JOURNAL OF MATERIALS SCIENCE 13 (1978) 1443–1448

A new approach to describe the tensile stress-strain curve of a glassy polymer

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The tensile stress–strain curve of a glassy polymer is compared to the response of a rheological system including a generalized non-linear Maxwell model. The treatment assumes that throughout the course of deformation, some structure initially present in the polymer is destroyed and that the initial spectrum of the Maxwell elements is converted to another spectrum. A law of transformation of these spectra as a function of deformation is proposed while their expression is assumed to be analogous to that of the spectrum of a structureless material, experimentally determined. Data are found to be fully consistent with the proposed treatment.

1. Introduction

The purpose of this paper is to compare the tensile stress–strain curve obtained for a glassy polymer with the one predicted by a rheological model, previously proposed [1]. This model, qualitatively useful to describe tensile creep tests, interrupted tensile tests and to explain the yield drop, consists of a modified generalized Maxwell model having the following characteristics:

(1) all the n elements include the same Hookean spring;

(2) each element is characterized by an Eyring-type dashpot, the deformation of which may be neglected as long as the stress it bears remains smaller than a definite value σ_i (σ_i is strain rate and temperature dependent);

(3) when σ_i is reached on an element, its deformation goes on under the action of a stress lower than σ_i. This condition, implied by interrupted tensile tests [1], could mean that the onset of viscous deformation requires the destruction of some structure initially present in the polymer. That is, the spectrum P_i of the σ_i values is converted to another spectrum, P_d, possessing a smaller lower limit, σ_{md}. It is the assumption of the existence of two spectra characterizing the polymer deformation which allows a yield drop to be obtained in the response of the model. This response is calculated in Appendix 1.

In order to take account of rather large deformations occurring beyond the yield point in a tensile test, we have completed the model here by inserting in parallel a rubber elasticity spring, following Haward and Thackray [2] on this point. The proposed system is shown in Fig. 1. From the theory, a tensile test may be described by the following expression including, besides the rubber elasticity contribution σ_R,

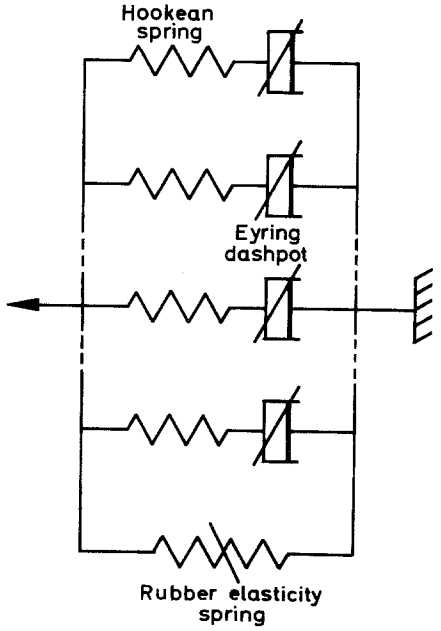

Figure 1 Proposed rheological model.

two terms related to the viscous deformed elements and the coexistent elastic ones repectively:

$$\sigma = \int_{\sigma_{md}}^{E\epsilon_A} E\epsilon P_d(E\epsilon)\,dE\epsilon + E\epsilon_A \int_{E\epsilon_A}^{\infty} P_i(E\epsilon)\,dE\epsilon + \sigma_R \quad (1)$$

where σ denotes the tensile stress corresponding to the deformation ϵ_A and E the resulting modulus of the Hookean springs. Equation 1 becomes quantitative if one knows P_i and P_d. The problem is to establish these spectra. There is no experimental data allowing a direct determination of P_i and P_d, but the spectrum P_s of a material whose initial structure has been destroyed prior to testing may be easily obtained.

The tensile curve of such a structureless material may be expressed by Equation 1 where P_i and P_d are replaced by P_s.

$$\sigma_s = \int_{\sigma_{md}}^{E\epsilon_A} E\epsilon P_s(E\epsilon)\,dE\epsilon + E\epsilon_A \int_{E\epsilon_A}^{\infty} P_s(E\epsilon)\,dE\epsilon + \sigma_R \quad (2)$$

from which it can be derived that:

$$P_s(E\epsilon) = -\frac{d^2\sigma_s}{d(E\epsilon)^2} \quad (3)$$

From a test-piece of the material possessing an initial structure, we intend to obtain a sample of a structureless material and to determine P_s from the tensile curve of such a sample. A plausible law for building P_d as a function of P_s and deformation is then assumed, while the expression for P_i is deduced from that for P_s by analogy. Under these conditions, the response of the model to a simple tensile test is calculated in order to check the validity of the proposed system and the hypothetical spectra.

2. Experimental

2.1. Materials

Our tests were performed on two different forms of PVC (Trovidur, Dynamit Nobel) "as-received" and structureless.

The shape of the test-pieces used was given elsewhere [3]. They were cut out of sheets 3 mm thick. The structureless material was obtained as follows. We thought that the hypothetical structure present in the "as-received" material was of the same kind as that formed by annealing the polymer just below its glass transition temperature, T_g [4, 5]. Mills [6] and Adam *et al.* [5] have shown that quenching or straining an annealed polymer beyond the yield point removes the effect of the annealing treatment. We thought that this structure might perhaps occur during the cooling of the polymer through its glass transition and we attempted to stop this happening. A test-piece of the "as-received" material was heated to about 30° C higher than T_g in order to destroy the structure. Afterwards, it was slowly cooled and during the cooling continuously deformed in alternated bending in such a way that the structure could not be formed. Finally, the test-piece was reshaped to its original dimensions.

2.2. Stress–strain curves

Stress–strain curves were measured in an Instron test machine at an imposed strain rate $\dot{\epsilon}_0$ equal to 4×10^{-4} sec^{-1}. All tests were conducted at room temperature. The extension was recorded using strain gauge extensometers of the Baldwin type as long as the deformation remained homogeneous (as is the case for the tensile curves given in Fig. 3). For larger deformations, necking occurred and spread along the test-piece, so we had to measure local deformation. For this purpose, 2 mm equidistant marks were traced along the test-piece. The elongation of the portion where the neck formed was measured, on a base of 4 mm, as a function of load and time, until the end of neck propagation. Therefore the stress–strain curve may be obtained entirely except in the small highly unstable region where the neck arises, inducing adiabatic heating even at low strain rates.

2.3. Evaluation of the engineering stress

The calculation of the Maxwell elements provided the true stress, σ, while σ_R was evaluated in terms of engineering stress. The graphs are drawn in engineering stresses, full lines representing experimental values, and dots the calculated ones. We used the following relationship between both types of stress, which is derived from considerations previously discussed [7]; that is

$$\sigma_{eng} = \frac{\sigma}{1+\epsilon} \quad (4)$$

3. Choice of the spectra P_i and P_d

The spectrum P_s may be easily obtained from the tensile curve of a test piece of the structureless material. Such a curve is given in Fig. 2. It does not exhibit a yield drop, a sign that the initial

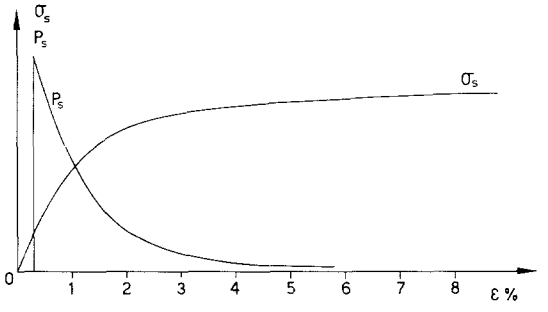

Figure 2 Tensile stress–strain curve of the structureless material and spectrum P_s derived from this curve.

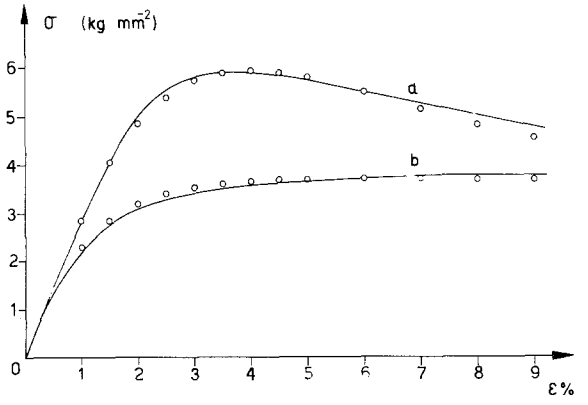

Figure 3 Comparison between the measured tensile stress–strain curves (full line) and the calculated response of the model (points). Curves (a) and (b) are related to the "as-received" and the structureless materials respectively. Deformations remain homogeneous throughout the test.

structure is practically absent. Young's modulus, E, can be obtained as a best fit to the slope of the first part of the curve, as is given in Table I. The value of σ_{md}, also given in this table, corresponds to the stress at which the curve first ceases to be linear. The spectrum derived from this curve using Equation 3 is given on the same figure. The shape of the right-hand-side leads us to approximate it by a decreasing exponential function given by;

$$P_s = \frac{1}{\sigma_{od}} \exp\left(-\frac{E\epsilon - \sigma_{md}}{\sigma_{od}}\right), \qquad (5)$$

where σ_{od}, given in Table I, is estimated from the mean value of the tangent at different points on the graph.

We know nothing about P_d except that it equals P_s for rather large deformations at which the initial structure can be considered as destroyed. For this reason, we will assume the following relationship between both spectra, for $\epsilon < \epsilon_A$;

$$P_d(E\epsilon) = K_{E\epsilon_A} P_s(E\epsilon), \qquad (6)$$

where $K_{E\epsilon_A}$ reaches unity for large deformations. The relationship of Equation 6 does not depend on the function chosen to approximate P_s and remains quite general. We have tried an expression analogous to that of P_s (Equation 5) to give an expression for P_i;

$$P_i = \frac{1}{\sigma_{oi}} \exp\left(-\frac{E\epsilon - \sigma_{mi}}{\sigma_{oi}}\right). \qquad (7)$$

The value of σ_{mi} can be obtained from the tensile curve of the material given in Fig. 3 (curve *a*, full line). Young's modulus was found to equal that of the structureless material. The constant σ_{oi} was determined by adjusting by trial and error the calculated response of the model at the yield point with the experimental value of the yield stress. The three constants of Equation 7 are given in Table II.

TABLE I Coefficients for structureless PVC

E (kg mm^{-2})	σ_{md} (kg mm^{-2})	σ_{od} (kg mm^{-2})
285	0.8	3

TABLE II Coefficients for "as-received" PVC

E (kg mm^{-2})	σ_{mi} (kg mm^{-2})	σ_{oi} (kg mm^{-2})
285	3.6	7*

*Optimized to adjust the maximum of the calculated curve to fit the experimental yield stress.

4. Response of the model submitted to a tensile test

4.1. Expression for the tensile curve for the structureless material

In this case, the tensile stress can be calculated from Equations 2 and 5:

$$\sigma_s = \sigma_{md} + \sigma_{od}\left[1 - \exp\left(-\frac{E\epsilon - \sigma_{md}}{\sigma_{od}}\right)\right] + \sigma_R \qquad (8)$$

4.2. Expression for the tensile curve for the material in its initial state

To establish the expression for the tensile stress, we must make the law of transformation of the elastic elements to the viscous elements, in the course of deformation, more explicit. Let C_i be the fraction of the Maxwell elements which

exhibit viscous flow at a given value $E\epsilon_A$. This fraction may be expressed as a function of P_i by:

$$C_i = \int_{\sigma_{mi}}^{E\epsilon_A} P_i(E\epsilon)\,dE\epsilon$$

However, these C_i elements no longer belong to P_i but to P_d, therefore, from Equation 6, one obtains:

$$C_i = \int_{\sigma_{md}}^{E\epsilon_A} P_d(E\epsilon)dE\epsilon = K_{E\epsilon_A}\int_{\sigma_{md}}^{E\epsilon_A} P_s(E\epsilon)dE\epsilon \quad (9)$$

and

$$K_{E\epsilon_A} = \frac{\int_{\sigma_{mi}}^{E\epsilon_A} P_i(E\epsilon)\,dE\epsilon}{\int_{\sigma_{md}}^{E\epsilon_A} P_s(E\epsilon)\,dE\epsilon} \quad (10)$$

If P_i and P_s are expressed by Equations 5 and 7, $K_{E\epsilon_A}$ becomes:

$$K_{E\epsilon_A} = \frac{1-\exp\left(-\frac{E\epsilon_A-\sigma_{mi}}{\sigma_{oi}}\right)}{1-\exp\left(-\frac{E\epsilon_A-\sigma_{md}}{\sigma_{od}}\right)} \quad (11)$$

The resulting stress borne by these C_i elements may also be expressed as function of P_s. Finally, from Equations 1, 5, 7 and 11, we can write that:

$$\sigma = \frac{1-\exp\left(-\frac{E\epsilon_A-\sigma_{mi}}{\sigma_{oi}}\right)}{1-\exp\left(-\frac{E\epsilon_A-\sigma_{md}}{\sigma_{od}}\right)} \times \int_{\sigma_{md}}^{E\epsilon_A}\frac{E\epsilon}{\sigma_{od}}\exp\left(-\frac{E\epsilon-\sigma_{md}}{\sigma_{od}}\right)dE\epsilon + \frac{E\epsilon_A}{\sigma_{oi}}\int_{E\epsilon_A}^{\infty}\exp\left(-\frac{E\epsilon-\sigma_{mi}}{\sigma_{oi}}\right)dE\epsilon + \sigma_R$$

$$= \left[1-\exp\left(-\frac{E\epsilon_A-\sigma_{mi}}{\sigma_{oi}}\right)\right]\times\left[\sigma_{od}+\sigma_{md}-\frac{E\epsilon_A-\sigma_{md}}{\exp\left(\frac{E\epsilon_A-\sigma_{md}}{\sigma_{od}}\right)-1}\right] + E\epsilon_A\exp\left(-\frac{E\epsilon_A-\sigma_{mi}}{\sigma_{oi}}\right)+\sigma_R. \quad (12)$$

5. Choice of the rubber spring

Instead of the Langevin spring, proposed by Haward and Thackray [2] and particularly convenient to describe very large deformations, we have chosen the following relation to express the rubber elasticity occurring at the level of strain we have considered:

$$\sigma_R\,(\mathrm{kg\,mm^{-2}}) = \frac{11}{14}\left(\alpha-\frac{1}{\alpha^2}\right)\times\left[1+\frac{4.25}{14}\left(\frac{3\alpha^3+4}{5\alpha}-1\right)\right], \quad (13)$$

with

$$\alpha = (1+\epsilon). \quad (14)$$

The numerical values are calculated in Appendix 2.

Equation 13 is the expression for the stress supported by an elastomer constituted by a non-Gaussian distribution of chains. This is a classical relation, given for example by K. J. Smith Jr [8]. The angle of rotation, ϕ, about the tetrahedral bonds of the chains was not restricted, so that $<\cos\phi>=0$, the front factor being taken equal to unity for the sake of simplicity.

By trial and error, N, the number of backbone links per segment, was optimized to obtain a best fit with the experimental curve; the value of $N=14$ was found. Of course, this is a rough approximation because N and the front factor certainly change during the course of deformation. For this reason we have not considered too large deformations.

6. Results

6.1. Tensile curve for the structureless material

This experimental curve is compared in Fig. 3 to the value of σ_s calculated using Equations 8 and 13 and Table I. As P_s approximates the spectrum derived from the same curve, the comparison is only given to show the validity of the approximation chosen.

6.2. Tensile curve for the "as-received" material (portion related to homogeneous deformation)

A comparison between experimental and calculated curves from Equations 12 and 13 is given in Fig. 3. The accuracy of the fit is quite satisfactory.

6.3. Tensile curves for the "as-received" material (portion related to the neck propagation)

When deformation becomes inhomogeneous, local strain rate ceases to remain constant. The graph

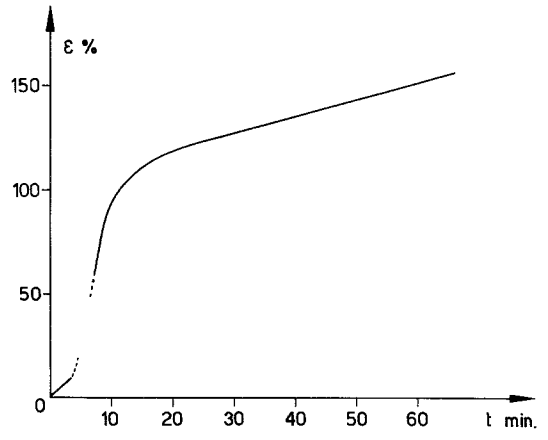

Figure 4 Variation of the measured local deformation as a function of time. Measurements are made within the region of the test-piece where the neck occurs.

representing the local strain variation as a function of time is given in Fig. 4. The comparison between the experimental tensile curve given in Fig. 5 (full line) and the response of the model requires a strain rate correction.

We have previously [1] established a linear dependence between the ratio σ/T, T being the absolute temperature, and the logarithm of the strain rate. The slope of the straight line giving this dependence was found to equal, for the as-received material,

$$A = 7.35 \times 10^{-4}\ \mathrm{kg\,mm^{-2}\,K^{-1}}. \qquad (15)$$

Points shown on Fig. 5 were therefore evaluated as follows. For a given value of ϵ, say ϵ_A, $\dot{\epsilon}_A$ is

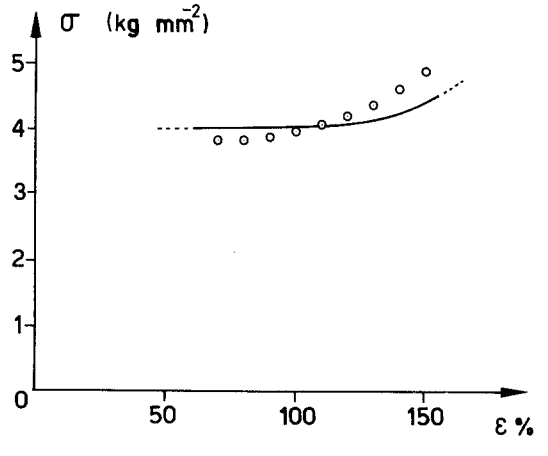

Figure 5 Comparison between the experimental stress–strain curve related to local deformation where the neck occurs (full curve) and the response of the model (points). A strain rate correction has been made using Equation 16.

calculated from the graph of Fig. 4. As the constants of Tables I and II are related to $\dot{\epsilon}_0 = 4 \times 10^{-4}$ $\mathrm{sec^{-1}}$, the value of σ_A corresponding to $\dot{\epsilon}_A$ equals:

$$\sigma_A = \sigma + AT(\ln \dot{\epsilon}_A - \ln \dot{\epsilon}_0) \qquad (16)$$

where σ is calculated from Equations 12 and 13 using the constants of Tables I and II. The results, shown in Fig. 5, give an accurate fit until rather large deformations.

7. Conclusions

The proposed model has been successfully applied to calculate the tensile stress–strain curve of a glassy polymer. The fit is accurate over the whole curve, except perhaps for very large deformations and for the highly unstable region where necking takes place. Only one parameter, i.e. σ_{oi}, has to be adjusted.

The basic idea of the proposed treatment is that viscous deformation requires the destruction of a structure initially present in the material. That is to say, the model exhibits two spectra of Maxwell elements P_i and P_d, and P_i is converted into P_d during the course of deformation. This paper is a first attempt to evaluate these spectra quantitatively; results are promising and may be considered as a first step towards the understanding of the dependence of the structure of a polymer on the viscous deformation in the glassy state.

Appendix 1
Response of the modified generalized Maxwell model

It is assumed that the n elements of the modified generalized Maxwell model include the same Hookean spring E, and that the deformation of the dashpot belonging to a given element j starts as soon as it bears the stress:

$$\sigma_{ij} = T[A \ln \dot{\epsilon} + B_{ij}(T)], \qquad (A1)$$

while it goes on under the action of a lower stress

$$\sigma_{dj} = T[A \ln \dot{\epsilon} + B_{dj}(T)] \qquad (A2)$$

Subscripts i and d recall that Equations A1 and A2 concern the initial and the increasing deformation of the dashpot respectively. The parameter A is kept constant; this means that the relationship between stress and strain rate is the same for all elements.

The macrocoscopic stress σ is the average of the stresses borne by the n elements:

$$\sigma = (1/n) \sum_{j=1}^{n} \sigma_j \qquad \text{(A3)}$$

The response of the model to a tensile test at constant strain rate may be expressed as a function of σ_v, the macroscopic stress related to the elements having a strained dashpot, and σ_E, the macroscopic stress related to the elements having a strained spring only. For a given value ϵ_A of the deformation, l dashpots are strained, we may therefore write that:

$$\sigma_v = (1/n) \sum_{j=1}^{l} \sigma_{dj} \qquad \text{(A4)}$$

and

$$\sigma_E = \epsilon_A/n) \sum_{j=l+1}^{n} E_j \qquad \text{(A5)}$$

By taking into account that $E_j = E$ for all the elements, Equation A5 becomes

$$\sigma_E = (1/n) E\epsilon_A (n-l) \qquad \text{(A6)}$$

while

$$\sigma_{il} = T[A \ln \dot{\epsilon} + B_{il}(T)] = E\epsilon_A \qquad \text{(A7)}$$

Let us define the following functions:

$$P_d(\sigma_{dj}) = \lim k \to j \left[\frac{j-k}{\sigma_{dj} - \sigma_{dk}}\right] \qquad \text{(A8)}$$

and

$$P_i(\sigma_{ij}) = \lim k \to j \left[\frac{j-k}{\sigma_{ij} - \sigma_{ik}}\right] \qquad \text{(A9)}$$

P_d and P_i are the distribution functions or spectra of the elements whose deformation is viscous and elastic respectively.

Therefore, the stress borne by the model at a given deformation ϵ_A is:

$$\sigma = \sigma_v + \sigma_E = \int_{\sigma_{d1}}^{E\epsilon_A} \sigma_d P_d(\sigma_d)\, d\sigma_d + E\epsilon_A \int_{E\epsilon_A}^{\infty} P_i(\sigma_i)\, d\sigma_i \qquad \text{(A10)}$$

Since $\sigma_{d1} = \sigma_{md}$, Equation A10 reduces to Equation 1 if one replaces σ_d and σ_i by $E\epsilon$ and takes into account the rubber elasticity contribution σ_R

Appendix 2

Response of the rubber spring

The relation given by K. J. Smith [8] may be written:

$$\sigma_R = \nu kT\eta(\alpha - 1/\alpha^2) \left\{1 + 20\delta/3 \left[1 - \frac{\eta}{5\alpha}(3\alpha^3 + 4)\right]\right\} \qquad \text{(A11)}$$

where η denotes the front factor of Tobolsky, ν the number of segments per unit volume, k the Boltzmann constant and T the absolute temperature.

For the calculations, we take $\eta = 1$ and $\delta = -51/80N$ for $<\cos\phi> = 0$, N denoting the number of backbone links per segment. Thus Equation A11 becomes:

$$\sigma_R = \frac{kT}{Nv_0}(\alpha - 1/\alpha^2)\left\{1 + \frac{4.25}{N}\left(\frac{3\alpha^3 + 4}{5\alpha} - 1\right)\right\} \qquad \text{(A12)}$$

where Nv_0 is the volume of a segment.

Taking into account that:

$$\frac{kT}{Nv_0} = \frac{\rho RT}{MN} \qquad \text{(A13)}$$

where R is the universal gas constant, ρ the specific weight ($1.4\,g\,cm^{-3}$) and M half the molecular weight of the monomer unit (32.25 g) one obtains at room temperature:

$$kT/v_0 = 11\,kg\,mm^{-2} \qquad \text{(A14)}$$

Therefore, with $N = 14$, Equation A12 becomes identical to Equation 13.

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Received 19 July and accepted 7 October 1977.