

## The Limits of Linear Viscoelasticity in Poly(methyl Methacrylate) and Poly(ethyl Methacrylate)

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### Synopsis

The limit of linear viscoelasticity is determined for poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) in uniaxial tension creep over the temperature range of 20° to  $T_g - 10^\circ\text{C}$ . The time span covered is from 10 to 1000 sec. The linear limit is defined as the point at which the creep compliance deviates by more than 1% from its mean value in the linear viscoelastic range. For both materials, the stress limit of linear viscoelasticity falls to a minimum or plateau level at a temperature below  $T_g$ . It is suggested that the  $\beta$ -mechanism plays an important role in the existence of this minimum.

### INTRODUCTION

The linear viscoelastic theory has long been a valuable tool in design work relating to thermoplastics. At uniaxial strains larger than 0.5–1%, however, most thermoplastics show a nonlinear viscoelastic behavior.

From the designer's point of view, it is important to know how the limit of linear viscoelasticity depends on time and temperature and to what extent the material will deviate from linear viscoelastic behavior above this limit of linearity.

From the polymer scientist's point of view it is necessary to describe, quantify, and explain both the nonlinear viscoelastic behavior and the transition from linear to nonlinear viscoelasticity. There are several ways of describing and quantifying nonlinear viscoelasticity. The most common attempts seem to be extensions of Boltzmann's superposition principle or multiple integral representation, briefly reviewed by Ward.<sup>1</sup> To explain the nonlinearity, however, the appearance of nonlinear viscoelasticity must be shown to relate to changes in the mobilities of molecular groups.

From the practical point of view, the meaning of the transition from linear to nonlinear viscoelastic behavior is quite clear. The question is whether this linear limit also has a physical significance and whether it can be explained in molecular terms. In isochronous stress-strain diagrams for ordinary thermoplastics, the linear limit is often rather vague, and it is easy to believe that the linear limit will decrease to a lower stress level if the accuracy of measurement is improved. If this is the case, the existence of linear viscoelasticity is only a question of a degree of approximation.

Many phenomena are, however, connected with stress-strain levels of the same magnitude as the linear limit, which leads us to believe that there is a

physical significance for the linear viscoelastic behavior and the stress and/or strain limit of the linear viscoelasticity.

1. Firstly, there are materials whose linear limit is quite sharp. In such cases, the range of linear viscoelasticity is certainly not a consequence of the accuracy and resolution of the viscoelastic measurements. Examples are poly(vinyl acetate)<sup>2</sup> and unsaturated polyester<sup>3</sup> at room temperature.

2. A shift of relaxation times to shorter times and a broadening of the relaxation spectra are observed when the viscoelastic behaviour becomes nonlinear.<sup>4</sup> These phenomena have been penetrated for ABS by Matsuoka et al.<sup>5</sup> and for PEMA by Jansson.<sup>6</sup>

3. Lunn and Yannas<sup>7</sup> have made measurements on the change in the IR-dichroic ratio in polycarbonate under uniaxial stress, and Yannas et al.<sup>8</sup> have concluded that segmental motions are accelerated when the polymer is strained beyond the limit where the theory of linear viscoelasticity is valid.

4. Menges and Schmidt<sup>9</sup> concluded from crazing observations on uniaxially loaded thermoplastics that a lower strain limit  $\epsilon = \epsilon_{\text{crit}}$  exists below which crazing cannot occur. This strain limit is of the same order of magnitude as that for linear viscoelasticity.

For polymers in the glassy state or in the main transition region just below the glass transition temperature, the transition from linear to nonlinear viscoelasticity occurs at small strains. In all known cases, the strain limit level lies at 1% uniaxial strain or less. The ostensible nonlinearity cannot, therefore, be explained as an effect due to "large strains" or due to the definition of strain used.

Studies of the transition from linear to nonlinear viscoelasticity and attempts to explain this transition and correlate it to other parameters and phenomena are rather sparse in the literature. Maxwell and Guimon<sup>10</sup> studied seven thermoplastics and a series of polyethylenes with different degrees of branching. A general tendency for the strain limit of linear viscoelastic response to increase with increasing heterogeneity of internal structure was found. The authors also indicate that there may be two or more stress regions for linear viscoelastic response. Yannas et al.<sup>11-13</sup> studied the transition from linear to nonlinear viscoelasticity for polycarbonate. Measurements were presented for both uniaxial creep and uniaxial stress relaxation, and a temperature range from room temperature up to 20°C above  $T_g$  was covered. It was shown that the stress limit of linear viscoelasticity for polycarbonate decreases when the temperature increases above 23°C and makes a pronounced drop when the temperature passes  $T_g$ . The strain limit increases, however, from about 1% to about 100% over the same temperature range. Ishai and Bodner<sup>14</sup> determined the limit of linear viscoelastic response of filled and unfilled epoxy resins. The authors also noted that exceeding the linear limit does not necessarily imply that irreversible changes take place. In all the work cited, both the temperature dependence and the time dependence of the linearity limits are well established.

In this report, results from creep measurements in uniaxial extension are given for poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA). The temperature range covered is 20° to  $T_g - 10^\circ\text{C}$ , and the time range is from 10 to 1000 sec. The maximum stress level at each temperature is approximately 1.2 times the stress limit of linear viscoelasticity. The aim of the study has been to determine how the stress and strain limits of linear viscoelasticity depend on temperature below the  $\alpha$ -transition temperature. It was also our intention to see in what way a disturbing  $\beta$ -transition influences the transition to non-

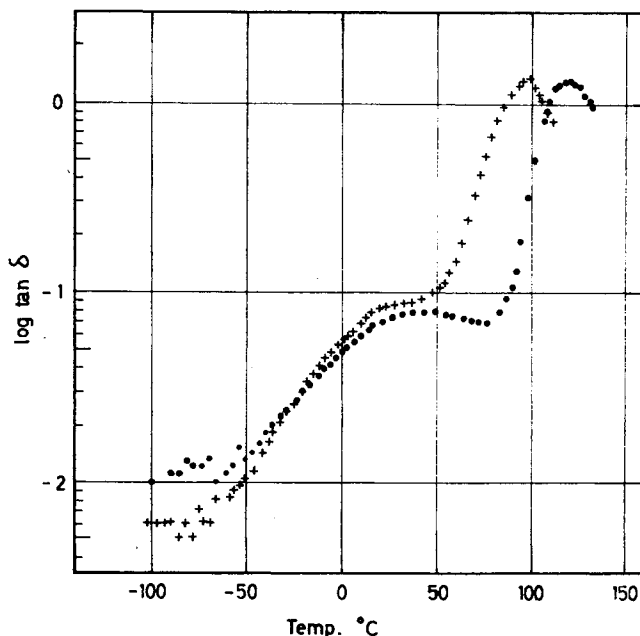


Fig. 1. Log  $\tan \delta$  vs. temperature for PMMA (●) and PEMA (+) from a dynamic tensile experiment, frequency 3.5 Hz.

linearity. For this reason, the two materials PMMA and PEMA were chosen since they have great similarities in structure and probably also in molecular deformation mechanisms, but a slight difference in the temperature span between  $\alpha$ - and  $\beta$ -transitions.

### MATERIALS AND SPECIMENS

The two materials studied, PMMA and PEMA, were pure bulk polymers with no additives other than the initiator, in this case azoisobutyronitrile. The materials were supplied by Bofors AB in the form of 2–3-mm-thick sheets. Determination of the glass temperature on a Perkin-Elmer DSC apparatus showed  $T_g = 95^\circ\text{C}$  for PMMA and  $T_g = 63^\circ\text{C}$  for PEMA. The width and intensity of the  $\beta$ -relaxation were determined on a Rheovibron DDV II B Dynamic viscoelastometer. Figure 1 shows log  $\tan \delta$  versus temperature for a frequency of 3.5 Hz. The  $\beta$ -peaks are located in the same temperature region, approximately  $40^\circ\text{C}$ , for the two materials, while the  $\alpha$ -peak value lies at  $100^\circ\text{C}$  for PEMA and at  $120^\circ\text{C}$  for PMMA. For PEMA, however, the  $\alpha$ -peak overlaps the  $\beta$ -peak to some degree. From the thermoplastic sheets, ordinary dumbbell-shaped specimens were machined out according to SIS 112116 (approximately according to ASTM D 638 Type II). Before being subjected to a creep test, each specimen was kept at a temperature of  $10^\circ\text{C}$  below  $T_g$  for 20 hr.

### EXPERIMENTAL

Two creep machines each with three specimen sites were used. The load is applied by means of cantilever arms (lever ratio 1:5). The loading weights are applied by hand, but this does not affect creep readings after five sec. The creep machines are thermostatically adjusted to an accuracy of  $\pm 0.5^\circ\text{C}$ , and

the temperature is checked with a thermocouple mounted close to each specimen.

The specimen clamps consists of clamp plates with a hole for a pin through the specimen. Most of the load is taken up by this pin, and the clamp plates act merely as spacing washers. Alignment is ensured by universal joints mounted on each side of the specimens and clamps. A polycarbonate sample was tested in the apparatus between crossed polarizers to check that the uniaxial stress was uniformly distributed in the narrow section of the specimen.

The creep extension was detected by an Instron (G-51-11 M) extensometer. The extensometer was connected to a carrier amplifier (Peekel Type 581 DNH) whose output was connected to a recorder. At each temperature, six specimens were used to obtain an isochronous diagram consisting of 15–20 experimental points. Each tested specimen was replaced by a fresh one if complete recovery was not obtained within a reasonable time. Only at 80° and 85°C at the highest stress levels were there strains that did not seem to be recoverable within 8 hr. The temperature range covered ended approximately 10°C below  $T_g$  since the material then became too soft for the type of extensometer used.

From the recorded creep curves, the strains at 10, 100, and 1000 sec creep time were determined in order to form isochronous stress-strain diagrams. From the points corresponding to the lowest stress and strain, a straight line can be drawn, corresponding to the linear viscoelasticity. The linear limit is defined as the point where the curve for best fit to the experimental points deviates by more than 1% from this straight line; 1% is arbitrarily chosen but it is of the same order of magnitude as the standard deviation of the experimental points in the linear viscoelastic region. The same values were obtained for the linear limits if the isochronous creep compliance was plotted against stress. So far, there is no standardized procedure for defining the linear limit, but the procedure described above is approximately in accordance with that due to Yannas.<sup>11–13</sup>

Strain values recorded in this work are computed throughout as  $\Delta L/L_0$ . There is a negligible difference between differently defined strains in the low strain region studied in this work. The stress values recorded were not corrected for the decrease in cross sectional area. The error in stress was found to be negligible for the stress levels concerned, assuming a Poisson ratio of 0.4.

It must be pointed out, however, that stress and strain limits of linear viscoelasticity reported in this work refer only to the case of uniaxial tension. There is so far no reason to suppose that the linear limits will be the same in other situations such as uniaxial compression, shear, multiaxial loadings, etc.

## RESULTS AND DISCUSSION

Creep measurements during periods up to 1000 sec were made at nine different temperatures for PMMA and at four different temperatures for PEMA. From the creep data, isochronous stress-strain diagrams were constructed to determine the stress and strain limits of linear viscoelasticity. The linear limits can also be determined from diagrams of creep compliance plotted against stress, as in Figures 2 and 3. The scattering of the experimental values is evident in the figures. The standard deviation amounts to 1–3% in the linear viscoelastic region. From Figures 2 and 3 it is clear that the transition from linear to non-linear viscoelasticity is more pronounced at higher temperatures and longer times. This phenomenon is more evident in the case of PEMA. Keeping in mind that the standard deviation of the experimental points in Figures 2 and 3

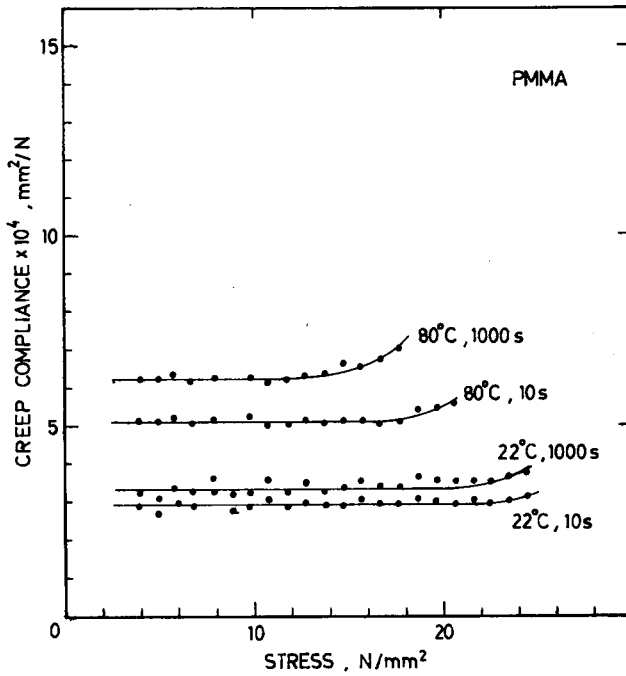


Fig. 2. Tensile creep compliance vs. stress for PMMA.

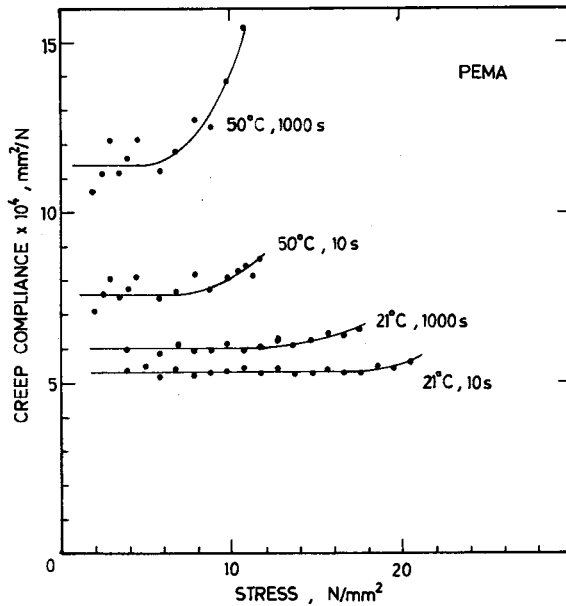


Fig. 3. Tensile creep compliance vs. stress for PEMA.

is not more than 3%, the diagrams indicate that within this uncertainty the deviation from linear viscoelasticity is at least less than 3% below a certain stress level. It must also be pointed out that the linear part of each curve is drawn on the basis of 10–20 experimental points.

The stress limit of linear viscoelasticity is shown as a function of temperature for PMMA in Figure 4 and for PEMA in Figure 5. In all creep experiments,

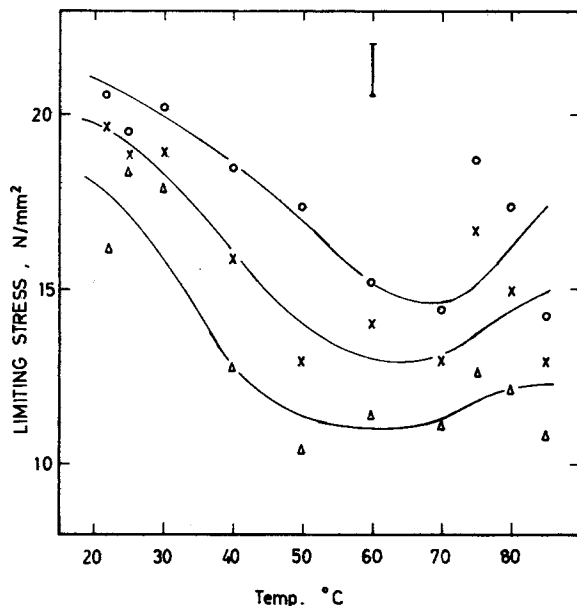


Fig. 4. Stress limit of linear viscoelasticity vs. temperature for PMMA at 10 sec (O), 100 sec (X), and 1000 sec ( $\Delta$ ) creep time.

the lateral contraction of the specimen has also been recorded simultaneously with the axial extension. Nonlinearity has been found to occur at the same stress level for both contraction and elongation, and the limiting stress data from the contraction measurements have been used to augment the extension data in the determination of limiting stresses.

The experimental points in Figures 4 and 5 are the average stress limits from the extension and contraction measurements. When the linear limit is determined either from isochronous stress-strain diagrams or from diagrams of compliance versus stress some uncertainty arises because of the uncertainty in determining the compliance in the linear region. Thus, the error bars shown in Figures 4 and 5 indicate the uncertainty from both the averaging procedure and from the determination of the linear viscoelastic compliance.

For both PMMA and PEMA, the stress limit of linear viscoelasticity passes through a minimum as the temperature increases. In the case of PMMA it is also possible to see a slight shift of this minimum toward lower temperatures at longer creep times. In view of the considerable scattering in the experimental points above 70°C in Figure 4, however, the upturn of the curve above that temperature is rather uncertain. It is therefore possible that the limiting stress decreases to a minimum plateau level, but that would not greatly affect the present discussion. A general decrease in the stress limit with increasing temperature is to be expected since the compliance increases on the same temperature region. An increase of the stress limit at a temperature 25°C below  $T_g$  is therefore rather unexpected, but at still higher temperatures, the stress limit will certainly decrease to a very low level since the compliance will then be very high. In this work, the high compliance has made it impossible to make any measurements in this temperature region. From the figures, it is also possible to discern that the decrease of the stress limit just before it reaches its minimum is more pronounced for PEMA than for PMMA. From Figure 1 and according to

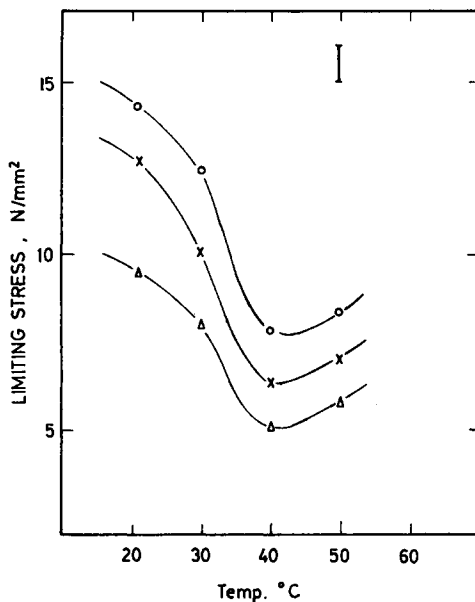


Fig. 5. Stress limit of linear viscoelasticity vs. temperature for PEMA at 10 sec (O), 100 sec (X), and 1000 sec ( $\Delta$ ) creep time.

Jansson,<sup>15</sup> it is clear that the  $\beta$ -transition occurs at the same temperature for PMMA and PEMA. Moreover, since the deformation mechanisms must be of the same type for the two materials since their structures are so similar, it is reasonable to suggest that the differences in behavior evident between Figure 4 and 5 are connected with the  $\beta$ -transition in the material or rather with the temperature span between the  $\alpha$ - and  $\beta$ -transitions.

Ishai and Bodner<sup>14</sup> have considered the linear viscoelastic limit to be a definite lower limit to the onset of irreversible structural changes in the material. It must, however, also be pointed out that a material can show a pronounced nonlinear viscoelastic behavior without any irreversible deformation. PMMA, for example, has been deformed in shear creep up to 5%, and yet the deformation has been fully recoverable (ref. 4, p. 483), although the linear limit is below 1%. It seems possible for nonlinear viscoelasticity to occur without involving any irreversible deformation mechanism or even any reversible molecular mechanism which when acting alone would give a nonlinear viscoelastic response.

We can suppose that a certain number of molecular processes with different relaxation times are responsible for the deformation of a material. All these processes or mechanisms are activated even at very low stress levels. If we further suppose that all these mechanisms act in proportion to individual intensities we have a discrete intensity distribution. As long as this distribution is independent of stress, the relaxation time spectrum is also independent of stress and we have linear viscoelastic behavior. But if this intensity distribution is disturbed at a certain stress level, i.e., a new molecular process is activated or the intensity relationship between two or more other processes is changed, a stress dependence of the relaxation spectrum develops which means that the viscoelastic behavior becomes nonlinear.

Segmental motions of the  $\alpha$ -transition type can be stress activated at temperatures far below the glass transition temperature.<sup>7</sup> Above the stress level neces-

sary for such activation, the viscoelastic behavior is linear since a new molecular mechanism contributes to the deformation. When the temperature rises, this stress level will decrease since the new mechanism will be introduced at a lower stress. Thus, for a material with an undisturbed  $\alpha$ -transition, the stress limit of linear viscoelasticity will show a monotonic decrease at temperatures below the glass transition temperature. In the case of PMMA and PEMA, however, there is a  $\beta$ -transition just below the  $\alpha$ -transition. We suggest that a coupling effect exists between the  $\alpha$ - and  $\beta$ -mechanisms, as discussed by Jansson.<sup>15,16</sup> This coupling effect to the  $\alpha$ -transition will activate large main chain movements, and a steeper decrease in the stress limit is therefore possible when the temperature increases in the range between the  $\beta$ - and  $\alpha$ -transitions. At the temperature where the  $\beta$ -mechanism is fully developed, there is no longer any need for the stress activation of the segmental movements caused by the coupling effect. This means that the stress limit will now be determined by the stress activation of the  $\alpha$ -mechanism, which lies at a higher level. The stress limit will therefore increase or show a plateau level when plotted versus temperature. This trend will be maintained up to the temperature level where the compliance will be so high that the stress limit will be greatly decreased for that reason. At that temperature, the strain limit will, however, rise to the very high level which is characteristic in the rubbery region.<sup>13</sup> The smaller the temperature span between the  $\alpha$ - and  $\beta$ -transitions, the more intensive is the coupling effect to be expected and the more pronounced is the minimum in stress limit of linear viscoelasticity which is found. It can be seen in Figure 1 that the temperature span between the  $\alpha$ - and  $\beta$ -peaks is narrower for PEMA than for PMMA. A more pronounced minimum in stress limit versus temperature can therefore be expected for that material, as is shown in Figure 4 and 5.

The development of nonlinear viscoelasticity and the role of the  $\beta$ -mechanism in this phenomenon will be further discussed in later reports based on data from other materials.

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