Physical Aging in Polymer Glasses
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Source: *Science*, New Series, Vol. 267, No. 5206 (Mar. 31, 1995), pp. 1945-1947
Published by: American Association for the Advancement of Science
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polymers, to which neutron scattering contributes, might have an impact on the development of new materials in the future.

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32. We gratefully acknowledge the fruitful collaboration with U. Buchenau, R. Zorn, and B. Farago in much of the presented work and the excellent sample preparation by L. J. Fetters.

Physical Aging in Polymer Glasses

Ian M. Hodge

Physical aging refers to structural relaxation of the glassy state toward the metastable equilibrium amorphous state, and it is accompanied by changes in almost all physical properties. These changes, which must be taken into account in the design, manufacture, and use of glassy polymer materials and devices, present a daunting challenge to theorists.

Glasses usually exist in a nonequilibrium state, and relaxation toward equilibrium is commonly referred to as physical aging. This term was first coined by Struik (*1*) to distinguish glassy state relaxation from other time-dependent processes such as recrystallization and chemical degradation. In the inorganic glass literature, it is traditionally referred to as structural relaxation, annealing, or stabilization. The variety of terminologies reflects the common occurrence and considerable practical importance of glassy state relaxation to a chemically diverse range of materials that includes polymers, inorganic glasses, composites, amorphous metals, and even foodstuffs. Physical aging is particularly important for polymers, because the rate of physical aging is determined in part by how far below the glass transition temperature T_g the polymer is used, and T_g values are lower for polymers than for most inorganic glasses. Physical aging also affects the characteristic time scale of dynamic properties, which are important for polymers. The coupling between thermodynamic and dynamic properties gives rise to the most practically important and technically difficult aspect of physical aging, its nonlinearity. Accurate prediction of changes in physical properties with aging can have significant economic implications, in part because of the obvious need to predict long-term behavior from accelerated short time tests. These and other issues are discussed in detail in several recent review articles and books (*1–5*), a report of a recent workshop at the National Institute of Standards and Technology (NIST) (*6*), and in the proceedings of two international conferences (*7*, *8*). Properties and applications affected by physical aging include the design, manufacture, and performance of polymer-based composites, automotive applications of polymers, adhesives, permeability of packaging materials, curling of photographic film supports, nonlinear optic materials, curing of epoxies, the optical, electrical, and mechanical properties of xerographic materials, and glass-to-metal seals.

In addition to being nonlinear, glassy state relaxations are also nonexponential and exhibit the memory effect, that is, relaxation from a particular state depends not only on what that state is, but also on how that state was reached. For example, physical aging of a polymer that has been injection molded will depend on the temperature T, hydrostatic pressure, and mechanical deformation history during the molding process, as well as the post-molding thermal and mechanical history before the polymer is put into service. The two essential ingredients of nonlinearity and nonexponentiality are illustrated by the effects of physical aging on viscoelastic creep shown in Fig. 1. The tensile creep compliance of poly(vinylchloride) (PVC) is shown as a function of creep time, measured after the indicated physical aging times, t_a, at 20°C after a quench from above T_g. The creep curves continue to move to longer creep times, even after almost 3 years of aging. The shapes of the individual curves are determined by the nonexponential compliance response function, which depends on material type, but is almost independent of t_a for these particular data. The latter independence allows a master creep compliance curve to be constructed by shifting the individual curves along the creep time axis (*9*), exemplified by the master curve at $t_a = 1000$ days. This procedure is not always possible for all properties and all polymers, however, because the response function often changes with annealing time. The effects of physical aging are erased by heating the glass above its T_g, indicating a close connection between aging and the glass transition. This effect is illustrated by the crossed data in Fig. 1, observed for a previously aged sample that had been heated to above T_g and aged again for 1 day, which essentially superimposed those of the original material after a day of aging.

The position of a curve on the creep time axis is determined by the average creep relaxation time, τ (*10*). Shifts along the creep time axis with aging can therefore be described in terms of τ increasing with aging time, t_a, approximated as:

$$\tau = \tau_0 t_a^{\mu} \qquad (1)$$

where μ is the Struik shift factor (*1*). Viscoelastic creep occurs because there is appreciable polymer chain mobility in the glassy state, and this mobility is determined by the free volume, v_f, and configurational entropy,

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S_c. Both v_f and S_c are functions of T, from which arise the well-known non-Arrhenius behavior of $\tau(T)$ above T_g (*11*). Importantly, S_c and v_f also decrease with aging time, resulting in the lengthening of τ with aging exhibited in Fig. 1. The value of τ also determines the rates of relaxation of v_f and S_c themselves, so that volume and entropy (isothermal enthalpy) relaxation is nonlinear. Both S_c and v_f are greater in the nonequilibrium glass than in the equilibrium amorphous state at the same temperature, producing a shortening of the nonequilibrium relaxation time that results in relaxation occurring within the lifetime of the glass, that is, physical aging occurs. Nonlinearity is therefore an essential cause of physical aging occurring on a practically important time scale. Nonlinearity becomes significant for changes in T as small as 2 K or so and must be incorporated in the analysis of almost all glassy state experiments. In contrast, the viscoelasticity of polymers, for example, remains linear up to practically significant levels of stress, strain, and strain rate.

Nonexponentiality is frequently described by the stretched exponential or Kohlrausch-Williams-Watts (KWW) decay function:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau_0}\right)^{\beta}\right] \quad 1 \geq \beta > 0 \tag{2}$$

This is a linear function as written, in the sense that τ_0 is constant and does not depend on aging time. Nonlinear extensions of $\phi(t)$ are obtained by using the reduced time:

$$\xi(t) = \int_0^t \frac{dt'}{\tau_0(t')} \tag{3}$$

where integration commences at the time the polymer was last in equilibrium. The nonlinear KWW function is then:

$$\phi(t) = \exp(-\xi^{\beta}) = \exp\left[-\left(\int_0^t \frac{dt'}{\tau_0(t')}\right)^{\beta}\right] \tag{4}$$

A more general method for describing nonlinearity is to specify the nonequilibrium state of the glass in terms of the fictive temperature, T_f, defined as the thermodynamic temperature at which some observed nonequilibrium excess property would be the equilibrium value, or with a parameter δ that is proportional to $T_f - T$ (*12*). The most frequently used expression for $\tau_0[T(t), T_f(t)]$ is the Narayanaswamy-Moynihan (NM) equation (*13*):

$$\tau_0 = A\exp\left(\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right) \tag{5}$$

where the parameter Δh^* is the effective equilibrium activation energy just above T_g, x is a measure of nonlinearity, and R is the gas constant. Experimental values of x depend on polymer type and the property being described, but typically lie between 0.1 and 0.5. The response to any given thermal history is then described in terms of Boltzmann superposition of responses linearized with the reduced time and $\tau_0[T(t), T_f(t)]$ or $\tau_0[T(t), \delta(t)]$. Usually, $T(t)$ is specified by the thermal history and $T_f(t)$ is the response to that history, although $T_f(t)$ can also be determined by nonthermal perturbations, because these can also change τ. Representative examples of τ-changing with applied stress have been described for PVC, polycarbonate, and polystyrene (*14*). The generally accepted explanation for this effect is that τ is shortened by volumetric dilation (*15*). This effect can give rise to what is commonly referred to as "rejuvenation," in which the effects of physical aging are partially reversed. Indeed, some researchers have interpreted yielding and brittle-to-ductile transitions in polymers in terms of the applied stresses decreasing the relaxation time to values characteristic of temperatures near or above T_g. Thus, accurate prediction of aging effects depends not only on knowledge of a polymer's history before use, but also of the stresses experienced as physical aging occurs. It is also important to recognize that, although physical aging occurs in a wide variety of glasses and affects a large number of properties, the aging kinetics of a particular material are generally different for different properties. Thus, changes in one property cannot in general be predicted using parameters obtained from another property.

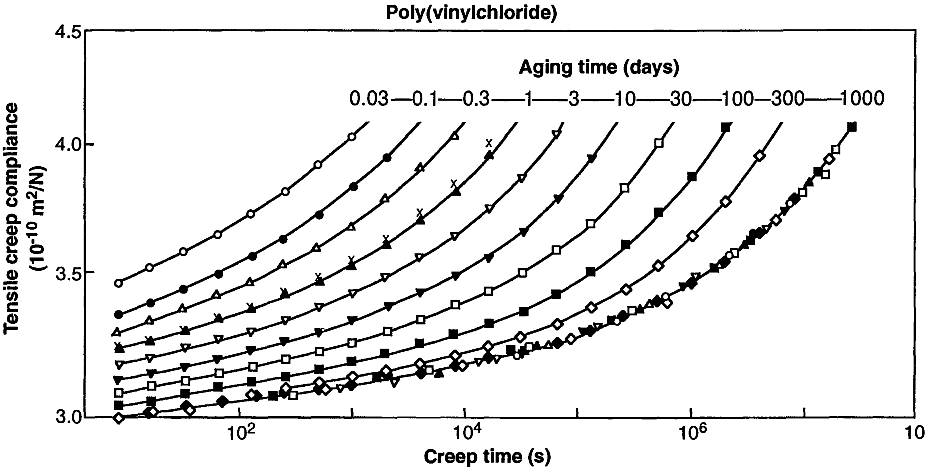

Fig. 1. Creep compliance for PVC as a function of creep time and physical aging time. [Adapted from (*1*) with permission, copyright Elsevier]

Physical aging is also coupled to gas solubility, absorption and desorption. As v_f decreases during aging, inert gas solubility decreases. Conversely, physical aging is slowed down by gas absorption because part of the free volume becomes occupied and τ lengthens. Physically aged polymers are more slowly swollen by solvent vapors, and rapid vapor desorption from a swollen polymer accelerates subsequent aging. Gas diffusivities are also influenced by aging.

The theoretical understanding of physical aging is primitive. Perhaps the best understanding to date is in terms of the heuristic nonlinear Adam-Gibbs equation (*3, 5, 16*):

$$\tau_0 = A'\exp\left(\frac{B}{T(1 - T_K/T_f)}\right) \tag{6}$$

where T_K is the thermodynamic Kauzmann temperature at which S_c extrapolates to zero and A' and B are constants. Theoretical implications of the nonlinear Adam-Gibbs theory are discussed in detail elsewhere (*3, 5, 16*); just a few are briefly mentioned here. Equation 6 simplifies to the Vogel-Tamman-Fulcher (VTF) equation in the equilibrium state above T_g, where $T_f = T$, so that the parameters A', B, and T_K can be obtained from fitting equilibrium data to the VTF equation and used to predict the glassy state effective activation energy $BR/(1 - T_K/T_g)$. Such predictions are often accurate for both polymeric and nonpolymeric materials, although the general relation between equilibrium (linear) and nonequilibrium (nonlinear) relaxation is not well understood. The parameter B is proportional to an activation energy per particle, $\Delta\mu$, that for polymers can be equated to an average energy barrier for bond rotation. Physically reasonable values for $\Delta\mu$ of 10 to 33 kJ mol^{-1} are obtained. Despite appearances, Eqs. 5 and 6 are essentially equivalent, with their parameters related by $x \approx 1 - T_K/T_g$ and $\Delta h^*/R \approx B/(1 - T_K/T_g)^2 \approx B/x^2$. The relation between x and T_K/T_g suggests that nonlinearity is determined by how close the kinetic T_g is to the thermodynamic T_K. It can be argued that $\Delta\mu$ determines T_K/T_g. If a linear relation between $\Delta\mu$ and T_K/T_g is assumed, observed correlations between the empirical NM parameters x and Δh^* and the KWW parameter β are correctly predicted. A correlation between Δh^* and β is also observed for polymers in the rubbery state above T_g, where relaxation is linear (*17*), and is consistent with the correlation between the same parameters observed under the nonlinear conditions prevailing below T_g. The ratio T_K/T_g is a measure of fragility in Angell's classification scheme for liquids (*17, 18*), implying that more fragile liquids produce more nonlinear glasses. This is borne out by the correlations between the NM and KWW parameters being consistent with the fragility classification scheme.

The description and prediction of physical aging effects is fraught with difficulties caused by the complexity of their nonlinear and nonexponential character. The problem is acute for polymers because of the coupling between aging and the dynamic and thermodynamic properties that are important in their applications. The current phenomenologies for purely thermal histories are adequate for many engineering applications, such as those for inorganic glasses, for example (*3*), but fail for glasses that are very far from equilibrium. The reasons for this failure are not known with certainty, although the handling of nonlinearity, or the methods for combining nonlinearity and nonexponentiality, or both are suspected by some (*5, 7, 8*). A generally accepted methodology for treating nonthermal perturbations to polymers has not yet been developed. Theoretical understanding of the glass transition, upon which a better understanding of physical aging will presumably be based, is at present too poorly developed to be of much help. New approaches to these long-standing problems are sorely needed.

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Metallic Glasses

A. Lindsay Greer

Amorphous metallic alloys, relative newcomers to the world of glasses, have properties that are unusual for solid metals. The metallic glasses, which exist in a very wide variety of compositions, combine fundamental interest with practical applications. They also serve as precursors for exciting new nanocrystalline materials. Their magnetic (soft and hard) and mechanical properties are of particular interest.

Materials with each of the major bonding types (ionic, covalent, van der Waals, hydrogen, and metallic) can be obtained in amorphous (that is, noncrystalline) solid forms. Metallic amorphous materials are comparative newcomers to this group. They first came to prominence with Duwez's demonstration in 1959 that an amorphous $Au_{75}Si_{25}$ alloy (the composition is given here, as throughout this article, in atomic percent) could be obtained by rapid cooling of the liquid (*1*). Formed when the liquid becomes increasingly viscous on cooling and fails to crystallize, such a material can correctly be termed a glass. Metallic glasses are but a subset of a range of metallic amorphous solids that can be made by a wide variety of techniques. Undoubtedly, amorphous metallic materials had been made, and even recognized as such, before Duwez's experiments; an example is early work on the condensation of thin films on substrates at liquid helium temperatures (*2*). The significance of Duwez's work, seen more clearly when the improved cooling technique of melt-spinning was developed (Fig. 1), was that vitrification of a liquid permits comparatively large quantities of an alloy to be made into the amorphous state, certainly much more than could be made by thin-film techniques.

In addition to their fundamental interest, metallic glasses were soon realized to have considerable commercial importance when iron-based compositions were found to have excellent soft magnetic properties (*3*). With their ready availability, fundamental interest, and properties of technological importance, metallic glasses in the late 1970s and 1980s were the focus of an explosion of academic and industrial research. Some years on, the novelty has faded. Some commercial applications are well established, and others are still awaited. Yet research on metallic glasses remains active, not least because of continuing discoveries that open up new possibilities. This article considers the current state of the field and focuses on recent developments. Further background material may be found, for example, in (*4, 5*).

How to Make a Metallic Glass

A glass is made if a liquid is cooled sufficiently rapidly to avoid crystallization. With conventional oxide glasses, the critical cooling rate is so low that it is not an important production parameter. For metallic glasses, however, critical cooling rates are usually rather high. Melt-spinning (Fig. 1) has been the main technique for metallic glass production, and it gives cooling rates of the order of 10^5 to 10^6 K s^{-1}. There are, of course, many other techniques for rapidly cooling an alloy liquid. For example, a jet of molten alloy can be ejected into a stream of water to produce wire, or (in any of the many variants of atomization) broken up to produce droplets. With such techniques, the cooling rate is comparable to that in melt-spinning and the interest is in the forms of the product. A contrasting example is pulsed laser quenching, in which a very thin (~100 nm) surface layer is melted by an incident beam of duration as short as a few picoseconds. The thin layer on top of a large cold substrate experiences ultrarapid cooling, as fast as 10^{14} K s^{-1} (*6*).

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