

# Property modeling across transition temperatures in polymers: a robust stiffness–temperature model

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## Abstract

The variation of stiffness with temperature in polymers is widely discussed in the literature. Previous studies have been concerned with the effects of temperature for highly specific materials and for limited ranges of temperature. Representations or predictions of stiffness variations for wide classes of polymers (thermosets, thermoplastics, amorphous, semi-crystalline, filled, unfilled, linear, crosslinked, etc.) and over wide ranges of temperature (from fully glassy to fully rubbery) have not been established. However, modern engineering design tools, especially those based on virtual design environments, require robust property models that apply over the entire range of temperatures that extend far below and substantially above the  $T_g$  of the matrix. The present paper addresses that need. The influence of temperature on secondary bonding in polymers is the basis of the approach. Weibull statistics are used to represent the failure of secondary bonds during the relaxation processes that lead to stiffness change over the full range of use temperatures. The feasibility of the approach was illustrated by applying the model to experimental data chosen at random from the literature. The behavior of six polymers of very different nature was successfully described. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords:* Stiffness; Temperature; Statistical model

## 1. Introduction

The mechanical properties of polymers are greatly influenced by temperature. Typically, the elastic modulus of a polymer can drop from  $10^9$  to  $10^6$  Pa between the glassy and rubbery state. However, polymers and their composites are more and more extensively used over wide ranges of service conditions. Therefore it becomes necessary to have an accurate description of the variations of the material properties under various and extreme conditions. For the present case, we will focus on temperature. To enable the use of polymer matrix composites within a transition region, we need to be able to analytically describe the changes of the polymer properties with temperature. In this paper, we will restrict our discussion to changes in the stiffness of the material.

The purpose of this study is to establish an explicit engineering relationship between stiffness and temperature of a polymer that can be easily integrated into micromechanics models and design codes. This relationship can be applied to any polymer (thermosets, thermoplastics, amorphous,

linear, semi-crystalline, crosslinked, low molecular weight, high molecular weight materials...) for the entire range of temperatures: from the glassy state to the flow region. This model will enable us to quantitatively describe stiffness changes across the transition regions (without making or testing the material).

In the literature, a very small number of studies deal with explicitly relating the changes in the modulus of a polymer caused by variations of temperature. In the rubbery region, however, the temperature dependence is fairly well established [1]. In this region, the modulus can be computed using Eq. (1):

$$E = \frac{\rho RT}{M_c} \quad (1)$$

where  $M_c$  is the molecular weight between crosslinks. However, this dependence can only be rigorously applied above the glass transition temperature of the material.

In the glassy state, different theories enable us to compute the modulus variations when they are small. For example, Van Krevelen [2] suggests the following set of relationships:

$$\frac{G_g(T)}{G_g(T_r)} = \frac{T_g/T_r + 2}{T_g/T_r + 2T/T_r} \text{ for } T < T_g \quad (2)$$

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$$\frac{G_c(T)}{G_c(T_r)} = \exp\left[-2.65 \frac{T_m/T_r - T_m/T}{T_m/T_r - 1}\right] \quad (3)$$

for  $T > T_r - 100$

$$G_{sc} = G_g + x_c^2(G_c - G_g) \quad (4)$$

where  $G$  is the shear modulus, and the subscripts g, c, sc, m, and r refer to glassy, crystalline, semi-crystalline, melting and reference. However, these equations only rigorously apply to the glassy state, and do not relate to the microstructure of the polymer.

Computational theories also enable an accurate description of the variation of the crystalline phase of the polymer modulus with temperature. These theories are complex and are usually restricted to one polymer and a fairly limited temperature range [3].

One can note that most of the literature focuses on the effect of time upon the stiffness of the polymer (KWW [4], Rouse [5], the traditional viscoelastic models [6] (springs and dashpots) and the time–temperature equivalence (WLF [7])). However, none of these equations explicitly relate modulus and temperature. Other shortcomings of these models are as follows:

- The KWW equation does not consider the details of the polymer microstructure and requires the use of relaxation times. The concept of relaxation time is not fully established and is still being discussed [8].
- The Rouse model does not apply over large temperature ranges [6].
- Viscoelastic models are phenomenological and were derived based on the assumption that the polymer is in the viscoelastic region (i.e.  $T > T_g$ ). These models were mathematically extended to the case of elastic behavior without reconsideration of the fundamental physical behavior. Impact and fast strain rate experiments illustrate the need for exact and accurate models to describe the instantaneous response of the material. Local fracture events also occur at high strain rates.
- The WLF equation is semi-empirical and is only a time–temperature equivalence tool. A relationship between modulus and temperature can not be obtained through the WLF equation (unless an accurate modulus versus time prediction scheme is established). As transition temperatures are easier to measure and interpret than relaxation times, we will therefore concentrate on expressing the stiffness of the material as an explicit function of temperature. Further work could focus on the rate or time-dependency of the modulus using time–temperature superposition schemes. However, this extension will not be included in the present paper.

We would like to adopt a more general approach than the existing theories listed above, be able to describe the polymer behavior over the entire temperature spectrum,

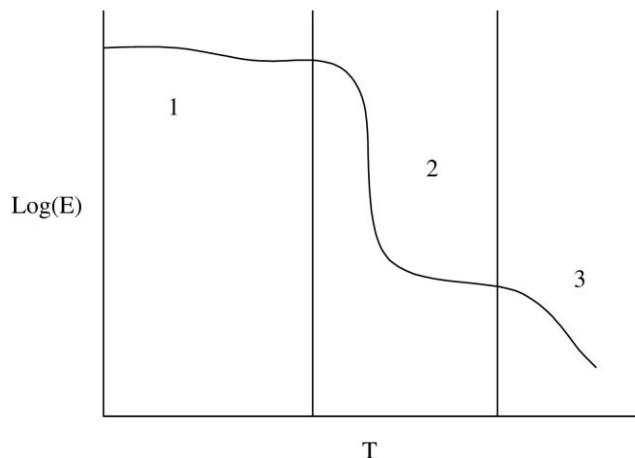


Fig. 1. Modulus versus temperature for a typical polymer.

including the transitions, and relate the mechanical response of the polymer to its microstructure.

## 2. Background

The well-known modulus versus temperature curve for a typical polymer exhibiting a secondary relaxation is illustrated by Fig. 1. We will not detail the molecular motions that have been carefully reviewed in other studies. We will rather focus on the behavior of the inter- and intra-molecular bonds, as discussed by Ashby [9].

The bonds in polymers can be divided into two major groups: primary bonds and secondary bonds. The first class includes the strong covalent intramolecular bonds. The disassociation energy [16,17] of such bonds varies between 50 and 200 kcal/mol. Secondary bonds include weaker bonds, e.g. hydrogen bonds (dissociation energy [16,17]: 3–7 kcal/mol), dipole interactions (1.5–3 kcal/mol), Van der Waals interactions (0.5–2 kcal/mol, and ionic 10–20 kcal/mol). The two types of bonds are shown schematically in Fig. 2.

From the glassy state to the flow region, the primary bonds of the molecule remain intact. However, the secondary bonds (hydrogen, dipole, Van der Waals) will be altered by the molecular motions during relaxation. We will call

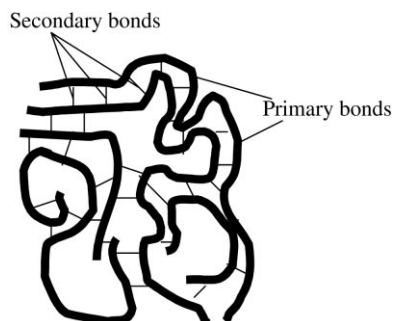


Fig. 2. Schematic of bonds in polymer materials.

“bond failure” the dissociation of a secondary bond (referred to as “bond melting” by Ashby [9]).

Region 1 in Fig. 1, commonly referred as the glassy region, is characterized by a quasi-elastic behavior of the polymer. The modulus is constant over a wide range of temperatures and most of the secondary bonds stretch without breaking. However, for some polymers, the thermal energy is high enough to allow rotation of side groups. For this situation, one (or several) secondary relaxations can be observed, characterized by a significant drop in the modulus. In this case, the secondary bonds need to break to allow the side groups to rearrange. However, the activation energy required for this very local movement is low, and these relaxations can occur at low temperatures (lower than the glass transition temperature).

The alpha transition, also referred as the glass transition, usually results in a dramatic drop in Young’s modulus (region 2) followed by a plateau (rubbery region). In region 2, the molecules start sliding against each other [9]. However, the movement of the molecules is still restricted by the presence of entanglement, crosslinks, crystallites, fillers, etc. The movements of a molecule can be thought as trapped in a tube (concept of reptation introduced by De Gennes [10]), where the molecule can move in a snake-like fashion. In order to be able to reptate, the molecule needs to break secondary bonds as in the case of the secondary relaxation, but over a larger part of each molecule. However, in this region, some elastic parts still survive and the molecular chain will keep some memory of its original position. As temperature is further increased, all of the secondary bonds are broken and the molecules can move freely (unless crosslinks are present); the modulus of the polymer starts dropping again (viscous flow, region 3).

### 3. Analysis

Spring and dashpot models lead us to discuss relaxation times as a representation of local behavior. The relationship between modulus and time is often written as:

$$E(t) = \sum_{i=1}^N E_i \exp(-t/\tau_i) \quad (5)$$

Where  $\tau_i$  are the relaxation times. One can define the distribution function  $H$  as:

$$H(\tau) = \tau E(\tau) \quad (6)$$

Eq. (5) can then be written as:

$$E(t) = \int_{-\infty}^{+\infty} H(\tau) \exp(-t/\tau) d(\ln \tau) \quad (7)$$

In the viscoelastic region, reptation is sometimes [9] modeled by an equation of the type:

$$E \propto \exp\left(-\frac{Q}{RT}\right) \quad (8)$$

Where  $Q$  is the activation energy of the process. However, when one bond breaks, there is a non-negligible influence on the other bonds. Secondary transitions, for example, are typically the result of highly localized molecular motions [18]. In order to allow side group motion or the motion of a few main chains, secondary bonds need to be broken. Due to the distance variations between atoms inducing a distribution in the strength of the interactions, the secondary bonds will break at different times. The failure of the first bond will change the interaction between the remaining atoms due to the spatial proximity of the event. If we consider the process of bond rupture, a Weibull distribution [11] would seem to be a more appropriate general form than the Boltzman distribution of Eq. (8). Let us first consider the beta transition. The mechanical response is driven by the motion of small chain segments (only a few monomers long). Considering the number and strength of the bonds involved in this relaxation process we can associate a Weibull coefficient  $m_1$  with the beta relaxation. In this case Eq. (5), for the beta transition becomes:

$$H_1(\tau) = \exp\left(-\left(\frac{t}{\tau_1}\right)^{m_1}\right) \quad (9)$$

or exchanging time for temperature [6] for instantaneous response and introducing a conversion constant:

$$H_1(T) = H_0^1 \exp\left(-\left(\frac{T}{\beta_1}\right)^{m_1}\right) \quad (10)$$

Where  $\beta_1$  is the characteristic temperature (i.e. beta transition temperature) and  $H_0^1$  a reference value for the beta transition (i.e. magnitude of the relaxation). For the following transitions (alpha, flow), the number of segments involved in the relaxation increases. For each relaxation, new Weibull coefficients related to the number of bond failures required for a given relaxation to occur and to the strength of the intermolecular bonds can be associated with the relaxation.

Finally, as we have different mechanisms occurring, we can sum the different components:

$$E = \sum_{i=1}^N H_i \exp\left(-\left(\frac{T_i}{T_{ref_i}}\right)^{m_i}\right) \quad (11)$$

In our case, we will consider one to three transitions ( $1 \leq N \leq 3N$ ). The  $H_i$  coefficients (magnitude of the transition step) can be obtained by different means. We can subtract the value of the material’s stiffness before and after the transition, leading to Eq. (12) (case of a material that does not undergo any transition prior to flowing), Eq. (13) (material with two transitions, e.g. glass and flow) and Eq. (14) (material undergoing three transitions, e.g. beta, glass and flow):

$$E = E_3 \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (12)$$

$$E = (E_2 - E_3) \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) + E_3 \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (13)$$

$$E = (E_1 - E_2) \exp\left(-\left(\frac{T}{T_1}\right)^{m_1}\right) + (E_2 - E_3) \exp\left(-\left(\frac{T}{T_2}\right)^{m_2}\right) + E_3 \exp\left(-\left(\frac{T}{T_3}\right)^{m_3}\right) \quad (14)$$

The  $T_i$  correspond to the temperatures at each transition (as given by the maximum of the peaks on the tangent delta versus temperature of a DMA curve, or by the inflection point of a DSC plot) in degrees Kelvin. The remaining difficulty is for the flow region. In this first approach, we will not try to detail the behavior of the material in the flow region. We will only show the applicability of this approach to the flow region by using flow temperatures given in the literature.

The  $E_i$  represent the instantaneous stiffness of the material at the beginning of each plateau or region.  $E_1$  is the instantaneous modulus at a very low temperature (far below  $T_g$ );  $E_2$  is the instantaneous modulus right after the beta transition and  $E_3$  is the instantaneous stiffness at the beginning of the rubbery plateau. A reliable experiment leading to consistent values for those stiffness measurements is the ultrasound method. The obtained modulus corresponds to a tensile experiment performed at very high strain rate or cyclic frequency. Various modeling methods can also be used to estimate the plateau stiffness values. The drops in modulus in the different regions ( $H_i$ ) represent the “importance” of the relaxation processes. These values depend on the chemistry of the polymer (stiffness of the backbone), molecular weight, crystallinity and degree of crosslinking. An increased crystallinity will produce only a slight increase in the glassy state stiffness but can produce a large rise in the value of the modulus of the rubbery plateau. Therefore, the magnitude of the glass transition step will decrease as the crystallinity is increased. The transition temperatures will also increase as the crystallinity impedes the rearrangement of the molecules under the applied stress. Increased molecular weight and crosslinking will stiffen the material to a lesser extent.

The last parameters ( $m_i$ ) are Weibull moduli, corresponding to the statistics of the bond breakage. To allow rotations of side groups for the secondary relaxations, the strength of the bonds that must be broken depends on the relative position of the side group to the other molecular chains. Therefore, there will be a wide distribution of bond strengths and we would expect  $m$  to be small. Reptation involves translation of the main chains. If the material is very homogenous (narrow distribution of bond strengths) as in the case of amorphous materials, we would expect  $m$  to be very large. However, this parameter is going to depend on the degree of impediment of the molecular motion (crosslinking, molecular weight and crystallinity...). If the movement of the molecular chains is severely restricted at precise locations

(by crosslinking, etc), we would expect  $m$  to be really low (approaching a Boltzman distribution). For crosslinked materials the slope of the drop in the viscous flow region will decrease with increasing degree of crosslinking. For heavily crosslinked materials, the flow region can even disappear.

#### 4. Validation

To validate the feasibility of our approach, we used data for some polymers selected at random from the literature. For details on how the experimental results were obtained, we will refer to the published work of the different investigators.

Eq. (14) was first used with PMMA. The experimental data from Ashby [9] were taken on the amorphous linear polymer.

The second set of experimental data used represented the variations of the storage shear modulus of PVDC from Schmieder and Wolf [12].

The storage modulus (measured at 1 Hz) of a high molar mass Thiophene-based poly(arylene ether ketone) from Brennan et al. [13]: poly(1,4-BFB, BisA),  $M_n = 20,000 \text{ g mol}^{-1}$  was also compared to our model.

The model was compared to the experimental data for the storage modulus of a polyethylene oxide–salt complex (PEO)<sub>0.82</sub>(Fe(SCN)<sub>3</sub>)<sub>0.18</sub> measured at 3 Hz ( $M_w = 600,000$ ) from Bartellota et al. [14].

Two poly(ether ether ketone)–polymethylsiloxane block copolymers were also studied using data from Risch et al. [15]. PEEK–PSX copolymers were obtained from the PEEK block with a number average molecular weight of 4900 (5k) and from PSX block number-average molecular weights of 3200 (3k) and 4900 (5k). In this case, we used Eq. (13) to model the presence of two glass transitions.

The results are shown in Figs. 3–8. Surprisingly the  $m_1$ ,  $m_2$ , and  $m_3$  coefficients were consistently equal to 5, 20, 20 for all materials except for the Thiophene-based poly(arylene ether ketone), where  $m_2 = 40$  and  $m_3 = 1$ .

#### 5. Discussion and conclusions

In order to use Eqs. (12)–(14) in a systematic manner, we need to be able to compute all the parameters or to obtain them from independent experiments. The biggest challenge is to understand the significance of the  $m_1$ ,  $m_2$ , and  $m_3$  parameters. The Weibull coefficients were calculated to obtain the best fit of the overall shapes of the experimental master curves. In the glassy region the effect of temperature on the modulus of the different polymers is small and the plateaus are fairly flat (Figs. 3–6). In the glass transition region, however, the modulus drops rapidly. The Weibull moduli associated with these transitions are high ( $m_2 = 20$ ) for PMMA and (PEO)<sub>0.82</sub>(Fe(SCN)<sub>3</sub>)<sub>0.18</sub>. High coefficients characterize a very deterministic and simultaneous failure

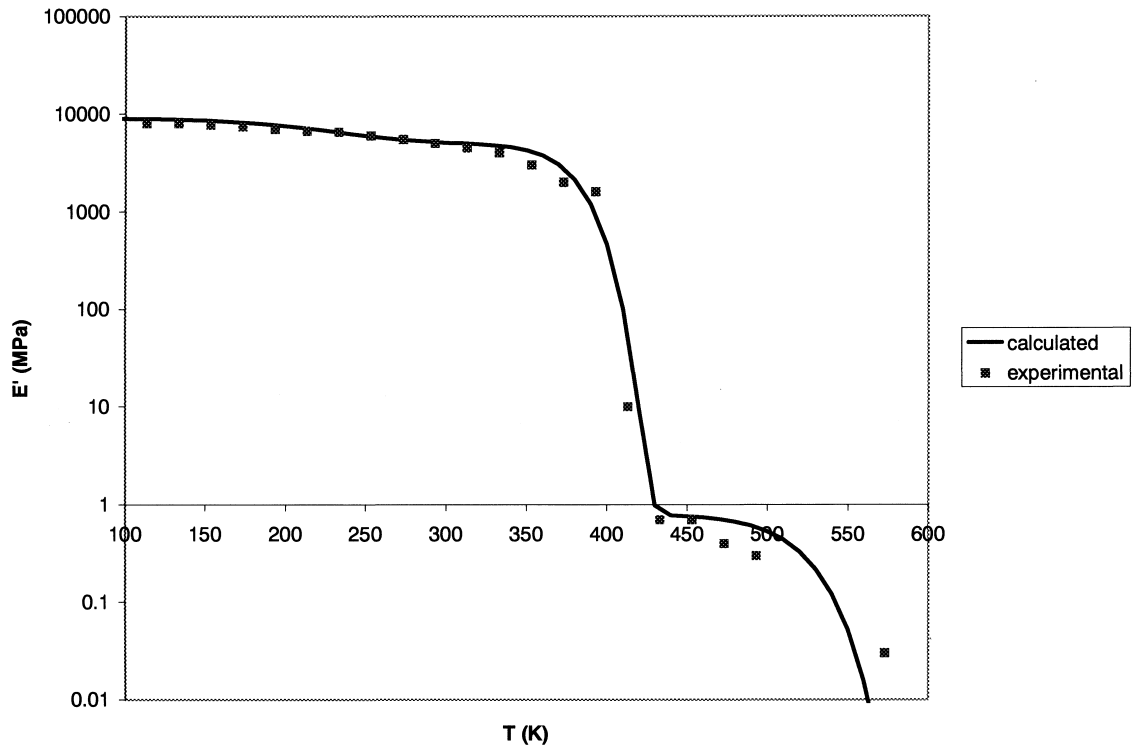


Fig. 3. PMMA.

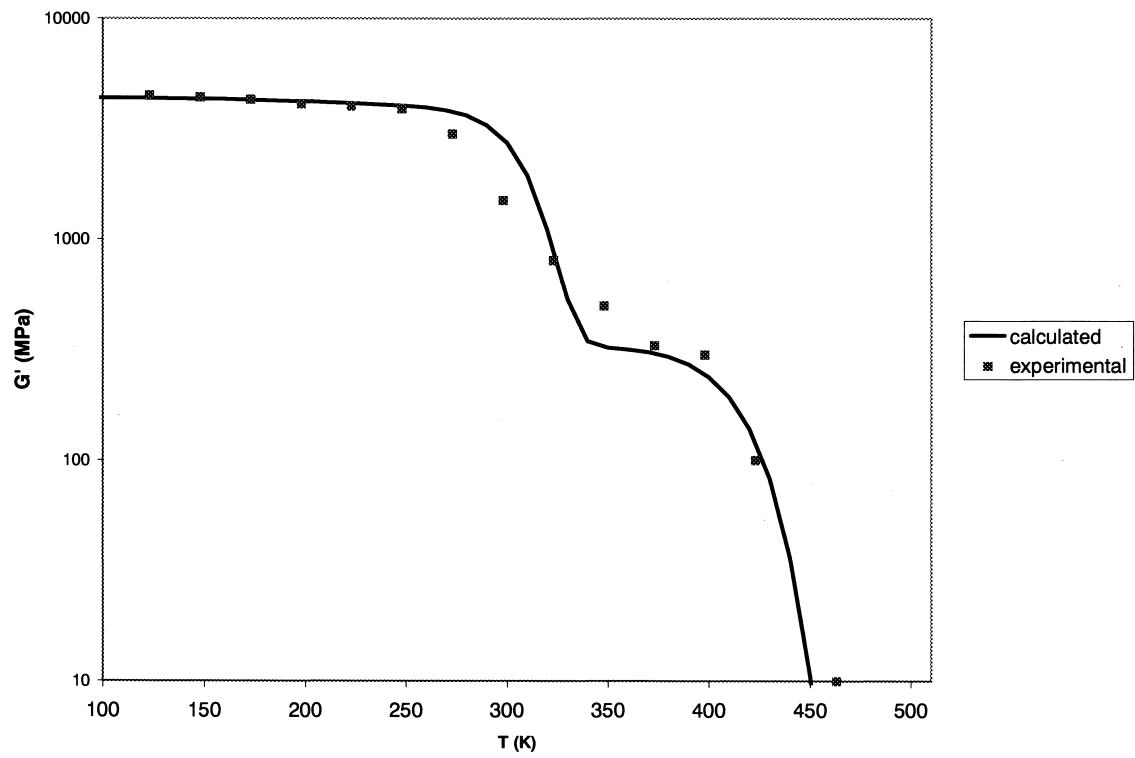


Fig. 4. PVDC.

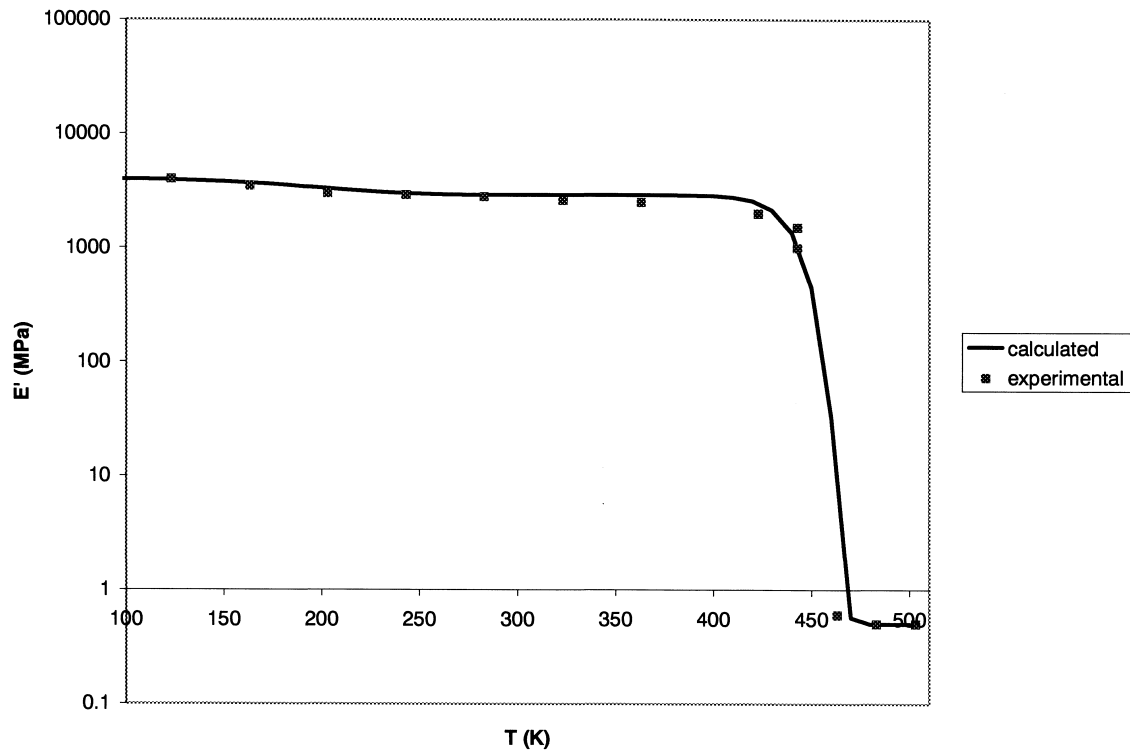
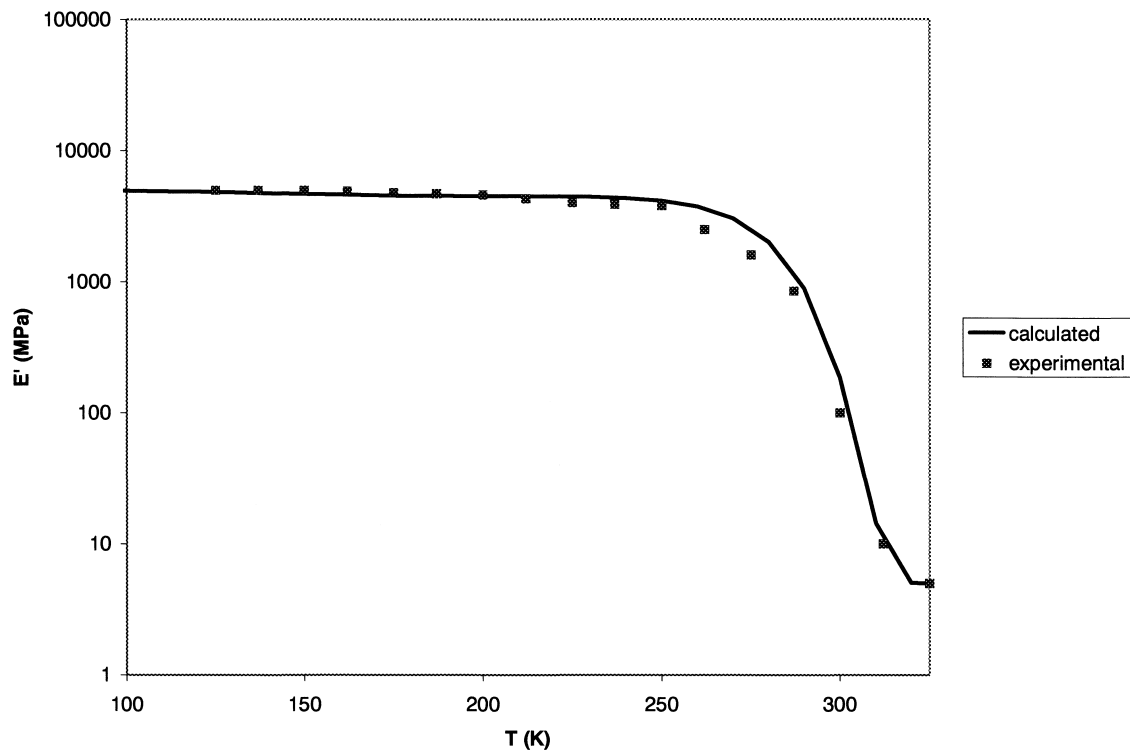


Fig. 5. Poly(1,4-BFB, Bis A).

process. For the Thiophene-based poly(arylene ether ketone) the curve is even steeper and a higher coefficient ( $m_2 = 40$ ) was required to describe the experimental data. This behavior probably denotes a very narrow distribution

of secondary bond strengths. The glass transition of PVDC is not as dramatic and a coefficient of 20 leads to a curve steeper than the experimental data, but remains acceptable. The main difference between the different polymers is the

Fig. 6.  $(\text{PEO})_{0.82}(\text{Fe}(\text{SCN})_3)_{0.18}$ .

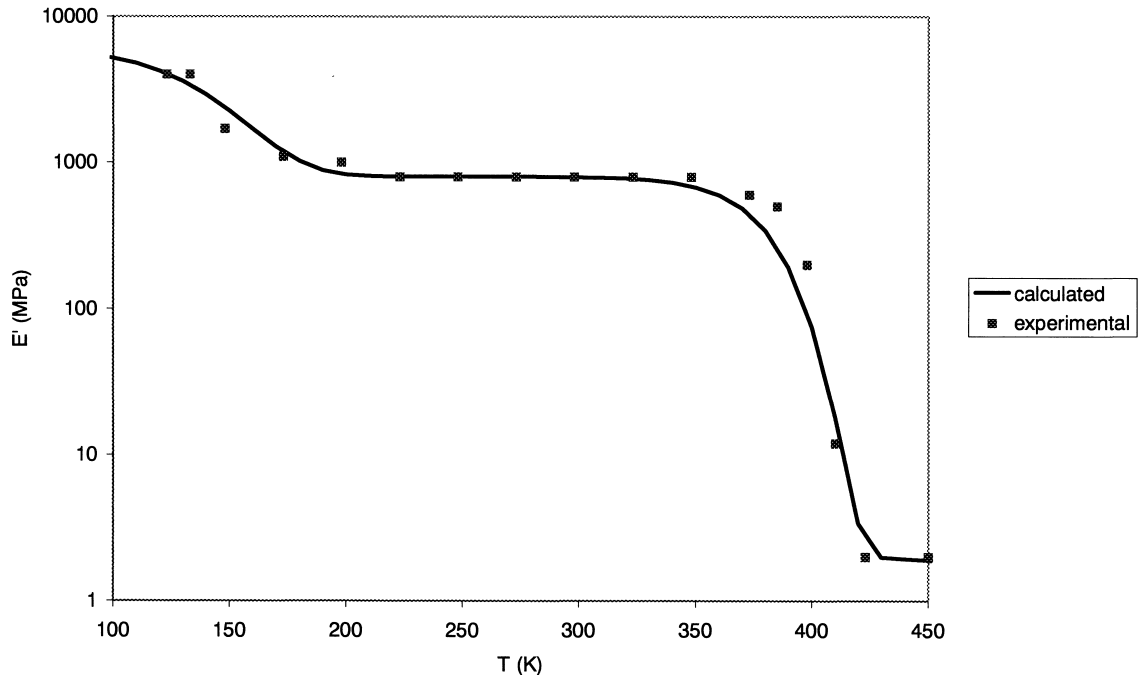


Fig. 7. PEEK(5k)PSX(3k).

length and height of the rubbery plateau. Eq. (13) can describe these differences. The copolymers exhibit the presence of two glass transitions (Figs. 7 and 8). The statistical coefficients associated with these two transitions were also found to be 20. The differences in the molecular

weights of the polymer block constituents did not significantly alter the shape of the transitions and only induced an expected vertical shift of the rubbery plateau. A flow region is shown for PMMA and PVDC (Figs. 3 and 4). After a threshold value, the modulus of the polymers decreases

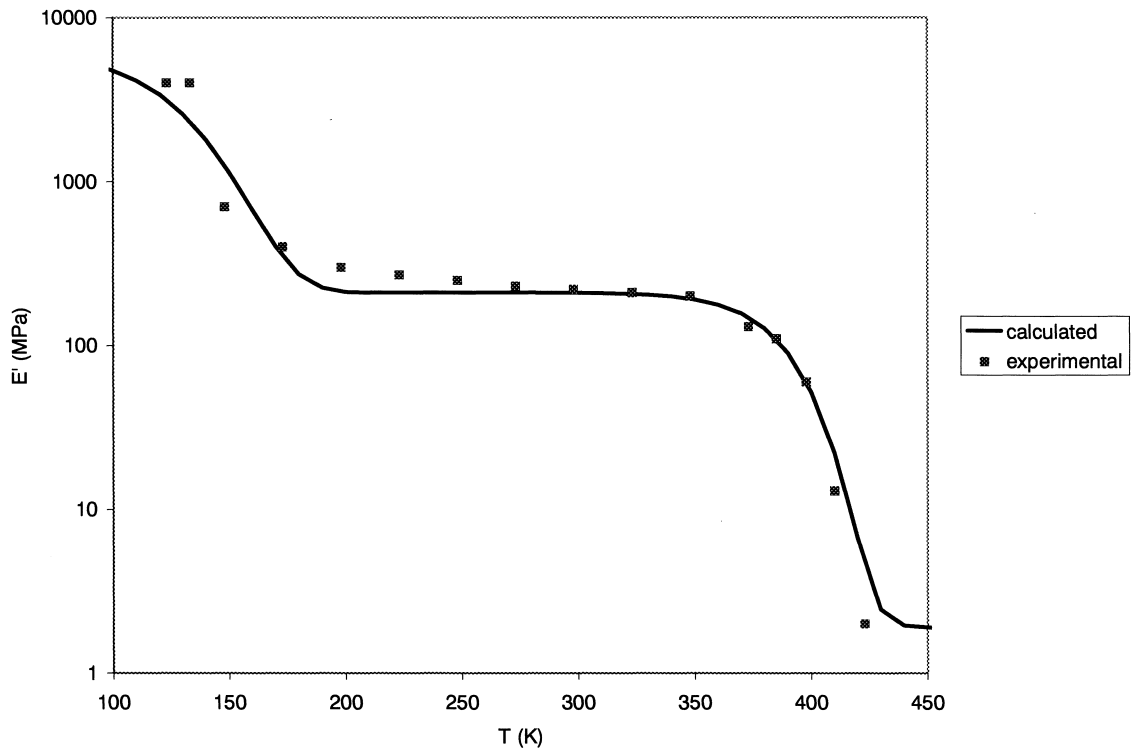


Fig. 8. PEEKt(5k)PSX(5k).

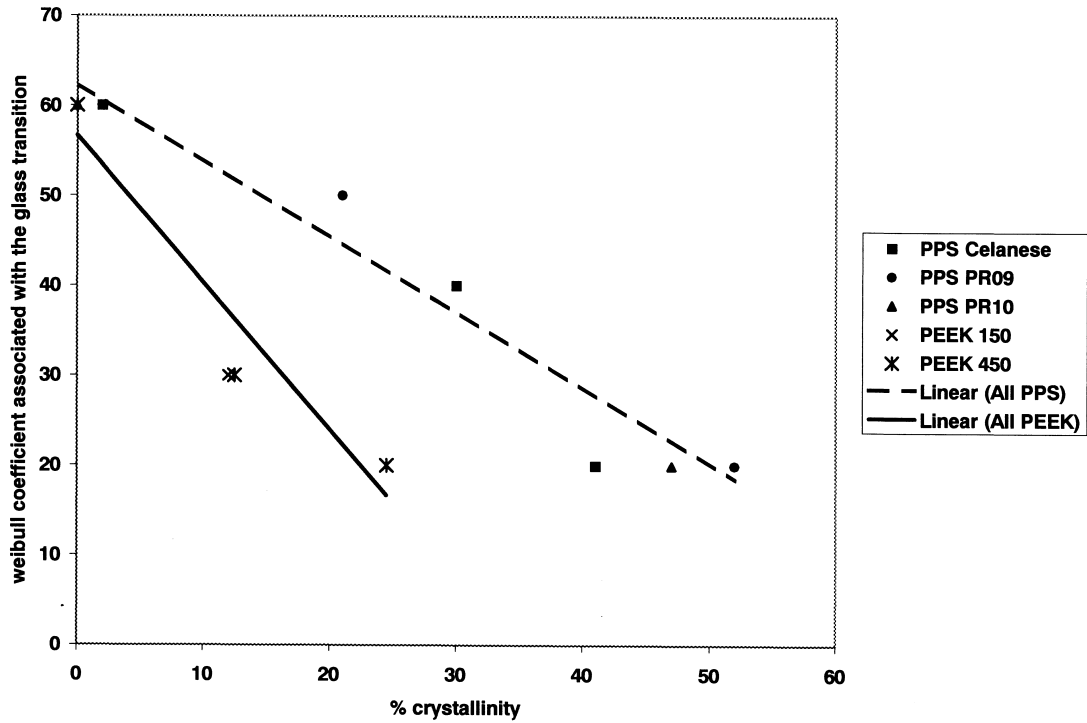


Fig. 9. Weibull coefficient associated with the glass transition versus degree of crystallinity for PPS and PEEK [20].

dramatically. For thermoplastics, the secondary bond failure process that results in flow is similar to the one observed during the glass transition, leading to a Weibull coefficient of 20. However, for crosslinked materials, the presence of

solid physical bonds, stops the material from flowing. Therefore, the distribution of the strength of bonds to be broken is infinitely broadened, leading to a Weibull coefficient of 1. This behavior is illustrated by the

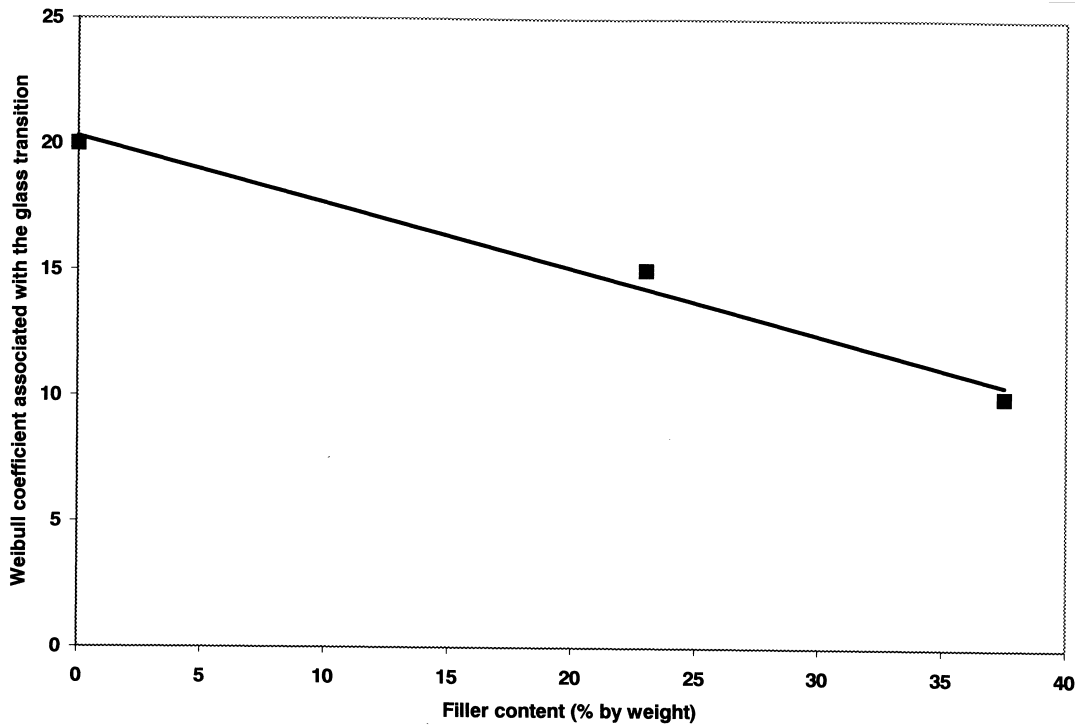


Fig. 10. Weibull coefficient associated with the glass transition versus amount of carbon black for polybutadiene [21].



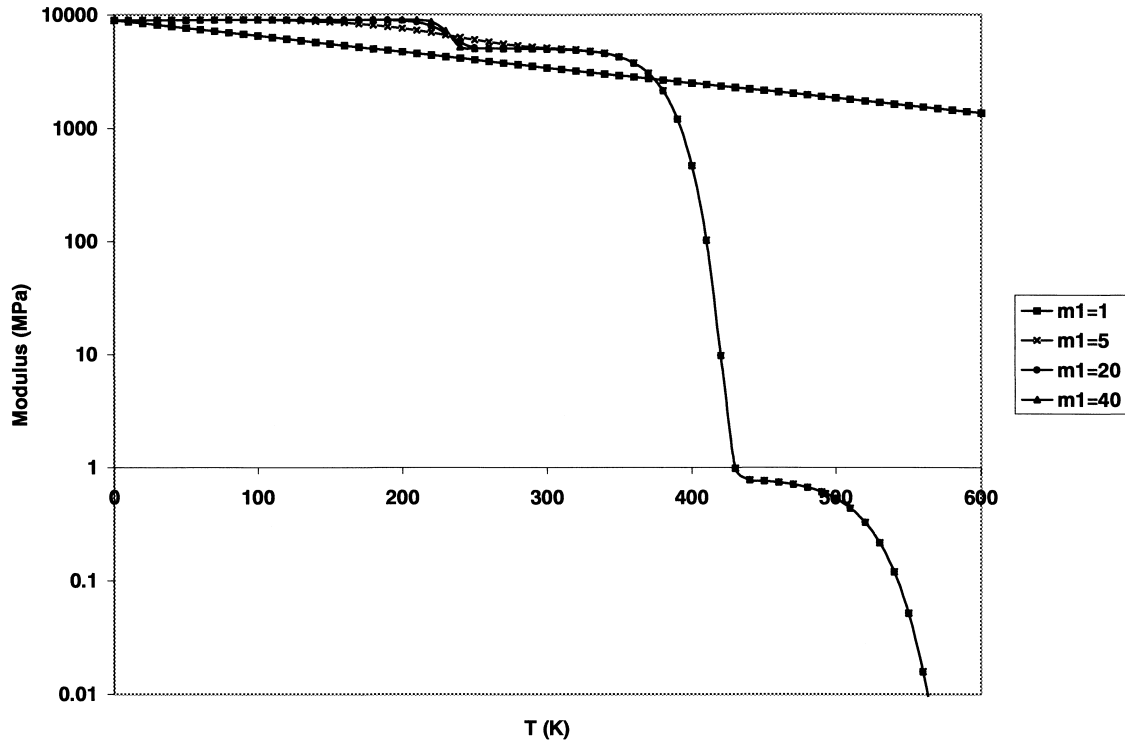


Fig. 11. Theoretical variations of the stiffness versus temperature curve.  $m_2 = 20$ ,  $m_3 = 20$ ,  $m_1 = 1, 5, 20$  and  $40$ .

Thiophene-based poly(arylene ether ketone) (Fig. 5). Intuitively, it seems that the Weibull coefficients associated with the glass transition ( $m_2$ ) and the flow region ( $m_3$ ) must be related to the degree of impediment of the molecular motion

in the different regions, i.e. crystallinity, crosslinking, molecular weight, etc.

These preliminary remarks have been verified by subsequent studies [19–21]. The details of the experiments are

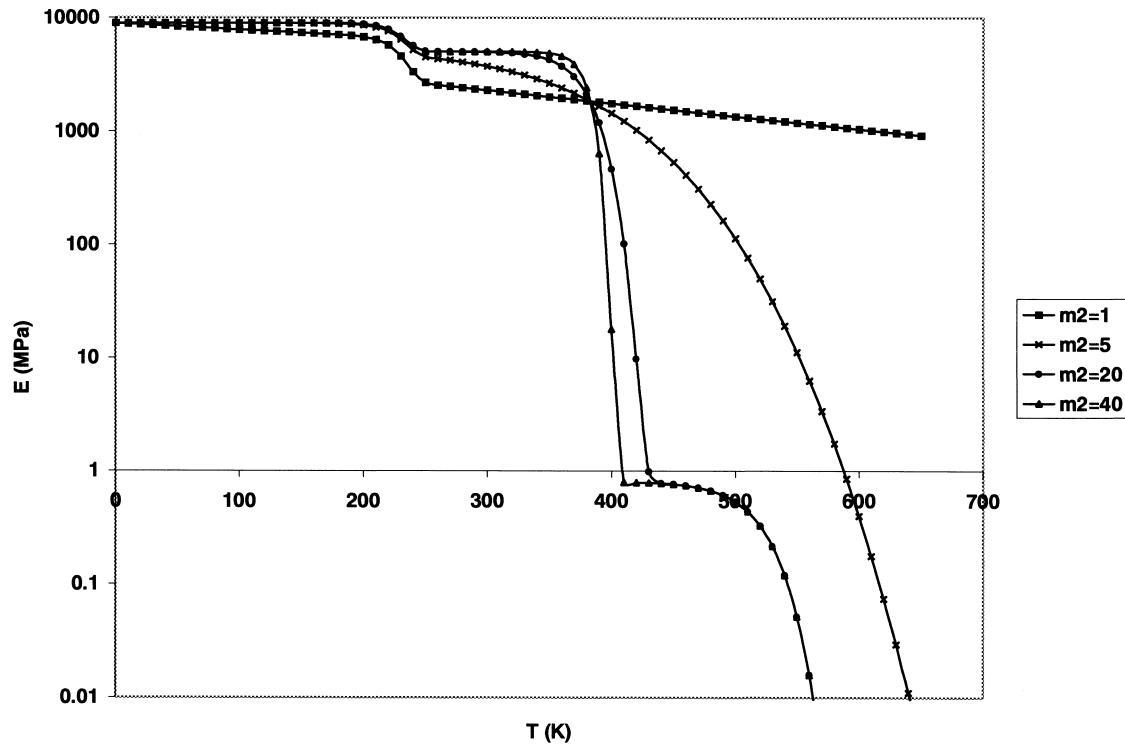


Fig. 12. Theoretical variations of the stiffness versus temperature curve.  $m_1 = 5$ ,  $m_3 = 20$ ,  $m_2 = 1, 5, 20$  and  $40$ .

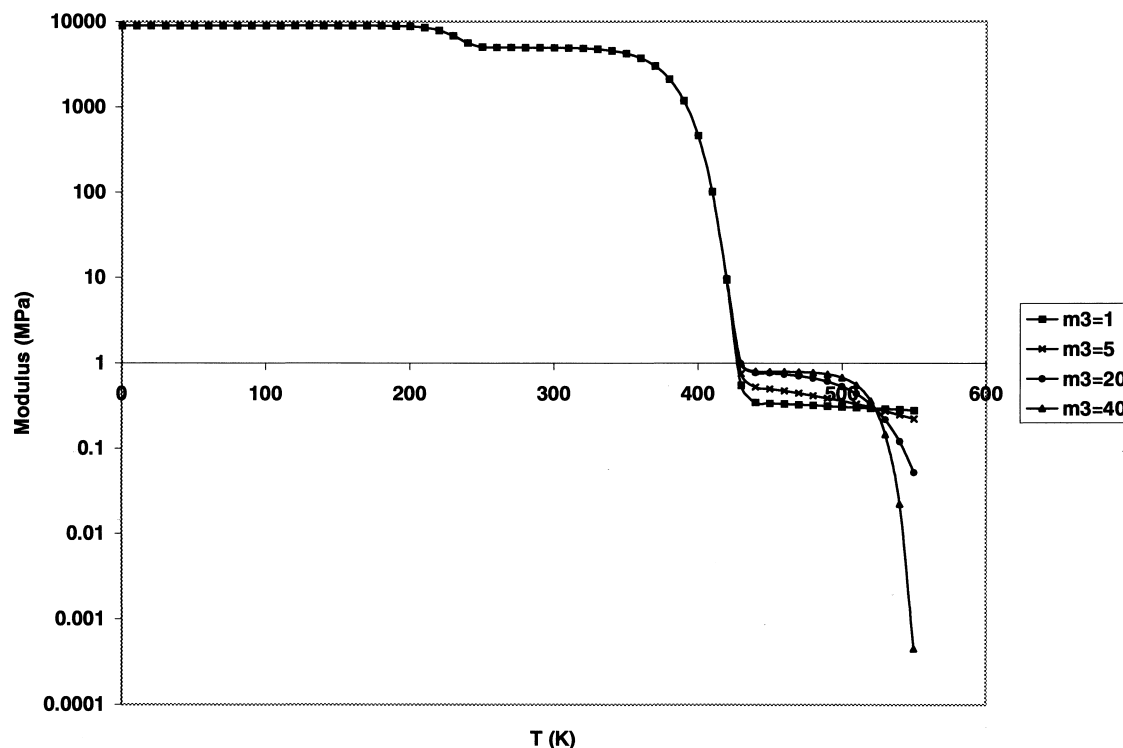


Fig. 13. Theoretical variations of the stiffness versus temperature curve.  $m_1 = 5$ ,  $m_2 = 20$ ,  $m_3 = 1, 5, 20$  and  $40$ .

beyond the scope of this introductory paper. However, examples of results supporting our physical interpretation of the Weibull coefficients are shown in Figs. 9 and 10. Experiments performed on carefully defined materials [19–21] have shown that Weibull moduli are strongly related to the microstructure of the polymer. Fig. 9 shows the variations of the Weibull coefficient associated with the glass transition with respect to the degree of crystallinity for various grades of PEEK and PPS [19,20]. Fig. 10 illustrates the relationship between  $m_2$  and the amount of carbon black filler in polybutadiene [21].

The sensitivity of the curves generated by Eq. (14) to the Weibull parameters is illustrated by Figs. 11–13. The modulus-temperature curves of Fig. 11 were obtained by varying  $m_1$  and keeping  $m_2$  and  $m_3$  equal to 20. For  $m_1$  coefficients greater than 1, the differences between the curves is small. Increasing  $m_1$  leads to a steeper step describing a more abrupt secondary relaxation and indicating a simultaneous process. Fig. 12 was obtained by keeping  $m_1$  equal to 5 and  $m_3$  equal to 20 and varying  $m_2$ . This last coefficient drives the slope of the glass transition. High values of the Weibull parameter describe a steep transition. Low values ( $m_2 = 5$  for example) lead to single transition curves: the glass transition becomes very broad and the polymer starts flowing before the end of the glass transition. The  $m_2$  coefficient was found to be almost constant for the cases previously studied, and might be related to the breadth of the molecular weight distribution or to the percent of crystallinity. However, it is difficult to get details on the chemical properties of the

materials used in the experiments excerpted from the literature. The curves of Fig. 13 were calculated for  $m_1$  equal to 5 and  $m_2$  equal to 20. The value of  $m_3$  slightly influences the height of the rubbery plateau and drives the slope of the curve in the flow region. For high values of  $m_3$ , the polymer softens rapidly. As previously discussed, the flow region disappears (the plateau is infinitely extended) for  $m_3$  equals 1, corresponding to the case of heavily crosslinked polymers.

Despite some discrepancies, the model fits the data successfully even for extreme temperatures. Eqs. (12)–(14) seem to describe the stiffness behavior of polymers with temperature. We must first remember that these equations have a physical basis: in order for the relaxations to occur, the secondary bonds need to break. In polymers, there is a distribution of these molecular bond strengths. The number of segments involved also varies from one relaxation to the other (always increases as the temperature increases). Finally when one of the secondary bonds breaks, other bonds are influenced (in the manner that broken fibers interact with unbroken fibers in a fiber bundle). Secondly, the reference temperatures and moduli can be independently measured or calculated. The reference temperatures correspond to the inflection point of the transitions and not the temperature ( $T_i$ ) corresponding to the plateau's height ( $E_i$ ). Therefore, we are not forcing the value of the modulus at any temperature. The reader might also notice the similarity of the mathematical form of Eq. (14) with the KWW equation [4]. These two equations are stretched exponentials.

However, the differences can be noted as follows:

- Eq. (14) is based on physical considerations (bond failure).
- Eq. (14) refers to measurable, well-defined physical quantities (transition temperatures and instantaneous stiffnesses).
- Eq. (14) is applicable over the entire temperature range (up to flow of the polymer).

Further experiments are required to study the statistical coefficients for polymers with very different properties (i.e. molecular weight, crystallinity, crosslinking and filler content). Some of these experiments are presently being conducted in our laboratory. However, this initial study seems to demonstrate the validity of our approach. Applications of the model have been discussed in other publications [19,22,23]: the model has been applied to a correct prediction of composite strength and life across transitions [19,23]. The determination of constants has been discussed in terms of other modeling approaches and rests on their validity in many cases [19–21]. This new model offers great potential in ultimately reducing the experimental work required to design new composites, and would enable the use of life prediction tools, over large temperature ranges including the matrix transitions.

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