Fracture of molecular glasses under tension and increasing their fracture resistance with polymer additives

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Abstract. The fracture of single-component molecular glasses has been characterized under tension. In-plane tension is created by cooling a liquid film below its glass transition temperature constrained on a substrate that is less thermally expansive. The fracture produces a network structure whose cell size is comparable to film thickness. For each system studied (indomethacin, *o*-terphenyl, and sucrose benzoate), the condition of fracture is well described by the fracture models for supported films and a characteristic energy release rate G_c . Agreement is found for a wide range of film thickness (10 – 250 μm) in both open and sandwich geometries. For the molecular glasses studied, $G_c \approx 1 \text{ J/m}^2$. *o*-terphenyl glasses become significantly more resistant to fracture with the addition of polystyrene; at 10 wt %, G_c increases with the molecular weight of polystyrene, by a factor of 5 at 1 million g/mol. The molecular-weight dependence is consistent with an increase of fracture surface area as the crack tip goes around the pervaded volume of each polymer chain encountered (sphere defined by the radius of gyration).

Keywords: Molecular Glass, Fracture Toughness, Polymer Additives, Brittle Fracture

Introduction

Glasses are important materials that combine the mechanical strength of crystals and the spatial uniformity of liquids. While better known glasses are inorganic and polymeric, organic glasses of relatively low molecular weights (“molecular glasses”) are being explored for applications in electronics [1,2,3,4], bio-preservation [5,6], and drug delivery [7,8]. Despite a growing knowledge of these materials, however, little is known about their mechanical properties, especially their fracture. Fracture can influence not only the functions of molecular glasses but also their processing (e.g., milling [9,10] and tableting [11,12]).

Another reason to study the fracture of molecular glasses is their high surface mobility [13,14] and fast surface crystallization [15,16]. Since it creates free surfaces, fracture is expected to accelerate crystallization in these materials. Indeed there have been reports of fracture-induced crystallization in molecular glasses [17,18]. In a recent proposal, fast crystal growth *in the interior* of molecular glasses is linked to a steady creation of micro-cracks [18,19]. This role of fracture in glass crystallization motivates a deeper understanding of the phenomenon in the development of stable amorphous materials.

While the solids of small organic molecules are relatively fragile, polymers are known to resist fracture. The mixing of polymers with small molecules can improve materials performance in pharmaceuticals [8,20,21] and electronics [22,23]. One goal of this study is to examine the effect of polymer additives on the fracture toughness of small-molecule glasses.

In this study, we characterized the tensile fracture of molecular glasses using a simple method that relies on cooling a liquid film adhered to a less thermally expansive substrate [24,25,26,27,28,29]. Tension is created in the organic layer owing to the mismatch of thermal expansion, and this tension is sufficient to cause fracture. This method of studying fracture under tension has been applied to ceramics [24] and organo-silicates [25] and has recently gained a firm theoretical foundation [27,28,29]. Although

alternative tests are available for measuring fracture properties, this method has proved simple and able to characterize fracture under the actual conditions of applications [24,25].

We report that under in-plane tension, the supported film of a molecular glass fractures comprehensively to a network structure whose cell size is comparable to film thickness. The condition of fracture is well described by the theoretical models and a material-specific energy release rate G_c . Agreement is found at a wide range of film thickness in both open and sandwich geometries. We report the first set of critical fracture energy release rates for organic glasses and a significant toughening effect of polymer additives on these materials.

Theoretical Portion

If a glass-forming liquid adheres to a solid substrate of a different thermal expansion coefficient (Figure 1), cooling creates a stress on the liquid. This stress is relaxed by liquid flow at high temperatures, but upon cooling toward the glass temperature T_g , viscous relaxation slows down and eventually fails to relax the stress on the timescale of cooling. Further cooling creates an in-plane stress in the material, which for a mechanically thin film is given by

$$\sigma_{//} = \frac{E}{1-\nu} \Delta\alpha(T_{set} - T) \quad (1)$$

where $\Delta\alpha$ is the difference in linear thermal expansion coefficients between the film and the substrate, E is Young's modulus of the film, ν is its Poisson's ratio, and T_{set} is the temperature at which the liquid begins to respond like an

Fig. 1. Illustration of fracture experiments in (a) sandwich and (b) open geometries. Fracture propagates through the organic glass film. h : film thickness. G_{ss} : energy release rate for steady-state propagation of fracture.

elastic solid. Rigorously speaking, eq. (1) holds only if $\Delta\alpha$ is constant; otherwise the right-hand side is an integral. Eq. (1) can accurately predict the stress observed in constrained films of ceramics [24], metals [30] and polymers [31,32]. In this study, the substrate (silicate glass) is less thermally expansive than the organic layer and the stress is tensile with cooling.

At temperatures sufficiently below T_{set} , the stress becomes high enough to fracture the organic film. The condition for a crack to propagate is that the energy release rate G exceeds some material-dependent critical value G_c . For a steadily propagating crack through the film without detachment from the substrate (termed “tunnel fracture” for a sandwich film and “channel fracture” for an open film; see Figure 1), G is given by [27,28,29]

$$G_{ss} = \frac{\psi^2 \sigma_{II}^2 h}{\bar{E}} \quad (2)$$

where h is film thickness, ψ is a dimensionless geometric factor, and $\bar{E}$ is $E/(1-\nu^2)$ (assuming a plane-strain condition). The subscript “ss” signifies the steady-state propagation of fracture. For an organic film on a silicate coverslip as used in this study, $\psi^2 = 1.2$ for an open film [27] and 0.5 for a sandwiched film [29]. As we report below, our films fracture at well-defined temperatures or stresses. We calculate the corresponding G_{ss} with eq. (2) and regard it as an estimate for the material’s G_c .

Equations 1 and 2 and the assumption $G_{ss} = G_c$ implies the following relation:

$$T_{\text{frac}} = T_{\text{set}} - k h^{-1/2} \quad (3)$$

where T_{frac} is the temperature of fracture and k is related to G_c by

$$G_c = \psi^2 k^2 \Delta\alpha^2 E \frac{1+\nu}{1-\nu} \quad (4)$$

As we show below, relationship given by eq. (3) is indeed observed, allowing the calculation of G_c by eq. (4). As a further test of consistency, we shall compare the G_c values obtained from measurements with open and sandwiched films for which the ψ values differ. Internal consistency requires that the same G_c be obtained from the two types of measurements, and we show that this consistency does exist.

A crack through a supported film (Figure 1) is expected to release the stress within some distance from the crack. Xia and Hutchinson predict that this characteristic distance is given by $l = \psi^2 h$, where ψ^2 is the same geometric factor in eq. (4) and h is film thickness [33]. For a film that has fractured in a cellular pattern, the average cell size d would be approximately $2l$; at this size, the local stress would fall below the critical value in the entire film. For an organic film sandwiched between silicates ($\psi^2 = 0.5$), the prediction is $d = h$. We shall see that the prediction agrees with the experimental results.

Experimental Section

Indomethacin (IMC), sucrose benzoate (SB), and *ortho*-terphenyl (OTP) were obtained from Sigma Aldrich and used as received. Table 1 collects the relevant properties of these materials. Polystyrene (PS) fractions used in this work were: “PS8.4k”: $M_w = 8400$ g/mol, PDI (polydispersity index) = 1.05; “PS16k”: $M_w = 15500$ g/mol, PDI = 1.04; “PS100k”: $M_w = 97400$ g/mol, PDI = 1.01; “PS1000k”: $M_w = 979800$ g/mol, PDI = 1.03. We obtained PS 16k from Polymer Source and all others from Scientific Polymer. PS-OTP solutions were prepared by dissolving 10 wt % PS in OTP at 353 K for at least 24 h.

To perform a fracture experiment in the sandwich geometry, a liquid film was prepared between two 15 mm diameter circular coverslips (150 μm thick; Schott D-263-M silicate glass). The thickness of the film was calculated from its mass, density and area; the calculated thickness was validated against direct measurements with a caliper of 1 μm precision. Each sample was placed on a hot/cold stage (Linkam THMS 6000), equilibrated in the liquid state (at $T_g + 5$ K), and then cooled at 10 K/min until fracture occurred. The 10 K/min cooling rate corresponds to a strain rate of approximately 10^{-5}s^{-1} . The entire cooling process was recorded on video through an Olympus BH2-UMA microscope. After fracture, the sample was heated to $T_g + 20$ K to heal the cracks and retested up to 3 times. For samples tested in the open geometry, a film was prepared between a 22 mm square coverslip and a 15 mm diameter circular

one and the square coverslip was removed. An open-surface sample was tested in the same protocol but used only once to avoid dewetting at high temperatures.

The density of an SB glass was measured at 295 K by volume displacement. Before measurement, the sample (ca. 0.4 g) was degassed at 370 K in vacuum. The sample was placed in a 2 mL volumetric flask and submerged in water to mark. The mass of the water was measured and its volume calculated from its known density. The density of SB was determined to be $1.31 \pm 0.01 \text{ g/cm}^3$ (3 independent measurements).

Table 1 Properties of the materials used.

Material	ρ , g/mL	T_g , K	E , GPa	α , ppm/K	ν	References
IMC	1.34	315	4.1	65	0.36	[34,35,36]
OTP	1.13	246	4.3	87	0.33	[37]
SB	1.31	332	2.5	70	0.33	[38]
Silicate coverslip	2.6	830	73	7.2	0.21	[39]

Notes: (1) IMC: ρ from Ref. 34, measured at room temperature; E and ν from Ref. 35; α is calculated from the ellipsometry TEC α_{obs} [36] using the relation $\alpha = \left(\frac{1-\nu}{1+\nu}\right)\alpha_{\text{obs}} + \left(\frac{2\nu}{1+\nu}\right)\alpha_s$, where α_s is the TEC of the substrate (silicon) [40].

(2) OTP: ρ and α are from Ref. 37 and given at 246 K. α is taken to be 1/3 of the volumetric value. E is calculated from isothermal compressibility [37] and assumed ν (0.33).

(3) SB: ρ is from this work, measured at 295 K; α and ν are assumed; E is calculated from the shear modulus [38] and ν .

(4) T_g is the onset glass transition temperature from differential scanning calorimetry during heating at 10 K/min.

(5) Coverslip: All data from the manufacturer [39].

Results

Figure 2 shows the stages of fracture observed during the cooling of an organic glass film sandwiched between two silicate coverslips. Before cooling, the film is in the liquid state and continuous (Figure 2a). During cooling, fracture typically occurs all-at-once within the field of view, producing a network structure (Figure 2b). The velocity of fracture tips is too fast to be measured by our video camera; it is at least 0.1 m/s judging from the 30s^{-1} frame rate and the 2 mm field of view. Further cooling leads to additional fracture of the isolated cells. This second stage of fracture makes the cells appear circular (Figure 2c); it is not all-at-once, with each cell “blinking in” during fracture. We attribute the first stage of fracture to tunnel fracture as shown in Figure 1a (channel fracture in the case of open films, Figure 1b) and the second stage to delamination. We will focus hereafter on the first-stage, all-at-once fracture.

Occasionally, a single long crack appears in the field of view at a slightly higher temperature before network fracture (Figure 2b). For some samples, the long cracks halt the wave of network fracture and allow the observation of multiple network fracture events at slightly different temperatures (a few K from each other). For such samples, we report an area-weighted average fracture temperature.

Fig. 2. Stages of fracture for a sandwiched 42 μm thick sucrose benzoate sample cooled at 10 K/min. (a) 338 K (no fracture). (b) 273K (tunnel fractures). (c) 253K (circular fracture).

Fig. 3. Effect of cooling rate on fracture temperature. The data are for sandwich IMC films $40 \pm 4 \mu\text{m}$ thick and referenced to T_{frac} at 10 K/min.

Figure 3 shows the effect of cooling rate on the temperature of fracture. Slower cooling slightly decreases T_{frac} . This effect is small: for a decrease of cooling rate from 30 to 1 K/min, T_{frac} decreases by 3 K. The effect is similar to that observed for the glass transition temperature [41], and likely reflects a reduction of T_{set} (the temperature at which tension begins to build) with slower cooling. The weak dependence of T_{frac} on cooling rate suggests that the stress at fracture (and thus the calculated G_c) is a weak function of strain rate. Similar observations were made for the brittle fracture of rocks [42] and tungsten [43] for even larger changes of strain rate.

Figure 4 shows the effect of film thickness h on the size of fracture cell d for sandwich films of SB. Thicker films fracture to create larger cells. The occasional black circles are air bubbles trapped in during sample preparation. These bubbles were never observed to be the initiation sites for fracture. Figure 5 plots d as a function

Fig. 4. Size of fracture cells (d) for sandwiched films of SB vs. film thickness (h) labeled for each sample.

of h for three molecular glasses (IMC, OTP, and SB) studied in the sandwich geometry. A standard method⁴⁴ was used to measure d . Despite considerable scatter, an overall trend is evident. The overall trend is the same for all three systems, described by $d = 1.2h$. This relation is in excellent agreement with the prediction made on the basis of the distance over which stress is relaxed from a crack.³³ This result supports the notion that network fracture reduces the

Fig. 5. Size of fracture cell d versus film thickness h . The data are for sandwich films. The line corresponds to $d = 1.2h$.

stress in the entire film below some critical value.

Figure 6 shows the temperature of network fracture T_{frac} as a function of film thickness h for the molecular glasses studied. All data were collected at a cooling rate of 10 K/min (strain rate approximately 10^{-5}s^{-1}). The data are plotted in the format T_{frac} vs $h^{-1/2}$ to test the relation (eq. 3) anticipated for the fracture of supported films. For IMC and SB, experiments were performed in both open and sandwich geometries; for OTP, only sandwich samples were measured because its sub-ambient T_g makes it difficult to prepare open-surface films. Note that the anticipated relation $T_{\text{frac}} \propto h^{-1/2}$ (eq. 3) is observed for all three molecular glasses and for IMC and SB, in both open and sandwich geometries. Later we shall see that the relation also holds for OTP doped with PS (Figure 7).

Table 2 shows the slope k and the intercept T_{set} for each fitting line in Figure 6. The value of T_{set} tracks closely the T_g (Table 1), with $T_g - T_{\text{set}} \approx 20$ K. T_{set} is roughly the endpoint of the glass transition measured during 10 K/min cooling. Note the smaller slope k for

the fracture of open-surface films, indicating that at the same thickness, an open film fractures at a higher temperature (lower tension) than a sandwich film. This difference is anticipated by the fracture

Fig. 6. Fracture temperature vs film thickness for three molecular glasses with cooling at 10K/min, along with best-fitting lines. $R^2 = 0.90$ (IMC open), 0.91 (IMC sandwich), 0.91 (SB open), 0.95 (SB sandwich), 0.86 (OTP sandwich).

models [27,28,29]. The predicted ratio for the slopes is $k_{\text{open}}/k_{\text{sandwich}} = \psi_{\text{sandwich}}/\psi_{\text{open}} = 1.6$, and this ratio is indeed observed. These consistencies indicate that the theory describes well our experimental results and justify the further calculation of G_c using eq. 4 for each system studied (see Table 2 for the results).

For IMC, Figure 6 shows additional data points (crosses) from experiments performed with open films that contained pre-formed flaws. These films were scratched with a scalpel down to the substrate to create flaws to see whether they could initiate new fractures. Tested in the same way, these samples showed no significant change in the fracture temperature from those without scratches. This result indicates that each film fractures at a well-defined critical tension, without significant undercooling or excess stress necessary to nucleate cracks.

Table 2. Fracture properties of molecular glasses

Material	Sample Geometry	ψ^2	T_{set}, K	$k, \text{K} \cdot \text{m}^{1/2}$	$K_c, \text{MPa} \cdot \text{m}^{1/2}$	$G_c, \text{J/m}^2$
IMC	Sandwich	0.5	291 (1)	0.27 (1)	0.071 (2)	1.08 (7)
	Open	1.2	298 (2)	0.17 (1)	0.069 (5)	1.0 (1)
OTP	Sandwich	0.5	225 (2)	0.18 (1)	0.066 (4)	0.9 (1)
SB	Sandwich	0.5	317 (1)	0.25 (1)	0.042 (1)	0.64 (4)
	Open	1.2	321 (3)	0.15 (2)	0.040 (5)	0.6 (1)
OTP 10% 8.4k	Sandwich	0.5	225	0.24 (1)	0.079 (4)	1.3 (2)
OTP 10% 16k	Sandwich	0.5	225	0.24 (2)	0.090 (5)	1.7 (2)
OTP 10% 100k	Sandwich	0.5	225	0.30 (1)	0.126 (5)	3.3 (2)
OTP 10% 1000k	Sandwich	0.5	225	0.36 (2)	0.147 (6)	4.5 (3)

Notes: The T_{set} of OTP-PS solutions was fixed at the OTP value (see text). The critical stress intensity factor K_c is related from G_c and the relation $G_c = \frac{K_c^2}{\bar{E}}$, where $\bar{E}$ is $E/(1-\nu^2)$ for fracture under the plane-strain condition. The T_{set} and k values are from fitting fracture temperatures measured at a cooling rate of 10 K/min. In parenthesis are the standard errors of fitting or propagated computational errors on the last digit. The accuracy of K_c and G_c also depends on the errors in the assumed quantities in Table 1.

Figure 7 shows the fracture temperature vs. film thickness for OTP glasses doped with 10 wt % PS of different molecular weights. These data were collected with sandwiched films only because of the sub-ambient T_g and given the consistency of results obtained for open and sandwich films. Note that in the presence of PS, the predicted relation (eq. 3) between T_{frac} and h still holds. We find the temperature T_{set} to be the same within experimental error as that for pure OTP (225 K). In

Fig. 7. Fracture temperature vs. film thickness for OTP containing 10 wt % PS of different molecular weights. Lines are best fits constrained by $T_{\text{set}} = 225$ K (the value for pure OTP). $R^2 = 0.92$ (10% PS 8.4K), 0.88 (10% PS 16K), 0.90 (10% PS 100K), 0.92 (10% PS 1000K).

contrast, the slope k depends strongly on the PS additive, increasing with its molecular weight. The similar T_{set} values for the PS-doped OTP samples are expected, given that 10 wt % PS raises the T_g of OTP only slightly (ca. 1 K). To better characterize the effect of molecular weight, the slope k was calculated with T_{set} fixed at 225 K (the value for pure OTP). The results are in Table 2.

From the value of k , we calculate G_c for PS-doped OTP glasses (Table 2). This calculation assumes that 10 wt % PS does not significantly change OTP's density, elastic modulus, thermal expansion coefficient, and Poisson's ratio. We find that the presence of PS in OTP makes the material significantly more resistant to fracture. At 10 wt %, the effect increases with the molecular weight of PS; at $M_w = 1$ million g/mol, G_c is increased by a factor of 5.

Discussion

We have studied the fracture of supported films of molecular glasses under in-plane tension. In-plane tension is created as an organic glass film is cooled on a substrate that is less thermally expansive. The fracture produces a network structure whose cell size is comparable to film thickness. For a given material, the condition of fracture is described by the fracture models [27,28,29] and a characteristic energy release rate G_c . Agreement with theory is found for films tested in both open and sandwich geometries at a wide range of thickness. For the single-component molecular glasses studied here, we find $G_c \approx 1 \text{ J/m}^2$ and $K_c = 0.04 - 0.07 \text{ MPa} \cdot \text{m}^{1/2}$. The addition of PS in OTP substantially increases its resistance to fracture, with the effect increasing with the molecular weight of PS; at 10 wt % PS at 1 million g/mole, the increase of G_c is a factor of 5 over pure OTP.

Figure 8a compares the values of K_c for several glasses obtained by observing spontaneous fracture of supported films by in-plane tension. The systems include inorganic oxide films baked onto silicon [24], $\text{SiO}_x\text{C}_y\text{N}_z\text{:H}$ films prepared by CVD onto silicon [25], and molecular glasses on silicate coverslips (this study). Applying this method, Shimbo obtained $K_c = 0.5 \text{ MPa} \cdot \text{m}^{1/2}$ for a silicate glass [24], in agreement with the values by other methods [45]. King and Gradner find broad agreement between their K_c values for silicate films and those of other studies [25]. Another check of consistency is to compare our values for molecular glasses with those for molecular crystals by nano-indentation [9,10,46,47]. We find broad agreement

Fig. 8. Comparison of the fracture of glass films constrained on substrates. (a) K_c vs E . (b) Fracture stress vs. film thickness (for open films).

between the two sets of values. Nano-indentation has been found to yield known fracture toughness for silicate glasses [45].

The various glasses in Figure 8a are labeled “soft” and “hard” according to their elastic moduli E . The soft group ($E = 3 - 9$ GPa) includes the molecular glasses studied here and organo-silicates [25]; the hard group ($E = 70 - 130$ GPa) consists of inorganic silicates [24,25]. Together, these glasses form a broad trend in which K_c increases with E (the line). This trend may reflect the fact that all these materials have brittle fracture. As a group, these materials lie at the bottom of the “fracture toughness vs modulus” diagram, below polymers and metals.

Figure 8b compares the conditions of tensile fracture for various glass films constrained on substrates. We plot the tension at fracture divided by the in-plane elastic modulus, $\sigma_c (1-\nu)/E$, as a function of film thickness. This normalized stress can be understood as the strain at fracture. All data in Figure 8b are for open films. For the molecular glasses (IMC and SB), the strain at fracture increases with decreasing thickness. Although our data do not go below $h = 10$ μm , the trend appears to continue to lower thickness with soft organo-silicate films [25]. This trend is indicated with the line in Figure 8b; it gives an empirical guide for predicting the fracture condition for a supported glass film of known thickness. This trend describes *soft* organic glass films. For hard silicate glass films, there appears to be a similar trend, although the strain at fracture is slightly lower. At the same thickness, the soft organic glasses are more resistant to fracture (can be strained to a greater extent).

Because fracture can be observed only if stress exceeds some critical value, it is important to evaluate the excess stress required for nucleating fracture. This excess stress is analogous to the undercooling required to nucleate crystals. We consider *open films* first and provide two arguments that excess stress is relatively small and has a minor effect on the fracture properties reported here. Recall the insensitivity of the fracture temperature to deliberately introduced scratches or pre-existing flaws (holes left behind

by occasional bubbles in the film after removing the top coverslip). If the films could be undercooled substantially without fracture, these defects would act as nucleation sites and reduce the stress required for fracture (raise the fracture temperature). Our observation therefore suggests that the excess stress is small. Recall also the consistency between the observed dependence of fracture temperature on film thickness and the predicted relation (eq. 3). The prediction assumes only a material-specific G_c without excess stress. Should it be significant, the eq. 3 relation need not hold.

Although the open-film experiments observed no evidence for nucleation barriers, our data suggest a small undercooling effect for *sandwiched films*. Note in Table 2 the slightly lower T_{set} for sandwich films (7 and 4 K for IMC and SB, respectively). This difference could reflect a higher barrier for fracture nucleation in sandwich films. This effect is quite small, however, judging from the agreement between the predicted ratio $k_{\text{open}}/k_{\text{sandwich}} = 1.6$ and the observed one. Again, had there been large excess stress in the sandwich films, this ratio might be altered. We conclude that the small undercooling observed with sandwich films will not affect the calculated fracture toughness.

Given that polymers are fracture resistant, their presence in small-molecule glasses is expected to increase fracture toughness. For pure polystyrene below the entanglement molecular weight, G_c approximately scales with $M_w^{0.5}$ and the relation is explained on the basis of a small craze at the crack tip [48,49]. At the interface between two immiscible polymers reinforced by their copolymer, the increase of G_c scales with M_w^2 , where M_w is the molecular weight of the polymer chains being pulled out [50]. Both models are formulated for neat polymers and are unlikely to hold for small-molecule glasses containing

Fig. 9. Molecular weight dependence for the increase of G_c by 10 wt % PS in OTP. The curve is predicted from eq. 9 with no adjusted parameters.

10 wt % polymer.

To study the effect of PS molecules on the fracture resistance of an OTP glass, we express the observed G_c as

$$G_c = G_{c0} + \Delta G_c \quad (5)$$

where G_{c0} is the critical fracture energy release rate of pure OTP and ΔG_c is the increase of G_c attributable to PS. Following Kramer and coworkers [50], we write

$$\Delta G_c = g \Sigma \quad (6)$$

where Σ is the number of unique polymer chains crossing the unit area of a fracture plane and g is the average contribution of each chain to fracture energy. Σ is calculated as

$$\Sigma = (c N_A / M) (2 R_g) \quad (7)$$

where c is the polymer concentration (kg/m^3), M is its molecular weight, R_g is its radius of gyration, and N_A is Avogadro's number. The term $c N_A / M$ is the number of chains per unit volume; its product with $(2 R_g)$ gives the number of chains whose centers of mass are within the distance R_g from a plane of unit area.

Next, we assume that upon encountering a crack tip, a polymer chain goes to either one side of the fracture or the other, and brings along matrix molecules (OTP in our case) within its pervaded volume (the sphere of radius R_g). Qualitatively, this would increase the area of fracture surface, leading to higher apparent toughness. Assuming the fracture surface enclosing each polymer chain has the shape of a spherical cap and the center of mass of each chain is randomly distributed, we obtain

$$g = (2\pi/3) R_g^2 G_{c0} \quad (8)$$

where $(2\pi/3) R_g^2$ is the average increase of the fracture surface area for each chain. Combining eqs. (6), (7), and (8) yields

$$\Delta G_c = (4\pi/3) (c N_A R_g^3 / M) G_{c0} \quad (9)$$

The curve in Figure 9 is the prediction of eq. (9). We have calculated the R_g of PS using $(N/6)^{1/2}b$, where N is the number of monomers and $b = 0.67$ nm [51]. There is reasonable agreement with the experimental data. It is noteworthy that this prediction is made with *no adjusted parameters*.

Conclusions

This study has investigated the fracture of molecular glasses indomethacin, *o*-terphenyl, and sucrose benzoate under tension. In-plane tension was created by cooling a liquid film below its glass transition temperature constrained on a substrate that is less thermally expansive. The fracture produces a network structure whose cell size is comparable to film thickness. The condition of fracture is well described by recently developed models and a material-specific energy release rate G_c ; agreement is found at all film thicknesses tested (10 – 250 μm) in both open and sandwich geometries. For the molecular glasses studied, we find $G_c \approx 1$ J/m². *o*-terphenyl glasses become significantly more resistant to fracture with the addition of polystyrene; the effect is explained by the increase of fracture surface area as a crack tip circumvents the pervaded volume of each polymer chain encountered.

This method of characterizing glass fracture is well suited for studying molecular glasses with relatively large coefficients of thermal expansion and low fracture toughness. It requires only milligrams of materials. Future work is warranted to validate this method against other techniques such as nano-indentation. An isothermal version of this method could be developed that uses deformable substrates. The method could be applied to study the effect of glass aging on fracture toughness and the difference between the fracture of crystals and glasses.^{52,53} The greater stress required to fracture smaller specimen suggests an approach to the theoretical limiting-tension; it would be of interest to conduct experiments to probe this limit. The mechanistic model for the effect of polymer additives on the fracture of small-

molecule glasses should be tested against additional data and microscopic examination of fracture surfaces.

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