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Young's modulus and β -relaxation of amorphous polymers

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Résumé. — Le comportement mécanique des polymères est fortement dépendant des conditions d'essais, notamment du temps de sollicitation et de la température. Il a ainsi été mis en évidence l'existence d'une température, ou d'une vitesse de déformation, correspondant à un changement dans le comportement du matériau ; celles-ci sont appelées température et vitesse critique et peuvent être associées à des phénomènes de relaxation. Cette étude portant sur le Poly Méthacrylate de Méthyle (P.M.M.A.) montre que cette relaxation correspond à la relaxation β . Pour de très faibles niveaux de déformation à faible vitesse (ce niveau augmentant avec la vitesse de déformation) les mécanismes provoquant la relaxation β sont bloqués : le comportement du P.M.M.A. est alors indépendant de la vitesse de déformation. Puis la plasticité apparaît, provoquée par des mécanismes de type diffusif.

Abstract. — The mechanical behaviour of polymers have been studied as a function of time and temperature. The influence of a critical temperature or critical strain rate have been pointed out which may be related to relaxation phenomena. This study, carried out on Poly Methyl Methacrylate, shows that this relaxation phenomena can be associated to the β -relaxation. When the process does not occur, for very low rate of strain at low strain rate (the higher the strain rate, the higher the rate of strain), the behaviour of P.M.M.A. is independent of the strain rate and the strain is proportional to the applied stress. When the β -relaxation can occur the deformation is no more linear, and is highly dependent on strain rate and plasticity is due to diffusional mechanism.

1. Introduction.

It is well known that all polymers are characterized by a temperature, called glass transition temperature T_g , beyond which they are in an equilibrium thermodynamic state. Below T_g , the whole or part of them will never reach this state. This transition is associated to a mechanical relaxation (called α -relaxation for amorphous polymers) which is due to motions of the main molecular chain parts [1-3] ; in the glassy state much more localized motions (secondary relaxation) may be identified by dielectrical or mechanical relaxation [4, 5].

These relaxation influences have been studied at low strain rate in a large range of temperature for instance by Bauwens *et al.* on Poly Methyl Methacrylate (P.M.M.A.), Polycarbonate (P.C.), Poly Vinyl Chloride (P.V.C.) [6-11].

Following Ree & Eyring, macromolecules relative motion is handled by cohesive forces but can be thermally activated. This leads to the following expression for the yield stress σ_y [12]:

$$\frac{\sigma_y}{T} = A_\alpha \left(\text{Ln} (2 \cdot C_\alpha \cdot \dot{\epsilon}) + \frac{E_\alpha}{RT} \right) \quad (1)$$

where T is the absolute temperature, $\dot{\epsilon}$ the strain-rate, E_α the α glass-transition activation energy and R the universal gas constant, A_α and C_α adjustable parameters. Note that this formula is very similar to the one obtained with the plasticity Escaig's model based on physical metallurgy concepts [13]:

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp \left(- \frac{Q - \sigma^* V^*}{kT} \right) \quad (2)$$

where σ^* is the effective stress, Q the activation energy and V^* is the activation volume which can be related to A_α .

$$A_\alpha \approx \frac{k}{V^*(\epsilon_y)} \quad (3)$$

where ϵ_y is the strain corresponding to the yield stress σ_y .

In a larger temperature range, when a secondary β -relaxation can be activated, equation (1) becomes:

$$\frac{\sigma_y}{T} = A_\alpha \left(\text{Ln} (2 \cdot C_\alpha \cdot \dot{\epsilon}) + \frac{E_\alpha}{RT} \right) + A_\beta \left(\text{Ln} (2 \cdot C_\beta \cdot \dot{\epsilon}) + \frac{E_\beta}{RT} \right) \quad (4)$$

taking into account the α and β molecular processes.

Owing to time temperature equivalence principle, a critical strain-rate $\dot{\epsilon}_c$ was found; below $\dot{\epsilon}_c$ the flow is due to α -relaxation, and beyond β -relaxation is activated:

$$\dot{\epsilon}_c = \frac{1}{2 C_\beta} \exp \left(- \frac{E_\beta}{RT} \right). \quad (5)$$

Such conclusions were also drawn for P.M.M.A. by Roetling [14-16] and extended to high strain rate on P.C. [17].

In fact this critical strain-rate is very closed to a characteristic time τ ; below τ there is no time for molecular rearrangement and relaxation phenomena cannot be observed. In the year 1950 (Lethersich [18]) two relaxation effects on P.M.M.A. at 30 °C were shown to exist: one observed in the range of 1 to 100 s after stressing, the other one beyond 10^7 s; the short time range effect was the first evidence of P.M.M.A. β -relaxation. Therefore we have revealed the relation between ϵ and the frequency at which the β loss peak occurs.

2. Experimental.

MACHINES AND SPECIMEN. — Low frequency internal friction measurements were performed at constant temperature with a torsional pendulum working in a 10^{-4} -10 Hz frequency range [19]. At frequencies low enough to permit initial forces neglect the internal friction

Q^{-1} is simply related to the phase lag δ between the stress (the applied force) and strain (the specimen displacement) :

$$Q^{-1} = \operatorname{tg} \delta . \quad (6)$$

— To achieve strain-rate up to 2 s^{-1} an INSTRON hydraulic machine was used, and the deformation was localized in a small part of the test specimen as shown in figure 1.

To determine the material mechanical response different parameters were monitored :

- force given by the load cell of the machine
- deformation given used by strain gauge glued on to test specimen
- time given and calculated by the internal timing of the 'acquisition system we developed [20].

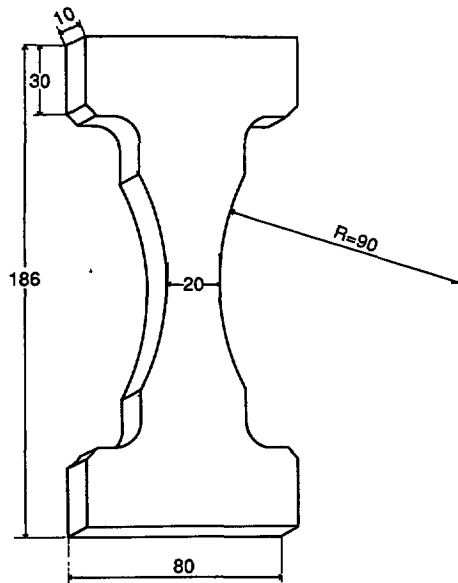


Fig. 1. — Tensile Test Specimen. Nota : a stress concentration factor $K = 1.07$ is induced by the form.

MATERIAL. — As we wanted to study the β -relaxation influence on the mechanical behaviour of polymer, we have chosen the P.M.M.A. whose β -peak is observed, at room temperature, at a frequency within 10 Hz.

This polymer was a commercial Altuglas delivered as a sheet so a thermal treatment at 140°C was applied to anneal the material. This treatment was stopped long time after they were no more volume expansion of a sample taken into the sheet. This expansion is due to a free volume growth which appears during the rubbery phase keeping. This free volume is kept when the sample specimen is air-quenched, then it tends to slowly decrease at room temperature : this is the physical ageing which is quite non-existent on P.M.M.A. at room-temperature.

TENSILE CURVES. — The acquisition system allowed us to follow the evolution of force and deformation *versus* time ; so we can plot the evolution of the true stress *versus* the true strain and compute to get the strain-rate.

As it was awaited the influence of strain rate is very important as shown in figure 2 where each tensile curves are shifted in order to distinguish them.

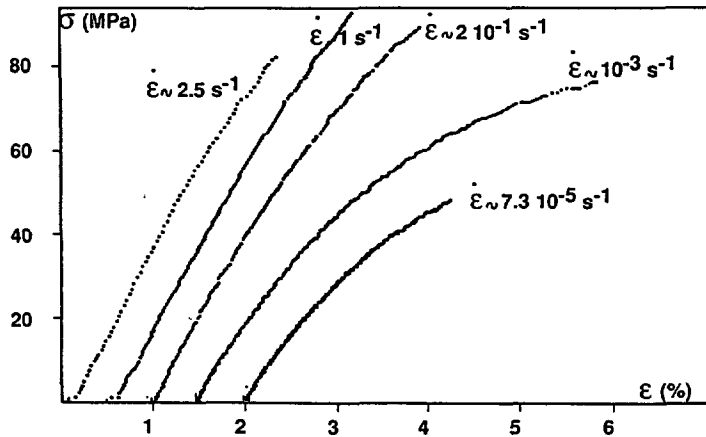


Fig. 2. — Tensile Curves of annealed P.M.M.A. for different indicated strain-rates (origins are displaced along x-axis).

It seems to be evident that for strain rate about 2 s^{-1} the deformation is elastic until failure, unlike for $\dot{\epsilon} \approx 10^{-4} \text{ s}^{-1}$ viscoelasticity appears as soon as the strain reaches 2×10^{-3}

3. Analysis.

LINEAR STAGE — ELASTIC MODULUS. — The simplest way to determine the linear stage hedge should be to construct the curve plotting the derivation to true stress σ with respect to the different strains ϵ against the considered strain ϵ (i.e.: $\left(\frac{\partial \sigma(\epsilon)}{\partial \epsilon}\right)(\epsilon)$) as a function of ϵ for instance ; but this method is not very efficient because of perturbations induced during the acquisition process.

In order to get a better idea of each different states corresponding to the different behaviour of the material the isostrain curve was drawn (Fig. 3) : the needed stress to reach a given strain is plotted against the strain-rate.

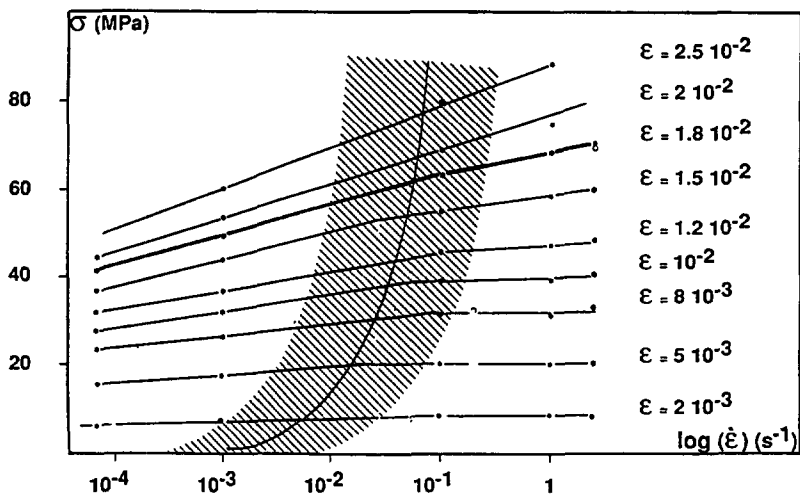


Fig. 3. — Isostrain Curves plotted in a $(\sigma, \ln(\dot{\epsilon}))$ graph.

In fact we can notice of figure 3, in the right side of the hatched area, the existence of a zone in which, considering a given rate of strain, the ratio of σ to ε is constant for every strain-rate. Furthermore this ratio is non-dependent of the rate of strain ε considered.

Consequently the material behaviour is non strain-rate dependent and in addition is linear ; it follows that it is an elastic behaviour. This stage is evident at high strain-rate and is to be found at very tiny rate of strain ($\varepsilon < 2 \times 10^{-3}$) for the lowest strain-rate.

The hatched zone corresponds to the beginning of relaxation process under low stress.

LINEAR STAGE HEDGE. — For a start we have to consider the β -relaxation peak of the same P.M.M.A. (test were carried out on specimen taken in the same sheet). It has been studied at a constant temperature of 28 °C as a function of the frequency and a strain amplitude about 10^{-4} [21].

This peak has its vertex at 10 Hz (Fig. 4). It is much more larger than a Debye's peak and exhibits a large relaxation time spectra : its influence is to be taken into account over three decades.

Owing to its 70 kJ.mol^{-1} activation energy, at 23 °C, which is our test temperature its vertex is at about 3 Hz. In figure 3, a 0.3 s isochronous solid line has been drawn which corresponds to this 3 Hz frequency ; this is the time needed for the β -relaxation to fully occur. The hatched area corresponds then to the β -relaxation influence :

- on the right of this zone β -relaxation has no time to occur and we reached a given strain at $\dot{\varepsilon} > \dot{\varepsilon}_c$
- otherwise on the left β -relaxation has been activated so the given strain is reached at $\dot{\varepsilon} < \dot{\varepsilon}_c$.

Consequently it seems to be clearly evident that the linear behaviour is limited by β -relaxation except for higher strain-rate for which the behaviour is no more linear before β -relaxation interfere ; this is due to damage owing to the gauge sticking [22].

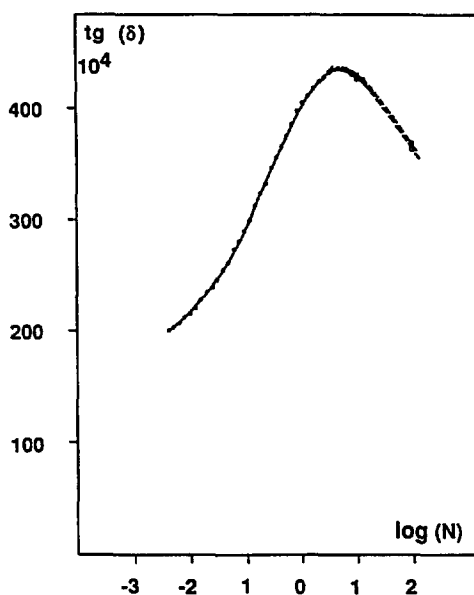


Fig. 4. — P.M.M.A. β -relaxation peak versus logarithm of frequency at 28 °C.

The elastic modulus value is $3\,900 \pm 200$ MPa for strain-rate greater than 10^{-2} s^{-1} there is then no use to increase the strain-rate to measure a higher modulus as the other secondary relaxations (δ and γ) which occurs at low temperature (i.e. high strain-rate) have a very weak influence.

At lowest strain-rate the behaviour is no longer linear for rate of strain about 10^{-3} that is to say after 100 s. The β -relaxation has fully occurred and the modulus is dropped of about 20 % [23].

ANELASTIC BEHAVIOUR. — This stage is characterized by loss of the material consistence. In fact the linear dependence of the needed stress to reach a given strain with $\text{Ln}(\dot{\epsilon})$ leads to an thermally activated process described by the Escaig's relation (2) :

$$\dot{\epsilon} = \dot{\epsilon}_0 \exp\left(-\frac{Q - \sigma^* V^*}{kT}\right)$$

where σ^* is the effective stress, V^* is the activation volume and Q the activation energy.

Some hypotheses are needed to evaluate V^* ; on the assumption that

- $\dot{\epsilon}_0$ is non dependent of $\dot{\epsilon}$ and σ ;
- the internal stress σ_i ($\sigma_i = \sigma - \sigma^*$) is proportional to strain : $\sigma_i = \alpha \epsilon$.

The value of V^* can then plotted against strain ϵ (Fig. 5).

In spite of our hypotheses the values of the activation volume are closed to Lefebvre's [24]. The activation volume decreases when the rate of strain increases as in metals at the beginning of the plastic deformation when the dislocation density increases.

Consequently in this stage two physical phenomena are involved : the β -relaxation and elements mobility which act as dislocations do in metals plasticity. This leads to the diffusionnal mechanism which is involved in the P.M.M.A. plastic deformation as Lefebvre [24] showed : the β -relaxation takes the same part as the vacancy migration in high temperature deformation of metals.

As the activation volume rapidly grows when the strain decreases we may consider that $\epsilon = 10^{-3}$ may be the lowest strain beyond which non linear process appears.

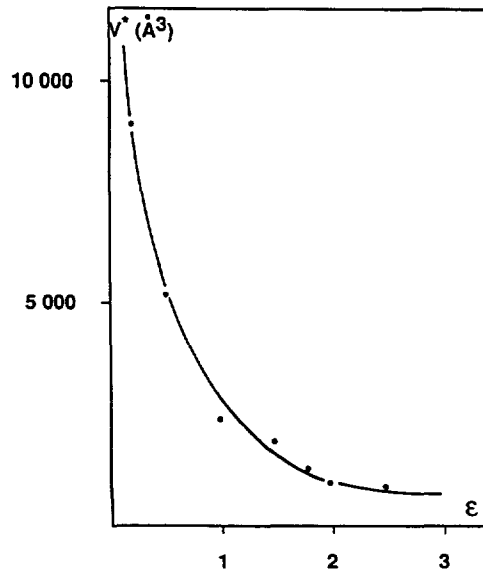


Fig. 5. — Activation volume versus strain (%).

4. Conclusion.

Two deformation stages have been shown : a linear elastic stage and anelastic one.

The deformation is linear until the strain reaches about 10^{-3} . As the strain rate increases the linear deformation concerns bigger rate of strain which reaches about 1.5 % when $\dot{\epsilon} = 1 \text{ s}^{-1}$. This stage is limited by the activation of the β -relaxation which appears as soon as 0.1 s at room temperature.

The value of the elastic modulus is $3\,900 \pm 200 \text{ MPa}$. For the lowest strain rate, when the elastic behaviour is edged at $\epsilon \approx 10^{-3}$, the apparent elastic modulus decreases of 20 % when β -relaxation may occur.

When the rate of strain is greater than 10^{-3} , the β -relaxation involves a new deformation process which is like the dislocations motion at the first stage of plastic metals deformation. It is a thermally activated process with an activation volume which increases when strain decreases. We have shown that the P.M.M.A. deformation at room temperature is bound to β -relaxation and the motion of defects which are thermally and mechanically activated. So it seems impossible to prefer one of the Ree-Eyring's or Esgaig's theory.

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