Prediction of Stress-Strain Relationships in Glassy and Crystalline Polymers

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ABSTRACT: A scheme is introduced for generating a stress strain curve at any constant strain rate, temperature, pressure, in tension, shear or compression, and the annealing history, from a set of experimental stress-strain data by parametric scaling. The parameters are determined for each polymer empirically first, but their study reveals much in terms of the structure-properties in glassy and crystalline polymers.

KEY WORDS   Viscoelasticity / Polymer Glass / Crystalline Polymers / Physical Aging / Stress-Strain Curves / Relaxation in Solids / Polymeric Solids / Viscoplasticity / Yield Phenomena / Time-Temperature Scaling Factor /

The primary object of this work is to introduce a scaling scheme for generating a stress-strain curve of polymeric solids at any strain rate, temperature, pressure, in tension, shear or compression, and the annealing history, from a set of stress-strain data stored in file. The scaling procedure is simple, but the physical reasoning for why it works can be complex.

THE STRAIN RATE DEPENDENCE

In the simplest case of linear viscoelastic behavior with a single relaxation time, τ, *i.e.,*

$$E(t) = E_0 \exp(-t/\tau) \qquad (1)$$

where $E(t)$ is the relaxation modulus, and E_0 is the initial elastic modulus. If we now consider a special case where the strain is made to increase at a constant rate, $\dot{\varepsilon}$, then the superposition principle is used to obtain the stress-strain relationship:

$$\sigma(\varepsilon) = E_0 \dot{\varepsilon}\tau(1 - \exp(-\varepsilon/\dot{\varepsilon}\tau)) \qquad (2)$$

where $\dot{\varepsilon}$ is the strain rate. The stress-strain curves calculated with various $\dot{\varepsilon}$ from eq 2 are shown in Figure 1, which exhibit the following two important features: (1) that increasing either the strain rate, $\dot{\varepsilon}$, or the relaxation time, τ, by the same multiplication factor will result in the identical stress-strain curve,

and (2) that by varying $\dot{\varepsilon}$ or τ, the stress-strain curve will grow or shrink both in the horizontal and vertical directions by the same amount, maintaining the same congruent shape as shown.

Glassy polymers, which neigher are linearly viscoelastic nor exhibit a single relaxation time, nevertheless exhibit stress-strain curves with both of the above two features, as evident from the curves for poly(vinyl chloride) shown in Figures 2 and 3. There are two major differences between the experimental curves of Figures 2 and 3 and the theoretical single relaxation curves of Figure 1. The first of these differences is that the "size" of the stress-strain curve in Figure 1 grows proportionately with the strain rate whereas the size of the experimental curve grows in the manner much less sensitive to a change in the strain rate, such as to some power, n, of the strain rate, with n being less than 1. Secondly, the curves in Figure 1 asymptotically approach the respective horizontal lines, whereas the experimental curves undergo the stress maximum.

The first of these major differences, *i.e.,* the linear *vs.* the less pronounced dependence of stresses and strains on the strain rate, is the consequence of the differences between a single *vs.* broadly distributed relaxation times. With real polymers, the time dependence of stress relaxation or creep is known to be much more gradual than can possibly be repre-
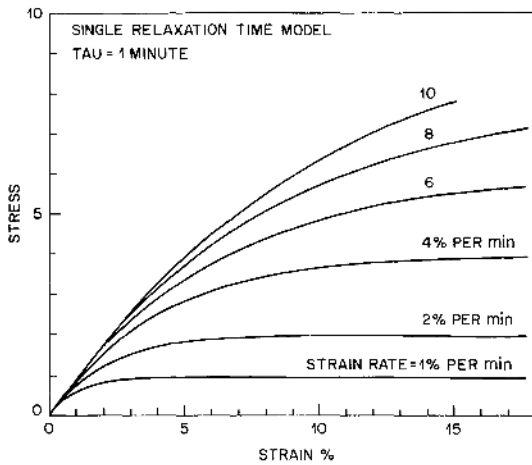
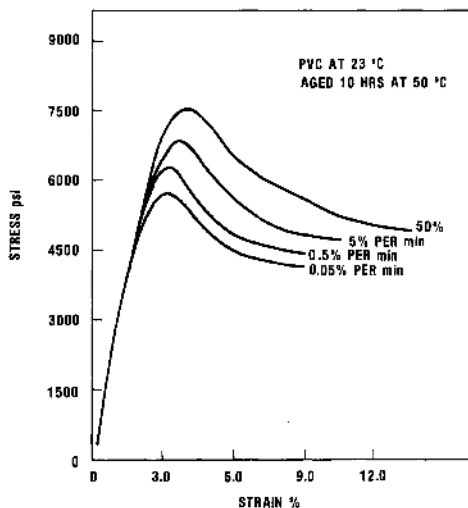**Figure 1.** Stress-strain curves for linear viscoelastic single relaxation time.

Figure 2. Stress-strain curves for poly(vinyl chloride) with various strain rates.

Figure 3. Stress-strain curves for poly(vinyl chloride) at various temperatures.

sented with a single relaxation time, manifesting a broad distribution of relaxation times. To represent such a spread in the distribution of relaxation times, the technique of substituting the time by the power of time is often used.

For example, the relaxation modulus in eq 1 is replaced by the so called "power law":

$$E(t) = E_0(t/t_0)^{-n} \quad \text{for} \quad t \geq t_0 \quad (3a)$$
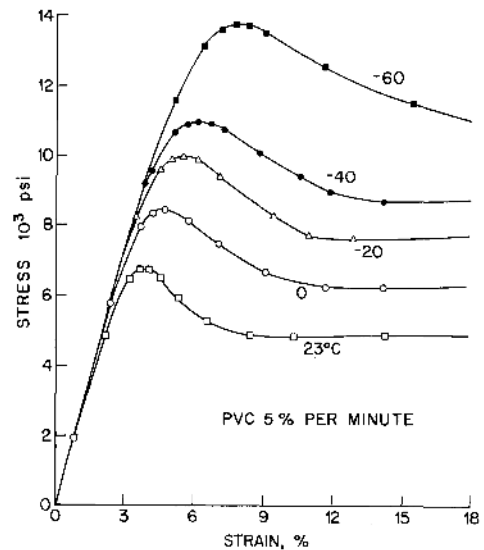
$$E(t) = E_0 \quad \text{for} \quad t < t_0 \quad (3b)$$

where n is an empirically determined number of less than unity. This form of approximation is good only for a limited time range, and never intended for use near $t = t_0$. The power law has been used for a variety of polymers in creep and relaxation analyses (Shapery,[12] Findley[4]), and in fact we will show that the power law works well with semicrystalline polymers with the amorphous regions in the rubbery state. The analytical models of Rouse[11] and Zimm[16] for the relaxation function of polymers in solution lead to the power law with $n = 1/2$ and $2/3$ respectively, and have been extended to polymer melts.[3]

The broad distribution of relaxation times has long been recognized by the workers concerned with dielectric relaxation phenomena.[1] The dynamic dielectric permittivity J^* with single relaxation time, τ:

$$J^* = J_\infty + \Delta J/(1 + j\omega\tau) \quad (4)$$

has been modified by Cole[2] into the form, known today as the Cole–Cole formula:

$$J^* = J_\infty + \Delta J/[1 + (j\omega\tau)^n] \quad (5)$$

to account for the distribution of relaxation times, where J_∞ is the limiting (unrelaxed) permittivity at the high frequency and ΔJ is the permittivity difference between the relaxed and unrelaxed values. ω is

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the circular frequency in radians, and n is an empirically determined number similar to n in eq 3.

The Cole–Cole formula, and others like it such as the Fuoss–Kirkwood and Cole–Davidson formulas, represent the spectrum of widely distributed relaxation times by essentially substituting the $(\omega\tau)$ term with the $(\omega\tau)^n$ term. We can follow a similar procedure in modifying the stress-strain equation for the single relaxation time in eq 2 by replacing the $(\dot{\varepsilon}\tau)$ term by $(\dot{\varepsilon}\tau)^n$ term to obtain:

$$\sigma(\varepsilon) = E_0(\dot{\varepsilon}\tau)^n\{1 - \exp[-\varepsilon/(\dot{\varepsilon}\tau)^n]\} \qquad (6)$$

The plot of this equation would have the same appearance as in Figure 1, but the "size" of the curves is proportional to ε^n instead of $\dot{\varepsilon}$. Thus, this is equivalent of a power law represention for the linear viscoelastic stress-strain curves with a distribution of relaxation time. The stress strain curves for poly(vinyl chloride) shown in Figure 2, though different in shape from these curves by the presence of the stress maximum, also can be *scaled* up or down by the factor $(\dot{\varepsilon}\tau)^n$ in the same way as with eq 6, with the value of $n \approx 0.04$. This value of n is in general nearly equal to the value of n in the power law of eq 3, or the negative slope of the $\log E(t)$ *vs.* $\log t$ plot.

While the power law is a fairly good approximation for many polymeric glasses at temperatures well below T_g, where the values of n typically range from 0.02 to 0.04, such as shown for polycarbonate at 23°C in figure 4a, it is not a good approximation at elevated temperatures, such as those shown in Figure 4b for polystyrene at 58 and 90°C. Another type of formula that will approximate curves which bend downward with the progress of time is clearly needed. An empirical form which can describe such a form has been introduced by Williams and Watts[15] and known by their names:

$$E(t) = E_0 \exp[-(t/\tau)^\beta] \qquad (7)$$

It is a two parameter equation which in fact approaches the power law when $\tau \gg t$, or when β is very small.

The slope of the logarithmic relaxation modulus *vs.* log time curve can be shown to be

$$d \log E(t)/d \log t = -\beta\left(\frac{t}{\tau}\right)^\beta \qquad (8)$$

and it is equal to β when $t = \tau$, as when $T \approx T_g$, and when t/τ is very small, it becomes more nearly
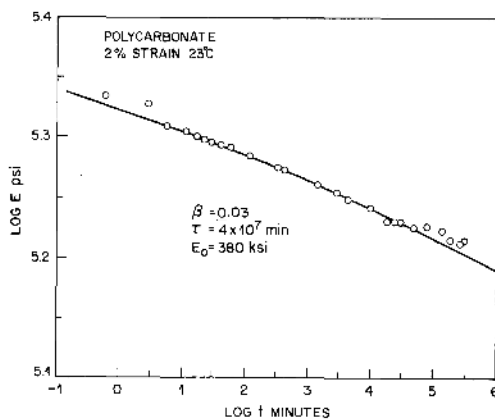

Figure 4a. Experimental relaxation modulus for polycarbonate at room temperature fitted with Williams–Watts formula, eq 7 with $\beta = 0.03$.
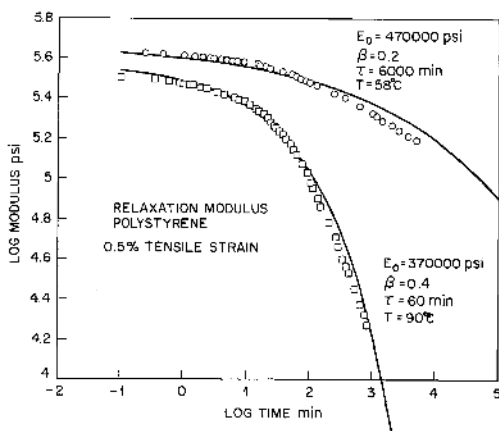

Figure 4b. Relaxation modulus of polystyrene at 58 and 90°C; both experiments were started after waiting for 15 h at respective temperatures.

constant over a greater time range.

Thus, the Williams–Watts formula is clearly preferable to the power law particularly for the creep[13] and relaxation of glassy polymers near the T_g where the effect of physical aging is often studied. If we redefine the parameter, $-n$, as the slope of the $\log E$ *vs.* lot t plot:

$$-n = -\beta\left(\frac{t}{\tau}\right)^\beta \qquad (9)$$

the power law may be considered as a speical case of the Williams–Watts formula where n is constant.

At a first glance, then, the Williams Watts formula might seem to work well not only in approx-
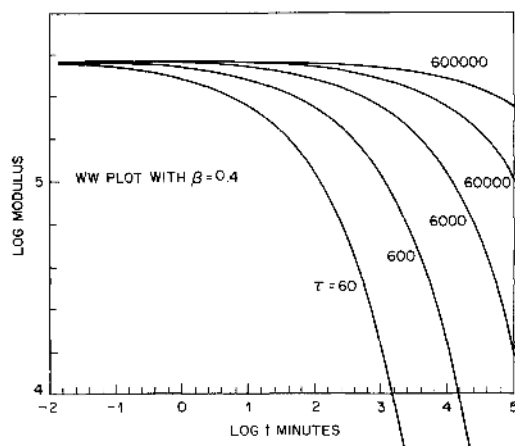
Figure 5. Relaxation modulus with Williams–Watts formula, eq 7, with $\beta = 0.4$.

Figure 6. Stress-strain curves calculated with the non-linear equation mentioned in the text.

imating the widely differing shapes of the curves over the temperature range, but also in approximating the effect of temperature on the shape of the relaxation curves through the variation only in the parameter τ without changing β. If this were in fact possible, the Williams–Watts formula would indeed have been considered as a simple but valuable bridge between structure and properties of glassy polymers. Unfortunately, we find that both τ *and β* must be changed with temperature in order to fit the data. In Figure 5 the curves are plotted using the Willams–Watts formula with $\beta = 0.4$ for various values of the parameter τ. This value of 0.4 for β has been frequently quoted for dielectric and mechanical relaxations near T_g (both above and below T_g), including our data for polystyrene at 90°C shown in Figure 4. The value of $\tau = 60$ minutes seems reasonable with the "average" relaxation times near but below T_g, although much discussion would have to be involved on what significance this value of τ might have. The main point here on these curves are not on the physical significance of the numerical values of τ but on the fact that the variation of τ alone in the Williams–Watts equation cannot produce a good fit to the relaxation data obtained at a much lower temperature such as the curve shown in Figure 3 for polycarbonate at 23°C. Rather, both τ *and β* must be changed with the temperature. The values of τ for many glassy polymers have been found to follow the Arrhenius type dependence with the activation enthalpy of 30 to 50 kcal. The value of β typically is reduced by one order of
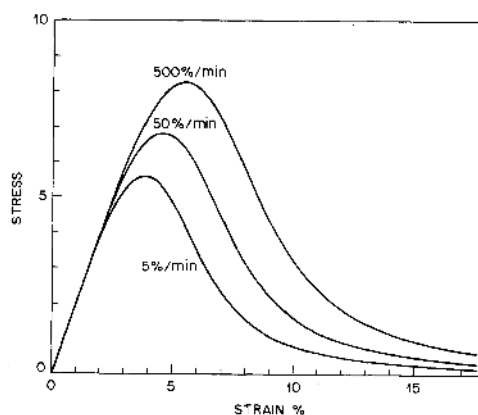
magnitude from $T \approx T_g$ to $T \approx T_g - 100°C$. The temperature dependence of both β and n suggests that the distribution of relaxation times becomes broader as the glassy state is removed further from the equilibrium state. The temperature dependence of the quantity n will be discussed further in the subsequent section.

The value of n can be determined empirically by comparing the stress-strain curves obtained at two different strain rates. It can be assumed to be nearly independent of $\dot{\varepsilon}$, but more precise value of n can be obtained by multiplying n by $(\dot{\varepsilon}/\dot{\varepsilon}_0)^n$.

While a linear viscoelastic formula such as eq 6 has been shown to enable one to predict the strain rate dependence of the stress-strain relationship for glassy polymers, such an equation cannot describe curves which undergo the stress maximum. In fact, the linear viscoelastic behavior precludes the existence of a maximum in stress because the tangential modulus, $d\sigma/d\varepsilon$, for the stress-strain curve, is equal to the relaxation modulus, $E(t)$, which cannot be a negative value. It is not intended to elaborate on the derivation of a stress-strain equation based on nonlinear viscoelasticity here. However, such an equation can be derived easily in the case where β is small, as with glassy polymers near the room temperature.

The calculated stress-strain curves are shown in Figure 6. The experimental curves will not continue to decrease as are shown by these calculated curves, because the "drawing" phenomenon intervenes where a steady state constant stress is maintained as the "drawn" portion is propagated throughout the

sample. The scaling law for the strain rates, $(\dot{\varepsilon}/\dot{\varepsilon}_0)^n$, apparently still applies to the stresses while the sample is in the drawing mode. Thus the entire stress-strain curve including the drawing portion can be scaled from one strain rate, $\dot{\varepsilon}_0\tau$, to another strain rate, $\dot{\varepsilon}\tau$, by the scaling factor, $(\dot{\varepsilon}/\dot{\varepsilon}_0)^n$. A question arises then whether β or n would remain small as the strain is increased and the relaxation times is reduced. If in fact β or n did depend on the strain, and if in fact the distribution of relaxation times did revert back to that of near T_g, i.e., $\beta \approx 0.4$, then the stress-strain curves would not have obeyed the congruency rule and in fact the simple scaling rule being introduced here would have failed.

The experimental relaxation and creep data show that the value of n remains constant nearly up to the yield strain, but unfortunately no data exist at the levels immediately beyond the yield. However, at the room temperature, the stress-strain data beyond the yield in the steady state elongation regime, where the necking is taking place, show that n is the same low value as were before the yield, and not a large value such as 0.4. Thus the flat shape of the relaxation spectrum is most likely maintained independently of the stress or strain levels at a given temperature. This steady-flow stress, such as observed in PVC in Figures 2 and 3 can also be scaled by the same scaling factor, which will be shown below. Thus, one parameter scaling scheme can be applied to the entire stress-strain curve including the regime of elongation-by-necking. We have used the engineering stress, i.e., the force divided by the initial zero-strain cross sectional area for all tensile data. The scaling factor, being empirical in origin, can include the change in the cross-sectional area with the change in the strain or the temperature. The effects from the nonuniformity in strain throughout a tensile test specimen is also built into the scaling factor and, as long as the pattern of the distribution of the strain remains unchanged, this scaling scheme will automatically include such an effect and will predict a realistic stress-strain relationship under widely varying conditions.

Scaling Rule No. 1 Strain Rate Effect for Glassy Polymer

To obtain a stress-strain curve at a strain rate $\dot{\varepsilon}$ from the stress-strain data obtained at $\dot{\varepsilon}_0$, multiply each stress and strain by $R_1 = (\dot{\varepsilon}/\dot{\varepsilon}_0)^n$, where n is either experimentally determined or calculated from

Table I. Parameters for scaling of stress-strain curves. The notations are given in the text

Polymer	T_c °C	n_0	H kcal	Crystalline C or glassy G
ABS	170	0.0287	41.5	G
Polystyrene	176	0.0250	45.8	G
Polycarbonate	217	0.027	33.4	G
Polyethylene (high density)	145	0.080	25.4	C
Polyethylene (low density)	120	0.050	48.0	C (G, $T < -35°C$)
Polypropylene	170	0.060	29.7	C (G, $T < 0°C$)
NORYL	160	0.032	40.0	G
PVC	100	0.037	45.5	G
Nylon	190	0.076	21.6	C (G, $T < 20°C$)
Polysulfone	295	0.025	23.8	G
PBT	110	0.048	42.0	G (C, $T > 85°C$)

n_0, tabulated for many polymers in Table I.

TEMPERATURE DEPENDENCE OF STRESS-STRAIN CURVES

The congruency of the stress-strain curves for PVC in Figure 3 with the temperature as the parameter turns out to be a typical feature for many glassy polymers. The congruency means that the stress and strain will increase or decrease by one scaling factor. The temperature dependence of the relaxation process in glassy polymers is complicated because of the temperature dependence of the distribution of relaxation times, and also because of the effects of the thermal history. There is no doubt, however, that the relaxation processes in glassy polymers are temperature dependent even if the free volume (or the fictive temperature) is deliberately kept constant through the controlled manipulation of their thermal history. We have found (Matsuoka[7]) that the temperature dependence of the ageing rate for the iso-free volume nonequilibrium polymeric glasses is of the Arrhenius type with a constant activation enthalpy of ca. 35 kcal. Superimposition of this Arrhenius process over the Williams–Landel–Ferry equation for the free volume[3] has been successfully applied to the analysis of the ageing process and the shift in mechanical and dielectric relaxation spectrum for several polymeric glasses. It is a curious fact that the

Arrhenius term disappears above T_g in the equilibrium state, whereas below T_g the free volume form of the Williams–Landel–Ferry (WLF) equation *without altering* the coeffcients must be applied together with the Arrhenius term to fit the data. Thus it must be concluded that the Arrhenius term arises only when the rate of rearranging the conformations is severely impaired. Empirically, the emergence of the Arrhenius term and the temperature dependence of the distribution of relaxation times are coincidental at T_g, and continued to persist at lower temperatures. This is probably related to the nature of the β process in glass. Taking all of these bits of information about the glassy polymer, we can assume that the dependence of the relaxation process in a polymeric glass can be separated into the history dependence and the temperature dependence. The history dependence is expressed by the free volume, the excess entropy, or the fictive temperature. This aspect will be discussed in detail in the later section. At present, we will be concerned with the glassy polymer with the exactly equivalent thermo-mechanical history. The temperature dependence of the relaxation process in such a polymer is described by the Arrhenius equation:

$$\ln \frac{\tau}{\tau_0} = \frac{H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{10}$$

where R is the universal gas constant, τ and τ_0 are the relaxation times at temperatures T and T_0 K, and H is the enthalpy of activation.

The contribution from the temperature variation towards the stress-strain curve, then, is described by the equation for the scaling factor R_0:

$$R_0 = \left[\frac{\dot{\varepsilon}}{\dot{\varepsilon}_0}\right]^n = \exp n \frac{H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) \tag{11}$$

where $\dot{\varepsilon}$ in this case is the *equivalent* strain rate at T_0, when in fact the strain rate of $\dot{\varepsilon}_0$ was employed at T. Thus the logarithm of the scaling factor is proportional to n and $1/T$, or

$$\ln R_0 = \ln\left[\frac{\sigma}{\sigma_0}\right] = n\frac{H}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right] \tag{12}$$

It is evident from eq 12 that the only way that n can remain independent of temperature is for the equivalent stress between the two curves, such as the corresponding yield stresses, to depend on the temperature in the Arrhenius manner. Experimental data point out that such is not the case, but far from
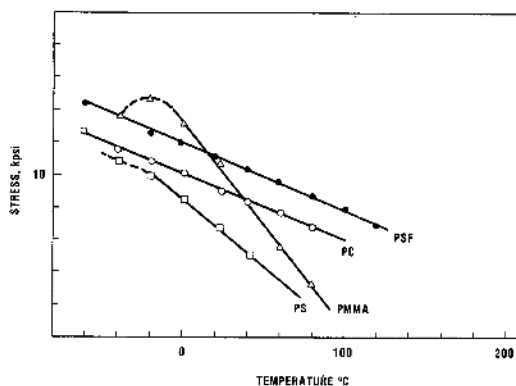

Figure 7. Yield stress at 5%/min *vs.* T for glassy polymers.

it. From the experimental curves of Figure 3, and many more to follow, the maximum or the yield stress is found to decrease in proportion to the negative of the temperature, following the equation:

$$R_0 = \left[\frac{\sigma(T)}{\sigma(T_0)}\right]_{\dot{\varepsilon}_0} = \frac{T_c - T}{T_c - T_0} \tag{13}$$

where T_c is an empirically derived temperature at which the yield stress at strain rate of $\dot{\varepsilon}$ is extrapolated to reduce to zero. This is shown in Figure 7 for four glassy polymers.

Equation 13 above can be derived if the stress is to reduce the free energy of activation for the relaxation process, following the concept of the rate process, or

$$H - T_0 S = H - C\sigma - TS \tag{14}$$

where C is an empirical constant. The above formula implies that at temperature T, the addition of the stress σ will cause the material to flow in the manner possible with an infinitesimally small stress at temperature T_c. The straight line relationship as dictated by eq 13 is supported by the plot for several glassy polymers shown in Figure 7. T_c is higher than T_g by about 30°C. When T_c and n at T_0 are empirically determined, the activation enthalpy can be evaluated from the formula:

$$H = \lim_{T \to T_0}\left[\ln\frac{T_c - T}{T_c - T_0} \Big/ \frac{n}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$$

and

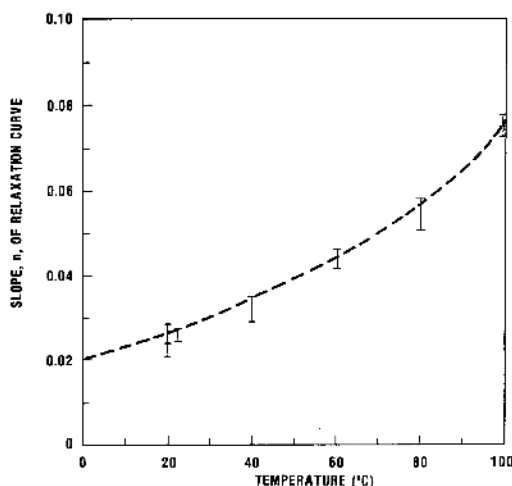$$H = \frac{RT_0^2}{T_c - T_0}\frac{1}{n_0} \tag{15}$$

Figure 8. Temperature dependence of parameter n for polycarbonate obtained from creep data.

as obtained by combining eq 12 and 13 and utilizing l'Hospital's rule, where n_0 is n at T_0, and the temperature must be in Kelvin degrees. The temperature dependence of n can now be determined from the formula:

$$n = \frac{RT^2}{H(T_c - T)} \qquad (16)$$

by the similar method. The temperature dependence of n has been obtained from creep data for polycarbonate and shown in Figure 8 for polycarbonate. The dotted line represents eq 16, and agrees well with the data. These parameters for many polymers are shown in Table I. Crystalline polymers have been included in the table. It turns out that the stress-strain curves of crystalline polymers are sharply different from those of glassy polymers, as neither the congruency of the stress-strain curves nor the temperature dependence of eq 13 is observed. However, many basic features of the scaling technique described here-to-fore on glassy polymers are applicable to crystalline polymers and, as it will be shown subsequently, the scaling of the nonlinear viscoelastic stress-strain curves for crystalline polymers is also possible. One very interesting aspect of data shown in Figure 8 is that each value of n at a given T can be obtained from n_0 at adjacent T_0 by the formula, $n = n_0 \exp(n_0 H(1/T_0 - 1/T)/R)$. This is another evidence that β for the Williams–Watts formula *must* change with the temperature.

The value of n can be refined by multiplying itself by the quantity, $(\dot{\varepsilon}/\dot{\varepsilon}_0)^{-n}$, or

$$n = \frac{RT^2}{H(T_c - T)} \left(\frac{\dot{\varepsilon}_0}{\dot{\varepsilon}} \right)^n \qquad (16')$$

which is equivalent to the Williams–Watts formula instead of the power law.

Scaling Rule No. 2 Temperature Effects on Glassy Polymer

To obtain a stress-strain curve at temperature T from the curve obtained at T_0, multiply each stress *and* strain by $R_0 = (T_c - T)/(T_c - T_0)$ where T_c is tabulated for several polymers in Table I. The parameter n is calculated from eq 16: $n = RT^2/H(T_c - T)$. The values of H, the activation enthalpy, for glassy polymers are similar, *ca.* 30 to 45 kcal. This is approximately the value involved in the physical aging process as measured by the decrease of volume or enthalpy as well as in the dielectric relaxation process in glassy polymers with equivalent thermal histories.

As the reader probably has recognized, the scaling technique is recommended to be centered around the room temperature. The reason for this is a practical one; the region where the most accurate prediction is needed is around the room temperature. However, because the emphasis has been placed on the room temperature behavior, the accuracy in the extrapolation to a temperature near T_g is sacrificed. If such a requirement should arise, the stress-strain data must be obtained at different strain rates at or near that temperature, and the values of Table I will be altered, in some cases substantially.

If T_g is taken as the reference temperature, then

$$\ln\left(\frac{\tau}{\tau_g} \right) = \frac{H}{R} \left(\frac{1}{T} - \frac{1}{T_g} \right) \qquad T < T_g \qquad (17)$$

and by combining with eq 11, sufficiently accurate stress-strain curves may be obtained in this temperature range. However, it must be cautioned that in this temperature range, the relaxation process is markedly influenced by the thermal aging, and a proper account must be taken following the procedure which will be explained in a subsequent section.

The stress-strain curves for polysulfone are shown in Figure 9. The lines are calculated utilizing the appropriate scaling procedure. This glassy poly-
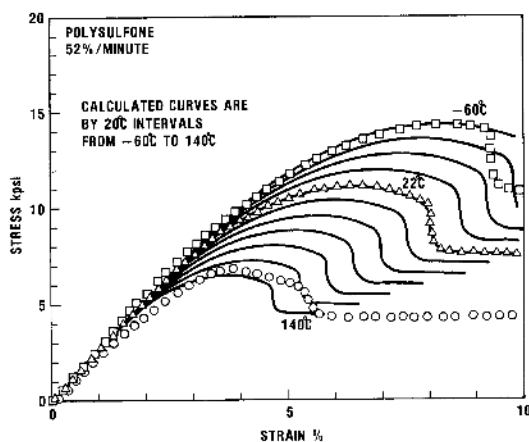
Figure 9. Stress-strain curves for polysulfone calculated by the scaling rule. Experimental points at only two extreme temperatures are shown, but all data in the intermediate temperatures agree with the curves.
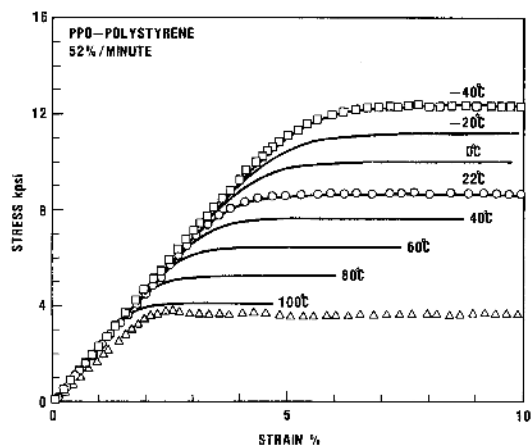

Figure 10. Similar plots for poly(phenylene oxide)–polystyrene mixture as Figure 9.
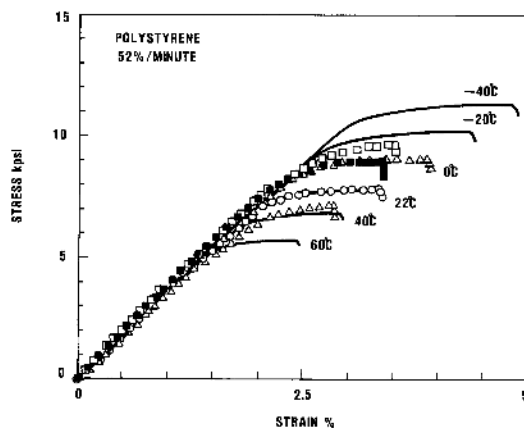

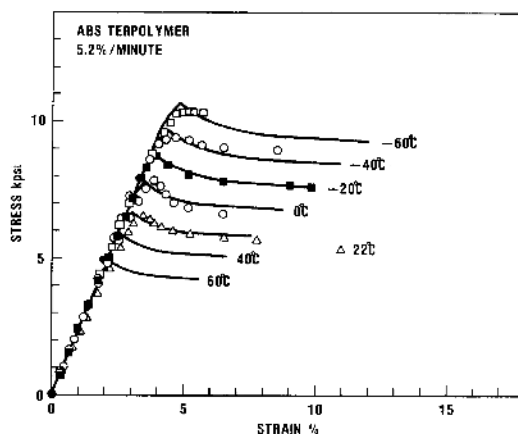Figure 11. Similar plot for polystyrene as Figure 9.

Figure 12. Stress-strain curves for ABS terpolymer with polybutadiene as the rubbery phase spheres dispersed in the glassy matrix. They behaves more like a glassy polymer than the two components typified by the crystalline polymer.

mer exhibits the viscoelastic behavior qualitatively very similar to polycarbonate, but it is less temperature dependent and the yield strain at the room temperarure is about the same as that of polycarbonate in spite of the fact that its T_g and T_c are both substantially higher. The stress-strain curves for the solid solution of poly(phenylene oxide) and polystyrene are shown in Figure 10. Similar curves for polystyrene are shown in Figure 11. These curves do not undergo a maximum in the stress, but they appear more like the linear viscoelasticity with eq 6, and go into the steady plastic flow process at yield. The essential features for the scaling rule are all

present, and the curves at various temperatures can be quite accurately reproduced from the 22°C curve by scaling with the parameters included in Table I.

We have not touched upon the subject of brittle failure. The brittle failure is less favored when the molecular weight of the polymer is higher, and whether brittle or ductile failure will ensure at a given strain rate at a given temperature can be established by another scaling rule incorporating the molecular weight and the critical stress. At a higher strain rate and/or for a lower molecular weight, the brittle failure will occur at a higher temperature. This will be discussed in the appro-

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priate chapter of this volume dealing with the time-history and temperature-dependent failure processes.

The stress-strain curves for an acrylonitrile-butadiene styrene system known as ABS are shown in Figure 12. The structure of this polymer composite is well known, that the rubbery polybutadiene spheres with acrylonitrile grafted skin are dispersed in the matrix of glassy acrylonitrile-styrene copolymer. The features of the stress-strain curves are basically those of a homogeneous glassy polymer, and as it will be shown, very different from a composite of hard and soft components exemplified by the semicrystalline polymers with a rubbery amorphous phase. However, the threshold of the brittle failure behavior is substantially extended toward the lower temperature as compared to unmodified styrene acrylonitrile copolymer of comparable molecular weight.

STRESS-STRAIN BEHAVIOR IN SHEAR

The microscopic shear deformation can be thought of as a combination of microscopic tensile and compressive components. The tensile component tends to shorten the relaxation time rapidly and accelerates the process further. The compressive component cannot easily lengthen the relaxation time when the latter is already too great for the given strain rate, and only responds reversibly and elastically. Thus the overall relaxation time under shear is predominantly determined by the rapidly shifting tensile component. The shift of the relaxation time in shear, as it will be shown, can be calculated if the shift due to the tensile deformation is known. Actually Robertson's model[9] for the strain-induced shift in the relaxation time can be identified with this concept on the molecular level.

The nonlinear viscoelastic stress-strain behavior at constant strain rates can be conveniently thought of as a nonlinear *elastic* behavior dealing with strain as the sole variable, for the conservative part of the viscoelastic deformation energy. For a conservative system, there is the elastic constitutive relationship:

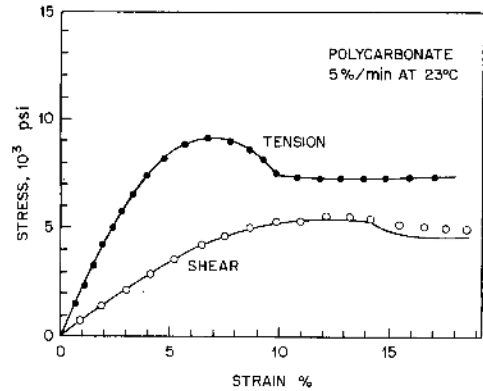$$\sigma = 2\mu\varepsilon + \lambda\varepsilon_{KK}\mathbf{1} \qquad (18)$$

Figure 13. Shear stress-strain curve is generated from the tensile data following the scaling rule for shear. Though slightly, the shear data also undergoes a maximum.

where "bold letters" denote a tensor notation, μ is the generalized secant modulus which depends on the strain and λ is the Lammé constant.* Rosenberg and Matsuoka[10] have shown that the introduction of the second invariant of the deviatoric strain

$$\Pi_\varepsilon = \frac{1}{2}\varepsilon_{ij}\varepsilon_{ij}$$

into the strain terms in eq 17 satisfies the energy requirements for the conservative component and because the following is true:

$$\Pi_\varepsilon^{1/2} = \frac{1+\nu}{\sqrt{3}}|\varepsilon_{11}| \qquad \text{tension} \qquad (19)$$

$$\Pi_\varepsilon^{1/2} = |\varepsilon_{12}| = \gamma/2 \qquad \text{shear} \qquad (20)$$

using the above pair of formulas, we can scale a tensile stress-strain curve to obtain a corresponding shear stress-strain curve by the following procedure:

(1) Multiply the tensile strain by the scaling factor, R_{sx}: $R_{sx} = 2(1+\nu)/\sqrt{3}$
(2) Multiply the tensile stress by the scaling factor, R_{sy}: $R_{sy} = 1/\sqrt{3}$
(3) Optionally, if the engineering stress-strain is used for tensile data, *i.e.*, the force divided by the *initial* area, then the tensile stress in (2) may be further *divided* by $(1-2\nu)$ (tensile strain).

The equivalence in the rates of strain in tension and

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* Note: λ is not a constant since we are dealing with a nonlinear case. However, the hydrostatic term is less important mechanically than the pressure effect entering as the thermodynamic intensive quantity and can be neglected in this case.

shear are established by the factor $2(1+v)/\sqrt{3}$ to correct the constant C, but this results in an error of order of 1% for the stress, hence it can be generally ignored. Figure 13 demonstrates how well the scaling scheme works for polycarbonate.

Scaling Rule No. 3 from Tension to Shear

Multiply the stress by R_{sy} and the strain by R_{sx} for all polymers.

CRYSTALLINE POLYMERS

Experimentally it is found that the stress-strain curves for crystalline polymers obtained at different strain rates and temperatures are not congruent.[14] This fact alone may seem to dash off any hope of generating a new and simple scaling rule comparable to that for glassy polymers. As it turns out, a scaling rule utilizing a different procedure works well with crystalline polymers. Although the congruency rule does not apply to the stress-strain curves for crystalline polymers at various strain rates and temperatures, the following features are applicable: (1) the stress levels increase with the power of strain rates, $\dot{\varepsilon}^n$, as were true for glassy polymers, (2) at the same time, the strains decrease with the negative power of strain rates, $\dot{\varepsilon}^{-n}$, *unlike* for glassy polymers, (3) the stress levels decrease linearly with $T(T_c - T)$ instead of $T_c - T$, as for glassy polymers, and (4) the values of n and H are about the same orders of magnitude as for the glassy polymers and are determined from experimental data in the similar manner as used for glassy polymers. Thus, the scaling of stress-strain data in crystalline polymers can be accommodated by multiplying the stress by R_1 and dividing the strain by R_1. In Figures 14 and 15 are shown examples of high and low density polyethylenes, one at one strain rate but at different temperatures, and the other at different strain rates but at the same temperature. In both cases, the lines drawn were actually calculated by scaling the stresses up by multiplying by R_1 but at the same time scaling the strains down by *dividing* by R_1. The stress-strain equation for glassy polymers where the congruency rule was observed to hold is *not* applicable to the crystalline polymers.

Although the effect of the temperature on the yield stress seems to be almost the same for crystalline polymers as for glassy polymers, a close exam-
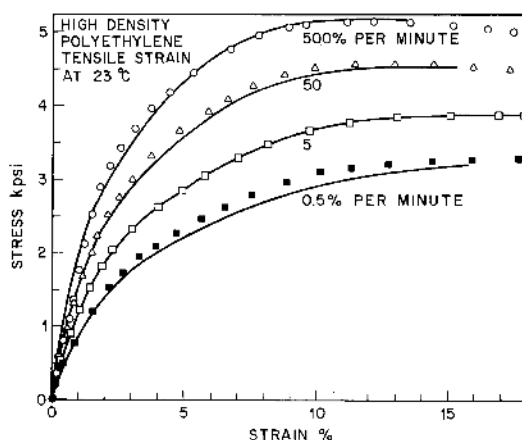

Figure 14. Stress-strain curves for high density polyethylene at various strain rates, fitted by the curves generated by the scaling rule for crystalline polymers.
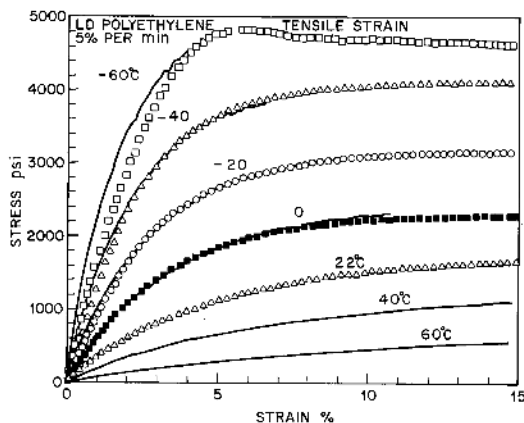

Figure 15. Stress-strain curves for low density polyethylene at various temperatures, fit curves generated by the scaling rule for crystalline polymers.

ination reveals that such is not the case. The yield stress for three kinds of crystalline polymers are plotted against the temperature in Figure 16. While such a plot was a straight line for the glassy polymer, these curves are definitely curved. When the data are plotted in a slightly different form, *i.e.*, $\sigma T/T_0$ *vs.* T, where T, T_0 are in degrees Kelvin, they become straight lines approaching the respective melting tempeature, T_m, as shown in Figure 17. Thus for crystalline polymers, the scaling factor R_0 is slightly different from eq 13, *i.e.*,

$$R_0 = \left[\frac{\sigma(T)}{\sigma(T_0)}\right]_{\dot{\varepsilon}_0} = \frac{T_0(T_c - T)}{T(T_c - T_0)} \qquad (21)$$
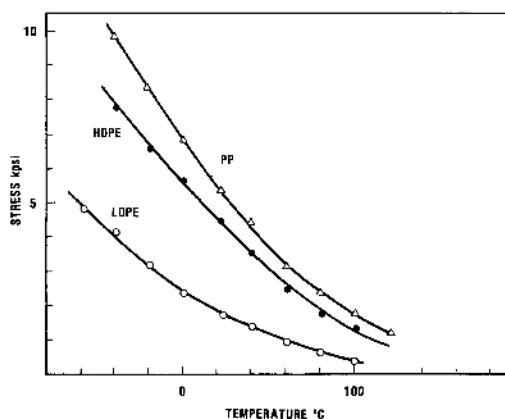
Figure 16. Temperature dependence of yield stress for crystalline polymers taken at 5%/min.
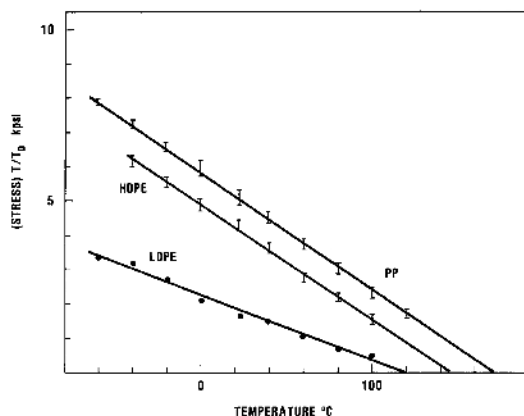

Figure 17. Replot of Figure 16 by multiplying the stress by T/T_0.

This formula can be derived if the stress will increase the activation entropy, *i.e.*,

$$H - T_c S = H - T(C_s \sigma + S) \tag{22}$$

where C_s is an empirical constant.

Similarly, from the empirically determined value of n_0 at T_0, the activation enthalpy H is determined by the formula:

$$H = \frac{R T_0 T_c}{n_0(T_c - T_0)} \tag{23}$$

and the temperature dependence of n is determined from the formula

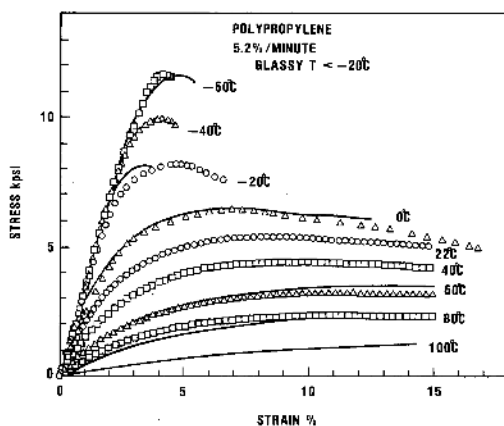$$n = \frac{R}{H} \frac{T T_c}{T_c - T} \tag{24}$$

Figure 18. Stress-strain data for polypropylene at various temperatures fitted (1) with the scaling rule for crystalline polymers above 0°C but (2) with the scaling rule for glassy polymers below −20°C.

T_c can be taken to be T_m, but our empirically determined values are shown in Table I.

The scaling factor $R_0 = T_0(T_c - T)/T(T_c - T_0)$ is used to multiply the stress and to divide the strain to scale from the data obtained at T_0 to the stress-strain curve at T. The temperature dependence of n is obtained from eq 24. Among all crystalline polymers we have studied in which the amorphous regions are in the rubbery state, $T > T_g$, this scaling rule has been found to apply. In the temperature and the strain rate range where the amorphous regions become glassy, the behavior reverts back to the model of congruency for glassy polymers, *i.e.*, the congruent stress-strain curves. T_g of polypropylene is observed at about 0°C by the specific heat measurement of 10°C min⁻¹. This transition is clearly observable in Figure 18 where the scaling formula for crystalline polymer was used above 0°C from data taken at 23°C, and the formula for glassy polymers was used for −20, −40, and −60°C curves based on the −40°C curve. When comparing various data obtained with different strain rates at 23°C, however, polypropylene behaves in a similar manner to the high and the low density polyethylenes, indicating the behavior typical of the crystalline rubber composites.

EFFECT OF PHYSICAL AGING ON VISCOELASTICITY

Polymer glasses typically undergo the physical

aging process accompanied by the decrease of volume, entropy, and enthalpy, during which time the dielectric relaxation spectrum can be observed to shift to the longer relaxation time. Although the thermodynamic treatment of the aging process is complex and the quantitative prediction for all types of history is difficult, a simple physical model can be followed to enable a sufficiently accurate prediction of the shift in viscoelastic functions due to the thermal history.[6] Kovacs[5] has shown that a free volume model such as is used in the WLF equation can be utilized in the formulation of the isothermal aging process following a sudden change in temperature from above to below T_g, i.e.,

$$-\frac{df}{dt} = kf \tag{25}$$

where f is the free volume fraction and k is the rate constant for the volume contraction. This rate constant is a rapidly diminishing function of the free volume fraction, and, in fact, it is within the magnitude of the reciprocal of the characteristic dielectric relaxation time, τ, i.e.,

$$\tau = \tau_0 \exp(1/f - 1/f_0) \tag{26}$$

where the subscript 0 denotes some reference time during the steady state contraction process. As the volume continues to contract during aging, τ continues to grow greater. Now, the rate of increase of τ is given, from eq 25 and 26, by

$$\frac{d}{dt}\left(\frac{1}{k}\right) = \frac{d\tau}{dt} = \frac{1}{f} \tag{27}$$

Since f is in the order of 10^{-2}, eq 25, 26, and 27 are approximately satisfied if

$$\frac{\tau}{t} = \frac{1}{f} - 1 \tag{28}$$

from which follows

$$\frac{d\log\tau}{d\log t} = \frac{1}{1-f} \approx 1 \tag{29}$$

The slope of $\log\tau$ vs. $\log t$ plot will eventually become nearly 1, provided that (1) the time t must become an oder of magnitude greater than the initial relaxation time, τ_0, to satisfy the steady state condition and (2) that the tempeature must not be near T_g where the glassy system is near equilibrium. If either of the above two conditions is not met, the slope of the $\log\tau$ vs. $\log t$ plot will be less than 1.
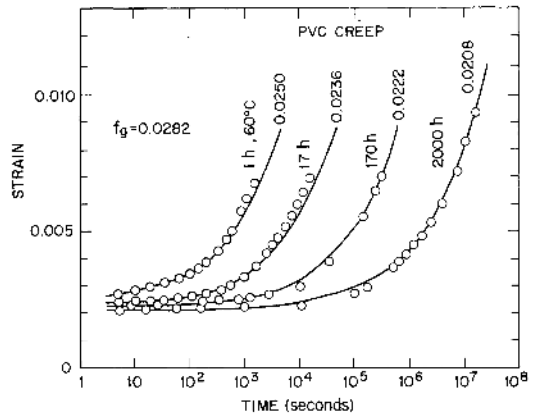

Figure 19. Creep data for PVC after aging for different periods of time. The parametric numbers are the fractional free volume at start of creep experiments, respectively.
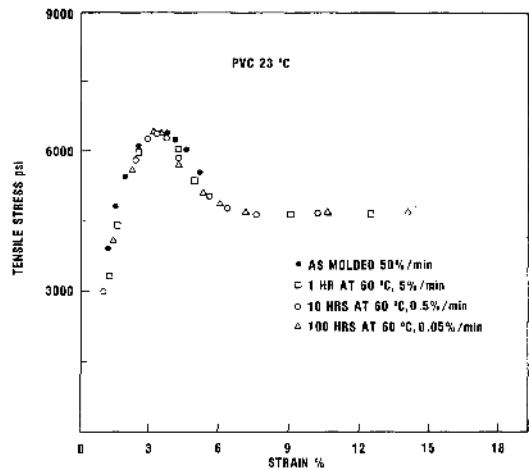

Figure 20. Stress-strain curves for PVC samples. Each aged one decade longer is superimposed when each test was conducted at one decade slower strain rate.

The distribution of relaxation times, perhaps due to fluctuations, is a topic of interest to many polymer physicists but will not be discussed here. The distribution itself would not change the relationship of eq 29, but the extreme components of τ will affect it.

The typical result is obtained following eq 29, expressing the rule that a decade increase in the logarithmic time for aging will increase the characteristic relaxation time by a decade. This is clearly denonstrated by the creep curves shown in Figure 19. A series of creep experiments were conducted at 60°C for poly(vinyl chloride), each following a

different time of aging, varied by about a decade, at the same temperature. It can be observed that an increase of logarithmic aging time by one decade will shift the creep curve by one decade, *i.e.*, the shift factor, or the logarithmic ratio of relaxation times to the time spent for aging, is unity as described by eq 29.

The effect of physical aging on viscoelastic stress-strain curves is illustrated in Figure 20 where the stress-strain curves of samples having undergone various thermal histories are compared. Curves were picked among the PVC stress-strain curves run at 23°C after having undergone the exposure to 50°C for 1, 10, and 100 h, with the strain rates of 5, 0.5, and 0.05%/min, respectively. They all superimpose on top of each other. The curve for the "as-molded" sample, run at 50%/min, also superimposed on top of the others. This graph clearly supports the rule described by eq 29 for the relaxation time and the aging time to be proportional to each other. As already pointed out, however, the aging will slow down and then cease to continue as the equilibrium (liquidus) state is approached when annealing is performed at a very high temperature near T_g. The aging will also not take place if the original sample has undergone a substantial aging already, *i.e.*, if the relaxation time at the aging temperature is substantially greater than the time to be spent on aging. According to eq 28, time t must be *at least* within one or two orders of magnitude of τ (since $f \sim 10^{-2}$) in order to observe an aging effect. The "as-molded" sample in Figure 20 was injection molded, and can be considered as having been rapidly cooled from the molten state, so its equivalent relaxation time at 60°C happened to be equivalent to 0.1 h. However, had this "as-molded" sample been cooled much more slowly, its relaxation time at 60°C would have been much greater. For example, suppose that its history were comparable to 10 h at 60°C. In such a case, annealing the sample for 1 or 10 h at 60°C would have made no difference on the stress-strain curves; they would have superposed on top of each other *without* changing the rate of strain, and the difference would have become observable only when the aging period exceeded 10 h at 60°C. Thus it is of utmost importance to know the equivalent thermal history of a sample that is being tested before the prediction can be made on the effect of physical aging. To do this, first subject a sample to a prescribed thermal history,
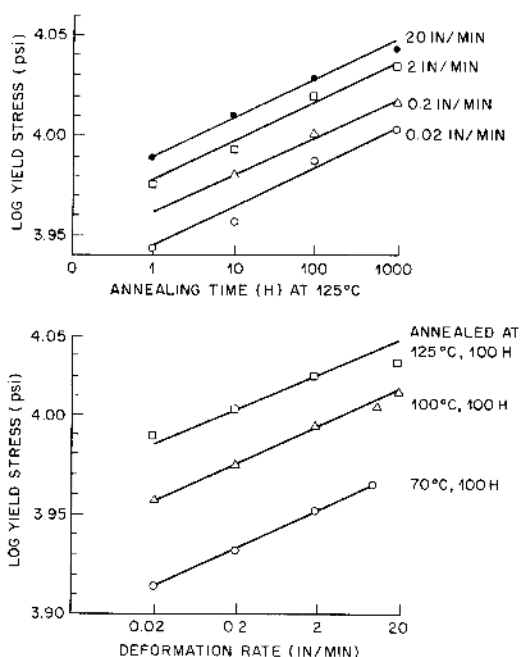

Figure 21. The dependence of the maximum stress on the annealing time and the strain rate for polycarbonate.

typically 100 h at a temperature, T_a, about 25°C below the value of T_g determined by the differential scanning calorimetry at *ca.* 1°C per min, and obtain the stress-strain curve at 5%/min. Now all other curves can be calibrated against this value, by using the scaling factor, R_2, for the thermal history:

$$R_2 = \left(\frac{t_a}{t_{a0}}\right)^n_{T_a, \dot{\varepsilon}_0} = \frac{\sigma}{\sigma_0} \tag{30}$$

where t_a is the time for aging, as recalculated to the reference condition with the tempeature T_a and the strain rate of $\dot{\varepsilon}_0$. The power n should be the value at the temperature of mechanical testing, and not at the temperature of aging; it should be the values in Table I if the test was run at 23°C. The equivalent annealing time can be converted to any temperature of annealing by the use of the formula:

$$\ln\left(\frac{t_{a,T}}{t_{a,T_{a0}}}\right) = \frac{H}{R}\left(\frac{1}{T} - \frac{1}{T_{a0}}\right) \tag{31}$$

where the same value of H as the one in Table I may be used. The equivalent annealing time is the minimum time spent on that specimen at that temperature. Any subsequent annealing time must be added to this time after being converted to the

equivalent time at the temperature of aging being considered. Any *additional* aging, such as leaving on the shelf for an extended period of time or subjecting it to annealing at elevated temperatures must be accounted for by adding the equivalent additional time t at T_a, *i.e.*,

$$R_2 = \left(\frac{t + t_a}{t_{a0}}\right)^n \tag{32}$$

where t can be calculated from eq 31. The interchangeability of the annealing time and the strain rate is shown also for polycarbonate in Figure 21.

The value of n depends slightly on the aging also, because it depends on the relaxation time τ which becomes longer with annealing. Recalling eq 9:

$$n = \beta \left(\frac{t}{\tau}\right)^{\beta} \tag{9}$$

and if τ is to be increased by 4 decades from 10^3 to 10^7 minutes, then for $\beta = 0.03$, n will decrease from 0.024 to 0.018. In some of the creep studies on glassy polymers, we have found that such would be the case.

NOMENCLATURE

C, C_1, C_2, etc. = empirical constants

$D(t), D(\varepsilon, t)$ = linear and nonlinear creep compliance at strain ε and time t

$E(t), E(\varepsilon, t)$ = linear and nonlinear stress relaxation modulus at strain ε and time t

E_0 = zero strain tensile modulus

E_f and E_p = zero strain moduli for filler and polymer

$f, \Delta f, f_0, f_\infty$ = fractional free volume

G = shear modulus

H = activation enthalpy for aging and for relaxation process for solid state having undergone the same or equivalent thermomechanical history

$I^*, I_e, \parallel I_\varepsilon$ = critical, the fist, and the second strain invariants

$J, J^*, J_\infty, \Delta J, J_0$ = shear compliance, J^* is the dynamic compliance

k = rate constant for the aging process

n, n_0 = the power for scaling time, relaxation time, or strain rate for viscoelastic function; n is the slope of log relaxation time against log time at constant strain or stress

p, p_0, p_c = pressure in psi; p_c is a parameter for scaling the pressure effect on the stress

R_0 = scaling factor for the temperature

R_1 = scaling factor for the strain rate

R_2 = scaling factor for the physical aging

R_f = scaling factor for the filler concentration

R_{sx}, R_{sy} = scaling factor to convert tensile to shear stress-strain

R = the gas constant

t = time

t_a, t_{a0} = annealing (physical aging) time

T, T_0, T_c = temperature in K, T_c is a parameter for scaling the temperature effect on the stress

U = strain energy

$V, \Delta V, V_f, V_p$ = specific volume; V_f and V_p are volumes of filler and polymer

Greek Letters

β = power for time in Williams–Watts formula

γ = shear strain

$\varepsilon, \varepsilon_0$ = tensile strain

ε^* = strain corresponding to the equal rate of energy increase for constant strain rate process

$\varepsilon, \varepsilon_{kk}, \varepsilon_{11}, \varepsilon_{12}$ = strains in tensor notation

η = viscosity

λ = Lammé constant

ν = Poisson ratio

$\sigma, \sigma_0, \sigma_1, \sigma_2, \sigma_3$ = stress (usually tensile)

$\sigma, \sigma_{11}, \sigma_{12}$ = streses in tensor notation

τ, τ_0, τ_g = relaxation time, τ_g is the extra-

polated value for T_g

ω = circular frequency

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