Rheology Reviews 2004; Walters, K., Bindings, D., Eds.; British Society of Rheology: Aberystwyth, U.K., 2004; p 1.

FAILURE AND RECOVERY OF ENTANGLED POLYMER MELTS IN ELONGATIONAL FLOW

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ABSTRACT

Entangled polymer melts exhibit failure in elongational flow, with different failure modes characteristic of different Weissenberg number regimes. Theoretical attempts to predict failure include Reiner's dynamical theory of strength, the Considère construction for the onset of necking, and a scaling theory that associates rupture with a critical recoverable strain. Reiner's theory is not consistent with the overall trend of available data, and the Considère construction does not appear to be applicable to melt flow in regimes with dissipation. The scaling theory is in qualitative agreement with available data but falls short quantitatively, and predictive capability of failure in elongational flow remains an elusive goal. An understanding of rupture and its relation to recovery, if any, is hindered by the extremely limited experimental database on rupture and recovery of well-characterized polymers.

KEYWORDS: elongational flow, entanglements, failure, necking, polymer melt, recoverable strain, recovery, rupture.

1. INTRODUCTION

Entangled polymer melts exhibit failure at high stress levels in a variety of processing flows. By *failure* we mean a gross change in the flow, perhaps accompanied by a discontinuity in the velocity field, with features that may be more typical of tears and fractures in solids than of one's usual notions of fluid behavior. Our focus in this chapter is on

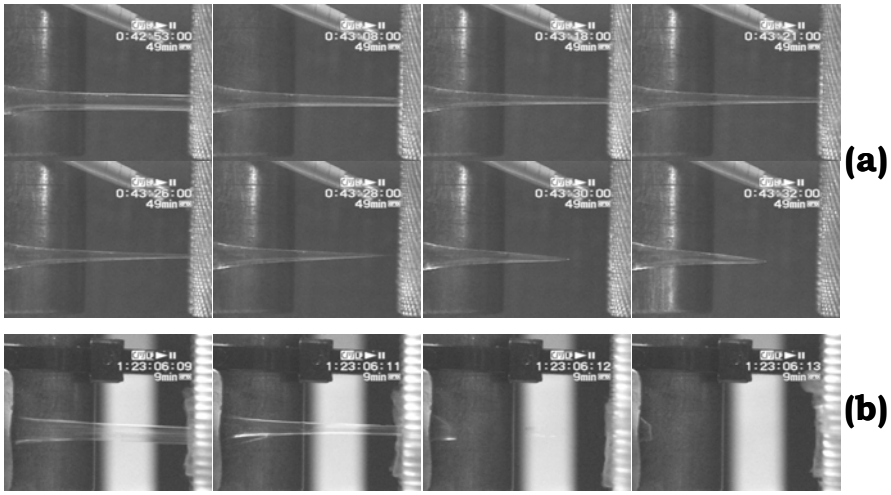

Figure 1: Polyisobutylene melt stretched (a) at 0.058s^{-1}, showing ductile failure, and (b) at 5.6 s^{-1}, showing cohesive failure. (Compliments of V. C. Barroso and J. M. Maia [1].)

the failure of entangled polymer melts in elongational flow. Figure 1 illustrates the subject with two examples of failure in elongational flow [1]. Figure 1a, which shows a time sequence of the elongation of an entangled polyisobutylene melt at a rate of 0.058 s^{-1}, illustrates a ductile failure, while Figure 1b, at an elongation rate of 5.6 s^{-1}, exemplifies what appears to be a cohesive failure, with nearly complete recovery of the extensional strain following rupture. The phenomenon known as *sharkskin* [2], which is characterized by regular distortions that have the appearance of tears on the surface of extruded melts, is probably also an extensional failure that results from the tensile stress concentration where the melt departs from the die.

Failure in elongational flow has been addressed by Petrie and Denn [3], Malkin and Petrie [4], and Ghijsels and coworkers [5]. Much of the relevant experimental literature was obtained prior to 1980, and there is a detailed tabulation of experimental studies in Petrie [6]. A good deal of useful empiricism regarding the onset of failure exists, but quantitative prediction based on sound molecular or continuum mechanisms has remained elusive. We believe a common theme runs through the various attempts to understand failure phenomena in shear and elongational flows, namely the existence of a rapid increase in chain disentanglement and a concomitant drop in flow resistance at what appears to be a failure surface. This theme associates failure with strain recovery, and we address what we believe to be the current state of understanding of both topics.

2.RUPTURE

A. Modes of Filament Breakup

Vinogradov and coworkers [7-11] carried out extensive experiments on failure in elongational flows of well-characterized entangled polymer melts, and they also measured the ultimate recovery following failure. They proposed four regimes of failure at increasing elongation rates, as shown schematically in Figure 2 (cf Malkin and Petrie [4]). The first regime occurs at low rates, where the response of the system is dominated by viscous flow and a steady-state stress can be attained at constant elongation rate. Surface tension effects are often important in this regime, and the filament ultimately breaks up into droplets in liquids of low viscosity and through a ductile failure ("necking") in liquids of high viscosity. The recoverable (elastic) strain increases with elongation rate, but it is very small relative to the total strain at failure.

The second regime, where the filament fails before reaching steady state, also involves substantial flow. The total strain at rupture decreases with increasing elongation rate in this regime, while the stress at rupture increases. The recoverable strain increases with elongation rate in the second regime and becomes comparable to that of the viscous (non-recoverable) strain. The response is mostly elastic in the third (*rubbery*) regime, where the total strain at rupture increases with the elongation rate and the strain is mostly recovered following failure. The stress at rupture increases with elongation rate in the rubbery regime. Figure 3, which contains data from Vinogradov's laboratory [7] on a polyisoprene with M_w = 575,000 and a polydispersity of 1.02 at T = 25 ˚C, illustrates regimes II and III. (Note that we use the Hencky (logarithmic) measure of strain throughout.)

At very high elongation rates, in the *glassy* regime, the filament undergoes brittle failure, the tensile stress and strain at rupture both decrease with elongation rate, and the strain is completely recoverable.

Based on the available experimental observations, Malkin and Petrie [4] proposed that a minimum recoverable Hencky strain of 0.5 units and a Weissenberg number (product of extension rate and a characteristic relaxation time) greater than 0.5 are required for rupture to occur in narrow-distribution entangled polymer melts. They showed a single linear correlation between the stress at rupture at different temperatures and the elastic (recoverable) strain for 1,4-polybutadienes, 1,2-polybutadienes, and 1,4-polyisoprenes. Malkin and Petrie further argued that the strength of a polymer melt is not constant, but depends on the "durability," which they define as the time to failure at a constant stress. Their durability criterion introduces a parameter with dimensions of specific energy that is

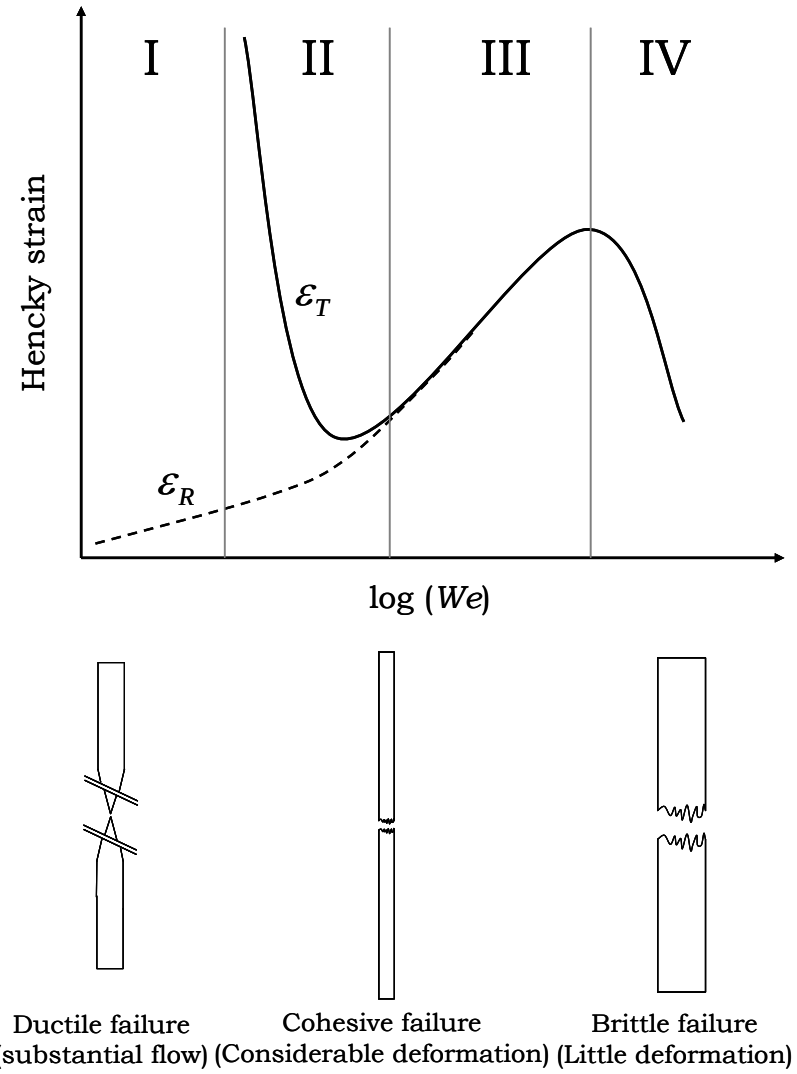

Figure 2: Schematic of regimes of failure, after Malkin and Petrie [4]. *We* is the product of elongational rate and a characteristic relaxation time.

nearly independent of polymer type, temperature, and molecular weight, and they suggest that there may be an energetic criterion for rupture.

There are few additional studies on the failure of well-characterized polymers. Maia and coworkers [12] studied rupture of the low-density polyethylene IUPAC-X and reported failure data that

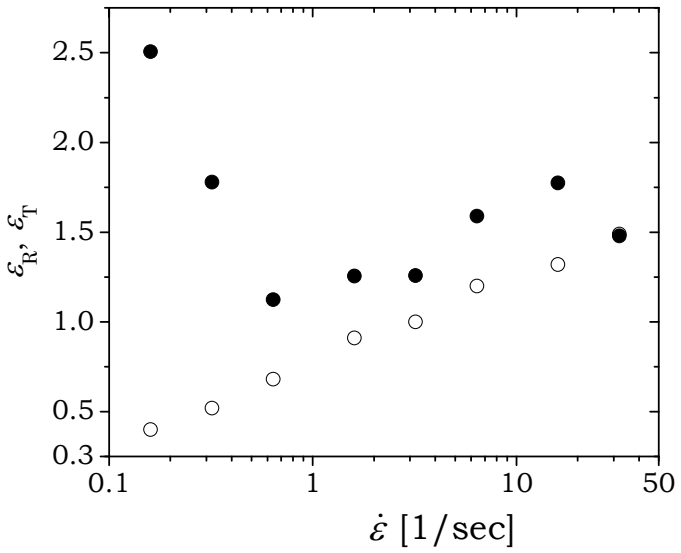

Figure 3: Total (●) and recoverable (○) strain at failure as a function of rate of elongation for a polyisoprene with Mw = 575,000 and a polydispersity of 1.02 at T = 25 ˚C. Data of Vinogradov and coworkers [8].

mapped out regimes II, III, and IV of Figure 2. They also reported rupture strains for a polyisobutylene for which recovery was nearly complete and the failure stress increased with extension rate, characteristic of regime III. Kamei and Onogi [13] studied rupture of various narrow and broad molecular weight distribution polystyrenes in constant velocity mode, and their overall observations of the various regimes are similar to those of Vinogradov and coworkers. Ide and White [14] studied the failure of low- (*LDPE*) and high-density (*HDPE*) polyethylenes, polypropylene, polystyrene, and poly (methyl methacrylate) (*PMMA*) with various molecular weights and molecular weight distributions. HDPE and polypropylene exhibited necking, while high molecular weight LDPE, polystyrene, and PMMA showed cohesive failure. Necking was more pronounced in the high molecular weight polypropylene and HDPE. Similar results regarding the polyethylenes were also reported by Chen and coworkers [15] and Ide and White [16]. In the case of PMMA, the strain at failure first decreased and then increased with the elongation rate, while the strain at failure for PS showed a slight increase with elongation rate.

Pearson and Connelly [17] studied failure in commercial PMMA, polystyrene, and a co-polyester. The failure strains were relatively insensitive to a Weissenberg number based on the maximum relaxation time over nearly four decades. Lee and coworkers [18] found that the critical strains at which necking failure was observed in an ABS melt were constant within experimental uncertainty with respect to both temperature and strain rate. These latter two studies are discussed further below.

B. Theories of Failure

i. Reiner's Dynamical Theory of Strength

Reiner proposed a "dynamical theory of strength" in a series of papers starting in 1938 [19]. The theory contains some phenomenology, but it reduces to the assumption that rupture occurs if the tensile stress exceeds a critical value equal to $(6KG)^{1/2}$, where G is the shear modulus and K is the "elastic energy per unit volume," or the "resilience." There is no obvious *a priori* way to estimate K, but we might assume that it would scale with G; in any event, we can parameterize the theory by taking $6K = \alpha^2 G$, in which case the critical stress is equal to αG, where we expect α to be at least 3 (rupture stress comparable to the extensional modulus) and more likely of order 10 or greater. The qualitative predictions of Reiner's theory are illustrated with the upper-convected Maxwell model, where the criterion for rupture is

$$\frac{We}{(1+We)(1-2We)}\left(3-2(1+We)e^{-\varepsilon\left(\frac{1}{We}-2\right)}-(1-2We)e^{-\varepsilon\left(\frac{1}{We}+1\right)}\right)\geq\alpha \quad \text{....(1)}$$

Here, ε is the Hencky strain and the Weissenberg number $We = \lambda\dot{\varepsilon}$ is the dimensionless elongation rate, where λ is the Maxwell relaxation time. For $We >> 1$ and $\alpha > 1$, the critical strain approaches an asymptotic value of $\varepsilon \sim \tfrac{1}{2}\ln\alpha$. Hence, the critical strain for rupture is predicted to be of order unity at high stretch rates and is relatively insensitive to the parameter α. Similarly, the predicted time to rupture, which is equal to the strain divided by the strain rate, is inversely proportional to the strain rate and less than the Maxwell relaxation time.

Figure 4 shows Reiner's rupture strain plotted against the Weissenberg number for a Maxwell liquid at various values of α. The strain to rupture decreases rapidly with increasing We at small values of the Weissenberg number, which is qualitatively consistent with the

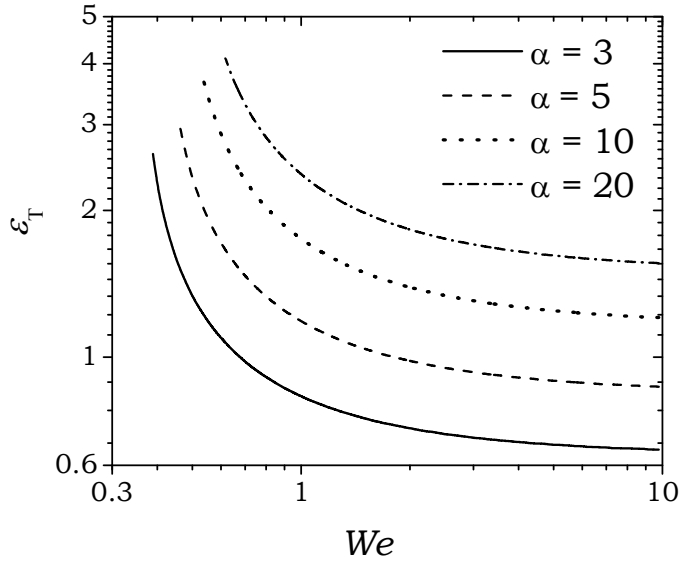

Figure 4: Strain at failure from Reiner's Dynamical Theory of Strength as a function of Weissenberg number for a Maxwell liquid. α is the ratio of the tensile strength to the shear modulus.

experimental data, and approaches the asymptote when We is in the range 1 to 10. The Maxwell liquid is rubber-like in the asymptotic regime, where $t < \lambda$, and the prediction of the theory is that rupture occurs at a critical strain that is independent of the stretch rate. The predicted magnitudes, of order unity, are in the range observed experimentally, but the theory is inconsistent with the trend of the data, which show a strain-rate independence for the failure strain in the rubbery regime and a stress at rupture that is rate dependent.

ii. Considère Construction

The Considère construction is a concept from solid mechanics that states that a material will fail in extension if the extensional force vs. strain curve goes through a maximum. The idea here is that the system can jump to a state in which more than one strain can be sustained by the same force, hence a ductile failure may occur. The concept seems first to have been applied to polymer melts by Cogswell

and Moore [20], who credit the idea to J. R. A. Pearson. The construction is most easily illustrated by considering a material that is in the rubbery regime, where the extensional stress is proportional to the Hencky strain. If the material is incompressible we may write

$$F = 3GA_0 e^{-\varepsilon}\varepsilon \qquad \text{.....(2)}$$

G is the shear modulus and A_0 is the initial area. For simplicity, we assume that G has a power dependence on strain of the form ε^p, where the material is strain hardening if $p > 0$ and strain softening if $p < 0$. The maximum in the force curve occurs for $\varepsilon = 1/(1-p)$, which, according to the underlying assumption of the construction, should be the limiting strain for which uniform extension can be guaranteed. Hence, limiting strains of order unity are predicted. The comparable result can be obtained rigorously for the Doi-Edwards and pom-pom models [21]. For the Doi-Edwards model, which is extension softening, the critical strain is approximately 0.86. For the pom-pom model with $q = 1$ (no branches), the critical strain is approximately 0.70. For pom-pom models with $q > 1$, which are extension hardening, the asymptotic value is approximately $0.55 + \ln q$; for $q = 10$, for example, the limiting strain in the rubbery regime is approximately 2.85.

The Considère construction can be applied to any viscoelastic constitutive equation [17, 18, 21, 22] by computing the stress and strain in transient uniform uniaxial (or other) extensional flow. Figure 5 shows the force and stress in an upper-convected Maxwell liquid stretched at a constant rate with We = 0.3. At this dimensionless stretch rate the Maxwell liquid reaches a steady-state elongational stress. As we see from Figure 5, the maximum in the force curve occurs at a relatively small strain, and well before steady state is reached in the stress. This calculation illustrates the problematic nature of the Considère construction when applied to situations in which there is dissipation. Since the area decreases as exp $(-\varepsilon)$, *any* liquid that can reach a steady-state stress in elongation must exhibit a maximum in the force curve. Hence, literal interpretation of the construction as a sufficient condition for failure would imply that uniform uniaxial extensional experiments could never be carried out past the force maximum, which often corresponds to a relatively low strain; such an interpretation is clearly contrary to substantial experimental experience in extensional rheometry.

We note in particular the experiments of Pearson and Connelly [17], who compared the Considère construction obtained with the K-BKZ model to experimental data on commercial PMMA, polystyrene,

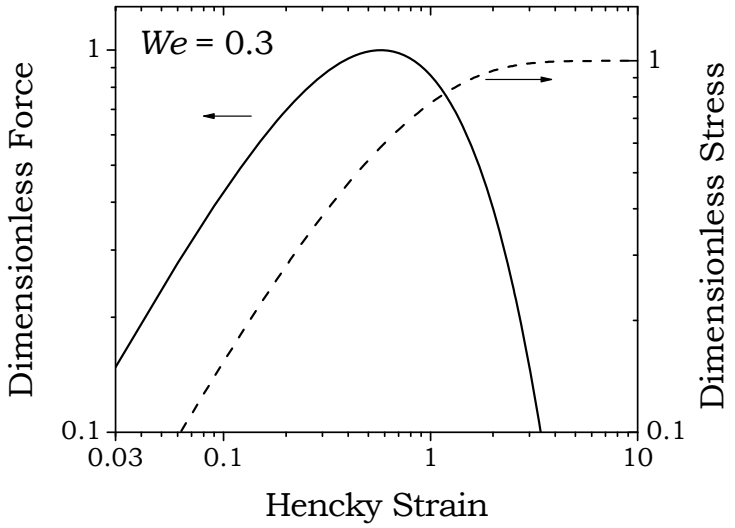

Figure 5: Force and stress as functions of strain during uniform uniaxial extension of a Maxwell liquid at We = 0.3.

and a co-polyester. The data for all three polymers superimposed when plotted as strain at the maximum force versus a Weissenberg number based on the maximum relaxation time, and the data were in generally good agreement with the computed Considère curve. While this study is often cited as an application of the Considère construction to melt failure, there is in fact no suggestion in the paper that Pearson and Connelly observed necking at the "failure" point, and such an observation would not have been possible with their experimental arrangement [23]; rather, the plot of the strain corresponding to the maximum force as a function of Weissenberg number seems to be simply another indication of the good fit of the K-BKZ model to their rheological data. Pearson and Connelly reported rupture at higher strains, and the rupture strains coincided with the critical strain from the Considère construction only at the highest Weissenberg number. Similarly, Lee and coworkers [18] reported that the critical strains at which necking was observed in an ABS melt were consistently higher than those from the Considère construction.

We believe that the Considère construction has only limited utility for understanding failure in polymer melts. The criterion is focused on necking, which typically occurs at low Weissenberg

numbers, where the application is problematic and the construction provides at best a conservative lower limit for the necking strain. The construction is likely to provide a good estimate of the onset of necking at high Weissenberg numbers, but failure under these conditions is typically from rupture (although we note that Lee and coworkers [18] reported necking just prior to cohesive failure under the sole experimental condition where the Considère construction predicted a failure stress that was comparable to that observed experimentally).

iii. Scaling Theory

Joshi and Denn [24] recently developed a scaling model for rupture in which catastrophic failure occurs when the frictional force on an entangled chain can no longer balance the tension in the chain. The approach is conceptually similar to the scaling analysis of Brochard and de Gennes [25] for failure in shear ("slip") near a solid surface, although different in substance. The chain tension is purely elastic, so rupture is identified with a critical value of the recoverable strain. According to the analysis, the recoverable strain at rupture ε_R is given by

$$\exp(3\varepsilon_R) - \exp(2\varepsilon_R) = \frac{4\pi^2\beta}{5N_e} N^{1/2} We_{\mathrm{Rep}} \qquad \text{.....(3)}$$

Here, $We_{\mathrm{Rep}} = \dot{\varepsilon}\tau_d$ is the Weissenberg number based on the reptation time τ_d, N_e is the average number of monomers between neighboring entanglements, and N is the number of entanglements per molecule. β is a scaling parameter of order unity. (Joshi and Denn [24] took β =1.) The only data set available to test the scaling theory is for the narrow-distribution polyisoprene of Vinogradov and coworkers [26] shown in Figure 3, which is repeated in dimensionless form in Figure 6 together with the prediction of Equation 3 with β =1. (The reptation time for this polymer has an uncertainty of about 50%, ranging from 18 sec to 32 sec, because of different reported values for the plateau modulus, and lines corresponding to both values bound the shaded region shown here.) The agreement is encouraging, especially the trend with Weissenberg number; quantitative agreement with the data is obtained for β ~2.5. This result suggests that the recoverable strain may be the key factor in predicting failure. Equation 3 is useful for predicting rupture only in the rubbery regime, however, where the total strain is nearly all recoverable. It must be combined with a recovery

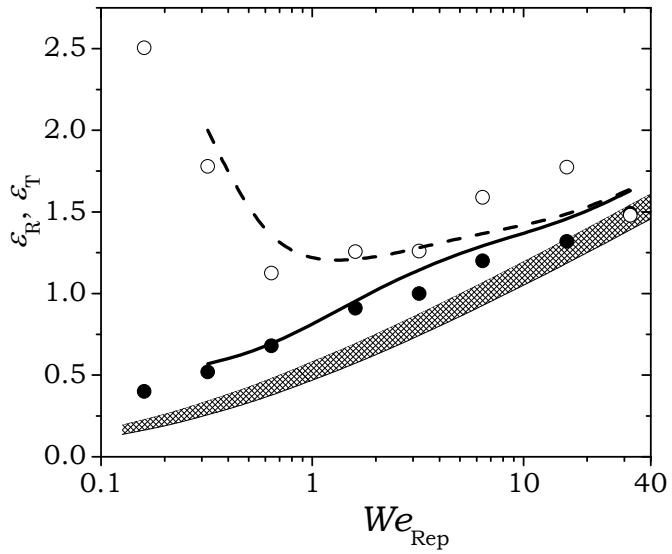

Figure 6: Failure data for polyisoprene as in Figure 3, plotted versus Weissenberg number based on reptation time. The fine lines bounding the shaded region are the predictions of the scaling theory, Equation (3), using estimated reptation times of 18 and 32 sec and β =1 The heavy continuous and broken lines are the predictions of recoverable and total strain, respectively, using the Wagner model and the experimental times to rupture. After Joshi and Denn [37].

calculation from a constitutive equation to be useful in Vinogradov's second regime, where there is dissipation.

3. RECOVERY

A. Experiments

The scaling argument cited above suggests that recoverable strain, which is a measure of chain extension, may play a significant role in understanding rupture in elongational flow. Recovery measurements following steady elongation are difficult, and the experimental database is very limited. Meissner [27] obtained recovery data following uniaxial elongation of a low-density polyethylene at 150

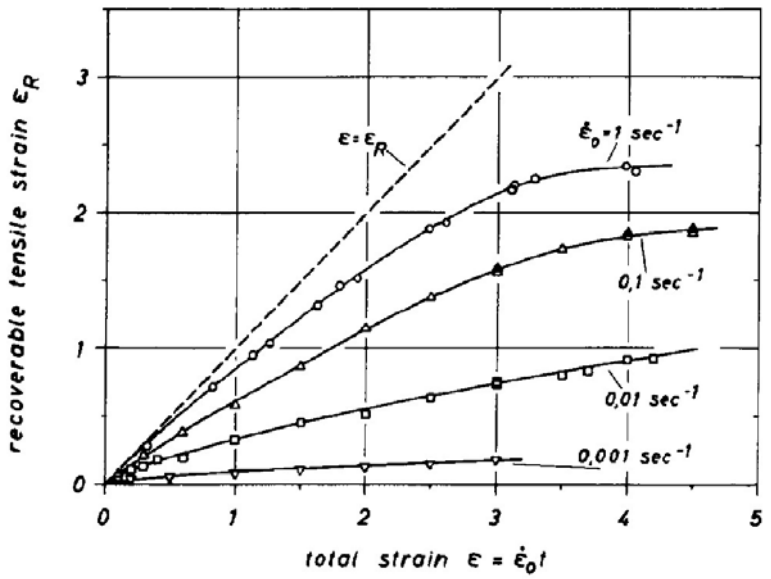

Figure 7: Recoverable strain as a function of total strain for low density polyethylene at 150 °C. Data of Meissner [27], reproduced with the permission of the Society of Rheology.

°C at various steady rates of elongation and total strains; recoverable strain as a function of total strain is plotted in Figure 7 with elongation rate as a parameter. The strain is almost completely recoverable at high elongation rates and small total strains, while at large total strains the recoverable strain reaches a constant asymptote. The strain is mostly dissipative at small elongation rates. Meissner and coworkers [28] observed a maximum in the recoverable strain as a function of total strain at the same strain at which the transient stress experiences a maximum in a stress growth experiment. Laun and Münstedt [29] showed that the steady-state recoverable strain for low-density polyethylene initially increases rapidly with increasing tensile stress or elongation rate, and then reaches a plateau at very high stresses and elongation rates. Similar behavior was shown for polystyrene by Münstedt [30] and for various high-density polyethylenes by Münstedt and Laun [31]. Münstedt and Laun [32] showed that recovery data for LDPE can be superposed using time-temperature superposition, and that the recoverable strain at constant stress is independent of temperature.

Vinogradov and coworkers [7-9, 11] measured the recoverable strain following rupture in elongational flow at constant rate and

constant stress for a variety of linear polymers with small polydispersity, including polyisoprene, polybutadiene, poly(vinyl chloride), and polystyrene. Their recoverable strain data for a polyisoprene were shown in Figure 3 to illustrate the experimental basis for the master curve for failure shown schematically in Figure 2. Recovery data for specific polymers can be superposed using time-temperature superposition and molecular-weight shift factors.

B. Theory

It is straightforward to compute recoverable strain following elongation for integral continuum models of the general Rivlin-Sawyers class, as well as for other integral models in which the strain appears explicitly in the integrand; the latter encompasses some tube models, including the recent model of Ianniruberto and Marrucci [33], but recovery has not been successfully computed for the popular Mead-Larson-Doi [34] model. We illustrate continuum recovery calculations following Wagner [35]. The Wagner model is a special case of the Rivlin-Sawyers class, with the extra-stress σ dependent on the Finger strain $\boldsymbol{C}^{-1}$ through the single integral

$$\boldsymbol{\sigma} = \int_{-\infty}^{t} \sum_k \frac{G_k}{\lambda_k} \exp\left(-\frac{t-t'}{\lambda_k}\right) h(I_1, I_2)\boldsymbol{C}^{-1}(t,t')\,dt' . \qquad \text{.....(4)}$$

The parameters $\{G_k, \lambda_k\}$ are obtained from linear viscoelastic data. The damping function $h(I_1, I_2)$ depends on the first and second invariants of the strain tensor. Wagner [35] suggested a particularly simple damping function for elongational flows with Hencky strains less than 2, which we use here for illustrative purpose for all strains:

$$h(I_1, I_2) = \exp\left(-m\left|\varepsilon(t,t')\right|\right), \qquad \text{.....(5)}$$

where $\varepsilon(t,t')$ is the Hencky strain experienced between times t' and t. (The use of the absolute value in the argument, which works well for the linear polymer melt described in the example here, is just one of several proposals by Wagner to deal with flow reversal.)

The elongation rate $\dot{\varepsilon}$ is taken to be constant until $t = t_0$, after which the sample is cut (or ruptures) and the stress is set to zero. The model exhibits both instantaneous and delayed recovery. It is straightforward to show that the instantaneous recovery is given by

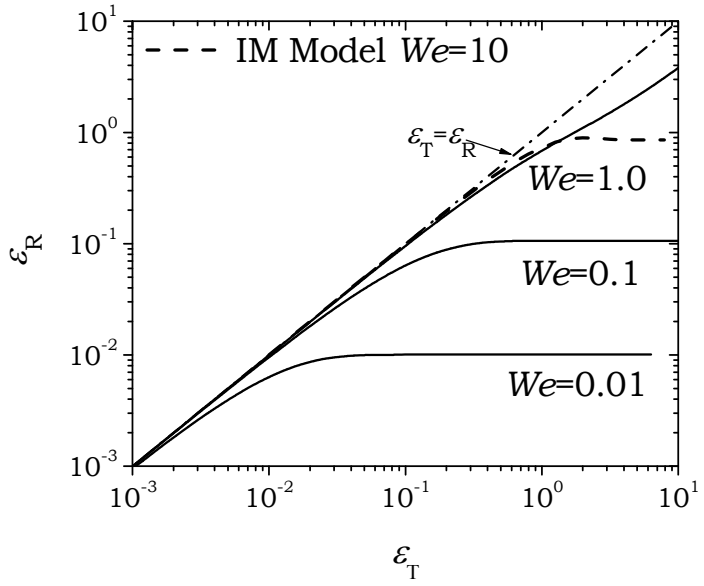

Figure 8: Recoverable strain as a function of total strain for a Maxwell liquid. The heavy broken line is the same calculation for an Iannirubertо-Marrucci tube model [33] at We = 10.

$$\varepsilon_R(t_0) = \varepsilon_T - \frac{1}{3}\ln\left\{\frac{\sum_k G_k e^{-t_0/\lambda_k}\left[\frac{\lambda_m e^{\varepsilon_T\left(\frac{\lambda_m}{\lambda_k We}+1+m\right)}+(1+m)\lambda_k We}{\lambda_m+(1+m)\lambda_k We}\right]}{\sum_k G_k e^{-t_0/\lambda_k}\left[\frac{\lambda_m e^{\varepsilon_T\left(\frac{\lambda_m}{l_k We}-2+m\right)}-(2-m)\lambda_k We}{\lambda_m-(2-m)\lambda_k We}\right]}\right\} \qquad \text{.....(6)}$$

Here, ε_T is the total strain prior to recovery and the Weissenberg number $We = \dot{\varepsilon}\lambda_m$ is computed using the *maximum* relaxation time λ_m. The multi-mode upper-convected Maxwell (or Lodge-Yamamoto) Model corresponds to m = 0. A single-mode model exhibits only instantaneous recovery. The ultimate recovery must be calculated numerically for a multimode model using a procedure given by Wagner and Stephenson [36] and Joshi and Denn [37].

The asymptotic behavior of Equation 6 is readily calculated for large strains, $\varepsilon_T >> 1$. For $We << 1$ we obtain a constant value $\varepsilon_R = We\bar{\lambda}/\lambda_m$, independent of m, where $\bar{\lambda} = \Sigma G_k \lambda_k / \Sigma G_k$. For $We >> 1$, for a single mode, we obtain $\varepsilon_R/\varepsilon_T = (2 - m - We^{-1})/3$; there is no simple form for the multimode model. The recoverable strain for a single-mode model is shown as a function of total strain in Figure 8, with We as a parameter and m = 0; the curves are simply shifted for $m \neq 0$. The qualitative form of the Meissner [27] data in Figure 7 is evident, and indeed Wagner has used the model with a value of $m = 0.3$ appropriate to low-density polyethylene to fit these data. The recovery calculation for the Ianniruberto-Marrucci tube model at *We* = 10 is also shown in Figure 8; this model exhibits very little recovery relative to the Wagner model. It is interesting to note, in the context of the experiments of Meissner and coworkers [28], that the ultimate recovery for the Ianniruberto-Marrucci model goes through a slight maximum before reaching the plateau.

Joshi and Denn [37] fit the linear viscoelastic data of Vinogradov and coworkers [26] for the polyisoprene shown in Figure 3 with a sum-of-exponentials memory function of the form used in Equation 4, and they determined the parameter m in the Wagner model by fitting one nonlinear transient experiment. The transient data for this narrow-distribution linear polymer for all experiments are best fit with *m* = 1. The calculated recovery is shown as a heavy continuous line in Figure 6 for τ_d = 32 sec, and the total strain at rupture corresponding to these parameters is shown as a heavy broken line in Figure 6. The model is in reasonable agreement with the data. The Ianniruberto-Marrucci [33] model is too "soft" to predict the recovery that is observed experimentally.

Recovery was calculated for a Phan-Tien/Tanner differential model by Langouche and Debbaut [38], who used an integrating factor to convert the differential model to an integral form over the period of instantaneous recovery. Borgbjerg and coworkers [39] solved the Curtiss-Bird model for recovery after steady elongational flow using an equivalent non-equilibrium Brownian dynamics formulation. The qualitative behavior is independent of the model, although quantitative results are highly model-dependent

C. Recovery and Failure

Joshi and Denn [37] used the scaling theory, Equation (3), and the relation between recoverable strain and total strain for the Wagner model, to predict the total strain at failure for the Vinogradov data. This is an *a priori* calculation that requires only the rheological

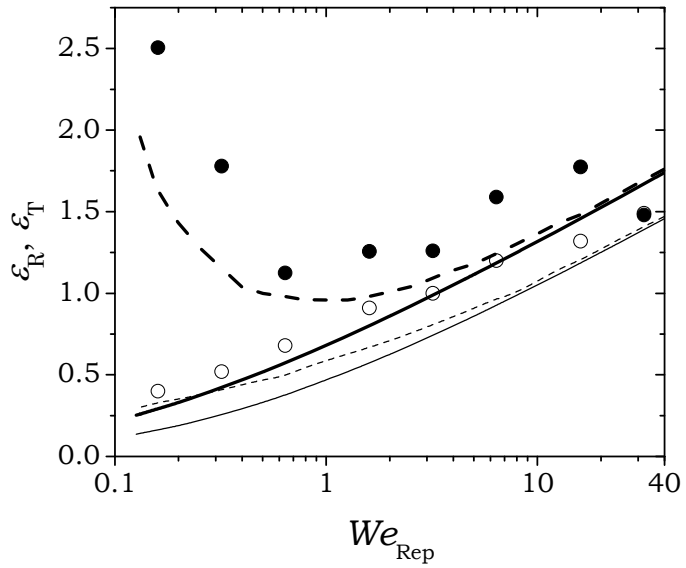

Figure 9: Failure data for polyisoprene as in Figure 3. The fine continuous and broken lines are the critical recoverable and total strain, respectively, from the scaling theory, Equation 3, with β =1 and τ_d = 32 sec. The heavy continuous and broken lines are the critical recoverable and total strain from the scaling theory with β =2.5. After Joshi and Denn [37].

parameters. The result is shown in Figure 9. The light lines, corresponding to the scaling theory with τ_d = 32 sec and β =1, show far too much recovery and greatly underpredict the total strain at failure. The heavy lines correspond to the same calculation, but with β =2.5 to bring the scaling theory curve closer to the recovery data. This calculation of total strain at failure is in qualitative agreement with the data and shows both Vinogradov's regimes II and III.

4. CONCLUSIONS

One major conclusion is that a fuller understanding of recovery and rupture, both separately and as they may relate to one another, is hindered by the extremely limited database for well-characterized

polymers. These are difficult experiments, but progress cannot be made without more careful experimentation in which both rupture strain and recovery are measured. The data set from the Vinogradov group used in Figures 3, 6, and 9 is more than thirty years old, and it is not obvious how reproducible these data are. In particular, the spread between the recoverable and total strain at high Weissenberg numbers seems too large, perhaps in part because of the difficulty of measuring complete recovery in a system having a longest relaxation time of several hundred seconds.

In terms of theory, we have grave doubts whether the Considère construction, which has received renewed attention in recent years, has any relevance to the onset of necking failure in entangled melts under conditions where the flow is dissipative. The construction predicts necking in extensional rheometry under conditions where uniform filaments are observed experimentally, and it underpredicts the onset of necking by a large amount in experiments where necking is observed.

Finally, it is clear that a predictive theory for rupture of entangled polymer melts remains an elusive goal. We are encouraged by the simplicity and qualitative properties of the scaling theory, and we believe there is a strong case for the notion of a critical recoverable strain at rupture, but a more fundamental analysis is needed.

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