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The Role of Entanglements in the Elastic Fracture of Polymer Solutions

INTRODUCTION

The literature contains numerous accounts of flow instabilities, or fracture, of polymer melts caused by extrusion through dies at high rates.[1,2] A similar phenomenon can occur with concentrated solutions of polymers; however, there are few references to this fact.[2] Undoubtedly, this is partly because fracture of solutions is somewhat more difficult to detect as Vinogradov et al.[3] have noted. The present authors reported recently[2] on some observations of fracture with solutions of a high molecular weight polystyrene ($\bar{M}_w = 2 \times 10^6$) in benzene. The central point of this paper was the observation that fracture of these solutions occurred at shear stress levels one to two orders of magnitude lower than that required to cause fracture of the same polymer in the undiluted melt.[4] A theory was developed which predicted that the critical shear stress for fracture should decrease as the polymer is diluted with solvent, and this theory gave good quantitative agreement with the solution data reported. The main feature of this theory was the hypothesis that fracture of solutions occurs at a critical recoverable shear strain which is the same as that for the melt.[2] The concentration dependence of the critical shear stress then stems from the reduction in the elastic modulus of the polymer when it is diluted by solvent.

After these data and their analysis were reported, some new results for solutions of lower molecular weight polystyrenes have been obtained. Also, Vinogradov et al.[3] have since published some very interesting data for polybutadiene solutions which show some of the same features as our earlier work. It is the purpose of this paper to present these new polystyrene data and to reexamine the analysis in light of both sets of new information.

EXPERIMENTAL

In contrast to extrudates of melts, the extrudates of solutions do not retain the deformed shape that results from the fracture instability. Thus, to examine the fracture of solutions, it was necessary to construct a visualization apparatus by which the onset of fracture could be defined photographically. The use of this equipment along with a description of the flow instability in the capillary entrance and exit regions were discussed in the earlier paper.[2] The critical shear stress for fracture initiation was defined as the onset of a continuous screw-thread or helical distortion pattern in the extrudate. The Instron rheometer used to drive the solution through the capillary did not have a continuously variable throughput control, and as a result, the flow rate where fracture initiated could not be pinpointed to closer than 10% to 20% about the true value in some cases.

The polystyrenes used were all narrow molecular weight distribution samples obtained from the Pressure Chemical Company, ($\bar{M}_w/\bar{M}_n$ less than 1.1). The solvent used was benzene, and concentrations were expressed as a volume fraction ϕ. All measurements were made at 26°C using capillaries described earlier. The observed shear stresses at the capillary wall, τ_{wc}, that initiated fracture are shown in Table I for each solution.

The polybutadiene used in the experiments by Vinogradov et al. referred to earlier had narrow molecular weight distributions with a microstructure similar to polymers synthesized using a butyllithium catalyst.[5] In one series of experiments, the $\bar{M}_w$ was held constant at 240,000 while the polymer volume fraction ϕ varied; but in another series, ϕ was held constant at 0.7 while $\bar{M}_w$ varied. The solvent in both cases was methylnaphthalene.

DATA ANALYSIS USING CONSTANT RECOVERABLE SHEAR STRAIN CRITERIA

For a viscoelastic fluid flowing through a capillary, the recoverable shear strain at the wall, S_w, is related to the wall shear stress τ_w via the elastic shear modulus G:

$$\tau_w = GS_w \tag{1}$$

Some of the most successful correlations for the critical shear stress for the onset of fracture, τ_{wc}, of polymer melts are based on the hypothesis that the criterion for fracture conditions is a constant critical recoverable shear strain value, S_{wc}, so that

$$\tau_{wc} = GS_{wc}. \tag{2}$$

The predictive value of this hypothesis then resides in the possibility of relating G to the variables of interest using theoretical or empirical relations. In our earlier paper,[2] we assumed that G for concentrated solutions could be predicted from the Rouse modulus expression G_R for dilute solutions

$$G_R = \frac{5}{2}\frac{cRT}{M} \quad \text{(Monodisperse)} \tag{3}$$

$$G_R = \frac{5}{2}\frac{\bar{M}_w^2}{\bar{M}_z \bar{M}_{z+1}}\frac{cRT}{\bar{M}_w} \quad \text{(Polydisperse)} \tag{4}$$

where c = polymer concentration (g/cm^3) by appropriate modification for the effect of entanglements, viz.,

$$G_0 = G_R f(E) \tag{5}$$

where $f(E)$ is an appropriate function of the entanglement density E, defined as

$$E = 2\phi\frac{\bar{M}_w}{M_c} \tag{6}$$

with $\phi = c/\rho$ (ρ = melt density) and M_c = a critical molecular weight for formation of entanglements that is characteristic of the polymer melt. Equation (5) is a generalization of a specific result proposed and used by Graessley[6] in which he takes

$$f(E) = a + bE \tag{7}$$

where a and b are empirical constants with values of a = 0.455 and b = 0.155 for polystyrene in n-butyl benzene. Combination of eqs. (2)–(7) yields

$$\tau_{wc} = \frac{5}{2}\frac{\phi\rho RT}{\bar{M}_w} S_{wc}\left(\frac{\bar{M}_w^2}{\bar{M}_z \bar{M}_{z+1}}\right)\left[a + 2b\phi\left(\frac{\bar{M}_w}{M_c}\right)\right]. \tag{8}$$

In our previous paper, we chose to take the ratio of stresses predicted by eq. (8) for a given polymer sample in solution of volume fraction ϕ, $(\tau_{wc})_{\text{soln}}$, to that predicted for the same polymer in the melt where $\phi = 1$, $(\tau_{wc})_{\text{melt}}$, which gives

$$\frac{(\tau_{wc})_{\text{soln}}}{(\tau_{wc})_{\text{mlet}}} = \phi\left[\frac{a + 2b\phi\left(\frac{\bar{M}_w}{M_c}\right)}{a + 2b\left(\frac{\bar{M}_w}{M_c}\right)}\right]. \tag{9}$$

Vlachopoulos and Alam[4] gave extensive data for $(\tau_{wc})_{\text{melt}}$ as a function of $\bar{M}_w$ and T. Since the melt cannot exist at the 26°C used in the solution work, a small problem of comparison arises which was circumvented in the earlier analysis[2] by bracketing the results using an arbitrary melt temperature of 200°C and a fictitious melt temperature of 26°C. For both cases, $(\tau_{wc})_{\text{melt}}$ was computed from an equation given by Vlachopoulos et al., eq. (20) of reference 2. We found that with these assignments, eq. (9) predicted very well our $(\tau_{wc})_{\text{soln}}$ values for polystyrene with $\bar{M}_w = 2 \times 10^6$ when Graessley's a and b values were used and M_c was taken[7] as 33,000. Similar calculations for $(\tau_{wc})_{\text{soln}}$ are shown in Table I for the new data. The prediction is quite good for solutions with large $\bar{M}_w$ but becomes much too low as $\bar{M}_w$ is decreased. It is now of interest to examine why this prediction becomes poor at low $\bar{M}_w$.

Because our earlier data were not very extensive, it was expedient to use eq. (9) which employed the comparison with melt data and made use of eq. (7) with values of a and b for a somewhat different system. Concerns about each of these practices were voiced earlier, and now with the new data we would like to abandon them (since this could be the origin of the problem noted above) and follow another approach. Equations (2) and (5) can be combined into a more general version of eq. (8), i.e.,

TABLE I

Polystyrene—Benzene Solution Fracture Results

		τ_{wc}, dynes/cm^2		
		Predicted by eq. (9) using melt temperatures of		Experimental data for
$\bar{M}_w$	ϕ	26°C	200°C	26°C
2,000,000	0.128	9,400	15,000	15,000
	0.150	12,600	20,000	19,000
	0.172	16,200	25,900	17,500
	0.195	20,600	32,800	25,000
	0.217	25,200	40,200	22,000
498,000	0.322	77,200	123,000	146,000
	0.420	124,000	199,000	200,000
200,000	0.466	237,000	379,000	545,000
	0.583	345,000	551,000	622,000
110,000	0.593	110,000	532,000	932,000

$$\tau_{wc} = G_R f(E) S_{wc} \tag{10}$$

which can be rearranged into the following form with the aid of eqs. (4) and (6):

$$\frac{\bar{M}_w \tau_{wc}}{\phi} = \frac{5}{2}\left(\frac{\bar{M}_w^{\,2}}{\bar{M}_z \bar{M}_{z+1}}\right)\rho RT S_{wc} f\left(2\frac{\phi \bar{M}_w}{\bar{M}_c}\right) \tag{11}$$

This equation suggests that for a polymer series with similar molecular weight distributions (e.g., monodisperse) at a fixed T, one should be able to form a unique relation by plotting experimental data as $\bar{M}_w \ \tau_{wc}/\phi$ versus $\phi \bar{M}_w$, since all other parameters in this equation (ρ, S_{wc}, $\bar{M}_w^2/\bar{M}_z\bar{M}_{z+1}$, and M_c) should be constant. The shape of this plot would depend on the nature of the function *f(E)*, but no assumptions about this nature nor the numerical parameters of this function are required. Figure 1 shows such a plot for all of the data in Table I. While there is a certain amount of scatter, there appears to be a unique relation (note that both ϕ and $\bar{M}_w$ vary). This plot is not consistent with Graessley's values of a and b. Statistically, the best representation of the data is a horizontal line, like the one shown. This implies that for this system, *f(E)* is constant and there is no effect of E. In terms of eq. (7), $b = 0$. Thus based on these new data, the critical shear stress for fracture, τ_{wc}, for this system is proportional to $\phi/\bar{M}_w$ (the limiting case for complete independence of entanglements[2]), which is somewhat different from the functionality employed earlier[2] using the procedures embodied in eq. (9) where a value of $b \neq 0$ was used. It is interesting to note that for very large values of $\bar{M}_w$ the predictions of eq. (9) are somewhat insensitive to the choice of b, which may explain in part why this procedure gave adequate predictions for $\bar{M}_w = 2 \times 10^6$.

It is of interest to examine the data of Vinogradov et al. by a similar plot. Figure 2 shows their data for a series of experiments in which $\bar{M}_w$ was held constant while ϕ varied from 0.2 to 1.0. These data for polybutadiene fall about a straight line (see solid line) with a very definite posi-

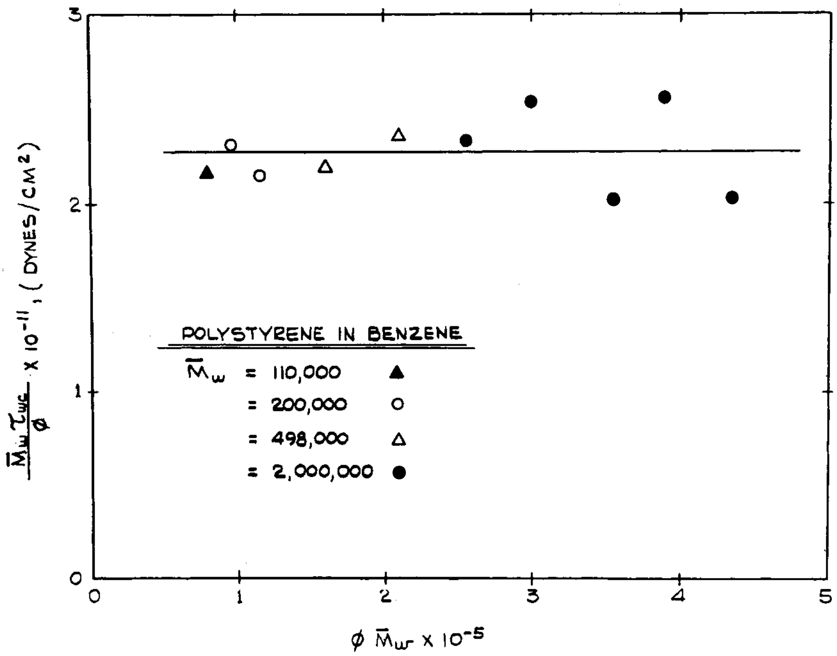

Fig. 1. Polystyrene fracture data at 26°C.

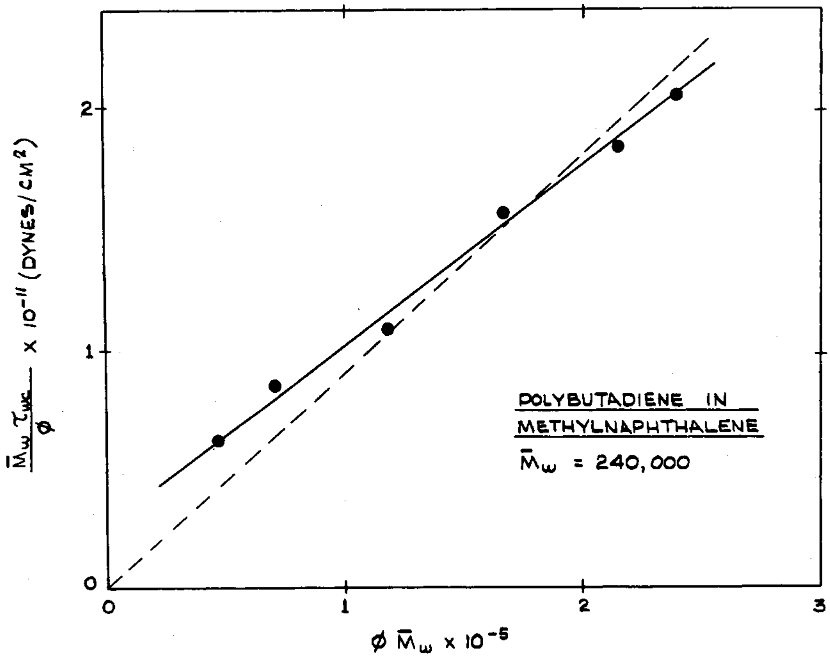

Fig. 2. Polybutadiene fracture data at 24°C.

tive slope, in contrast to the polystyrene data. This form is also consistent with eq. (7). The arbitrary solid line drawn through the data in Figure 2 gives a small value for the intercept on the ordinate, which suggests that the parameter a is very small. There are other indications from the Vinogradov et al. work that would suggest this parameter is in fact zero. In a series of experiments with polybutadiene, where ϕ was held constant at 0.7 and $\bar{M}_w$ varied from 76,000 to 580,000, these authors report that τ_{wc} remained constant. From eq. (8), we see that this independence of $\bar{M}_w$ would result if $a = 0$, $b \neq 0$. The dotted line in Figure 2 corresponds to this case, and it gives a reasonable representation of the data there (especially when one considers the accuracy of such data). Thus, we conclude for the polybutadiene–methylnaphthalene system that $a \approx 0$. This means that for this system, τ_{wc} is proportional to ϕ^2 and is independent of $\bar{M}_w$. This is the limiting case for complete dominance by entangements.[2] Possible reasons for the divergent behavior of polybutadiene and polystyrene are examined in the next section.

SUMMARY

From Figures 1 and 2, it appears that the combinations of variables used in the ordinate $\tau_{wc} \bar{M}_w/\phi$ and the abscissa $\phi \bar{M}_w$ are appropriate in order to represent solution fracture data (where both ϕ and $\bar{M}_w$ are variable) as a single function, although there seems to be a separate function for each system. This method of plotting was suggested on the basis of the critical shear strain hypothesis and the pseudotheoretical eq. (5) to represent the elastic modulus of concentrated solutions, and the present successes would support the validity of this theory. However, considerably more work on a variety of systems is needed before any definitive conclusion regarding this theoretical basis can be made.

It is of interest to speculate on why the two systems shown in Figures 1 and 2 exhibit such different behavior in these plots. To do so, we will assume that the theoretical basis for these plots has sufficient merit so that we can interpret this behavior in terms of the relative importance of entanglements in the two systems. In this connection, there are two facts that are relevant. First, the parameter M_c, which is proportional to the entanglement coupling spacing,[8] is quite different for the two systems: $M_c = 33{,}000$ for polystyrene[7] and $M_c = 5{,}600$ for polybutadiene.[9] This means that for the same value of $\phi \bar{M}_w$, the entanglement density E would be approximately six times greater for a polybutadiene solution than a polystyrene solution. Second, we observed that the polystyrene solutions fractured at shear rates considerably beyond the lower Newtonian plateau, whereas Vinogradov et al. always observed fracture of the polybutadiene solutions in the Newtonian region. Equation (6) only gives the entanglement density in this Newtonian limit; and as the shear rate is increased into the non-Newtonian region, the molecules become progressively more disentangled because of insufficient time for entanglements to reform at these high deformation rates.[6] Based on this, the relative state of entanglement at the point of fracture for polystyrene compared to polybutadiene would be even less than eq. (6) indicates from M_c considerations. These factors are qualitatively consistent with the conclusions arrived at above that polybutadiene solution fracture is initiated as the result of critical changes in the entanglement density, whereas the polystyrene fracture phenomenon is independent of entanglements at the concentrations examined.

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