

# The Impact Fracture Toughness of Plasticized Cellulose Acetate and the Relationship with the Secondary Loss Transition

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## Synopsis

The impact fracture toughness of plasticized cellulose acetate has been determined by linear elastic fracture mechanics over the temperature range 20–70°C. A major peak in fracture toughness at –10°C has been found to correspond to a secondary loss transition in the dynamic mechanical loss spectrum of plasticized cellulose acetate. At –10°C, the fracture toughness is directly proportional to the log of the maximum strain rate.

## INTRODUCTION

At present there is a great deal of interest in the relationship between propellant fracture and anomalous gun ballistics. Propellant fracture during the ballistic cycle, especially at low temperatures, is thought to result in additional unprogrammed burning surface, causing unexpectedly high chamber pressures in the gun, and occasionally catastrophic breech blows. Propellant fracture during the ballistic cycle is generally a brittle failure process, especially during low temperature gun firings. As the large majority of gun propellants in current service contain nitrocellulose and other cellulosic polymers, considerable effort is currently being expended into devising laboratory methods of evaluating brittle fracture of cellulosic polymers under high strain rate impact conditions. Such conditions are thought to be a reasonable facsimile of the extremely large and rapid forces exerted upon the propellant during the ballistic cycle.

Plati and Williams<sup>1,2</sup> have used a linear elastic fracture mechanics approach to derive the fracture toughness  $G_c$  of various polymers under impact (three-point bend) conditions. Unlike many of the criteria used to measure impact strength or impact resistance of materials,  $G_c$  is a true material parameter which is independent of specimen geometry.

The impact fracture properties and dynamic mechanical properties of polymeric materials has provided strong evidence that the presence of significant secondary loss transitions is strongly related to the high impact strength of the materials.<sup>3</sup> Loss transitions in dynamic mechanical spectroscopy (or other forms of relaxation spectroscopy such as NMR, dielectric, ultrasonic) indicate the presence of various molecular motions of the polymer main chain or side chain which can dissipate applied energy (mechanical energy in DMA, radio-frequency energy in NMR, etc.). Thus polymeric materials which exhibit significant loss

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transitions (especially secondary transitions) may be expected to show high impact strength by virtue of the fact that the polymer chain rapidly dissipates the applied impact stress hence avoiding localized stress concentration. The frequencies of these molecular motions must substantially match the frequencies of the applied impact stress to provide effective energy dissipation.<sup>4</sup>

## EXPERIMENTAL

Specimen bars of plasticized cellulose acetate of length  $L$ , breadth  $B$ , and depth  $D$  were carefully manually notched with fresh razor blades to a depth  $a$  and tested in the Charpy three-point bend mode. A Hounsfield impact tester, which had been previously modified to allow variation of the effective specimen test length, was used in the study. The effective test lengths used were 39.6, 54.5, 74.8, and 94.8 mm, while the breadth and depth of the specimens varied from 4.5 to 8.4 mm. The  $a/D$  values varied from 0.05 to 0.4. Low-temperature measurements were made by storing the notched specimen bars at the required temperature for at least 60 min, then quickly testing the specimens within 20–25 s. The low-temperature cabinet was cooled with carbon dioxide. All fracture surfaces were examined with a calibrated moderate power microscope to accurately measure the notch depth and observe the fracture surfaces for signs of crazing. Specimens whose fracture surfaces showed signs of crazing, especially at the crack tip, were excluded from further consideration.

The cellulose acetate (2.0–2.5 acetate groups per glucose unit) was plasticized with 41% triacetin and 5% carbamate. The specimen bars were machined from thick sheets (9–10 mm) of the plastic. The plasticized cellulose acetate has a softening point of approximately 60°C.

The impact test conditions and specimens were essentially those previously described in the literature.<sup>1,2</sup> The four different test lengths were used at each temperature, and values of  $a$ ,  $B$ , and  $D$  were chosen to cover the range of  $BD\Phi$  (see text) 0–200  $\times 10^{-6}$  m. Each impact energy determination for a particular geometry was median value of 10 readings. For each test length at a particular temperature, four values of  $BD\Phi$  were used; hence 160 specimens were tested at each temperature.

## RESULTS AND DISCUSSION

It has been shown<sup>1,2</sup> that the impact energy  $W$  required to break a sharply notched specimen can be related to the fracture toughness (or critical strain energy release rate)  $G_c$  by the equation

$$W = G_c BD\Phi + KE \quad (1)$$

where

$$\Phi = C \frac{dC}{d(a/D)} \quad (2)$$

and  $C$  is the compliance while  $KE$  is the kinetic energy component of the impact test. Values of  $\Phi$ , the geometrical calibration factor for the Charpy three-point bend mode, have been previously tabulated.<sup>2</sup> Thus a plot of  $W$  vs.  $BD\Phi$  will give a straight line of slope  $G_c$  for brittle fracture conditions. The kinetic energy

imparted to the test specimen during impact will manifest itself as a positive intercept on the impact energy axis.

The fracture toughness of plasticized cellulose acetate has been determined at 20°C, 5°C, -10°C, -25°C, -40°C, -55°C, and -70°C. The corresponding values of  $G_c$  (determined from the slope of the lower limit line<sup>5,6</sup>) for the respective temperatures were: 0.85, 0.20, 0.34, 0.20, 0.145, 0.095, and 0.085 kJ/m<sup>2</sup> (average error estimates  $\pm 0.02$  kJ/m<sup>2</sup>). Values of  $KE$  varied from approximately 0 to  $0.07 \times 10^{-2}$  J for the various temperatures. The effect of temperature on  $G_c$  for the seven temperatures studied is shown in Figure 1. A pronounced peak at -10°C is immediately obvious, indicating that the plasticized cellulose acetate is far more resistant to crack propagation at subambient temperatures than would be expected for an isotropic brittle material. The peak in  $G_c$  at -10°C is quite authentic, the observed value of  $0.34 \pm 0.02$  kJ/m<sup>2</sup> being well outside the conservative error estimates of the  $G_c$  values at 5°C and -25°C. It is important to note that all fracture surfaces considered in this analysis were consistent with completely brittle fracture processes having occurred.

The observed temperature dependence of  $G_c$  can be rationalized in terms of the empirical relationship between the impact strength and the presence of significant secondary loss transitions in many polymers. After allowing for frequency differences between the impact fracture frequency and the frequency of the dynamic mechanical measurements, it has been observed that the temperature at which pronounced peaks occur in impact strength correspond closely to temperatures at which secondary loss transitions occur in many polymeric materials.<sup>4,5</sup>

Russel and Von Kerpel<sup>7</sup> have determined the dynamic mechanical spectra of cellulose triacetate, cellulose diacetate, and various plasticized cellulose triacetates and diacetates. Cellulose diacetates containing equal portions of a

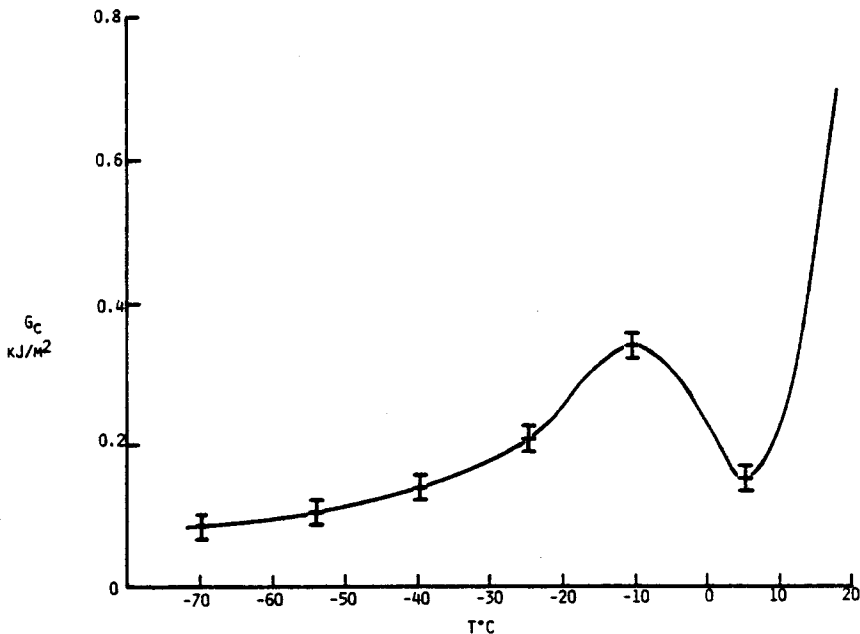


Fig. 1. Fracture toughness  $G_c$ , vs. temperature (°C) for plasticized cellulose acetate.

variety of plasticizers show strong secondary loss peaks in the region from  $-10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$  at a frequency of 1 Hz. Thus cellulose diacetate equally plasticized with methylphthalylethylglycollate has a secondary loss peak at  $-10^{\circ}\text{C}$ . As methylphthalylethylglycollate is a triester, we may expect<sup>8</sup> cellulose acetate (containing 2.0–2.5 acetate units per glucose unit) equally plasticized with triacetin to show a similar secondary loss peak at approximately  $-10^{\circ}\text{C}$ .

The frequency of fracture,  $f$ , can be calculated from the expression

$$f = \dot{\epsilon}_{\max}/4e_y \quad (3)$$

where

$$\dot{\epsilon}_{\max} = 6(V/D)(D/L^2) \quad (4)$$

and  $\dot{\epsilon}_{\max}$  is the maximum strain rate,  $e_y$  is the yield strain,  $V$  is the striker velocity during impact (2.5 m/s). At  $0^{\circ}\text{C}$  and an impact striker velocity of 0.61 m/s,  $e_y$  for plasticized cellulose acetate has previously been calculated<sup>9</sup> to be 0.058, 0.060, and 0.062 for  $L = 33.5$ , 44.7, and 55.9 mm, respectively. As the impact velocity in this case is 2.5 m/s,  $f$  can be roughly approximated to be in the range 925–155  $\text{s}^{-1}$ . It is generally found that  $e_y$  is usually independent of rate and temperature in many polymers,<sup>6</sup> a result confirmed in this study for impact conditions.

Thus, while the frequency of fracture of plasticized cellulose acetate lies in the range of 925–155  $\text{s}^{-1}$ , which is far greater than the frequency of the dynamic mechanical measurements (1 Hz), it has been previously shown that the Fourier spectrum of an impact pulse is composed of a broad distribution of frequencies. For an idealized brittle fracture, the normalized magnitude is largest from 0 to approximately 1200 Hz,<sup>4</sup> although the frequency distribution extends to far higher frequencies.<sup>10</sup> Hence, since the frequency of fracture for plasticized cellulose acetate lies within this range, it may be anticipated that the secondary loss transition determined at 1 Hz should closely correspond to the peak in impact fracture toughness. From a molecular relaxation standpoint, the various plasticized cellulose acetate polymer chains will exhibit a normalized frequency distribution of segmental main chain molecular motions, any combination of which may be excited by the applied impact stress. It has been shown that it is the main chain relaxation mechanisms rather than side chain mechanisms of the polymer which are effective in dissipating impact energy.<sup>10,11</sup> Kisbenyi et al.<sup>5</sup> have also observed a correlation between impact fracture toughness and  $\tan \delta$  (for both the  $\beta$  and  $\gamma$  transitions) of rubber-modified polystyrene. The peaks in  $G_c$  were related to the rubber content, indicating that the rubber particles were more effective in dissipating the applied impact energy than were the polystyrene chains. In this case the rubber particles are far more efficient in providing molecular relaxation mechanisms than the triacetin plasticizers molecules in the cellulose acetate.

In a search for possible relationships between  $G_c$  and  $\dot{\epsilon}_{\max}$ , it was found that only at  $-10^{\circ}\text{C}$  did such a relationship exist. Although only four data points are available, it appears as if  $G_c$  is directly proportional to  $\ln \dot{\epsilon}_{\max}$  (Fig. 2). It is noteworthy that the line of best fit does pass through the origin as expected. Significantly,  $G_c$  is proportional to  $\ln \dot{\epsilon}_{\max}$  at  $-10^{\circ}\text{C}$ , the temperature at which a peak in fracture toughness occurs. It was also observed that the brittle fracture surfaces at  $-10^{\circ}\text{C}$  were much squarer than those observed at other temperatures. A tentative explanation of this observed relationship between  $G_c$  and  $\ln \dot{\epsilon}_{\max}$

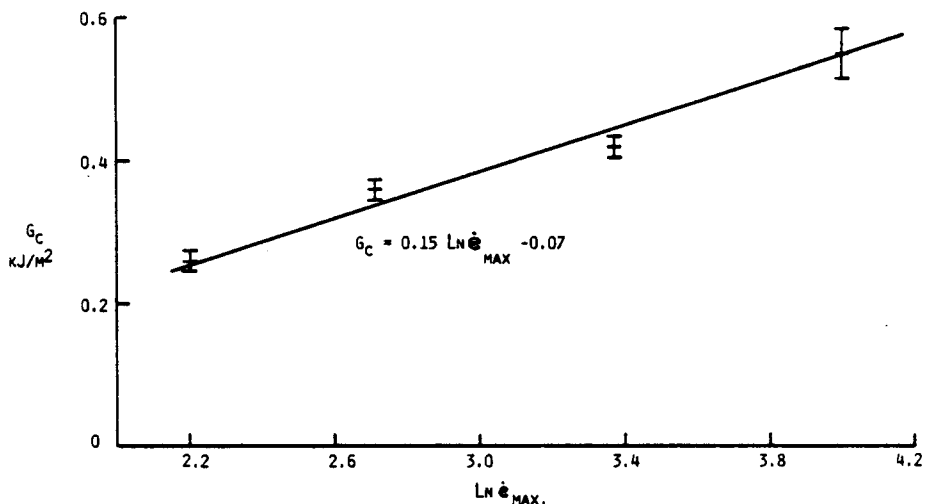


Fig. 2. Fracture toughness  $G_c$ , vs. the log of maximum strain rate for plasticized cellulose acetate at  $-10^\circ\text{C}$ .

may lie with the particular frequency distributions of the polymer chain motions at  $-10^\circ\text{C}$  (as reflected in the secondary loss peak) compared to the other temperatures. If the frequencies of the chain motions which are most active at  $-10^\circ\text{C}$  correspond to the major frequency distribution of the impact event, it can be expected that a relationship between the strain rate and the frequencies of the polymer chain motions may very well exist. While relationships between strain rates and frequencies of segmental main chain motions may exist at other temperatures, it is only at  $-10^\circ\text{C}$  that the magnitude of these effects are experimentally detectable.

## CONCLUSIONS

The impact fracture toughness  $G_c$  of plasticized cellulose acetate has been determined by linear elastic fracture mechanics in the Charpy mode over the temperature range from  $20^\circ\text{C}$  to  $-70^\circ\text{C}$ . A major peak in fracture toughness at  $-10^\circ\text{C}$  has been found to correspond to a secondary loss transition in the dynamic mechanical loss spectrum measured at 1 Hz. Although the frequency of fracture covers the range  $925\text{--}115\text{ s}^{-1}$ , it has been shown that this range is still within the range of frequencies for a brittle fracture process during impact. The observed relationships between  $G_c$  and the secondary loss transition,  $\dot{\epsilon}_{\text{max}}$  are both rationalized in terms of the molecular relaxation processes associated with the segmental main chain motion of the cellulose acetate polymer.

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