

# History- and temperature-dependent yield phenomena of polycarbonate related to its rate of physical ageing

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The yield force (or stress) of polycarbonate in simple extension was studied to determine its dependence on deformation history, including the stretching rate, and temperature. At different temperatures, the stretching of a specimen at a constant rate was interrupted both before yielding and during cold drawing to allow the occurrence of stress relaxation and the accompanying physical ageing (hardening). When a test was resumed, progressive erasure of ageing occurred, leading to a yield force whose value compared to that obtained by continuous stretching can be explained qualitatively in terms of the rate of physical ageing, determined earlier at an extension of 2.6% over a wide temperature range. In addition, the present data support the conclusion reached previously that physical ageing occurs during stress relaxation at a fixed deformation. Also determined were the yield and drawing stresses and the yield strain from  $-90$  to  $100^{\circ}\text{C}$ .

(Keywords: yield phenomena; cold drawing; stress relaxation; physical ageing; erasure of ageing; de-ageing)

## INTRODUCTION

Phenomenological and theoretical aspects of yield processes in polymers have been reviewed by Ward<sup>1</sup>. His review includes a discussion of the Eyring equation for non-Newtonian viscosity and its extensive use to account for the dependence of the yield stress on strain (deformation) rate and temperature<sup>1,2</sup>. When a specimen is deformed progressively, the mobility of molecular segments increases continuously until eventually it is sufficiently high so that for an infinitesimal increase in strain, at the imposed strain rate, the force remains constant. These concepts, commonly stated somewhat differently, provide the basis for using the Eyring equation to account for factors that affect yield-stress data. Other widely recognized theories are those of Robertson<sup>3</sup> and Argon<sup>4</sup>. Although these theories are developed in substantially different ways, they are partially based on activated processes and so contain elements of the Eyring approach.

In this paper results are discussed from experiments made on bisphenol-A polycarbonate which clearly show that the yield stress depends on a deformation- and time-dependent segmental mobility. Our yield-stress data, determined in non-conventional ways at several temperatures, are related qualitatively to the rate of physical ageing (hardening) of polycarbonate determined at different temperatures on specimens maintained at 2.6% extension<sup>5</sup>.

In a previous study<sup>5</sup> and other studies<sup>6-8</sup>, the segmental mobility was not determined directly or quantitatively. Each study was made by first applying a static deformation to a specimen, usually  $>1\%$ , and then modulating it intermittently with a sinusoidal strain of small amplitude

to obtain the storage modulus,  $E'$ , of the deformed specimen; in one study<sup>7</sup> both  $E'$  and the loss modulus,  $E''$ , were determined. After applying a static strain,  $E'$  was found to be significantly less than that for the undeformed specimen. This decrease in  $E'$  is attributed primarily to an increase in the mobility of short molecular segments in much the same manner as that produced by an increase in temperature. The reduction in  $E'$  reflects a softening of the specimen and can be termed partial erasure of physical ageing<sup>9</sup> or rejuvenation<sup>10</sup> or de-ageing<sup>5</sup>. Following the initial decrease in  $E'$ , it increased continuously with time, a reflection of a progressive decrease in the segmental mobility. The continuous increase in  $E'$  is a hardening process that is commonly called physical ageing, a term coined by Struik<sup>9</sup>.

McKenna and Zapas<sup>11</sup> have questioned the above interpretation of our data. They contend that the initial decrease in  $E'$  effected by a static strain and its subsequent progressive increase is just a reflection of non-linear viscoelastic processes. They obtained experimental data on a 16% solution of polyisobutylene that are phenomenologically similar to de-ageing and physical ageing and that can be represented by the non-linear Bernstein-Kearsley-Zapas (BKZ) theory. Their experimental findings clearly result from an initial decrease in the concentration of entanglements produced by the application of a large shear strain, and this is followed by the progressive reformation of the entanglements, as shown some years ago<sup>12</sup>. Hence, the data on the polyisobutylene solution are not relevant to the behaviour of a glassy polymer. They also obtained data in a similar way on poly(methyl methacrylate) but were unable to represent them by the BKZ theory. Of course, it is probably true that a proper non-linear viscoelastic theory could represent the strain-induced de-ageing and physical ageing of a glassy polymer but such a treatment would not

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invalidate our viewpoint. Another discussion refuting the ideas of McKenna and Zapas has been given by Yee *et al.*<sup>13</sup>.

Recently, Lee and McKenna<sup>14</sup> have given a restrictive definition of physical ageing that differs from certain other viewpoints. They agree that physical ageing occurs with a reduction in molecular mobility but they also consider that the thermodynamic state of the glass must change concurrently. By the latter, they mean 'the state defined by the PVT (pressure-volume-temperature) surface, for example, recognizing that the application of a stress or deformation has thermodynamics involved with it as well'. They also state 'for simplicity we will keep the mechanical response part of the thermodynamics separate from the PVT . . . response'. In our opinion, the latter is not realistic and is incorrect. They also claim that application of a large strain or stress does not produce rejuvenation and that the response only results from a memory effect 'due to the non-linear viscoelastic response of the material . . .'. However, their supporting data<sup>14</sup> are inconclusive.

The terms physical ageing and erasure of ageing were first introduced by Struik<sup>9</sup> to characterize phenomena similar to those presented previously<sup>5-9</sup> and also in this paper. Struik defined ageing and de-ageing in terms of changes in molecular mobility, although he also invoked free volume concepts. However, he pointed out that none of the available definitions of free volume are suitable to explain his data (see Ch. 13 in ref. 9). Furthermore, he proposed that free volume is generated by mechanical deformations, specifically energy dissipation (pp. 83-85, ref. 9), even in simple compression. In fact, static strains in simple compression have been shown to effect de-ageing followed by physical ageing<sup>6</sup>. We propose that the original definitions of ageing and de-ageing be retained and that a restrictive definition not be used. Of course, ageing and de-ageing can be termed time-dependent hardening and strain-softening processes, as has been done on occasion.

From studies of the intensities of X-rays scattered at small and intermediate angles from specimens of polystyrene whose volume had been changed in five different ways, Song and Roe<sup>15</sup> have proposed explanations for a number of the unusual properties exhibited by glassy polymers. To explain the partial erasure of physical ageing by applied deformations in either simple compression or torsion, they consider that the local packing of segments are changed into a 'more disordered state of higher energy' and that during the subsequent physical ageing the local packing becomes more highly ordered along with a concurrent decrease in energy.

## EXPERIMENTAL

Studies of the yield force (or stress), determined in non-conventional ways, and the subsequent force of cold drawing (or nominal stress) were made with an Instron tester equipped with a chamber whose temperature could be controlled to  $\pm 1^\circ\text{C}$ . Measurements were made on an as-received polycarbonate film (0.13 mm thick; Lexan, General Electric Co.), except for one test made on the annealed polycarbonate film, mentioned below. At temperatures from  $-90$  to  $100^\circ\text{C}$ , measurements were made of the nominal yield stress, the nominal stress for cold drawing and the strain at yield at a constant extension rate of  $0.2 \text{ min}^{-1}$ .

As discussed elsewhere<sup>5</sup>, the rate of physical ageing (hardening rate) at an extension of 2.6% was determined with a Dynastat (Imass Inc., Hingham, MA) on specimens of the polycarbonate film that had been annealed for 1 h at  $160^\circ\text{C}$  and then for 1 month at  $120^\circ\text{C}$ . To determine the ageing rate, a specimen was stretched rapidly to 2.6% with the Dynastat. Then this static strain was modulated intermittently with a sinusoidal strain of small amplitude ( $\sim \leq 0.1\%$ ) at frequencies usually from 0.4 to 25 Hz. In this way,  $E'$  of the stretched specimen was obtained as a function of frequency and elapsed (ageing) time,  $t_e$ , from  $> 100 \text{ s}$  to between 2.2 h and 10 h, depending on the temperature. From such data, the ageing rate,  $d \log E'/d \log t_e$ , was derived at temperatures from  $-110$  to  $110^\circ\text{C}$  and found to be independent of both  $t_e$  and frequency, at least from 0.4 to 25 Hz.

## RESULTS AND DISCUSSION

### *Rate of physical ageing at a constant extension and its dependence on temperature*

Figure 1 shows  $d \log E'/d \log t_e$ , obtained as outlined above and discussed in detail elsewhere<sup>5</sup>, plotted against temperature. With a progressive reduction of temperature from  $110^\circ\text{C}$ , the ageing rate first decreases until it reaches a minimum at  $\approx 30^\circ\text{C}$ , then it increases until it passes through a pronounced maximum at  $-40^\circ\text{C}$ , and finally it decreases and becomes nearly zero at  $-110^\circ\text{C}$ . For almost all of the following discussions of yield phenomena, it is only necessary to remember that the ageing rate increases from near room temperature to  $110^\circ\text{C}$ .

### *Yield phenomena related to the rate of physical ageing*

Figure 2 shows phenomena, similar to those first reported by Vincent<sup>16</sup>, obtained on the as-received polycarbonate film at 20 and  $60^\circ\text{C}$ . At each temperature, a specimen 1.0 cm wide and 5.0 cm long between the grips was stretched at a crosshead speed of  $1.0 \text{ mm s}^{-1}$ . The plots of tensile force against displacement show that the yield point for each specimen is followed by a drop in load, which is accompanied with the formation of a neck. During continued stretching, the length of the necked, or cold-drawn material, increases as the undrawn portion of a specimen is continuously being converted into drawn material. At a displacement of  $\sim 14 \text{ mm}$ , the crosshead was stopped for 1 h during which stress relaxation

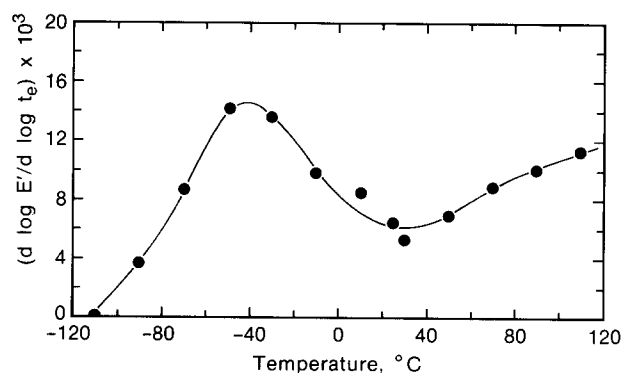
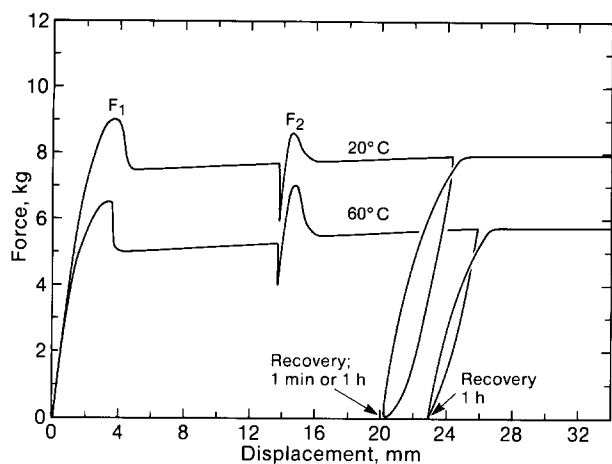


Figure 1 Temperature dependence of the ageing rate,  $d \log E'/d \log t_e$ , of the well annealed polycarbonate film at a static elongation of 2.6%. (Data from ref. 5)



**Figure 2** Dependence of the tensile force on elongation determined at a crosshead speed of  $0.1 \text{ mm s}^{-1}$  and at 20 and  $60^\circ\text{C}$ . The yield force  $F_2$  was obtained when the crosshead was restarted after stress relaxation had occurred for 1 h. Subsequently, the cold-drawing force was removed for 1 h, and for 1 min in a second test at  $20^\circ\text{C}$ , and then the crosshead was restarted, causing the force to return to its former value

occurred. When the crosshead was restarted, a yield peak developed in each specimen but the drawing force remained almost the same as that after the first yield point. This second peak is not accompanied by the formation of a neck as during the initial load drop. (The reason for this behaviour is mentioned later.) The force at the second yield peak depends on the duration of stress relaxation, other variables being the same. At a larger displacement, the load on each specimen was removed for 1 h, or for 1 min in a duplicate experiment at  $20^\circ\text{C}$ . Upon restarting the crosshead, the force increased until it reached the same drawing force as before. These and related phenomena have previously been studied in detail but only at room temperature<sup>17</sup>.

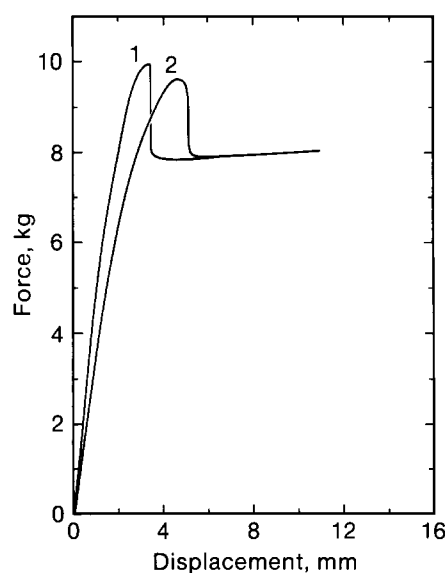
During stress relaxation for 1 h at each temperature (Figure 2), the segmental mobility decreased continuously, i.e. physical ageing occurred. The ageing rate is greater at  $60^\circ\text{C}$  than at  $20^\circ\text{C}$ , as shown in Figure 1. Consequently, when the crosshead was restarted, the increment of force,  $(f_y - f_d)$ , needed to attain the segmental mobility required to effect yielding is greater at  $60^\circ\text{C}$  than at  $20^\circ\text{C}$ , where  $f_y$  and  $f_d$  are the yield force and the drawing force, respectively. Figure 2 also shows that the force  $F_2$  at the second yield point exceeds that at the first yield point  $F_1$  at  $60^\circ\text{C}$  but not at  $20^\circ\text{C}$ . Again, this occurs because the ageing rate is greater at  $60^\circ\text{C}$  than at  $20^\circ\text{C}$ . An early example of hardening (ageing) during the stress relaxation of poly(vinyl formal) after yielding has occurred at room temperature and of the dependence of the yield stress of polystyrene on five different stress fields, including simple compression, have been given along with an example of the volume changes that accompany the yield process in simple compression<sup>18</sup>.

Curve 1 in Figure 3 was determined on a specimen of the annealed polycarbonate film at room temperature. Then the undrawn section of the specimen, following the load drop, was tested in the same way as the initial specimen. The resulting curve 2 shows that the yield force is smaller and the width of the curve on both sides of the yield point is greater than in curve 1. These changes result because the first specimen became partially de-aged during its test, and so curve 2 is similar to that shown for the as-received specimen in Figure 2 at  $20^\circ\text{C}$ . Of some,

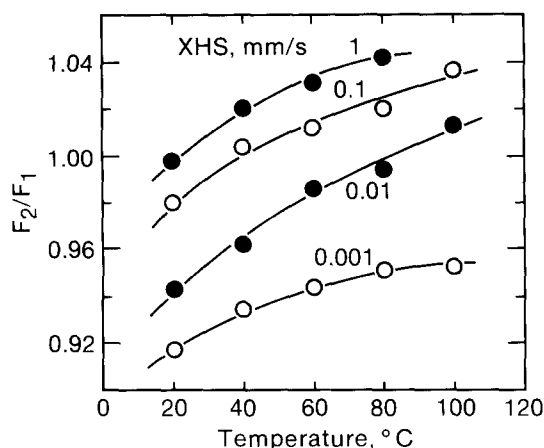
and possibly of substantial significance, is the observation that the drawing force is the same for both specimens. This behaviour suggests, but does not prove conclusively, that the drawing force is independent of, or does not depend strongly on, the age of a specimen.

As mentioned above, Figure 2 shows that after the force required for cold drawing is removed for 1 h, or even for 1 min, the same force as before, or nearly so, is reached at each temperature when the crosshead is restarted. An unquestionable explanation for this phenomenon cannot be given now, although some relevant observations can be mentioned. For example, the data in Figure 3 suggest that the age of a specimen has little or no effect on the drawing force. Also, Struik<sup>9</sup> showed that a cold-drawn specimen ages rapidly after the drawing force is removed. In agreement with Struik's findings, and as mentioned later, we have found that the ageing rate of a cold-drawn specimen at a static strain of 2.6% is significantly greater than that for a well annealed specimen under the same experimental conditions. Also, in some recent experiments<sup>19</sup>, rigid specimens of polycarbonate were subjected for a number of hours to a fixed strain of  $\sim 3\%$ . When the strain was returned to zero, or to a small strain of 0.6%, ageing occurred rapidly. These observations and those of Struik show that ageing occurs quite rapidly in a cold-drawn specimen when the force is removed. When the crosshead is restarted later, de-ageing occurs, and in spite of these various changes, the force returns to the original drawing force. So the observation mentioned above, namely that the drawing force may be independent of the age of the specimen, is possibly correct.

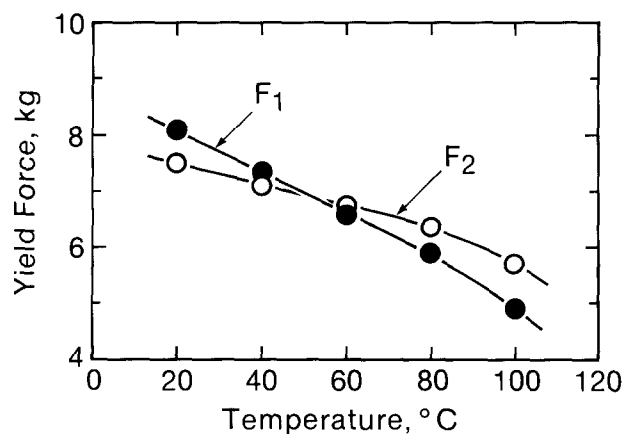
Determinations were made of  $F_1$  and  $F_2$  at four crosshead speeds from  $0.001$  to  $1 \text{ mm s}^{-1}$  and at temperatures from  $20$  to  $100^\circ\text{C}$ . In each instance,  $F_2$  was obtained after stress relaxation had occurred for 1 h, as was done previously (Figure 2). Figure 4 shows the dependence of  $F_2/F_1$  on temperature and crosshead speed; the latter is given on each curve.



**Figure 3** Dependence of the tensile force on elongation determined at a crosshead speed of  $1 \text{ mm s}^{-1}$ . Curve 1 was measured on a specimen of the well annealed polycarbonate film, and curve 2 was determined on the undrawn section of the first specimen following the yielding process



**Figure 4** Dependence of  $F_2/F_1$  on temperature and crosshead speed (XHS). Each value of  $F_2$  was determined after stress relaxation occurred for 1 h, the same as used previously (Figure 2)



**Figure 5** Temperature dependence of  $F_1$  and  $F_2$  determined at a crosshead speed of  $0.1 \text{ mm s}^{-1}$ .  $F_2$  was determined the same as before (Figure 2)

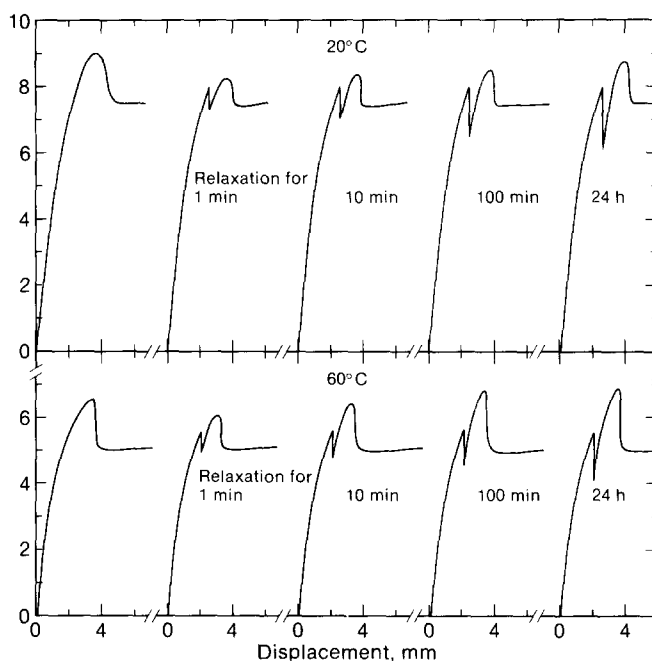
The data in Figure 4 at each temperature show directly that  $F_2$  increases faster than  $F_1$  with the crosshead speed. At each crosshead speed,  $F_2/F_1$  increases with temperature because the amount of physical ageing, during stress relaxation for 1 h, increases with temperature (Figure 1). The latter statement is true because, as shown in Figure 5,  $F_2$  decreases more slowly than  $F_1$  with an increase in temperature. It follows that  $F_2/F_1$  will increase with temperature, as shown in Figure 4.

#### Stress relaxation at a strain less than the yield strain

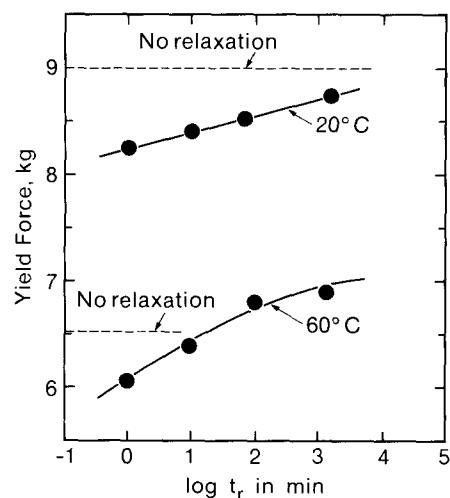
Shown on the left-hand side of Figure 6 are the usual type of stress-strain curves, including the yielding process, the load drop, and the early stage of the cold-drawing process. These curves were determined at 20 and 60°C and at a stretching rate of  $0.1 \text{ mm s}^{-1}$ . The next group of curves at each temperature shows the effect on the yield force of stress relaxation for 1, 10 and 100 min and 24 h at a strain slightly less than the yield strain as obtained by continuous stretching. Figure 7 shows the yield force plotted against the logarithm of the time of stress relaxation. When the stress-relaxation time at 60°C exceeds 10 min, the yield force exceeds that obtained by stretching a specimen continuously. This occurs because the segmental mobility decreases sufficiently during stress-relaxation periods longer than 10 min so that the

force needed to effect yielding exceeds that required when no stress relaxation occurs. Because the ageing rate at 20°C is less than at 60°C (Figure 1), the decrease in mobility even during 24 h of relaxation at 20°C is not sufficient to cause the yield force to exceed that determined in the usual way.

To explain further the significance of the data in Figures 6 and 7, assume first (incorrectly) that the mobility remains constant during each stress-relaxation period. Then the nominal yield stress  $\sigma_y$  obtained after a relaxation period would be  $\sigma_y = \sigma_y^0 - (\sigma_i - \sigma_f)$  where  $\sigma_y^0$  is the yield stress when a specimen is stretched continuously and  $(\sigma_i - \sigma_f)$  is the decrease in stress during the relaxation period. That is, if the mobility remained constant during stress relaxation, the yield stress would



**Figure 6** Force-elongation curves at 20 and 60°C determined at an extension rate of  $0.1 \text{ mm s}^{-1}$ . Except for the first curve at each temperature, the others were made by allowing stress relaxation to occur for 1, 10 and 100 min and 24 h at a strain slightly less than the yield strain obtained by continuous stretching. After each relaxation period, the crosshead was restarted



**Figure 7** Values of the yield force from Figure 6 plotted against  $\log t_r$ , where  $t_r$  is the stress-relaxation period

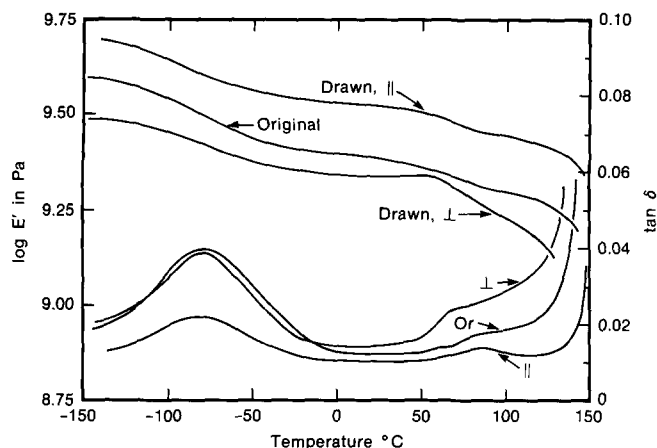


Figure 8 Temperature dependence of  $\log E'$  and  $\tan \delta$  determined at 10 Hz on three types of polycarbonate specimens: original as-received film and those cut parallel and perpendicular from an oversized cold-drawn specimen

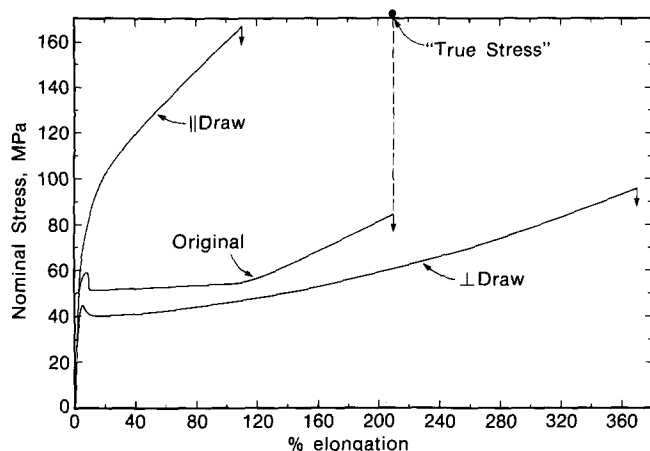


Figure 9 Plots of nominal stress against percentage elongation for a specimen of the as-received polycarbonate film and specimens cut parallel and perpendicular from an oversized cold-drawn specimen

decrease with an increase in the relaxation period. If the mobility decreases during stress relaxation, as in fact occurs, then  $\sigma_y > \sigma_y^0 - (\sigma_i - \sigma_r)$ . Hence, the increase in the yield stress (Figure 7) with the time of stress relaxation results from a reduction in the segmental mobility during the relaxation periods. These considerations provide additional evidence that the mobility does decrease during stress relaxation.

#### Temperature dependence of other mechanical quantities

Figure 8 shows the temperature dependence of  $\log E'$  and  $\tan \delta$  at 10 Hz for specimens cut from a wide cold-drawn specimen, parallel and perpendicular to the draw direction and also for a specimen cut from the as-received polycarbonate. At 0°C, for example,  $E'$  for the specimen cut parallel to the draw direction is ~50% greater than that for the specimen cut perpendicular to the draw direction, a consequence of the high degree of orientation in the former specimen. For the as-received (original) specimen, values of  $E'$  and  $\tan \delta$  are rather close to those for the specimen cut perpendicular to the draw direction, except in the upper portion of the temperature scale.

Figure 9 shows that a specimen cut parallel to the draw

direction, from a cold-drawn specimen, does not undergo yielding when stretched continuously, a fact not surprising because the specimen had undergone yielding when stretched the first time. The nominal stress increases continuously until fracture occurs at ~165 MPa and 110% elongation. The specimen cut perpendicular to the draw direction and the specimen from the 'original' as-received polycarbonate, isotropic or nearly so, both show the usual type of yielding but the yield stress is less for the former than for the as-received material.

The natural draw ratio for the 'original' isotropic specimen is ~2.15 (Figure 9). Subsequently, the stress increases until fracture occurs at an extension of 200% and at ~80 MPa, based on the initial cross-sectional area. The stress for the specimen cut parallel to the draw direction is based, as expected, on its initial cross-section. For the isotropic specimen, the cross-section after completion of drawing is  $0.465A_i$ , where  $A_i$  is the initial cross-section and 0.465 is derived from the natural draw ratio. Hence, the fracture stress of the isotropic specimen, when based on the cross-section after cold drawing is complete, is  $80/0.465 = 172$  MPa which is rather close to that (165 MPa) for the specimen cut parallel to the draw direction.

The yield stress  $\sigma_1$  determined at an extension rate of  $0.2 \text{ min}^{-1}$  and at temperatures from  $-90$  to  $100^\circ\text{C}$  is shown by the closed symbols in Figure 10. The open symbols, which represent  $\sigma_2$ , were obtained from values of  $F_2$  determined in the same way as those in Figure 2, except the crosshead speed there was  $0.1 \text{ mm s}^{-1}$  but here it was  $0.167 \text{ mm s}^{-1}$ . Above  $40^\circ\text{C}$ ,  $\sigma_2$  exceeds  $\sigma_1$ , as expected from the results in Figure 4. At  $-30$  and  $-50^\circ\text{C}$ ,  $\sigma_2$  again exceeds  $\sigma_1$ , as expected because the rate of physical ageing at these temperatures is quite high (Figure 1).

Figure 11 shows that the yield strain, also determined at an extension rate of  $0.2 \text{ min}^{-1}$ , increases from 5% at  $100^\circ\text{C}$  to 15% at  $-90^\circ\text{C}$ , a three-fold increase. But the yield stress  $\sigma_1$  (Figure 10) increases only by a factor of 2.4, and so the yield strain changes more than the yield stress with temperature.

Figure 12 shows the temperature dependence of  $\sigma_y/\sigma_D$ , where  $\sigma_y$  is the yield stress from Figure 10 (closed symbols) and  $\sigma_D$  is the nominal drawing stress. From 100 to  $-30^\circ\text{C}$ ,  $\sigma_D$  clearly increases faster than  $\sigma_y$ , but the opposite occurs from  $-30$  to  $-90^\circ\text{C}$ . So  $\sigma_y/\sigma_D$  is a

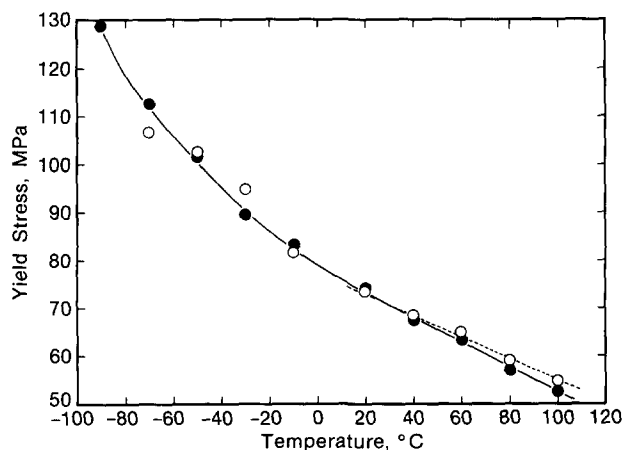


Figure 10 Temperature dependence of the yield stress  $\sigma_1$  (●) and  $\sigma_2$  (○) obtained from  $F_2$  determined the same as before (Figure 2), except here the extension rate is  $0.2 \text{ min}^{-1}$

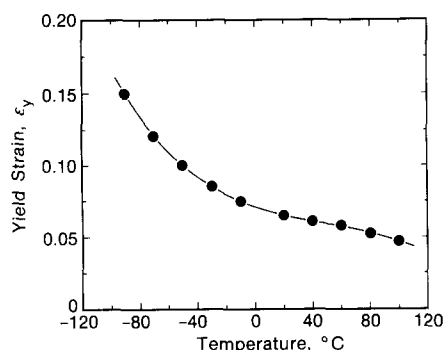


Figure 11 Temperature dependence of the yield strain determined at an extension rate of  $0.2 \text{ min}^{-1}$

minimum at  $-30^\circ\text{C}$ , at which temperature the ratio is only slightly greater than unity. No explanation is apparent for these data, and in fact the ratio  $\sigma_y/\sigma_D$  over a wide temperature range presumably has not been reported previously.

#### Additional results and comments

Stress-relaxation rates were determined at an extension of 2.6% on the annealed polycarbonate film and on a cold-drawn specimen at  $30^\circ\text{C}$  and were found to be 1.3 and 8.75% decay of stress per decade of time, respectively. Also,  $d \log E'/d \log t_e$  at  $50^\circ\text{C}$  and again at an elongation of 2.6% was determined on a cold-drawn specimen and found to be  $9.5 \times 10^{-3}$  which is significantly larger than  $6.7 \times 10^{-3}$  for the annealed film determined under the same experimental conditions. These results show that the segmental mobility in the drawn film, when measured in the draw direction, is greater than in the annealed film, as might be expected because a substantial increase in mobility is needed to reach the yield point and to enable cold drawing.

In fact, it has been suggested some years ago by Andrews<sup>20</sup> that yielding or drawing results from a stress-induced glass transition. There are a number of references in the literature about stress or strain softening<sup>16,21</sup> and also of 'structural softening and hardening'<sup>22</sup> to explain phenomena like those shown in Figure 2. Hence, the concepts of physical ageing and erasure of ageing are not really new but are now better defined, and the consequences of such phenomena are better understood, as illustrated by the data and discussions in this paper.

#### CONCLUSIONS

The initial yield force  $F_1$  (or stress) for polycarbonate was determined at four rates of extension and usually at five temperatures from 20 to  $100^\circ\text{C}$ . During the subsequent cold drawing, the crosshead was stopped for 1 h in each experiment to allow stress relaxation and the accompanying physical ageing. When the crosshead was restarted, another yield peak developed at a force  $F_2$ . The ratio  $F_2/F_1$  increases with the crosshead speed, which was varied from 0.001 to  $1 \text{ mm s}^{-1}$ , and also with the temperature from 20 to  $100^\circ\text{C}$ . The increase of this ratio with temperature results because the amount of ageing during stress relaxation increases with the temperature in the range covered, as found in a previous study of the ageing rate of polycarbonate specimens at a static extension of 2.6%. It was also found that  $F_2$

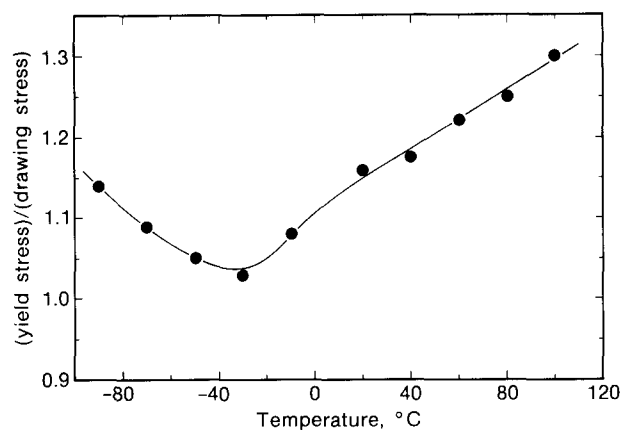


Figure 12 Temperature dependence of the yield stress divided by the drawing stress (nominal) determined at an extension rate of  $0.2 \text{ min}^{-1}$

exceeds  $F_1$  in a significant fraction of the tests made, especially at the higher temperatures and extension rates.

In other sets of experiments at 20 and  $60^\circ\text{C}$ , stress relaxation was allowed to take place for four periods of time from 1 min to 24 h at an extension somewhat less than the yield strain obtained by continuous stretching. When stretching was resumed, yielding occurred at a force that increased with the time of stress relaxation. In all experiments, the yield force was higher at 60 than at  $20^\circ\text{C}$ , again because ageing occurs faster during the relaxation period at the higher temperature. An analysis of these data shows, independent of results from previous studies, that physical ageing occurs during stress relaxation.

Stress-strain curves and dynamic measurements at 10 Hz were made on specimens cut parallel and perpendicular to the draw direction from a large cold-drawn specimen. The specimen cut parallel does not exhibit yielding because the orientation is high and the material had already undergone yielding. Also, the yield stress  $\sigma_y$ , the yield strain  $\epsilon_y$ , and the drawing stress (nominal)  $\sigma_D$  were determined at temperatures from  $-90$  to  $100^\circ\text{C}$  at an extension rate of  $0.2 \text{ min}^{-1}$ . With the decrease in temperature,  $\sigma_y$  increases by a factor of 2.4 but  $\epsilon_y$  increases three-fold. The ratio  $\sigma_y/\sigma_D$  decreases with a reduction in temperature until it reaches a minimum value of  $\sim 1.02$  at  $-30^\circ\text{C}$ , and then it increases with a further reduction in temperature. The cause of the temperature dependence of this ratio is not known, and the present data seemingly are the first that have been reported over such a wide temperature range.

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