Extensional Viscosity of Amorphous Polystyrene

INTRODUCTION

Under the restriction of constant volume, uniaxial extensional flow is described by a velocity field of the form

$$V_i = \left(\Gamma(t)x_1, \; -\frac{1}{2}\Gamma(t)x_2, \; -\frac{1}{2}\Gamma(t)x_3 \right) \tag{1}$$

where (x_1, x_2, x_3) are Cartesian coordinates and $\Gamma(t)$ is the extension rate which may be an arbitrary function of time. For this flow, the fluid is characterized by an extensional viscosity $\bar{\eta}$, defined by

$$\bar{\eta} = \frac{S_{11}}{\Gamma} \tag{2}$$

where S_{11} is the axial stress. For the case of zero force acting on the surface of the material perpendicular to the direction of extension (i.e., $S_{22} = S_{33} = 0$), $\bar{\eta}$ may be expressed in terms of the primary normal stress difference, i.e.,

$$\bar{\eta} = \frac{S_{11} - S_{22}}{\Gamma} = \frac{N_1}{\Gamma}. \tag{3}$$

Theoretical predictions for $\bar{\eta}$ vary widely among existing constitutive theories.[1-5] However, many of these theories predict in common the existence of a critical extension rate for polymeric materials. For example, at the onset of a constant extension rate in an initially unstressed fluid, the convected Maxwell model yields the following expression for $\bar{\eta}$:

$$\bar{\eta} = \frac{3\mu}{(1 - 2\lambda\Gamma)(1 + \lambda\Gamma)} - \frac{2\mu \exp[-(1 - 2\lambda\Gamma)t/\lambda]}{1 - 2\lambda\Gamma} - \mu \frac{\exp[-(1 + \lambda\Gamma)t/\lambda]}{1 + \lambda\Gamma} \tag{4}$$

where μ is the shear viscosity, λ is the relaxation time, and t is the time elapsed since the onset of flow. In this case, the critical extension rate is given by

$$\Gamma_c = \frac{1}{2\lambda} \tag{5}$$

and for $\Gamma < \Gamma_c$ this model predicts the attainment of a steady-state extensional viscosity, whereas for $\Gamma \geq \Gamma_c$ a solid-like response is predicted, with the extensional viscosity (stress) increasing rapidly with time (strain). Although the predicted value of Γ_c varies among constitutive theories, the qualitative material behavior described above is common to most viscoelastic models.

In recent years, extensional viscosity measurements at constant extension rate have been reported in the literature.[3,6-10] Furthermore, in all cases for which a sufficiently wide range of deformation rates was examined,[3,8-10] the results indicated a rapid stress growth at high extension rates, rather than attainment of steady state. For Meissner's results, in particular, the onset of the rapid stress growth was found to occur at a critical value of the total strain,[8] which was approximately independent of the deformation rate. These experimental results were thus in qualitative agreement with the theoretical predictions described above.

It is interesting to note, however, that in all of the extensional viscosity measurements referred to above, the experiments were performed using molten polymers which contained crystalline material in the solid state. This raises a question, therefore, as to the origin of the experimentally observed transient stress increase. Although these results were interpreted as confirming the theoretical predictions of the transient nature of material properties in extensional flow, one could also hypothesize that a stress- (or strain)-induced crystallization systematically occurred during the experiments which would also yield similar solid-like manifestations. Indeed, stress-(strain)-induced crystallization has been observed numerous times under extensional flow conditions,[11] and the low temperatures (required for measurably large tensile stresses) utilized in the

extensional viscosity measurements referenced above would enhance the probability of its occurrence.

In the present note, this uncertainty in the interpretation of experimental results is eliminated through extensional viscosity measurements on a molten *amorphous* polystyrene. The effect of extension rate on $\bar{\eta}$ is thus examined for apparently the first time under conditions for which crystallization is not a factor.

EXPERIMENTS AND DISCUSSION OF RESULTS

The material used in the present study was an amorphous, commercial polystyrene (Lustrex GC 505, manufactured by Monsanto Company) having an M_w of 2.5×10^5 and M_n of 6.0×10^4. This material was characterized in steady shearing flow at 155°C in both an Instron extrusion rheometer and the cone-and-plate mode of a Rheometrics Mechanical Spectrometer. The steady shear viscosity results are plotted in Figure 1.

A method of measuring extensional viscosity similar to that originally proposed by Macosko and Lorntson[9] was used in the present study. The apparatus, which is similar to the rotating clamp device of Meissner,[8] is illustrated in Figure 2. The test material was held in a stationary clamp at one end and wrapped around a winder rod at the other end. The stationary clamp was mounted on the Mechanical Spectrometer transducer, which detected the tensile force in the sample. The winder rod was connected to the drive system of the Mechanical Spectrometer and could be rotated over a wide range of speeds. The experiments were carried out in the forced convection heating chamber of the Mechanical Spectrometer, which maintained temperature control to within ± 0.2°K. A silicone oil bath was constructed to support the sample, but was found unnecessary as the high viscosity material was easily supported by the heated air stream used for temperature control.

With the apparatus of Figure 2, a constant extension rate given by

$$\Gamma = \frac{WD}{2L} \tag{6}$$

is attained if the sample deforms uniformly and incompressibly between the clamp and the winder rod. Here, D is the winder diameter, W is the constant winder rotational speed, and L is the sample length. Under these conditions, the total extensional strain ϵ increases linearly with time, i.e.,
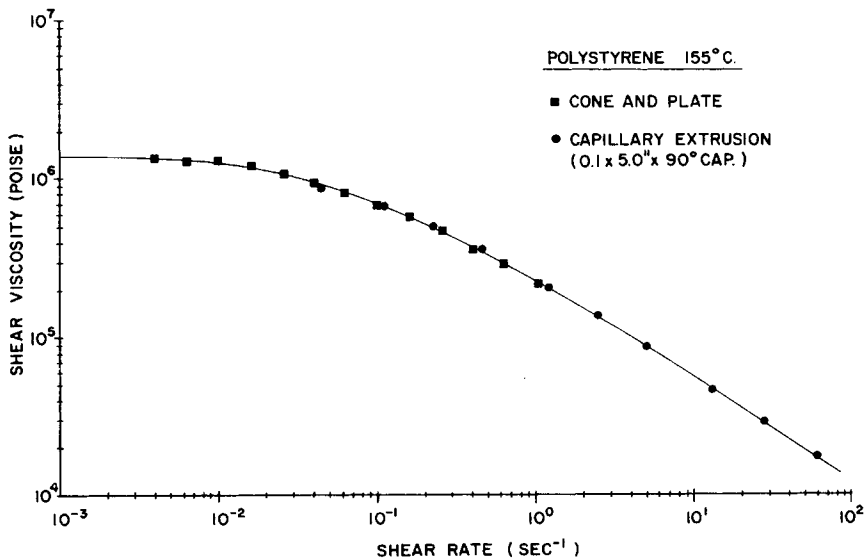
$$\epsilon = \ln(x/x_0) = \Gamma t$$

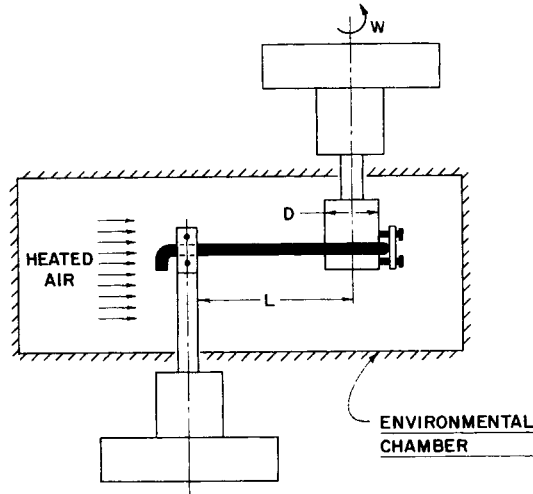Fig. 1. Steady shear viscosity vs. shear rate for amorphous polystyrene at 155°C.

Fig. 2. Experimental apparatus for extensional viscosity measurement, $D = 1.651$ cm, $L = 2.0$ cm.

where x and x_0 are lengths of material elements at time t and zero, respectively. Neglecting gravity, inertia, and surface tension effects, the normal stress difference in the sample is given by

$$S_{11} - S_{22} = \frac{F(t)}{A(t)} \tag{7}$$

where $F(t)$ is the measured tensile force and $A(t)$ is the sample cross-sectional area. For this flow, $A(t)$ attenuates according to the following expression:

$$A(t) = A_0 \exp(-\Gamma t) \tag{8}$$

where A_0 is the initial cross-sectional area. Thus, from eq. (3), the extensional viscosity is given
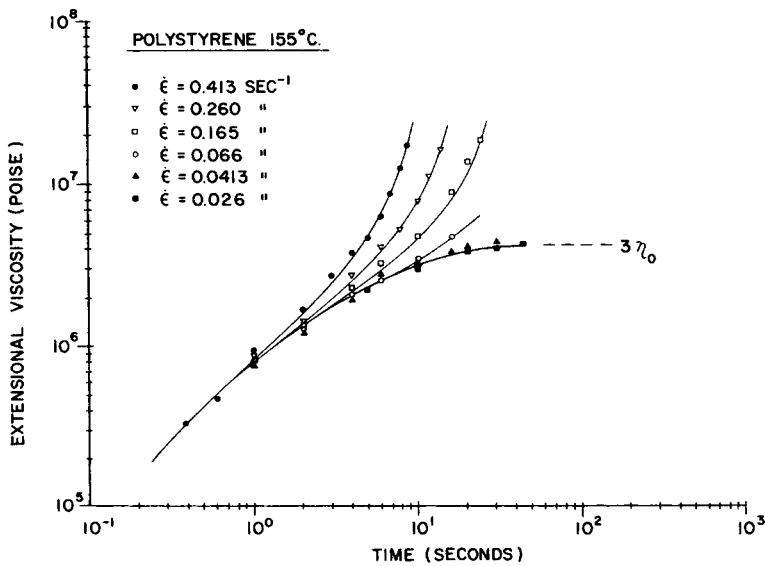

Fig. 3. Extensional viscosity of amorphous polystyrene at 155°C.

TABLE I
Critical Total Strain at Onset of Rapid Stress Growth

Material	Extension rate, sec^{-1}	Critical total strain[a]
Amorphous polystyrene at 155°C	0.413	0.8
(present work)	0.260	1.0
	0.165	1.0
	0.066	0.9
Linear polyethylenes at 180°C[10]	1.15	0.9
(M-1 and M-2)	0.461	0.9
	0.115	0.9
	0.0726	0.8
Low-density polyethylene at 150°C[9]	1.00	0.8
(melt I)	0.50	0.8
	0.10	0.9
	0.05	1.0
	0.01	1.0

[a] Total strain at which stress attained level 10% greater than linear viscoelastic curve.

by

$$\bar{\eta}(t) = \frac{F(t)}{\Gamma A_0 \exp(-\Gamma t)}. \tag{9}$$

The extensional viscosity results for the amorphous polystyrene are presented in Figure 3. Here we have plotted extensional viscosity versus time for a series of extension rates and have also indicated the experimentally measured Trouton viscosity $3\eta_0$. The results are quite similar to those previously obtained using crystallizable polymers. At the lower extension rates, the extensional viscosity attains a steady-state value of $3\eta_0$, as would be expected of a linear viscoelastic material. At higher extension rates, however, a rapid transient stress growth is observed with no steady-state viscosity level attained.

It is also interesting to note that the onset of the rapid stress growth in the present experiments occurred at an approximately constant value of the total strain. Similar observations were reported by Meissner[8] for a low-density polyethylene, and the data presented by Macosco and Lorntson[9] for two linear polyethylenes also indicate a similar result. In Table I, we have tabulated the critical total Hencky strain at which the observed stress level attained a value 10% greater than the linear viscoelastic (i.e., low extension rate) curve for all of these materials. The results indicate that the critical total strain at the onset of the rapid stress growth is essentially independent of the extension rate and has an approximately constant value of 0.9 for all of these materials. The apparent independence of the critical strain on detailed polymer structure suggests that the rapid stress growth may be due to the deformation of an entanglement network structure, having the same degree of chain extensibility due to tortuosity between entanglement points, which is presumably present in all flexible polymeric materials of sufficiently high molecular weight to entangle. Indeed, Cogswell[12] has observed that a wide variety of polymeric materials exhibit a constant *maximum* recoverable extensional Hencky strain of approximately 2.0, which further suggests that an elastic deformation of a network structure may occur which is essentially independent of the particular polymer involved.

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