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Elastic Breakup in Uniaxial Extension of Entangled Polymer Melts

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Five entangled melts, with the number of entanglements per chain ranging from 25 to 160, have been studied to illustrate how cohesive strength can be overcome in either continuous or interrupted extension (i.e., during or after uniaxial stretching). The internal elastic stress due to chain deformation from imposed strain appears to be the cause of the observed yielding behavior that reveals scaling laws. The visual signature of the elastic breakup is the occurrence of nonuniform extension. The yield phenomena may be understood at a force level.

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Because of various internal microscopic structures, complex fluids exhibit rich viscoelastic behavior. When subjected to a rate of deformation much greater than their dominant relaxation rates, these materials respond elastically or solidlike and are expected to fail in either a ductile or brittle manner. In this context, cohesive strength for materials that are capable of flowing at long times has been a rather fundamental yet often elusive concept. A clear understanding of how the material integrity is overcome during external deformation is highly valuable for more effective processing. Spray of paints (colloids), application of shampoos, fiber spinning, film blowing (to produce grocery bags), blow-molding (to make milk bottles) of molten polymers all involve extensional flow. So it is important to examine the basic understanding on a leading aspect of flow behavior in a major class of viscoelastic materials. For entangled polymeric liquids, we have little knowledge about what factors determine their melt strength despite numerous references to this concept in the literature.

Recently, an interesting picture emerged, leading to a fresh account of nonlinear shear flow behavior [1(a)–1(g)]. Apparently, entangled polymeric liquids suffer structural disintegration on short time scales, plausibly through chain disentanglement, in each of the three popular forms of shear deformation: startup continuous shear [1(b),1(c)], large amplitude oscillatory shear [1(d),1(e)] and large step shear [1(f),1(g)]. Specifically, our recent particle-tracking velocimetric study revealed that the well-known shear stress overshoot in startup shear coincides with development of inhomogeneous shear and that the sample relaxation is nonquiescent after an interrupted shear.

In this Letter, we discover universal features associated with both continuous and interrupted extensional deformations of an important class of viscoelastic materials, i.e., polymer melts, against a background of extensive experimental literature on yield and rupture phenomena during extensional flow of polymer melts [2–5] as well as extensional flow behavior of molten thermoplastics [6–11] and entangled solutions [12–14]. The new results offer insight into extensional deformation behavior of any highly viscoelastic complex fluids well beyond polymeric materials.

Parallel to a recent study on the scaling behavior of yielding in shear deformation [15], we study extensional deformation behavior of polymers during startup flow and after flow cession. Using a new experimental setup known as SER fixture [16] coupled to an Anton Paar MCR 301 rotational rheometer, we can apply constant (Hencky) strain rate $\dot{\varepsilon}$ in uniaxial stretching. The materials under study are a series of four monodisperse styrene-butadiene rubbers (SBR) plus a polyisoprene (PIP) made at Bridgestone-America. Our cylindrical filaments are capillary extrudates with a radius r controlled around 1 mm, except for PIP specimen in the shape of a strip. See Table I for a list of parameters at room temperature including the terminal and Rouse relaxation times τ and τ_R evaluated as $\tau(M_e/M_W)$.

For the purpose of comparison among these samples of different molecular weight, we typically chose extension rate $\dot{\varepsilon}$ such that the dimensionless product $\dot{\varepsilon}\tau_R$ is a constant. To explore scaling behavior that has been seen in shear deformation [15], we principally explored the regime of $\dot{\varepsilon}\tau_R > 1$. Figure 1 shows the typical results of a series of uniaxial stretching experiments on SBR(250 K), at five different values of $\dot{\varepsilon}$. Similar to the familiar stress overshoot phenomena [17–19] in continuous shear, the measured tensile force also exhibited a maximum at the various times for the different applied rates. Beyond the tensile force maximum, the sample undergoes transient nonuniform extension before breakup. This is a structural failure because it occurs within just a few strain units on a time scale much shorter than τ to produce the decline of the measured tensile force as shown in Fig. 1.

The Doi-Edwards tube model [20] depicts a force maximum during startup shear without anticipating any structural yielding and thus is not pertaining to the present observations. A recent pair of theoretical studies [21] attempted to depict rupture of continuously stretched entangled melts. It was suggested that a specimen would break when the tension in a chain exceeds a time-independent frictional force, which appears to be a steady condition rather than a failure criterion.

TABLE I. Material characteristics based on linear viscoelastic measurements.

Samples	M_w	M_w/M_n	M_e	G_N^0 (MPa)	M_W/M_e	$\tau(s)$	τ_R
SBR(100 K)	94 800	1.05	4000	0.55	24	25	1.1
SBR(170 K)	174 000	1.07	3300	0.67	53	120	2.3
SBR(250 K)	250 000	1.04	3300	0.68	76	310	4.1
SBR(500 K)	497 000	1.19	3100	0.72	160	2100	13
PIP(550 K)	547 000	1.1	5100	0.40	107	54	0.5

To search for the origin of nonquiescent relaxation after a step shear, we came to realize [1(f)] that the entropic retraction force f_{retract} arising from deformation of a Gaussian chain network, if unbalanced, might cause chain disentanglement. The cohesion provided by chain entanglement is rather weak and can be exceeded at higher elastic deformations.

In our startup uniaxial stretching experiments, an elastic (entropic) force f_{retract} grows in time, resulting from the system resisting against the conformational entropy loss associated with the chain deformation that is obviously caused by an intermolecular gripping force f_{img}. The action of f_{img} is conventionally depicted to result in affine deformation of the entanglement network or the primitive chain in a tube model. At first, f_{img} balances f_{retract}. Over time, f_{retract} increases until it reaches the same magnitude as f_{img}. Beyond this point, cohesive failure must take place. It is reasonable to identify the maxima in Fig. 1 as a yielding condition where we have

$$f_{\text{img}}(t_{\max}, \dot{\varepsilon}) = f_{\text{retract}}(\dot{\varepsilon} t_{\max}). \tag{1}$$

To estimate the magnitude of the retraction force f_{retract} produced up to the yield point, we carry out further analysis of data such as those in Fig. 1 and find a master curve in Fig. 2 that

$$f_{\text{retract}}(\dot{\varepsilon} t_{\max}) \sim \varepsilon_y = \dot{\varepsilon} t_{\max}, \tag{2}$$

for all five different samples at various extensional rates. Furthermore, Fig. 1 reveals

$$f_{\text{img}}(t_{\max}, \dot{\varepsilon}) \sim t_{\max}{}^{-1/2}. \tag{3}$$

Insertion of Eq. (2) and (3) into Eq. (1) produces $\varepsilon_y \sim (\dot{\varepsilon}\tau_R)^{1/3}$. Indeed, Fig. 3 confirms that such a master curve exists to indicate how the yield point shifts to higher strains at higher extensional rates. It is important to point out that our startup shear experiments [15,19] on entangled polybutadiene solutions also exhibit the same scaling behavior of $\sigma_y \sim \gamma_y$ and $\gamma_y \sim (\dot{\gamma}\tau_R)^{1/3}$.

Guided by the idea of and evidence for force imbalance, we examined a simpler yet more surprising aspect of extensional deformation. We interrupted the extension well before the yield point was reached. In such step

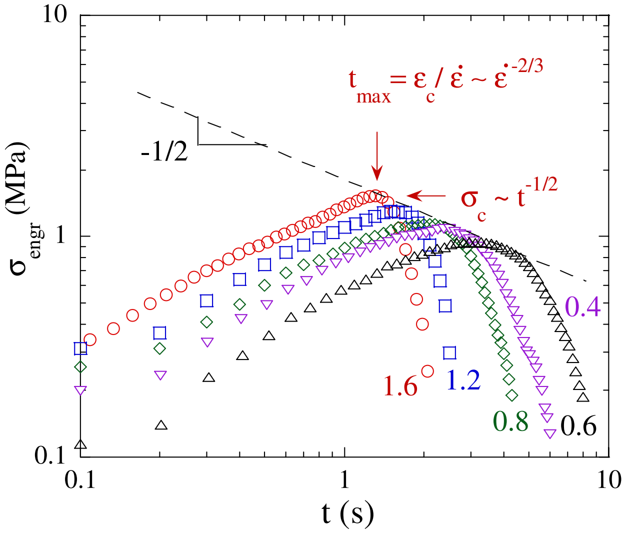

FIG. 1 (color online). The measured tensile force resulting from five discrete continuous uniaxial stretching experiments, expressed in the form of the engineering stress σ_{engr}, where the numbers 0.4 to 1.6 s^{-1} indicate the rate of extension. The coordinates of the force maximum (yield point) are designated by $t_{\max}$ and σ_y.

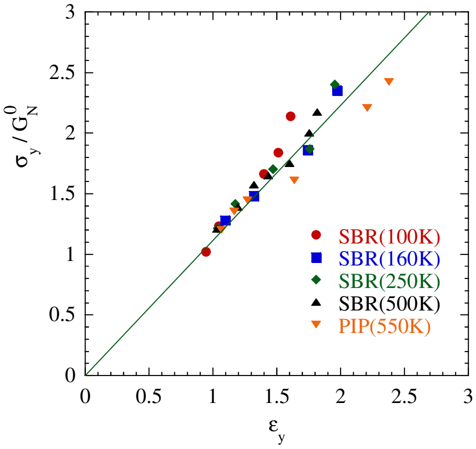

FIG. 2 (color online). The normalized "yield stress" σ_y/G_N^0 from such experiments as shown in Fig. 1 as a function of the "yield" strain, ε_y, for all four SBR samples as well as the PIP melt, where instead of a cylindrical filament, the PIP specimen has a rectangular cross section of dimensions: 5.1 mm × 1.0 mm. The rates applied are SBR(100 K) 8, 6.4, 4.8, 3.2, 1.6, and 0.8 s^{-1}; SBR(170 K) 4.8, 3.2, 1.6, 0.8, 0.4, and 0.24 s^{-1}; SBR(250 K) 3.2, 1.6, 1.2, 0.8, 0.4, 0.24, and 0.16 s^{-1}; SBR(500 K) 0.56, 0.48, 0.4, 0.32, 0.24, 0.16, and 0.08 s^{-1}; PIP(550 K) 29, 19, 9.6, 4.8, 2.9, 1.9 s^{-1}.

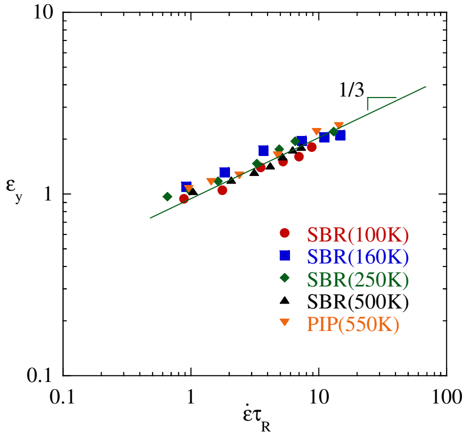

FIG. 3 (color online). The yield strain ε_y as a function of the applied rate of extension, revealing a master curve with a scaling exponent 1/3 for the same five samples after normalizing the strain rate with the Rouse relaxation time τ_R.

extension experiments [22] involving strain ε as low as 0.8, the SBR melt could not remain intact during the relaxation. On the other hand, the same sample would not go unstable until $\varepsilon_c \approx 2.0$ in continuous stretching. Figure 4(a) shows a series of interrupted stretching tests corresponding to three different amplitudes of strain. At $\varepsilon = 0.6$, the sample clearly remained intact after the step strain, where the measured tensile force started to decay rapidly only beyond the terminal relaxation time τ. At $\varepsilon = 1.0$, the stretched filament actually yielded and broke apart, on a time scale considerably shorter than the terminal relaxation time τ yet considerably longer than the Rouse time τ_R, leading to a final loss of measurable force as shown. The structural integrity was lost more quickly [23] when the sample was strained to higher amplitude of 1.4. Figure 4(b) further indicates that the dynamics leading to the sample failure appear similar for different rates all higher than or equal to $1/\tau_R$, as long as the different tests involves the same amplitude of step extension.

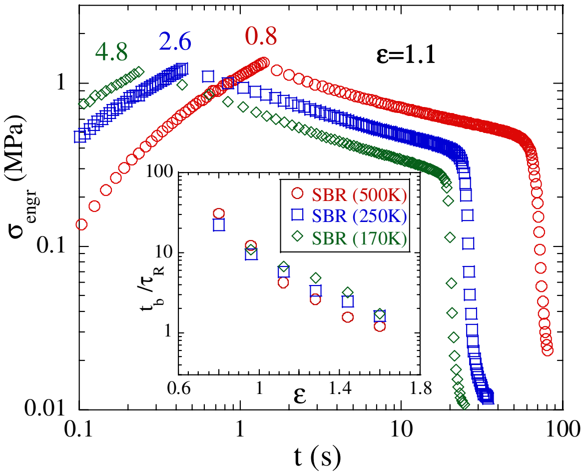

FIG. 5 (color online). A strain of $\varepsilon = 1.1$ performed on three different SBR samples using strain rates proportional to the reciprocal Rouse time. Taking the time to break as t_b, the inset plots the normalized breakup time t_b/τ_R as a function of a series of such interrupted stretching experiments for the three samples, revealing exponential dependence of t_b on ε: $t_b(M_w) = \tau_R(M_w)\exp(-A\varepsilon)$ where the constant A is rather insensitive to the level of chain entanglement.

Ide and White [5] attempted to describe failure during extensional flow of melts by introducing critical stress criterion. However, their analysis does not anticipate any elastic breakup after a step extension. It is interesting to note that cross-linked SBR rubbers also suffer a delayed breakup after a step extension [24]. Like the rupture during stretching [25], the failure produces sharp mirrorlike partitions at the point of break. Unlike the present case, cross-linking prevents "erosion" of the network through individual chain disentanglement. Nevertheless, the origin of breakup is elastic: the residual entropic force caused chain

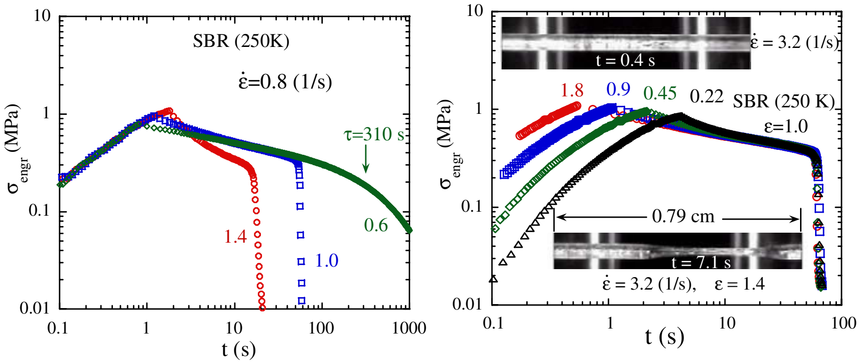

FIG. 4 (color online). (a) Three interrupted extension experiments involving amplitudes of 0.6, 1.0, and 1.4, respectively. The specimen remains uniform, i.e., intact for $\varepsilon = 0.6$. However, the higher amplitudes of step strain produce samples that are only temporarily stable. The breakup yields a sharp decline in the measured force. (b) A strain of amplitude 1.0 produced at four different rates of extension, all higher than the reciprocal Rouse time τ_R, for SRB(250 K), shows the same breakup time. Two photos show another step extension experiment where the applied rate $\dot{\varepsilon}$, the strain ε where the stretching was interrupted and times when pictures were taken, are all specified.

disentanglement and network dissociation. The breakup of a stretched filament on a wide range of time scales suggests to us that the residual entropic force has overcome the cohesion provided by the chain entanglement.

Figure 5 show that after an interrupted extension at an amplitude of $\varepsilon = 1.1$, all three SBR samples suffered ductile failure, i.e., unable to maintain their uniform dimensions and unable to stay motionless within the terminal relaxation time τ of each respective sample. At higher strains, the filaments collapsed faster as summarized in the inset. It appears that the dependence of the breaking time t_b on the amplitude of step strain is exponential, resembling an activation process, for the three different samples. To describe the failure process requires a many-body molecular theory and a full stability analysis [5] based on appropriate viscoelastic constitutive equations, and is a task beyond the scope of the present study.

In summary, the present work examined a long-standing issue of whether entangled melts could undergo indefinite uniform uniaxial extension on time scales much shorter than the terminal relaxation. Contrary to the consensus, we show that these liquids break down cohesively during continuous extension. A step strain of amplitude as low as 0.8 also causes yielding within a stretched sample. These yielding phenomena have the same physical origin: elastic breakdown of the entanglement network, and are completely analogous to those revealed by particle-tracking velocimetric studies of shear flow of entangled polymer solutions [1(a)–1(g)]. Actually, both extensional and shear flow behaviors exhibit the same scaling characteristics associated with the yield point. The observed universality offers hope for development of detailed phenomenology concerning nonlinear flow behavior of entangled polymeric liquids.

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