Effect of Physical Aging on the Properties of Films of Amorphous Poly(ether ether ketone) (PEEK)

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ABSTRACT: Physical aging of films of poly(ether ether ketone) kept for 2 months at 120°C was studied. The extent of aging was evaluated with different techniques. Aged samples show different thermal behavior and exhibit different mechanical, transport, and viscoelastic properties. An attempt was made to establish the accuracy of different techniques and their reliability in detecting the extent of physical aging. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 2635–2641, 1997

Key words: poly(ether ether ketone); physical aging; glassy polymers; mechanical properties; transport properties

INTRODUCTION

In recent years, particular attention has been devoted to the study of the physical aging of polymeric materials for at least two reasons: The first concerns the use of plastics which experience physical aging and are used as manufactured articles. In this case, knowledge of aging behavior is indispensable for the prediction of their long-term behavior from short-term tests. The second, no less important reason, concerns the theoretical aspects involved in physical aging. In particular, it is interesting to understand what occurs at the molecular level during aging.

Glassy polymers, when rapidly cooled below their glass transition, are not in the thermodynamic equilibrium, having an excess of free volume.[1] The achievement of the equilibrium in the glassy state is hindered by kinetic phenomena. The free volume excess decreases with time with a consequent decrease of chain mobility that produces a slowing down of the overall process that is therefore defined as "self-retarding."

Polymers having glass transition temperatures above the temperature at which they are used can therefore exhibit a change of some physical properties during the course of normal use. Poly(ether ether ketone)(PEEK) is one of them and is used in several applications as a matrix for high-performance composites because of its good mechanical properties along with high-temperature stability and resistance to chemical attack.[2,3] Several studies have dealt with the physical aging of PEEK.[4–9] In these studies, the extent of physical aging was measured by different techniques. One of us[9] found that, besides the reduction of free volume, the aging at a temperature slightly lower than the glass transition temperature decreases the sorption of dichloromethane at low activity. This led to the suggestion that ordered domains, impermeable to the vapor at low activity, are formed at a "sub-T_g" temperature.

The purpose of this study was therefore to investigate the physical aging at a temperature slightly lower than the T_g, with different techniques, in order to analyze their reliability in detecting variations due to the reduction of free volume or to the formation of ordered domains. One of the techniques used in this work is the transport of gases through polymeric films. It is partic-
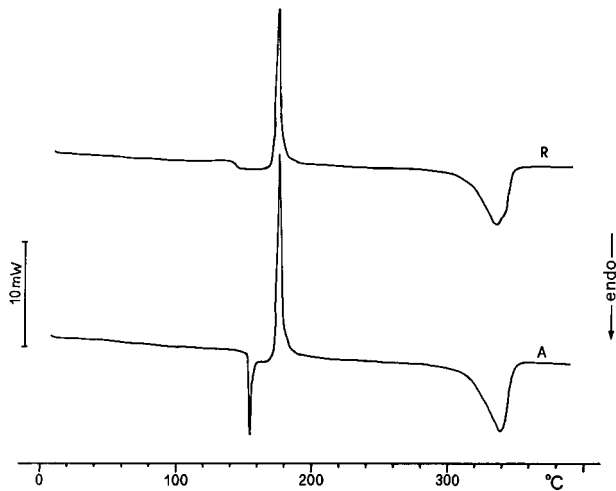
Figure 1   DSC traces for samples R and A.

ularly helpful in detecting the state of the amorphous phase since the molecules of the diffusant are able to pass only through the amorphous component.

EXPERIMENTAL

Amorphous PEEK film (STABAR) 0.10 mm thick was kindly supplied by ICI. The film as received was used as a reference (sample R) and was compared with the same film aged at 120°C for 2 months (sample A). Density measurements were performed using the floating method, using a solution of zinc chloride and distilled water.

Differential scanning calorimetry (DSC) was carried out on the two samples R and A over the temperature range of 0–400°C, using a Mettler TA 3000 DSC, purged with nitrogen and chilled with liquid nitrogen. Runs were conducted on samples of about 12 mg at the heating rate of 20°C/min. Different strips of samples R and A were drawn at 80, 120, and 140°C, using an air-heated Instron dynamometer at an extension rate of 10 mm/min on samples with a thickness of 0.10 mm; width, 6 mm; and length, 15 mm. The actual strain, λ_N, defined as the ratio between the length of the deformed sample and the initial length, was determined by photographic recording of the displacement of fiducial marks placed on the sample. Further details are reported elsewhere.[10]

The measurements of gas transport were performed using equipment described by Koros et al.,[11] based on the detection of the gas pressure as a function of time; the pressure decay gives the quantitative measurements of the gas transferred

from the gas phase to the sample, and therefore sorption and diffusion coefficients can be calculated. The pressure transducer had a sensitivity of ±100 Pa. Measurements were performed at the temperature of 25°C.
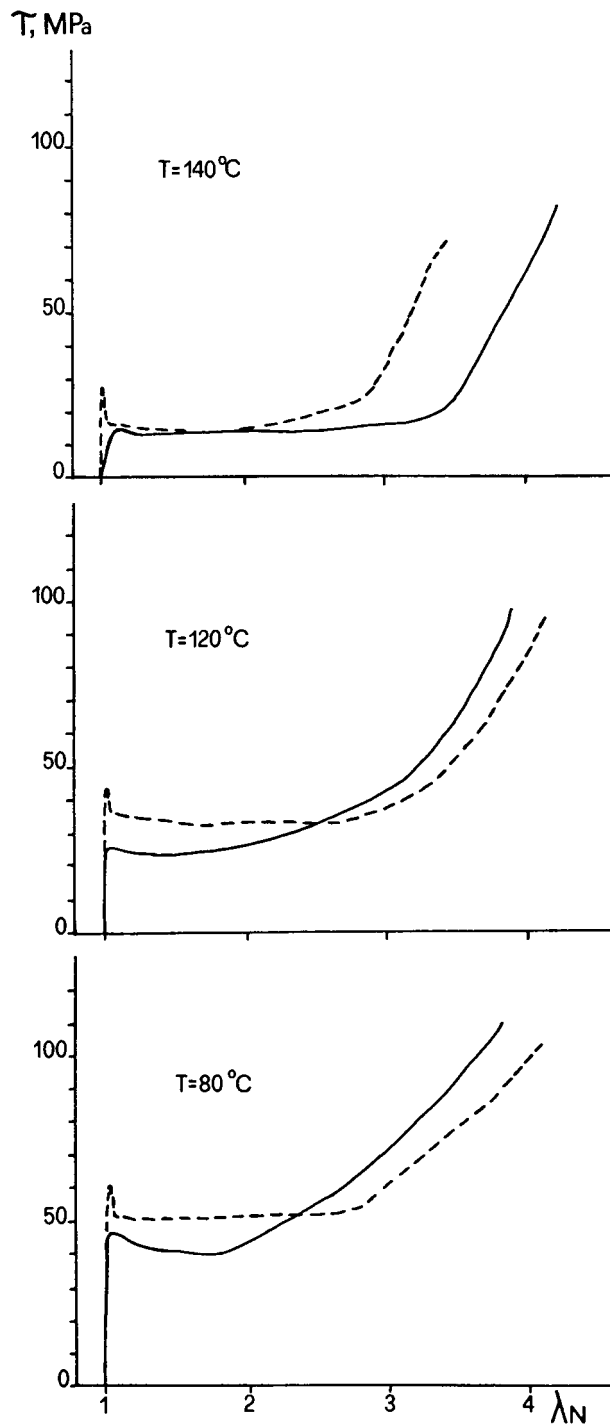
Dynamic mechanical properties and creep mea-

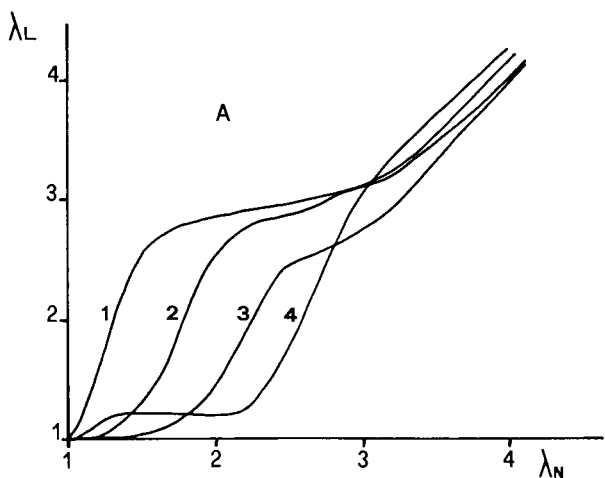**Figure 2**   Stress–strain curves for samples (——) R and (------) A drawn at different temperatures.
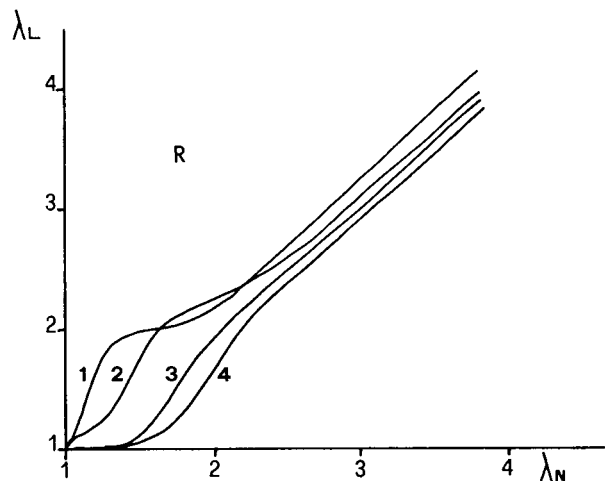
Figure 3 Local deformation (λ_L) versus nominal deformation (λ_N) for samples R and A drawn at 80°C.

surements were performed using a Polymer Laboratories dynamic mechanical thermal analyzer interfaced with a Polymer Laboratories temperature controller. Dynamic mechanical spectra were recorded in the tension mode, at a frequency of 1 Hz and a heating rate of 3°C/min, in the range 120–220°C. Creep measurements were performed at 130°C with a stress of 2 MPa.

RESULTS AND DISCUSSION

The aging phenomenon, after the reference sample R is kept at 120°C for 2 months, influences several physical properties. We analyze now some of them and the results will be compared to estab-

lish the most reliable techniques able to better detect physical aging.

Density

The difference in terms of density in the two samples R and A is not remarkable. In fact, the density of sample R is 1.2641 g/mL, while that of sample A is 1.2669 g/mL.

Differential Scanning Calorimetry

In Figure 1, the DSC traces of samples R and A are reported. In sample R, the glass transition at 145°C is followed by a sharp exotherm at 179°C due to the cold crystallization. A broad endothermic peak centered at 338°C indicates the presence of a broad distribution of crystal sizes formed during the crystallization. In sample A, in the glass transition region, a sharp endothermic peak appears. The increase of the glass transition temperature is due to the decreased mobility in the aged
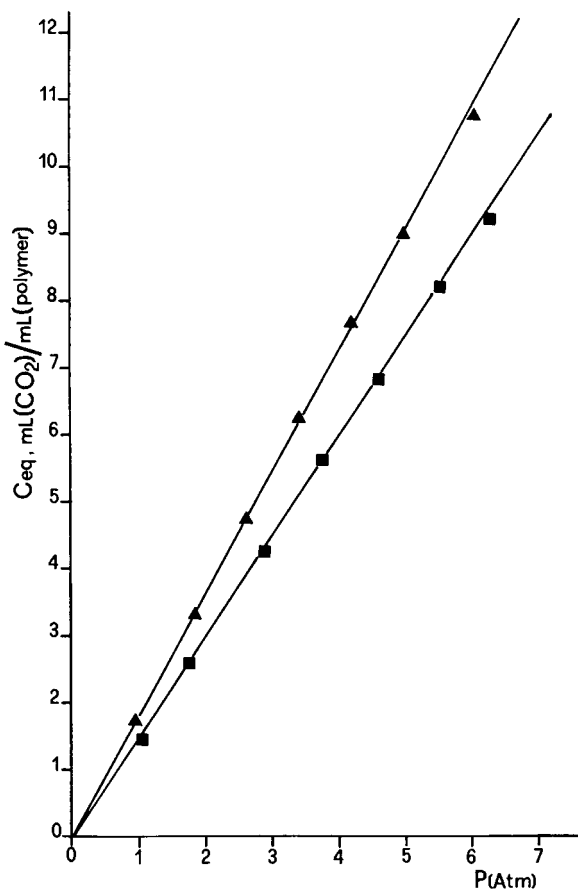

Figure 4 The equilibrium concentration of carbon dioxide expressed as mL gas (STP)/mL bulk polymer for samples (▲) R and (■) A.
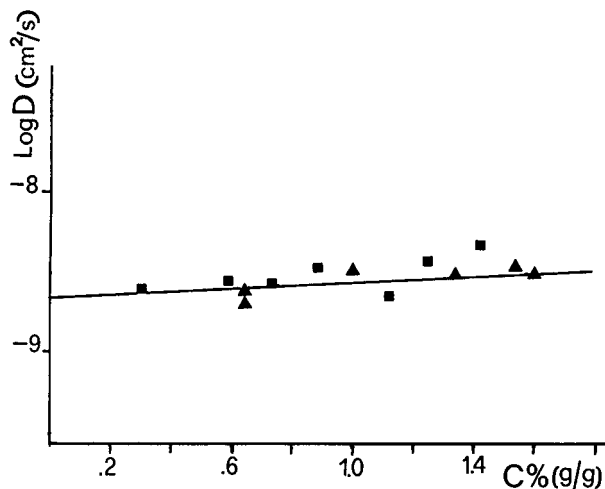
Figure 5 The diffusion coefficient, D, as a function of the equilibrium concentration for samples (▲) R and (■) A.

samples. The appearance of the endotherm at T_g for other systems was explained as due to the kinetics of the glass transformation.[12] In particular, the thermal energy absorbed at T_g is related to the time required for the system to reach the degree of freedom at a given heating rate. The endotherm at T_g is usually used to evaluate the extent of the physical aging and it has been proved that it increases logarithmically with aging time.[13,14] The glass transition of the aged sample is not reported since the endotherm at T_g does not allow the detection of this temperature in an accurate way. The two samples do not show any difference in terms of temperature of crystallization and temperature of melting.

Drawing Behavior

Stress–strain curves for samples R and A drawn at 80, 120, and 140°C are reported in Figure 2. At all the temperatures, the samples deform with neck propagation. The aged samples drawn at 80 and 120°C, after the yielding, deform at a stress level greater than that of the reference sample. This is because the mechanical deformation generates free volume; more work, and therefore a greater stress level, is needed to deform aged samples. This is proved by the fact that the endothermic process observed in DSC measurements at the glass transition on aged specimens is entirely removed after yielding.[1] The additional work needed to deform aged samples can also be considered as a measure of the extent of physical aging. On the other hand, the presence of ordered do-

mains also would explain the increase of the stress level during the deformation.

In Figure 2 also evident is the increased rate of fall in stress on yielding for aged samples. This phenomenon has been reported for aged glassy polymers[4,13] and explained in terms of the formation of localized necks forming at 90° to the draw direction in aged samples. The presence of slip bands, at 45° with respect to the draw direction, at the initial point of neck formation was also observed in aged PEEK.[4] The presence of crazing and shear yielding, with an interspacing ranging 10–100 nm, was also noticed, in well-aged and deformed glassy polymers, by Brady and Yeh.[15] They hypothesized that a not homogeneous microstructure existed in the aged samples due to the presence of ordered regions. In this case, therefore, either the decrease of free volume or the formation of ordered domains could explain the different drawing behavior in sample A.

In Figure 2, we notice that the drawing at 140°C does not produce a different stress level during the deformation. This is reasonable since 140°C is a temperature quite close to the glass transition and the consequent increase of chain mobility is able to erase the changes caused by the physical aging in sample A.

Another noteworthy difference in the stress–strain curves between samples R and A concerns the larger interval of necking registered in aged samples. This is evident in Figure 3 in which the local deformation λ_L detected in four different volume elements is reported versus the nominal deformation λ_N detected by recording the displacement of the extreme marks. In Figure 3, the four regions are indicated by the numbers 1–4. Figure 3 refers to the samples R and A drawn at 80°C, but the neck formation and propagation at 120 and 140°C are similar. This phenomenon can be explained in terms of a larger deformation in sample A needed to erase the aging and therefore to restore a similar free volume as that of sample R.

Transport Properties

The experimental approach used in this work is able to determine the sorption and the diffusion of carbon dioxide in samples R and A as a function of the pressure. The pressure decay is measured at different pressures of carbon dioxide. At any pressure, the ratio $(P_0 - P_t)/(P_0 - P_{eq})$ is detected as a function of time; P_0 is the initial pressure of the test gas before sorption starts, while P_{eq} and P_t are the pressures at equilibrium and at the time t, respectively. The ratio $(P_0 - P_t)/(P_0 - P_{eq})$
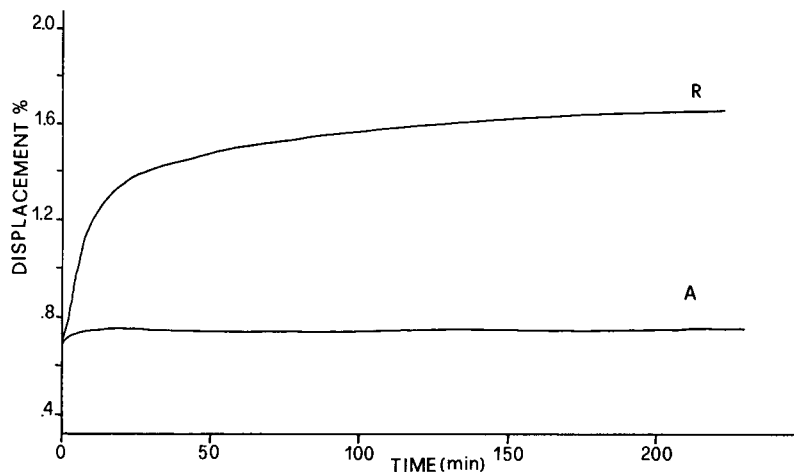
Figure 6 Creep curves for samples R and A.

is numerically equal to C_t/C_{eq}, where C_t and C_{eq} are the concentration of gas in the polymer at time t and at equilibrium.

The curves for samples R and A at different pressures of carbon dioxide show a linear increase of gas sorbed by the sample with the square root of time, a downward curvature, and the equilibrium value of vapor concentration. This behavior is typical of Fickian sorption curves; it is therefore possible, at each pressure, to derive a mean diffusion coefficient, $\bar{D}$ (cm^2 s^{-1}), from the equation

$$\frac{C_t}{C_{eq}} = \frac{4}{d}\left(\frac{\bar{D}\cdot t}{\pi}\right)^{1/2} \tag{1}$$

where d is the thickness (cm) of the sample.

In Figure 4, C_{eq}, expressed in mL (STP) of carbon dioxide per mL of bulk polymer, is reported for samples R and A as a function of the pressure. Although the experiment was performed at 25°C, i.e., well below the glass transition of PEEK, we observe that the solubility was a linear function of the pressure P, according to Henry's law:

$$C_{eq} = S \cdot P \tag{2}$$

where S is the sorption coefficient. It is important to point out that the pressure range studied is very restricted, limiting the possibility to see any "dual mode" curvature within this range. In Figure 4, we see that the aged sample has a lower sorption coefficient.

In Figure 5, the diffusion coefficient D, derived from the early stage of increase of weight of the sample using eq. (1), is reported as a function of equilibrium concentration for samples R and A.

The coefficient D can be dependent on the pressure and on the equilibrium concentration, C_{eq}. Generally, in systems following Henry's law, the coefficient D is independent of pressure, and at any pressure, it can be assumed, in the range of the experimental error, equal to D_0, the thermodynamic diffusion coefficient. In Figure 5, we see that the diffusion in both samples R and A is slightly dependent on concentration; the experimental points fit the same straight line extrapolating to $D_0 = 2.2 \cdot 10^{-9}$ cm^2/s. The coincidence of the diffusion and the lower sorption of sample A in respect to sample R can be better explained with the formation in the former of ordered domains impermeable to the gas. In fact, if the reduction of free volume were responsible of the lower sorption, we would have measured a much more reduced diffusion. This parameter is, in fact, more dependent on the fractional free volume than on the sorption. Instead, if we assume that the reduction of sorption is ascribed to a reduction of the permeable phase, the same diffusion for the remaining permeable phase is reasonable.

Viscoelastic Analysis

Structural changes associated with the physical aging of polymers affect the viscoelastic behavior.[1,17–19] In Figure 6, the displacement caused by the application of a constant stress at the temperature of 130°C is reported for samples R and A. As expected, the aged sample becomes less compliant. In Figure 7, the storage modulus (E') and the loss tangent (tan δ) are reported versus temperature. The measurements were performed in the vicinity of the glass transition. As previously
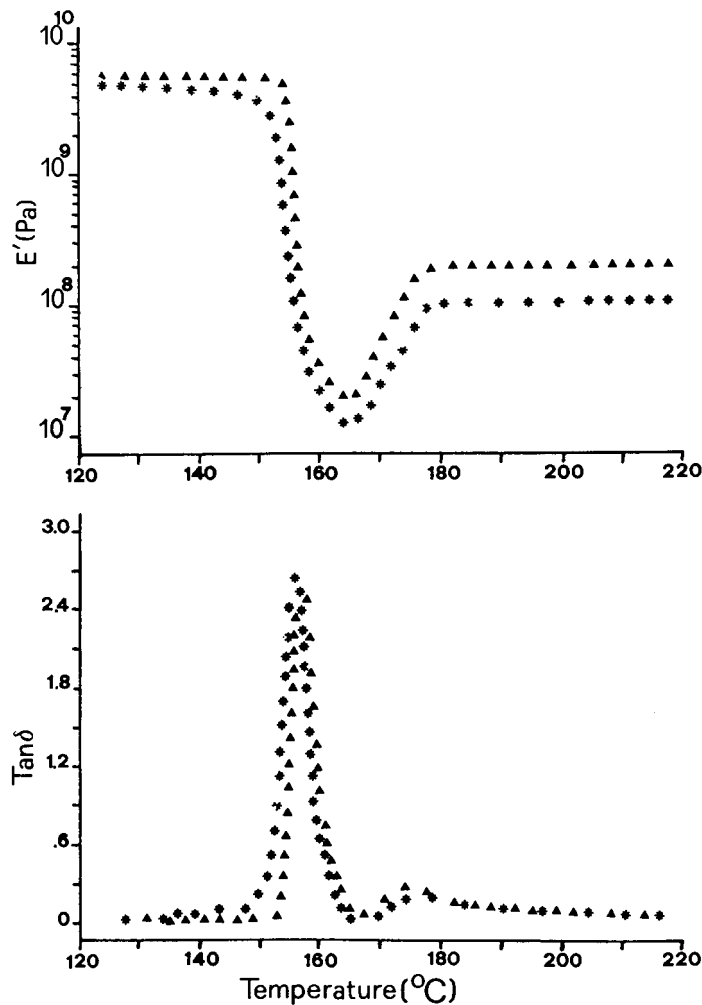
Figure 7 Storage modulus (E') and loss factor (tan δ) as a function of temperature for samples (∗) R and (▲) A.

reported,[20-22] the α relaxation in the amorphous PEEK, associated with the glass transition, is accompanied by a dramatic drop of the storage modulus and a sharp loss peak. Moreover, in the proximity of the glass transition, cold crystallization takes place with a consequent increase of the storage modulus. Immediately after the α relaxation, a broad shoulder appears. This relaxation corresponds to the amorphous phase which is now constrained by the presence of crystals formed during the cold-crystallization.[22] In Figure 7, we notice that, before the α relaxation occurs, sample A shows a higher storage modulus and a lower tan δ when compared with sample R. This is not surprising and it is in agreement with other data; it is caused by the densification of the material that reduces the molecular mobility. After the glass transition, the two samples show profiles in tan δ that are almost identical. On the other hand, the

storage modulus after the α relaxation is different for the two samples. Sample A exhibits a higher modulus and this can be explained in terms of a higher crystallinity and/or a better crystalline phase formed during the heating scan. This could be supported by the presence of small domains in the aged sample that act as nuclei of crystallization.

CONCLUDING REMARKS

In this work, several experimental approaches have been used in order to evaluate the extent of the physical aging. Not all the investigated techniques have the same sensibility. In addition to the endotherm at the glass transition in the DSC measurements, the stress–strain measurements can be considered particularly reliable in which

the different profile, in the rate of falling of the stress after the yield as well as the increased work to deform the sample, can be related to the extent of physical aging.

The reduced amount of carbon dioxide sorbed by the aged sample can be related to the presence of impermeable domains, besides the reduction of free volume. The physical aging affects the viscoelastic properties. In fact, the aged sample in the creep measurements is less compliant and the profiles of the storage modulus shows some significant differences.

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