

# NOTES

## *Viscous Heating Effects In Polymer Mechanochemistry*

### INTRODUCTION

Alberghini and Sukanek<sup>1</sup> suggested that viscous dissipation could play a major role in the analysis of mechanical degradation experiments and could perhaps be responsible for the observed changes in molecular weight. They examined a model degradation experiment in a capillary rheometer and calculated the average rate of degradation across the capillary cross section. The rate of reaction was taken to be an exponential function of temperature with a positive activation energy. Temperature profiles in the capillary were assumed to be fully developed and the viscosity to be an exponential function of temperature. They found that the rate of degradation when plotted against the wall temperature had the same temperature dependence as is observed in practice: the rate decreased, passed through a minimum, and increased as the capillary wall temperature increased. The calculated maximum temperatures were sufficiently high to cause thermal degradation based on a comparison with oven experiments.<sup>2</sup> In addition, the calculated temperatures at which the rate was a minimum were close to the observed values for polystyrene, natural rubber, and polyisobutene.

Casale<sup>3</sup> attempted to refute these arguments. His reasoning, which is also given in the recent comprehensive book on the entire area of mechanochemistry,<sup>4</sup> is not conclusive. Some data on surface temperatures in rubber mastication were presented which showed that viscous dissipation was important. However, it is impossible to determine the actual polymer temperature, as opposed to the surface temperature, from these data. Casale also noted that in the experiments of Whitlock and Porter<sup>5</sup> more degradation was observed near the capillary wall than at the centerline, where the temperatures calculated by Alberghini and Sukanek<sup>1</sup> were a maximum. This, too, does not rule out a purely thermal mechanism since as the capillary wall departs from isothermal behavior, the maximum temperature moves closer to the wall. Indeed, Gerrard, Stiedler, and Appeldoorn<sup>6</sup> indicated that the true behavior of a capillary wall was more nearly adiabatic than isothermal. Finally, apparently through a misinterpretation of one of the curves in reference 1, Casale indicated that the viscosity of a fluid in an experiment such as described in reference 1 would be a double-valued function of wall temperature. This, however, is not the case.<sup>7</sup>

The purpose of this note is to present some data on temperature effects in a mechanochemistry experiment. As will be seen, the data clearly indicate that the observed temperature rise, which is in agreement with calculations based on viscous dissipation, is well below what would be required to achieve any thermal degradation.

### EXPERIMENTAL

All experiments were performed using Vistanex LM-MS polyisobutene (PIB) supplied by Exxon Chemical Company. The samples were sheared in a Contraves Model RM-30 rotational viscometer using cup-and-bob measuring system E. The bob radius was 0.002, m, and the cup radius, 0.0075 m. The cup was surrounded by a constant-temperature jacket through which water was circulated by a Haake Model FT constant-temperature circulator. Wall temperatures in the range of 30° to 90°C were investigated.

PIB was loaded into the cup and the bob inserted. The sample was allowed to sit for approximately 2 hr before a run was begun. The bob was set in motion at one of the 30 possible rotational speeds. Torque was recorded with time on a Hewlett-Packard Model 7044-A *x-y* plotter. At the end of the run, the bob was slowly raised and a small sample of polymer adhering to the bob was removed. Degradation was determined by changes in the intrinsic viscosity of PIB in toluene at 30°C, where molecular weight and intrinsic viscosity are related by<sup>8</sup>

$$[\eta] = 0.02M_{2w}^{0.67}. \quad (1)$$

Chromel–constantan thermocouples were used to measure polymer temperature. The thermocouple wires, with a diameter of about  $10^{-4}$  m, were passed through two holes in a ceramic shaft. The bead diameter was about three times that of the wire. The ceramic shaft was attached to a traverser which could move vertically in the annular region between the cup and bob, as well as across this region. Vertical distance was measured by means of etchings on the bob shaft. Distance from the bob was indicated by a micrometer.

No temperature measurements were made while the polymer was flowing because of the disturbances to the flow field caused by the thermocouple. Rather, after the flow had proceeded for some time, the bob was stopped and the thermocouple inserted. Because of the low thermal diffusivity of the material ( $\alpha \sim 10^{-7}$  m<sup>2</sup>/sec), the temperature profiles, once established, take a relatively long time to return to the constant, no-flow condition. Since the time for insertion and measurement of temperature is much shorter than the thermal relaxation time, the thermocouple reading gave an approximate indication of the temperature rise resulting from viscous dissipation.

## RESULTS AND DISCUSSION

### Flow Behavior and Observed Degradation

The observed flow behavior of the PIB, with a nominal molecular weight of approximately 70,000, is shown in Figure 1. These data show both a temperature dependence as well as a shear rate dependence. Since the temperature profiles which result from viscous dissipation take a relatively long time to develop (see below), the temperature and shear rate effects can be separated.

This viscosity function has meaning only after the flow is fully developed. While in a purely viscous fluid, the time to achieve steady state is relatively fast (on the order of  $10^{-6}$  sec); viscoelastic materials take a longer time (on the order of 10 sec). At short times, elastic effects become important. At and above some critical shear rate, the stress overshoots the equilibrium level. Such behavior was observed for the PIB used in this study. Typical shear stress–time histories are shown in Figure 2 for several shear rates.

Shear degradation experiments were carried out at a variety of temperatures, shear rates, and exposure times. The data are in agreement with previous reports. At low shear rates, no degradation occurs. As the shear rate is increased, the extent of the degradation increases. This behavior is illustrated in Figure 3, which shows the intrinsic viscosity versus shear rate at 50°C. As the temperature increases, the degradation decreases. This latter observation is indicative of the negative activation energy of mechanochemical reactions.

### Viscous Heating Effects

In order to determine the possible effects of the temperature rise from viscous dissipation on the observed degradation, the temperature profile in the instrument was predicted as well as measured. Three factors may be important in this assessment: the time required for the temperature profiles

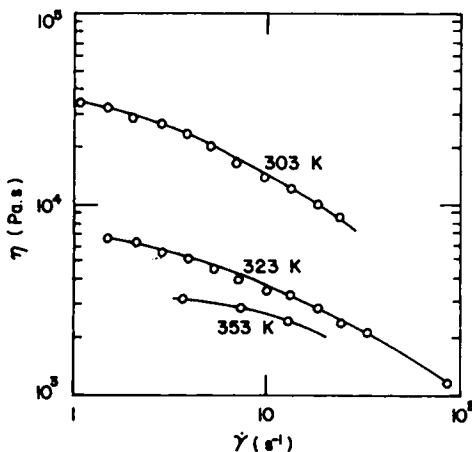


Fig. 1. Viscosity–shear rate behavior of PIB.

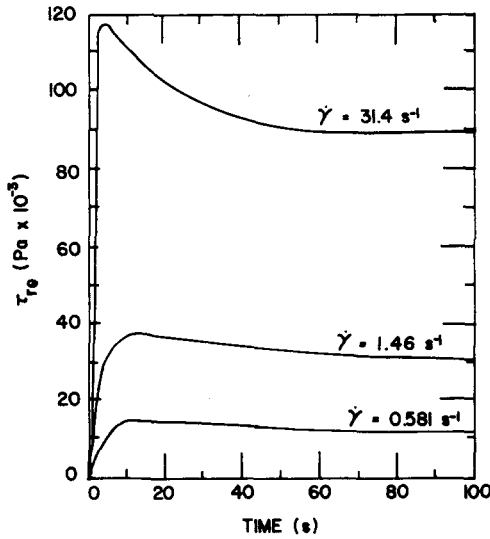


Fig. 2. Stress overshoot observed at  $60^\circ\text{C}$  for various shear rates.

to reach their steady-state values, the effect of the stress overshoot on the temperature profiles, and the magnitude of the final temperature rise.

To obtain a first estimate of the relative importance of the first two parameters (i.e., time and overshoot), a particularly simple geometry and constitutive equation for the fluid can be employed. Consider the plane Couette flow of a fluid whose shear stress–shear rate behavior can be described by

$$\tau + \lambda \frac{\partial \tau}{\partial g} = \eta_0 \Delta + \sigma \Delta^2 \tag{2}$$

where  $\partial/\partial t$  is the convected or Oldroyd derivative.

Equation (2) is by no means a realistic equation for the PIB melt examined in this study, and its use is in no way meant to imply its acceptance as a viable model. Nonetheless, this simplified equation does demonstrate two features important in the present context. The viscosity is a function of shear rate:

$$\eta = \eta_0 \left( 1 - \frac{\sigma \dot{\gamma}_\infty^2 \lambda}{\eta_0} \right) \tag{3}$$

and the stress does overshoot the steady-state value for a jump in shear rate from 0 to  $\dot{\gamma}_\infty$ :

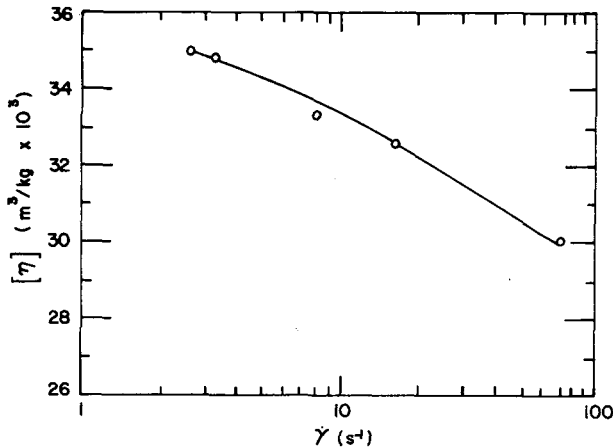


Fig. 3. Changes in intrinsic viscosity (molecular weight) as a function of shear rate at  $50^\circ\text{C}$ .

$$\eta^+(t, \gamma_\infty) = \eta_0 \left[ \left( 1 - \frac{\sigma \dot{\gamma}_\infty^2 \lambda}{\eta_0} \right) (1 - e^{-t/\lambda}) + \frac{\sigma \dot{\gamma}_\infty^2 \lambda}{\eta_0} \frac{t}{\lambda} e^{-t/\lambda} \right] \quad (4)$$

Assume that the two plates are separated by a distance  $h$ , and at time  $t = 0$  the upper plate starts to move in the  $x$ -direction with a velocity  $U$ . If the velocity profile develops much more rapidly than the temperature profile and there is no elastic contribution to the internal energy of the fluid, the temperature distribution is governed by

$$\frac{\partial \vartheta}{\partial \tau} = \frac{\partial^2 \vartheta}{\partial \xi^2} + (1 - B)(1 - e^{-\Omega \tau}) + B \Omega \tau e^{-\Omega \tau} \quad (5)$$

where

$$\begin{aligned} \vartheta &= \frac{k(T - T_0)}{\eta_0 U^2} \\ \xi &= y/h \\ \tau &= tk/\rho C_p h^2 \\ B &= \frac{\sigma U^2 \lambda}{h^2 \eta_0} \\ \Omega &= \frac{\rho C_p h^2}{k \lambda} \end{aligned} \quad (6)$$

The solution to eq. (5) for isothermal boundaries is

$$\begin{aligned} \vartheta = \sum_{n=0}^{\infty} \frac{4 \sin l\pi \xi}{l\pi} \left\{ (1 - B) \left[ \frac{1 - e^{-l^2 \pi^2 \tau}}{l^2 \pi^2} - \frac{e^{-\Omega \tau} - e^{-l^2 \pi^2 \tau}}{l^2 \pi^2 - \Omega} \right] \right. \\ \left. + \frac{B}{(l^2 \pi^2 - \Omega)^2} \left[ e^{-\Omega \tau} [(l^2 \pi^2 - \Omega)\tau - 1] + e^{-l^2 \pi^2 \tau} \right] \right\} \end{aligned} \quad (7)$$

where

$$l = 2n + 1 \quad (8)$$

At steady state ( $\tau \rightarrow \infty$ ), the temperature profile is given by

$$\vartheta_\infty = \frac{1 - B}{2} (\xi - \xi^2) \quad (9)$$

In order to estimate the history of the temperature profiles, the parameters  $B$  and  $\Omega$  must be

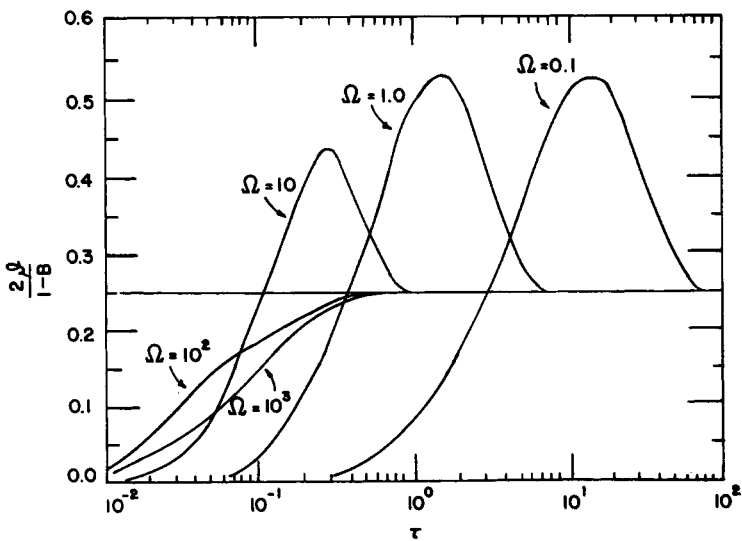


Fig. 4. Predicted centerline temperature vs. time in plane Couette flow for a fluid given by eq. (3).

TABLE I  
Predicted and Measured Temperature Rise from Viscous Heating

$T_0$ , K	$\dot{\gamma}_N^a$ , sec <sup>-1</sup>	$\mu_{app}^d$ , Pa-sec	Newtonian fluid		Power law fluid		Measured $\Delta T$ , K
			constant viscosity		variable viscosity		
			$\Delta T_{ISO}^b$ , K	$\Delta T_{AD}^c$ , K	$\Delta T_{ISO}$ , K	$\Delta T_{AD}$ , K	
303	12.5	$1.38 \times 10^4$	5	31	0.8	26	5
313	78.9	2070	30	184	0.2	20	7
323	78.9	1940	28	173	2.5	31	9

<sup>a</sup> Newtonian shear rate.

<sup>b</sup> Assuming the inner cylinder is isothermal.

<sup>c</sup> Assuming the inner cylinder is adiabatic.

<sup>d</sup> Apparent (Newtonian) viscosity.

specified.  $B$  is a measure of the non-Newtonian effects in the fluid. The larger  $B$  is ( $0 \leq B < 1$ ), the more shear thinning the fluid and the larger the magnitude of the stress overshoot. The parameter  $\Omega$  is the ratio of thermal times ( $h^2/\alpha$ ) and elastic times ( $\lambda$ ) for the fluid. To find these parameters, the values of the "material constants,"  $\lambda$  and  $\sigma$ , are required. These can be estimated by using the time at which the maximum shear stress is reached ( $\sim 10$  sec) and the magnitude of the overshoot relative to the steady-state value ( $\sim 2$ ). With these numbers and assuming  $\eta_0 \sim 10^4$  Pa-sec and  $\dot{\gamma}_\infty \sim 80$  sec<sup>-1</sup>, the values of  $\lambda$  and  $\sigma$  are 8 sec and 0.156 Pa-sec<sup>2</sup>, respectively. Using the density, thermal conductivity, and heat capacity of PIB reported in reference 8, the parameters  $B$  and  $\Omega$  are

$$B = 0.8 \quad (10)$$

$$\Omega = 4.5 \times 10^3$$

Figure 4 shows the variation of the maximum temperature with time for several values of the parameter  $\Omega$ . As expected, for small  $\Omega$  the temperature profiles develop fairly quickly compared to the stress profiles, and so the overshoot in stress is manifested by a similar overshoot in temperature. However, for large  $\Omega$ , which is more characteristic of real fluids, the temperature profiles develop essentially independently from the stress profiles. In the present experiments stress overshoot does not affect the temperature. It is sufficient to examine the steady-state profiles. Also, it should be noted that eq. (7) predicts that the steady-state profiles will be achieved at a dimensionless time  $\tau$  of about 0.5. With the properties of PIB and the system geometry, this corresponds to  $t \cong 230$  sec.

An estimate of the steady-state temperature rise brought about by viscous heating may be obtained by extending the theory of Gavis and Laurence<sup>9</sup> to account for shear rate-dependent viscosity. For the present material, a power law model was used. Table I compares the calculated maximum temperature rise using this theory with the temperature rise predicted for a Newtonian fluid with temperature-independent viscosity\* for three different outer wall temperatures. Also shown in the table is the measured value of  $\Delta T$  for each case. As can be seen, the assumption of constant viscosity leads to a significant overprediction of the temperature increase. The measured temperature falls within the extremes of isothermal and adiabatic inner cylinders. Had a more exact boundary condition been employed,<sup>7</sup> the agreement would be much improved.

In any event, it is the magnitude of the temperature rise which is important in the present context of degradation. This temperature rise is certainly too small to result in any thermally induced degradation. In addition, the time scale over which mechanical degradation takes place ( $\leq 60$  sec for the present experiments) is much less than the time required to develop the temperature profiles. Viscous heating, while it may in some circumstances augment the mechanical degradation observed experimentally, cannot be the sole cause of bond rupture in shear.

\* The Newtonian viscosity used in these calculations was the ratio of the measured shear stress to the apparent shear rate.

References

1. D. P. Alberghini and P. C. Sukanek, *J. Appl. Polym. Sci.*, **16**, 1701 (1972).
2. K. Arisawa and R. S. Porter, *J. Appl. Polym. Sci.*, **14**, 879 (1970).
3. A. Casale, *J. Appl. Polym. Sci.*, **19**, 1461 (1975).
4. A. Casale and R. S. Porter, *Polymer Stress Reactions*, Academic Press, New York, 1978, pp. 96-101.
5. L. R. Whitlock and R. S. Porter, *J Polym. Sci. A2*, **10**, 877 (1972).
6. J. D. Gerrard, F. E. Stiedler, and J. K. Appeldoorn, *Ind. Eng. Chem., Fundam.*, **4**, 332 (1965).
7. P. C. Sukanek and R. L. Laurence, *AIChE J.*, **20**, 474 (1974).
8. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, p. IV-8.
9. J. Gavis and R. L. Laurence, *Ind. Eng. Chem., Fundam.*, **7**, 232 (1968).

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Received October 19, 1978  
Revised July 10, 1979

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