

Phenomenological Description of Strain Rate and Temperature-Dependent Yield Stress of PMMA

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SYNOPSIS

A constitutive equation to describe the yield behavior of poly(methyl methacrylate) (PMMA) is useful not only from the technological point of view, but also for the comprehension of the nonlinear mechanisms acting in the material. In both compression and tension, the yield stress is usually represented as a function of the strain rate at different temperatures. In PMMA and other glassy polymers these curves are related by scaling, that is, they can be matched to form a master curve. Particularly in PMMA the temperature and strain rate dependence of the master curve has been characterized by two different models. The first involves two thermally activated rate processes, one acting only at high strain rates. The second model interprets the yield process as a cooperative movement of several independent structural units, all with the same activation energy. In this article it is demonstrated that only the second phenomenological model is correct because it provides a good fit to the master curve of PMMA both in compression and tension, and verifies the properties of a set of curves related by scaling. Moreover, it is pointed out that the first model leads to severe inconsistencies because it does not consider the nonlinear behavior of PMMA. Finally, the physical parameters obtained (internal stress, activation volume, and enthalpy) are compared with those given in the literature. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The dependence of the yield behavior on strain rate and temperature is useful not only to predict simple failure criteria, but to describe the mechanisms acting in a nonlinear isotropic viscoelastic material as well. Particularly, the yield process of glassy polymers has been examined from two different aspects: the molecular and structural theories, and the phenomenological models.

The molecular theories assume that the nonrecoverable deformation is due to permanent changes in the polymeric chains. For instance, Robertson¹ considered that the intramolecular forces were the primary factor for deformation, its rate being a function of temperature. Moreover, Duckett et al.² modified this theory by including the effect of the hydrostatic pressure. This modified model satisfactorily accounts for the plastic resistance near the

glass transition temperature, but fails at low temperatures over a wide strain-rate range.

Some years later, Argon³ developed a molecular theory by assuming that the deformation was a consequence of the formation of a pair of molecular kinks. The energy required to create the kink pair arose from the elastic interactions between molecules (intermolecular forces). Argon also suggested that the yield process could not merely evolve through the formation of double kinks, but should require the cooperative change of several adjacent molecular segments. Although this theory turned out to be more relevant at very low temperatures, there are no general physical models to describe the yield behavior over a wide range of both temperature and strain rate.

On the other hand, the phenomenological research is based on the theory of thermally activated rate processes generally applied to dilute polymeric solutions.⁴ This theory assumes that the plastic deformation is due to partial motions of chain molecules over a potential energy barrier. It is not established whether the potential energy is associated

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with intra- or intermolecular forces, but in any case on applying a stress σ the barrier is reduced in σv , v being an activation volume. According to this model, glassy polymers follow a logarithmic dependence of the yield stress on the strain rate.

Haward and Thackray⁶ determined that the activation volumes of several glassy polymers were 2–10 times larger than the volume of the “statistical random link,” so they suggested that yield involved the cooperative movement of a larger number of chain segments than for dilute solutions. Even in this case they considered a log(strain rate) dependence for the yield stress.

Roetling⁷ and Bauwens et al.^{8–10} also determined that more than one activated rate process is involved in the yield behavior. However, they do not consider a larger activation volume but the addition of the stresses corresponding to the different acting mechanisms. For example, Bauwens–Crowet¹⁰ tried to fit the strain-rate dependent yield stress curves of poly(methyl methacrylate) (PMMA) by two processes associated with the dynamical α and β relaxations.

Otherwise Fotheringham and Cherry¹¹ described the yield curves of PMMA 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.^{11,12}

In summary, the molecular theories, associated with inter- or intramolecular forces, seem to provide scanty information to describe the whole evolution of the yield behavior of glassy polymers. On the contrary, there is a good agreement between the yield data of glassy polymers and several phenomenological models. These models, however, are based on completely different physical concepts: an activation volume greater than the volume of the polymeric unit, the presence of several mechanisms with different activation volumes acting independently, or the cooperative motion of n identical elements leading to a non log strain-rate dependence of the yield stress.

Therefore, it was the purpose of this article to determine how the correct constitutive equation associated with the strain rate and temperature dependence of the yield stress can be calculated. This determination requires, first, to analyze if the set of yield stress vs. log(strain-rate) curves measured at different temperatures satisfy the scaling conditions. If these conditions are fulfilled, the derivatives of the master curve will discern which phenomenolog-

ical description is correct. In particular the procedure will be applied to the compression and tensile yield stresses of PMMA,¹⁰ giving a detailed interpretation of the calculated parameters.

THEORETICAL CONSIDERATIONS

Strain Rate Dependence of Yield Point

In the Introduction it was pointed out that the log(strain-rate) dependence of the yield stress curves measured at a fixed temperature is linear for several glassy polymers such as polycarbonate.⁸ However, this is not the case for PMMA whose yield curves exhibit a definite curvature. As this curvature is rather smooth, how yield depends on log(strain rate) can be established only if the curves are measured over many orders of strain rate, or if a master curve is built. Effectively, the yield curves of several glassy polymers, particularly PMMA, can be related by scaling^{8,11} in such a way that, through translations along a certain direction, the curves measured at different temperatures can be superposed onto one measured at a temperature T_s , taken as a reference, leading to a master curve. This master curve usually covers several decades of the strain rate scale, so a phenomenological model that fits it properly should give a correct description of the yield process. Therefore, several researchers intended to characterize the yield behavior of PMMA by adjusting its yield master curve.

An easy phenomenological description of the master curve of PMMA is based on assuming that a single thermally activated rate process is acting. For this process, the relationship between the yield stress σ and the strain rate $\dot{\epsilon}$ is⁴

$$\frac{\sigma}{T} = \frac{2k}{v} \sinh^{-1}\left(\frac{\dot{\epsilon}}{\dot{\epsilon}^*}\right) \quad (1)$$

with k being Boltzmann's constant. The parameters v and $\dot{\epsilon}^*$ represent an activation volume and a characteristic strain rate of the process, respectively, and usually depend on the temperature T . It must be noticed that at small strain rates the yield stress tends slowly to zero, while for large deformation rates eq. (1) reduces to

$$\frac{\sigma}{T} = \frac{2k}{v} \ln\left(\frac{2\dot{\epsilon}}{\dot{\epsilon}^*}\right) \quad (2)$$

which is the equation of a slanted asymptote of the yield curve in the σ/T against $\log \dot{\epsilon}$ plot. According to eq. (2), once the linear asymptote of the empirical

master curve is determined, the parameters of this model can be calculated straightforward from its slope and abscissa to the origin.

A different interpretation of the yield behavior of PMMA was given by Bauwens-Crowet and collaborators, on assuming that the empirical master curve has not only a slanted asymptote at high but at low strain rates, as well. This model proposes a combination of two thermally activated rate processes, namely α and β .⁸ The first one appears at small strain rates where the smooth dependence of the master curve is characterized by a rather flat slanted asymptote. The second one describes the behavior at high strain rates, where the curve reaches a sharper slanted asymptote. Thus, on considering Ree-Eyring's theory,¹³ they described these asymptotes as

$$\frac{\sigma}{T} = A_{\alpha} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) \quad (3)$$

and

$$\frac{\sigma}{T} = A_{\alpha} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + A_{\beta} \left(\ln 2C_{\beta} \dot{\epsilon} + \frac{Q_{\beta}}{RT} \right) \quad (4)$$

where the subscripts α and β refer to the processes acting at low and high strain rates, respectively. The parameters A_{α} and A_{β} are derived from the slopes of the corresponding asymptotes while the ordinates to the origin lead to $[Q_{\alpha}/RT \ln C_{\alpha}]$ and $[Q_{\beta}/RT \ln C_{\beta}]$, respectively. It must be pointed out that the values of C_{α} , Q_{α} , C_{β} , and Q_{β} can be determined only if the asymptotes are evaluated at different temperatures.

Using this model, Bauwens-Crowet et al.⁸ also intended to fit the measured yield curve according to

$$\frac{\sigma}{T} = A_{\alpha} \left(\ln 2C_{\alpha} \dot{\epsilon} + \frac{Q_{\alpha}}{RT} \right) + A_{\beta} \sinh^{-1} (C_{\beta} \dot{\epsilon} \exp(Q_{\beta}/RT)), \quad (5)$$

but this expression did not fit the data except, of course, in the asymptotes. However, it was used as an approximation of the curve passing through the experimental points.

A better description of the yield master curve is obtained on considering the same single activated rate process as in eq. (1), but introducing an effective yield stress $\sigma^* = \sigma - \sigma_i$, where σ_i is an internal stress associated with the elastic recovery process before and after yield.^{6,11} Moreover, if it is assumed that the yield point is reached when

n segments of PMMA move simultaneously, that is in a cooperative way, the measured strain rate results in the product of the strain rate of each process. Particularly, if all the segments are equal, the relationship between $\dot{\epsilon}$ and the yield stress σ , turns out to be

$$\dot{\epsilon} = \dot{\epsilon}^* \sinh^n \left(\frac{(\sigma - \sigma_i)v}{2kT} \right). \quad (6)$$

Furthermore, an Arrhenius' temperature dependence for $\dot{\epsilon}^*$ is usually assumed, $\dot{\epsilon}_0$ being the preexponential factor, and ΔH , the activation enthalpy of the cooperative process, thus eq. (6) can be written as

$$\dot{\epsilon} = \dot{\epsilon}_0 e^{-\Delta H/kT} \sinh^n \left(\frac{(\sigma - \sigma_i)v}{2kT} \right). \quad (7)$$

It must be noted that eq. (6) reduces to eq. (1) if $n = 1$ and $\sigma_i = 0$, while if $\sigma_i \neq 0$, it gives an approximation of eq. (5). In fact, Bauwens-Crowet determined that the asymptote of the master curve of PMMA for the lowest measured strain rates is rather flat so, the stress of the α process can be approximated by a constant.¹⁰ On defining this constant as the internal stress σ_i , eq. (5) can be rewritten as eq. (6) with $n = 1$.

Equation (6) includes four adjustable parameters to fit the empirical master curve. In a previous work,¹¹ the parameters of PMMA were determined by fitting the master curve at the glass transition temperature where the yield stress is lower, so it was assumed that $\sigma_i = 0$. Nevertheless, the four parameters of eq. (6) can be calculated without any assumption, if not only the master curve but also its derivative are considered. Effectively, eq. (6) can be rewritten as

$$\frac{\sigma}{T} = \frac{\sigma_i}{T} + B \sinh^{-1} \left[\left(\frac{\dot{\epsilon}}{\dot{\epsilon}^*} \right)^{1/n} \right] \quad (8)$$

with $\dot{\epsilon}^* = \dot{\epsilon}_0 \exp(-\Delta H/kT)$ and $B = 2k/v$. Then, its partial derivative with respect to $\log \dot{\epsilon}$ is

$$\left. \frac{\partial \sigma}{\partial \log \dot{\epsilon}} \right|_T = \log \left(\frac{2.303B}{n} \right) + \frac{1}{n} (\log \dot{\epsilon} - \log \dot{\epsilon}^*) - \frac{1}{2} \log [1 + 10^{2(\log \dot{\epsilon} - \log \dot{\epsilon}^*)/n}]. \quad (9)$$

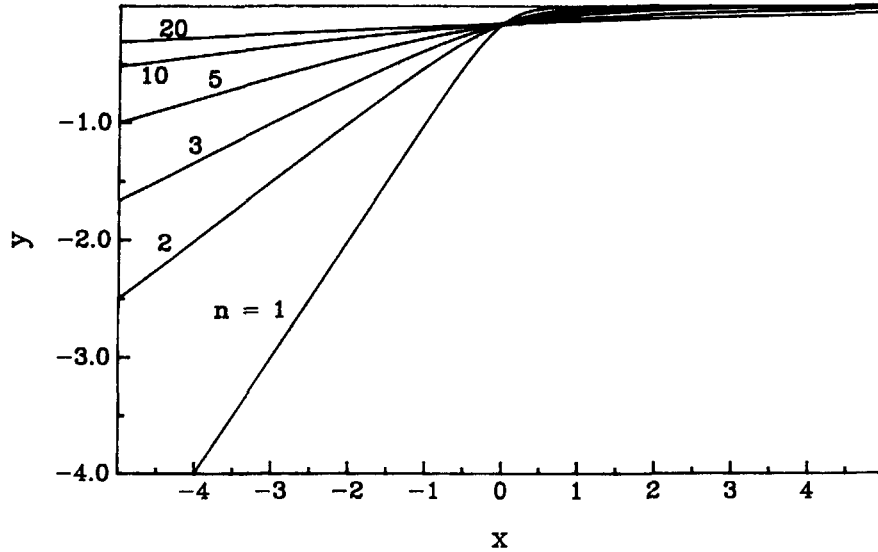


Figure 1 Pattern of $\log(\partial(\sigma/T)/\partial \log \dot{\epsilon}|_T)$ vs. $\log \dot{\epsilon}$ curves calculated from eq. (12).

This expression has three adjustable parameters: B , $\log \dot{\epsilon}^*$, and n . However, on defining the shifted variables

$$x = \log \dot{\epsilon} - \log \dot{\epsilon}^* \quad (10)$$

$$y = \log\left(\frac{\partial \sigma}{\partial \log \dot{\epsilon}} \Big|_T\right) - \log\left(\frac{2.303B}{n}\right), \quad (11)$$

a normalized plot can be built¹⁴ and eq. (9) can be rewritten as

$$y = \frac{1}{n} x - \frac{1}{2} \log(1 + 10^{2x/n}). \quad (12)$$

This equation has only one adjustable parameter n . This parameter modifies the shape of the $\log(\text{strain-rate})$ dependence of the shifted derivative of the yield stress, as shown in Figure 1.

Hence, if the derivatives of the master curve represented in a double-log plot can be superposed onto one of the curves of Figure 1 only by horizontal and vertical translations, the parameters n , B , and $\dot{\epsilon}^*$ 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 origins of both coordinate systems give $\log \dot{\epsilon}^*$ and $\log(2.303 B/n)$, respectively.

Once n , B , and $\dot{\epsilon}^*$ are known, going back to eq. (8), the internal stress σ_i is determined in order to provide a good fit to the experimental points of the master curve.

Temperature Dependence of Yield Curves

The phenomenological equation derived from the fitting to the master curve provides the dependence of the yield stress on the strain rate, but not on temperature. Effectively, if the master curve is referred to another temperature T'_s , the functional relationship between σ and $\dot{\epsilon}$ will be the same as for the master curve at T_s , but the parameters will be different because, in principle, they depend on temperature. This dependence can be determined if the translation paths employed to form the master curve, and the formalism developed to characterize a set of curves related by scaling are employed.¹⁵

The most important features of this formalism can be summarized on considering two curves in the (x, y) plane, as the ones shown in Figure 2. These

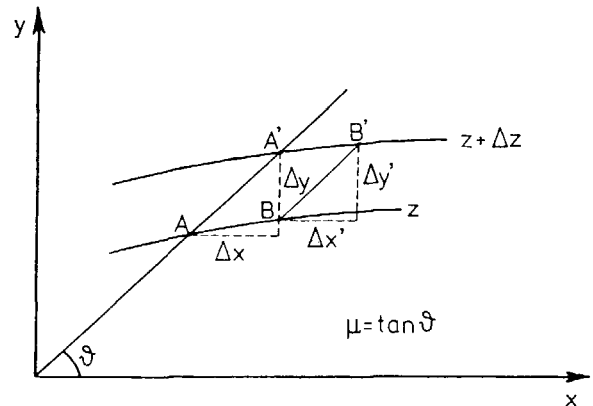


Figure 2 Two curves in the (x, y) plane, parametrized in z , related by scaling along the translation path of slope μ . Points A, A' or B, B' have the same derivatives.

curves, parametrized in z or in an arbitrary function $h(z)$, are related by scaling along a translation path of slope μ . This means that the points A, B are translated to A', B' by making the increments $(\Delta x, \Delta y)$ and $(\Delta x', \Delta y')$, respectively, in such a way that the following holds:

1. Points of equal derivatives must be superposed, that is,

$$\begin{aligned} y_x(x + \Delta x, z + \Delta z) &= y_x(x, z) \\ y_x(x + \Delta x + \Delta x', z + \Delta z) &= y_x(x + \Delta x, z) \end{aligned} \quad (13)$$

where the subindex indicates a partial derivative with respect to the corresponding variable.

2. The slope of the translation path must be independent from the variables, that is,

$$\frac{\Delta y}{\Delta x} = \frac{\Delta y'}{\Delta x'} = \mu = \text{constant}. \quad (14)$$

Moreover, the representations in the $(y, h(z))$ and $(h(z), x)$ planes are also related by scaling, their slopes of translation being

$$\frac{\Delta h(z)}{\Delta y} = \alpha = \text{constant} \quad (15)$$

and

$$\frac{\Delta x}{\Delta h(z)} = \beta = \text{constant}, \quad (16)$$

respectively. Then, it is easy to show that

$$\alpha\beta\mu = 1. \quad (17)$$

3. Because the translation is rigid, the square of the hypotenuse of the triangle defined by the increments of the variables x and y depends only on the increments of the parameter z , that is,

$$\begin{aligned} [(\Delta x)^2 + (\Delta y)^2]^{1/2} \\ = [(\Delta x')^2 + (\Delta y')^2]^{1/2} = M(\Delta h(z)) \end{aligned} \quad (18)$$

where M is a function of $\Delta h(z)$.

Consequently, the increment in $h(z)$ can be calculated once the horizontal and vertical translation paths in the (x, y) plane as well as the slopes α and β are known. For the determination of these slopes the curves should be represented in the other two

planes; however, that procedure can be widely simplified on considering the functional dependence of curves related by scaling.

If the scaling conditions are fulfilled, then the curves will belong to the same family; they are described by the implicit function

$$F(y - \mu x, x - \beta h(z)) = 0 \quad (19)$$

or equivalently,

$$F(x - \beta h(z), h(z) - \alpha y) = 0. \quad (20)$$

In fact, when evaluated on points related by scaling, according to eqs. (14)–(16), the arguments of both implicit functions remain constant. Therefore, if a constitutive equation has been proposed to fit the $y(x)$ curves, it must be rewritten as the implicit function F . On doing this, the slopes μ and β , or α and β are determined, as well as the function of parametrization $h(z)$.

As an application of this formalism, the temperature dependence of the parameters v and $\dot{\epsilon}^*$ for the single thermally activated rate process given by eq. (1) will be determined. Being $\Delta(\log \dot{\epsilon})$ and $\Delta(\sigma/T)$ the horizontal and vertical shift paths of the yield curves, respectively, and defining the variables

$$x = \log \dot{\epsilon}$$

$$y = \log(\sigma/T)$$

$$z = T.$$

Equation (1) can be rewritten as

$$y - \log\left(\frac{2k}{v}\right) - \log(\sinh^{-1}(10^{x - \log \dot{\epsilon}^*})) = 0. \quad (21)$$

If $\log \dot{\epsilon}^* = h(z)$ then the argument $[x - \beta h(z)]$ appears in eq. (21), being $\beta = 1$. Moreover, if v is constant, it is found also the argument $[y - \mu x]$, being $\mu = 0$. Otherwise, the implicit function is the one given in eq. (20) if

$$y - \log\left(\frac{2k}{v}\right) = y - \frac{h(z)}{\alpha}. \quad (22)$$

Even if the scaling conditions are fulfilled, the definition of y points out that the curves can be translated only if the vertical axis is logarithmic. However, the yield curves are shifted in the $(\log \dot{\epsilon}, \sigma/T)$ plane, so the model of a single activated rate process cannot be used to describe the yield curves of PMMA.

Nevertheless this example illustrates the useful information derived from the scaling conditions. For example, $\mu = 0$, i.e., a horizontal translation, implies that $\log(2k/v)$ is not a function of T . On the other hand, when $\alpha \neq 0$, from eq. (22), the dependence of the activation volume on temperature results

$$\log(2k/v) = h(z)/\alpha + \text{constant} \quad (23)$$

and taking into account that $h(z) = \log \dot{\epsilon}^*$, it follows that

$$v = C\dot{\epsilon}^{*\mu} \quad (24)$$

where C is a constant.

Further, because the arguments evaluated at two points measured at different temperatures and related by scaling must remain invariable, the parameters $\dot{\epsilon}^*$ and v corresponding to the individual curve measured at T can be calculated from those of the master curve considering that

$$\log \dot{\epsilon}^*(T) - \log \dot{\epsilon}^*(T_s) = \Delta \log \dot{\epsilon} \quad (25)$$

$$\log v(T) - \log v(T_s) = -\Delta \log(\sigma/T) \quad (26)$$

where $\Delta \log \dot{\epsilon}$ and $\Delta \log(\sigma/T)$ are the horizontal and vertical shift paths used to superpose the curve measured at a temperature T onto the master curve at T_s .

RESULTS

Scaling Properties of Phenomenological Models

In the previous section it was shown that the yield curves of PMMA cannot be described by Eyring's equation. Now, we open the discussion about the yield behavior of PMMA, which is associated to two different processes, according to Bauwens-Crowet,^{10,16} and to a cooperative thermally activated mechanism, according to Fotheringham and Cherry.¹¹ In order to solve this discrepancy, first it will be analyzed whether any of these models fulfills the scaling conditions. If this is not so, then the model will be immediately invalidated because the empirical yield curves can be matched to form a master curve.

Bauwens-Crowet and coworkers proposed a phenomenological model with a constitutive equation that did not fit the whole yield curve of PMMA, but only its α and $\alpha + \beta$ asymptotes. The first one, determined at very low strain rates, is associated to the α process while the other is observed at high strain rates where both the α and β processes appear.

Moreover, the yield curves measured at different temperatures, particularly their asymptotes, can be superposed to form a master curve. Therefore, the equations of the asymptotes should verify the scaling conditions. On introducing the parameters

$$\dot{\epsilon}_\alpha^* = \left[2C_\alpha \exp\left(\frac{Q_\alpha}{RT}\right) \right]^{-1} \quad (27)$$

$$\dot{\epsilon}_\beta^* = \left[2C_\beta \exp\left(\frac{Q_\beta}{RT}\right) \right]^{-1} \quad (28)$$

the α and $\alpha + \beta$ asymptotes given in eqs. (3) and (4) can be expressed as

$$\frac{\sigma}{T} = A_\alpha \ln\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_\alpha^*}\right) \quad (29)$$

and

$$\frac{\sigma}{T} = A_\alpha \ln\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_\alpha^*}\right) + A_\beta \ln\left(\frac{\dot{\epsilon}}{\dot{\epsilon}_\beta^*}\right), \quad (30)$$

respectively.

Bauwens-Crowet¹⁰ established that, for PMMA, the slopes of both asymptotes A_α and $A_\alpha + A_\beta$ were constants while the ordinates $\ln \dot{\epsilon}_\alpha^*$ and $\ln \dot{\epsilon}_\beta^*$ depended on temperature according to eqs. (27) and (28), respectively. Thus, the α asymptotes determined at different temperatures constitute a set of parallel straight lines, and the same happens to the $\alpha + \beta$ asymptotes, achieving another set of parallel lines with a different slope.

It can be easily shown that a set of parallel straight lines can be superposed by translations in any direction; however, as the translation of the yield curves is rigid, both the α and the $\alpha + \beta$ asymptotes must be shifted along the same direction and with the same horizontal and vertical translation paths. Therefore, in the Appendix it is demonstrated that, in order to fulfill the scaling conditions, the slope of translation must be

$$\mu = \frac{(Q_\beta - Q_\alpha)A_\alpha}{Q_\beta}. \quad (31)$$

From the graphic superposition of the yield curves of PMMA at different temperatures, Bauwens-Crowet established that the mean slope of translation corresponding to the compression tests was $\mu = -4.5 \times 10^4$ Pa/K.¹⁰ Taking into account the parameters of the curves derived in her publication, summarized in Table I, eq. (31) gives $\mu = -7.5 \times 10^4$ Pa/K, that is, a hardly sharper slope that does

Table I Parameters of Yield Curves of PMMA at 373 K

A_{α_c}	= 6958 Pa
A_{α_t}	= 5390 Pa
A_{β}	= 36652 Pa
C_{α}	= 5×10^{-52} s
C_{β}	= 4.67×10^{-17} s
Q_{α}	= 412 kJ/mol
Q_{β}	= 107 kJ/mol

not modify the master curve within the experimental error. On the other hand, using the parameters determined from the tensile yield curves, eq. (31) leads to $\mu = -3.6 \times 10^4$ Pa/K, which is equal to the empirical value derived graphically. Therefore, both in tension and compression, the asymptotes of the yield curves of PMMA might be well represented by the model of two processes because it verifies the scaling properties. This model, however, is valid only for extrapolations at very low or high strain rates, so the second phenomenological model, based on the cooperative motion of n simultaneous processes, will be considered. The strain rate dependence of the yield stress of this model is given in eq. (8) so, first it will be analyzed if this equation obeys the scaling conditions. That is to say, it will be determined if, in principle, the model guarantees the properties of translation of the yield curves of PMMA.

On defining the variables

$$\begin{aligned} x &= \log \dot{\epsilon}, \\ y &= \sigma/T, \\ z &= T, \end{aligned}$$

eq. (8) can be expressed as

$$\left(y - \frac{\sigma_i}{T}\right) \frac{v}{2k} - \sinh^{-1}[10^{(x - \log \dot{\epsilon}^*)/n}] = 0. \quad (32)$$

This equation can be written in the form of the implicit functions given in eqs. (19) or (20) if n and v are constants, and if $\log \dot{\epsilon}^*$ depends only on T . In this way it can be defined $h(z) = \log \dot{\epsilon}^*(T)$, getting the argument $[x - \beta h(z)]$ with $\beta = 1$.

Then, eq. (32) takes the form given in eq. (19) if

$$y - \frac{\sigma_i}{T} = y - \mu x + C \quad (33)$$

where C is a constant. Because σ_i does not depend on x , eq. (33) is fulfilled only if $\mu = 0$, i.e., if the yield curves are translated horizontally, being $\sigma_i/T = C$.

As this is not the case, eq. (32) must be written using the arguments of the implicit function given in eq. (20). The first argument, $[x - \beta h(z)]$, has already been determined; the second one, $[h(z) - \alpha y]$ or equivalently $[y - h(z)/\alpha]$, leads to

$$\frac{\sigma_i}{T} = \frac{h(z)}{\alpha} + C. \quad (34)$$

On considering the definition of $h(z)$ and eq. (17), the parameters σ_i and $\dot{\epsilon}^*$ of the yield curve become related by

$$\frac{\sigma_i}{T} = \mu \log \dot{\epsilon}^* + C. \quad (35)$$

Moreover, once the parameters of the master curve are known, the scaling properties lead to the temperature dependence of the parameters of the individual yield curves. Effectively, the horizontal and vertical shift paths $\Delta x = \Delta \log \dot{\epsilon}$ and $\Delta y = \Delta(\sigma/T)$, respectively, are related to the increments of the parameters σ_i and $\log \dot{\epsilon}^*$, according to

$$\log \dot{\epsilon}^*(T) = \log \dot{\epsilon}^*(T_s) + \Delta(\log \dot{\epsilon}) \quad (36)$$

$$\frac{\sigma_i(T)}{T} = \frac{\sigma_i(T_s)}{T_s} + \Delta\left(\frac{\sigma}{T}\right). \quad (37)$$

Furthermore, if the Arrhenius' dependence on temperature employed in eq. (7) is assumed for $\dot{\epsilon}^*$, eq. (35) leads to

$$\sigma_i = \mu \log \dot{\epsilon}_0 T - \left[\mu \frac{\Delta H}{k} + C \right]. \quad (38)$$

In summary, both the model of two processes, α and β , as well as the cooperative model fulfill the scaling properties of a set of curves with a slope of translation μ . However, the former only fits the asymptotes of the yield master curve of PMMA, so it does not represent its yield behavior properly. Then, the question is: Does the cooperative model provide a good fitting to the whole master curve of PMMA?

Constitutive Equation of Yield Behavior of PMMA

The cooperative model, characterized by eq. (8), have four parameters: the number of cooperative units, n ; the activation volume, v ; the internal stress, σ_i ; and the characteristic strain rate, $\dot{\epsilon}^*$. These parameters can be determined using the procedure detailed previously. Then, to determine whether the yield

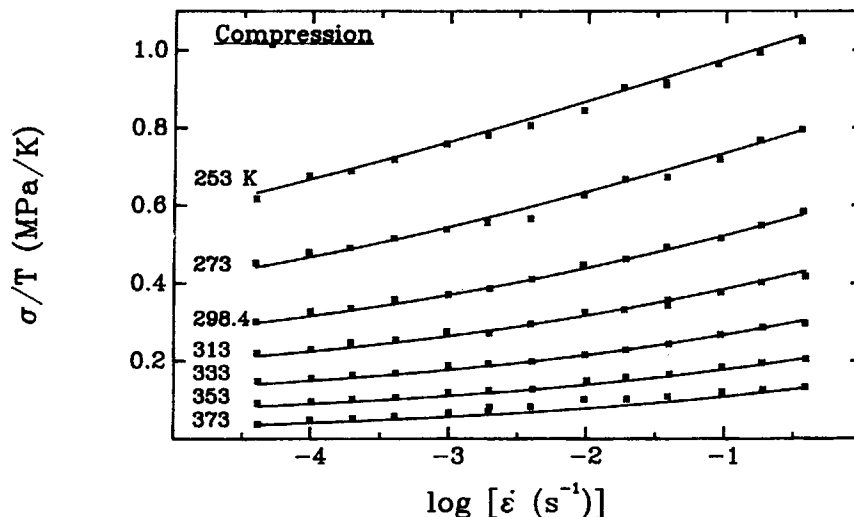


Figure 3 Compression yield curves at different temperatures. (*) Values measured by Bauwens-Crowet.¹⁰ The full curves correspond to the cooperative model described by eq. (8) with the parameters given in Table III.

behavior of PMMA is described by this cooperative model, the procedure will be applied to both the compression and tensile yield curves of PMMA measured at different temperatures,¹⁰ which are represented in Figures 3 and 4, respectively.

The parameter n can be determined by the graphical superposition of $\partial(\sigma/T)/\partial \log \dot{\epsilon}$ against $\dot{\epsilon}$ represented in a double-log plot, onto the pattern of the family of curves given in Figure 1. Then, the first attempt is to calculate the derivatives of the compression yield curves measured at different temperatures. These derivatives, represented in the double-log plot shown in Figure 5, are rather smooth, except at the highest temperature where its numer-

ical determination is difficult because of the great experimental error. Anyway, even at the lower temperatures, the strain rate interval of the individual curves is so narrow that any derivative can be a piece of several of the pattern curves given in Figure 1.

Thus, in order to get a larger strain rate interval, the yield master curve of the compression data referred to 373 K is derived numerically.¹⁰ Figures 6 and 7 show the compression master curve and its derivative, respectively. Because the derivative is extended over nearly 12 orders of magnitude, its su-

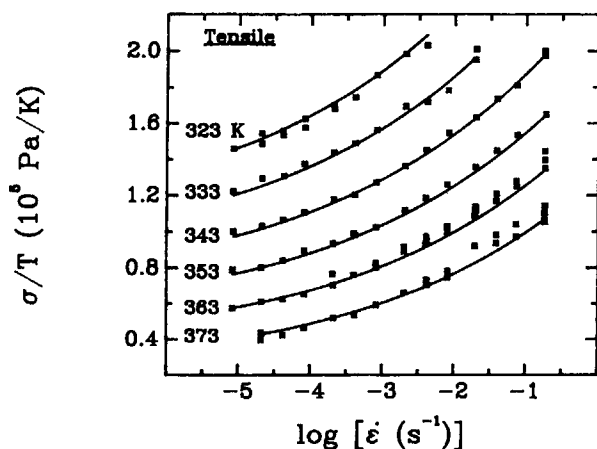


Figure 4 Tensile yield curves at different temperatures. (*) Values measured by Bauwens-Crowet.¹⁰ The full curves correspond to the cooperative model described by eq. (8) with the parameters given in Table III.

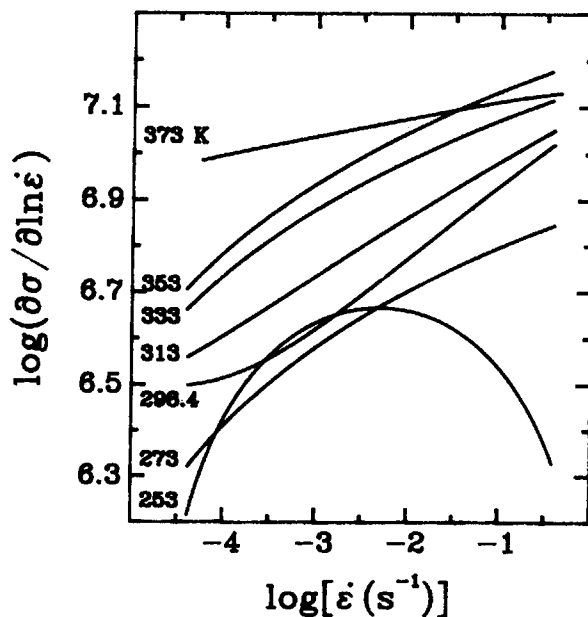


Figure 5 Double-log plot of the derivatives of the compression yield curves given in Figure 3.

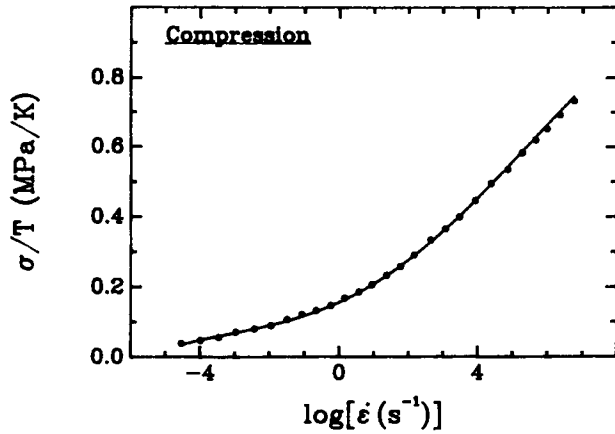


Figure 6 Compression yield master curve of PMMA at 373 K. (●) Measurements translated by Bauwens-Crowet.¹⁰ The full curve is derived from eq. (8) with the parameters given in Table II.

position onto the pattern curves determines that $5 < n < 10$. Effectively, if n is lower than 5 or greater than 10, the pattern curves are sharper or smoother than the derivative of the master curve, respectively. In order to arrive at the precise value of n , eq. (12) was fitted numerically to the derivative of the compression master curve, leading to $n = 6.65$.

Moreover, according to eq. (10) the horizontal shift between the coordinate frames, namely Δx , is directly equal to $\log \dot{\epsilon}^*$ while from eq. (11), the vertical shift Δy is equal to $\log(2.303B/n)$, leading to the activation volume because $B = 2k/v$. Once n , v , and $\log \dot{\epsilon}^*$ are determined, σ_i is adjusted numerically in order that eq. (8) provides a good fitting to the master yield curve, as shown in Figure 6. The parameters calculated from the master yield curve of the compression data are summarized in the first column of Table II.

The same procedure is also applied to the master yield curve of PMMA in tension, leading to the fit-

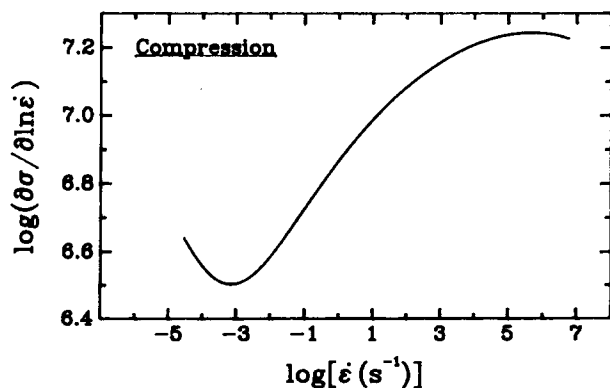


Figure 7 Double-log plot of the derivative of the master curve represented by (*) in Figure 6.

Table II Parameters of Cooperative Model for Compression and Tensile Master Yield Curves of PMMA¹⁰ at 373 K

n	Compression 6.65	Tension 6.65
$\log \dot{\epsilon}^*$	2.15	2.15
v (m ³)	8.39×10^{-29}	1.15×10^{-28}
σ_i (MPa)	0.46	0.00
$\dot{\epsilon}_0$ (s ⁻¹)	1.6×10^{17}	9.6×10^{16}
ΔH (kJ/mol)	107	105.9

ting shown in Figure 8, with the parameters detailed in the second column of Table II. Consequently, the cooperative model can be used to characterize the yield behavior of PMMA.

Now, on considering the horizontal and vertical translation paths employed by Bauwens-Crowet to form the master curves, the parameters $\log \dot{\epsilon}^*$ and σ_i of the individual curves can be calculated.¹⁰ Effectively, on replacing the parameters of the master curves and the translation paths given in Table III into eqs. (36) and (37), the internal stress and the characteristic strain rate at each temperature, summarized in Table III, are obtained.

Finally, Figure 9 shows that the parameter $\log \dot{\epsilon}^*$ of the individual yield curves is linearly related to $1/T$ both in compression and tension. In fact, a least squares fitting to these representations give correlation coefficients -0.9998 and -0.9999 for

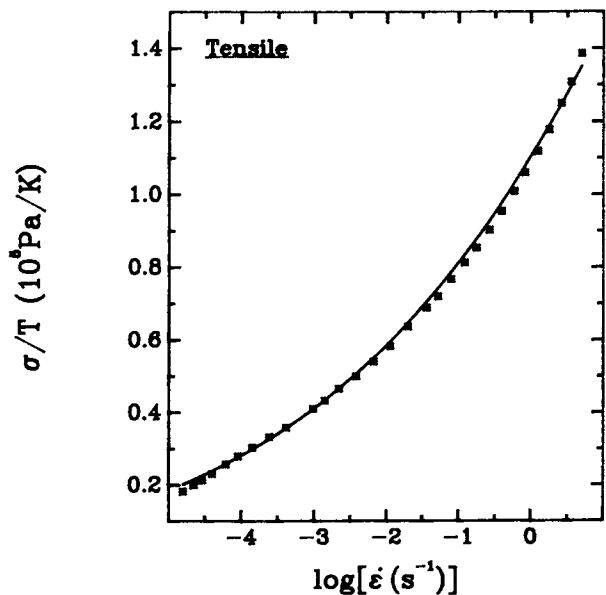


Figure 8 Tensile yield master curve of PMMA at 373 K. (*) Values measured by Bauwens-Crowet.¹⁰ The full curves correspond to the cooperative model described by eq. (8) with the parameters given in Table III.

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

T (K)	$\Delta \log \dot{\epsilon}$	$\Delta(\sigma/T)$ (10^4 Pa/K)	$\log \dot{\epsilon}^*$	σ_i (MPa)
Compression				
253	7.090	-29.0	-4.94	73.7
273	5.418	-23.0	-3.27	63.1
298.4	3.866	-17.7	-1.72	52.5
313	2.766	-12.6	-0.61	39.8
333	1.638	-7.60	0.51	25.7
353	0.776	-3.60	1.37	13.1
373	—	—	2.15	0.45
Tension				
323	2.291	-8.14	-0.14	26.3
333	1.797	-6.38	0.35	21.3
343	1.303	-4.63	0.85	15.9
353	0.844	-3.00	1.31	10.6
363	0.422	-1.50	1.73	5.44
373	—	—	2.15	0.00

compression and tension, respectively. That is, the Arrhenius' dependence of $\log \dot{\epsilon}^*$ given in eq. (7) is also verified, with the values of $\dot{\epsilon}_0$ and ΔH detailed in the last two rows of Table II.

DISCUSSION

In the previous section it was shown that the phenomenological models proposed by Bauwens-Crowet¹⁰ and Fotheringham and Cherry¹¹ satisfy the scaling conditions. However, the latter provides a good fitting to the empirical master curve, while the

former approaches only the asymptotes. According to these results, the cooperative model should provide a correct description of the yield behavior of PMMA. Nevertheless, Bauwens-Crowet argued the existence of two different processes based not only on the asymptotes of the master curve, but also on a relationship between the internal friction peak and the temperature dependence of the yield point. Thus, the following comments on the assumptions involved in her relationship intend to clarify this apparent discrepancy.

First, the parameters determined by Bauwens-Crowet to fit the asymptotes should be considered with caution. Particularly $C_\alpha = 5 \times 10^{-52}$ s, that represents the inverse of the jump frequency associated to the α process, is extremely small because it should be at least of the order of the Debye's frequency. Furthermore, in order to get an acceptable value for the yield stress of the α process, she derived an activation energy of 412 kJ/mol. This value is high when it is compared, for example, with the activation energy of 176 kJ/mol determined by Thompson¹⁷ for the α relaxation. The differences both in C_α and ΔH_α come from the assumption that a slanted asymptote is reached at low strain rates. Actually this is not the case because eq. (8), which gives a good fitting to the whole empirical master curve, does not exhibit a slanted asymptote but approaches slowly to the internal stress σ_i as the deformation rate goes to zero. That is, the yield stress against strain-rate curves cannot be characterized by two different sets of parameters, but must be associated to a unique mechanical process.

Second, Bauwens-Crowet considered that the yield process was produced by two mechanisms because the internal friction peak could be decomposed in several hypothetical individual peaks, two of them

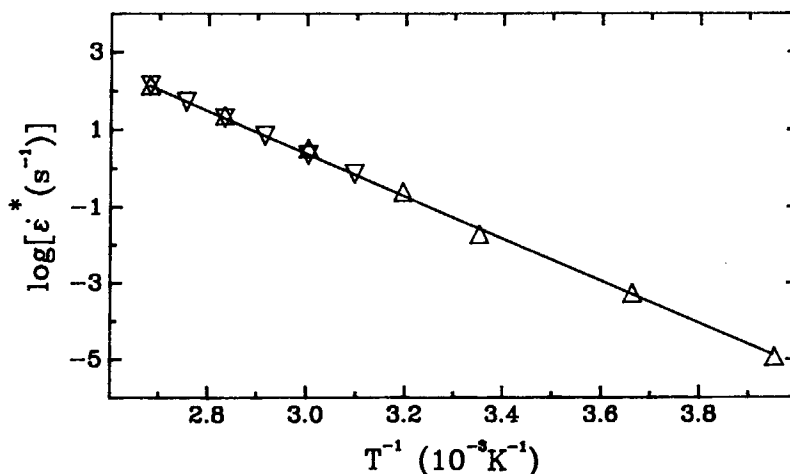


Figure 9 Temperature dependence of $\log \dot{\epsilon}^*$: (Δ) in compression and (∇) in tension.

with the same energies as the ones derived from the yield curves. It is noticed that instead of the subjective splitting of the internal friction peak, a rigorous procedure¹⁹ should be used. This analysis is beyond the scope of this article, so the following comments refer only to the hypothetical splitting.

Bauwens-Crowet determined that the β relaxation could be characterized by the peak whose activation energy was similar to the one corresponding to the β process. Then, she calculated the temperature dependence of the partial yield stress associated to the β process, namely σ_β , from the internal friction peak of the β relaxation determined as a function of temperature at a given frequency. To do that, she assumed that a Newtonian viscosity

$$\eta_\beta = 1/\sqrt{3}C_\beta A_\beta T \exp[Q_\beta/kT]$$

could be defined to relate linearly σ_β and the strain rate. This linear relationship is possible only if $\sigma_\beta \ll A_\beta T$, imposing a restriction to the interval of temperature where Bauwens-Crowet's treatment should be applied. For example, it is not valid at 253 K because the previous condition gives $\sigma_\beta \ll 92.9$ MPa while the measured yield stress minus the stress associated to the α process leads to $\sigma_\beta = 72$ MPa.

On considering only the temperature range where the previous assumption is valid, Bauwens-Crowet followed the description of the β peak using a phenomenological model of three elements. This inelastic element was characterized by a relaxation time $\tau = \eta_\beta/G_\beta$, G_β being a shear modulus in such a way that τ depended on the parameters C_β , A_β , Q_β , and G_β . She also supposed that the peaks measured at different temperatures had all the same shape and were only horizontally shifted in such a way that the product between the frequency and the temperature of the peak was constant. Further, she established that the β relaxation was not due to a single relaxation time but to a distribution $P(C_\beta)$ corresponding to different values of C_β . Therefore, she calculated the derivative of σ_β as

$$\frac{\partial \sigma_\beta}{\partial T} = \int_0^\infty \frac{\partial \sigma_\beta(C_\beta)}{\partial T} P(C_\beta) d(\ln C_\beta) \quad (39)$$

where $K = \partial \sigma_\beta(C_\beta)/\partial T \approx A_\beta \ln(2C_\beta \dot{\epsilon})$ and $d(\ln C_\beta) = (-Q_\beta/R)d(1/T)$, leading to

$$\frac{\partial \sigma_\beta}{\partial T} = K \frac{\int_0^{1/T} P(1/T) d(1/T)}{\int_0^\infty P(1/T) d(1/T)} \quad (40)$$

omitting that K depends on C_β and, in consequence, on temperature.

Moreover, assuming that the strength of relaxation $\Delta = G_o/G_\beta \ll 1$, Bauwens-Crowet found that the distribution P was proportional to the internal friction. In this way, she calculated σ_β from the double integration of the internal friction peak multiplied by a fitting constant that should not be directly K but a mean value of the derivative of σ_β .

In summary, the more important assumptions made by Bauwens-Crowet were:

- a linear relationship between σ_β and the strain rate, according to a phenomenological model of three parameters, and
- an internal friction peak whose shape does not depend either on frequency or on the amplitude of deformation.

The first assumption does not correspond to the fact that the asymptotes of the σ against $\log \dot{\epsilon}$ curves were described by a nonlinear relationship. The second supposition is not valid because, for instance, Heijboer²⁰ measured that not only the position of the maximum of the loss tangent peak, but also its shape changes as the frequency increases. Moreover, recently it has been measured that the internal friction depends strongly on the strain amplitude.²¹ In consequence, the double integral of the internal friction peaks measured at the same frequency but at different deformation levels would lead to yield stresses σ_β that depend on the deformation level. Therefore, these severe inconsistencies lead straightforward to set aside the model of two processes acting independently.

On the other hand, a very good approximation of the master curve is found on considering the cooperative model proposed by Fotheringham and Cherry.¹¹ Practically the same values of n , $\dot{\epsilon}^*$, $\dot{\epsilon}_o$, ΔH , and v are determined both in tension and compression. Moreover, nearly the same values were found for the internal stress, σ_i , either in compression or in tension, at the same temperature. This is expected because σ_i is related to the past thermo-mechanical history. An interesting point is that the values of σ_i , given in Table III, vary with temperature, both in tension and compression, according to the law

$$\sigma_i = \sigma_{io}(T_c - T) \quad (41)$$

with $\sigma_{io} = 0.64$ MPa, $T_c = 372$ K, and a correlation coefficient of 0.993. We do not have a physical model at the moment to explain this temperature depen-

dence of σ_i . T_c is very close to the glass transition temperature of PMMA.²²

A quite different analysis of the yield stress data of PMMA has been performed by Haussy et al.²³ and Lefebvre and Escaig.²⁴ In fact, the strain rate is expressed by these authors as

$$\dot{\epsilon} = \dot{\epsilon}^*(\sigma, T) \exp\left[-\frac{\Delta G_a(\sigma, T)}{kT}\right] \quad (42)$$

where both the preexponential factor and the Gibbs free energy of activation are assumed stress and temperature dependent. They gave a procedure to obtain ΔG_a from the experimental data by assuming $\dot{\epsilon}^* \propto (\sigma - \sigma_i)^m$, where m is a constant. The operational activation volume, v_o , defined as

$$v_o = kT \left(\frac{\partial \ln \dot{\epsilon}}{\partial \sigma} \right)_{T, \text{struct}} \quad (43)$$

where struct means any structural variable, is given by

$$v_o = \frac{nkT}{(\sigma - \sigma_i)} + v_a, \quad (44)$$

v_a being the true activation volume, that is,

$$v_a = - \left(\frac{\partial \Delta G_a}{\partial \sigma} \right)_{T, \text{struct}}. \quad (45)$$

v_a gives the size of the activation event (that is, the number of atoms activated) coherently. These authors, however, do not give any information either on v_a or on σ_i . A comparison can be made between our and their analysis of the data in the following way: on considering eq. (6) v_o is given by

$$v_o = \frac{nv}{2} \frac{1}{\tanh\left[\frac{(\sigma - \sigma_i)v}{2kT}\right]} \quad (46)$$

with $n = 6.65$ and $v = 8.30 \times 10^{-29} \text{ m}^3$. This equation gives values for v_o that are in the range of 0.3–0.6 nm^3 , for $\sigma_i = 0$. Values between 0.3 and 1 nm^3 are obtained if the internal stresses indicated in Table III are used, in the range of strain rates covered by Figure 2. The values for v_o calculated by means of eq. (46) are similar to those reported in table II of

Lefebvre and Escaig.²⁴ Moreover, the apparent activation enthalpy is given by

$$\Delta H_o = kT^2 \left(\frac{\partial \ln \dot{\epsilon}}{\partial T} \right)_{\sigma, \text{struct}} \quad (47)$$

that, on using eq. (7) reduces to

$$\Delta H_o = \Delta H - \frac{nv}{2} \frac{(\sigma - \sigma_i)}{\tanh\left[\frac{(\sigma - \sigma_i)v}{2kT}\right]}. \quad (48)$$

This equation, with $\Delta H = 107 \text{ kJ/mol}$ and $v = 8.39 \times 10^{-29} \text{ m}^3$, gives values for ΔH_o quite similar to those reported in table II of Lefebvre and Escaig²⁴ for $\sigma_i = 0$. Slightly higher values are obtained for $\sigma_i \neq 0$. It should be pointed out that, according to their table II,²⁴ ΔH_o tends to ΔH at high temperatures, as expected from eq. (48). Finally, in the formalism used by them,^{23,24} it is difficult to explain the superposition of the different curves to form a master curve.

In summary, it can be stated that some of the physical parameters obtained in this work are compatible with those reported in the literature,^{23,24} which were calculated by means of a thermal activation analysis of the data. As stated previously, the works reported^{23,24} do not give any information on v_a . It might be possible that $v_a = v$, so that v , as found in this article is the true activation volume. It is clear that further work is needed. Moreover, within the formalism used by several authors,^{23,24} it is very difficult to explain the superposition of the individual σ/T against $\log \dot{\epsilon}$ curves to form a master curve.

The activation volume, v , is very similar to the values given in the literature by Argon and Bessonov.²⁵ These authors treat the plastic deformation behavior of several glassy polymers, showing that when the stiff units become more complex, the plastic deformation becomes less local. From experimental and structural data, their treatment leads to determine the average number of molecular segments in the activated configuration as well as to classify if these segments move together in a linear chain or if they act collectively as a microbundle. Particularly for PMMA, it is determined that the ratio of the monomer unit is practically the same as that of the polymer segment, while the ratio between the lengths of a rotation segment and of a segment between natural hinges is equal to 5.3. Therefore, the yield behavior of PMMA is governed by a linear chain where more than five stiff units move cooperatively. This result is very similar to the one de-

rived on fitting the experimental data using eq. (8) where $n = 6.65$. Further, Argon and Bessonov established that this parameter does not depend significantly on temperature. This characteristic has also been derived directly from the scaling conditions of the yield curves.

CONCLUSIONS

It was intended in this article to determine whether any of the phenomenological models proposed by Bauwens-Crowet and Fotheringham and Cherry really describes the yield behavior of PMMA. This determination would provide not only the best approximation of the empirical yield curves, and also might clarify the response of the molecular structure during the yield process.

The tools employed to discern these models are, on one hand, the scaling properties of a set of curves related by scaling and, on the other hand, an accurate method to determine adjusting parameters fitting not only the curve but also its derivative. On applying these tools, it is established that the yield behavior of PMMA is described properly by Fotheringham and Cherry's cooperative model.¹¹

The numerical procedure developed here also achieves the calculation of the whole set of parameters without any hypothesis. For instance, instead of assuming that the internal stress is zero,¹¹ its value is derived by fitting the master curve.

The other parameters also provide fairly interesting information about the structure. Particularly the activation volume and the adjusting parameter n can be used to characterize the cooperative movement of the segments of each PMMA molecule in the glassy state. Furthermore, the apparent activation volumes and enthalpies are quite similar to those obtained by a thermal activation analysis of the tensile data.

Finally, it must be noticed that the same methodology can be applied to other nonlinear polymers, giving a quantitative description of the molecular movements. However, more effort must be devoted principally to determine whether the intermolecular or intramolecular forces govern the local rearrangement, in order to understand the yield behavior of glassy polymers.

This work has been supported partially by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), the University of Buenos Aires, the Proyecto Multinacional de Investigación y Desarrollo en Materiales OAS-CNEA, and the Antorchas Foundation. One of the authors (E.H.) thanks the Alexander von Humboldt

Foundation for a scholarship to work at the Max Planck Institut für Metallforschung, Institut für Physik.

APPENDIX

On considering the variables

$$x = \ln \dot{\epsilon}$$

$$y = \sigma/T$$

$$z = T$$

$$h_\alpha(z) = \dot{\epsilon}_\alpha^*(T)$$

$$h_\beta(z) = \dot{\epsilon}_\beta^*(T),$$

it is immediate that the asymptotes given in eqs. (29) and (30), can be written as

$$y = A_\alpha x + A_\alpha h_\alpha(z)$$

and

$$y = (A_\alpha + A_\beta)x + A_\alpha h_\alpha(z) + A_\beta h_\beta(z)$$

for the low and high strain rates, respectively. Now, when the asymptotes parametrized in $z + \Delta z$ are superposed onto those determined at z with a slope of translation μ , the horizontal and vertical displacements of the α asymptote are related by

$$\Delta y_1 = \mu \Delta x_1 = A_\alpha \Delta x_1 + A_\alpha \Delta h_\alpha \quad (\text{A.1})$$

and analogously, for those of the $\alpha + \beta$ asymptote it results

$$\begin{aligned} \Delta y_2 &= \mu \Delta x_2 \\ &= (A_\alpha + A_\beta) \Delta x_2 + A_\alpha \Delta h_\alpha + A_\beta \Delta h_\beta. \end{aligned} \quad (\text{A.2})$$

From eqs. (A.1) and (A.2) it is easy to show that

$$\Delta x_1 = \frac{A_\alpha \Delta h_\alpha}{\mu - A_\alpha} \quad (\text{A.3})$$

$$\Delta x_2 = \frac{A_\alpha \Delta h_\alpha + A_\beta \Delta h_\beta}{\mu - (A_\alpha + A_\beta)}. \quad (\text{A.4})$$

Moreover, as the shift of the yield curve must be rigid, the increments of the variables x and y corresponding to the asymptote α must be the same as those of the asymptote $\alpha + \beta$, that is,

$$\Delta x_1 = \Delta x_2$$

$$\Delta y_1 = \Delta y_2.$$

Then, eqs. (A.3) and (A.4) lead to

$$\mu = \frac{A_\alpha[\Delta h_\beta(z) - \Delta h_\alpha(z)]}{\Delta h_\beta(z)}. \quad (\text{A.5})$$

Hence, on considering eqs. (27) and (28), the increment of h_α can be written as

$$\Delta h_\alpha = \frac{Q_\alpha}{R} \Delta \left(\frac{1}{T} \right) \quad (\text{A.6})$$

and an analogous expression results for h_β . Then, the slope of translation results in

$$\mu = \frac{(Q_\beta - Q_\alpha)A_\alpha}{Q_\beta}, \quad (\text{A.7})$$

giving a relationship among the activation energies and A_α .

Bauwens-Crowet¹⁰ established that the parameters A_α and A_β could be determined from the slopes of the asymptotes, and the activation energies could be calculated using an equation that considered the horizontal distances between the asymptotes. It is now shown that this equation can also be derived straightforward from the scaling conditions. Effectively, on considering the α asymptote at two different temperatures, T and T_s , the horizontal distances between them, calculated from eq. (A.1) on considering that $\Delta y = 0$ results in

$$\Delta x_\alpha = \Delta h_\alpha(z). \quad (\text{A.8})$$

Similarly, from eq. (A.2) the horizontal distance between the $\alpha + \beta$ asymptotes at T and subscript s gives

$$\Delta x_{\alpha+\beta} = \Delta h_\alpha(z) + \Delta h_\beta(z). \quad (\text{A.9})$$

Finally, taking into account eqs. (27) and (28), it follows

$$\Delta x_\alpha = Q_\alpha \left(\frac{1}{T} - \frac{1}{T_s} \right) \quad (\text{A.10})$$

$$\Delta x_{\alpha+\beta} = (Q_\alpha + Q_\beta) \left(\frac{1}{T} - \frac{1}{T_s} \right), \quad (\text{A.11})$$

which are the expressions suggested by Bauwens-Crowet,¹⁰ but without demonstration.

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Received March 21, 1994

Accepted March 24, 1995