

Phenomenology of plastic recovery in high polymer glasses[☆]

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Dedicated to Wayne Mattice on the occasion of his 60th birthday

Abstract

Deformations in isotropic, strain-free polymer glasses are usually completely recoverable (at the test temperature or after warming to T_g), in sharp contrast with the behavior of low molecular weight glasses and crystals. The apparent ‘plastic strain’ which remains at the end of a creep or stress relaxation experiment does not recover at the test temperature, but only after the sample is heated. It is proposed that the long time scales needed for entanglement reorganization in the glass are responsible for this delayed recovery. A phenomenological network model for thermally activated strain recovery in polymer glasses is analyzed. A superposition relation between the stress and the strain history using a KWW (stretched exponential) memory kernel is employed. The recovery of plastic (i.e. residual) strain in non-crosslinked amorphous thermoplastics is a two-step process that may be interpreted in terms of the network model. In particular, recovery at sub- T_g temperatures is associated with entanglement slippage, while recovery near- T_g is believed to involve reorganization at or near chain ends. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The molecular mechanisms of stress relaxation, creep, and strain recovery in polymer glasses have been, and continue to be, subjects of considerable interest and investigation. Some years ago, the authors suggested [1] that the diffusion and migration of conformational and packing defects within and between individual polymer molecules in the glassy state could rationalize observations on mechanical response for varying thermal, stress, and strain conditions and histories below the T_g . For example (see Fig. 1), strain and birefringence recovery following either stress relaxation or creep was interpreted in terms of an anelastic response caused by the motion and/or reorganization of packing and segmental defects in chain segments between entanglement points, while motion of defects across entanglements and subsequent loss or entrapment at the chain ends was proposed to account for the origin of persistent (‘plastic’ or residual) strain. It was suggested that defects might move easily past an entanglement when the polymer is stressed or strained, but

that the barrier to return in the absence of applied stress or strain is higher, thereby reducing the rate of defect recovery to the original distribution. While considering experimental ways to confirm or disprove that two or more persistent (plastic) processes had occurred during stress relaxation or creep, it was recognized that the diffusive processes responsible might be thermally activated; i.e. that the rates might increase with temperature. The current article focuses on a simple phenomenological model to describe some experimental aspects of thermally stimulated mechanical recovery, and discusses briefly experimental methods used to test these ideas. The experimental results and methods, which will be described in detail at a later date, are closely related to investigations previously reported by others and used to study shrinkage or retraction of hot and cold drawn glassy polymers as well as crazed thermoplastics [2–6].

2. Background: strain recovery following stress relaxation

The recovery of polymers after creep is a well-known phenomenon and has been extensively used to separate the secondary flow response from the elastic and anelastic responses [7]. In contrast, strain/birefringence recovery following stress relaxation [8–12] is less often reported though we have found it of use in practical studies of

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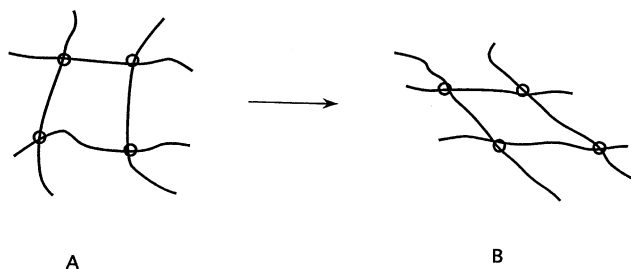


Fig. 1. Portion of the entanglement network (A) unstrained, and (B) strained. Under load, stress concentration occurs at entanglement points, allowing partial movement and relaxation of chain displacements past entanglements to chain ends. When the load is released, these displacements are 'trapped' until the sample is heated.

structural resilience. Leaderman in his classic book [8] states that it is difficult to analyze recovery behavior after stress relaxation:

A third type of test is represented in Fig. 3(sic). In this, a given deformation is applied at zero time, and after a time t_1 the specimen is released. The load falls at this instant from some value smaller than the initial value to zero; there is thus a residual deformation, which gradually disappears with time. If the relaxation with time is small during the time under strain (as in glass at room temperature), the residual deformation in the test of Fig. 3 then approximates to that in the test of Fig. 1 (i.e. recovery following creep); otherwise no simple interpretation of this test is possible. This type of test was in fact widely used by early workers following Weber, on materials such as glass and silver [8].

In spite of Leaderman's pessimism, it is not difficult to analyze some representative cases, and probably the simplest solution is found in Eq. (7). The objective of the present work is to emphasize that recovery experiments contain important information that complements stress relaxation studies. During stress relaxation, several types of deformation occur simultaneously, elastic, anelastic, and plastic. During recovery (i.e. after the load is removed), the elastic deformation disappears, the plastic deformation ceases, and the only time-varying component is the anelastic strain. Recovery experiments are thus uniquely capable of isolating and quantifying anelastic and plastic components of polymer glass deformation. Furthermore, recovery results can be used to predict the anelastic contributions to stress relaxation and creep. By comparing predicted (anelastic) creep and stress relaxation behavior with the actual behavior, the plastic contributions to each may be determined.

As a simple example of recovery, the dash pot model in Fig. 2 will be used to illustrate residual strain. The solution of this model for stress relaxation at constant applied strain and temperature is well known and is

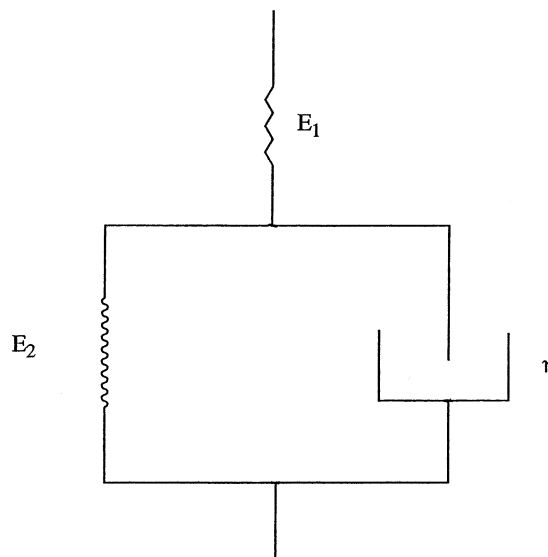


Fig. 2. Simple dash pot model for stress relaxation and recovery (Eqs. (1)–(7)).

given by

$$\sigma(t) = \varepsilon_0 \{E_r + \Delta E \exp[-(t/\tau)]\} \quad (1)$$

where ε_0 is the constant applied strain,

$$E_r = \frac{E_1 E_2}{(E_1 + E_2)} \quad (2)$$

$$E_u = E_1 \quad (3)$$

and

$$\Delta E = (E_u - E_r) \quad (4)$$

t is the duration of the strain application, and $\tau = \eta/(E_1 + E_2)$. The amount of strain in the Kelvin–Voigt element at any time t during the stress relaxation portion of the experiment is given by

$$\varepsilon_{kv}(t) = \varepsilon_0 - \frac{\sigma(t)}{E_u} \quad (5)$$

and upon substituting Eq. (1) into Eq. (5) yields the result

$$\varepsilon_{kv}(t) = \frac{\varepsilon_0 \Delta E}{E_u} \left\{ 1 - \exp\left[-\left(\frac{t}{\tau}\right)\right] \right\} \quad (6)$$

Finally, when the load is released after a hold time t_h , the strain remaining (and now recovering) in the Kelvin–Voigt

element is

$$\varepsilon_{\text{rec}}(t^* + t_h) = \frac{\varepsilon_0 \Delta E}{E_u} \left\{ 1 - \exp\left[-\left(\frac{t_h}{\tau}\right)\right] \right\} \exp\left[-\left(\frac{t^*}{\tau_2}\right)\right] \quad (7)$$

where t^* is the time elapsed since the load release and $\tau_2 = \eta/E_2$. Note that at $t^* = \infty$, $\varepsilon_{\text{rec}} = 0$, and this model shows complete recovery.

Consider now a continuous distribution of Kelvin–Voigt elements, for which the Boltzmann superposition relation holds between the stress at a time t and the strain history from time $t = 0$,

$$\sigma(t) = E_u \varepsilon(t) - (E_u - E_r) \int_0^t g(t - t') \varepsilon(t') dt' \quad (8)$$

and in practice one could assume that Eq. (8) is nearly true for the tensile stress produced by a succession of small tensile strains $\{\varepsilon(\tau)\}$ in the polymer glass. Based on earlier work by others and ourselves, we will approximate the memory function $g(t)$ in Eq. (8) by the Kohlrausch–Williams/Watts (KWW) form:

$$g(t) = -\frac{d}{dt} \{\exp[-(t/\tau)^\alpha]\} \quad \text{where } 0 \leq \alpha \leq 1 \quad (9)$$

Combining Eqs. (8) and (9) gives

$$\sigma(t) = E_u \varepsilon(t) + (E_u - E_r) \times \int_0^t \frac{d}{dt} (\exp\{-[(t - t')/\tau]^\alpha\}) \varepsilon(t') dt' \quad (10)$$

We have found that an efficient iteration procedure exists to solve Eq. (10) by taking advantage of several variable changes [13]. In particular, let

$$\frac{t}{\tau} = s, \quad \frac{t'}{\tau} = s', \quad \frac{\sigma(t)}{E_u} = \sigma_2(t), \quad \frac{E_r}{E_u} = k \quad (11)$$

and

$$\sigma_2(t) = \sigma_2(\tau s) = g(s)$$

$$\varepsilon(t) = \varepsilon(\tau s) = f(s)$$

Then Eq. (10) becomes

$$f(s) = g(s) + (1 - k) \int_0^s \frac{d}{ds'} \{\exp[-(s - s')^\alpha]\} f(s') ds' \quad (12)$$

$$0 \leq s \leq \infty$$

Introducing new variables

$$x = 1 - \exp(-s^\alpha), \quad y = 1 - \exp(-s'^\alpha) \quad (13)$$

into Eq. (12) and integrating by parts once gives

$$f(x) = g(x) + (1 - k)[f(x) - (1 - x)f(0)] - (1 - k) \int_0^x K(x, y) f(y) dy \quad 0 \leq x \leq 1 \quad (14)$$

where

$$K(x, y) = (1 - x) \left\{ - \left[\frac{\log(1 - y)}{\log(1 - x)} \right] \frac{1}{\alpha} \right\}^\alpha, \quad 0 \leq \alpha \leq 1 \quad (15)$$

The transformations of Eq. (13) map the semi-infinite range ($0 \leq \tau \leq \infty$) to a finite range ($0 \leq x \leq 1$) and allow solutions of Eqs. (10) or (12) to be studied over very long times [13]. A useful fact about the transformed kernel in Eq. (15) is that it is close to $(1 - x)$ over much of its range. Eq. (14) is, therefore, closely approximated by

$$f_0(x) = g(x) + (1 - k)[f_0(x) - (1 - x)f_0(0)] - (1 - k) \int_0^x (1 - x) f_0(y) dy \quad 0 \leq x \leq 1 \quad (16)$$

which is readily solved for $f_0(x)$;

$$f_0(x) = \frac{g(x)}{1 - (1 - k)x} = \frac{g(x)}{1 - (1 - k)[1 - \exp(-s^\alpha)]} \quad (17)$$

and in terms of the original variables,

$$\varepsilon(t) \approx \frac{\sigma(t)}{E_r + \Delta E \left\{ 1 - \exp\left[-\left(\frac{t}{\tau}\right)^\alpha\right] \right\}} \quad (18)$$

The same asymptotic methods used to derive Eq. (18) can also be used to solve for strain recovery following stress relaxation. The (leading-term) result is

$$\varepsilon_{\text{rec}}(t' + t_h) = \varepsilon \left[1 - \frac{E_r + \Delta E \exp\left[-\left(\frac{t' + t_h}{\tau}\right)^\alpha\right]}{E_r + \Delta E \exp\left[-\left(\frac{t'}{\tau}\right)^\alpha\right]} \right] \quad (19)$$

which generalizes Eq. (7), replacing exponential time decay functions by stretched exponentials. The precise relationship (and differences) between models leading to Eqs. (7) and (19) will be discussed elsewhere. Numerically they are quite similar, especially for long

hold times. In Section 3, we consider the case when the time-scale parameter, τ , in Eq. (19) is different (e.g. much larger) in recovery than in the relaxation stage. This shift in τ with stress level is adopted as a simple tractable model of stress activation [14–16], and we assume it is the principal cause of plastic and persistent strains.

3. Recovery with τ shift

One explanation for the appearance of plastic or persistent strain is that the rate of chain reorganization is slower in the absence of applied stress, hence some anelastic deformation that occurs during the first part of the experiment becomes frozen-in after load release. Here, we model such behavior by using one time-scale parameter, τ , for the relaxation portion of the experiment and another, τ' , for recovery. The expression for strain recovery, Eq. (19),

$$\varepsilon(t + t_h) = \varepsilon \left(1 - \frac{E_r + \Delta E_1 \exp\{-[(t + t_h)/\tau_1]^{\alpha_1}\} + \Delta E_2 \exp\{-[(t + t_h)/\tau_2]^{\alpha_2}\}}{E_r + \Delta E_1 \exp[-(t/\tau_1)^{\alpha_1}] + \Delta E_2 \exp[-(t/\tau_2)^{\alpha_2}]} \right) \quad (23)$$

4. Recovery solution for two relaxation mechanisms

Eqs. (8)–(10) are easily generalized to two relaxation processes, each having its own relaxation strength and (dispersive) kinetics:

$$\sigma(t) = E_u \varepsilon(t) + \Delta E_1 \int_0^t \frac{d}{dt'} (\exp\{-[(t - t')/\tau_1]^{\alpha_1}\}) \varepsilon(t') dt' + \Delta E_2 \int_0^t \frac{d}{dt'} (\exp\{-[(t - t')/\tau_2]^{\alpha_2}\}) \varepsilon(t') dt' \quad (22)$$

where ΔE_1 , τ_1 and α_1 are the relaxation strength and KWW kinetic parameters for process 1 and ΔE_2 , τ_2 and α_2 are the corresponding parameters for process 2. Strain recovery for Eq. (22) is then given by

Finally, if process 1 has a relaxation time shift $\tau_1 \rightarrow \tau'_1$ during recovery, Eq. (23) becomes

$$\varepsilon_{\text{rec}}(t + t_h) = \varepsilon \left(1 - \frac{E_r + \Delta E_1 \exp[(t_h/\tau'_1)^{\alpha_1}] - (t_h/\tau_1)^{\alpha_1} \exp\{-[(t + t_h)/\tau'_1]^{\alpha_1}\} + \Delta E_2 \exp\{-[(t + t_h)/\tau_2]^{\alpha_2}\}}{E_r + \Delta E_1 \exp[-(t/\tau'_1)^{\alpha_1}] + \Delta E_2 \exp[-(t/\tau_2)^{\alpha_2}]} \right) \quad (24)$$

and if $\tau'_1 \rightarrow \infty$ (i.e. it is very much larger than the experimental time scale), then

$$\varepsilon_{\text{rec}}(t + t_h) = \varepsilon \left(1 - \frac{E_r + \Delta E_1 \exp[-(t_h/\tau_1)^{\alpha_1}] + \Delta E_2 \exp\{-[(t + t_h)/\tau_2]^{\alpha_2}\}}{E_r + \Delta E_1 + \Delta E_2 \exp[-(t/\tau_2)^{\alpha_2}]} \right) \quad (25)$$

then becomes

$$\varepsilon_{\text{rec}}(t' + t_h) = \varepsilon \left\{ 1 - \frac{E_r + \Delta E \exp\left[\left(\frac{t_h}{\tau'}\right)^\alpha - \left(\frac{t_h}{\tau}\right)^\alpha\right] \exp\left[-\left(\frac{t' + t_h}{\tau'}\right)^\alpha\right]}{E_r + \Delta E \exp\left[-\left(\frac{t'}{\tau'}\right)^\alpha\right]} \right\} \quad (20)$$

In the special case when $\tau' = \infty$,

$$\varepsilon_{\text{rec}} = \varepsilon \left\{ 1 - \frac{E_r + \Delta E \exp\left[-\left(\frac{t_h}{\tau}\right)^\alpha\right]}{E_r + \Delta E} \right\} \quad (21)$$

and no recovery occurs on the time scale of the experiment. Calculations using parameter values appropriate to polycarbonate at room temperature indicate that small shifts in τ — i.e. less than a factor of 10 — will be difficult, if not impossible, to detect.

At very long times after load release, Eq. (25) reaches the limiting value

$$\varepsilon_{\text{rec}}(\infty) \rightarrow \varepsilon \left\{ 1 - \frac{E_r + \Delta E_1 \exp[-(t_h/\tau_1)^{\alpha_1}]}{E_r + \Delta E_1} \right\} \quad (26)$$

and Eq. (26) corresponds to residual ‘plastic’ strain produced by the stress-activated shift in the relaxation time for process 1, τ_1 .

5. Thermally activated strain recovery

We now consider the case when a fraction of the anelastic strain appears to be ‘frozen’ because of the very long recovery times at the relaxation test temperature, and we then accelerate the recovery by heating the sample. This is easily treated using Eq. (24). The recovery time τ'_1 is assumed to be very large ($\tau'_1 \gg \tau_2$),

although not infinite, and if one waits a time t' much longer than τ_2 , then Eq. (24) becomes

$$\varepsilon_{\text{rec}}(t' + t_h) = \varepsilon \left\{ 1 - \frac{E_r + \Delta E_1 \exp[(t_h/\tau_1)^{\alpha_1} - (t_h/\tau_1)^{\alpha_1}] \exp\left[-\left(\frac{t' + t_h}{\tau_1}\right)^{\alpha_1}\right]}{E_r + \Delta E_1 \exp[-(t'/\tau_1)^{\alpha_1}]} \right\} \quad (27)$$

for $\tau_2 \ll t' \ll \tau_1'$. The right hand side of Eq. (27) is essentially independent of time, and the strain (which is recoverable, in principle) acts as a plastic or persistent contribution. If the relaxation time τ_1' is temperature dependent, then heating the sample permits the ‘frozen strain’ to recover. For Arrhenius activation,

$$\tau_1' = \tau_\infty \exp(E_{\text{act}}/RT) \quad (28)$$

where τ_∞ is the high-temperature attempt period, E_{act} is the activation energy, and RT is the product of the gas constant and the absolute temperature.

A final and straightforward extension of Eq. (27) to two shifted recovery times yields

$$\varepsilon_{\text{rec}}(t' + t_h) = \varepsilon \left\{ 1 - \frac{E_r + \Delta E_1 \phi_1(t' + t_h) + \Delta E_2 \phi_2(t' + t_h)}{E_r + \Delta E_1 \exp[-(t'/\tau_1)^{\alpha_1}] + \Delta E_2 \exp[-(t'/\tau_2)^{\alpha_2}]} \right\} \quad (29)$$

where

$$\phi_1(t' + t_h) = \exp[(t_h/\tau_1)^{\alpha_1} - (t_h/\tau_1)^{\alpha_1}] \exp\{ - [(t' + t_h)/\tau_1]^{\alpha_1} \}$$

and

$$\phi_2(t' + t_h) = \exp[(t_h/\tau_2)^{\alpha_2} - (t_h/\tau_2)^{\alpha_2}] \exp\{ - [(t' + t_h)/\tau_2]^{\alpha_2} \}$$

Eq. (29) is used to analyze thermally activated recovery for an amorphous polyetherimide polymer.

6. Experimental

Two experimental methods were used to study the thermally activated strain recovery of samples that had undergone either stress relaxation or creep. With the first method (Fig. 3), the residual birefringence of the sample is measured at various temperatures using both a Babinet and a Soleil compensator in series. The resultant birefringence measurements are then converted to residual strains using the strain-optical coefficient for the polymer. This measurement is based on the linear relationship between

the strain and birefringence, which has been previously noted for polycarbonate, and on comparative measurements of strain and birefringence during early strain recovery [9]. The advantage of this measurement is that while temperature has a small effect on the refractive index, the birefringence is not significantly altered. In contrast, a second method (not represented here) involves direct measurement of the longitudinal strain using an extensometer. In this second type of test, an increase in temperature leads to thermal expansion of the sample, which is then followed by a slow decrease of the longitudinal expansion to a new equilibrium value. The temperature is then again increased, and the thermal expansion is again followed by uniaxial contraction. This procedure must be repeated until the contraction caused by the residual strain is within the noise of the measurement, and such measurements (leading to results in agreement with those mentioned here) will be described at a later time.

7. Results and discussion

Strain recovery for polyetherimide (PEI) samples was first studied at room temperature. The samples had undergone stress relaxation at room temperature for 500,000 s. They were then allowed to recover unrestrained for several million seconds at room temperature and at the end of this hold time a small but measurable residual strain was still present. These results are similar to those reported by other investigators; this residual strain has been denoted as either

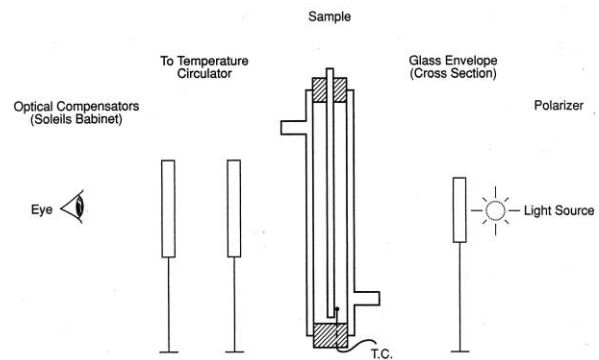


Fig. 3. A schematic of the apparatus for measuring residual strain using birefringence.

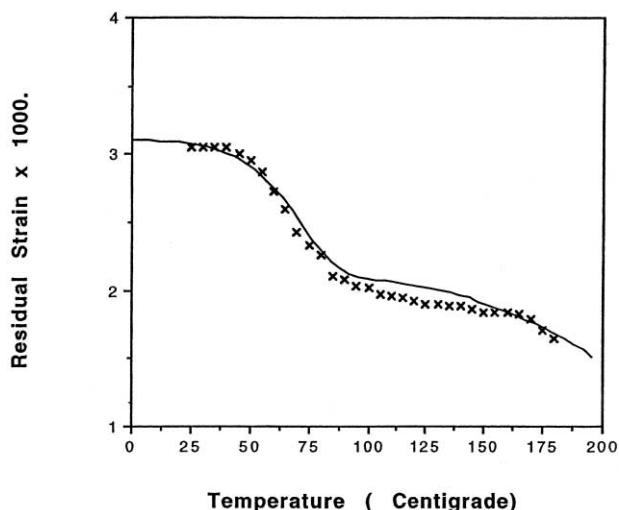


Fig. 4. Thermally activated strain recovery for polyetherimide (following stress relaxation at a strain of 2% for 500,000 s at 24°C, and strain recovery at room temperature for about 3 Ma s). The solid line is a simulation using Eq. (29), with $E_r = 2.7$ GPa, $\Delta E_2 = 0.45$ GPa, $\Delta E_1 = 0.45$ GPa, $\alpha_1 = 0.30$, $\alpha_2 = 0.50$, $\tau_\infty = 10^{-13}$ s, $E_1^{\text{act}} = 133.9$ kJ/mol, $E_2^{\text{act}} = 186.2$ kJ/mol. The simulation curve is illustrative and not a 'best fit', and it uses the numerical values of E_r , ΔE_1 , and ΔE_2 that were also used to fit stress relaxation and strain recovery (at room temperature) for the same sample.

plastic or persistent [5,6]. The amount of residual strain for these PEI samples (and many other glassy polymers studied, is found to vary with thermal histories, test conditions, and T_g s, consistent with other studies [13]. For example, thermally quenched samples exhibited more residual strain than annealed samples when tested under the same conditions. An increased strain during stress relaxation, an increased stress during creep, and an increased hold time and/or temperature will all increase the final level of residual strain in the sample.

The thermally activated strain recovery for one PEI sample which underwent stress relaxation for 50,000 s at 25°C is presented in Fig. 4, along with a simulation curve generated using Eq. (29). It is obvious that the recovery process does not begin until the sample is heated to a temperature approximately 20°C above the original test temperature. PEI tested at room temperature shows an initial recovery process approximately 150°C below T_g but also retains a residual strain, which only recovers near the T_g at 217°C.

8. Conclusions

A model is presented to interpret various aspects of strain recovery and thermally activated strain recovery following stress relaxation. The effects of applied stresses on relaxation and recovery times are modeled and discussed. Two experimental techniques are described to measure residual plastic strain recovery as a function of temperature. The experiments and model simulations are consistent with a network model of a polymer glass in which the motion of defects past entanglement points and the subsequent loss at chain ends leads to residual plastic strain. Analysis of both static and kinetic data as a function of temperature suggests that two different processes are involved in the case of uncrosslinked thermoplastics.

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