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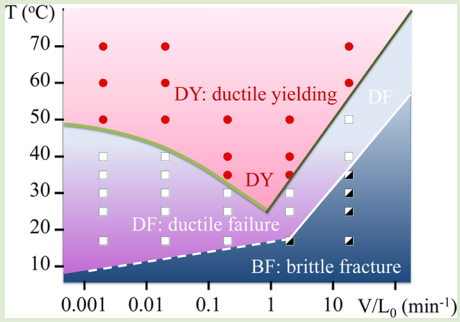
Mapping Brittle and Ductile Behaviors of Polymeric Glasses under Large Extension

Xiaoxiao Li and Shi-Qing Wang*

Morton Institutes of Polymer Science and Engineering, University of Akron, Akron, Ohio 44325, United States

Supporting Information

ABSTRACT: We have carried out a series of tensile extension tests on the two most common polymer glasses to describe their generic mechanical responses as a function of deformation rate at different temperatures. The essentially defect-free polystyrene and poly(methyl methacrylate) both show remarkable re-entrant failure: being ductile at intermediate rates and showing diminishing toughness at both higher and lower rates. We draw phase diagrams to map out the relationship between brittle-like and yield-like states in terms of temperature, rate, and stress. A coherent understanding of the rich phenomenology requires us to describe in more detail the interplay between the chain network and the primary structure bonded by intersegmental van der Waals forces.



Structural failure of solid polymers under mechanical deformation is a difficult subject to study in polymer science. Contrary to low molar-mass organic glasses that are always brittle, polymer glasses of high molecular weight can be highly ductile, drawn to double their initial length during uniaxial extension. Their mechanical response switches from ductile to brittle when they are sufficiently below T_g. Despite decades of continuous investigations,[1−3] it has remained an elusive objective to propose a coherent molecular mechanism for the brittle-to-ductile transition (BDT) in most glassy polymers, located in a small temperature range indicated by T_{BD}.

The textbook explanation for BDT is empirical, based on the Ludwik−Davidenov−Wittman−Orowan (LDWO) hypothesis,[1,4−6] which treats yielding and brittle fracture as independent and competing events in a continuum. At high temperatures, yield stress σ_Y is lower than brittle stress σ_B so that plastic flow would take place instead of fracture. Below T_{BD}, σ_Y would be higher than σ_B since σ_Y has been observed to increase significantly with decreasing temperature. The BDT phenomenon is usually examined by tensile extension of glassy polymers at a constant rate over a temperature range that covers T_{BD}. It is widely understood that plastic flow in polymer glasses takes place when the deformation rate is comparable to the internal material relaxation rate.[7−9] Thus, a lower extensional rate is expected to favor a more ductile response.[2] There are several known characteristics associated with the ductility of polymers glasses. (a) A most ductile glassy polymer, that is, bisphenol A polycarbonate (PC), loses its ductility upon reduction of its molecular weight below a critical value. (b) Mechanical "rejuvenation", that is, certain types of large-magnitude mechanical deformation at $T < T_g$, can make a brittle glass behave in a ductile manner. (c) Upon physical aging, even the ductile PC turns brittle. (d) Brittle polystyrene (PS) and poly(methyl methacrylate) (PMMA) become ductile at room temperature after melt extension to a sufficient degree.[10,11] (e) PS can be as ductile as PC under sufficiently high hydrostatic pressure.[12] (f) Incorporation of some plasticizing small-molecule additives into polystyrene makes it turn more brittle.[13] To provide a coherent account for all these six factors, we need a molecular picture[14] that recognizes the role of a global network formed by sufficiently long chains.[15,16]

In this Letter, we investigate the effect of deformation rate on nonlinear mechanical responses of typical polymer glasses. Specifically, by minimizing structural defects using extruded rods or polished dogbone-shaped specimens, we have discovered a remarkable "re-entry" phenomenon and constructed generic "phase diagrams" to depict the mechanical behavior of two common polymer glasses at different temperatures and applied rates. Specifically, we find that PMMA and PS are brittle at the highest applied rate, ductile at intermediate rates and become much less ductile as the extensional rate further decreases.

The polymer glasses under study are PMMA from Plaskolite West Inc. (item number CA-86), having a molecular weight of M_w = 125 kg/mol and polydispersity PDI = 1.43, and PS from Dow (Styron 663) with M_w = 319 kg/mol and polydispersity PDI = 1.44. Samples in this study are either cylindrical specimens from capillary extrusion or dogbone-shaped, cut from isotropic hot-pressed sheets, both described in some detail in Supporting Information (SI). Tensile extension was carried out using an Instron 5543 equipped with a customer-made environmental chamber for temperature control. Each test was repeated at least three times to assess the reproducibility.

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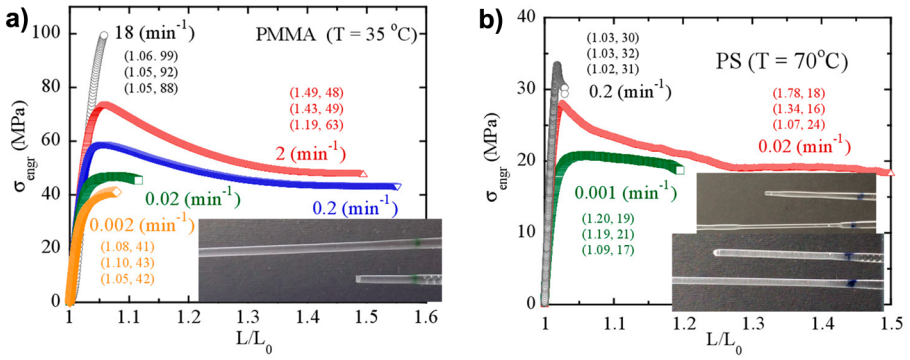

Figure 1. Engineering stress σ_{engr} vs draw ratio L/L_0 from various tensile extension tests on (a) PMMA at 35 °C at the different initial rates defined by V/L_0 ranging from 18 to 0.002 min^{-1}, showing brittle fracture (circles), ductile drawing (triangles), and premature failure (squares and diamonds) and (b) PS at 70 °C showing similar behavior to (a). The numbers in the brackets are $(L/L_0, \sigma_{engr})$ in the units of mm and MPa, respectively, at breaking, for three runs, with the top numbers corresponding to the data presented in the figures. Here, L_0 = 50 mm is the original effective length of specimen that is undergoing extension, and $(L - L_0)$ measures the lengthening of the specimen of initial length L_0. At 0.2 and 2 min^{-1} in (a), the ductile drawing was nearly uniform: no visible neck front, and there was only a small smooth variation in the specimen diameter of 5% or so from the thinnest section to the thickest section, as shown by the photo (0.2 min^{-1}) in the inset. At 0.02 min^{-1} in (b), there is shear yielding leading to necking with multiple neck fronts, visible from the top photo in (b). The diameter of specimen shrinks to 0.66 mm, whereas the original diameter is 1.16 mm, amounting to a large local draw ratio of 3.1. At 0.001 min^{-1}, the drawing is uniform as shown in the second photo in the inset until breaking at L/L_0 = 1.2.

Effects of deformational rate on yielding behavior of polymer glasses are well understood.[1,3] In Eyring's spirit,[7] segmental dynamics can be accelerated by the deformation, and yielding as well as plastic flow can take place when segmental relaxation rate become as high as the deformation rate. More advanced microscopic theories have been recently developed to go well beyond the notion of stress-induced activation.[9,17,18] Usually, polymer glasses are more brittle at higher rates according to the literature.[19−21] Figure 1a shows brittle failure at 18 min^{-1} and ductile drawing at either 2 or 0.2 min^{-1}. However, when the extensional rate is further reduced to either 0.02 or 0.002 min^{-1}, PMMA loses its toughness, becoming unable to draw, breaking after about 10% uniform extension. To examine the universality of this surprising result, we carried out a comparable set of extensional tests on PS. Figure 1b shows similar behavior to that in Figure 1a: PS is completely ductile at 0.02 min^{-1}, but suffers a "premature" structural failure at 0.001 min^{-1} after 20% visibly homogeneous extension. Thus, both PMMA and PS lost its ability to draw significantly when the extensional rate is sufficiently lowered. In passing, it is worth mentioning that, at the low rates, for example, 0.2 min^{-1} or lower, both PMMA and PS specimens are full of crazes. Based on data such as those in Figure 1a,b, we can evaluate the overall toughness at different rates and indicate that it is strongly nonmonotonic, as shown in Figure 2, at several temperatures for PMMA and at 70 °C for PS. To the best of our knowledge, such a dramatic and unexpected loss of toughness with lowering rate has not previously been reported in the literature and challenges the conventional wisdom.

To thoroughly explore the extraordinary behavior, we also probed PS at other temperatures within the range of accessible extensional rate. Table 1 summarizes the results, where the data in the boxed row are from Figure 1b, and the different colors designate the different responses, indicating, respectively, brittle fracture (BF) at the high rates, blue, ductile yielding (DY) at the intermediate rates, red, and dynamical or ductile failure (DF) at the low rates, violet. Reading "vertically", for example, at V/L_0 = 0.2 min^{-1}, we see in Table 1 that, as the temperature

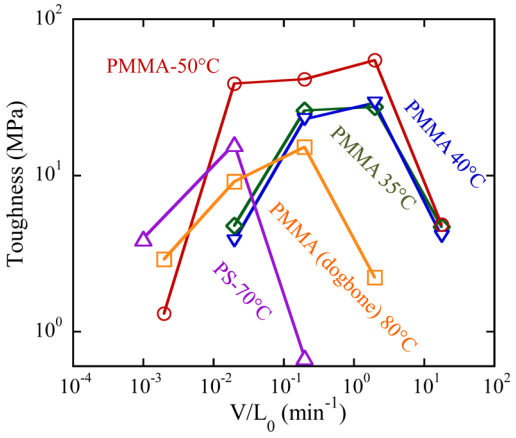

Figure 2. Toughness at different rates for extruded PS at 70 °C, extruded PMMA at three temperatures (35, 40, and 50 °C) and dogbone-shaped PMMA at 80 °C, evaluated from data such as those in Figure 1a,b according to $\int_1^{\lambda_{break}} \sigma_{engr}(\lambda)d\lambda$.

Table 1. Characteristic Stress Levels of PS at Different Temperatures and Rates[a]

T (°C)/ Rate (min^{-1})	0.001	0.02	0.2	2
90			**24**	
80	**15**	**21**	**30**	**35**
70	**21**	**28**	**33**	
60	**24**	**34**	**37**	
50	**29**	**36**		
17	**40**		**42**	**42**

[a]Numbers in bold face are the values of either yield (peak) stress or breaking stress.

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rises, the brittle PS (at 70 °C) first experiences DF at 80 °C before becoming ductile at 90 °C. PMMA shows a similar variation of the response to temperature: As shown in Figure 3,

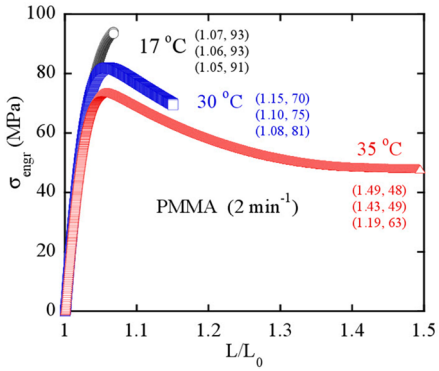

Figure 3. Engineering stress vs draw ratio from three tensile extension tests on PMMA at three temperatures, showing ductile response at 35 °C, premature failure at 30 °C, and brittle failure at 17 °C. The numbers in the brackets are (L/L_0, σ_{engr}) at breaking for three runs, with the top numbers corresponding to the data presented in the figure.

it is ductile (DY) at 35 °C and loses drawability at 30 °C (DF) before turning brittle at 17 °C under V/L_0 = 2 min^{-1}. As the test temperature is lowered, the emergence of DF on the way from DY to BF is perhaps unsurprising. On the other hand, at a fixed temperature, as the deformation rate decreases, how can polymer glasses turn from DY to DF and lose toughness?

We have shown the two ways to access DF, either by varying applied rate or changing temperature. As the applied rate V/L_0 increases the response of PS changes from DF to DY and then back to DF again before reaching BF, at 80 °C, reading Table 1 horizontally. In other words, DF is accessible at both low and relatively high rates, sandwiching a regime of DY. DF can also show up as a function of temperature, for example, PMMA at 30 °C for 2 min^{-1}, as shown in Figure 3.

Based on many additional sets of experiments on PMMA, similar to Figures 1a and 3, we can construct a "phase diagram" involving the test temperature as Y axis and the extensional rate as X axis, as shown in Figure 4. Here the borderlines between the "phases" of BF and DF, as well as among DY, DF, and BF at

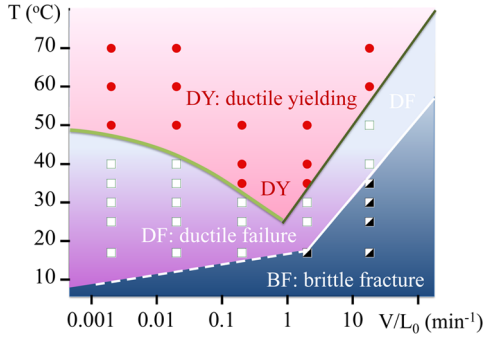

Figure 4. Quantitative phase diagram depicting various mechanical responses at different temperatures T and rates V/L_0 based on "defect-free" PMMA, showing brittle fracture (dark blue) at low temperatures, ductile failure at intermediate temperatures (violet), and ductile yielding (pink) at high temperatures. As a function of rate or temperature, PMMA shows BDT passing through ductile failure (DF). As a function of the applied rate, DF actually emerges twice.

higher rates are of illustrative purpose and need not be straight lines. Read "vertically", the diagram shows at various rates how the mechanical response of PMMA changes from ductile yielding (DY) to failure that includes both DF and BF as the temperature is reduced. More interestingly, when reading "horizontally", either Figure 4 or Table 1, at various fixed temperatures, we also observe BDT-like behavior with respect to the applied rate. In particular, at temperatures above 30 °C but below 50 °C, the various "phases" show up in the order of BF, DF, DY, and DF for PMMA as the extensional rate decreases.

The rich phenomenology, extracted from the numerous experiments and depicted in Figure 4, can be represented in another insightful way. Plotting the peak tensile stress at different temperatures for various applied rates, we show in Figure 5 the transitions between DF and DY as well as between

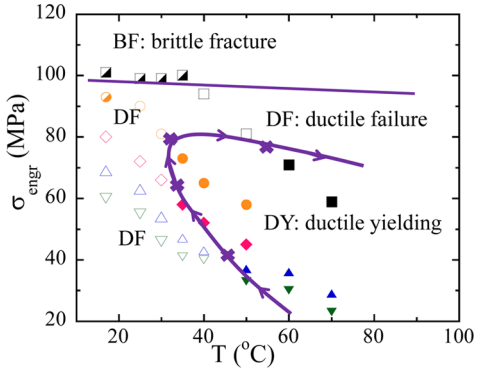

Figure 5. Either brittle stress or peak stress from tensile extension of PMMA as a function of temperature for different applied rates of V/L_0 = 18 (squares), 2 (circles), 0.2 (diamonds), 0.02 (upward pointed triangles), and 0.002 (downward pointed triangles) min^{-1}. Inside the U-shaped region resides the ductile yielding (DY). Above the near-horizontal line there is brittle fracture (BY). Ductile failure (DF) occurs in the rest of the space. Here x on the curve denotes the points of separation between DF and DY.

DF and BF, respectively. The U-shaped purple curve is a borderline dividing DF from DY, with the arrows in the curve indicating the direction of increasing rate. The transition between DY and DF first shifts to lower temperatures with increasing rate, which is abnormal, before switching the sense of directionality, going to higher temperatures with increasing rate. The abnormality stems from the re-entrant DY at low rates, as depicted in Figure 4.

To show that the phenomenon is not special to only specimens prepared with capillary extrusion, PMMA sheets were cut into dog-bone shaped specimens (cf. SI). Unlike the extruded rods, the dog-bone specimens suffer from uncontrollable defects due to the cutting, pushing the BDT to a much higher temperature, making it difficult to observe DF. To minimize defects, we polished edges of the dogbone-shaped specimens. Detailed extension experiments on dogbone-shaped PMMA at 80 °C shows similar nonmonotonicity in the toughness, as a function of the extensional rate, as summarized by the squares in Figure 2.

To interpret the observed nonmonotonicity, we postulate a molecular mechanism for the observed specimen failure under tensile extension. The structural failure is due to breakdown of the chain network via chain pullout, according to our recently proposed theoretical picture for the BDT[14] that regards a

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polymer glass of high molecular weight under large deformation as a structural hybrid made of a primary structure bonded by short-ranged van der Waals attractions and a chain network arising from intermolecular uncrossability. Brittle fracture (BF) involves spontaneous pullout before the chain network could cause the glass to reach the point of yielding. We suggest that the emergent ductile failure (DF) associated with the toughness nonmonotonicity, as an activation process via chain pullout, can take place even after yielding during plastic deformation. At such low rates, pullout could nucleate over time to terminate the slow plastic extension.

At higher temperatures, such chain pullout might take a long time to produce breakdown of the chain network because only a lower level of chain tension could emerge during the extension. Consequently, given the limited range of accessible extensional rate explored in this study, the nonmonotonicity or re-entry could only be observed in a narrow temperature window, which diminishes in presence of man-made defects. For extruded PMMA, the window is just between about 30 and 50 °C. For PS, we indicated in Figure 1b that the nonmonotonicity can occur at and above 70 °C. Similarly, for dogbone-shaped PMMA, we saw analogous nonmonotonicity at 80 °C within the available rate range.

In summary, a remarkable nonmonotonic change of ductility with deformation rate can be observed when artificial structural defects are minimized in PMMA and PS of high molecular weight using extruded rods and polished dogbone-shaped specimens. Such unexpected behavior requires improved theoretical understanding and stimulate development of a molecular-fracture-mechanical approach. Clearly, beyond the zeroth order picture,[14] we must include the rate effect when depicting the BDT in polymer glasses. Apparently, the chain network in polymer glasses can undergo structural breakdown (through chain pullout) over time at lower rates even though yielding has already taken place. The phenomenon of re-entrant failure (or loss of toughness) with decreasing rate and the corresponding molecular-level explanation may have far reaching implications and consequences. The present work may also simulate new optical photobleaching experiments[22−24] to further probe the relationship among segmental mobility, deformational rate, and state of the polymer glass and prompt additional molecular dynamics simulations[23,25−30] to quantify the condition for chain pullout. For the nearly ideal (defect-free) specimens, we have constructed two "phase diagrams" in Figures 4 and 5 to depict the borderlines between the various "phases" that are either ductile yielding (DY), dynamical/ductile failure (DF), or brittle fracture (BF). The description should qualitatively apply to other polymer glasses of high molecular weight.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00554.

The detailed materials, sample preparation, and protocol information on these samples (PDF).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: swang@uakron.edu.

Notes

The authors declare no competing financial interest.

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