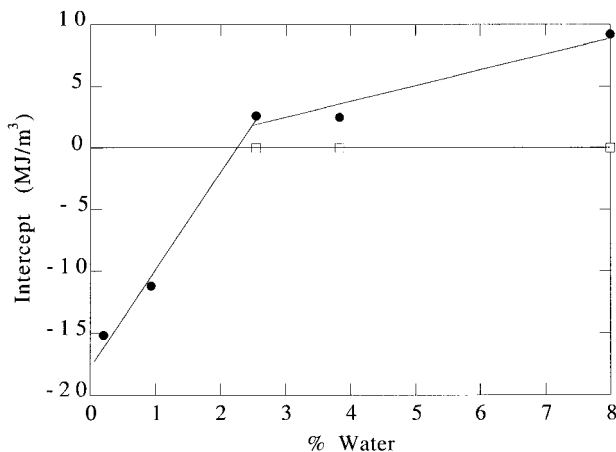

Figure 1   Intercepts of the strain energy density *vs.* $1/(aY^2)$ (●) and for the same data after making the plastic zone correction (□).

centage of water has been substituted for RH[4] in ref. 3. There is a sharp break in this curve, as the intercept passes from negative to positive, which suggests a change in mechanism for the intercept.

A common correction in fracture mechanics is the Irwin or Dugdale plastic zone correction.[5] In these cases, the apparent crack size is slightly larger than the real crack size due to plastic deformation just ahead of the crack tip. The majority of the energy required to break the specimen has been attributed to the energy required to create and propagate this plastic zone. When this correction is made to the samples with water content > 2.3% in such a way as to force the intercepts to zero (open symbols in Figure 1), the results in Table I (columns 4 and 5) are obtained. All of the plastic zone sizes are within the experimental error of their average in this study. Interestingly, when this correction is applied, G_{Ic} for moisture contents > 2.3% becomes a constant (25.3 kJ m^{-2}).

The plastic zone correction cannot reasonably be applied to the cases of moisture content < 2.3%, because this would require a negative plastic zone size, which is of course impossible. A good explanation of the negative intercepts is still elusive.

Because G_{Ic} is constant in these fibers for moderate and high moisture contents, it is interesting to compare G_{Ic} with the required fracture energies for various possible fracture mechanisms. Table II lists several proposed mechanisms to account for G_{Ic}, the relevant equations, the calculated G, and the ratio of the measured G_{Ic} to calculated G. The last column is the thickness of material used to convert from the associated energy density to the energy per unit crack area.

In this table, γ is the surface tension, which for

Table II Fracture Energies

Process	Fracture Energy	G	G_{Ic}/G	Thickness
Experiment	$G = G_{Ic}$	25 kJ m^{-2}		
Surface free energy	$G_{\gamma} = 2\gamma$	92 mJ m^{-2}	3×10^5	
Bond breakage	$G_{BB} = \dfrac{\text{energy}}{\text{bond}} \times \dfrac{\text{no. of bonds broken}}{\text{unit area}}$ $\approx \dfrac{\text{energy}}{\text{bond}} \times \dfrac{t\rho}{M}$	3.8 J m^{-2}	7×10^3	0.15 nm
"Melting" of crystals in plastic zone	$G_{m,pz} \cong t\rho\Delta H_m^*(1 - T/T_m^*)$	4.5 kJ m^{-2}	5.6	100 μm
"Melting" of crystals in plastic zone, with $\Delta S \approx 0$	$G_{m,pz}^{\Delta S \approx 0} = t\rho\Delta H_m^*$	10 kJ m^{-2}	2.5	100 μm

nylon 6,6 is 46 mJ m^{-2}, the energy per broken bond is ~ 350 kJ mol^{-1} and the number of bonds broken is just thickness of a plane of bonds, t, or the length of a bond ($l = t = 1.54 \times 10^{-10}$ m, times the density, $\rho = 1.14 \times 10^3$ kg m^{-3}) divided by the molecular weight per backbone bond, $M = 16 \times 10^{-3}$ kg mol^{-1}.

Calculation pertaining to "melting" of crystals in Table II is based on Abhiraman's postulate[6] that the plastic deformation in the fracture of crystalline materials is a manifestation of strain energy-induced melting at the crack tip. The maximum reversible work (strain energy) per unit mass at the crack tip is given by

$$W_{rev}^{max}(T) \cong \Delta H_m^*(1 - T/T_m^*), \qquad (1)$$

where ΔH_m^* and T_m^* are the enthalpy of melting per unit mass and the equilibrium melting temperature of the undeformed material, respectively. T is the test temperature. Conversion of W^{max} to melting energy per unit area of crack growth, $G_{m,pz}$ is given by:

$$G_{m,pz} = t\rho W^{max} \qquad (2)$$

Taking the simplest case of a cylindrical plastic zone, the thickness of the zone is just twice its radius, or, in the present case, 100 μm. $\Delta H_m^* = 88.5$ J g^{-1} and $T_m^* = 265°$C were measured by differential scanning calorimetry. This gives $G_{m,pz} = 4.5$ kJ m^{-2} and is by far the closest agreement with experiment of any of the models presented so far.

Equation (1) is the general case for melting any material. However, in polymers, the high stresses required to pull a crystal apart are also high enough to straighten the chains nearly as much

as they straighten when they crystallize. Then $\Delta S_m \sim 0$. In this case, eq. (1) becomes

$$W^{max} \cong \Delta H_m^* \qquad (3)$$

and

$$G_{Ic} = t\rho W^{max} = G_{m,pz}^{\Delta S \approx 0} \qquad (4)$$

as given in the last line of Table II. Again, using the cylindrical plastic zone approximation gives a value for $G_{m,pz}^{\Delta S \approx 0} = 10$ kJ m^{-2}, which is within a factor of 2.5 of the measured value.

A better approximation for the shape of the plastic zone is given by Williams.[7] For small scale yielding, where the plastic zone is much smaller than the thickness of the sample, the thickness of the plastic zone is roughly 30% larger than given by the spherical approximation. In this case, $G_{Ic}/G_{m,pz}^{\Delta S \approx 0} \sim 1.9$. As the thickness of the fiber approaches the length of the plastic zone in front of the crack (i.e., 50 μm in the present case), the thickness of the plastic zone normal to the plane of crack growth increases, and the ratio $G_{Ic}/G_{m,pz}^{\Delta S \approx 0}$ decreases further.

CONCLUSIONS

Clearly, the energy required to form a new surface area and to break any bonds crossing the fracture plane as the crack grows is so small, compared with the measured fracture energy release rate that they contribute insignificantly to the fracture energy. Although both of these processes undoubtedly occur, their effect on the fracture energy is insignificant. On the other hand, the energy re-

quired to disrupt, or melt, the crystals in the plastic zone approaches the fracture energy. This aspect should be considered explicitly in future analyses of fracture in crystalline polymers.

REFERENCES

1. A. A. Griffith, *Philos. Trans. R. Soc.,* **A221,** 163 (1920).

2. S. Michielsen, *J. Mater. Sci. Lett.,* **11,** 982 (1992).
3. S. Michielsen, *J. Appl. Polym. Sci.,* **52,** 1081 (1994).
4. Anonymous, *Design Handbook for DuPont Engineering Plastics, Module II,* available from DuPont Engineering Polymers.
5. D. Broek, *Elementary Engineering Fracture Mechanics,* 4th ed., Marinus Nijhoff Publishers, Boston, 1986.
6. A. S. Abhiraman, *Proc. Roy. Soc. Lond. A,* **453,** 1649 (1997).
7. J. G. Williams, *Fracture Mechanics of Polymers,* Wiley, New York, 1984, p. 98.