Physical Aging in Plastics and Other Glassy Materials

L. C. E. STRUIK
Centraal Laboratorium TNO
Delft, The Netherlands

This paper surveys the basic aspects of physical aging. It shows that aging is a general and important phenomenon found in all organic and inorganic glasses and in some metals as well. Moreover, the behavior of all these materials is very similar. It further shows that aging cannot be ignored in the testing of plastics, particularly in the prediction of their long-term behavior.

INTRODUCTION

It has been known for many years (see, e.g., Kovacs (1)) that amorphous materials are not in thermodynamic equilibrium at temperatures below their glass transition. As solidified supercooled liquids they have a higher volume, entropy, etc., than they would have in the equilibrium state (see Fig. 1). Volume relaxation studies (1) reveal that below $T_A$, the molecular mobility is not quite zero. There is a slow and gradual approach to equilibrium, and this process, called physical aging, changes many properties of material (2-5). In fact, the aging is a gradual continuation of the vitrification around $T_v$. Therefore, it will affect all those properties which in their dependence on temperature, undergo drastic changes at $T_v$. During aging the material becomes more and more glass-like and less rubber-(liquid)-like. It becomes stiffer and more brittle, its damping decreases, and so do its creep- and stress-relaxation rates, dielectric constant, loss, etc.

We have studied this aging for some 35 plastics and other organic glasses and for a variety of mechanical properties. The main conclusions of the study are:

- Aging occurs in broad temperature ranges below $T_v$. In general, the aging range runs from $T_v$ down to the first (highest) secondary transition, $T_B$ (see Fig. 1).
- Thus, for polyvinyl chloride (PVC) it runs from +70 to about $-50^\circ$C, for polycarbonate (PC) from +150 to about $-100^\circ$C, etc. The aging range of many plastics includes the temperature range of practical interest.
- In the aging range defined above, aging is a very important phenomenon. At least the small-strain mechanical properties of the material are determined mainly by the parameter aging time. Aging has to be considered in the testing of plastics, particularly in the prediction of their long-term behavior.
- In the aging range, all polymers age in the same way, and even their mechanical behavior at small strains is very similar. Thus, there is little difference in behavior between PVC, polymethyl methacrylate (PMMA), PC, polystyrene (PS), polyethylene terephthalate (PET), etc.; their behavior is primarily determined by their being glassy amorphous substances.
- Nearly all aspects of aging can be explained in a straightforward way from the free-volume concept.

Although our work was mainly concerned with synthetic amorphous polymers, the results are not restricted to this particular class of materials. The same mechanical and aging behavior as shown by plastics has been found in organic glasses such as bitumen, shellac, amorphous sugar, and compression molded dry cheese powder. In addition, several polycrystalline metals such as lead, tin and Wood's metal turned out to behave in the same way, which prompted us to suggest (11) that physical aging is a basic feature of the solid state in general.

In the next sections aging will be discussed systematically for amorphous polymers. Starting from the free-volume concept, we will derive the basic aspects of aging one by one and illustrate them by experimental data. Details about experimental techniques are omitted; they are given in Refs. (5-10).

THE FREE VOLUME CONCEPT AND THE ORIGIN OF AGING

This concept states (see Fig. 2) that in every system of particles, molecules, etc., the transport mobility $M$, primarily depends on the degree of packing, or in other terms on the free volume, $v_f$. This idea is very general and, according to Robertson (12), very old, much older...
than the idea that mobility is determined by temperature.

In deriving the various aspects of aging, we apply the free-volume concept in its crude qualitative form. We do not use the quantitative free-volume models proposed in the literature (compare (1)), first because we do not in fact need them, and second because we believe that the problem of quantifying the free-volume concept and defining free-volume in terms of measurable quantities has not yet been solved.

Let us now turn to polymers and consider what will happen when such a material is cooled from a temperature $T_0 > T_g$ to $T_1 < T_g$ (see Fig. 2B). In polymers, transport mobility should be identified with the segmental mobility, i.e., the rate factor for changes in chain configuration. Since above $T_g$ the polymer behaves as a rubber or a fluid, even at very small strains, the segmental mobility must be large, and the free volume, $v_f$, must also be large.

On cooling there will be a simultaneous decrease in $v_f$ and $M$. Free volume is made up of holes. Since molecules attract one another, the generation of free volume will be accompanied with an increase in internal energy by an amount $\Delta U$ that increases with $v_f$. Free volume actually exists because its generation is also accompanied with an increase, $\Delta S$, in entropy. In fact, $v_f$ will attain that value for which $\Delta U$ balances $T\Delta S$. A lowering of the temperature decreases the importance of the term $T\Delta S$, and $v_f$ and the mobility, $M$, will decrease simultaneously (13). In Fig. 2, this behavior above $T_g$ is shown schematically.

The changes in $v_f$ are brought about by a redistribution of the holes. The rate of this process is determined by the segmental mobility, $M$, so we have the following closed-loop scheme: $v_f$ determines $M$, while $M$ determines the rate, $\frac{dv_f}{dt}$, at which $v_f$ changes, in symbols:

$$ v_f \Rightarrow M \Rightarrow \frac{dv_f}{dt} \tag{1} $$

This closed-loop scheme is essential for an understanding of glass transition and aging (1, 5). First, it shows that during cooling the decrease in $v_f$ cannot continue beyond certain limits. Below a certain temperature, $M$ becomes so small that the changes in $v_f$ fail to keep pace with those of the temperature. The material then passes through its glass transition. Upon further cooling, $v_f$ remains to a first approximation constant. The rapid changes of $M$ with $T$ also come to an end, and only a slight decrease in mobility $M$ remains because of the attendant decrease in thermal activation.

A second consequence of Eq 1 is that below $T_g$, the mobility cannot simply become zero*. For a decrease in $M$, $v_f$ must be decreased, and for this some mobility must be available. Therefore, $M$ cannot vanish in a finite time; the state of zero mobility can only be approached asymptotically.

Consequently, when after cooling the polymer is kept at some constant temperature below $T_g$, the mobility $M$ will be small but not zero. Since $v_f$ exceeds its equilibrium value, a slow and gradual volume contraction will remain (1). It will be accompanied with simultaneous changes in mobility $M$, and in all properties of the glassy polymer which in any way depend on $M$ (see Fig. 1).

**THE BASIC ASPECTS OF AGING**

The simple picture of the above section suffices for deriving most aspects of aging. They are listed and explained below, and we have illustrated them by experimental data, confining ourselves to the mechanical behavior at small strains.

**Aging Affects Properties Primarily Through Changes in the Relaxation Times**

Since the very property that changes during aging is the mobility, $M$, and the relaxation times are directly related to $M$, this conclusion is obvious from the above picture. So creep or stress-relaxation curves will be shifted along the logarithmic (loading) time scale, the more the longer the aging time.

An example is given in Fig. 3, which refers to rigid PVC and shows the creep curves at various times, $\epsilon$, elapsed after a quench from 90 to 40°C**. We observe drastic changes in the creep properties, the creep curves shifting by no less than 4.5 decades. At a fixed creep time, the compliance changes by about 50 percent for an

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* For refinements, see section below.

** For details about the experiment, see Refs. (5) and (6).

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*Fig. 3. Small-strain tensile creep curves of rigid PVC quenched from 90°C (i.e., about 100°C above $T_g$) to 40°C and further kept at 40 ± 0.1°C for a period of 4 years. The different curves were measured for various values of the time $t$, elapsed after the quench. The master curve gives the result of a superposition by shifts which were almost horizontal, the shifting direction is indicated by the arrow. The crosses refer to another sample quenched in the same way, but measured for creep at a $t$, of 1 day only.
increase in \( t_a \), from 0.03 to 1000 days. All individual creep curves of Fig. 3 can be superimposed to give a single master curve. The necessary shifts are almost horizontal, which proves that the aging effects are indeed due to changes in the relaxation times. These even change all in the same way. Similar results were obtained for all other materials investigated.

A final point to be mentioned with regard to Fig. 3 concerns the fact that the creep curves were obtained by a sequence of creep and recovery tests performed on a single sample (compare Refs. (5, 6)). This raised the questions to what extent the results are due to the sequential testing (mechanical aging) rather than to a spontaneous aging occurring in the material, irrespective of whether it is tested for creep or not. It could be ascertained that in the present results mechanical aging is of no importance, simply because the tests were done at small strains (<0.3 percent, for details, see (6)). The proof is given in Fig. 3 by the crosses, which refer to another sample quenched in exactly the same way as the first. The creep tests at 0.03, 0.1 and 0.3 days were omitted, but the results at a \( t_a \) of 1 day still agree to within 2 percent with those obtained on the first sample.

**Aging Is Thermoreversible**

According to the above picture, we have to expect the following: when the material is heated to above \( T_p \) it readily reaches thermodynamic equilibrium. By definition, the history of the sample has been "forgotten", any previous aging that occurred below \( T_p \) has been erased. Aging therefore is a thermoreversible process that can be reproduced as an arbitrary number of times on the same sample. This can be done by restarting every time at the same temperature above \( T_p \).

An example showing this thermoreversibility is given in Fig. 4. The aging during the 1000-day period at 20°C is erased by heating the sample to 90°C for only 20 min. and after quenching the aging is resumed. The data (crosses) measured 1 day after quenching agree to within 2 percent with those measured 1 day after the quench which the sample had undergone 4 years earlier.

Thermoreversibility is a typical feature of physical aging. It is not, of course, found in chemical aging (photo-oxidation, thermal breakdown, etc.), the effects of which certainly cannot be erased by short heating to above \( T_p \). In fact, to determine whether, for an amorphous polymer, a certain aging effect (e.g., embrittlement) is due to the physical aging described in this paper, it suffices to check whether the original properties of the material can be restored by heating to just above \( T_p \).

**Aging Does Not Affect Secondary Relaxations**

Below \( T_p \), \( \gamma_r \) shrinks to a value at which segmental motion becomes strongly hindered, though it remains possible. In general, secondary motions require much less space than the motion of the segment as a whole. Therefore, \( \gamma_r \) will always remain sufficiently large to permit these small-scale secondary motions to occur.

This was tested for 22 polymers. An example of the results is given in Fig. 5; for other examples, see Refs. (14) (15). The changes in free volume were brought about by quenching and slow cooling rather than by isothermal aging. We observe a pronounced effect of thermal history, especially on the damping. However, these effects are only seen in the temperature region between the secondary peak and \( T_p \). For all polymers in which the secondary peak is pronounced and well separated from the glass transition, the location and height of the secondary peak was unaffected by changes in thermal history. This confirms the prediction that aging and thermal history will leave the secondary relaxations unchanged. The effects seen in Fig. 5 are then to be attributed to changes in the low-temperature tail of the glass-transition peak.

Complications have thus to be expected for those polymers whose secondary peak is not well separated from the glass transition. An example is given in Fig. 6. The secondary peak has now apparently changed, but these changes can still be attributed to shifts of the low-temperature tail of the glass transition (compare Fig. 8 of (14)).

**The Aging Range Runs From \( T_a \) to \( T_B \)**

Figure 5 shows that below the secondary transition, \( T_B \), modulus and damping are unaffected by the changes in \( \gamma_r \) produced by rapid instead of slow cooling. An

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**Fig. 4.** As Fig. 3, but now for PVC quenched from 90 to 20°C. The crosses were found when, after 1000 days of aging, the sample was reheated to 90°C, quenched to 20°C, and remeasured for a \( t_a \) of 1 day. They show that the aging is thermoreversible.

**Fig. 5.** Shear modulus and damping at 1 Hz for rigid PVC (mass polymer), measured during heating from -170 to +65°C at a rate of 2°C/min. Tests (1), (2) and (3) refer to different thermal histories (see diagram), and were done in succession on one sample. The agreement between the results of tests (1) and (3) again shows that the effects are thermoreversibly.
observation related to this is that below $T_a$ the aging effects disappear, i.e., no aging is found after a quench from above $T_a$ to below $T_b$. Experimental data showing this are given in Fig. 7.

This figure requires some explanation. We observed that aging produces an almost horizontal shifting of the creep curves (Figs. 3 and 4). We can take one of the creep curves, e.g., the one for $t_e = 1$ day as a reference curve, and then determine how the horizontal shift $\log a$ varies with $\log t_e$. It appears that nearly always $\log a$ varies linearly with $\log t_e$. Therefore, the intensity of the aging can be characterized by the double-logarithmic shift-rate, $\mu$, defined as:

$$\mu = \frac{d \log a}{d \log t_e}$$  \hspace{1cm} (2)

For many polymers, this shift rate has been measured at various temperatures, some of the results being presented in Fig. 7. The following general picture emerges from such data:

- Above $T_a$ there is (of course) no aging, and $\mu$ is zero.
- At $T_a$, $\mu$ jumps to a value of about unity for all polymers (the explanation is given below). This means that the creep curve shifts one decade to the right for each tenfold increase in aging time $t_e$ (this can easily be seen in Figs. 3 and 4). In other words, the relaxation times increase proportionally to aging time $t_e$.

![Fig. 6. As Fig. 5, but for a post-chlorinated PVC.](image)

- At low temperatures, $\mu$ begins to decrease, and the aging effects begin to disappear. Roughly, this occurs at the temperature $T_a$ of the highest secondary transition (values for $T_a$'s and $T_b$'s can be found in (16)).

A possible explanation of the last point above is the following: When the polymer is cooled through the $T_a$ range, the polymer segments will (partly) lose their flexibility. However, above $T_a$ the free volume has already shrunk to such a low value that the motion of the still flexible segments is strongly hindered. It will therefore be much more hindered, or even become impossible, at temperatures below $T_a$. Below $T_a$, the segmental motion, and therefore the aging also, will practically disappear.

Several remarks can be made in this context:

(a) In the way explained above, secondary motion is a prerequisite for segmental motion. This conclusion can probably be generalized. Experiments by Mikhailov (17), Koppelman (18), and Johari (19) show that at high frequencies and high temperatures, the $\alpha$-peak (glass transition) merges with the $\beta$-peak. The combined peak then follows the same Arrhenius line as the separated $\beta$-peak does at low frequencies (see Fig. 8).

(b) According to the picture here presented, segmental motion ceases at temperatures below $T_a$. The material then reaches the "truly glassy state" (see Fig. 1), and behaves as expected for a glass. One of the features of glassy behavior is brittleness, and indeed all polymers are brittle below $T_a$. On the other hand, the temperature range of ductility roughly coincides with that of aging (see Fig. 7). Polymers such as PC, polyphenylene oxide (PPO), and polysulphone, which are ductile over wide temperature ranges also age over wide ranges; polymers with a narrow aging range (PS, styrene acrylonitrile SAN, PMMA) lose their ductility at temperatures not very far below $T_a$. A possible explanation for this remarkable correlation is that for both aging and ductility, some segmental mobility must be available. This also sheds new light on the role of the secondary transitions. These, in the first place, do not enhance the toughness of the material. For ductility over a wide temperature range, the $\beta$-transition has to lie at temperatures as low as possible. On the other hand, the enhanced ductility has to be paid for by an increase of the temperature range in which the polymer is sensitive to aging and thermal history.

![Fig. 7. The shift rate, $\mu$, vs temperature for various polymers. For explanation, see text.](image)

![Fig. 8. The merging of $\alpha$- and $\beta$-peaks at high frequencies. Schematic after Refs. 17-19; $f_{max}$, is the frequency of maximum loss.](image)
(c) Problems arise with materials which have no clear secondary transition. The aging range may then extend to very low temperatures, and this appears to be the case with PPO (polyphenylene oxide) and PPPO (polytriphenylene oxide). Another possibility is that the chain segments lose their flexibility gradually, so that segmental motion and aging gradually disappear over a wide temperature range.

**In the Aging Range, Shift Rate $\mu$ Is About Unity for All Polymers**

This experimental observation (see Fig. 7) can be explained from the fact that aging is a strongly self-delaying process (the mobility decreases continuously, see Fig. 2). For such processes it can be derived that, as long as the self-delaying effects are strong, mobility $M$ will decrease in inverse proportion to aging time $t_r$, or:

$$M \sim \frac{\text{constant}}{t_r}$$

The general derivation of Eq 3 will be given in a subsequent paper (for the special case of volume relaxation, see (1)). Here, it suffices to say that the equation holds for all strongly self-delaying processes. Examples are: aging in organic glasses (present work); aging in inorganic glasses (whose viscosity increases proportionally with time (20, 21)); setting of stirred powders; nonlinear stress relaxation in plastics and metals (the relaxation is accelerated by the high stress, but since this stress decreases, the process is self-delaying); and an adiabatic endothermal chemical reaction, started by a short initial heating.

**Equation 3** implies that during aging the creep curves will shift at a constant rate (compare Figs. 3 and 4) and, moreover, that this rate will be about unity:

$$\mu = \frac{d \log a}{d \log t_r} = \frac{d \log M}{d \log t_r} \sim 1$$

An example showing how this prediction is confirmed by experiment is given in Fig. 9. The data were derived from Figs. 3 and 4 and from similar data for a measuring temperature of $0^\circ$C. Apart from some deviations at short times, $\log a$ varies linearly with $\log t_r$, and the slope of the line is 0.95. An important consequence of Eq 3 and 4 is that in their aging ranges all polymers will age in exactly the same way, there will hardly be any dependence on the specific chemical structure of the material.

**Aging Is a General Phenomenon**

According to the picture developed above, aging is a basic feature of the glassy state. It should be found in all glasses, irrespective of their specific chemical, polymeric or monomeric structure. Moreover, Eqs 3 and 4 must be expected to hold generally.

This has been confirmed by the present work. Very similar aging effects were found in all amorphous glassy polymers. Examples are given in Figs. 3, 4, 10 and 11.

This same aging effects were observed in other glassy materials such as bitumen, shellac, and amorphous sugar. Some results are given in Figs. 12, 13, and 14.

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**Fig. 9.** The shifting of the creep curves of rigid PVC quenched from $90^\circ$C to 0, 20, and $40^\circ$C. Log $a$ is the shift relative to the creep curve measured at a $t$, of 1 day.

**Fig. 10.** As Fig. 3, but for the small-strain torsional creep of PS (Styron 666) quenched from 100 to $50^\circ$C.

**Fig. 11.** As Fig. 10, but for an Epoxy resin cured at $200^\circ$C and quenched from 177 to $147^\circ$C.

**Fig. 12.** As Fig. 10, but for a heavy roofing bitumen quenched from 20 to $0^\circ$C.
As an extreme example, we investigated compression molded dry cheese powder. The structure of this material is highly complicated and unknown. However, the material shows a softening around 170°C which resembles a glass transition. Therefore, the above theory suggests that the material will show aging similar to that found in synthetic polymers. Figure 15 shows that this is indeed the case. These results for organic glasses together with literature data on inorganic glasses (20, 21) prove that physical aging is a basic feature of the glassy state.

The Aging Process Persists for very Long Periods of Time

The time $t_\infty$ needed for the establishment of equilibrium at $T < T_g$ can be estimated from free volume theory (1). It follows that $t_\infty$ increases almost exponentially with $T_g - T$, roughly by a factor of 10 per 3°C. At a temperature of no more than 20°C below $T_g$, $t_\infty$ reaches a value of 100 years, which implies that practically speaking, the aging will persist for the entire lifetime of a plastic product.

The results of Figs. 3, 4, and 9 strongly support this conclusion. The shift rate is constant over a 4.5 decade change in aging time (0.03-1000 days); there are no indications for any change in the remaining decade from 3-30 years.

For a definite check, we designed the following experiment in which we start with a PVC tube of known age, say, 20 years. We measure its creep curve at 20°C, reheat it to $T_g$ and recool it to 20°C. From the creep curves measured at 0.1, 1, 10, and 100 days after recrystallizing, we can predict the location of the curve after a $t_e$ of 20 years. Comparison with the true creep curve measured after 20 years of aging will reveal whether the predictions based on free-volume theory are correct or not.

This experiment is in progress now, and the results will be published in due course. If the test is successful, we will attempt similar experiments on much older glassy substances in order to find out whether this method can be used for dating materials.

In the Aging Range, Aging Time Is the Most Relevant Material Parameter

The meaning of this is illustrated in Fig. 16. This shows creep curves of rigid PVC at 0, 20, and 40°C, at 6°C for $t_e$ of 0.03 day, at 40°C for $t_e$ of 1000 days, and at 20°C for $t_e$ of 0.1, 1, 10, 100, and 1000 days.

It is generally assumed that heating accelerates creep. This effect is, however, small and easily overshadowed by the much stronger aging effects. At 0°C and for $t_e$ of 0.03 days, the material can therefore creep faster than at 40°C for $t_e$ of 1000 days. In fact, Fig. 6 shows that around room temperature the aging effects in PVC are
stronger than the effects produced by temperature changes of no less than 40°C.

Similar results were obtained for other polymers. They show, in agreement with the picture above, that the parameter aging time is the most relevant one in specifying the small-strain mechanical behavior in the aging range.

In the Aging Range, the Small-Strain Behavior of all Polymers Is Almost Identical

To explain the meaning of this empirical finding, we consider Fig. 17. This shows that the effect of aging and temperature on the creep of PVC can be reduced to horizontal and vertical shifts. When plotted in a double-logarithmic diagram, all creep curves have the same shape, irrespective of the values of temperature and aging time. The only restriction is that the curves are momentary creep curves, i.e., referring to creep tests of short duration compared with the previous aging time \( t << t_0 \).

Similar results were obtained for all other polymers. Incidentally, we found that for certain groups of materials, the resulting master curves have identical shapes. This is shown in Fig. 18, which includes results for a metal (lead). The meaning of this similarity of behavior between metals and plastics will be discussed below. In fact, the differences in shape of the two curves of Fig. 18 are only small. When they are superimposed and supplemented with data on PMMA and PPO, we obtain Fig. 19. The scatter around the master curve is about 2 percent.

These results show that the creep curves of all polymers have the same shape, at least in the aging range*. All individual creep curves can be derived from the master curve of Fig. 19, viz., by horizontal and vertical shifts.

Linear viscoelastic theory indicates that this result can be generalized. If the creep curves of all polymers have the same shape, then the same rule must hold for the stress-relaxation curves, the curves of dynamic modulus vs frequency, etc.

**DISCUSSION**

The Practical Importance of the Aging Effects

We can be brief about this (for a more detailed discussion, see (6)): the data given above have demonstrated that in the creep testing of plastics physical aging cannot be ignored. Figure 16 shows that it is indeed of little use.

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* Below the aging range, the shape of the creep curve depends on the specific structure of the material.
to measure the creep with an accurate instrument equipped with an accurate thermostat, if aging is not taken into consideration.

In addition, the methods for predicting long-term creep from short-time tests have to be revised. During long-term creep, say over 50 years, the creep is accompanied by simultaneous aging, and this fact has to be accounted for in the prediction method. For the case of small-strain creep and stress relaxation, such revised methods have been developed and tested; they will soon be published.

On the other hand, the finding that all polymers behave similarly (see above) implies that the testing of plastics can be considerably simplified.

Effects of Aging on Other Properties of Plastics
The present paper has been confined to aging effects on the small-strain properties after a simple thermal history, viz., a quench. How aging proceeds after more complicated thermal histories, or at large stresses (nonlinear creep, yielding, impact) has also been investigated; the results will be published in the near future.

Work on the electrical properties of plastics has been initiated. Aging effects which seem to be similar to those in the creep properties have been found in the low-frequency dielectric properties (4, 23).

Aging in Polycrystalline Metals
At high temperatures and very small strains, the creep in metals is supposed to be due to vacancy diffusion (24). Furthermore, the equilibrium concentration of the vacancies is temperature dependent.

Obviously, there is some similarity between this picture and the free-volume picture developed above. This prompted us also to study the aging in some metals. We had to select metals with a low melting point because our present instruments, being designed for tests on plastics, can only be used to temperatures of about 300°C. An example of the results is given in Fig. 20, which shows that lead ages in just the same way as PVC and sugar. Similar results were obtained for Wood’s metal and for tin.

The General Creep Equation and the Similarity Between Plastics and Metals
A simple formula describing the master curve of Fig. 19 is the following:

$$J(T) = J_o e^{t_0 m}; m \sim 1/3$$  \hspace{1cm} (5)

In this formula, $J(t)$ denotes the creep compliance whilst $J_o$ and $t_o$ are the vertical and horizontal shift factors which depend on temperature, aging time, and the type of material. The exponent, $m$, however, is always the same, i.e., equal to about $1/3$.

This empirical formula goes back to Kohlrausch (1866), who applied it to the creep of glass and even once thought it to be the universal formula for creep (compare Leuderman (25)).

An exploration for Eq 5 has not yet been found. However, its wide applicability (plastics, sugar, lead) suggests that the creep mechanism in polymers must be of a very general nature. It is not primarily determined by the specified chemical structure of the polymer (all polymers behave in the same way), nor by the polymeric structure (PVC behaves like sugar), nor by the glassy structure (PVC behaves like lead). Possibly, Eq 5 describes the general phenomenon of how a solid material, below its softening point, gradually loses its rigidity and begins to become a fluid.

A similar generality of behavior has been found by Kubat (26). He measured the stress relaxation of various polymers (synthetic and natural) and metals. On a

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**Fig. 19.** As Fig. 18 but, now, the results obtained for all materials are superimposed.

**Fig. 20.** Torsional creep of lead at very small strains (<0.004 percent). The sample was cast in a mold and then rapidly cooled to 20°C. After being placed in the creep tester, the specimen was rapidly heated to 180°C, kept at that temperature and tested for creep at $t_s$ of 1.5, 3, 6, and 22 hrs. The master curve was obtained as described in the caption to Fig. 3.
logarithmic time scale, the stress relaxation curve appears to be sigmoidal, the maximum slope being given by:

\[ F = \left\{ -\frac{d\sigma}{d \ln t} \right\}_{\text{max}} = A(\sigma_0 - \sigma_a) \quad (6) \]

in which \( \sigma \) is the stress, and \( \sigma_a \) and \( \sigma_0 \) the values of \( \sigma \) for \( t = 0 \) and \( t = \infty \).

For a wide range of materials, the constant \( A \) turned out to be equal to about 0.1, and at least for the small-strain behavior, this result can also be derived from our general creep equation. This can be converted (27-30) into a stress-relaxation formula. As a first approximation, we get:

\[ \sigma(t) = \sigma_0 e^{-\alpha t \omega^m}; m \sim 1/3 \quad (7) \]

For the maximum slope we find:

\[ F = \frac{m}{e} \sigma_a \sim 0.12 \sigma_a \quad (8) \]

Since in our case, \( \sigma_a \) is zero (see Eq 7), Kubat's formula reduces to

\[ F \sim 0.10 \sigma_a \quad (9) \]

Obviously, the two results agree reasonably well, and therefore support each other.

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