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A formulation of the cooperative model for the yield stress of amorphous polymers for a wide range of strain rates and temperatures

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Abstract

The mechanical response of solid amorphous polymers is strongly dependent on the temperature and strain rate. More specifically, the yield stress increases dramatically for the low temperatures as well as for the high strain rates. To describe this behavior, we propose a new formulation of the cooperative model of Fotheringham and Cherry where the final mathematical form of the model is derived according to the strain rate/temperature superposition principle of the yield stress. According to our development, the yield behavior can be correlated to the secondary relaxation and we propose an extension of the model to temperatures above the glass transition temperature. For a wide range of temperatures and strain rates (including the impact strain rates), the predicted compressive yield stresses obtained for the polycarbonate (PC) and the polymethylmethacrylate (PMMA) are in excellent agreement with the experimental data found in the literature.

Keywords: Yield stress; Modeling; Amorphous polymers

1. Introduction

Many molecular theories have been proposed for the prediction of the yield stress of amorphous polymers. These theories consider the yield behavior as a thermally activated process and account for temperature and strain rate effects. One of the first models was the Eyring transition state theory [1] where the fundamental process of yielding consists of the jump of macromolecule segments from one equilibrium position to another. Later, Robertson [2] proposed an approach explaining how a shear stress can induce flow in an amorphous polymer by changing the actual structure of the polymer chain. Argon [3] developed a model that takes into account the intermolecular resistance to shear yielding with the rotation of chain segments generating two kinks in the chain. Other theories are based on the dislocation concept, such as in the work of Bowden and Raha [4] who calculated the thermal energy necessary for the nucleation of a sheared region (dislocation loop) under an applied stress.

Most of the previous models give an acceptable prediction for the yield stress but only on a specific domain of temperatures and/or strain rates [5]. As a matter of fact, the yield stress increases more rapidly at higher strain rates or lower temperatures than it does at lower strain rates or higher temperatures. In accordance with the Ree-Eyring theory of non-Newtonian viscosity [6], many processes may be required to obtain a good description over a wide range of temperatures and strain rates. For many amorphous polymers, Bauwens-Crowet, Bauwens and co-workers [7–12] have shown that generally two rheological processes are necessary for the modeling of the yield stress. The equation resulting from the Ree-Eyring theory involves two activation processes, α and β. It is given by:

$$\frac{\sigma_y}{T} = A_\alpha \cdot \left(\ln(2C_\alpha \dot{\varepsilon}) + \frac{Q_\alpha}{kT} \right) + A_\beta \cdot \sinh^{-1}\left(C_\beta \dot{\varepsilon} \exp\left\{ \frac{Q_\beta}{kT} \right\} \right) \qquad (1)$$

where σ_y is the yield stress under uniaxial loading, T is the absolute temperature, k is the Boltzmann constant, $\dot{\varepsilon}$ is the strain rate, Q_i(i = α,β) are activation energies for the two processes α and β, and finally A_i and C_i are activation parameters. The process α refers to low strain rates and high

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temperatures, whereas the β process refers to high strain rates and low temperatures. The pressure effect on the yield stress can also be considered in the preceding formulation where it has been shown that hydrostatic pressure increases activation energies [13,14]. Moreover it was shown that the use of two Eyring processes acting in parallel also permits to successfully model the yield stress of semi-crystalline polymers [14]. However, in this later case, it is necessary to consider three distinct activated processes each with its own temperature, strain-rate and pressure dependences. Many authors have tried to link the different yield processes of the Ree-Eyring formulation to molecular motions [9–12,14]. The main difficulty in these attempts is that some of the parameters used in the modeling are non-physical quantities. In particular, the values taken by the activation parameters C_i can rarely be related to a physical process.

Within the past 10 years, it has been shown, for amorphous polymers by Povolo and co-workers [15,16] and for semi-crystalline polymers by Brooks et al. [17], that the two Eyring processes acting in parallel for the description of the yield stress on a wide range of temperatures and strain rates can be substituted with the cooperative model of Fotheringham and Cherry [18,19]. In line with these previous studies, we propose a new formulation of the cooperative model for amorphous polymers with the assumption that yield stress must obey the strain rate/temperature superposition principle of Bauwens-Crowet et al. [7]. This assumption allowed us to clearly identify the temperature and strain rate dependence of the model. In a second part of this work, we propose an extension of the model to the glass transition domain (above the glass transition temperature). To the best of our knowledge, this is the first time that: (1) temperature and strain rate dependencies are demonstrated in a very clear and simple way; (2) the activation energy of the cooperative model for amorphous polymers is identified as the energy of the β relaxation; and (3) the cooperative approach is extended to predict yielding above the glass transition point. For a wide range of strain rates and temperatures, the predicted compressive yield stresses obtained for the polycarbonate (PC) and the polymethylmethacrylate (PMMA) give a good agreement in comparison with the experimental results of the literature. In the discussion part of this paper, we emphasize the physical meaning of the proposed model parameters.

2. The cooperative model

2.1. Background

The cooperative model, also called cooperative jump model or Eyring cooperative model, was originally due to the work of Fotheringham and Cherry [18,19]. Two modifications were granted to the original Eyring equation [1]. First, it is assumed that there exists an internal stress σ_i such that the effective stress σ^* is given by:

$$\sigma^* = \sigma_y - \sigma_i \tag{2}$$

This internal stress is a structural parameter, which depicts the arrangement of defects inherited from past thermal history. It provides a better way of expressing the observed macroscopic properties of polymeric materials. Second, the flow in the polymer will be permitted when several polymer chain segments are moving cooperatively [20]. Such a concept was developed to take into account the significance of activation volume in the yield process. According to Fotheringham and Cherry [18,19], the cooperative movement of chain segments involves the occurrence of n elementary transitions. The resulting strain rate $\dot{\varepsilon}$ is given by:

$$\dot{\varepsilon} = \dot{\varepsilon}^* \sinh^n\left(\frac{\sigma^* V}{2kT}\right) \tag{3}$$

where V is an arbitrary activation volume and $\dot{\varepsilon}^*$ is the characteristic strain rate. To write an expression of the yield stress, we get σ^* from Eq. (2) and according to Eq. (3) we obtain the following form:

$$\frac{\sigma_y}{T} = \frac{\sigma_i}{T} + \frac{2k}{V}\sinh^{-1}\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^*}\right)^{1/n} \tag{4}$$

In the next paragraphs, by assuming the strain rate/temperature superposition principle [7], we will determine the forms of the internal stress σ_i and the characteristic strain rate $\dot{\varepsilon}^*$.

2.2. Strain rate/temperature superposition principle

As it is classically observed, the mechanical behavior of polymers at low temperatures is comparable to the behavior at high strain rates. An increase in temperature will have the same effect on the yield stress as a decrease in strain rate. These observations originate most likely from the well-known time/temperature superposition principle, which describes the equivalence of time (or frequency, herein assimilated as the strain rate) and temperature. For the yield stress of amorphous polymers, Bauwens-Crowet et al. [7] have established that the Eyring plots (i.e. curves representing the reduced yield stress σ_y/T versus the logarithm of the strain rate $\log \dot{\varepsilon}$ for various temperatures) can be shifted to create a master curve for a reference temperature T_{ref}. To illustrate this, Fig. 1 shows a schematic of the Eyring plots for the reference temperature T_{ref} and for other temperatures. From Fig. 1, we can see that the shifts with respect to the master curve are both horizontal and vertical. The expression of these shifts is given by:

$$\begin{cases} \Delta(\log \dot{\varepsilon}) = \log \dot{\varepsilon}(T_{ref}) - \log \dot{\varepsilon}(T) \\ \Delta\left(\dfrac{\sigma_y}{T}\right) = \dfrac{\sigma_y(T_{ref})}{T_{ref}} - \dfrac{\sigma_y(T)}{T} \end{cases} \tag{5}$$

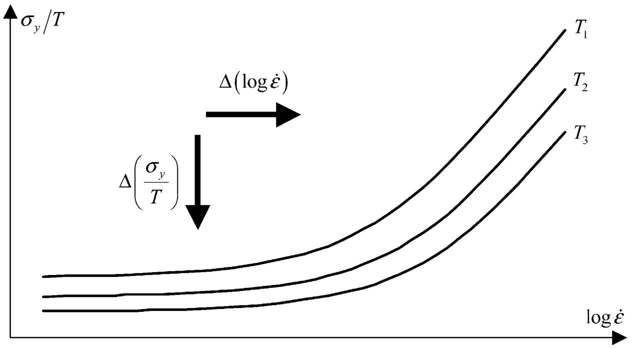

Fig. 1. Illustration of the strain rate/temperature superposition principle of the Eyring plots for three different temperatures $T_1<T_2<T_3$. The curves drawn for T_1 and T_3 can be superposed to the curve given for T_2.

where $\Delta(\log\dot{\varepsilon})$ is the horizontal shift and $\Delta(\sigma_y/T)$ is the vertical shift. A fortiori, the strain rate $\dot{\varepsilon}$ does not depend on the temperature. The form $\dot{\varepsilon}(T)$ is only used for referencing the temperature at which the Eyring plot is represented. Moreover, as it will be introduced in the next paragraph, the shifts $\Delta(\log\dot{\varepsilon})$ and $\Delta(\sigma_y/T)$ are only temperature dependent functions.

The shift properties of the cooperative model have been previously studied within the past 10 years. By determining the effective stress (Eq. (2)) through transient dip experiments, Brooks et al. only needed to consider a horizontal shift [17]. While Povolo and co-workers studied directly the yield stress and showed that the horizontal and vertical shifts are respectively related to the characteristic strain rate $\dot{\varepsilon}^*$ and to the internal stress σ_i [15,16]. This later result was found after a very lengthy reasoning method. In what follows, we propose a rather simple mathematical demonstration for this latter corollary. By inserting Eq. (4) into the expression of the vertical shift given by the second equation of Eq. (5), we obtain:

$$\Delta\left(\frac{\sigma_y}{T}\right)=\frac{\sigma_i(T_{\mathrm{ref}})}{T_{\mathrm{ref}}}-\frac{\sigma_i(T)}{T}+\frac{2k}{V}\left(\sinh^{-1}\left(\frac{\dot{\varepsilon}(T_{\mathrm{ref}})}{\dot{\varepsilon}^*(T_{\mathrm{ref}})}\right)^{1/n}-\sinh^{-1}\left(\frac{\dot{\varepsilon}(T)}{\dot{\varepsilon}^*(T)}\right)^{1/n}\right) \tag{6}$$

Since, the vertical shift is independent of the strain rate $\dot{\varepsilon}(T)$ [7], the last term of the right hand side of Eq. (6) should vanish. This allows us to express the shifts of Eq. (5) as function of $\dot{\varepsilon}^*$ and σ_i:

$$\begin{cases}\Delta(\log\dot{\varepsilon})=\log\dot{\varepsilon}^*(T_{\mathrm{ref}})-\log\dot{\varepsilon}^*(T)\\ \Delta\left(\dfrac{\sigma_y}{T}\right)=\dfrac{\sigma_i(T_{\mathrm{ref}})}{T_{\mathrm{ref}}}-\dfrac{\sigma_i(T)}{T}\end{cases} \tag{7}$$

This result is of great interest since it shows that the physics of the superposition principle expressed by the shifts in Eq. (5) is reduced to the physical meaning of the intrinsic parameters $\dot{\varepsilon}^*$ and σ_i as expressed by Eq. (7).

2.3. Temperature dependence of the shifts

For the polymethylmethacrylate (PMMA) and for the polyvinylchloride (PVC), Povolo and co-workers [15,16] proposed an Arrhenius-like temperature dependence for $\dot{\varepsilon}^*(T)$ and a linear temperature dependence for $\sigma_i(T)$. They obtained these results by fitting Eq. (4) for different temperatures to the experimental data. In what follows we propose to demonstrate that the same laws can be established by making abstraction of the fitting to the experimental data.

When Bauwens-Crowet et al. [7] introduced the strain rate/temperature superposition principle for the yield stress, they also pointed up that both shifts have to follow a linearized Arrhenius law given by:

$$\begin{cases}\Delta(\log\dot{\varepsilon})=A\left(\dfrac{1}{T}-\dfrac{1}{T_{\mathrm{ref}}}\right)\\ \Delta\left(\dfrac{\sigma_y}{T}\right)=B\left(\dfrac{1}{T}-\dfrac{1}{T_{\mathrm{ref}}}\right)\end{cases} \tag{8}$$

where A and B are material parameters. Originally, these relations were obtained by making an asymptotic development of the Ree-Eyring model at low and high strain rates. In the present work, we assume that the cooperative model follows the linearized Arrhenius law for both shifts (Eq. (8)). This assumption will allow us to calculate explicitly the characteristic strain rate $\dot{\varepsilon}^*(T)$ and the internal stress $\sigma_i(T)$.

To determine the form of the characteristic strain rate, we equate the right hand side of the first equations of Eqs. (7) and (8), and making use of the relationship between the decimal and the natural logarithm, to obtain:

$$\dot{\varepsilon}^*(T)=\dot{\varepsilon}_0\exp\left(-\frac{\Delta H_\beta}{kT}\right)$$

$$\text{with}\quad\begin{cases}\Delta H_\beta=Ak\ln 10\\ \dot{\varepsilon}_0=\dot{\varepsilon}^*(T_{\mathrm{ref}})\exp\left(\dfrac{\Delta H_\beta}{kT_{\mathrm{ref}}}\right)\end{cases} \tag{9}$$

Here ΔH_β is the β activation energy (see later) and $\dot{\varepsilon}_0$ is a constant pre-exponential strain rate, which does not depend on T_{ref}. The unicity of $\dot{\varepsilon}_0$ can be easily demonstrated ab absurdo.

We use a similar procedure to determine the internal stress. By equating the right hand side of the second equations of Eqs. (7) and (8), we obtain:

$$\sigma_i(T)=\sigma_i(0)-mT$$

$$\text{with}\quad\begin{cases}\sigma_i(0)=-B\\ m=\dfrac{1}{T_{\mathrm{ref}}}(\sigma_i(0)-\sigma_i(T_{\mathrm{ref}}))\end{cases} \tag{10}$$

Here $\sigma_i(0)$ is the internal stress at 0 K and m is a material constant which does not depend on T_{ref}. The unicity of m can also be demonstrated ab absurdo. This linear dependence of

σ_i on temperature was intuitively postulated by Povolo and Hermida [15]. This result is now clearly demonstrated.

The final expression of the cooperative model for temperatures below the glass transition temperature (T_g) is obtained by substituting Eqs. (9) and (10) into Eq. (4):

$$\sigma_y = \sigma_i(0) - mT + \frac{2kT}{V}\sinh^{-1}\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0 \exp\left(-\frac{\Delta H_\beta}{kT}\right)}\right)^{1/n} \tag{11}$$

Concerning the expression of the shift parameters A and B, an interesting parallel can be made with the Ree-Eyring model. As a matter of fact, following the work of Bauwens-Crowet et al. [7], A and B can be expressed as a function of the Ree-Eyring parameters (Eq. (1)):

$$\begin{cases} A = \dfrac{Q_\beta}{k \ln 10} \\ B = -\dfrac{A_\alpha(Q_\alpha - Q_\beta)}{k} \end{cases} \tag{12}$$

In accordance with the fact that the Ree-Eyring model is a good description of the yield stress, we suppose that the parameters for the horizontal and vertical shifts calculated using this model are also very good estimates. To generalize this, we can assume that any model leading to an acceptable predictive capability of the yield stress can be used to correctly estimate these shift parameters. We can therefore postulate that the expression of the shift parameters should be independent of the model. Consequently, by identification of the parameters A and B using Eqs. (9), (10) and (12), we get:

$$\begin{cases} \Delta H_\beta = Q_\beta \\ \sigma_i(0) = \dfrac{A_\alpha(Q_\alpha - Q_\beta)}{k} \end{cases} \tag{13}$$

It is worth noticing that both the cooperative and the Ree-Eyring models consider the same β activation energy.

2.4. Extension of the model above the glass transition temperature

For the modeling of the mechanical properties of amorphous polymers, the glass transition temperature T_g can be seen as a useful parameter to differentiate the solid state from the rubbery state. However, the glass transition does not occur for a single temperature but for a large temperature domain. According to these considerations, the yield stress of amorphous polymers vanishes at a temperature higher than T_g. Several authors [2,8,21] have previously studied the yield stress properties of amorphous polymers above T_g. For the modeling of the yield stress in this region, they considered the WLF equation [22] according to the fact that the molecular motions are of much greater amplitude than below T_g. Under the same consideration, the linearized Arrhenius dependence of the shifts cannot be used anymore and the WLF equation will be used for the modeling above T_g.

For the determination of $\dot{\varepsilon}^*(T \geq T_g)$, we will use a similar procedure as described in the previous paragraph. We have first to know the mathematical form of the horizontal shift before trying to calculate $\dot{\varepsilon}^*(T \geq T_g)$. Here, the idea is to divide the horizontal shift $\Delta(\log \dot{\varepsilon})$ in two parts, one below T_g and one above T_g:

$$\Delta(\log \dot{\varepsilon})_{T_{ref} \to T} = \Delta(\log \dot{\varepsilon})_{T_{ref} \to T_g} + \Delta(\log \dot{\varepsilon})_{T_g \to T} \tag{14}$$

According to Eqs. (8) and (9), the first term is given by:

$$\Delta(\log \dot{\varepsilon})_{T_{ref} \to T_g} = \frac{\Delta H_\beta}{k \ln 10}\left(\frac{1}{T_g} - \frac{1}{T_{ref}}\right) \tag{15}$$

For the second term, we use the WLF equation:

$$\Delta(\log \dot{\varepsilon})_{T_g \to T} = \log\frac{\dot{\varepsilon}(T_g)}{\dot{\varepsilon}(T)} = \frac{-c_1^g(T - T_g)}{c_2^g + (T - T_g)} \tag{16}$$

where c_1^g and c_2^g are the WLF parameters. The use of the WLF equation can be justified by drawing a parallel between the strain rate of a uniaxial loading test and the frequency of dynamic measurements (i.e. damping test). For a dynamic mechanical test carried out at a frequency f and for a maximal strain γ_{max}, the equivalent uniaxial strain rate $\dot{\varepsilon}$ is classically given by $\dot{\varepsilon} = 4f\gamma_{max}$ [23]. As a result, the quantities $f(T_g)/f(T)$ and $\dot{\varepsilon}(T_g)/\dot{\varepsilon}(T)$ are equal and allow us to demonstrate the validity of Eq. (16). The horizontal shift is then given by substituting Eqs. (15) and (16) into Eq. (14). Subsequently, the characteristic strain rate above T_g can be expressed as:

$$\dot{\varepsilon}^*(T \geq T_g) = \dot{\varepsilon}_0 \exp\left(-\frac{\Delta H_\beta}{kT_g}\right)\exp\left(\frac{\ln 10 \times c_1^g(T - T_g)}{c_2^g + T - T_g}\right) \tag{17}$$

In Eq. (17) all parameters have been defined previously. It can be noted that $\dot{\varepsilon}^*(T)$, as defined by Eq. (9) for $T < T_g$ and by Eq. (17) for $T \geq T_g$, is a continuous function of T.

For the determination of $\sigma_i(T \geq T_g)$, as it was suggested by Fotheringham and Cherry [18], we simply consider a vanishing internal stress above T_g:

$$\sigma_i(T \geq T_g) = 0 \tag{18}$$

According to this assumption, the proposed model for the yield stress will not be continuous through the glass transition. Moreover, we have postulated that the glass transition occurs for a single temperature, even though it is universally known that it occurs for a large domain of temperature. We have considered other models for the expression of σ_i such as a WLF temperature dependence, but the diverse results obtained were not very different from the drastic approximation proposed by Eq. (18). Another point to be made is that the glass transition is known to be dependent on the viscoelastic properties and so it varies with the rate of applied load [24]. Here, we neglect this effect by taking T_g constant for any given strain rates.

Finally, by substituting Eqs. (17) and (18) into Eq. (4), the expression of the cooperative model above T_g is given by:

$$\sigma_y = \frac{2kT}{V}\sinh^{-1}\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0 \exp\left(-\frac{\Delta H_\beta}{kT_g}\right)\exp\left(\frac{\ln 10 \times c_1^g (T-T_g)}{c_2^g + T - T_g}\right)}\right)^{1/n} \tag{19}$$

3. Results and discussion

3.1. Identification of the model parameters

Like in the Ree-Eyring model, the number of the parameters in our formulation of the cooperative model for amorphous polymers is six (n, V, $\dot{\varepsilon}_0$, ΔH_β, $\sigma_i(0)$ and m). Since, we will compare our model predictions to those from the Ree-Eyring model, we will first analyze the parameters for each model. The models parameters are given for three amorphous polymers (PC, PMMA and PVC). The parameters of both models were obtained from the same experimental data ([25] for PC, [12] for PMMA and [7] for PVC). In Table 1, the six parameters of the Ree-Eyring model were calculated according to an asymptotic development of the model at the low and high strain rates [12]. For the cooperative model, the six parameters are presented in Table 2. For PMMA and PVC, we used the work of Povolo and co-workers [15,16] to identify the model parameters for our proposed formulation. For PC, we used a somewhat similar method as the one of Brooks et al. [17]. We first choose a reference temperature and we determine the horizontal and vertical shifts according to Eqs. (8) and (12) to build a master curve for the chosen reference temperature ($T_{ref} = 20$ °C, see Fig. 2). If the Ree-Eyring parameters are not known, the shifts can be determined by eye with a decent accuracy. Then using a curve-fitting software, we numerically calculate the parameters for the cooperative model (Eq. (4)). From the best fit, the parameters n, V, $\dot{\varepsilon}^*(T_{ref})$ and $\sigma_i = (T_{ref})$ are obtained. According to Eqs. (9) and (10), we are able to calculate $\dot{\varepsilon}_0$, ΔH_β, $\sigma_i(0)$ and m. We note that this method for the parameters identification is based on the herein proposed strain rate/temperature superposition principle. This is different from the identification method used by Povolo co-workers [15,16]. However, the results from both methods are similar, that is why we used the results of Povolo and co-workers to get the model parameters for PMMA and PVC.

3.2. Strain rate dependence

Fig. 3 shows, for PC and PMMA, a comparison of the strain rate dependence for the compressive yield stress between the cooperative model, the Ree-Eyring model and experimental data from the literature. The cooperative model provides an excellent agreement of the data for different strain rates and at different temperatures. For PC, thanks to the data of Steer (Ref. [25]) the cooperative model is validated for the first time at high strain rates. This result justifies our assumption concerning the strain rate—temperature superposition principle. In the case of the Ree-Eyring model, the yield stress dependence on strain rate is also well described for different temperatures. However, in the case of PMMA and for medium strain rates, this model does not fit well the experimental data. This effect is mainly due to the writing of the model in two distinct processes [15].

Despite, we have given the activation parameters of PVC, we are not showing any results for the yield stress of this material. The main reason is that PVC presents a similar behavior as PMMA. Nonetheless, we can state that the results for PVC are in excellent agreement with the results found in the literature [7]. Like for PMMA, these experimental results are limited to the low and medium strain rates.

3.3. Temperature dependence

Concerning the temperature dependence of the compressive yield stress, the results for PC and PMMA are shown in Fig. 4. For both models, the predictions are in good agreement with the experimental data. As it was explained previously, the parameters were obtained after experimental data of the yield stress plotted as function of the strain rate. Consequently, it is quite remarkable that the same parameters can be used to correctly predict the data of the yield stress plotted as function of the temperature. This

Table 1
Parameters for the Ree-Eyring model

Parameter	PC (after Ref. [25])	PMMA (after Ref. [12])	PVC (after Ref. [7])
A_α (Pa)	6000	6958	6860
C_α (s)	4.10×10^{-30}	5.00×10^{-52}	1.00×10^{-38}
Q_α (J/mol)	284,240	412,000	294,700
A_β (Pa)	54,000	36,652	9898
C_β (s)	2.90×10^{-7}	4.67×10^{-17}	4.26×10^{-10}
Q_β (J/mol)	20,900	107,000	58,520

Table 2
Parameters for the proposed cooperative model

Parameter	PC (authors)	PMMA (adapted from Refs. [15,26])	PVC (adapted from Ref. [16])
n	3.91	6.65	10.00
V (m^3)	4.66×10^{-29}	8.39×10^{-29}	10.50×10^{-29}
$\sigma_i(0)$ (MPa)	190	210	199
m (Mpa/K)	0.384	0.538	0.570
$\dot{\varepsilon}_0^*$ [1/s]	1.25×10^{9}	3.60×10^{17}	2.97×10^{12}
ΔH_β (J/mol)	20,900	109,031	58,387
T_g (K)	413	378	348
c_1^g	17.44	9	17.44
c_2^g [°C]	51.6	36	51.6

observation is another validation of the strain rate/temperature superposition principle.

For PC, we make a comparison with data adapted from the work of G'Sell and Gopez [27] (Fig. 4) since, these authors have carried out few measurements above T_g. The PC used by G'Sell and Gopez (a 'Makrolon' PC manufactured by Bayer) was different from the PC used by Steer (a 'Lexan' PC from the company GE Plastics). Moreover the data from G'Sell and Gopez were obtained for shear tests. Hence, the shear stresses were corrected with the von Mises factor relating shear and tensile stresses (or strain rates). Despite these remarks and contrary to the Ree-Eyring model, the predictions of the cooperative model are in good agreement with the experimental data. We obtained a satisfactory agreement for the description of the definite drop of the yield stress of PC in the glass transition domain as it was previously observed by other authors [28].

For PMMA, the experimental data are those of Bauwens-Crowet [12]. Below T_g, for the strain rate of $4\times10^{-1}\ \mathrm{s}^{-1}$, there is a discrepancy between the two models at temperatures near T_g (Fig. 4). The cooperative model seems to be the most suitable according to the experimental data. Above T_g, the Ree-Eyring model can give erroneous results. Fig. 4 shows that the Ree-Eyring model presents non physical results for PMMA at the high temperatures while the yield stress given by the cooperative model tends logically towards the zero value. Unfortunately, we do not have experimental data above T_g for PMMA to bear out the predictions of the proposed cooperative model. By a comparison, the Robertson model [2] presents as well a faster decrease of the yield stress with temperature above T_g. However, Robertson proposed a quasi-linear dependence of the yield stress on temperature above T_g whereas, we considered a strong non-linear dependence on temperature.

3.4. Role of the secondary relaxation in the yield process

It is widely recognized that the localized movements of the secondary relaxations of amorphous polymers are related to the mechanical behavior of these materials. More recently, authors like Yee and co-workers [23,29–31] and Halary and co-workers [32,33] have emphasized the correlation existing between yielding and segmental mobility associated to the secondary relaxation motions. Bauwens-Crowet and co-workers [9–12] have shown that the process β of the Ree-Eyring equation can be associated

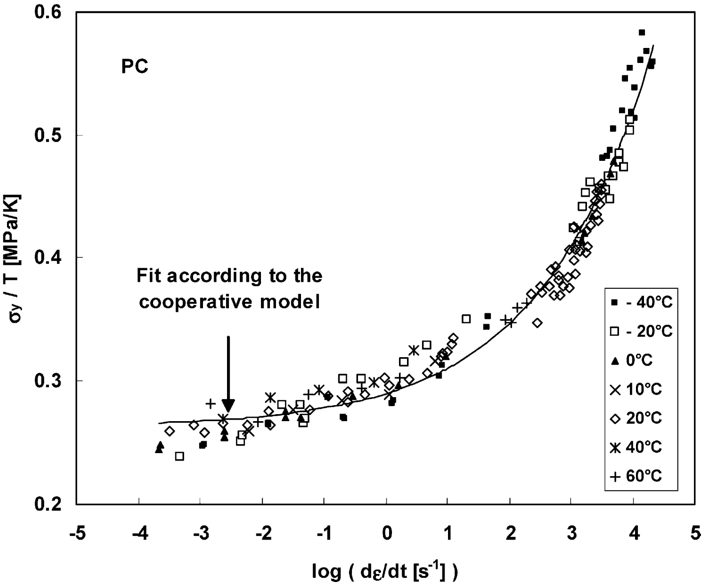

Fig. 2. Master curve built at 20 °C for a PC tested under uniaxial compression after the data of Steer in Ref. [25].

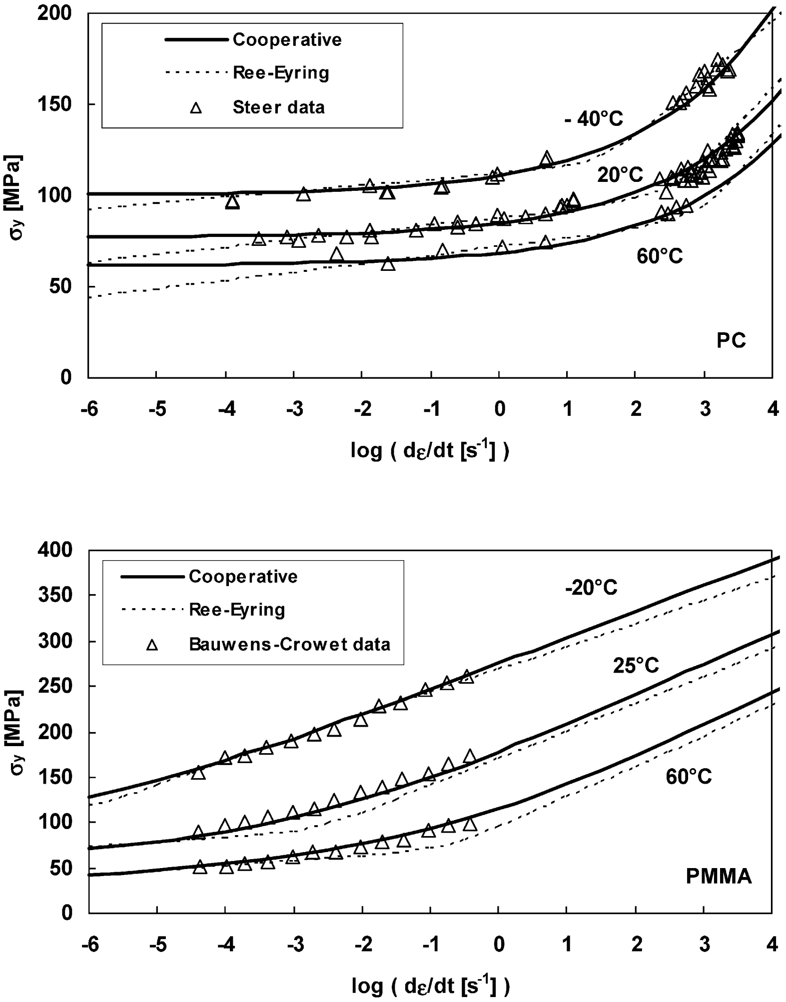

Fig. 3. Variation of the compressive yield stress with strain rate for PC and PMMA.

to the β mechanical loss peak revealed by oscillatory measurements. The same authors showed that, for at least five glassy polymers, the same molecular movements are involved for the β yield process and for the β loss peak since the activation energies associated to each process are identical [9–12]. On the other hand, it has been shown that there is no connection between the rheological process α of the Ree-Eyring model and the glass transition [10].

In the case of the cooperative model, we have demonstrated that ΔH_{β} is equal to Q_{β} (Eq. (13)). To validate this result we compared the numerical values of these energies in Table 3, which shows that we have an excellent agreement. This result implies therefore that the cooperative model takes into account the secondary relaxation. Originally in the case of amorphous polymers, nor Fotheringham and Cherry [18,19], neither Povolo and coworkers [15,16], have provided any information on the nature of the activation energy related to the cooperative model. It is worth noting that our formulation of the cooperative model considers a physical process that has been identified as a plasticity precursor. However, authors like Chen et al. [30] think that the quantitative link existing between the β process of the Ree-Eyring model and the dynamic mechanical secondary relaxation is more suggestive than substantial.

The other parameter to be discussed in this paragraph is the pre-exponential strain rate $\dot{\varepsilon}_0$ given in Eq. (9). As it is generally the case, the β movements follow an Arrhenius law with a pre-exponential factor of about 10^{12}–10^{14} Hz [34]. For the cooperative model, below T_g, $\dot{\varepsilon}^*(T)$ follows an Arrhenius law but the values are not of the same order of what was expected (Table 3). Nonetheless, in comparison with the Ree-Eyring theory, the values of $\dot{\varepsilon}_0$ are more physical. For instance, the α process of the Ree-Eyring theory is completely out of range in comparison to physical quantities such as the Debye frequency given by kT/h (h being the Planck constant).

As a final comment concerning the semi-crystalline polymers, authors like Truss et al. [14] found also a strong correlation of the different activation energies of the Ree-Eyring processes with specific molecular motions such as γ relaxation, α relaxation and melting. This work will be

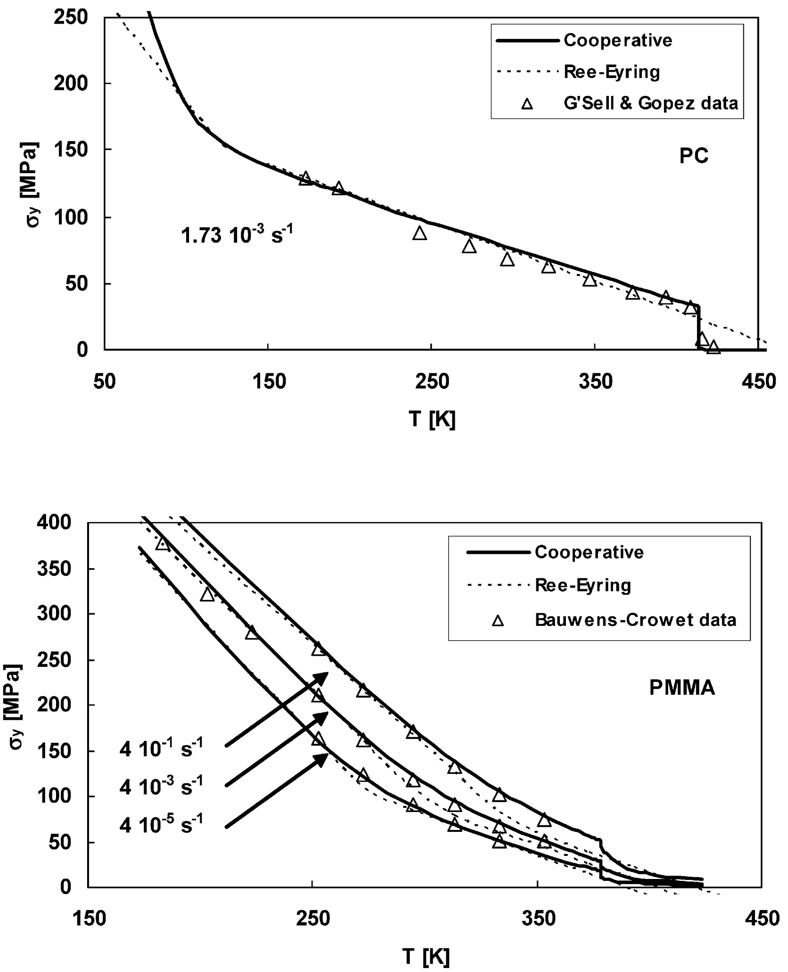

Fig. 4. Variation of the compressive yield stress with temperature for PC and PMMA.

helpful for the development of specific formulations of the cooperative model to semi-crystalline polymers.

3.5. Activation volume

Even if there are still doubts of what clearly represents the activation volume, it is well established that molecular yield processes are both intermolecular and intramolecular [30]. In Eq. (3), V is not the actual activation volume of the flow process and n does not represent the number of statistical links involved during yielding. The actual activation volume must be temperature and strain rate dependent according to the development of Escaig, Lefebvre and co-workers [35,36]. An unpublished study of ours [37] has shown that the actual activation volume of amorphous polymers is activated by temperature and bears the stamp of the secondary relaxation and of the glass transition. In the same study, we have also shown that the critical value of $nV/2$ corresponds to the theoretical least size of the actual activation volume.

Table 3
Comparison of the activation parameters for the Ree-Eyring and the cooperative models

Model	Parameter	PC	PMMA	PVC
Cooperative	ΔH_β (J/mol)	20,900	109,031	58,387
Ree-Eyring	Q_β (J/mol)	20,900	107,000	58,520
Cooperative	$\dot{\varepsilon}_0$ [1/s]	1.25×10^{9}	3.60×10^{17}	2.97×10^{12}
Ree-Eyring	$1/C_\alpha$ (1/s)	2.44×10^{29}	2.00×10^{51}	1.00×10^{38}
Ree-Eyring	$1/C_\beta$ (1/s)	3.45×10^{6}	2.14×10^{16}	2.35×10^{9}
Cooperative	$\sigma_i(0)$ (MPa)	190	210	199
Ree-Eyring	$A_\alpha(Q_\alpha-Q_\beta)/k$ (MPa)	190	255	195
Cooperative	m (MPa/K)	0.384	0.538	0.570
Cooperative	$\sigma_i(0)/T_g$ (MPa/K)	0.460	0.555	0.570

3.6. A physical model for the linear dependence of the internal stress

For the cooperative model, we have shown in Section 2.3 that the linear dependence of $\sigma_i(T)$ finds a justification in the strain rate/temperature superposition principle. Nonetheless, a very interesting parallel can be drawn between our results and the work of Rault [38]. This author has applied the compensation law to the yielding of amorphous and semi-crystalline polymers to find out that the yield stress may be written as:

$$\sigma_y = \sigma_0 - \frac{\sigma_0}{T_g} T + 2.3 \frac{kT}{V} \log \frac{\dot{\varepsilon}}{\dot{\varepsilon}_0} \tag{20}$$

In this, Rault interprets σ_0 as the yield stress at 0 K. Our form of the cooperative model below T_g given by Eq. (11) is comparable with Eq. (20). However, to be consistent with Eq. (11), it is not $\sigma_y(0)$ that should be used in Eq. (20), but rather $\sigma_i(0)$. As a matter fact, our parameter m should verify $m \approx \sigma_i(0)/T_g$ which is confirmed in Table 3. For PMMA and PVC, there is no discrepancy between m and the ratio $\sigma_i(0)/T_g$. For PC, the result is not as good due to the drop of the yield stress in the glass transition domain (Fig. 4).

4. Conclusions

The proposed formulation for the cooperative model is valid for a wide range of strain rates and temperatures: from quasi-static to impact loading rates and for low temperatures to above the glass transition temperature. Our contributions to this formulation can be summarized as: (1) the strain rate and temperature dependencies are clearly demonstrated using simple mathematics; (2) the activation energy of the cooperative model is identified as the energy of the β relaxation; (3) the cooperative model is extended to predict yield above the glass transition temperature; (4) the cooperative model is validated, for the first time, for impact loading rates. Our predicted results are in fine agreement with the experimental ones.

Many perspectives of this work are envisaged: (1) to implement the cooperative model in the formalism of the large deformation behavior [39] for the prediction of the stress–strain response. This work is under way and the first results are already encouraging [40]; (2) to extend the cooperative model to semi-crystalline polymers via a micromechanical development. We note that both the cooperative approach and the Ree-Eyring approach have already been used for semi-crystalline polymers [19,14,17].

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