

# A unified model for stiffness modulus of amorphous polymers across transition temperatures and strain rates

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## Abstract

In many applications, polymer materials undergo a large variety of mechanical loading conditions, wherein the influences of temperature and strain rate are of prime importance. Mahieux and Reifsnider [Mahieux CA, Reifsnider KL. *Polymer* 2001;42:3281. [19]] have proposed a statistical model to describe the stiffness variation of polymers over a wide range of temperatures. However, this model does not consider any frequency/strain rate dependence of the stiffness modulus. Starting from this consideration, we propose here to transform this latter model into a robust physically based model for the prediction of the stiffness modulus for a wide range of temperatures and frequencies/strain rates. This new formulation has been successfully validated for two amorphous polymers, polymethylmethacrylate (PMMA) and polycarbonate (PC), using dynamic mechanical analysis and uniaxial compression testing. Good agreement has been found between theory and experiment for the non-linear behavior of the initial Young's modulus, at the very high strain rates.

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**Keywords:** Stiffness modulus; Temperature; High strain rate

## 1. Introduction

The mechanical response of amorphous polymers is known to be strongly influenced by testing conditions. For this reason, the development of material constitutive models must consider both temperature and strain rate dependence. Over the years, many models have been proposed for the determination of the yield stress [1–12]. However, Richeton et al. [13] have revealed that these models are either unable to account for the dramatic increase of the yield stress at very high strain rates or are not valid in the glass transition region. In this spirit, Cady et al. [14] suggested that technologically advanced applications of polymers requires the development of physically-based models with a detailed quantitative knowledge of the separate and synergistic effects of temperature and strain rate on the mechanical response of the material. Starting from these considerations,

Richeton et al. [15,16] have proposed a new formulation of the cooperative model for the determination of the yield stress to be valid over a wide range of temperatures and strain rates. However, the use of this model for the prediction of the initial stage of the stress–strain response did not give satisfactory results. The main reason is that the Young's modulus is also strongly influenced by temperature and strain rate. In line with the recommendations of Cady et al. [14], there is also a real need to develop robust constitutive models for the stiffness modulus. These models should incorporate the temperature dependence below and above  $T_g$ , as well as the strain rate effect for quasi-static and dynamic loading cases ( $\dot{\epsilon} > (1/s^{-1})$ ).

The temperature dependence of the Young's modulus used in constitutive models is generally given by phenomenological descriptions. In the glassy region, the initial Young's modulus of amorphous polymers,  $E$ , is found to decrease with increasing temperature in the following manner [17]:

$$\log E(T) = \log E(T^{\text{ref}}) - a \cdot (T - T^{\text{ref}}) \quad (1)$$

where  $E(T^{\text{ref}})$  is the Young's modulus at the reference temperature  $T^{\text{ref}}$  and  $a$  is a parameter characterizing the

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temperature sensitivity of the material. However, this equation is not valid in the vicinity of the glass transition region due to the abrupt drop in stiffness between the glassy and the rubbery state. To take into account the effect of the glass transition, Drozdov [18] proposed the following temperature dependence for  $E$ :

$$E(T) = E_0 - \frac{E_1}{T_g - T} \quad (2)$$

where  $E_0$  and  $E_1$  are material parameters and  $T_g$  is the glass transition temperature. However, this equation is only slightly better than Eq. (1), as it can only be used to describe the very beginning of the glass transition, but not the rubbery plateau. To the best of our knowledge, the only model to be valid from fully glassy to fully rubbery is due to the work of Mahieux and Reifsnider [19,20]. These authors have recently developed a statistical model for the temperature dependence of the storage modulus. The basis of their approach is the influence of temperature on secondary bonding in polymers. Their concept can be summarized as follows (full excerpt from *J Mater Sci*, 2002;37:912):

Any transition in the polymer (secondary relaxation, glass transition, flow) requires breakage of secondary bonds (e.g. van der Waals, polar attraction). By breakage we mean cessation of the attractive interaction between the specific atoms involved in the molecular motion corresponding to the specific relaxation, i.e. rotation of a side group (e.g. beta relaxation), reptation of the main chains (e.g. glass transition) or global translations (e.g. flow). A distribution of strengths exists for the bonds between the macromolecules due to the different nature of bonds present in the material (e.g. Van der Waals, crosslinking) and the spatial arrangement of the molecules (Van der Waals interactions depending on the proximity of atoms).

The idea of Mahieux and Reifsnider [19,20] was to use Weibull statistics to represent the failure of these secondary bonds during the relaxation processes that lead to stiffness change over a wide range of temperatures. Although it has been shown that their model can be used to model all types of polymers (with different chemical nature, molecular weights and crystallinity contents), we will restrict its application here to amorphous polymers. These materials undergo three main transitions ( $\beta$ -transition, glass transition and flow). The storage modulus is given by:

$$\begin{aligned} E(T) = & (E_1 - E_2) \cdot \exp\left(-\left(\frac{T}{T_\beta}\right)^{m_1}\right) \\ & + (E_2 - E_3) \cdot \exp\left(-\left(\frac{T}{T_g}\right)^{m_2}\right) \\ & + E_3 \cdot \exp\left(-\left(\frac{T}{T_f}\right)^{m_3}\right) \end{aligned} \quad (3)$$

where  $T_\beta$  is the  $\beta$ -transition temperature,  $T_g$  is the glass transition temperature and  $T_f$  is the temperature marking the beginning of the flow region. The moduli,  $E_i$ , are the instantaneous stiffness of the material at the beginning of each region. The parameters  $m_i$  are the Weibull moduli, corresponding to the statistics of the bond breakage.

The physical considerations of the statistical model offer great potential for the modeling of the mechanical properties of polymers, however, the model unfortunately does not consider any frequency dependence of the storage modulus. Therefore, we propose in this paper to improve the original theory of Mahieux and Reifsnider [19,20] by incorporating a physical frequency/strain rate dependence for both the storage modulus and for the initial Young's modulus. Our work will be validated on two amorphous polymers, polymethylmethacrylate (PMMA) and polycarbonate (PC), with dynamic mechanical analysis measurements for the storage modulus and uniaxial compression tests for the initial Young's modulus.

## 2. Dynamic mechanical analysis

### 2.1. Experimental work

Dynamic mechanical analysis (DMA) measurements were carried out on amorphous polymer samples: polymethylmethacrylate (Degussa AG Plexiglas<sup>®</sup> PMMA) and polycarbonate (GE Plastics Lexan<sup>®</sup> PC). A dual cantilever setup was used for the deformation geometry; the DMA equipment was a rheometrics solids analyzer (RSA II). The dimensions of the samples were of 45 mm in length, 8 mm in width and 2 mm of thickness. Each sample was deformed to a strain of 1% for different frequencies: 0.1, 1, 10 and 100 Hz. The PMMA was tested from  $-60$  up to  $165$  °C, and PC was tested from  $25$  up to  $185$  °C. We tested PMMA at the very low temperatures to take into account the effect of the secondary transition ( $T_\beta \approx 0$  °C). For PC, we started the experiments at  $25$  °C because our experimental setup did not allow us to reach the secondary transition temperature of this material (about  $-100$  °C). The acquisition of experimental values was done every  $5$  °C. Furthermore to ensure that the center of the sample has reached the desired temperature, a time delay between two measurements of  $5$  min was employed.

### 2.2. Modeling of the frequency effect on the storage modulus

Starting from the original equation of Mahieux and Reifsnider [19,20] (Eq. (3)), we suggest the following temperature and frequency dependence for the storage modulus,  $E$ :

$$\begin{aligned}
 E(T, f) = & (E_1(f) - E_1(f)) \cdot \exp\left(-\left(\frac{T}{T_\beta(f)}\right)^{m_1}\right) \\
 & + (E_2(f) - E_3(f)) \cdot \exp\left(-\left(\frac{T}{T_g(f)}\right)^{m_2}\right) \\
 & + E_3(f) \cdot \exp\left(-\left(\frac{T}{T_f(f)}\right)^{m_3}\right) \quad (4)
 \end{aligned}$$

where the instantaneous stiffness,  $E_i(f)$ , are only frequency dependent, at each of the three transition temperatures  $T_\beta(f)$ ,  $T_g(f)$  and  $T_f(f)$ . The Weibull moduli,  $m_i$  remain constant parameters with the same value as in Eq. (3). The frequency dependence of each of the preceding parameter will be discussed according to physical considerations.

Concerning the determination of  $T_\beta(f)$ , the secondary relaxation temperature at the frequency,  $f$ , we rely on the fact that the  $\beta$ -movements (localized movements corresponding generally to the rotation of lateral groups around the main chain) are activated by an Arrhenius process:

$$\nu = \nu_0 \exp\left(\frac{-\Delta H_\beta}{kT}\right) \quad (5)$$

where  $\nu$  is the frequency at which the polymer chain segments are moving,  $\nu_0$  is the fundamental vibration frequency,  $\Delta H_\beta$  is the  $\beta$ -activation energy, and  $k$  is the Boltzmann constant. If one considers this latter expression for  $\nu^{\text{ref}}$  and  $\nu$ , the following form can be derived:

$$\ln\left(\frac{\nu^{\text{ref}}}{\nu}\right) = \frac{-\Delta H_\beta}{k} \left(\frac{1}{T^{\text{ref}}} - \frac{1}{T}\right) \quad (6)$$

By assuming that the vibration frequency  $\nu$  is directly related to the frequency  $f$  of the DMA tests, the expression of  $T_\beta$  at the frequency  $f$  can be given as function of  $T_\beta^{\text{ref}}$  at reference frequency,  $f^{\text{ref}}$ :

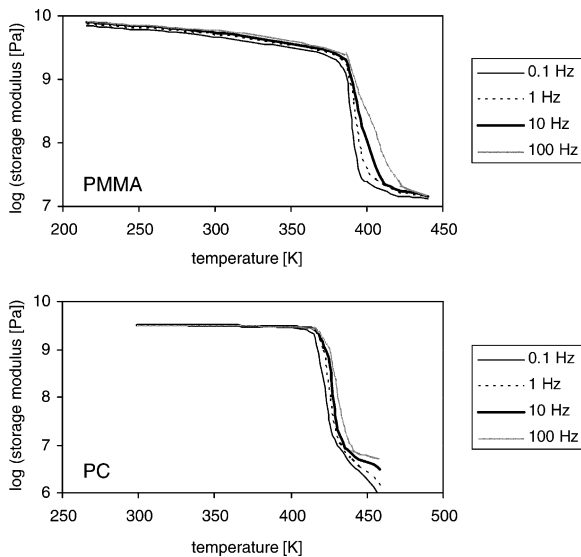


Fig. 1. Experimental results for the storage modulus of PMMA and PC for different frequencies.

$$\frac{1}{T_\beta} = \frac{1}{T_\beta^{\text{ref}}} + \frac{k}{\Delta H_\beta} \ln\left(\frac{f^{\text{ref}}}{f}\right) \quad (7)$$

For the determination of  $T_g(f)$ , the glass transition temperature at frequency,  $f$ , we rely on the time-temperature equivalence of the glass transition viscoelastic behavior and on the associated equation of Williams-Landel-Ferry (WLF) [21]:

$$\log a_{T_g \rightarrow T} = \log \frac{f(T_g)}{f(T)} = \frac{-c_1^g (T - T_g)}{c_2^g + T - T_g} \quad (8)$$

where  $c_1^g$  and  $c_2^g$  are the WLF parameters relative to  $T_g$ . This equation can also be written in term of  $T_g^{\text{ref}}$ , the glass transition temperature at the reference frequency  $f^{\text{ref}}$ , and in term of  $T_g$ , the glass transition temperature at frequency,  $f$ :

$$\log \frac{f(T_g^{\text{ref}})}{f(T_g)} = \log \frac{f^{\text{ref}}}{f} = \frac{-c_1^{\text{ref}} (T_g - T_g^{\text{ref}})}{c_2^{\text{ref}} + T_g - T_g^{\text{ref}}} \quad (9)$$

Subsequently the expression of  $T_g$  at frequency,  $f$ , can be expressed as a function of  $T_g^{\text{ref}}$ :

$$T_g = T_g^{\text{ref}} + \frac{-c_2^{\text{ref}} \log(f^{\text{ref}}/f)}{c_1^{\text{ref}} + \log(f^{\text{ref}}/f)} \quad (10)$$

For the determination of  $T_f$ , the flow temperature at frequency,  $f$ , we propose to use a phenomenological dependence on frequency as follows:

$$T_f = T_f^{\text{ref}} \left(1 + 0.01 \log\left(\frac{f}{f^{\text{ref}}}\right)\right) \quad (11)$$

Due to a lack of data in the flow region (Figs. 2 and 3), the value of 0.01 was arbitrary chosen for the pre-logarithmic constant in Eq. (11) for both polymers. The use of a logarithm function was driven by the fact that mechanical properties of polymer systems are usually sensitive to the logarithm of the rate of loading.

In the same way, we propose a similar, frequency dependence for  $E_i$ , the instantaneous moduli at the frequency,  $f$ :

$$E_i = E_i^{\text{ref}} \left(1 + s \log\left(\frac{f}{f^{\text{ref}}}\right)\right) \quad (12)$$

where  $E_i^{\text{ref}}$  is the instantaneous stiffness at the reference frequency and  $s$  is the sensitivity of the modulus to frequency. We postulate that  $s$  is a constant parameter for a given polymer. As is already the case for the three transition temperatures, there is a reasonable chance that  $s$  has a specific value for the different moduli,  $E_i$ . However, the main advantage of this latter assumption is to consider one single parameter instead of a set of three different parameters.

As a final point, the temperature and frequency dependent expression of the storage modulus is derived by inserting Eqs. (7), (10)–(12) into Eq. (4). In addition, due to the large range of frequencies that the material can be evaluated at, it is preferable to choose an intermediate value

for the reference frequency. A value of 1 Hz for  $f^{\text{ref}}$  appears to be a judicious choice.

### 2.3. DMA versus model: Results and discussion

Fig. 1 presents the storage modulus of PMMA and PC as determined from the experimental results of the DMA testing. The influence of the frequency on the glass transition is easily observable for both polymers. PMMA appears to be more sensitive to frequency than PC. First, the modulus of PMMA in the glassy region is sensitive to frequency, whereas the modulus of PC is almost constant. This difference in mechanical behavior is due to the fact that the secondary transition,  $T_\beta$ , of PMMA starts near room temperature, whereas the  $T_\beta$  of PC is much lower (about  $-100^\circ\text{C}$ ). Secondly, it is observed that the shift of  $T_g$  due to frequency occurs over a larger temperature domain for PMMA than for PC. In addition, PC does not show a definite rubbery plateau region of modulus like PMMA, but passes directly from the viscoelastic region to the region of permanent flow. This phenomenon could be attributed to the fact that PC has a lower molecular weight than PMMA.

The modeling results for the storage modulus are presented in Fig. 2 for PMMA and in Fig. 3 for PC. The agreement between theory and experiments is reasonable good for both polymers and for the four frequencies. The parameters used for the model are given in Table 1. The nine reference parameters were easily determined for both polymers since they refer to well-defined, measurable physical quantities according to the description of Mahieux and Reifsnider [19,20]. The values of  $c_1^g$  and  $c_2^g$  were those given by Ferry [21]. For the value of the  $\beta$ -energy, we took the values from our previous work carried out on the exact same materials [16]. The frequency sensitivity,  $s$ , was obtained from an average value of the experimental data. Furthermore, in the case of PMMA, our values are slightly different from those of Mahieux and Reifsnider at 20 Hz [20]. In particular, we had to use a higher

value for the Weibull modulus,  $m_2$ , due to the abrupt drop at the glass transition.

## 3. Uniaxial testing

### 3.1. Experimental work

Both quasi-static uniaxial compression tests and dynamic uniaxial compression tests were carried out on PMMA and PC. The quasi-static uniaxial compression tests were conducted on a servohydraulic load frame. The samples were tested to different temperatures, ranging from  $-40^\circ\text{C}$  to temperatures above  $T_g$  and at different constant extension rates, leading to strain rates ranging from  $10^{-4}$  to  $10\text{ s}^{-1}$ . The dynamic uniaxial compression tests were conducted for different temperatures at high strain rates of about  $800\text{--}5000\text{ s}^{-1}$  using a split Hopkinson pressure bar setup. More information concerning these experimental procedures can be found in our previous paper on the yield stress of amorphous polymers [16].

### 3.2. Modeling of strain rate effect on the initial Young's modulus

For the modeling of temperature and strain rate dependence of the initial Young's modulus, we will use a similar development as in the Section 3.2. We propose to write the initial Young's modulus,  $E$ , as:

$$E(T, \dot{\epsilon}) = (E_1(\dot{\epsilon}) - E_1(\dot{\epsilon})) \cdot \exp\left(-\left(\frac{T}{T_\beta(\dot{\epsilon})}\right)^{m_1}\right) + (E_2(\dot{\epsilon}) - E_3(\dot{\epsilon})) \cdot \exp\left(-\left(\frac{T}{T_g(\dot{\epsilon})}\right)^{m_2}\right) + E_3(\dot{\epsilon}) \cdot \exp\left(-\left(\frac{T}{T_f(\dot{\epsilon})}\right)^{m_3}\right) \quad (13)$$

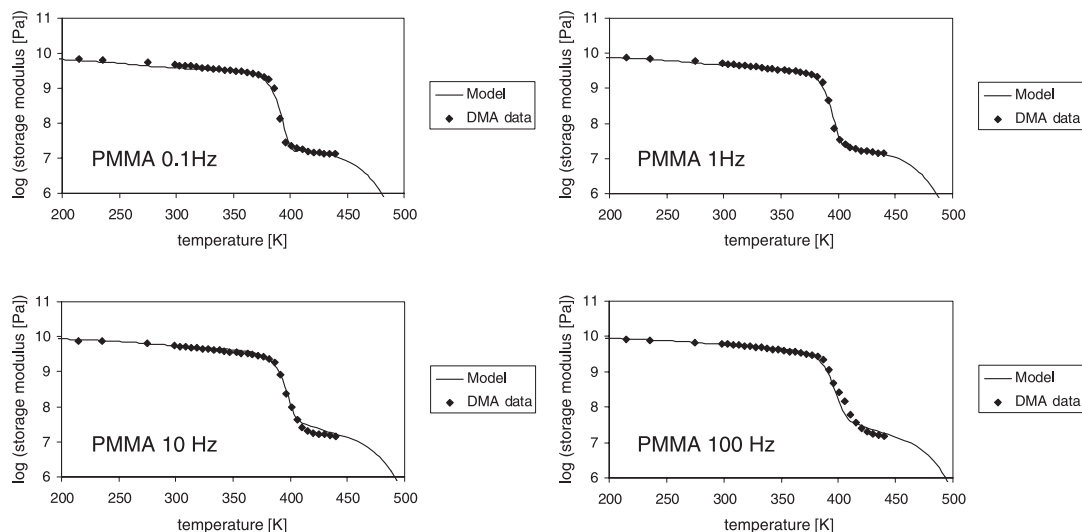


Fig. 2. Experimental and theoretical results for the storage modulus of PMMA.

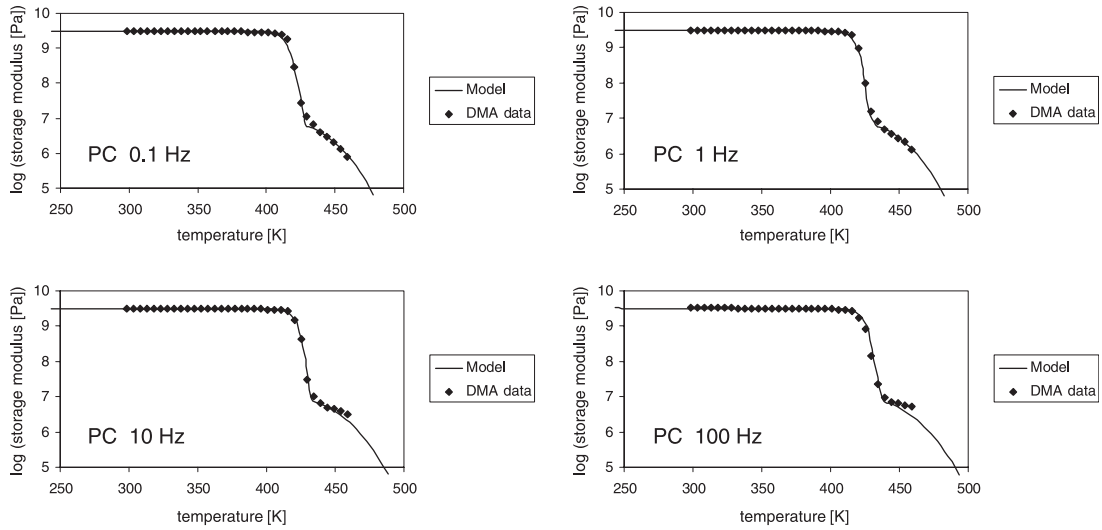


Fig. 3. Experimental and theoretical results for the storage modulus of PC.

where all parameters have the same meaning as before. The Weibull moduli,  $m_i$ , are the same constant parameters. The strain rate dependence of the three transition temperatures and of the instantaneous stiffness,  $E_i$ , is based on a relationship between the oscillatory dynamic mechanical testing (DMA) and the uniaxial testing (UT). This formula is expressed as [22]:

$$\dot{\varepsilon}^{\text{UT}} \approx 4f^{\text{DMA}} \varepsilon_{\text{max}}^{\text{DMA}} \quad (14)$$

where  $\dot{\varepsilon}^{\text{UT}}$  is the strain rate for uniaxial testing,  $f^{\text{DMA}}$  is the frequency of the DMA test and  $\varepsilon_{\text{max}}^{\text{DMA}}$  corresponds to the maximum strain value taken by the oscillatory deformation; an illustration of this result can be found in Xiao et al. [22]. Consequently, the relationship in Eq. (14) between the DMA results and the uniaxial results allows the following relationship to be obtained:

$$\frac{f^{\text{ref}}}{f} = \frac{\dot{\varepsilon}^{\text{ref}}}{\dot{\varepsilon}} \quad (15)$$

Table 1  
Parameters for the modeling of the storage modulus

	PMMA	PC
$f^{\text{ref}}$ (Hz)	1	1
$E_1^{\text{ref}}$ (MPa)	8600	3500
$E_2^{\text{ref}}$ (MPa)	3600	3100
$E_3^{\text{ref}}$ (MPa)	20	20
$T_{\beta}^{\text{ref}}$ (K)	270	173
$T_g^{\text{ref}}$ (K)	384	419
$T_f^{\text{ref}}$ (K)	460	430
$m_1$	5	5
$m_2$	40	80
$m_1$	20	15
$s$	0.087	0.011
$\Delta H_{\beta}$ (kJ/mol)	90	40
$c_1^g$	34.00	17.44
$c_2^g$ (°C)	80.0	51.6

Finally the strain rate dependence of the three transition temperatures is given by the following three relations (based on Eqs. (7), (10) and (11)):

$$\begin{cases} \frac{1}{T_{\beta}} = \frac{1}{T_{\beta}^{\text{ref}}} + \frac{k}{\Delta H_{\beta}} \ln\left(\frac{\dot{\varepsilon}^{\text{ref}}}{\dot{\varepsilon}}\right) \\ T_g = T_g^{\text{ref}} + \frac{-c_2^{\text{ref}} \log(\dot{\varepsilon}^{\text{ref}}/\dot{\varepsilon})}{c_1^{\text{ref}} + \log(\dot{\varepsilon}^{\text{ref}}/\dot{\varepsilon})} \\ T_f = T_f^{\text{ref}} \left(1 + 0.01 \log\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^{\text{ref}}}\right)\right) \end{cases} \quad (16)$$

A value of  $1 \text{ s}^{-1}$  is chosen for the reference strain rate,  $\dot{\varepsilon}^{\text{ref}}$ . However, it should be mentioned that the three reference transition temperatures used for the modeling of the storage modulus in the previous section will not have the same value of the reference temperatures used for the modeling of the initial Young's modulus. Indeed, in accordance with Eq. (14), a reference strain rate of  $1 \text{ s}^{-1}$  has an equivalent frequency value of about 25 Hz for an oscillatory deformation of 1%.

In addition, the WLF parameters also have to be corrected since  $T_g$  takes a different value depending on the testing mode. The following relation can be used [23]:

$$\begin{cases} c_2^{\text{DMA}} - T_g^{\text{DMA}} = c_2^{\text{UT}} - T_g^{\text{UT}} \\ c_1^{\text{DMA}} c_2^{\text{DMA}} = c_1^{\text{UT}} c_2^{\text{UT}} \end{cases} \quad (17)$$

where  $c_1^{\text{DMA}}$  and  $c_2^{\text{DMA}}$  are the WLF parameters associated to  $T_g^{\text{DMA}}$ , the glass transition temperature derived from a DMA measurement at 1 Hz, and  $c_1^{\text{UT}}$  and  $c_2^{\text{UT}}$  are the WLF parameters associated to  $T_g^{\text{UT}}$ , the glass transition temperature derived from an uniaxial testing at  $1 \text{ s}^{-1}$ .

The strain rate dependence of the instantaneous stiffness is given by:

$$E_i = E_i^{\text{ref}} \left(1 + s \log\left(\frac{\dot{\varepsilon}}{\dot{\varepsilon}^{\text{ref}}}\right)\right) \quad (18)$$

Table 2  
Parameters for the modeling of the compression modulus

	PMMA	PC
$\dot{\epsilon}_i^{\text{ref}}$ (s <sup>-1</sup> )	1 ( $\approx$ 25 Hz)	1 ( $\approx$ 25 Hz)
$E_1^{\text{ref}}$ (MPa)	5100	3500
$E_2^{\text{ref}}$ (MPa)	2700	1700
$E_3^{\text{ref}}$ (MPa)	20	20
$T_\beta^{\text{ref}}$ (K)	290	195
$T_g^{\text{ref}}$ (K)	387	423
$T_i^{\text{ref}}$ (K)	466	436
$m_1$	5	5
$m_2$	40	80
$m_3$	20	15
$s$	0.087	0.011
$\Delta H_\beta$ (kJ/mol)	90	40
$c_1^g$	32.58	16.19
$c_2^g$ (°C)	83.5	55.6

According to Eq. (14), a strain rate of 1 s<sup>-1</sup> is roughly equal to a frequency of 25 Hz.

The strain rate sensitivity,  $s$ , keeps the same value as in Section 2. However, the values of the reference instantaneous stiffness,  $E_i^{\text{ref}}$ , cannot be the same in oscillatory testing and in compression testing. It is widely known that polymers are extremely sensitive to the effect of hydrostatic pressure [16,24, 25]. In particular, the compressive yield stress was found to be greater than the tensile yield stress. The explanation lies in the fact that the hydrostatic pressure is positive in compression and negative in tension. According to the elastic linear relation between Young’s modulus and the stress at the small deformations, it could be envisaged that a similar effect has to be detected for the initial Young’s modulus. Paradoxically, the compressive modulus found in typical polymer databases (Ref. [26]) is usually smaller than the tensile modulus. In our study, this paradox is verified for the  $E_i^{\text{ref}}$  (Tables 1 and 2). Finding a physically-based model that could explain this paradox is definitely a challenging subject matter.

### 3.3. Compression versus model: Results and discussion

The modeling results for the initial Young’s modulus are presented for four different strain rates in Fig. 4 for PMMA and in Fig. 5 for PC. As expected, the experimental results are more dispersed for the uniaxial testing compared with the DMA measurements, since uniaxial mechanical testing is inherently less accurate for modulus measurements. Moreover, each data point in Figs. 4 and 5 corresponds to a different sample, whereas DMA tests were done on the same specimen, but at different frequencies and temperatures. In the case of PC at very low temperatures, the Young’s modulus appears to decrease with a decreasing temperature. This phenomenon is obviously an experimental artifact due to our specific experimental setup for the low temperature testing (Ref. [16]). Despite these considerations, the agreement between the modeling and the experiment remains satisfactory. With the exception made for the instantaneous stiffness,  $E_i^{\text{ref}}$ , all parameters were deduced from the DMA study. A recap of the recalculated parameters can be found in Table 2.

We have also presented in Fig. 6 the strain rate dependence of the Young’s modulus of PMMA and PC at 25 °C for a wide range of strain rates. The initial Young’s modulus exhibits a non-linear dependence on strain rate. A similar effect has been previously observed for the yield stress at high strain rates [15,16,27]. Several authors, such as Yee and co-workers [22,28] or Halary and co-workers [29, 30], have emphasized the existing correlation between yielding and segmental mobility associated with the  $\beta$ -relaxation process. This is also the case for the yield stress, wherein the increase of the initial Young’s modulus can be accounted for by a decrease of the  $\beta$ -movements of the polymer chains [15,16]. An increase of strain rate will diminish the molecular mobility of the chains by preventing their relaxation. The non-linear dependence of the Young’s

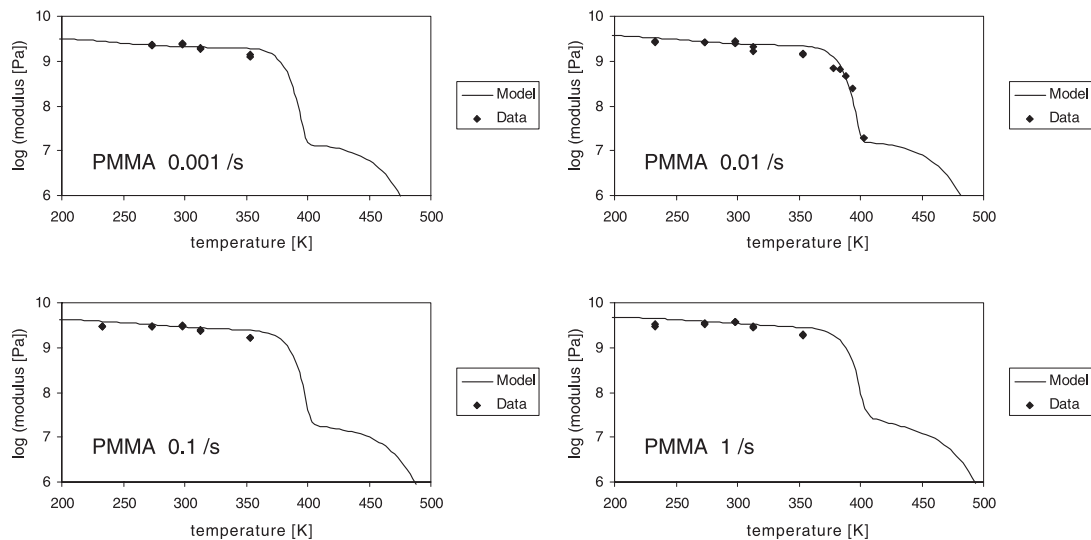


Fig. 4. Experimental and theoretical results for the compressive modulus of PMMA.

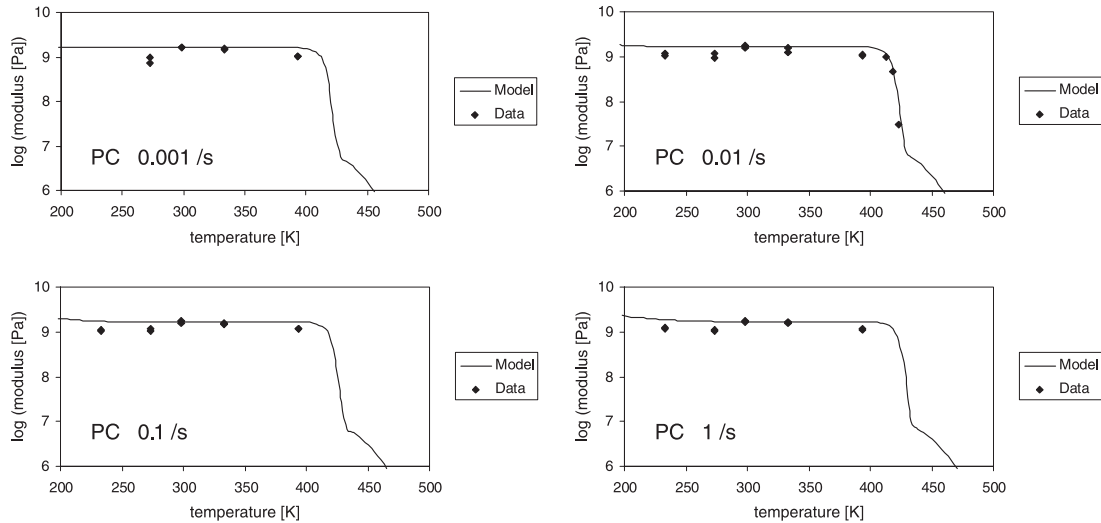


Fig. 5. Experimental and theoretical results for the compressive modulus of PC.

modulus at high strain rates is particularly noticeable for PC. Concerning PMMA, this effect is biased, since the secondary transition temperature of this material occurs nearly at room temperature. The curve obtained for PMMA can be seen as the extreme right portion of the curve obtained for PC. In fact, the transition regime of PMMA starts at very low strain rates. Fortunately, our physical development of the previous section allows us to recover the non-linear dependence of the modulus on the decimal logarithm of the strain rate. The use of an Arrhenius relation for the description of the secondary molecular movements (Eq. (7)) can definitely be seen as a key factor for the good modeling results at the high strain rates. Furthermore, our predicted results neglect any temperature rise generated by the elastic deformation at high strain rates, which would be

expected to be minimal under elastic deformation conditions [17,31].

Fig. 7 represents the modulus dependence of PMMA and PC for a wide range of temperatures and strain rates. In agreement with the observations of Cady et al. [14], the glass transition is dependent on strain rate. Without a doubt, this effect cannot be neglected in the modeling of mechanical properties at high strain rates. Concerning the modeling results for PMMA, the rate effect becomes even more important at the very high strain rates, where a deviation in the predicted curves is observed. The main reason for this outcome is that the apparent temperature gap between  $T_\beta$  and  $T_g$  is getting smaller with increasing strain rate. At  $10,000 \text{ s}^{-1}$ ,  $T_\beta$  is even slightly larger than  $T_g$ . When the bifurcation point between the  $\beta$ - and  $\alpha$ -processes is reached, the WLF equation cannot be used anymore. It will

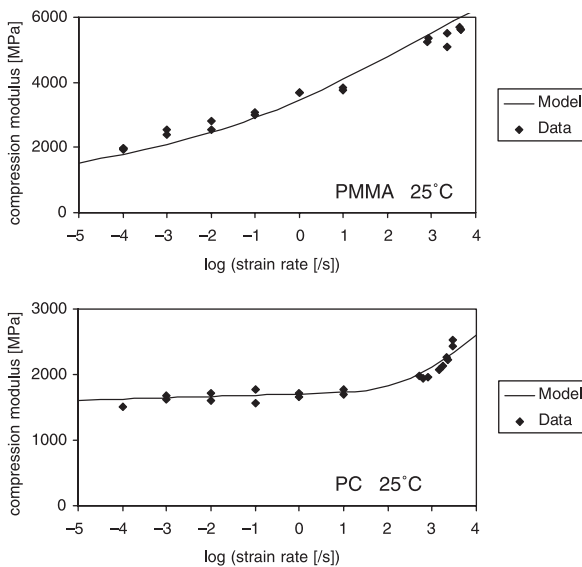


Fig. 6. Influence of the strain rate on the experimental and theoretical results for the compressive modulus of PMMA and PC.

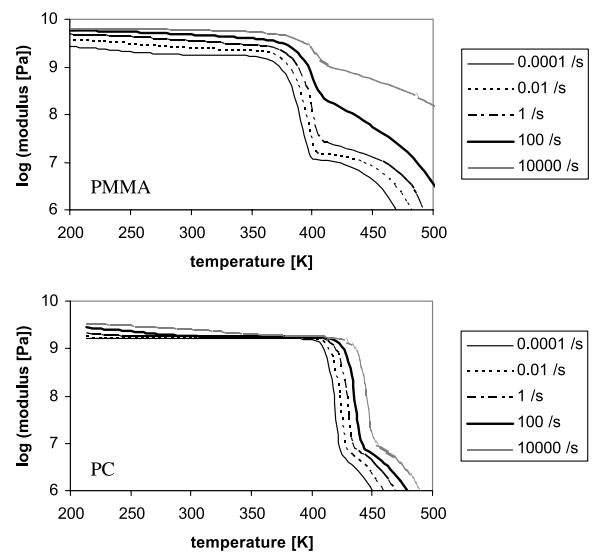


Fig. 7. Theoretical results for the compressive modulus of PMMA and PC for a wide range of strain rates.

be very interesting to confirm whether the predicted results of PMMA are experimentally verified or not, at the very high strain rates in the above  $-T_g$  region. In the case of PC, this occurrence is not observed because  $T_\beta$  remains much lower than  $T_g$  even for the highest strain rates.

#### 4. Conclusions

A model has been derived to account for the temperature and frequency/strain rate dependence of the stiffness modulus of amorphous polymers. This model is basically an extension of the work of Mahieux and Reifsnider [19,20]. The storage modulus has been modeled with Weibull statistics to describe the stiffness change over a wide range of temperatures, and with physically-based equations to account for the frequency/strain rate sensitivity.

In the case of dynamic mechanical analysis, our proposed dependence on frequency shows good agreement with the experimental data on both PMMA and PC. The effect of frequency on the glass transition was successfully modeled.

In the case of uniaxial compression testing, the initial Young's modulus is greatly influenced by strain rate. In particular, the high strain rate effect was correctly predicted for PMMA and PC with the same physical parameters as those obtained in the DMA testing. These results are another confirmation of the importance of the secondary relaxation in the deformation process of amorphous polymers. The temperature and strain rate dependence of the initial Young's modulus presented in this paper can be seen as a robust physically-based model for the prediction of the mechanical properties beyond the scope, where experimental data exist.

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#### References

- [1] Eyring H. *J Chem Phys* 1936;4:283.
- [2] Ree T, Eyring H. *J Appl Phys* 1955;26:793.
- [3] Robertson RE. *J Chem Phys* 1966;44:3950.
- [4] Bauwens-Crowet C, Bauwens JC, Homès G. *J Polym Sci A2* 1969;7:735.
- [5] Bauwens-Crowet C, Bauwens JC, Homès G. *J Mater Sci* 1972;7:176.
- [6] Bauwens-Crowet C. *J Mater Sci* 1973;8:968.
- [7] Argon AS. *Philos Mag* 1973;28:839.
- [8] Bowden PB, Raha S. *Philos Mag* 1974;29:149.
- [9] Fotheringham D, Cherry BW. *J Mater Sci* 1976;11:1368.
- [10] Fotheringham D, Cherry BW. *J Mater Sci* 1978;13:951.
- [11] Povoio F, Hermida EB. *J Appl Polym Sci* 1995;58:55.
- [12] Povoio F, Schwartz G, Hermida EB. *J Appl Polym Sci* 1996;61:109.
- [13] Richeton J, Ahzi A, Daridon L, Rémond Y. *J Phys IV* 2003;110:39.
- [14] Cady CM, Blumenthal WR, Gray III GT, Idar DJ. *J Phys IV* 2003;110:27.
- [15] Richeton J, Ahzi A, Daridon L, Rémond Y. *Polymer* 2005;46:6035.
- [16] Richeton J, Ahzi A, Vecchio KS, Jiang FC, Adharapurapu RR. *Int J Sol Struct*, accepted.
- [17] Arruda EM, Boyce MC. *Int J Plast* 1993;9:697.
- [18] Drozdov AD. *Eur Polym J* 2000;36:2063.
- [19] Mahieux CA, Reifsnider KL. *Polymer* 2001;42:3281.
- [20] Mahieux CA, Reifsnider KL. *J Mater Sci* 2002;37:911.
- [21] Ferry JD. *Viscoelastic properties of polymers*. 3rd ed. New York: Wiley; 1980.
- [22] Xiao C, Jho JY, Yee AF. *Macromolecules* 1994;27:2761.
- [23] Kausch HH, Heymans N, Plummer CJ, Decroly P. *Matériaux polymères: Propriétés mécaniques et physiques*. Lausanne: Presses Polytechniques et Universitaires Romandes; 2001.
- [24] Rabinowitz S, Ward IM, Parry JSC. *J Mater Sci* 1970;5:29.
- [25] Spitzig WA, Richmond O. *Polym Eng Sci* 1979;19:1129.
- [26] <http://www.polymersdatabase.com/>, edited by CRC Press.
- [27] Rietsch F, Bouette B. *Eur Polym J* 1990;10:1071.
- [28] Chen LP, Yee AF, Moskala EJ. *Macromolecules* 1999;32:5944.
- [29] Brulé B, Halary JL, Monnerie L. *Polymer* 2001;42:9073.
- [30] Rana D, Sauvart V, Halary JL. *J Mater Sci* 2002;37:5267.
- [31] Rittel D. *Mech Mater* 1999;31:131.