

New possibilities for the study of deformation kinetics and relaxations in polymers using a laser interferometer

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(Received 28 January 1993; accepted 27 October 1993)

Abstract

An original precise technique for measuring creep rate using a laser interferometer has been developed. This makes it possible to obtain information on creep kinetics at any point on the creep curve over wide ranges of temperatures and deformation values. Some regularities in the deformation kinetics of glassy polymers have been found. The relationships obtained between activation energy and activation volume, and cohesion energy confirm the intermolecular origin of the potential barriers to deformation. The possibilities of studying microplasticity in different materials, including brittle materials, have been demonstrated. On this basis, the Creep Rate Spectra (CRS) method is suggested as a low-frequency and high-resolution procedure for application in relaxation spectrometry.

INTRODUCTION

Explanations of inelastic deformation of glassy polymers are based on the classical treatments of Frenkel [1] and of Eyring and coworkers [2, 3], who considered an elementary plastic flow event as a transition of a particle from one quasi-equilibrium state to another by means of the overcoming of a potential barrier under the influence of thermal fluctuations. From refs. 3–7, it follows that the polymer deformation rate can be described, in a certain temperature range, by an expression of the type

$$\begin{aligned}\dot{\epsilon} &= \dot{\epsilon}_0 \exp\left(-\frac{Q_0 - \alpha t_m}{RT}\right) = \dot{\epsilon}_0 \exp\left(-\frac{Q(t_m)}{RT}\right) \\ &= N\epsilon_0^* v_0 \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{Q(t_m)}{RT}\right)\end{aligned}\quad (1)$$

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where $t_m = \sigma/2$ is the maximum tangential stress, Q_0 is an empirical activation energy, $Q(t_m) = \Delta H$ is an activation enthalpy, α is an activation volume, ΔS is the entropy of activation, N is the number of “flow kinetic units” or any elementary shear regions, ε_0^* is the contribution of each unit to the total strain, R is the gas constant, T is the absolute temperature, $\dot{\varepsilon}_0$ is the “frequency factor”, and $\nu_0 \approx 10^{13} \text{ s}^{-1}$.

The different deformation theories [2–13] involve expressions similar to eqn. (1). Frenkel’s treatment has been expanded to consider the conditions for displacement of a kinetic unit over a potential barrier, assuming that its height is lowered by stress. It has also been presumed that the magnitude of the kinetic units corresponds closely to the activation volume of deformation, as well as to the different kinds of motion, namely the rotation–translation displacement of one segment or several neighbouring segments. In addition, the disclination [10] or dislocation [11] models have been discussed.

However, eqn. (1), assuming a process with constant values of Q_0 and α , can only be applied within a narrow range of varying experimental conditions. In the more usual determination of kinetic parameters, the values of $Q(t_m)$ and α are found from the slopes of the $\ln \dot{\varepsilon}$ against T^{-1} and $\ln \dot{\varepsilon}$ against t_m plots, which requires a certain averaging of the results for wide ranges of stresses and temperatures and may introduce considerable errors.

Application by Sherby and Dorn’s method of “jumps” in stress or temperature [14], with inaccurate measuring of the creep rates, also led to rough estimates of the kinetic parameters and to the conclusion that they are approximately constant within certain ranges of temperatures or strains.

Meanwhile, the diversity of the molecular motions inherent in polymers resulted in a description of their mechanical properties with respect to their relaxation transitions [15, 16] that made it possible to predict the temperature anomalies observed for their deformation, fracture stress or longevity under load [17–19]. This description predicted, in principle, the inconstancy of deformation kinetic parameters over a wide range of temperatures. However, there were no systematic studies of the deformation kinetics of polymers measured at the different stages of the process of creep, i.e. as a function of the magnitude of deformation. The reason for this is that the techniques adopted were unsuitable for these experiments.

The important problem in developing any specific model of deformation is to define the physical nature of its potential barriers, i.e. the activation energy of the process. As postulated many years ago [2–4, 6, 7], the deformation of glassy polymers involves overcoming the barrier of intra- and intermolecular (non-chemical) interactions; the dominant role of the latter has also been assumed in specific models [10–12]. By combining the mechanical, spectroscopic and calorimetric techniques, the present authors [20–23] confirmed experimentally the transformations in an equilibrium

system of intermolecular bonds during a deformation process, and obtained direct correlations between the resistance to deformation and the energy of the intermolecular interactions in glassy polymers.

However, the values of Q_0 obtained for polymers by generally accepted techniques were often contradictory and were as large as tens or hundreds of kilocalories per mole [4, 5, 12, 24], i.e. much more than the energy of a single "intermolecular bond" or an internal rotation barrier. Moreover, the activation energies of the processes that are due to the breaking of chemical bonds in chains, namely mechanical fracture or thermal degradation, are of the same order of magnitude as the creep process [8, 13]. It is also noteworthy that the activation volumes of creep are characterized by the large values of α , approx. 10^3 – 10^4 Å³ [12, 13, 24]. All these data made it difficult to come to any conclusions regarding the nature of the activation energy of deformation.

We succeeded in resolving these problems by the elaboration of a new high-precision method for studying deformation kinetics, based on recording the creep rates by laser interferometer [25, 26]. This technique made it possible not only to increase markedly the accuracy of the measurements, but also to study the creep and microcreep kinetics under formerly inaccessible conditions, i.e. to obtain complete kinetic information at any temperature and any stage of the deformation process.

This paper includes a brief review of studies carried out using this method.

PRINCIPLES OF THE INTERFEROMETRIC TECHNIQUE FOR DEFORMATION RATE MEASUREMENTS

The laser interferometer method was the first technique to yield creep rates of about 10^{-10} – 10^{-4} m s⁻¹ with an accuracy of 1% at any stage of the deformation process, from measurements of the deformation increment of only a few thousandths of a percent, i.e. about 0.1 μm [27–34].

Figure 1 shows a scheme of one of the set-ups being considered, that for the compression test. A Michelson interferometer was used, with a low-powered He–Ne laser of wavelength $\lambda = 0.63$ μm. The optical scheme (Fig. 1) consists of three semi-transparent (half-silvered) mirrors and three opaque mirrors, one of which (2) is rigidly connected with a puncheon that follows the deformation of a specimen. The laser beam reflected from the moving mirror (2) changes its frequency as a result of the Doppler effect. Interference of the initial beam with a beam of changed frequency yields low-frequency beats in the resultant light beam whose intensity is transformed by photocells into an electric signal of the same frequency. The frequency ν of this signal may be measured by standard instruments.

The evolution of the deformation with time was registered by a recorder

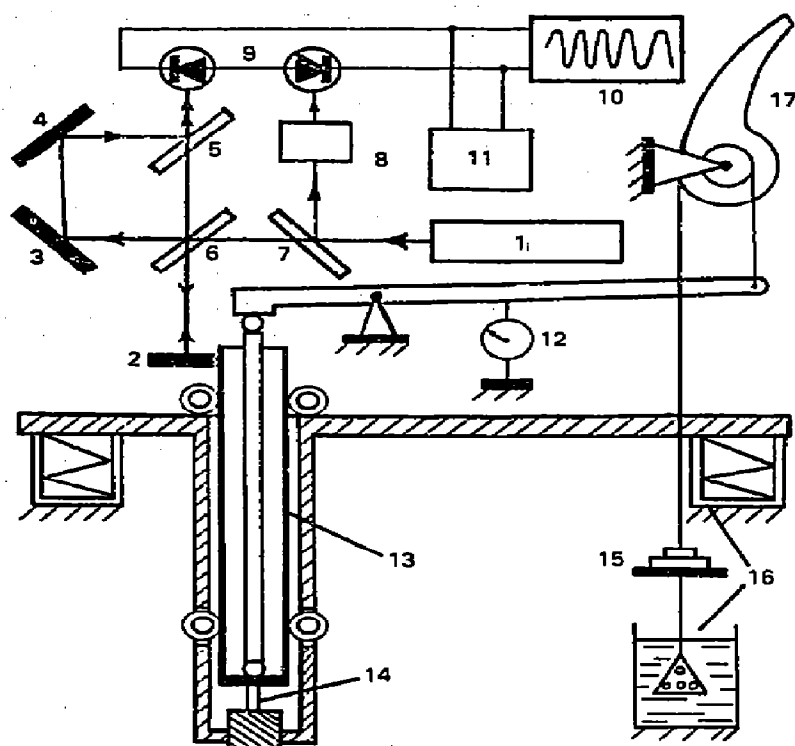


Fig. 1. Scheme of the interferometric setup: 1, laser; 2–7, mirrors; 8, polarizer; 9, photocells; 10, recorder; 11, automatic section; 12, indicator of displacements; 13, active puncheon; 14, sample; 15, load; 16, dampers; 17, figured lever providing constant α .

as a sequence of beats where the beat frequency ν yields the creep rate $\dot{\epsilon}$, and the number of oscillations N yields the deformation value ϵ

$$\dot{\epsilon} = \frac{\lambda \nu}{2l_0} \quad (2)$$

and

$$\epsilon = \frac{\lambda N}{2l_0} \quad (3)$$

where l_0 is the initial length of specimen.

Cylindrical specimens, 6 or 10 mm in length and 3 mm in diameter, were used in compression tests, and film samples, 15 mm in length, were used in the extension experiments. In this case, according to eqn. (3), the real minimum deformation increment allowing determination of the creep rate was equal to $0.15 \mu\text{m}$ (half of one oscillation), i.e. about 0.001%–0.003%. The error in the determination of $\dot{\epsilon}$ was equal to 1%.

The interferometric method has many advantages, such as the combination of a wide range of permissible displacements, from approx. 10^{-7} m up to 10^{-1} m, with constant resolution and high accuracy, and the possibility of studying the inelastic deformation of different solids, including ultralow creep rates and microplasticity in brittle materials. In addition, this

technique does not require calibration and allows a computer to be used for automatic plotting of $\dot{\epsilon} = f(t)$, $\dot{\epsilon} = f(\epsilon)$ and $\epsilon = f(t)$ curves during the course of the experiment [26]. Moreover, in this unique set-up there is no mechanical contact between the gauging scheme and the specimen.

The approach to the determination of the deformation kinetic parameters by this technique must be considered in more detail: a series of studies of this kind [27–34] are described below.

It is known [35] that the main difficulty in the correct estimation of the Q_0 and α values is the need to maintain the structure of the polymers during their measurement: this is, strictly speaking, impossible.

In refs. 27–34, the kinetic parameters Q_0 and α were determined by the method of temperature and stress “jumps” [14], which was greatly improved by using a laser interferometer to measure the strain rate.

In our opinion, the possibility of determining the insignificant changes of rate $\dot{\epsilon}$ using ultra-small changes in the strain (approx. 0.005%) in the jump allows the condition of invariability in the polymer structure to be approached during the test. Therefore, the parameters Q_0 , α and $\dot{\epsilon}_0$ in eqn. (1) may be regarded as constants for any given “point” of the creep process. In the sensitive method for the determination of creep rate, it is possible to change the temperature by only 3–5°C during the measurement of Q_0 . The jump method is also attractive because at any given temperature we can determine the kinetic parameters for a single sample at different stages of its deformation.

Thus, we assume that, in principle, all three kinetic parameters are a function of the temperature, strain and stress, but in each experiment, involving an abrupt but small change in temperature or stress, these parameters in eqn. (1) may be considered as constants; then, the relevant change in the creep rate $\dot{\epsilon}$ is associated only with changes in T or t_m .

The criterion of constancy of the structure was the reversibility of the strain rate $\dot{\epsilon}$ after a reverse jump, Δt_m or ΔT .

The method of jumps of ΔT or Δt_m was used to find the values of $Q(t_m)$, Q_0 and α at any “point” on the creep curve, using the equations

$$Q(t_m) = R \left(\frac{\ln \dot{\epsilon}_2 / \dot{\epsilon}_1}{T_1^{-1} - T_2^{-1}} \right)_{t_m} \quad (4)$$

$$\alpha = RT \left(\frac{\ln \dot{\epsilon}_2 / \dot{\epsilon}_1}{\Delta t_m} \right)_T \quad (5)$$

and

$$Q_0 = Q(t_m) + \alpha t_m \quad (6)$$

where $\dot{\epsilon}_1$ and $\dot{\epsilon}_2$ are the creep rates before and after a jump of $\Delta T = T_2 - T_1$ ($\approx 5^\circ\text{C}$) or Δt_m ($< 0.1 t_m$).

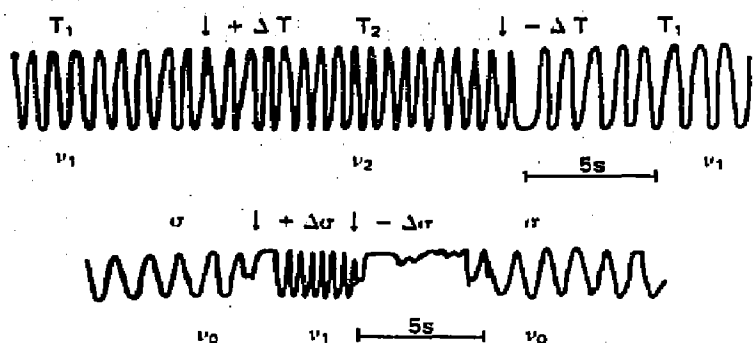


Fig. 2. Typical interferograms of the creep recorded during a temperature jump ΔT and a stress jump $\Delta\sigma$. One oscillation represents a strain of $0.3 \mu\text{m}$ (approx. 0.005%).

Equation (4) was used to determine the parameter $Q(t_m)$, and then eqn. (1) yields $\dot{\epsilon}_0$

$$(\ln \dot{\epsilon}_0)_{\sigma, T} = \ln \dot{\epsilon} + Q(t_m)/RT \quad (7)$$

The temperature jump was produced by passing a current along a flexible helix which, at low temperature, was wound around the sample but, at $T > 20^\circ\text{C}$, was achieved by immersion of the sample in an inert liquid. A period of about 30 s was sufficient to heat a sample. Typical interferograms before and after jumps of Δt_m or ΔT are shown in Fig. 2.

The coefficient α was determined by making a change Δt_m at constant T so that the dependence $\alpha(T)$ did not complicate the procedure of determining this coefficient.

When measuring $Q(t_m)$, a change in temperature was required. For polymers, one can expect a weak dependence of $Q(t_m)$ on T for certain temperature ranges [17, 19]. In those cases, the derivative dQ/dT was extremely small and the determination of Q_0 was the most correct.

Below, we briefly consider the results of our studies on glassy polymers using the technique described. Some specific aspects of the methodology will also be noted in the relevant parts.

ANALYSIS OF THERMALLY ACTIVATED CREEP

Process parameters versus deformation value

The creep curves under compression for all the glassy polymers studied were of the type shown schematically in Fig. 3, curve 2. The ϵ_y strain corresponds to a bend in the creep curve and to a maximum in the

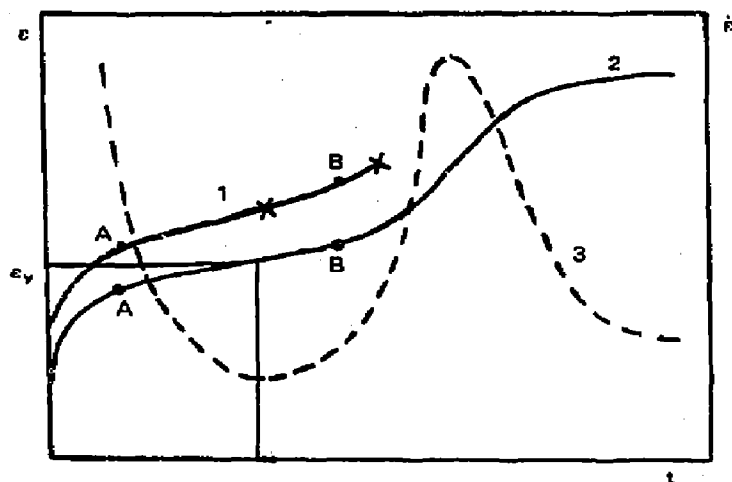


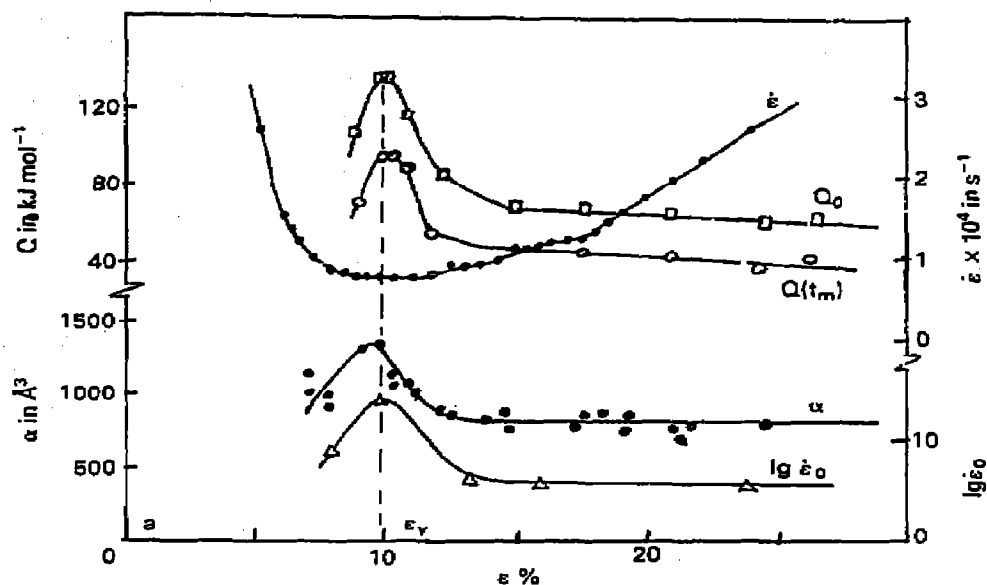
Fig. 3. Schematic representation of typical creep curves for stretching (1) or compression (2) of glassy polymers, and the creep rate alteration during the creep process (3): X, points of fracture in stretching.

stress–strain curve, yielding a stress σ_y [36–38]. The creep curve obtained in tension is often broken at AB, the creep stage. The activation parameter values cited in the literature as the “constants” of the materials [5, 8, 12, 14, 24] correspond to this steady-state creep, characterized by the constant rate, as assumed.

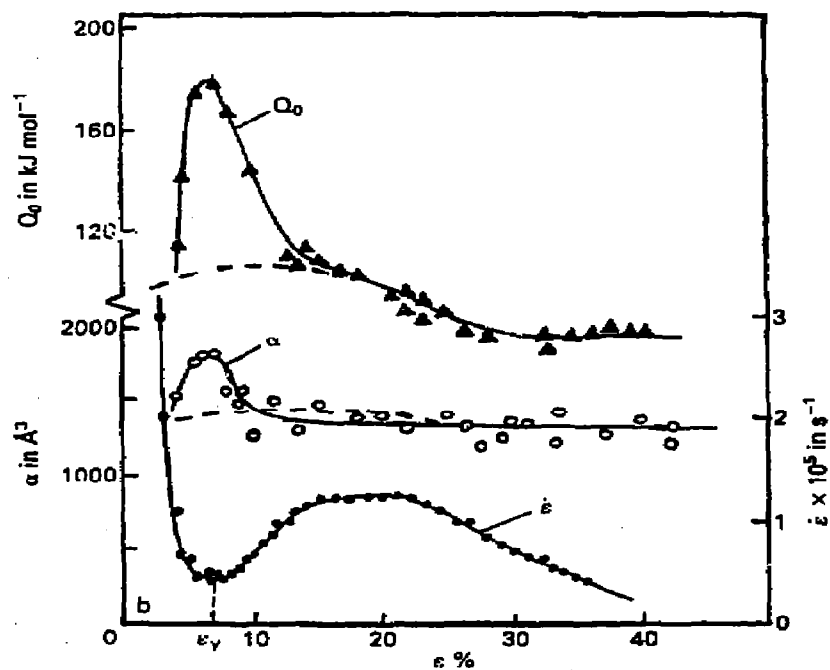
Meanwhile, precise measurements by laser interferometer of the $\dot{\epsilon} = f(\epsilon)$ plot show [19, 29] that if t_m and T are constant, the creep rate $\dot{\epsilon}$ varies continuously with increasing strain (see Figs. 3 and 4), so that $\dot{\epsilon}$ is minimum at ϵ_v . This result suggested that the values of Q_0 , α and $\dot{\epsilon}_0$ would also change during the course of the deformation.

We have carried out a systematic experimental evaluation of the creep kinetic parameters using the new technique [25–34] for a number of glassy polymers, see Fig. 6 caption, below. These data, combined with the spectroscopic and calorimetric measurements of the intermolecular interactions for the initial and pre-strained samples [20, 22, 23], made it possible to extend considerably the description of the nature of creep.

Figure 4 shows as an example the kinetic parameters versus total creep deformation dependences obtained for PVC and PMMA. The values of $Q(t_m)$, Q_0 , α and $\dot{\epsilon}_0$, determined from various points of the creep curves were found to depend on the degree of strain in a similar way for all the polymers studied (PMMA, PVB, PS, styrene copolymers, PC, PVC, etc.). As seen in Fig. 4, at constant σ and T , all the creep parameters depend strongly on strain. The magnitudes of $Q(t_m)$, Q_0 , α and $\lg \dot{\epsilon}_0$, reached their maximum values at ϵ_v ; thereafter they reduced, and at $\epsilon > 10\%$ – 15% the changes became insignificant; this is when “cold-flow” deformation occurs throughout the sample.



(a)



(b)

Fig. 4. Strain dependences of the creep parameters at $T \approx 20^\circ\text{C}$: a, poly(methyl methacrylate), $\sigma = 90\text{ MPa}$, b, poly(vinyl chloride), $\sigma = 50\text{ MPa}$. The broken curves correspond to the preliminarily stretched and twisted sample.

Over the range $\varepsilon \cong 10\%–40\%$, the value of α remained constant, to a first approximation, while Q_0 decreased slightly.

Table 1 gives the values of Q_0 and α for several polymers at $\varepsilon = \varepsilon_y$ and $\varepsilon = 20\%$. The largest values of the activation energy Q_0 vary within this polymer series in the range of about $130–280 \text{ kJ mol}^{-1}$; at the stage of fast creep (Fig. 3), this parameter decreases by 1.5–2 times.

It was shown in ref. 29 that pre-straining or quenching of glassy polymers could lower the “peak” values of the α and Q_0 parameters at point ε_y , with total disappearance of maxima (Fig. 4b). This result reflects the dependence of these parameters on structural changes in the polymers.

The strain dependences of the creep activation energy Q_0 were in good agreement with the results obtained by IR spectroscopy and DSC techniques. Thus, as was shown in refs. 20, 22 and 23, the pre-straining of glassy polymers at $\varepsilon > \varepsilon_y$ broke an initial equilibrium system of intermolecular bonds which resulted in a decrease in the interactions between molecules and, simultaneously, in a change in the kinetic parameters of deformation (Fig. 4). The value of the frequency factor $\lg \dot{\varepsilon}_0$ also depended on the degree of strain, changing from about 13 down to 7–8 [19, 27]. It was assumed that this was due to the changes in the entropy of activation ($\Delta S \neq 0$) [39].

Thus, for an isotropic linear polymer, in general the creep curve cannot be described by eqn. (1) with invariable values of the coefficients Q_0 , α and $\dot{\varepsilon}_0$.

The similarity of the $\alpha(\varepsilon)$, $Q_0(\varepsilon)$ and $\lg \dot{\varepsilon}_0$ versus ε curves has demonstrated their interrelationship and revealed the complex integral nature of Q_0 as a potential barrier. It can be tentatively assumed that the latter includes a number of “elementary” q_i energy barriers, overcome by a kinetic deformation unit commensurable with α in its volume. Indeed, this approach made it possible to proceed with the study of the nature of the activation energy [27–34].

Let us imagine a unit event of a creep process, without considering specific deformation models, as a displacement and transition of a section of the macromolecule equal in volume to $\alpha = mV$, over the potential barrier $Q_0 = \sum q_i = mq_i$ [19, 27–29]. Here $V = M/\rho N_A$ is the volume of one monomeric unit, m is their number per kinetic unit of deformation, and M , ρ , N_A are the molecular mass of the monomeric unit, the density of the polymer and Avogadro's constant, respectively. The “elementary” barrier q_i is a partial contribution to the potential barrier, being related to one monomeric unit.

Table 1, together with the kinetic characteristics, gives some values of $q_i = Q_0/m$ calculated from experimental data obtained at approx. 20°C for the point $\varepsilon = \varepsilon_y$, when the initial structure remains undamaged by shear, and at deformation $\varepsilon = 20\%$, i.e. in the “cold flow” range.

If the initial assumption is correct, the barrier q_i should be conditioned

TABLE I
Relationship between the activation parameters of polymer creep at about 20°C and the cohesion energy

Polymer	Activation energy Q_0 /kJ mol ⁻¹	Activation volume $\alpha/\text{Å}^3$ ^a	Molar volume $V/\text{Å}^3$	Number of monomer units $m = \alpha/V$	$q_0/(\text{kJ mol}^{-1}) = Q_0/m$	$E_f/(\text{kJ mol}^{-1}) = E_{coh}/3$ [40, 41]
	$\epsilon = \epsilon_y$ $\epsilon = 20\%$	$\epsilon = \epsilon_y$ $\epsilon = 20\%$		$\epsilon = \epsilon_y$ $\epsilon = 20\%$	$\epsilon = \epsilon_y$ $\epsilon = 20\%$	
Polyvinylbutyral, PVB	143	2240	163	14	10	7.5
Poly(methyl methacrylate), PMMA	134	1340	155	9	14.7	11.2
Polystyrene, PS	134	1400	166	9	15	10.7
Polyvinylchloride, PVC	167	1800	73	25	6.7	5.5
Polycarbonate, PC	252	2700	363	7.5	33.6	24
Polyacrylonitrile, PAN	210	1400	75	19	10.9	-
Poly(ethylene terephthalate), PET	278	2800	240	12	23	-

^a The activation volumes α in kcal mol⁻¹ Kg⁻¹ mm² were estimated from eqn. (1); 1 kcal mol⁻¹ Kg⁻¹ mm² = 700 Å³. The absolute errors are $\Delta Q = 4-8$ kJ mol⁻¹, $\Delta\alpha = 50$ Å³, $\Delta m = 0.3$, and $\Delta q_0 = 1.5$ kJ mol⁻¹.

primarily by the chemical structure of the monomeric unit and mainly corresponds to the intermolecular interaction barrier that is overcome being reduced to one mole of monomeric units, i.e. it is related to the cohesion energy E_{coh} . As known, E_{coh} is the energy required to break all the intermolecular contacts of a small molecule with its environment. However, when this kinetic unit is surrounded by similar particles, the effective intermolecular barrier to motion is equal to $E_f \approx E_{\text{coh}}/3$, as was shown for the flow of many low-molecular liquids [2, 3].

Table 1 gives E_f values estimated from the E_{coh} values of low-molecular organic substances [40, 41], whose chemical structure is the same as the monomer unit of the chain. In all cases, for polymers varying in structure the values of q_i were close to $E_{\text{coh}}/3$, although both characteristics varied for these polymers in a few cases.

Because the inelastic deformation of glassy polymers may somewhat reduce the intermolecular interaction energy [20, 22, 42], the barrier q_i might reflect this process. Some decrease in the q_i values was indeed observed for $\varepsilon \gg \varepsilon_y$ [19] (see also Table 1).

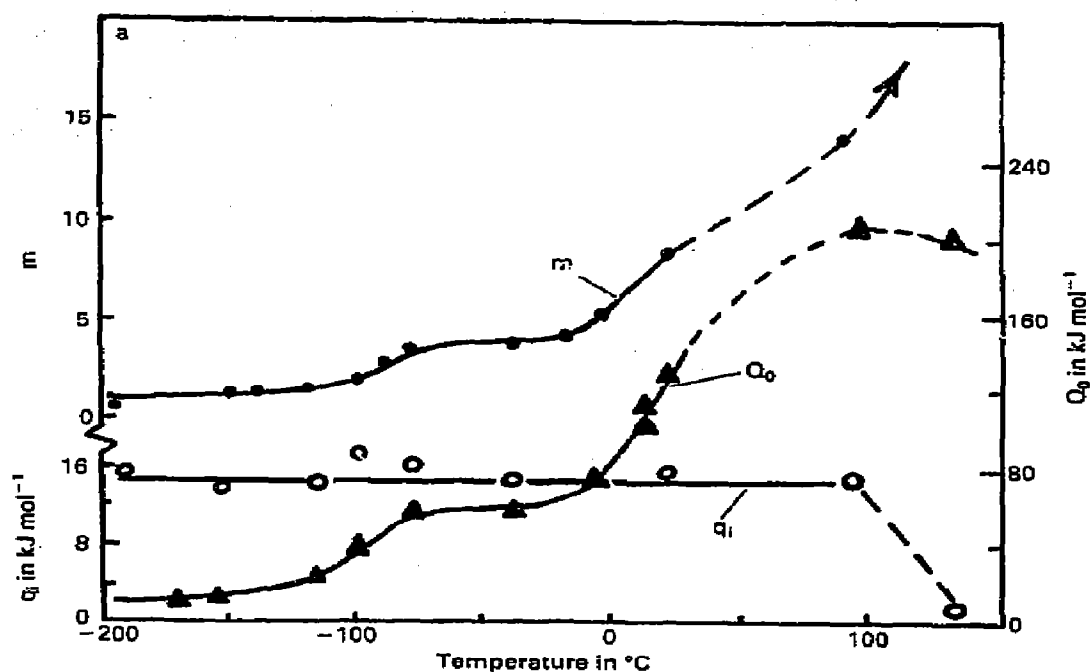
It might be thought that the correspondence found was not accidental but reflected the similarity between creep processes in glassy polymers and viscous flow in low-molecular substances. Of course, the mechanism of the deformation of solid polymers must undoubtedly be much more complex, but in each case it basically involves an overcoming of intermolecular interaction barriers.

Temperature dependences of kinetic parameters

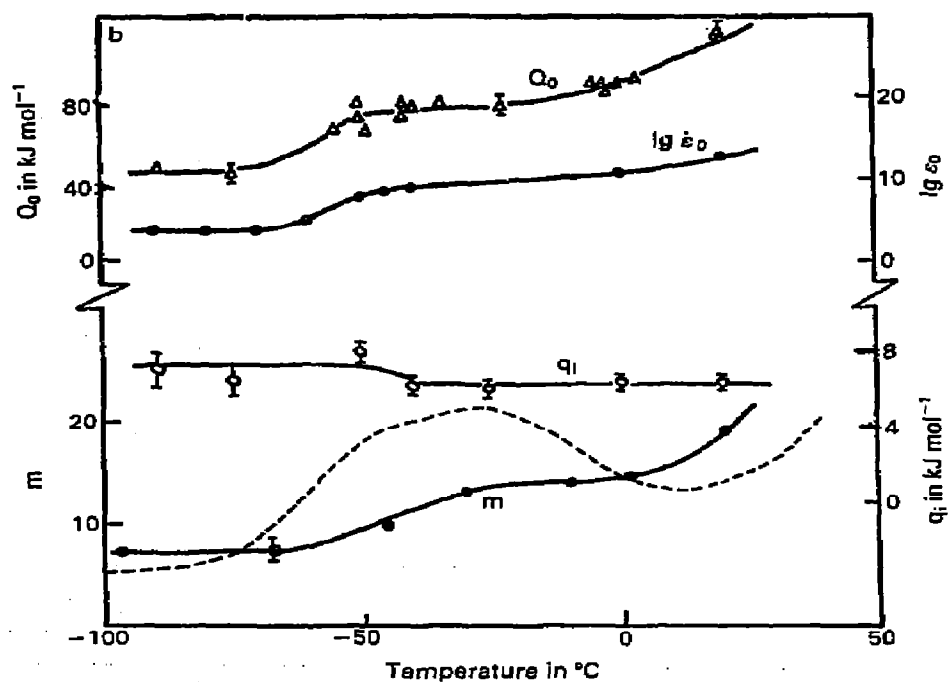
The potential barriers of intermolecular interactions in glassy polymers cannot vary greatly when the temperature is changed. In our experiments, a considerable variability in the deformation kinetic parameters were obtained over a wide temperature range for each polymer [19, 29–34].

Figure 5 shows the experimental Q_0 , m and $\log \dot{\varepsilon}_0$ versus temperature dependences obtained for PMMA and PVC at $\varepsilon \approx 20\%$. Similarities are observed (as, also, for PE, PS, PC, epoxy resins and other polymers [19, 29–34]), i.e. all three kinetic parameters of deformation change in a similar way, increasing with temperature several times over the range from -196°C to T_g . As seen, the curves indicate either regions of slight changes in the parameters with temperature, or intervals in which they change sharply.

These results are not surprising. According to earlier data [15–19], the deformability of solid polymers varies with temperature in a step-like manner because of the abrupt changes in the nature of the dominant type of molecular motion in the relaxation transitions. This is particularly obvious when comparing the kinetic curves obtained for PVC and PMMA with their mechanical loss spectra (Fig. 5).



(a)



(b)

Fig. 5. Temperature dependences of the creep parameters: a, poly(methyl methacrylate); b, poly(vinyl chloride). The broken line in b indicates the contour of the mechanical loss spectrum at approx. 1 Hz ($m = \alpha/V$ where the volumes of the monomer unit V are 155 and 72 \AA^3 for PMMA and PVC, respectively).

As shown in refs. 37 and 38, the deformation consists of the stress activation of the part of the relaxation time spectrum in the polymer located above the temperature of the deformation experiment. Therefore, the mechanical loss spectrum has been successfully used to describe the deformation properties of glassy polymers. Consequently, the values of Q_0 and α at each temperature characterize a certain effective kinetic unit formed by the relevant part of the spectrum.

In our treatment, eqn. (1) describes a process with a single effective relaxation time, characteristic of a given narrow temperature interval of $T_i + \Delta T$ and of a given strain $\varepsilon_i + 0.01\%$. In principle, at each subsequent "point" of the creep process, the effective relaxation time and, consequently, the measured kinetic parameters, can have different values. If we determine Q_0 , α and $\dot{\varepsilon}_0$ in a wide range of temperatures, we in fact obtain a temperature spectrum of their magnitudes.

Bearing these points in mind, we return to the curves in Fig. 5. The rise in the values of α and Q_0 with an increase in temperature means that at low temperatures the main contribution to the deformation is made by small-scale kinetic units, whose motion involves overcoming low-energy barriers with small thermal fluctuations.

On heating, the relaxation times for these units become much less than the experimental time, so that these motions contribute only to the instantaneous deformation, and the creep rate is governed by the stress activation of the motion of larger-scale kinetic units [19, 37, 38]. The fall in the $\dot{\varepsilon}_0$ value on cooling may be explained as the result of the decrease in the activation entropy ΔS , in case of the smaller kinetic units, and of the reduction in the contribution ε_0^* for each of these units to the deformation, see eqn. (1).

As Q_0 depends on deformation temperature (Fig. 5), its values do not provide sufficient information concerning the nature of the activation energy.

Meanwhile, the estimation of an "elementary" barrier q_i related to one monomer unit and achieved at completely different temperatures, allowed us to arrive at the following important conclusion. Despite the large changes in the values of Q_0 and m , the barrier of $q_i = [Q_0(T) \cdot V]/\alpha(T)$ is approximately constant within the limits of accuracy of 10–15%, throughout the temperature range of the glassy state of the polymer (Fig. 5).

In Fig. 6, the values of q_i obtained in our creep experiments ($\varepsilon > \varepsilon_y$) for 14 polymers of varying chemical structure, are compared with their cohesion energies; the latter were taken from refs. 40, 41 and 43. For the crosslinked polymers studied, we assumed that the kinetic units were located within the segments between crosslinks and were similar to those in linear polymers [44].

As seen in Fig. 6, all of the polymers studied fit satisfactorily to a linear dependence of $q_i \approx E_{\text{coh}}/3$, which was true for any temperature for the

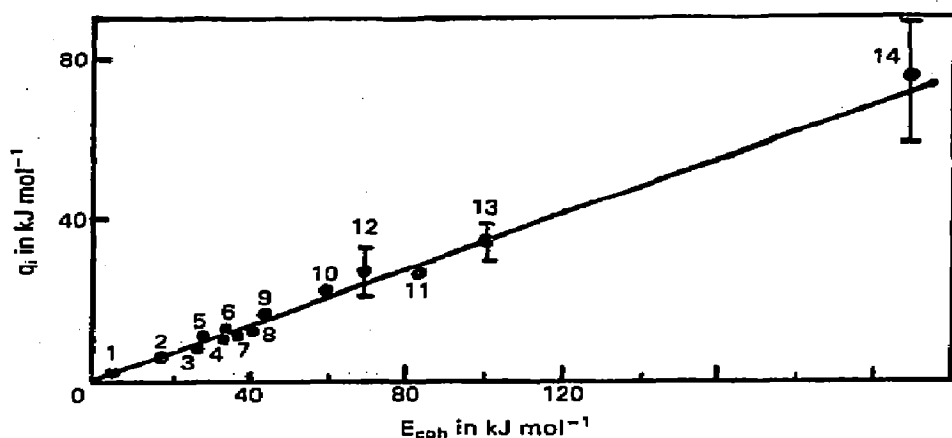


Fig. 6. Relationship between q_i , representing the partial activation barrier to creep, reduced to a monomer unit, and the cohesion energy: 1, polyethylene; 2, poly(vinyl chloride); 3, poly(vinyl butyral); 4, polyacrylonitrile; 5, polystyrene; 6, poly(methyl methacrylate); 7, styrene/methacrylic acid copolymer, 84:16; 8, styrene/methacrylic acid copolymer, 67:33; 9, styrene/methacrylic acid copolymer 40:60; 10, poly(ethylene terephthalate); 11, polycarbonate; 12, ebonite; 13, epoxy resin I; 14, epoxy resin II.

glassy state of the polymer. It should be noted that the connection between the deformation characteristics of polymers and the cohesion energy was also observed by Struik [80].

This relationship between the barrier q_i in the deformation ("cold flow") of solid polymers and $E_{coh}/3$, i.e. the activation energy of viscous flow for relevant monomeric liquids, turned out to be a general feature for amorphous and semi-crystalline polymers at $T < T_g$ including both isotropic and slightly drawn samples [29, 31].

Some tendency observed for q_i to decrease with increasing temperature (Fig. 5) may reflect a small change in the intermolecular interactions, estimated, in particular, by spectroscopy, see ref. 45. The latter effect was in fact accompanied by a considerable decrease in q_i values at $T > T_g$ (Fig. 5a) which is clearly the result of cooperative motional processes and the increasing role of an entropy factor.

However, study of the deformation kinetics for a series of glassy styrene–methacrylic acid (S-MAA) copolymers with different concentrations of MAA, i.e. of intermolecular hydrogen bonds, showed that an increase in intermolecular interactions resulted, as expected, in a regular rise in q_i values [29]. This could be considered as an additional corroboration of the intermolecular nature of the deformation energy barrier in glassy polymers.

It is also noteworthy that the values of Q_0 and α found in tension tests might be somewhat larger than in compression tests. However, the parameter q_i , which we consider as a certain criterion for recognizing the nature of the deformation, did not differ considerably under moderate

strains [34]. Thus, the value of $q_i \approx E_{\text{coh}}/3$ found from the macroscopic creep experiments enabled us to conclude that, irrespective of the specific deformation model, the deformation process for glassy polymers involved mainly the surmounting of intermolecular interaction barriers; this is similar, in essence, to the viscous flow of the oligomer which is equal in its volume to the activation volume, $\alpha = mV$, in the deformation process of the polymer. In other words, the activation barrier of deformation to be overcome

$$Q_0 = \frac{\alpha(T, \varepsilon)}{V} q_i \approx \frac{\alpha(T, \varepsilon) E_{\text{coh}}}{V \cdot 3} \approx m \frac{E_{\text{coh}}}{3} \quad (8)$$

is governed by the intermolecular interaction energy E_{coh} and by the scale of the kinetic units (in numbers of monomers m) [19].

It is interesting that eqn. (8) gives an independent approximate estimate of the E_{coh} value of glassy polymers, from only two experimental determinations of Q_0 and α for any point on the creep curve and any temperature.

As indicated above, the changes in the kinetic parameters with temperature occur to the greatest extent in the regions of relaxation transitions (Fig. 5) [17, 30–32, 46]. Consequently, the spectrum of relaxation times or, more exactly, the type of motion prevailing in the given relaxation region determines the possibility of deformation shear under stress at each temperature.

Therefore, the results of a large series of new experimental studies concerning the nature of the α , β , γ , and δ relaxations in polymers are of great interest; they have been published over the last decade and have recently been summarized in a book [47] and in review papers [48, 49]. These studies have made it possible to establish the interrelationship and common nature of the transitions for polymers of varying structure, in order to obtain relationships between the parameters of the transitions and the molecular characteristics of the polymers, and to provide techniques for the prediction of relaxations.

Thus, it was shown that the low-temperature δ -relaxation can be assigned to the small-angle torsional vibration of a monomer unit as a whole; the γ -relaxation (except in two specific cases) corresponds to localized torsional motions involving two or three neighbouring monomer units in the chain. The main transitions, β and α , turned out to be associated with the rotational motion within a chain segment close in size to a "correlation length", i.e. the statistical (Kuhn) segment, with participation of one-barrier conformational ($T \rightleftharpoons G$) transition in these events. The segmental motion can be realized as either quasi-independent (β) or cooperative (α) (in the intermolecular sense). The Kuhn segment also manifests itself as a motional unit in the rubber-like elasticity and flow regions [47, 49].

Two points should be emphasized. First, the potential barriers of the

above transitions, as for those in the deformation process, were found to be proportional to the cohesion energy and the scale of the motional unit. Thus, not only activation energies, which is well known, but also the estimated activation volumes [50, 51] of the relaxation transitions decrease step by step (from α - to β -, from β - to γ -relaxation) as the temperature is reduced. This regularity is, in fact, similar to that observed for the behaviour of the deformation activation parameters (Fig. 5). However, in the temperature region of the β -relaxation, as predicted, the activation volume of deformation is approximately $m_K V$ where m_K is the number of monomer units in the Kuhn segment [29].

Here, we do not take into account the specific models of polymer deformation. The dislocation analogy [11, 37, 38, 52], disclination [10] and combined dislocation–disclination [53, 54] models have been suggested; some experimental examination of these models was carried out in refs. 37 and 38. Satisfactory agreement between the theory and the experimental $Q_0(T)$ and $\alpha(T)$ dependences was shown in ref. 55. It is necessary to stress, however, that in these models a decisive influence of the intermolecular interactions and the molecular motion spectrum on the deformation kinetics is maintained as a result of the shear modulus versus temperature dependence used.

In summary, we can conclude that the activation energy, activation volume and pre-exponential factor cannot be regarded as stable characteristics of the deformation in a glassy polymer. The values of these parameters are interconnected, and depend on the degree of deformation and the temperature. Moreover, their changes are related in a regular manner to structural alterations in the polymer and to its spectrum of molecular motions. The polymer deformation mechanism is realized as shear, the potential barriers of the intermolecular interactions being mainly overcome.

Emphasizing the changeability of the deformation kinetic parameters we have to rewrite eqn. (1) as follows

$$\dot{\varepsilon} = \dot{\varepsilon}_0(T, \varepsilon) \exp\left(-\frac{Q_0(T, \varepsilon) - \alpha(T, \varepsilon)l_m}{RT}\right) \quad (9)$$

KINETICS OF SMALL DEFORMATIONS: MICROPLASTICITY

Creep rate spectra of glassy polymers

The precise laser-interferometric method was effectively applied to study the viscoelastic strain region of solids, i.e. the microplasticity at stresses much below the yield stress (“retarded elastic deformation”). Studies of polymers and of other materials have shown that peaks of small

deformation rates appear on the $\dot{\epsilon}(T)$ dependences measured at constant stress [56–60] or on the $\dot{\epsilon}(t_m)$ plots obtained at constant temperature [61, 62]. Curves of both these kinds are known as “creep rate spectra”.

These microplasticity effects, for instance from the $\dot{\epsilon}(T)$ spectra, were observed as follows. The sample was cooled to the lowest point of the temperature range under study, and a stress, about 5–10 times smaller than the yield stress at the highest temperature of the experiments, that could cause a small creep deformation without essential structure distortions, was applied. After accumulation of a deformation of approx. 0.01%, necessary for reliable measuring of the creep rate, the sample was unloaded and heated to a temperature 5–10°C higher; then it was again loaded up to the same stress, etc.

The creep rates were estimated from the interferograms, the same time after loading for each temperature, and the $\dot{\epsilon}$ versus T dependences were plotted. As shown, the nature of the loading is insignificant in these experiments; we mostly used a uniaxial compression test. The creep rates observed were about 10^{-7} – 10^{-5} s $^{-1}$.

The temperature regions of an increased microplasticity, i.e. the location of the creep rate peaks, corresponded approximately to the relaxation transitions in the polymers at frequencies of 10^{-4} – 10^{-2} Hz [19, 56, 58, 59] differing considerably, however, in resolution.

A typical creep rate spectrum for PMMA is shown in Fig. 7 (curve 2). For comparison, we also give the mechanical loss spectrum at 1 Hz [38] and the fracture stress versus temperature plot for this polymer [16, 63]. As can be seen, unlike the mechanical loss spectrum, the creep rate spectrum of

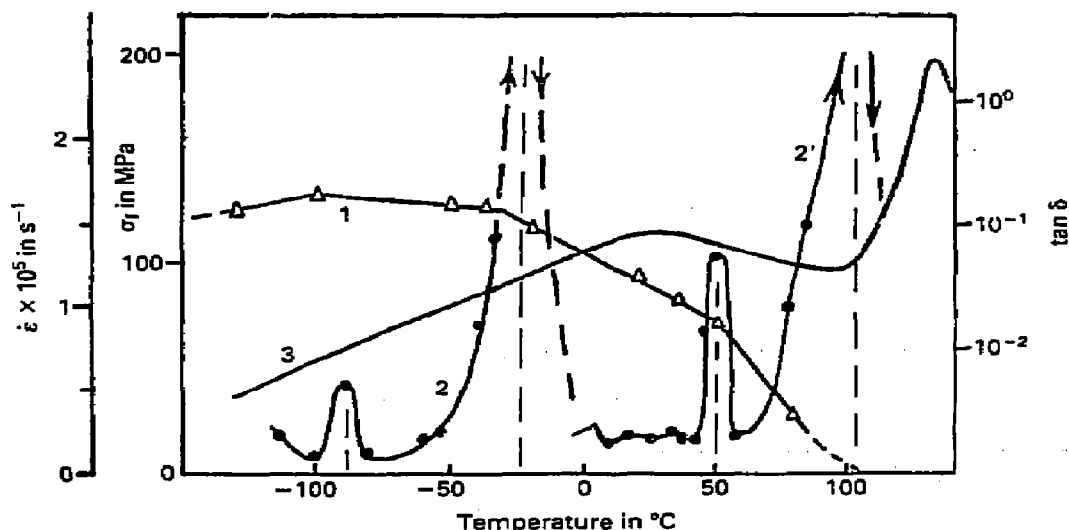


Fig. 7. Poly(methyl methacrylate): 1, the temperature dependences of the fracture stress σ_r for 10 s longevity under load; 2, the creep rate $\dot{\epsilon}$, $\sigma = 10$ MPa; 2', $\sigma = 1$ MPa; and 3, the mechanical loss spectrum, 1 Hz.

glassy PMMA is complicated and characterized by four pronounced narrow peaks of increasing micro-plasticity, at 100, -25 , -90 and 50°C , corresponding to the α , β (shifted to -25°C due to lower frequency), γ (most probably due to moisture) and "intermediate" (of unknown origin) relaxations, respectively. The considerably improved resolution of the latter technique is obvious.

Of practical importance was the fact that the peaks of the microplasticity were more distinctly correlated with the bends in the temperature dependence of the fracture stress σ_f , than with the wide β -peak in the mechanical loss spectrum (Fig. 7, curves 1 and 3).

Studies [56–59, 63] have also confirmed the new possibilities provided by the creep rate spectrum (CRS) interferometric method as a non-destructive technique for prediction of anomalies in the mechanical strength and deformation properties of glassy polymers. The anomalies manifest themselves at certain temperatures as increased microplasticity, including the region of brittle–ductile transition [63, 64].

The high resolution of the CRS method can also be illustrated by the data obtained for β -relaxation region in PC [58] which are compared to those obtained by two other relaxation techniques in Fig. 8. The rise in resolution on passing from the mechanical loss spectrum [65] to the thermally stimulated current depolarization method (TSD) [66] and, especially, to our CRS technique is clearly seen. The high sensitivity of the creep rate spectra technique has been proved experimentally. However,

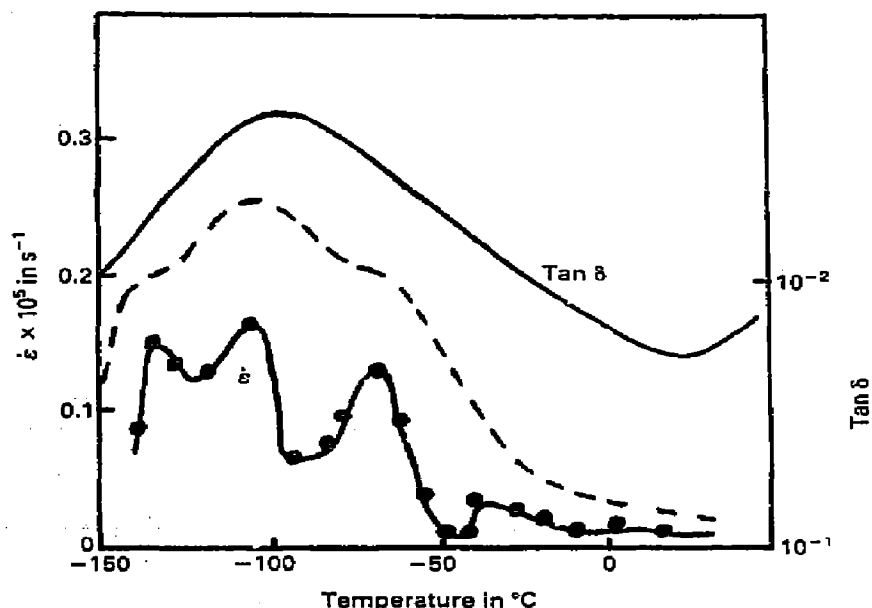


Fig. 8. Temperature dependences of the mechanical loss [65] and the creep rate $\dot{\epsilon}$ at $\sigma \approx 0.1 \sigma_f$ for polycarbonate. The broken line indicates the contour of the thermally stimulated depolarization current spectrum [66].

the adopted approximation for creep curve description using the mechanical models do not permit fine effects to be revealed. In addition, it should be noted that at low frequencies the spectrum becomes sensitive to moisture and physical ageing.

The direct connection between the complex structures of polymers, particularly crosslinked ones, and the relevant creep rate spectra, displaying multiple $\dot{\epsilon}$ peaks, was also shown in refs. 33 and 59. It should be stressed that the peaks corresponding to the different relaxation regions reflect different responses to the same external influence (thermal treatment, etc.); analogous changes in the dependences of mechanical properties versus temperature were observed in refs. 33, 58 and 59. Hence, the CRS method can be considered as a high-resolution, low-frequency approach for the study of relaxations including low-temperature transitions. Moreover, this technique enables changes in the plasticity and microplasticity of the polymer to be predicted in different temperature regions as well as at the relevant critical temperatures.

Studies of brittle materials

The CRS method permitted us to carry out microplasticity studies for a number of materials in their brittle and super-brittle states that were previously practically impossible. Below we shall only summarize some fine effects obtained in these experiments.

(i) As shown in ref. 67, the temperature position and height of the creep rate peak in the spectra of carbon steels at low deformations provide a comparison of their tendency towards the brittle fracture and a prediction of the critical brittle temperatures.

(ii) For the first time, the total kinetic analysis of very small inelastic deformations ($\epsilon = 0.01\%$) was achieved for silicate glasses over the temperature range from -120 to 350°C [32]. The polymer-like behaviour of the glass deformation kinetics, namely the inconstancy of the Q_0 , α and $\dot{\epsilon}_0$ parameters, the relationship between their temperature dependences and the relaxation spectra, as well as the low values of q_i , were observed.

(iii) Microplasticity at low temperatures and stresses was discovered and studied, even for extremely brittle glass ceramics and silicone nitride [68]. Their spectra of small deformation rates manifested maxima in the vicinity of -50°C which separated the regions of different local relaxation abilities. The influence of stress value and thermal history on the creep rate spectra of these superbrittle solids was determined.

(iv) The CRS technique was successfully employed for the investigation of small inelastic deformations in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics in their superconducting and "normal" states in the temperature range 77 – 300 K [69, 70]. Three creep rate peaks, including one close to the temperature T_c of the superconducting transition, were observed. The influence of the

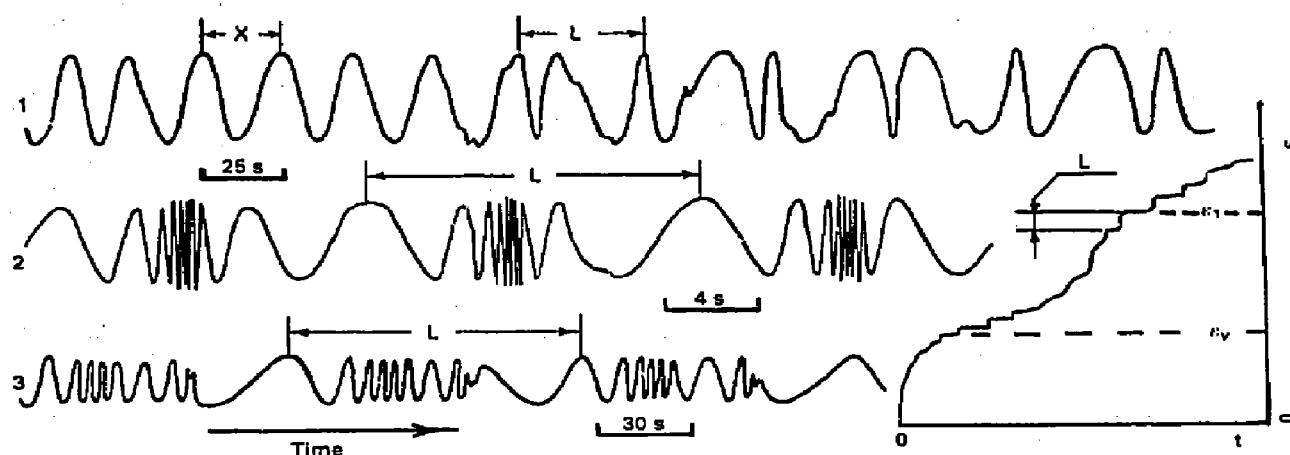


Fig. 9. Typical interferograms and scheme of the polymer step-like creep: 1, manifestation of the inhomogeneity in creep rate (steps) near ε_y ; 2 and 3, examples of the distinct periodic increments of deformation near ε_y ($\dot{\varepsilon} \approx x^{-1}$).

oxygen concentration changes in the ceramics, and of other factors, on the microplasticity was discovered [69].

THE STEP-LIKE DEFORMATION OF SOLID POLYMERS

The phenomenon of step-like or jump deformation of metals and crystals [71] can be regarded as a process characterized by an inhomogeneous rate. A similar effect in the form of periodic stress fluctuations in the $\sigma(\varepsilon)$ curve has been observed for crystallizing polymers during high stretching ratios [72].

The interferometric method enabled us to analyse the creep rate inhomogeneity more accurately and, thence, also to discover deformation increments ("steps") on a submicron or micron scale in isotropic amorphous polymers [73–76]. The step-like deformation can be illustrated by the interferograms and the scheme in Fig. 9. The steps were described by two parameters: the increase in the strain L corresponding to the height of a step in this scheme; and the ratio h of the maximum ($\dot{\varepsilon}_{\max}$) to minimum ($\dot{\varepsilon}_{\min}$) creep rates within the period L , i.e. parameter h corresponds to the slope of the step in the scheme of Fig. 9.

As found in refs. 73–75, the parameters h and L varied in a regular manner during the course of a creep process. So, for all the materials studied, the maximum in h was observed near the point ε_y , i.e. at the moment of breaking the initial structural state of the polymer. The h and L values increased with development of the deformation process.

Together with other observations, these results have suggested relationships between the step-like deformation and polymer structural heterogeneity of different degrees [73–76]. The study of shear deformation

processes in ultra-thin organic films [77] can be considered as supporting this approach.

Finally, it should be mentioned that the method considered was successfully applied to the study of changes in the creep curves of polymers after being subjected to magnetic fields [78] or γ -irradiation [79].

CONCLUSIONS

Thus, the laser-interferometric method developed provided broad, new possibilities for studying deformation kinetics in polymers and other materials, as well as new information concerning the physics of polymer plasticity. Relationships between deformation kinetics and the barriers to intermolecular interactions and relaxation spectra were found.

The results obtained show that this high-precision technique converts the creep method into a valid high-resolution mechanical spectrometric technique which allows both the plasticity and microplasticity kinetics in solids to be studied under different conditions, including the brittle and super-brittle states, even under the influence of fine structural effects. The compressive or tensile experiments can be carried out for massive samples, films, or fibres.

It is particularly important that the new technique was useful in the prediction of anomalous changes in mechanical behaviour, including the brittle-ductile transition.

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