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# The Assessment of Internal Stresses in Plastics by a Stress Relaxation Method

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When plotting the slope of stress relaxation curves (stress vs. log time) against the initial stress, straight lines are obtained intersecting the axis at a stress value which appears to be associated with the internal stress level of the sample. For injection molded samples, the internal stresses are negative, i.e. frozen-in compressive stresses. They disappear on annealing. Both tensile and compressive stresses can be introduced into stress-free samples by suitable thermal treatment when in a state of compression or tensile strain.

## INTRODUCTION

Problems associated with the assessment of internal stresses in plastics belong to an area of polymer physics where the similarities in the mechanical behavior of polymers and metals seem not to have been fully exploited. For instance for metals it is known that the kinetics of creep and stress relaxation is dependent on the internal stress level.<sup>1-4</sup> For obvious reasons this is known to be so for polymers too, but the possibility to use some of the simple methods for the assessment of the internal stress level as for instance the analysis of creep or stress relaxation curves appears to have been neglected hitherto. A contributing factor is the somewhat different way in approaching the physical aspects of flow in metals and polymers, respectively. In polymers, flow is often interpreted in terms of relaxation time spectra, changes in free volume, etc., that is to say in terms of approaches where internal stresses do not appear explicitly.<sup>5</sup> The normal approach to flow kinetics in metals is a power or exponential type relation between flow rate and effective stress, the latter quantity being set equal to the difference between the applied and internal

stresses.<sup>3</sup> Such a simple description of kinetics appears also to be applicable to polymers.<sup>6</sup> The physical reasons for this are not well understood, even though cooperative mechanisms may play an important role in this connection.<sup>7</sup>

The purpose of the present paper is to describe a stress relaxation method for determining a parameter which appears to be directly related to the internal stress level of a polymeric sample. The method is based on recording a number of stress relaxation curves with different initial stresses. When the maximum slope of the curves, as determined from stress-log time diagrams, is plotted against the initial stress, straight lines are obtained. The intercept of these lines with the stress axis is taken as a measure of the internal stress level.

From this method one obtains that samples rapidly cooled when slightly elongated or compressed above room temperature give a positive or a negative value, respectively, of the internal stress parameters. Injection molded samples give a negative value, which could be due to frozen-in negative stresses, while well annealed samples appear as stress-free according to this method.

The method described below is somewhat reminiscent of that proposed by Li.<sup>1</sup> It has been used earlier for studying internal stresses in cellulose and paper.<sup>8,9</sup> According to Li, under certain assumptions the internal stress can be obtained from a single flow curve, while the procedure proposed here requires a number of relaxation curves with varying initial stress. The advantages and drawbacks of the two methods are discussed below.

## SYMBOLS

- $\sigma, \epsilon$  stress and strain, respectively, in uniaxial extension  
 $\sigma_0$  initial stress, at the moment the straining is stopped  
 $t$  time, measured from the moment the straining is stopped  
 $F$  maximum slope of  $\sigma(\log t)$ , given numerically as  $(-d\sigma/d \ln t)_{max}$   
 $\sigma_i$  internal stress parameter, the extrapolated value of the  $\sigma_0$  intercept at  $F = 0$  of the  $F(\sigma_0)$  relationship  
 $E$  Young's modulus  
 $n$  exponent of the power law.

## THEORETICAL BACKGROUND—THE POWER LAW

In order to describe our relaxation curves in terms of formulae in common use in the metal field, we apply a power law here which for uniaxial extension can be written as follows:

$$\dot{\sigma}/E + B\sigma^n = \dot{\epsilon} \quad (1)$$

Here  $E$  is the modulus of elasticity and  $B$  and  $n$  are constants. As  $\dot{\epsilon} = 0$  in stress relaxation, Eq. (1) reduces to

$$\dot{\sigma} = -B E \sigma^n. \quad (2)$$

For steady-state creep,  $\dot{\epsilon} = A \sigma^n$  with the same value of  $n$ .<sup>1</sup> On the other hand, we do not make any decision as to whether the stress relaxation at comparatively low initial stresses corresponds to transient or steady-state flow. The mathematical formalism used does not allow such decisions.

Generally, relations of this type are justified by earlier findings<sup>10</sup> relating to the velocity of dislocations, which show an  $n$ -power dependence on the shear stress acting on them. In polymers such an explanation cannot be given without difficulties.

When the role of internal stresses is considered, the stress  $\sigma$  in Eqs. (1) and (2) is to be replaced by an effective stress,  $\sigma_{eff} = \sigma - \sigma_i$ . As  $\dot{\sigma}_i = 0$ , the internal stress level being assumed to remain unaffected by flow, Eq. (2) can be written as

$$\dot{\sigma} = -EB(\sigma - \sigma_i)^n. \quad (3)$$

The solution of Eq. (3) is

$$\sigma = (\sigma_0 - \sigma_i) (1 + mKt)^{-1/m} + \sigma_i \quad (4)$$

where  $\sigma_0$  is the initial stress,  $K = EB(\sigma_0 - \sigma_i)^m$  and  $m = n - 1$ .

The slope of the relaxation curves,  $d\sigma/d \ln t$ , is as follows

$$s = -K(\sigma_0 - \sigma_i)t (1 + mKt)^{-(m+1)/m}. \quad (5)$$

Eliminating  $t$  gives

$$-s = (\sigma - \sigma_i)/m \{ 1 + [(\sigma - \sigma_i)/(\sigma_0 - \sigma_i)]^m \}. \quad (6)$$

Eq. (6) enables us to calculate the internal stress  $\sigma_i$  from the value of the slope of the relaxation curves plotted as  $\sigma$  vs.  $\log t$ . This is the method proposed by Li.<sup>1</sup> According to Li,  $-s$  is plotted vs.  $\sigma$  and the intercept with the  $\sigma$ -axis gives the  $\sigma_i$ -value. This method uses  $s$ - and  $\sigma$ -values taken from the same curve, i.e. a single experiment is sufficient. However, this can lead to difficulties when the curvature is low. In the present case the method cannot be used, as the  $\sigma(\log t)$ -curves are practically linear. Despite this, Li's method has been described here as it may prove very useful when the experimental design is slightly modified. The second reason for describing this method is that it can be formally related to the procedure used here which was proposed many years ago by one of the present authors for the assessment of the internal stresses in cellulose and paper.<sup>8,9</sup>

The method used here is, as already mentioned, based on the determination of the maximum slope of a number of relaxation curves with different

$\sigma_0$ -values. Denoting this maximum slope by  $F$ , we calculate from Eq. (6)

$$F = n^{-n/(n-1)} (\sigma_0 - \sigma_i). \quad (7)$$

A plot of  $F$  vs. the initial stress  $\sigma_0$  thus results in a straight line, cutting the  $\sigma_0$ -axis at  $\sigma_i$ . This is the theoretical background of the procedure used in this paper. The slope of the  $F(\sigma_0)$ -lines is  $n^{-n/(n-1)}$ . For samples free from internal stresses one obtains

$$F/\sigma_0 = n^{-n/(n-1)}. \quad (8)$$

### The slope $m$ of $\log(\sigma - \sigma_i)$ vs. $\log t$

For metals, the value of the slope of the  $\log(\sigma - \sigma_i)$ - $\log t$ -plots, denoted  $1/m$ , is often used to gain information as to the mechanism of the flow process under study. When the power law is obeyed it follows that such plots are linear, i.e.

$$\log(\sigma - \sigma_i) = \text{const} - (1/m) \cdot \log(t + 1/mK). \quad (9)$$

The slope  $1/m$  is thus obtained at least for  $t \gg 1/mK$ .

### Stress relaxation measurements

A stress relaxation experiment is carried out by deforming the sample, keeping the deformation constant and recording the stress decay. In the present case, the experiments were performed in a conventional tensile testing machine (L. & W. Alwetron, type TCS 250). The initial deformation was performed at a rate of  $\dot{\epsilon} = 6.10 \cdot 10^{-3} \text{ s}^{-1}$ . A new sample was used for each relaxation curve. The initial stresses were chosen so as to be distributed evenly along the initial part of the stress-strain curve of the material under study.

The resulting relaxation curves were plotted in stress-log time diagrams. The maximum slope of these curves was determined as

$$F = (-d\sigma/d \ln t)_{max} \quad (10)$$

and plotted in another diagram vs. the initial stress  $\sigma_0$  of the relaxation curves.

It can be remarked that relaxation curves for any material when plotted as  $\sigma(\log t)$  are sigmoid in shape if the initial and final parts are included. In normal measurements, covering comparatively short time periods only, the curvature due to the initial and final portions of the curves is not recorded (very short and very long time, respectively). In the present case the rectilinear portions were shown to be identical with the rectilinear inflexion portion of the sigmoid curves, this portion covering about two decades of time.<sup>11</sup> This is of importance when the physical background of the relaxation kinetics is considered.

The measurements were carried out at  $22 \pm 1^\circ \text{C}$  and 65 percent relative humidity. Exceptions were the polystyrene samples, where the temperature

was set at 50°C in order to obtain easily measurable relaxation rates. Possibly, this temperature rise could influence the internal stress. Nevertheless, since the measuring time is relatively short compared with the time required to anneal the sample at 50°C, the internal stress measured at this temperature gives an estimate of the stress at room temperature.

The expected independence of the  $\sigma_i$ -value of temperature, at least at the comparatively low temperatures used in measuring the relaxation in polystyrene, is supported by data obtained with HDPE at 22°C and 40°C. Even though in that case the slope of the  $F(\sigma_0)$ -lines obtained at the two temperatures was slightly different, the intercept with the  $\sigma_0$ -axis, that is to say the  $\sigma_i$ -value, was almost identical. This is, however, not to be taken as an indication of the secondary role of the temperature. On the contrary, when approaching  $T_g$  or  $T_m$  of the polymer under study, internal stresses will be released almost immediately, and correspondingly the  $\sigma_i$ -parameter is reduced to zero.

### Samples

For introduction of tensile and compressive thermal stresses in polymer samples we used low density polyethylene (Lupolen 1810 H, BASF,  $\rho = 0.917$ – $0.918$  g/cm<sup>3</sup>, melt index = 1.2–1.7 g/10 min MFI 190/2). Injection molded samples of the following polymers were used: high density (HD-) and low density (LD-) polyethylene (PE), polypropylene (PP), polystyrene (PS) and acrylonitrile butadiene styrene (ABS). Their physical characteristics are given in Table I along with the injection molding conditions.

TABLE I  
Materials and moulding conditions

Material	Density (g/cm <sup>3</sup> )	Melt index (g/10 min) ASTM DI238	Nozzle temperature (°C)	Injection pressure (Pa · 10 <sup>-5</sup> ) (kp/cm <sup>2</sup> )
LD-PE Unifos DYOB	0.917	20.0	200	300
HD-PE Union Carbide DMDJ 7008	0.962	8.0	220	320
PP Enjay (Esso) GPCD 398	0.903	5.0	220	410
PS BP KLP	1.05–1.07		230	420
ABS Bayer Novodur PH/AT	1.06		240	1080

The temperature of the mold was set at 30°C, the cooling time at 30 s.

The dimensions of the samples were: length 224 mm, width 14 mm and thickness 3 mm, thus their cross section was 0.42 cm<sup>2</sup>.

Details of the annealing procedure and other treatments used in order to release the internal stress or to change their level are given below in connection with the presentation of the results.

## RESULTS

The general appearance of the stress relaxation curves used as the basis of the method presented here is illustrated in Figure 1, giving three  $\sigma(\log t)$ -curves for HD-PE, LD-PE and ABS. For the comparatively short measuring

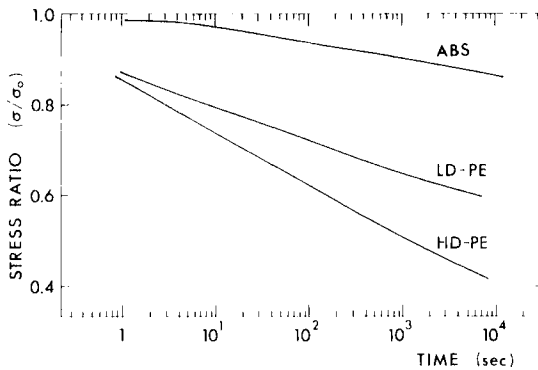


FIGURE 1 Stress relaxation curves for injection molded HD-PE, LD-PE and ABS at 22°C.

time used in these experiments it is obviously a good approximation to treat the relaxation curves as linear for 2–3 decades of time. In Figure 2 are markings denoting the initial stress  $\sigma_0$  on the corresponding stress-strain curve for HD-PE. It is seen that the  $\sigma_0$ -values occurring in this case are comparatively low and confined to the nearly linear part of the  $\sigma(\epsilon)$ -curve. This applies also to the remainder of the samples.

The first example of a  $\sigma_t$ -determination according to the present method is given in Figure 3 relating to the introduction of thermal residual tensile and compressive stresses in LD-PE. One sample was elongated a few percent, the other slightly compressed at 80°C and then rapidly cooled in water. The compressed sample gave a negative value of the intercept between  $F(\sigma_0)$  and  $\sigma_0$  (left line in Figure 3), while the elongated sample gave a positive value (right line). The line in the middle corresponds to a sample annealed at 90°C for 12 h which thus appears to be stress-free.

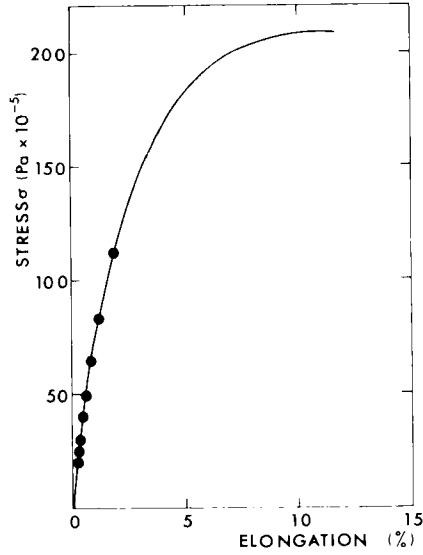


FIGURE 2 Stress-strain curve for injection molded HD-PE at 22°C. The dots denote the initial stress values of the stress relaxation experiments evaluated in Figure 5.

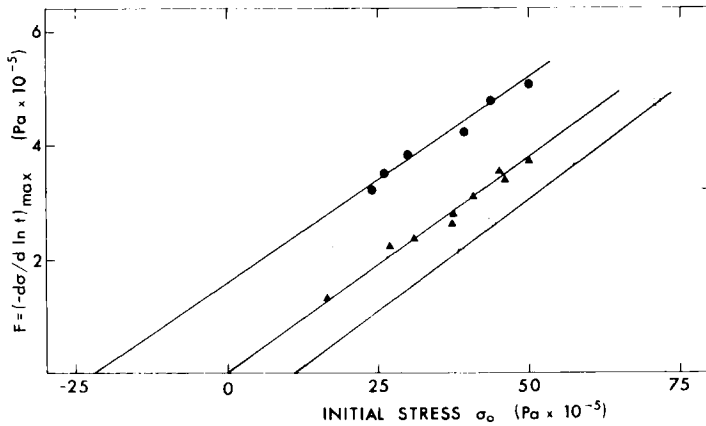


FIGURE 3 Determination of internal stress from the  $F(\sigma_0)$ -plot in LD-PE which has been compressed (left) or elongated (right) at 80°C and then rapidly cooled in water. The line in the middle relates to samples annealed at 90°C for 12 h.



The injection molded sample of LD-PE gives a negative value of the internal stress parameter  $\sigma_i$ , Figure 4, i.e. a value indicating the presence of frozen-in compressive stresses. Annealing the samples at 70°C for 5 days and slow cooling results in a markedly different, although plausible  $F(\sigma_0)$ -line. This time the intercept is close to  $\sigma_0 = 0$  indicating an almost complete release of the internal stresses originally present in the molded samples. Furthermore, there is a significant increase in the slope of the  $F(\sigma_0)$ -line.

The behavior observed with samples of HD-PE, Figure 5, is similar, i.e. a decrease in the  $\sigma_i$ -level after annealing (80°C, 5 days) and an increase in the

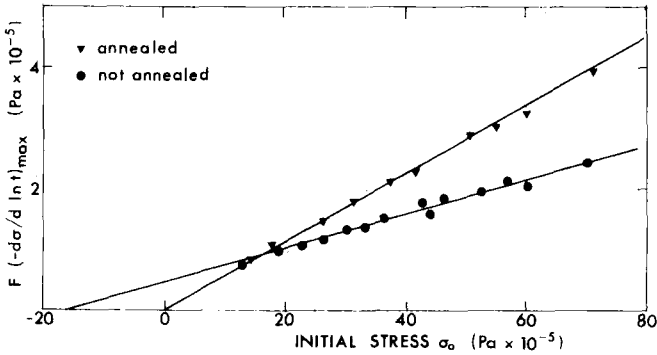


FIGURE 4 Determination of internal stress from the  $F(\sigma_0)$ -plot in injection molded LD-PE and LD-PE annealed at 70°C for 5 days.

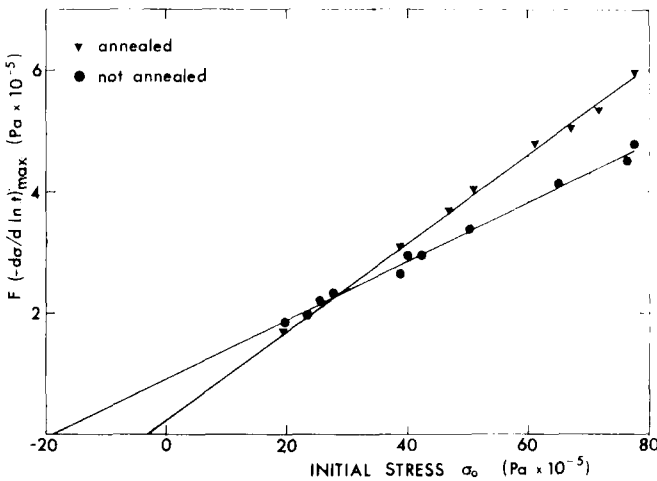


FIGURE 5 Determination of internal stress from the  $F(\sigma_0)$ -plot in injection molded HD-PE and HD-PE annealed at 80°C for 5 days.

slope of the  $F(\sigma_0)$ -line is found. It can be seen, however, that the release due to annealing is not complete, part of the internal stress level resisting such treatment. The third example of a polyolefine plastic is PP with a complete  $\sigma_i$ -release after annealing ( $110^\circ\text{C}$ , 5 days), Figure 6.

A slightly different picture is provided by the results relating to PS and reproduced in Figure 7. The internal stress level measured as the  $F(\sigma_0) - \sigma_0$ -intercept is substantially higher here. Also in this case, annealing produced

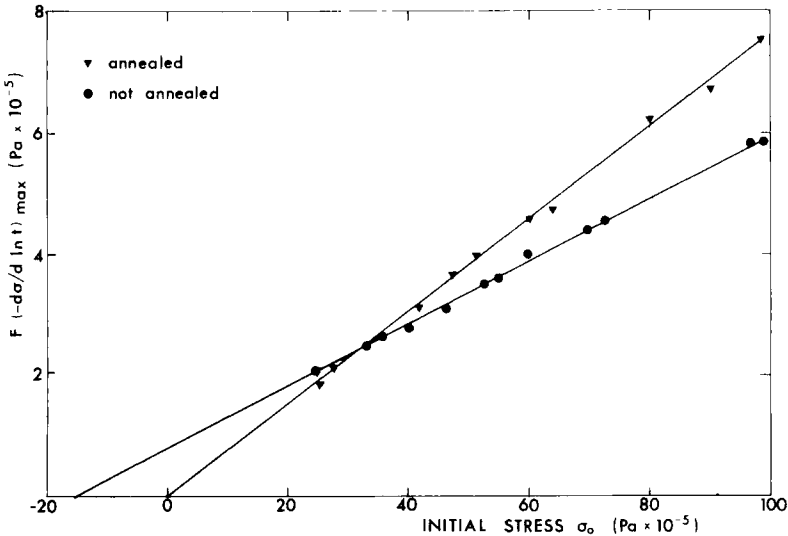


FIGURE 6 Determination of internal stress from the  $F(\sigma_0)$ -plot in injection molded PP and PP annealed at  $110^\circ\text{C}$  for 5 days.

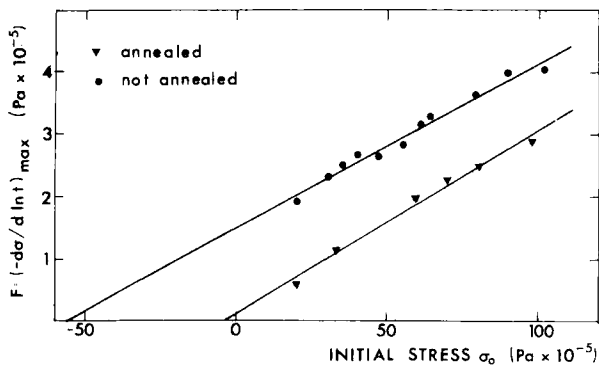


FIGURE 7 Determination of internal stress from the  $F(\sigma_0)$ -plot in injection molded PS and PS annealed at  $70^\circ\text{C}$  for 5 days.

almost complete release of the frozen-in stresses. On the other hand, the change in slope of the  $F(\sigma_0)$ -lines is not as pronounced as with LD-PE, for example.

With ABS finally, the  $\sigma_i$ -level was still higher than in the preceding case, Figure 8. Annealing at 80°C for 5 days brought about substantial but not complete release of the internal stresses, about 15 percent of the original  $\sigma_i$ -level remaining after the annealing treatment.

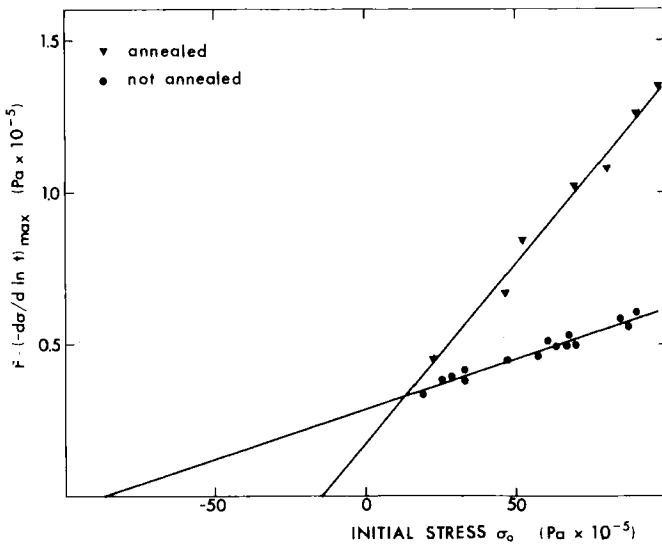


FIGURE 8 Determination of internal stress from the  $F(\sigma_0)$ -plot in injection molded ABS and ABS annealed at 80°C for 5 days.

The conditions of annealing in the above examples were chosen to give careful annealing within a practical time limit without melting the samples.

For polymers the value of  $m$  seems to be dependent on the injection molding treatment. As Table II shows, a marked decrease in the  $m$ -values is caused by their annealing. The values of  $m$  can also be calculated from the slope of the  $F(\sigma_0)$ -lines. However, this method is not recommended as small changes in the slope of those lines,  $(m + 1)^{-(m+1)/m}$ , correspond to very large changes in  $m$ .

One may recall in this connection that the value of  $m$  is connected with that of  $n$  in Eq. (3) by  $m = n - 1$ . For comparison, typical  $m$ -values for metals are in general lower than the  $m$ -values found here.<sup>12</sup>

TABLE II  
Summary of the experimental results on  $\sigma_i$  and  $m$ .  
( $m$  is calculated from the slope of  $\log(\sigma - \sigma_i)$  vs.  $\log t$ ).

Polymer	$\sigma_i$ -value		m-value	
	as molded	annealed	as molded	annealed
	MPa			
LD-PE	$-1.6 \pm 0.2$	0	22	10
HD-PE	$-1.9 \pm 0.2$	$-0.3 \pm 0.2$	11	9
PP	$1.5 \pm 0.2$	0	14	9
PS	$-5.6 \pm 0.4$	$-0.3 \pm 0.4$	32	29
ABS	$-8.7 \pm 0.4$	$-1.5 \pm 0.4$	100	70
LD-PE (thermal frozen-in stresses)				
elongated	$1.1 \pm 0.2$	0	9	9
compressed	$-2.2 \pm 0.2$		10	

## DISCUSSION

It is well evident from the data presented above that the  $F - \sigma_0$ -intercept represents a quantity which qualitatively and possibly even quantitatively appears to be related to the internal stress level in the polymer samples under study. The plausibility of such an assumption is supported by all the results presented above. Not only are internal stresses in injection molded samples of the compressive type, as they should be, but they diminish gradually during an annealing treatment and eventually disappear. Another strong support can be found in the experiments where compressive or tensile stresses were introduced into the samples by a suitable heat treatment under compression or elongation, respectively. Such a treatment results in shifts of the  $F(\sigma_0)$ -lines in the direction of compressive or tensile stresses. Again, these internal stresses, as measured by the intercept of the  $F(\sigma_0)$ -lines with the  $\sigma_0$ -axis, can be made to disappear by a sufficiently long and intense annealing.

With regard to the  $\sigma_i$ -values determined for the various samples, it may be noted that amorphous polymers like PS and ABS seem to have higher internal stress levels than polymers of the crystalline type, like PE and PP.

When interpreting the presence of compressive frozen-in stresses in injection molded samples one should take into account the complicated stress distribution in such samples, even when their geometrical shape is simple. In general the compressive stresses appear to be concentrated to the surface, while tensile stresses predominate in the central parts remote from the surface. It is, in principle, possible to analyse the relaxation of such a structure in terms of the power law, even though it would necessitate stress relaxation measurements on sectioned samples, a procedure not attempted here.

It may appear somewhat confusing that in the discussion above the theoretical background of the procedure is based on a power law, giving linear  $\log(\sigma - \sigma_i)$  vs.  $\log t$ -plots, while at the same time the slope  $F$  is evaluated from  $\sigma$  vs.  $\log t$ -plots. However, it so happens, that with the polymers under study both the  $\sigma$  vs.  $\log t$ -plots and  $\log(\sigma - \sigma_i)$  vs.  $\log t$ -plots are linear with sufficient accuracy. To decide which of the plots is to be preferred is not possible, which also means that one cannot decide on whether the flow rate has a  $\sigma^n$  or an  $\exp A\sigma$ -type dependence on the stress. On the other hand, such a situation is quite common when flow in solids is considered; it partly explains the present weakness of the various theories of flow.

If the stress relaxation curves are to be interpreted of using the  $\exp A\sigma$ -law this can be done as follows.

Since the curves are linear for about 2-3 decades of time, the stress can be written as:

$$\sigma = C - D \ln t \quad (11)$$

where  $C$  and  $D$  are constants.

$D$  is then set equal to the slope  $F$  from the power law, i.e.

$$F = (m + 1)^{-(m+1)/m} (\sigma_0 - \sigma_i). \quad (12)$$

Equations (11) and (12) give, together with appropriate boundary conditions,

$$\dot{\sigma} = \text{constant} \cdot \exp((\sigma - \sigma_i)/F) \quad (13)$$

which is the exponential  $\sigma$ -law.

It follows from what has been shown above that the method proposed here can be justified using both the power law and the exponential law connecting  $\dot{\sigma}$  and  $\sigma - \sigma_i$ . It should, however, be noted that the two approaches are not independent of each other, the reason for this being as follows.

It is well known that the maximum slopes of the  $\sigma$ - $\log t$ -curves are proportional to the initial stress  $\sigma_0$ .<sup>11</sup> Such a linear dependence is implicit to the power law. The exponential law does not lead to this linearity without additional assumptions. The equivalence between the two laws with regard to internal stresses in the above treatment is due to the fact that the constant  $F$  in the exponential law has been replaced by the corresponding quantity calculated from the power law thus providing an  $F(\sigma_0 - \sigma_i)$ -linearity. The results obtained can be justified using the exponential law only. In that case, however, the experimentally observed linearity between  $F$  and  $\sigma_0$  is to be introduced as an additional constraint.

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