Supporting Information

Enhanced Crystal Nucleation in Glass-Forming Liquids by Tensile Fracture in the Glassy State

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1. Material and Methods

Griseofulvin(2R,6'S)-7-chloro-2',4,6-trimethoxy-6'-methyl-3H,4'H-spiro[1-benzofuran-2,1'-cyclohex[2]ene]-3,4'-dione) was purchased from J&K scientific Co. Ltd., China (purity > 99.0%).

Differential Scanning Calorimetry (DSC): DSC measurements were conducted in a healed aluminum pan using a Q2000 (TA Instruments, New Castle, DE) unit under 50 mL/min N_2 purge. The instrument was calibrated for temperature and enthalpy using indium and sapphire. A total of 2~3 mg of materials was loaded in a healed aluminum pan for thermal analysis.

Probability of fracture and crystallization with different cooling temperatures: Commercial powder was heated to 503 K and held isothermally for 10 min in Run 1. In Run 2, the melt was cooled at a cooling rate of 15 K min^{-1} to desire cooling temperatures (T_c) (323, 313, 303, 293, 283, 278, 273, 268, 263 and 243 K). The resulting glasses were then reheated to 503 K at a heating rate of 10 K min^{-1} to study the recrystallization probability (Run 3). The formation of fracture was determined by a sharp exothermal peak in Run 2. 30 samples were performed for each T_c.

Probability of fracture and crystallization with different heating rates: The probability of crystallization of GSF glasses with different reheating rates was investigated. As shown in Scheme 1, in Run 1, commercial powder was heated to 503 K and held isothermally for 10 min. The melt was then cooled to 243 K in Run 2. Run 3 consisted of two different reheating processes. The cooled melt first heated to 453 K (Run 3a) at the three different heating rates (10, 20 or 50 K min^{-1}). Samples were annealed at 453 K (where GSF exhibits the fastest growth rate[1, 2]) for 10 min to allow crystal growth, and then heated at a rate of 10 K min^{-1} to 503 K (Run 3b). The probability of fracture in Run 2 and crystallization in Run 3b were summarized in Table S1.

2. Calculation of the critical energy release rate G_c

For a glass-forming liquid film cooled on a substrate of lower thermal expansion coefficient, tensile stress builds up in the glassy state according to[3]

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

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 elastic solid (approximately the endpoint of the glass transition during cooling). As T decreases, σ increases and may eventually exceed the critical value for fracture. The condition for this is $G > G_c$, where G is the energy release rate as a crack extends and G_c is a material property (fracture toughness). For our supported film, G is given by: [4, 5]

$$G = \frac{\psi^2 \sigma^2 h}{\bar{E}} \quad (2)$$

where ψ^2 is a geometric factor (1.2 for our open-surface sample) and $\bar{E} = E/(1-\nu^2)$.

Together, eqs. (1) and (2), for a thin film constrained on a more rigid substrate, the critical energy release rate G_c is[4, 5]

$$G_C = \frac{\psi^2 \Delta\alpha^2 (T_{set} - T_{frac})^2 E h (1+\nu)}{(1-\nu)} \quad (3)$$

The probability of fracture increases sharply with cooling near 278 K which was taken as T_{frac}. The linear thermal expansion coefficient α of GSF is taken to be 1/3 of its volumetric value of form I[2] and α for aluminum is obtained from Ref. 6. E and ν are assumed by using the value of a typical molecular glass – indomethacin glass.[4] T_{set} is approximately the end point temperature of the glass transition on cooling by reading from the DSC curve. h is the average thickness of the film, which is calculated by assuming the film uniformly adheres to the aluminum substrate. For the diameter of the aluminum pan is 5.4 mm, average weight of GSF material is 2.5 mg and ρ of amorphous GSF is from Ref. 7, h is calculated as 81 μm. We obtain $G_c = 3.4$ J/m^2 for GSF.

The values of above parameter are listed in the following table:

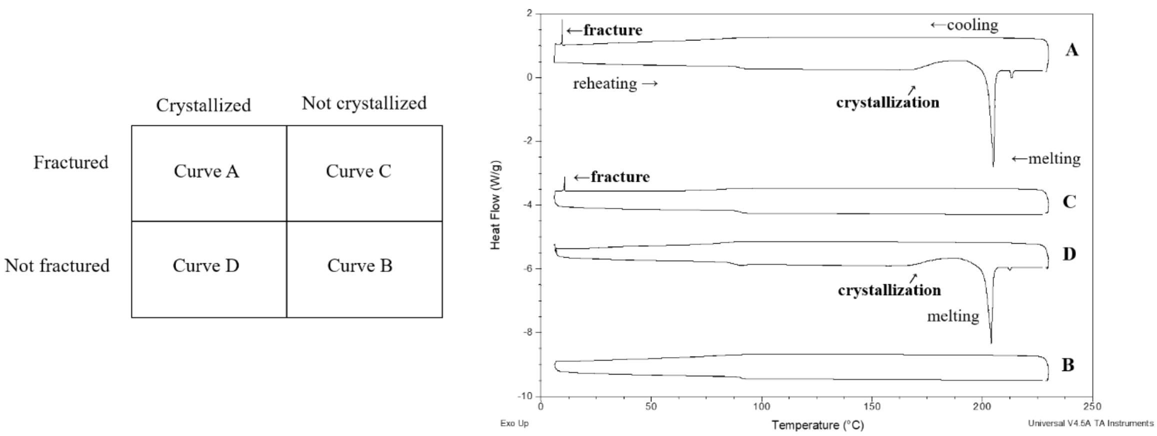
Parameter	Value	References
ψ^2	1.2	4
α_{GSF}, $10^{-6}K^{-1}$	59.67	2
$\alpha_{alumium}$, $10^{-6}K^{-1}$	23	6

T_{set}, K	333	this work
T_{frac}, K	278	this work
E, Gpa	4.1	4
v	0.36	4
ρ, g/cm^3	1.35	7

3. Table S1. Number and probability of samples fractured in Run 2 and crystallized in Run 3 at each heating rate of Run 3a. 30 samples were performed at each heating rate.

Heating rate of Run 3a, K/min	Number of samples fractured in Run 2	Probability of fracture, %	Number of samples crystallized in Run 3	Probability of crystallization, %
10	30	100.0	30	100.0
20	30	100.0	12	40.0
50	30	100.0	2	6.7

4. Figure S1. The typical DSC curves for different categories of crystallization behaviors.



5. Reference

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