

## Tensile Yield-Stress Behavior of Poly(vinyl Chloride) and Polycarbonate in the Glass Transition Region

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### Synopsis

The yield-stress behavior of two glassy polymers is studied through the glass transition region over a wide range of strain rates. For temperatures below the glass transition temperature, the yield stress behavior could be described as a non-Newtonian flow in agreement with Eyring's theory, if one excepts a narrow range relating to the slowest strain rates. For temperatures above  $T_g$ , the yield-stress behavior is still nonlinear but fits the relations based on the concept of free volume.

### INTRODUCTION

In a previous paper,<sup>1</sup> the tensile yield stress behavior of polycarbonate and poly(vinyl chloride) (PVC) over a fairly wide range of temperatures and rates of strain below the glass temperature  $T_g$  was reported. It was shown that at the yield stress, glassy polymers exhibit viscous flow which is in agreement with the generalized theory of Eyring.<sup>2</sup>

We have now studied in detail the tensile yield-stress behavior of these same two polymers through the glass transition region.

### EXPERIMENTAL

Experimental conditions and procedure were the same as described previously;<sup>1</sup> they are briefly recalled here.

The tensile stress-strain curves were obtained with an Instron tensile machine. The temperature was regulated by using an Instron environmental chamber and measured with a thermometer placed near the specimen in the chamber. The tests were made after the specimen had remained in the chamber for half an hour at the required temperature. The yield stress was taken as the peak or maximum stress on the stress-strain curve. At the yield point, strain rates were calculated from the crosshead speed. The values obtained agree well with extensometer determinations.

Tests specimens of Makrolon polycarbonate (Bayer) were cut from commercially available sheets 0.2 cm thick; the length of the specimens was 4 cm and their width 0.8 cm. Tests specimens of Solvic 227 PVC (Solvay et Cie) were 0.18 cm thick, 4 cm long, and 0.8 cm wide.

## RESULTS

The results of the measurements on the polycarbonate and PVC specimens are shown in Figures 1 and 2, where the ratio of the yield stress  $\sigma_y$ , to the absolute temperature  $T$  is plotted versus  $\log \dot{\epsilon}$  ( $\dot{\epsilon}$  denotes strain rate) for each of several constant temperatures both above and below  $T_g$ . Each point on the graph corresponds to the mean value of three tests. At each

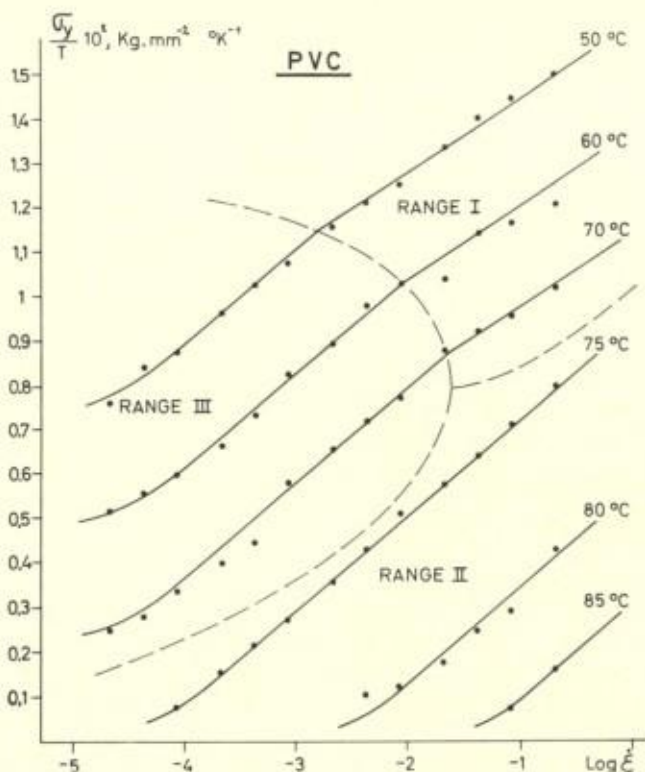


Fig. 1. Measured ratio of yield stress  $\sigma_y$  to temperature as a function of logarithm of strain rate ( $\dot{\epsilon}$  in  $\text{sec}^{-1}$ ). The dashed lines indicate the frontiers between three ranges (highly schematic). The curves in range I are calculated from eq. (2). The curves in range II are the set of parallel curves which best fits the experimental data. The curves in range III are a best fit of the experimental data.

temperature, we have found the existence of a critical strain rate below which the yield point disappears from the tensile curve; it was therefore not possible to measure the yield stress over the entire range of available rates. We give in Figure 3 examples of tensile curves of three types: (a) with a well defined yield point; (b) with a vanishing yield point; (c) without definite elastic limit.

We can measure at each temperature a critical value of  $\sigma_y$  corresponding to the critical strain rate at which the yield point vanishes. For tests performed at temperatures above  $T_g$ , the critical yield stress is very small.

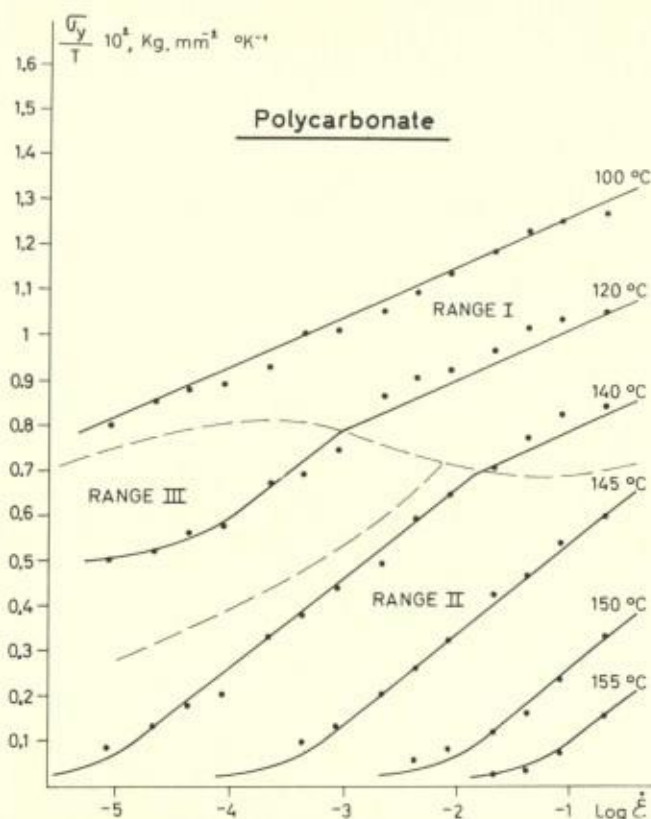


Fig. 2. Measured ratio of yield stress  $\sigma_y$  to temperature as a function of logarithm of strain rate ( $\dot{\epsilon}$  in  $\text{sec}^{-1}$ ). The dashed lines indicate the boundaries between three ranges (highly schematic). The curves belonging to range II are the set of parallel curves which best fit the experimental data. The curves belonging to range III are a best fit of the experimental data.

We can roughly separate the graphs of Figures 1 and 2 into three different ranges indicated as I, II, and III on the figures. Each of these ranges is discussed below.

## DISCUSSION

The yield point of a tensile curve has the appearance of a momentary condition of viscous flow because there, the rate of change of stress is zero although the strain is increasing at a constant rate. At this point the strain does not exceed 2% and appears to be uniform. Some authors, including Lazurkin,<sup>3</sup> Robertson,<sup>4</sup> Roetling,<sup>5-7</sup> and ourselves,<sup>1,8</sup> have made the assumption that pure viscous flow just begins at this point; this amounts to neglect of the processes whose contribution is insignificant compared to the viscous one.

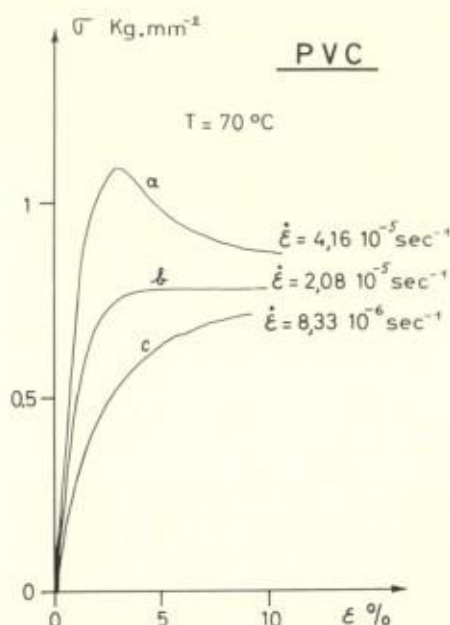


Fig. 3. Illustrative examples of stress-elongation curves obtained near the glass temperature at different strain rates: (a) with a well defined yield point; (b) with a vanishing yield point; (c) without definite elastic limit.

### Curves Belonging to Range I

The authors mentioned above have shown that the yield stress behavior of glassy polymers below  $T_g$  may be fairly well described by the Eyring equation of non-Newtonian flow.<sup>2</sup> In the Eyring theory, deformation is a rate process which corresponds in high polymers to the jump of segments of macromolecules. When no stress is acting, the jump frequency  $J$  may be written:

$$J = J_0 \exp \left\{ -Q/RT \right\} \quad (1)$$

where  $J_0$  is a rate constant containing an entropy factor,  $Q$  is the activation energy, and  $R$  is the universal gas constant.

If a stress is applied, Eyring derives from eq. (1) an expression for the shear rate. In tensile tests, we must write Eyring's equation for normal stresses and take into account the relations between normal and shear stresses and between normal and shear rates as established by Bauwens.<sup>9</sup>

In the special case where

$$\sinh x \approx \frac{1}{2} \exp \{x\}$$

and when a single process is involved in the deformation, the following expression for the yield stress is derived:

$$\begin{aligned} \sigma_y/T &= (4\sqrt{3}k/v_0\gamma_0) [\ln (\sqrt{3}/2\gamma_0 J_0 \dot{\epsilon} + (Q/RT))] \\ &= A [\ln 2 C \dot{\epsilon} + (Q/RT)] \end{aligned} \quad (2)$$

where  $v_0$  is the shear volume,  $\gamma_0$  is the elementary shear strain,  $k$  is Boltzmann's constant, and  $A$  and  $C$  are given by

$$A = 4\sqrt{3k/v_0\gamma_0}$$

$$C = \sqrt{3/4}\gamma_0 J_0$$

The segments of parallel straight lines within range I in Figures 1 and 2, have been calculated from eq. (2), with values of the constants  $A$ ,  $C$ , and  $Q$  taken from our previous work.<sup>1</sup> These values are recalled in Table I and were so chosen as to give the best fit of eq. (2) to the data over a range of temperatures from  $(T_g - 120^\circ\text{C})$  to  $(T_g - 20^\circ\text{C})$ .

TABLE I  
Constants of Equation (2)

	$A \times 10^4$ , kg/mm <sup>2</sup> °K	$C$ , sec	$Q$ , kcal/mole
Polycarbonate	4.16	$10^{-21}$	75.5
PVC	7	$10^{-28}$	70.5

From the reasonably good agreement between calculated and experimental values, it appears that range I corresponds to the glassy state where the Eyring theory can be applied. This theory is valid over an interval of temperatures covering at least  $120^\circ\text{C}$  for both materials.

In range I, let  $\log a_1(T)$  be the horizontal distance between two segments of parallel straight lines corresponding to temperatures  $T_1$  and  $T_2$ , with  $T_1 < T_2$ . It then follows from eq. (2) that  $\log a_1(T)$ , which we may call the shift factor relating to range I, is given by

$$\log a_1(T) = (Q/2.303 R)[(1/T_1) - (1/T_2)] \quad (3)$$

### Curves Belonging to Range II, $T \geq T_g$

For the strain rates we have considered, the data corresponding to temperatures above  $T_g$  no longer fit the curves derived from eq. (2). However, if one considers the data of Figures 1 and 2 for range II, it is possible to represent this data by a set of parallel curves for temperatures  $T \geq T_g$ . Except at very small stresses, these parallel curves may be considered as straight lines.

As these curves are parallel, they fit the time-temperature-superposition principle; let  $\log a_{II}(T)$  be the shift factor. In Figure 4 we have plotted  $\log a_{II}(T)$  versus  $\Delta T$  for both materials ( $\Delta T$  was chosen equal to  $T - 75.7^\circ\text{C}$  for PVC and  $T - 141^\circ\text{C}$  for polycarbonate; according to these values of  $\Delta T$  the points on the graph follow the same curve for both materials).

In order to give an interpretation of the curves  $\sigma_y/T = f(\ln \dot{\epsilon})$  for  $T \geq T_g$  and of the graph of Figure 4, we will apply the treatment of Fox<sup>10a</sup> to give a justification of the semiempirical WLF relation.

According to Eyring<sup>11</sup> and Bueche,<sup>12</sup> the activation energy  $Q$  in relations (1), (2), and (3) may be considered the sum of two terms: the one represents the energy required to make a void, the other, very much smaller, represents the energy a segment needs to free itself from its neighbors and move into the void. For temperatures above  $T_g$ , the free volume is no longer frozen in; it can therefore diffuse and form voids according to the

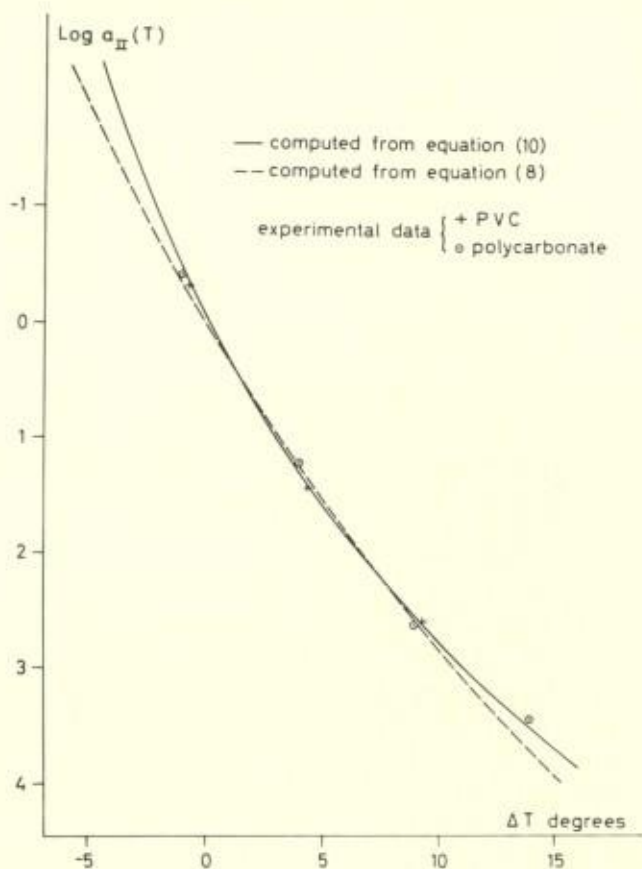


Fig. 4. A plot of  $\log a_{II}(T)$  vs.  $\Delta T$  for both materials. Experimental data are compared to theoretical equations.

theories based on the free volume concept. Then, for the elementary jump process, no more energy is required to create voids. The activation energy is, in this case, reduced to  $Q_{II}$ , the activation energy a segment requires to break loose from its neighbors. The jump frequency, however, will strongly depend on the probability  $Z(T)$  that the segment is vibrating in the proper direction at just the right time to enter a void constituted by the meeting of holes. The jump frequency is then related to the number of

holes present in the material and must be highly temperature-sensitive; eq. (1), valid in the glassy range, becomes for temperatures above  $T_g$ :

$$J = v_0 Z(T) \exp \{-Q_{II}/RT\} \quad (4)$$

where  $v_0$  is the vibration frequency of a segment.

From eq. (4) we may derive an expression for  $\sigma_y/T$  by analogy with the methods used previously in the glassy range, the desired expression is:

$$\begin{aligned} \sigma_y/T &= (4\sqrt{3} k/\sigma_{v0II}\gamma_{0II}) [\ln (\sqrt{3}/2\gamma_{0II}v_0)\dot{\epsilon} + (Q_{II}/RT) - \ln Z(T)] \quad (5) \\ &= A_{II} [\ln 2C_{II}\dot{\epsilon} + (Q_{II}/RT) - \ln Z(T)] \end{aligned}$$

where  $A_{II}$  and  $C_{II}$  differ from the previous  $A$  and  $C$  because the size of the segment relating to the deformation process above  $T_g$  may differ from the size of the segment relating to the deformation process in the glassy range.

From eq. (5) we obtain the following expression for  $\log a_{II}(T)$ , if we reduce the curves to temperature  $T_g$ :

$$\log a_{II}(T) = (Q_{II}/2.303R) [(1/T_g) - (1/T)] + \log Z(T) - \log Z(T_g) \quad (6)$$

The problem is now to evaluate  $Z(T)$  and different theories may be applied. If it is assumed that:

$$Z(T) = \exp \{-V/\phi\} \quad (7)$$

where  $V$  is the volume of a void a segment needs to jump and  $\phi$  the average free volume per segment, Cohen and Turnbull<sup>13</sup> find for  $\log Z(T)$  an expression which may be identified with the WLF relation. If we make the same assumption, eq. (6) becomes:

$$\begin{aligned} \log a_{II}(T) &= [Q_{II}(T - T_g)/2.303RTT_g] \\ &\quad + \{17.44 (T - T_g)/[51.6 + (T - T_g)]\} \quad (8) \end{aligned}$$

In previous work Bauwens<sup>14</sup> has made a different assumption to explain the segmental mobility above  $T_g$ . The following mechanism of deformation was proposed. Above  $T_g$ , the jump of a segment of a macromolecule requires a void formed by the meeting of  $n_0$  holes at least. According to the theory of Gibbs and di Marzio,<sup>15</sup> the increase of the fractional free volume  $\alpha$  formed by holes may be evaluated, so that the value of  $\log Z(T)$  calculated near  $T_g$  is:

$$\log Z(T) = n_0 \log \alpha = n_0 \log (T - T_0) + K \quad (9)$$

where  $K$  is a constant and  $T_0$  the temperature at which  $\alpha$  vanishes. In this case, eq. (6) reduced to temperature  $T_g$  becomes:

$$\log a_{II}(T) = [Q_{II}(T - T_g)/2.303RTT_g] + n_0 \log [(T - T_0)/(T_g - T_0)] \quad (10)$$

On the graph of Figure 4 we have drawn the curve computed from eq. (8) neglecting the first term, which varies only insignificantly with  $T$ . The values of  $T_g$  are given in Table II; they are obtained from the curve

TABLE II  
 Constants of Equations (5), (8), and (10)

	$T_g$ , °C		$T_0$ from eq. (10), °C	$A_{II} \times 10^4$ , kg/mm <sup>2</sup> °K (measured)
	From eq. (8)	Deter- mined dila- tometri- cally		
PVC	75.7	75	64.6	9.4
Polycar- bonate	141	143	129.9	8.7

which agrees best with the data. The values of  $T_g$  determined dilatometrically<sup>16,17</sup> are given for comparison.

We have also drawn on the same graph the curve computed from eq. (10), neglecting the first term. We have taken  $n_0 = 10$ , which is a quite reasonable value according to different methods of computation.<sup>10b</sup> The values of  $T_0$  estimated by assuming that eq. (10) was applicable, are given in Table II.

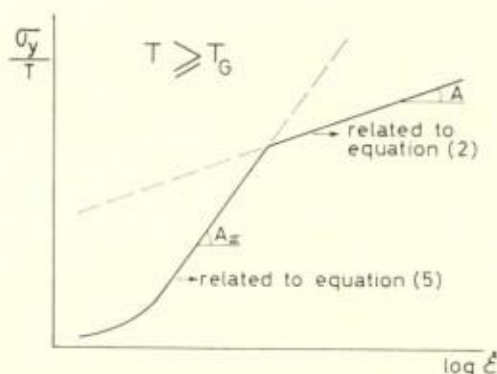


Fig. 5. Possible yield behavior above the glass temperature. At sufficiently high strain rates, Eyring's mechanism of deformation becomes the most probable.

In the range of temperatures explored, the two curves obtained from eqs. (8) and (10) are very close together and both fit the data fairly well. Equation (8), as well as eq. (10), seems to be valid here, although the stresses are relatively high and the behavior is nonlinear.

As the presumed value of  $Q_{II}$  is very small (a few kilocalories, according to Fox<sup>10a</sup>) it was not possible to measure it or the constant  $C_{II}$  which depends on  $Q_{II}$ . Only the slope  $A_{II}$  of  $\sigma_y/T = f(\log \dot{\epsilon})$  at  $T \geq T_g$  can be evaluated: the results are given in Table II. It will be noted that  $A_{II}$  is greater than  $A$ , the slope in range I. Therefore at a given temperature  $T \geq T_g$ , a critical strain rate may exist above which the Eyring process is the most probable (this case is represented schematically in Fig. 5). Our results do not reveal the existence of this critical rate; perhaps, because



we have not reached sufficiently high strain rates. However the results of Roetling<sup>6</sup> on poly(ethylmethacrylate), have shown that the Eyring viscosity theory may still be valid above the glass temperature.

### Curves in Range III

Unfortunately we are not able yet to give an interpretation of the segments of curves within range III. These curves exhibit a well defined asymptote which depends on the temperature and relates to the fading of the yield point (the tensile stress-strain curves corresponding to the data of region III are of the *b* type: see Fig. 3). Because of the existence of this level, it was not possible to apply the time-temperature superposition principle. It may be that the slope  $\sigma_y/T = f(\log \dot{\epsilon})$  is equal to  $A_{II}$ , but this is not certain because range III is narrow and results are more scattered than in the other ranges.

### CONCLUSIONS

(1) Tensile curves obtained in the glass transition region may exhibit a well defined yield point, even at temperatures above  $T_g$ .

(2) In the range of strain rates we have explored, the curves  $\sigma_y/T = f(\log \dot{\epsilon})$  at  $T \geq T_g$  fit the time-temperature superposition principle. Though the behavior is nonlinear, the shift factor agrees with the relations based on the concept of free volume (the WLF equation, for example).

(3) The yield stresses obtained at temperatures just below  $T_g$  fit the Eyring theory fairly well, if one excepts a narrow range (range III) relating to the slowest strain rates.

(4) The molecular process involved in the deformation at the yield point in range I (Eyring's theory) differs from the molecular process involved in the deformation at the yield point in range II (theories based on the concept of free volume), because the slope of  $\sigma_y/T = f(\log \dot{\epsilon})$  differs from one range to the other.

(5) It may happen that the yield stresses still fit the Eyring theory even above the glass transition temperature  $T_g$ , provided the strain rates are sufficiently high.

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