

# Temperature and Strain Rate Dependence of the Tensile Yield Stress of PVC

FRANCISCO POVOLO, GUSTAVO SCHWARTZ, and ÉLIDA B. HERMIDA

Depto. de Física, Fac. de Ciencias Exactas y Naturales (UBA), Pabellón I, Ciudad Universitaria, 1428 Buenos Aires, Argentina; and Depto. de Materiales, Comisión Nacional de Energía Atómica, Av. del Libertador 8250, 1429 Buenos Aires, Argentina

## SYNOPSIS

Data on the tensile yield behavior of poly(vinyl chloride) (PVC), reported in the literature, are interpreted in terms of a model involving a cooperative movement of several independent structural units, all with the same activation enthalpy. This analysis leads to physical parameters such as the internal stress, activation volume, and enthalpy, etc. These values are discussed and compared with those determined from thermodynamical considerations using stress relaxation tests and tensile curves at a constant strain rate. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Bauwens-Crowet et al.<sup>1</sup> reported data on the temperature and strain rate dependence of the tensile yield stress of PVC. According to the authors, the data could be described by an equation derived from the Ree-Eyring theory:

$$\frac{\sigma}{T} = A_{\alpha} \left[ \ln(2C_{\alpha}\dot{\epsilon}) + \frac{Q_{\alpha}}{kT} \right] + A_{\beta} \sinh^{-1} \left( C_{\beta}\dot{\epsilon} \exp \left[ \frac{Q_{\beta}}{kT} \right] \right) \quad (1)$$

where  $\sigma$  is the yield stress,  $\dot{\epsilon}$  the strain rate,  $T$  the absolute temperature,  $k$  Boltzmann's constant and  $Q_{\alpha}$ ,  $Q_{\beta}$  the activation energies for the  $\alpha$  and  $\beta$  transitions, respectively. The yield stress against log (strain rate) curves, at different temperatures, could be fitted by eq. (1) with the following values for the parameters:

$$A_{\alpha} = 68.6 \times 10^{-4} \text{ MPa/K}$$

$$Q_{\alpha} = 249.7 \text{ kJ/mol}; \quad C_{\alpha} = 10^{-38} \text{ s}$$

$$A_{\beta} = 98.98 \times 10^{-4} \text{ MPa/K};$$

$$Q_{\beta} = 58.52 \text{ kJ/mol}; \quad C_{\beta} = 4.26 \times 10^{-10} \text{ s}$$

The set of parallel  $\sigma/T$  against  $\log \dot{\epsilon}$  curves, at each temperature, can be looked upon as generated by the shift of one curve along line  $d$ , which joins the intersections of the asymptotes of the  $\sigma(\dot{\epsilon})$  curves at each temperature. In this way the authors built a master curve for a reference temperature of 273 K. The slope of the straight line  $d$  was found to be

$$\mu = \frac{\Delta(\sigma/T)}{\Delta(\log \dot{\epsilon})} = -6.37 \times 10^{-2} \text{ MPa/K}$$

The master curve covers several decades of the strain rate scale and it is possible to extrapolate the yield stress to rates which cannot be reached experimentally. Furthermore, Bauwens-Crowet et al.<sup>1</sup> interpreted the data in terms of two processes:

- the  $\alpha$  range, below the straight line  $d$ , where the second term of eq. (1), containing the parameters of the  $\beta$ -process, can be neglected. The molecular motions which take place under the action of the yield stress in this range may correspond to translations of the main chains.

- the  $\beta$  range, above  $d$ , where the two terms of eq. (1) are important. Furthermore, the intersection of every  $\sigma/T$  against  $\log \dot{\epsilon}$  curve with  $d$  has, according to the authors, the character of a secondary transition, that is, the  $\beta$  transition. This secondary transition is associated to local relaxation movements of the macromolecular chains.

Similar considerations were made by Bauwens-Crowet<sup>2</sup> for data of the yield stress against  $\log$  strain rate of poly(methyl methacrylate) (PMMA). Fotheringham and Cherry,<sup>3,4</sup> however, described the yield stress of PMMA and PVC using a model based on  $n$  activated rate processes. They determined the probability of a successful cooperative event as the product of the probabilities of the simultaneous occurrence of the  $n$  transitions. That is to say, they considered that the yield stress of a cooperative system has the strain rate dependence of a single activated rate process, but to the  $n$ th power. More recently, Povoło and Hermida<sup>5</sup> have discussed in detail the different models used to describe the temperature and strain rate dependence of the yield stress of PMMA. It was concluded that the data can be very well described as a cooperative movement of several independent structural units, all with the same activation enthalpy.

It is the purpose of this paper to show that also the tensile yield stress of PVC can be described with the same cooperative model and the physical parameters obtained (activation volume and enthalpy and internal stress) are discussed and compared with the values obtained through a thermodynamic analysis of the plastic deformation of glassy polymers.

### Theoretical Considerations

According to the cooperative model, the relationship between the yield stress and the strain rate is given by<sup>3,4</sup>

$$\dot{\epsilon} = \dot{\epsilon}^* \sinh^n \left[ \frac{(\sigma - \sigma_i)v}{2kT} \right] \quad (2)$$

where  $\sigma_i$  is the internal stress associated to the elastic recovery process before and after yield and  $v$  is the activation volume. Furthermore, an Arrhenius temperature dependence for  $\dot{\epsilon}^*$  is usually assumed, that is,

$$\dot{\epsilon}^* = \dot{\epsilon}_0 e^{-\Delta H/kT} \quad (3)$$

being  $\dot{\epsilon}_0$  the preexponential factor and  $\Delta H$  the activation enthalpy of the cooperative process. From eq. (2) it follows that

$$\frac{\sigma}{T} = \frac{\sigma_i}{T} + B \sinh^{-1} \left[ \left( \frac{\dot{\epsilon}}{\dot{\epsilon}^*} \right)^{1/n} \right] \quad (4)$$

with  $B = 2k/v$ . Thus, eq. (4) describes the yield stress against  $\log \dot{\epsilon}$  curves for the cooperative model. This equation, however, has four adjustable parameters:  $n$ ,  $\sigma_i$ ,  $B$ , or  $v$  and  $\dot{\epsilon}^*$ . Since each individual curve, measured at a given temperature, covers only few decades of the  $\log \dot{\epsilon}$  scale, it is difficult to determine the parameters for a single curve. This problem can be solved on building a master curve, that is, on superposing the individual segments onto one measured at a temperature  $T_s$ . In fact, the master curve covers several decades of the strain rate scale and lets to determine the parameters of eq. (4) with greater accuracy. The scaling conditions for this equation have been discussed elsewhere,<sup>5</sup> together with the procedure employed to calculate the parameters. Briefly, the derivative of eq. (4) can be represented in a normalized plot<sup>6</sup> as

$$y = \frac{x}{n} + \frac{1}{2} \log(1 + 10^{2x/n}) \quad (5)$$

with

$$x = \log \dot{\epsilon} - \log \dot{\epsilon}^*$$

and

$$y = \log \left( \frac{\partial \sigma}{\partial \log \dot{\epsilon}} \Big|_T \right) - \log \left( \frac{2.303B}{n} \right)$$

Eq. (5) has only one adjustable parameter:  $n$ . Hence, if the derivative of the master curve represented in a double-log plot can be superposed onto one of the curves of  $y$  against  $x$ , given by eq. (5)—only by horizontal and vertical translations—the parameters  $n$ ,  $B$ , and  $\dot{\epsilon}^*$  of eq. (4) can be established. Effectively,  $n$  comes out straightforward from the parameter of the curve fitted to the derivative of the master curve. The horizontal and vertical shifts needed to superpose the origin of both coordinate systems give  $\log \dot{\epsilon}^*$  and  $\log(2.303B/n)$ , respectively. Once  $n$ ,  $B$ , and  $\dot{\epsilon}^*$  are known, going back to eq. (4), the internal stress is determined in order to provide a good fit to the experimental points of the master curve. Furthermore, the scaling conditions lead to the following

relationship between the parameters of eq. (4) and the translation paths

$$\begin{aligned}\sigma_i &= (\mu \log \dot{\epsilon}^* + C)T \\ &= \mu \left[ T \log \dot{\epsilon}_0 - \frac{\Delta H}{2.303k} \right] + CT \quad (6)\end{aligned}$$

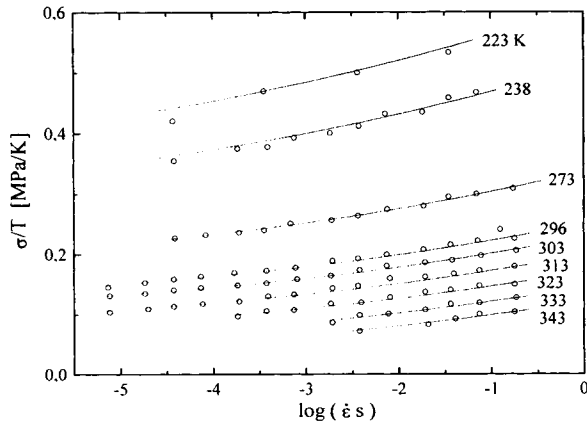
$$\log \dot{\epsilon}^*(T) = \log \dot{\epsilon}^*(T_s) - \Delta \log \dot{\epsilon} \quad (7)$$

$$\frac{\sigma_i(T)}{T} = \frac{\sigma_i(T_s)}{T_s} - \Delta \left( \frac{\sigma}{T} \right) \quad (8)$$

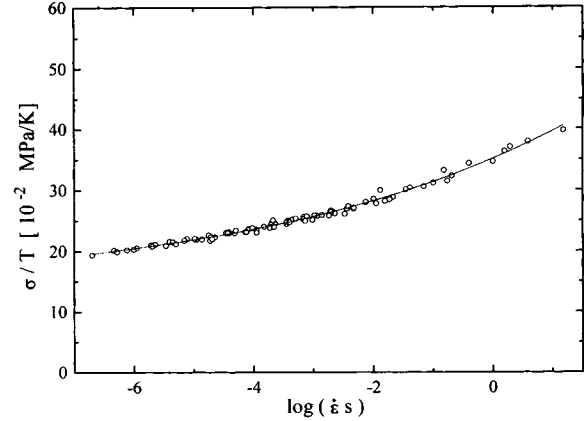
where  $\Delta \log \dot{\epsilon}$  and  $\Delta(\sigma/T)$  are the horizontal and vertical shift paths used to superpose the curve measured at a temperature  $T$  onto the master curve at  $T_s$ ;  $\mu$  is the slope of the translation path used to build the master curve. Then, once  $\sigma_i(T_s)$  and  $\dot{\epsilon}^*(T_s)$  are known for the master curve it is possible to determine these parameters for each of the individual curves by using eqs. (7) and (8).

## RESULTS

The tensile yield data for PVC reported by Bauwens-Crowet et al.<sup>1</sup> are shown in Figure 1. The experimental details are indicated in the original publication. A computer program described elsewhere<sup>7</sup> was used to obtain the master curve and the translation paths, finding essentially the same values as those reported by Bauwens-Crowet et al. It is noticed that the shape of the master curve obtained through this program is independent of the temperature chosen as reference. The master curve for  $T_s = 273$



**Figure 1** Tensile yield data, at the indicated temperatures, for PVC<sup>1</sup>. The full curves correspond to eq. (2) with the parameters given in Tables I and II.



**Figure 2** Master curve of the segments represented in Figure 1, built at 273 K, with the translation paths given by Bauwens-Crowet et al.<sup>1</sup>

K is shown in Figure 2. Its derivative was fitted to eq. (5) leading to the values of  $n$ ,  $\log \dot{\epsilon}^*$  and  $v$  indicated in Table I. Also  $\sigma_i$ , as determined from eq. (4), is given in the same table. It should be pointed out that the parameters of Table I fit not only the master curve of Figure 2 but also its derivative. The quality of the fitting to the master curve through eq. (4) is indicated by the full curve in the same figure. Once the parameters of the master curve, that is at  $T = T_s$ , are known, it is possible to determine the parameters at the other temperatures by using eqs. (7) and (8) and the translation paths  $\Delta \log \dot{\epsilon}$  and  $\Delta(\sigma/T)$  reported by Bauwens-Crowet et al.<sup>1</sup>. The results obtained in this way are indicated in Table II and the fitting to the individual curves is represented by the full curves of Figure 1. Figure 3 shows that the parameter  $\log \dot{\epsilon}^*$  of the individual yield curves is linearly related to  $1/T$ . In fact, a least square fitting of this representation gives a straight line with an excellent correlation coefficient, that is, the Arrhenius dependence given in eq. (3) is verified with the values of  $\dot{\epsilon}_0$  and  $\Delta H$  detailed in Table I. Finally, the values of  $\Delta H$ ,  $\dot{\epsilon}_0$  and  $\mu$  given in Table I and the values of  $\sigma_i$  given in Table II lead to the average value of  $C$  for eq. (6) indicated in Table I. Thus, the temperature dependence of  $\sigma_i$  results

$$\sigma_i(T) = \sigma_i(0) + (C + \mu \log \dot{\epsilon}_0) T \quad (9)$$

with

$$\sigma_i(0) = -\frac{\mu \Delta H}{2.303k} = 195.4 \text{ MPa} \quad (10)$$

**Table I Parameters for the Master Tensile Yield Curve of PVC<sup>1</sup> at 273 K**

$n = 10$	$\nu = 0.105 \text{ nm}^3$
$\sigma_i = 42.8 \text{ MPa}$	$\log(\dot{\epsilon}^* \text{ s}) = 1.3$
$\mu = -6.37 \times 10^{-2} \text{ MPa/K}$	$C = 0.24 \text{ MPa/K}$
$\log(\dot{\epsilon}_0 \text{ s}) = 12.47$	$\Delta H = 58.5 \text{ kJ/mol}$

## DISCUSSION

### The Two Processes and the Cooperative Model

In the model proposed by Bauwens-Crowet et al.<sup>1</sup> and Bauwens<sup>8</sup> the analysis in terms of eq. (1) leads to abnormally high values for the reciprocal of the frequency factor and the activation energy for the  $\alpha$ -process, namely,  $C_\alpha$  and  $Q_\alpha$ . A comparison between the yield stress data and the loss peak in the  $\beta$ -transition rate for PVC leads also to inconsistencies, the same as those determined for an equivalent analysis of the yield stress curves of PMMA.<sup>5</sup> These points have been discussed very recently<sup>5</sup> and will not be repeated here.

Fotheringham and Cherry<sup>3</sup> have used the master curve of Bauwens-Crowet et al.,<sup>1</sup> reduced to 353 K, to fit the data of the yield stress of PVC to eq. (2). This temperature was selected since it can be reasonably assumed that  $\sigma_i = 0$ . The author used a computer to optimize the parameters obtaining  $n = 7.69$  and  $\nu = 0.18 \text{ nm}^3$ . No information was given about  $\dot{\epsilon}^*$ . These parameters, however, do not fit the derivative of the master curve. In fact, a much higher activation volume is needed to fit the derivative of the master curve of Figure 2 of Fotheringham and Cherry's paper<sup>3</sup> to eq. (5). In other words, the parameters proposed by these authors do not fit both

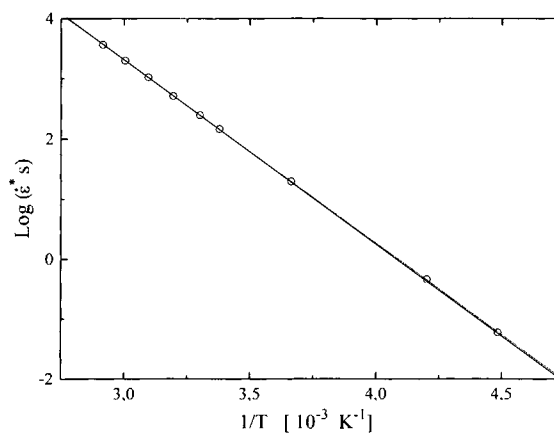
the master curve and its derivative, which is not the case when the master curve of Figure 2 is fitted to eq. (4) with the parameters given in Table I. In effect, there are some inconsistencies with the parameters proposed by these authors. However, the cooperative model with the parameters determined in this paper describes all the features of the master curve.

### Thermally Activated Process

It is interesting to compare the results obtained in this work with those given by a kinetic and thermodynamic analysis of plastic flow in polymeric glasses. Haussy et al.,<sup>9</sup> Escaig<sup>10</sup> and Lefebvre and Escaig<sup>11</sup> have studied the thermally activated deformation of glassy polymers. Pink<sup>12,13</sup> and Pink et al.<sup>14,15</sup> have applied this formalism to analyze the plastic deformation of PVC. All these authors have used the procedure developed by Schoek<sup>16</sup> for a thermodynamic analysis of the rate equation for dislocations moving by thermal activation under internal and external stresses. Cagnon<sup>17</sup> has extended this formalism by suggesting a new procedure to determine the Gibbs free energy from the stress dependence of the activation volume. According to the thermal activation analysis, the plastic strain rate is given by

**Table II Horizontal [ $\Delta \log(\dot{\epsilon})$ ] and Vertical [ $\Delta(\sigma/T)$ ] Shift Paths, and Parameters of Individual Yield Curves Measured at Temperature  $T$** 

$T$ (K)	$\Delta \log(\dot{\epsilon} \text{ s})$	$\Delta(\sigma/T)$ (MPa/K)	$\log(\dot{\epsilon}^* \text{ s})$	$\sigma_i$ (MPa)
223	2.52	-0.164	-1.22	71.5
238	1.64	-0.107	-0.34	62.8
273	0	0	1.30	42.8
296	-0.87	0.056	2.17	29.8
303	-1.1	0.072	2.40	25.7
313	-1.42	0.093	2.72	20.0
323	-1.73	0.112	3.03	14.5
333	-2.01	0.131	3.31	8.6
343	-2.27	0.148	3.57	3.0

**Figure 3**  $\log \dot{\epsilon}^*$  against  $1/T$  according to Table II. The full line corresponds to eq. (3) with the parameters given in Table I.

$$\dot{\epsilon} = \tilde{\epsilon}_0(\sigma, T) \exp\left[-\frac{\Delta G_a(\sigma, T)}{kT}\right] \quad (11)$$

where  $\tilde{\epsilon}_0(\sigma, T)$  is the preexponential factor and  $\Delta G_a(\sigma, T)$  is the Gibbs free activation energy, both assumed to be stress and temperature dependent. The true activation volume is

$$V_a = -\left.\frac{\partial \Delta G_a}{\partial \sigma}\right|_{T, \text{Struct.}} \quad (12)$$

which gives the size of the activation event, that is, the number of atoms activated coherently.

Struct. means any structural variable. The apparent activation enthalpy is

$$\Delta H_0 = kT^2 \left.\frac{\partial \ln \dot{\epsilon}}{\partial T}\right|_{\sigma, \text{Struct.}} \quad (13)$$

which, according to eq. (11) reduces to

$$\Delta H_0 = \Delta G_a + T\Delta S_a + kT^2 \left.\frac{\partial \ln \tilde{\epsilon}_0}{\partial T}\right|_{\sigma, \text{Struct.}} \quad (14)$$

where  $\Delta S_a$  is the activation entropy. Escaig establishes that eq. (14) becomes simply<sup>10</sup>

$$\Delta H_0 = \Delta G_a + T\Delta S_a = \Delta H_a \quad (15)$$

with  $\Delta H_a$  the true activation enthalpy "if the temperature derivative of  $\tilde{\epsilon}_0$  is taking as negligible when compared with  $\Delta H_a$ ; for, it should usually be screened out by the dominant exponential  $T$ -dependence from the  $\Delta G_a$  term. Therefore, as far as  $\Delta H_0$  is measured under condition of constant microstructure, we can have good confidence in taking it for the true activation enthalpy  $\Delta H_a$ ."<sup>10</sup>

The apparent activation volume is given by

$$V_0 = kT \left.\frac{\partial \ln \dot{\epsilon}}{\partial \sigma}\right|_{T, \text{Struct.}} \quad (16)$$

Let us assume that the structure is constant, then  $\dot{\epsilon}$  is only a function of  $\sigma$  and  $T$  [see eq. (11)]; because of that, in what follows the subscript Struct. will be dropped from eqs. (12) to (14) and (16). Consequently, a Maxwell-type relationship for the deformation rate is written as

$$d(\ln \dot{\epsilon}) = \left.\frac{\partial \ln \dot{\epsilon}}{\partial T}\right|_{\sigma} dT + \left.\frac{\partial \ln \dot{\epsilon}}{\partial \sigma}\right|_T d\sigma \quad (17)$$

so that, making  $\dot{\epsilon} = \text{constant}$  [ $d(\ln \dot{\epsilon}) = 0$ ] and substituting eqs. (13) and (16) into the derivatives it follows

$$\Delta H_0 = -TV_0 \left.\frac{\partial \sigma}{\partial T}\right|_{\dot{\epsilon}} \quad (18)$$

It is generally assumed in the literature<sup>9-17</sup> that the stress and temperature dependence of  $\tilde{\epsilon}_0$  of eq. (11) can be neglected, in comparison with the much stronger dependence of  $\Delta G_a$  on these variables, in such a way that  $\Delta H_0 \approx \Delta H_a$  and  $V_0 \approx V_a$ . Then, eq. (18) can be used to calculate  $\Delta H_a$  from tensile data, obtained at  $\dot{\epsilon} = \text{constant}$ .  $V_0$  can be obtained either through the changes in the strain rate during the tensile test or through stress relaxation experiments. All the previous concepts will be applied to the constitutive equation used in this paper to describe the tensile yield behavior of PVC, that is, to eq. (2). On differentiating this equation it is easy to show that

$$V_0 = \frac{nv}{2} \left( \tanh\left[\frac{(\sigma - \sigma_i)v}{2kT}\right] \right)^{-1} \quad (19)$$

and

$$\begin{aligned} \Delta H_0 &= \Delta H - \frac{nv}{2} \left[ \sigma - \sigma_i + T \frac{d\sigma_i}{dT} \right] \left( \tanh\left[\frac{(\sigma - \sigma_i)v}{2kT}\right] \right)^{-1} \\ &= \Delta H - V_0 \left[ \sigma - \sigma_i + T \frac{d\sigma_i}{dT} \right] \end{aligned} \quad (20)$$

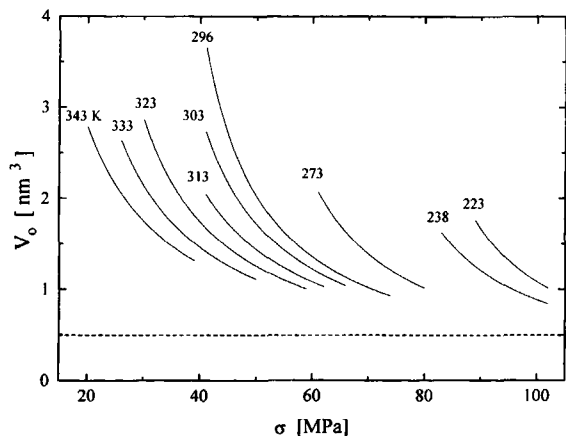
with  $n$ ,  $v$ ,  $\Delta H$  and  $\sigma_i$  given in Tables I and II. On taking into account eq. (9), eq. (20) can be rewritten as

$$\Delta H_0 = \Delta H - V_0[\sigma - \sigma_i(0)] \quad (21)$$

Furthermore, it can be easily shown that eqs. (20) or (21) are equivalent to eq. (18).

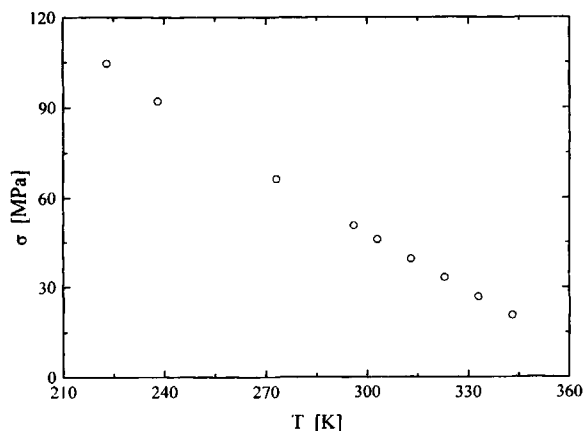
### Correlation Between Parameters Determined from Stress Relaxation or Tensile Tests and Using the Constitutive Equation

The activation volumes, calculated with eq. (19), are shown in Figure 4 against stress. Pink<sup>12,13</sup> and Pink et al.<sup>14,15</sup> have measured the apparent activation volume of PVC through tensile and stress relaxation experiments. The values shown in Figure 4 are quite

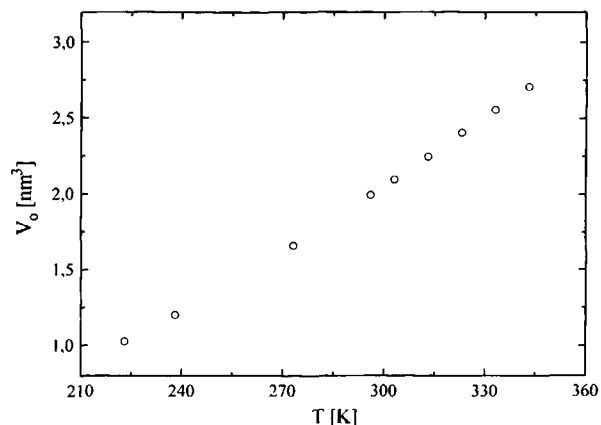


**Figure 4** Apparent activation volume against yield stress calculated with eq. (19).

similar to those reported in Figure 10 of Pink et al.<sup>15</sup> as obtained by stress relaxation in PVC. The values obtained by analyzing the stress relaxation data through Feltham's method<sup>18</sup> are quite similar to the limiting value  $nv/2$  of eq. (19), when  $[(\sigma - \sigma_i)v/2kT] \gg 1$ . This asymptotic value is indicated by the broken straight line in Figure 4. Feltham's method is based on the assumption that the stress relaxation curves give a linear plot  $\sigma$  (log time). Pink<sup>13</sup> calculated the activation enthalpy by using eq. (18) and the temperature dependence of the yield point, both in tension and compression, at a strain rate of  $3.4 \times 10^{-4} \text{ s}^{-1}$ . The activation volumes were measured by strain rate changes, at the same initial strain rate at each temperature. In our constitutive equation, the yield stress, at a fixed strain rate, can be expressed as a function of temperature on considering eq. (4) with  $\dot{\epsilon} = 3.4 \times 10^{-4} \text{ s}^{-1}$  and the calculated parameters  $\sigma_i$ ,  $v$ ,  $n$  and  $\dot{\epsilon}^*$ . The values obtained for the yield stress

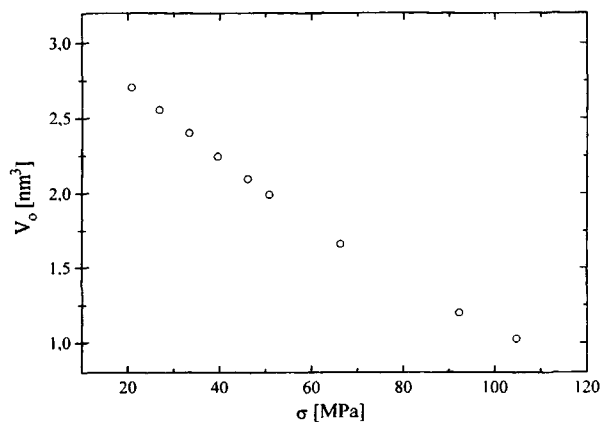


**Figure 5** Tensile yield stress against temperature at  $\dot{\epsilon} = 3.4 \times 10^{-4} \text{ s}^{-1}$ , calculated with eq. (4).

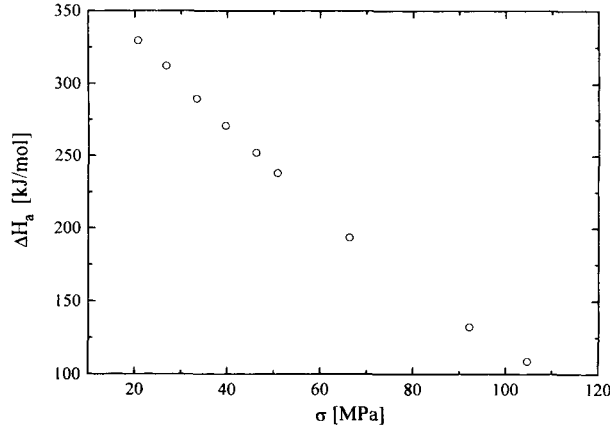


**Figure 6** Temperature dependence of the apparent activation volume at  $\dot{\epsilon} = 3.4 \times 10^{-4} \text{ s}^{-1}$ .

at this strain rate are indicated in Figure 5; they result quite similar to those of Figure 2 of Pink<sup>13</sup> at the same temperatures. Moreover, eq. (19) and (4) are employed also to calculate the apparent activation volumes at constant strain rate; these values are represented in Figure 6 as a function of temperature and in Figure 7 as a function of stress. Again, Figure 7 agrees with the dependence calculated by Pink,<sup>13</sup> and shown in Figure 5 of his paper. By using eqs. (4), (16), and (21) it is possible to calculate the activation enthalpy at a fixed strain rate. The results, obtained for  $\dot{\epsilon} = 3.4 \times 10^{-4} \text{ s}^{-1}$  and represented in Figure 8 as a function of  $\sigma$ , exhibit a good concordance with the ones reported in Figure 6 of Pink.<sup>13</sup> Furthermore, according to Figure 8, for very low stresses,  $\Delta H_o$  tends to have a limiting value of the order of 361 kJ/mol. This value is nearly the same as the one suggested by Pink when  $\sigma$  tends to zero<sup>13</sup>:  $\Delta H_o \approx \Delta H_a \approx 5.6 \times 10^{-19} \text{ J}$  (337 kJ/mol).



**Figure 7** Apparent activation volume against yield stress at  $\dot{\epsilon} = 3.4 \times 10^{-4} \text{ s}^{-1}$ .



**Figure 8** Apparent activation enthalpy against the yield stress at  $\dot{\epsilon} = 3.4 \times 10^{-4} \text{ s}^{-1}$ .

According to Schoek,<sup>16</sup> the Gibbs free activation energy is given by

$$\Delta G_a = \frac{\Delta H_0 + \sigma V_0 T (d \ln \mathcal{G} / dT)}{1 - T (d \ln \mathcal{G} / dT)} \quad (22)$$

where  $\mathcal{G}$  is the shear modulus.  $\Delta G_a$  calculated using eq. (22) with the values of  $\sigma$ ,  $V_0$  and  $\Delta H_0$  given in Figures 5, 6 and 7 and  $\mathcal{G} = E/3$ , being  $E$  the Young's modulus as determined by Pink<sup>13</sup>—up to 300 K through a tensile test at  $\dot{\epsilon} = 3.4 \times 10^{-4} \text{ s}^{-1}$ —is shown in the curve (a) of Figure 9. Curve (b) in Figure 9 shows the values of  $\Delta G_a$  obtained with the same equation but with the shear modulus determined by Heijboer,<sup>19</sup> in a more extended interval of temperatures with a torsion pendulum at a frequency of the order of 1 Hz. The value of  $\Delta G_a$  obtained with the shear modulus of Pink are quite similar to those reported by this author in Figure 8 of his paper.<sup>13</sup> In summary, it can be stated that the activation parameters obtained by using the constitutive equation given by the cooperative model are quite similar to those obtained through tensile and stress relaxation experiments. Pink et al.<sup>15</sup> have measured the internal stresses as a function of temperature in PVC through stress relaxation experiments. The reported values are slightly higher than those given in Table II. The author, however, have pointed out that the stress relaxation was not completed and the internal stress was extrapolated, certainly obtaining higher values than the real ones.

Finally, it is noticed that recent stress relaxation experiments in PVC<sup>20</sup> performed at stresses below the yield stress lead to internal stresses quite similar to those given in Table II.

### Comparison Between the Cooperative and the Thermal Activation Models

According to eq. (11) the apparent activation volume is given by

$$V_0 = kT \left. \frac{\partial \ln \tilde{\epsilon}_0}{\partial \sigma} \right|_T - \left. \frac{\partial \Delta G_a}{\partial \sigma} \right|_T \quad (23)$$

and the apparent activation enthalpy by

$$\Delta H_0 = kT^2 \left. \frac{\partial \ln \tilde{\epsilon}_0}{\partial T} \right|_\sigma - T^2 \left. \frac{\partial (\Delta G_a / T)}{\partial T} \right|_\sigma \quad (24)$$

If  $\tilde{\epsilon}_0$  is constant, on combining eqs. (23) and (24) with eqs. (19) and (20) it follows

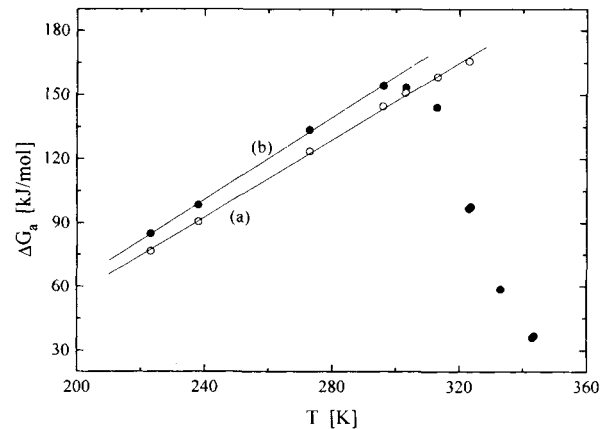
$$-\left. \frac{\partial \Delta G_a}{\partial \sigma} \right|_T = \frac{nv}{2} \left( \tanh \left[ \frac{(\sigma - \sigma_i)v}{2kT} \right] \right)^{-1} \quad (25)$$

and

$$\begin{aligned} -T^2 \left. \frac{\partial (\Delta G_a / T)}{\partial T} \right|_\sigma \\ = \Delta H - \frac{nv}{2} [\sigma - \sigma_i(0)] \left( \tanh \left[ \frac{(\sigma - \sigma_i)v}{2kT} \right] \right)^{-1} \end{aligned} \quad (26)$$

Furthermore, the integration of eq. (25) gives

$$-\Delta G_a = nkT \ln \left\{ \sinh \left[ \frac{(\sigma - \sigma_i)v}{2kT} \right] \right\} + F(T) \quad (27)$$



**Figure 9** Gibbs free activation energy against temperature calculated using eq. (22) with the modulus reported by: (○) Pink<sup>13</sup> and (●) Heijboer.<sup>19</sup> The full lines—(a) and (b)—are the linear regressions of both curves at low temperatures.

where  $F(T)$  is a function of temperature. On substituting eq. (27) into eq. (26) it results

$$F(T) = -\Delta H + \text{constant} \quad (28)$$

which, replaced into eq. (27) and taking into account eqs. (2) and (3) finally gives

$$\begin{aligned} \Delta G_a &= kT \ln(\dot{\epsilon}_0/\dot{\epsilon}) + \text{constant} \\ &= kT \ln(\dot{\epsilon}_0/\dot{\epsilon}) + \Delta G_0 \\ &= \alpha kT + \Delta G_0 \end{aligned} \quad (29)$$

with

$$\alpha = \ln(\dot{\epsilon}_0/\dot{\epsilon}) \quad (30)$$

Eq. (30) with  $\dot{\epsilon} = 3.4 \times 10^{-4} \text{ s}^{-1}$  and the value of  $\dot{\epsilon}_0$  given in Table I leads to

$$\alpha_t = 36.7 \quad (31)$$

The slope of the straight line of Figure 9(a) gives

$$\alpha_a = 7.32 \quad (32)$$

and the one of curve (b) leads to

$$\alpha_b = 8.14 \quad (33)$$

The values of  $\alpha$  given by eqs. (32) and (33) are much lower than the theoretical value given by eq. (30). Furthermore, according to Escaig,<sup>10</sup> on reverting eq. (11) it is possible to write at constant strain rate

$$\Delta G_a = kT \ln(\dot{\epsilon}_0/\dot{\epsilon}) = \alpha kT \quad (34)$$

with  $\alpha$  of the order of 20 for thermoplastics and strain rates between  $10^{-4}$  and  $10^{-5} \text{ s}^{-1}$ . Eq. (34) assumes that  $\dot{\epsilon}_0$  does not depend on temperature. On comparing eqs. (34) and (29) it is easy to show that both equations are equal only if

$$\dot{\epsilon}_0 = \dot{\epsilon}_0 e^{\Delta G_0/kT} \quad (35)$$

which is incompatible with the assumption made in eq. (34), that is,  $\dot{\epsilon}_0$  independent of  $T$ .

In summary, there are some inconsistencies in the assumption that  $\dot{\epsilon}_0$  of eq. (11) does not depend neither on  $\sigma$  nor on  $T$  and, consequently, in the calculation of  $\Delta G_a$  by means of eq. (22). Moreover, if the material obeys the constitutive eq. (2) then, if  $(\sigma - \sigma_i)v/2kT \ll 1$ ,

$$\sinh\left[\frac{(\sigma - \sigma_i)v}{2kT}\right] \approx \left[\frac{(\sigma - \sigma_i)v}{2kT}\right]$$

and

$$\dot{\epsilon} = \dot{\epsilon}_0 \left[\frac{(\sigma - \sigma_i)v}{2kT}\right]^n e^{-\Delta H/kT} \quad (36)$$

showing that, in this limit, eq. (2) is equivalent to eq. (11) with a constant activation free energy and a preexponential factor which depends on  $\sigma$  and  $T$ . In the other limit, that is, when  $(\sigma - \sigma_i)v/2kT \gg 1$ , eq. (2) reduces to

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp\{-[\Delta H - nv(\sigma - \sigma_i)]/2kT\} \quad (37)$$

establishing that eq. (2) is equivalent to eq. (11) with an activation free energy depending on stress and temperature—through  $\sigma_i$ —and a constant preexponential factor. The problem is that in our experimental range, that is, in the range of stresses and temperatures covered by Figure 1,  $(\sigma - \sigma_i)v/2kT$  varies between approximately 0.1 and 0.7 showing that none of the limits imposed by eqs. (36) and (37) are satisfied. In this situation it is difficult to reduce eq. (2) to eq. (11) and the values of  $V_a$ ,  $\Delta H_a$  and  $\Delta G_a$  obtained through the thermal activation analysis should be considered with caution. Further work is needed in order to solve this problem.

It is also interesting to point out that Pink<sup>13</sup> observed that “. . . the deformation cannot be studied below 185 K since brittle fracture takes place in a pre-yield region. The variation of this ductile-brittle transition temperature with strain rate can be analyzed in terms of an Arrhenius equation leading to a pre-exponential value of  $10^{12} \text{ s}^{-1}$  and to an “activation energy” of 62.3 kJ/mol.” These values are very closed to those of  $\dot{\epsilon}_0$  and  $\Delta H$  indicated in Table I.

Finally, it is pointed out that eq. (2) gives more information on the material than a simple tensile curve of the yield stress vs. temperature, at constant strain rate. Effectively, eq. (2) relates the mechanical variables  $\sigma$ ,  $\sigma_i$ , and  $\dot{\epsilon}$  with temperature, leading to describe not only tensile tests but also other mechanical experiments.

## CONCLUSIONS

In this paper, a cooperative model based on the simultaneous evolution of  $n$  independent processes is applied to tensile yield data in PVC. The constitutive



equation associated to this model is characterized by four parameters:  $\sigma_i$ ,  $n$ ,  $\dot{\epsilon}^*$ , and  $v$ . These parameters are calculated not only for the master curve but for the individual segments as well, providing a good fitting of the experimental data. Furthermore, the translation paths employed to build a master curve let to establish that  $\dot{\epsilon}^*$  is thermally activated, giving an activation enthalpy.

On the other hand, thermodynamic parameters such as the apparent activation volume and enthalpy and the Gibbs free energy are calculated using the constitutive equation. These values are in good agreement with the ones determined from stress relaxation curves and  $\sigma(T)$  plots at constant  $\dot{\epsilon}$ .

Consequently, the improvements of the constitutive equation to characterize the tensile yield evolution of PVC are clear since this equation not only enables to calculate thermodynamic parameters but also provides an analytical relationship between the temperature and the mechanical variables.

This work has been supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), the Proyecto Multinacional de Investigación y Desarrollo en Materiales OAS-CNEA, the Fundación Antorchas and the University of Buenos Aires.

## REFERENCES

1. C. Bauwens-Crowet, J. C. Bauwens, and G. Homés, *J. Polym. Sci.*, **7**, Part A-2, (1969).
2. C. Bauwens-Crowet, *J. Mater. Sci.*, **8**, 968 (1973).
3. D. Fotheringham and B. W. Cherry, *J. Mater. Sci. Lett.*, **11**, 1368 (1976).
4. D. Fotheringham and B. W. Cherry, *J. Mater. Sci. Lett.*, **13**, 951 (1978).
5. F. Povolò and É. B. Hermida, *J. Appl. Polym. Sci.*, **58**, 55 (1995).
6. F. Povolò, *J. Nucl. Mater.*, **96**, 178 (1981).
7. É. B. Hermida and F. Povolò, *Polymer J.*, **26**, 1054 (1994).
8. J. C. Bauwens, *J. Polym. Sci.*, **33**, Part C, 123 (1971).
9. J. Haussy, J. P. Cavrot, B. J. Escaig, and J. M. Lefebvre, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 311 (1980).
10. B. J. Escaig, in *Plastic Deformation of Amorphous and Semi-Crystalline Materials*, B. J. Escaig and C. G'sell, Eds., Les Editions de Physique, Paris, 1982, pp. 187-225.
11. J. M. Lefebvre and B. J. Escaig, *J. Mater. Sci.*, **20**, 438 (1985).
12. E. Pink, *Mater. Sci. Eng.*, **22**, 85 (1976).
13. E. Pink, *Mater. Sci. Eng.*, **24**, 275 (1976).
14. E. Pink, H. Bäck, and B. Ortner, *Phys. Stat. Sol. (a)*, **55**, 751 (1979).
15. E. Pink, V. Bouda, and H. Bäck, *Mater. Sci. Eng.*, **38**, 89 (1979).
16. G. Schoek, *Phys. Stat. Sol.*, **8**, 1499 (1965).
17. M. Cagnon, *Phil. Mag.*, **24**, 1465 (1971).
18. T. Feltham, *J. Inst. Met.*, **89**, 210 (1961).
19. J. Heijboer, in *Molecular Basis of Transition and Relaxation*, D. J. Maier, Ed., Gordon and Bridge Science Publishers, New York, 1978, pp. 75-102.
20. F. Povolò, G. Schwartz, and É. B. Hermida, *J. Polym. Sci., Polym. Phys. Ed.*, in press.

Received October 30, 1995

Accepted January 4, 1996