

# The Effect of Physical Aging on Long-term Properties of Poly-Ether-Ketone (PEEK) and PEEK-Based Composites

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## Synopsis

The viscoelastic properties of the amorphous and semicrystalline PEEK and of a PEEK-based composite (APC2) have been analyzed as a function of the aging time and related free volume relaxation, at temperatures close to the glass transition temperature. The effect of thermal treatments (physical aging) on the polymer amorphous phase of the three systems is presented. Creep tests approaching the "zero stress" were performed on samples subjected to different thermal histories. The presence of a second phase, namely crystallites and fibers, determines a loss of the mobility of the polymeric amorphous chains and consequently a decrease of the rate of free volume relaxation.

## INTRODUCTION

In last years increasing attention has been devoted to the use of thermoplastic polymers as matrices for high performance composites. In such a view, semicrystalline PEEK (poly-ether-ether-ketone) was regarded as a potential substitute for the epoxy resins. PEEK possesses the inherent properties of the thermoplastic resins, namely easy formability, bonding and reprocessing capability, coupled with good impact resistance and low moisture and solvents sensitivity.

Several studies have been published on the characterization of PEEK-based materials. Blundell and co-workers<sup>1-3</sup> described the crystallization kinetics, obtaining the basic information for the processing of PEEK-based composites. The mechanical properties at elevated temperatures<sup>4</sup> of semicrystalline PEEK were studied and compared to those of currently used epoxies. Physical aging has also been extensively investigated. Enthalpy relaxations, associated with volume relaxations, were examined by Kemmish and Hay<sup>5</sup> by differential scanning calorimetry (DSC). The presence in the glass transition region of well-defined endothermic peaks were quantitatively associated with volume relaxation induced by the physical aging.

The characterization of effects of aging on the viscoelastic properties is necessary to predict the end use limits of the material in extreme conditions. Preliminary results were presented by Ogale and McCullough<sup>6</sup> for samples with different degrees of crystallinity while Carfagna et al.<sup>7</sup> recently analyzed the aging of the amorphous PEEK by means of DSC, X-ray diffraction, water

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sorption, and infrared spectroscopy (FTIR). They emphasized the effect of the aging on the amorphous PEEK free volume reduction and on the related significant morphological modifications.

In view of the application of PEEK as matrix for composites, we have studied the effect of aging on amorphous and semicrystalline (32% crystallinity) PEEK and on APC2 (a commercial product based on carbon fibers embedded in a PEEK matrix) by means of dynamic mechanical and transient tests. Fibers, similarly to crystallites in semicrystalline samples, can be considered as constraints to the mobility of the polymer segments of the amorphous phase. It could be expected that an increase of the amount of inclusions should result in a lower sensitivity of the material to the physical aging. Creep tests on amorphous and semicrystalline PEEK and APC2 are reported, and an analysis of the aging effects is presented.

### PHYSICAL AGING

The origin of aging is attributed to the out of equilibrium state of the sample when cooled below the glass transition temperature  $T_g$ .<sup>8</sup> The free volume excess decreases with time as a consequence of the material tendency to reach the true equilibrium. The mobility  $M$  of the polymer chains in the amorphous state is influenced by the available free volume. On the other hand, the rate of reduction of the free volume depends on the chain mobilities. The process is therefore self-retarding. At temperatures higher than the glass transition temperature, the chain mobility  $M$  is sufficiently high to permit an instantaneous volume relaxation. In this case, no aging effects are expected. Conversely, at temperatures much lower than  $T_g$ , i.e., below the temperature of the secondary transition  $T_b$ , mobility is negligible and hence volume relaxation is not observed. Therefore, it is only at temperatures close to the glass transition that the relaxation phenomenon becomes more evident.

The simplest analysis of aging is made on quenched materials. Samples are first annealed for a short time above  $T_g$  in order to recover the polymer equilibrium free volume and to erase any aging effect due to previous sub- $T_g$  thermal histories, and finally quenched to the temperature of interest. The aging time  $t_e$  is then measured as the elapsed time. It is expected that the free volume will decrease monotonically as a function of  $t_e$ .

Utilizing quite general assumptions on self-retarding processes, Struik described the mobility as inversely proportional to the aging time  $t_e$ ,

$$M = k/t_e \quad (1)$$

where  $k$  is a constant. The conditions on which eq. (1) is based are:

- (i) The process must be strongly self-retarding.
- (ii) The process must be far enough from the initial state.
- (iii) The process must be far enough from equilibrium.

The linear viscoelastic properties, which are determined by a spectrum of relaxation times, are inversely proportional to the mobility  $M$  and, hence,

according to eq. (1), proportional to the aging time:

$$\tau_i = k_i t_e \quad (2)$$

The  $k_i$ 's in eq. (2) are constants. Longer agings are then expected to increase the material stiffness. In order to properly characterize the viscoelastic behavior, creep tests should be, therefore, carried out for times much shorter than the aging time  $t_e$ . Indeed, only in these conditions, free volume changes during the creep test can be considered negligible with respect to the total decrease occurred during  $t_e$ . These are called "momentary" tests and allow to clearly characterize the viscoelastic properties relative to a specific aging time.

The isothermal creep curves referred to different aging times will appear shifted horizontally by a factor  $a_t$ . A measure of the effect of aging with respect to the annealing time  $t_e$  is the shift rate  $\mu$  defined as

$$\mu = d \log(a_t) / d \log(t_e) \quad (3)$$

The horizontal shift is proportional to variations of the relaxation times. Therefore, using eq. (2), one obtains

$$\mu = 1 \quad (4)$$

The validity of eq. (4) derives from the conditions (i)–(iii). The failure of one of these conditions will give in general

$$0 < \mu < 1 \quad (5)$$

From this point of view the lack of aging effects at temperatures lower than the secondary transition temperature  $T_b$  or higher than the glass transition temperature  $T_g$  (i.e.,  $\mu = 0$ ) can be attributed to the failure of the conditions (ii) and (iii), respectively.

The crystalline phase and the fibers are stable and do not undergo any aging. They represent a constraint to the segmental mobility, at least in the vicinity of the inclusion boundaries.<sup>9</sup> The presence of inclusions is then expected to shift the glass transition to higher temperatures, and to broaden the glass transition over a larger temperature range. For this reason aging effects may be expected for semicrystalline polymers and their composites also at temperature slightly higher than the glass transition temperature of the completely amorphous materials. Moreover, the presence of inclusions in the amorphous phase cannot accomplish condition (i). In this case, in fact, the mobility  $M$  depends on both free volume and constraints. Therefore, a decrease of the free volume can have minor effects on  $M$ , and the process can become slightly self-retarding, with a shift ratio  $\mu < 1$ .

## EXPERIMENTAL

Samples having length  $L_0 = 25$  mm and width  $W = 4$  mm were cut from sheets 0.25 mm thick of both amorphous (crystallinity less than 2%) and semicrystalline (crystallinity 32%) PEEK. APC2 samples having length 40 mm, width 4 mm, and thickness 1 mm, with unidirectional fibers oriented at

90° and 45° with respect to the direction of the applied stress were cut from a lamina. The amount of fibers is about 62% of the total volume.

Transient (creep) and dynamic mechanical tests were carried out on a DYNASTAT (IMASS) instrument, capable of performing an accurate step function (20 ms rise time, and no overshoot), and clean sine waves. The temperature was controlled by the DYNATHERM within 0.1°C.

The experiments at different aging times have been performed on the same samples allowing for full recovery after each creep test. This procedure avoids problems related with the possible changes in shape, gripping, and alignment, which often affect the results of tests performed on different samples. For practical purpose, long aging time tests ( $t_e > 1/2$  day) were performed by transferring the samples from an oven to the Dynastat cell. Samples have been then subjected to a large change of temperature over a very short time. Nonetheless, based on the volume relaxation theory, this fact should not affect the aging, except that on a short transient time as will be discussed further on.

## RESULTS AND DISCUSSION

### Dynamic Mechanical Tests

Dynamic mechanical tests have been performed on amorphous, semicrystalline, and composite samples in order to achieve a preliminary characterization of these materials. The influence of temperature on dynamic moduli and loss factors is shown in Figure 1. Amorphous PEEK exhibits a curve interrupted at 145°C since beyond this temperature the polymer undergoes cold crystallization. As previously indicated, smoothing of the glass transition in the systems with internal constraints (both crystallites and fibers) is evident from the three curves. The glass transition temperature of crystalline PEEK is increased by 10°C with respect to that of amorphous PEEK ( $T_g = 145^\circ\text{C}$ ). This fact can be attributed to the reduced mobility of the amorphous phase of the semicrystalline samples.

In the case of APC2 the maximum of loss factor curve is located at a temperature lower than expected, in contrast with the trend shown by the crystalline PEEK. This could be due to the probable presence in the APC2 of additives which change the material viscoelastic properties or to the different morphology of the inclusions. As already described for PET, the glass transition temperature grows with crystallinity but decreases once the crystallites tend to form clusters, leaving a greater freedom to the segmental mobility.<sup>10</sup>

### Volume Relaxation

The concept of free volume is often presented in a qualitative manner. A precise definition is not simple; nonetheless, changes in the total volume can be directly associated to changes of the free volume. The total volume relaxation has been observed in a *zero-stress isothermal creep experiment*. The results have been reported as displacement of an arbitrary initial value of the sample length. For this reason the zero of such relaxation curves is meaningless.

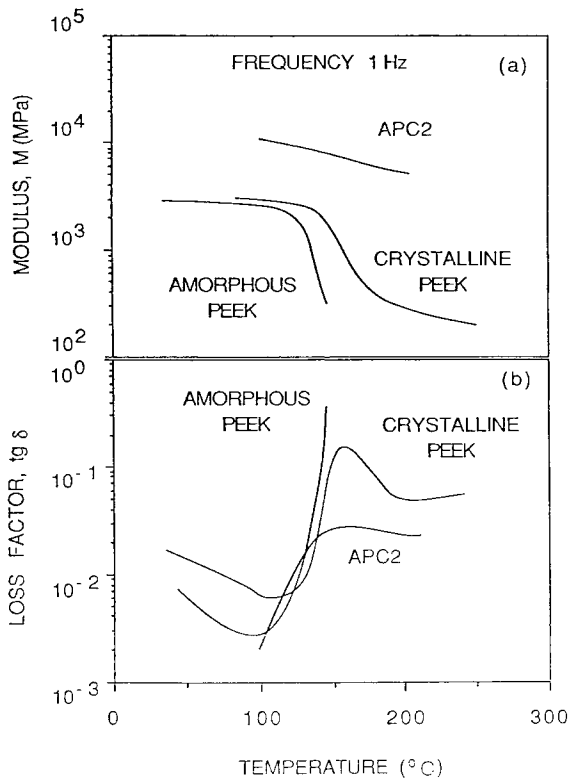


Fig. 1. (a) Dynamic modulus and (b) loss factor versus temperature for amorphous and semicrystalline PEEK and APC2.

The variation of sample length versus time for a quenched crystalline PEEK sample is reported in Figure 2. Length and hence volume decreases monotonically as previously discussed. The same procedure cannot be applied to the amorphous PEEK since it undergoes cold crystallization when heated slightly above its glass transition temperature. This case requires different procedures and thermal histories.

The results reported in Figure 3 are relative to the same creep test carried out on amorphous and semicrystalline PEEK samples heated from room temperature to 130°C. The thermal history can be considered as a down-quench/storage/upquench (the material is rapidly quenched from the melt, stored at room temperature, and finally heated up to the test temperature). The curve of the amorphous sample exhibits a maximum localized around 1000 s while that of the semicrystalline sample increases with time and does not reach any appreciable maximum, at least in the time range of the experiment. The presence of a maximum in the curves of samples subjected to complex thermal histories is explained by describing the free volume variations in terms of a relaxation times spectrum associating each relaxation time with distinct chain motions. If a sample is annealed at temperature  $T_1$  for a time  $t_1$ , only the polymer segments characterized by motions with relaxation times lower than  $t_1$  are allowed to relax to the equilibrium values, while the

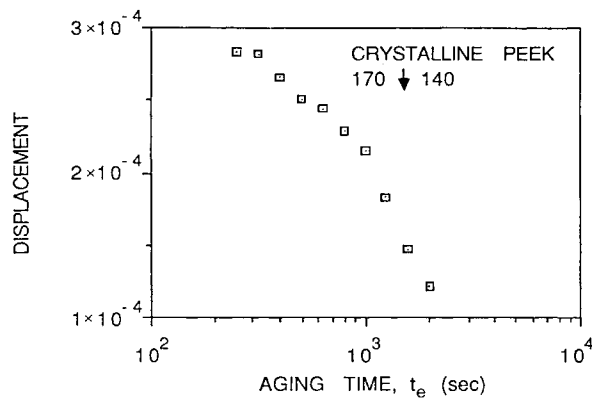


Fig. 2. Zero stress creep experiment: Displacement versus aging time for a crystalline PEEK sample subjected to a downquench from 170 to 140°C.

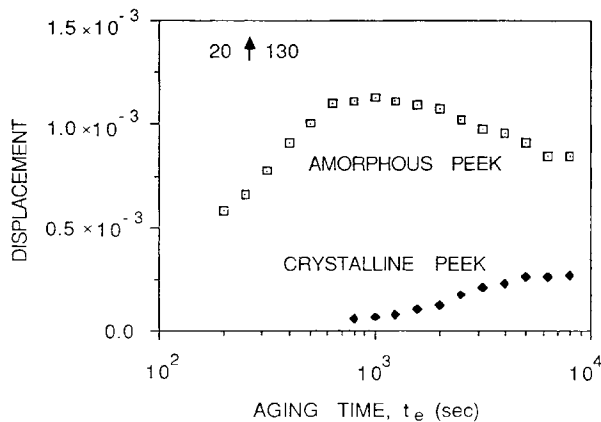


Fig. 3. Zero stress creep experiments: Displacement versus aging time for amorphous and crystalline samples subjected to an upquench from room temperature to 130°C.

other ones remain substantially far from equilibrium. Upon heating to a higher test temperature  $T_2$ , all the chain segments already relaxed tend to the new equilibrium configurations relative to the new temperature, leading to a volume increase. However, due to the temperature activation, these additional relaxations occur in a shorter time ( $t_2$ ). The out of equilibrium segments characterized by higher relaxation times (not allowed to relax at  $T_1$ ) only slightly relax in reaching the new temperature ( $T_2$ ) and still persist above the new equilibrium configuration. Finally, at times greater than  $t_2$ , only these motions remain active leading to the same relaxation behavior attained by a system directly quenched from the melt (8). This characteristic time ( $t_2$ ), associated with the maximum in the volume-time curve, strongly depends upon test and storage temperatures, respectively  $T_2$  and  $T_1$ . For example, as indicated in Figure 3, the amorphous PEEK behaves as a quenched material after an annealing time at  $T_2$  of the order of  $10^3$  s, even if previously stored for a long time (few months) at the temperature  $T_1$  (room temperature). The fact that the characteristic time  $t_2$  for the semicrystalline sample is greater than

that for the amorphous sample is probably due to either the lower cooling rate, from the melt needed to permit almost full crystallization of the material, and to the increase of the volume relaxation times induced by the crystals constraint.

These results justify, for the amorphous sample, the use of upquench procedures in order to obtain data on the aging phenomena comparable to those previously obtained by downquenching. The same argument also justifies the ineffectiveness of short time transfers from the oven to the Dynastat on the overall aging of the samples.

### Linear Viscoelasticity in Creep Experiments

As indicated in the previous section, tests of volume relaxation vs. time have been performed as *zero stress* creep experiments. Therefore, care must be taken on the assessment of linear viscoelastic limits. In fact, it can be assumed that the overall displacement exhibited by a withstanding constant load is

$$d = d_v + d_s \quad (6)$$

where  $d_v$  and  $d_s$  are, respectively, the contribution due to volume relaxation and applied stress.

Rigorously, the two contributions,  $d_v$  and  $d_s$ , are not independent since while the volume relaxation affects the relaxation times of viscoelastic phenomena, at the same time large stresses can induce free volume recovery.<sup>8</sup> Nonetheless, in low stress momentary creep tests the two effects do not interact significantly. In this case three distinct ranges of the applied stresses can be defined, according to the relative ratio between  $d_v$  and  $d_s$

$$\begin{aligned} \text{(I)} \quad & 0 < \sigma < \sigma_1, & d_v \gg d_s \\ \text{(II)} \quad & \sigma_1 < \sigma < \sigma_2, & d_v = d_s \\ \text{(III)} \quad & \sigma_2 < \sigma, & d_v \ll d_s \end{aligned}$$

In region I only volume relaxations can be detected. This is not a field of linearity since a change in stress does not induce appreciable displacement, while the compliance is varying. The tests reported in the previous section fulfill this condition.

For  $\sigma_2 < \sigma$  (region III) the displacement due to the creep overcomes the volume relaxation. When  $\sigma_2$  is smaller than the onset of the nonlinear viscoelastic behavior, it is possible to approach linearity. Again region II is a transition interval where linearity does not occur. Creep experiments are, hence, nonstandard cases in which the small value of the stress assures linear viscoelasticity. Dynamic experiments on the contrary do not suffer this shortcoming. In our creep experiments linearity has been checked directly by performing tests at different stress levels. Thereafter, the stress has been fixed to be 2 and 4 MPa for the amorphous and crystalline samples, respectively, and 12 MPa for APC2 samples.

### Creep Tests

Figure 4 shows the creep compliance at 130°C of a sample of amorphous PEEK aged for different times. An increase of stiffness with aging is observed.

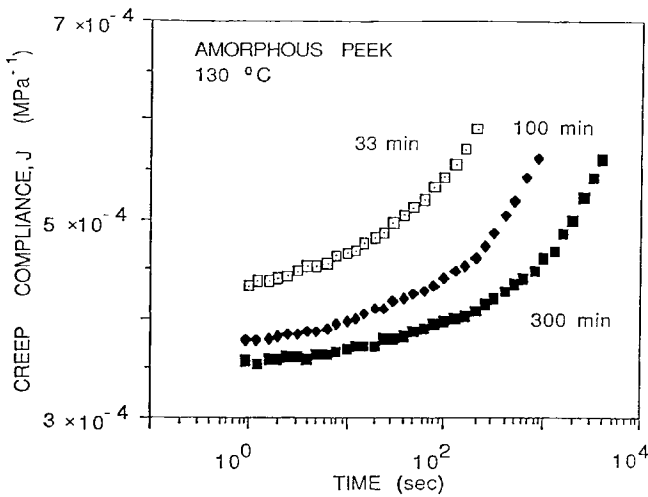


Fig. 4. Creep compliance of amorphous PEEK at 130°C for three different aging times:  $t_e = 33, 100, 300$  min.

The creep compliance curves are approximately modeled by the Findley expression

$$J = J_0 + A(t/t_0)^n \quad (7)$$

where  $A (= 1 \text{ MPa}^{-1})$  is a constant introduced for dimensional reasons. The use of this kind of formalism, rather than the expression used by Struik,<sup>8</sup> is made in view of an extension to the nonlinear behavior, when the Findley expression will be substituted by the more general Schapery equation.<sup>11</sup> Moreover, a power law such as eq. (7) allows an analytical evaluation of the spectrum of relaxation times and of the dynamic compliance  $J(\omega)$ .<sup>12</sup> On the other hand, eq. (7) can be seen as the development of Struik expression up to first order in  $(t/t_0)^n$ .

The results have been fitted into eq. (7) by a least square procedure and then the shift of the creep curves computed analytically. The possibility of a superposition of curves at different aging time relies on the constancy of the exponent  $n$  in eq. (7), since it hardly varies during aging. In order to be self-consistent, a mean value of  $n$  has been assumed, and then the fitting procedure reperformed. The continuous curves in Figure 4 are obtained by using this procedure.

Some experimental evidence exists about the necessity of a vertical shift, i.e., a dependence of  $J_0$  on aging time. This event has been observed during the aging at 130°C of an amorphous sample dynamically tested at a frequency of 10 Hz. Ninomiya and Ferry<sup>13</sup> showed that

$$J(t) = J'(\omega) + 0.4J''(0.4\omega) - 0.014J'''(10\omega)_{\omega=1/t} \quad (8)$$

which correlates the creep compliance to the storage and loss compliance. According to eq. (8) the behavior of  $J'(10 \text{ Hz})$  is almost the same as that of  $J_0$ . The curve  $J'(10 \text{ Hz})$  vs. time reported in Figure 5 is similar to the volume



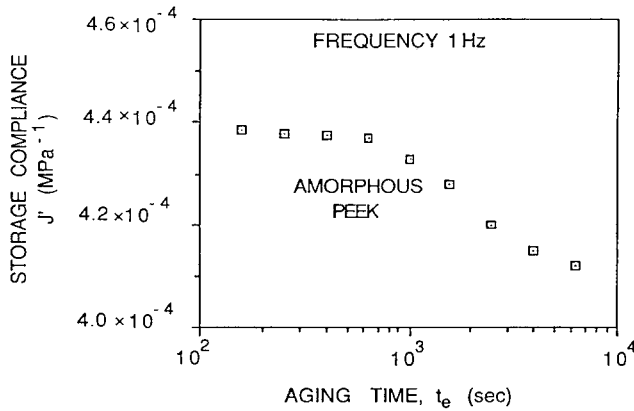


Fig. 5. Storage compliance versus aging time at a frequency of 1 Hz for amorphous PEEK at 130°C.

relaxation curve of Figure 3, confirming the influence of the aging also for the instantaneous compliance. The correct horizontal shift procedure must be then performed on the net compliance  $J(t) - J_0$ . The data shown in Figure 4 have been scaled in terms of  $J(t) - J_0$  and are reported in Figure 6 on a log-log scale plot. The experimental data are well described by eq. (7). Three different values of the parameter  $t_0$  are obtained, from which the shift parameter is defined:

$$a_t = t_0(t_e) / t_0(t_{e \text{ reference}}) \tag{9}$$

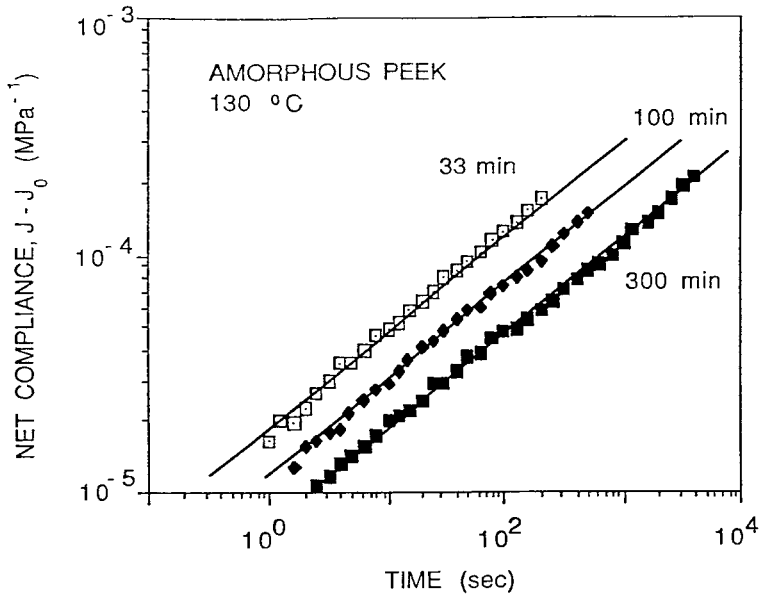


Fig. 6. Net creep compliance ( $J - J_0$ ) of amorphous PEEK at 130°C. The data are the same of those reported in Fig. 4.

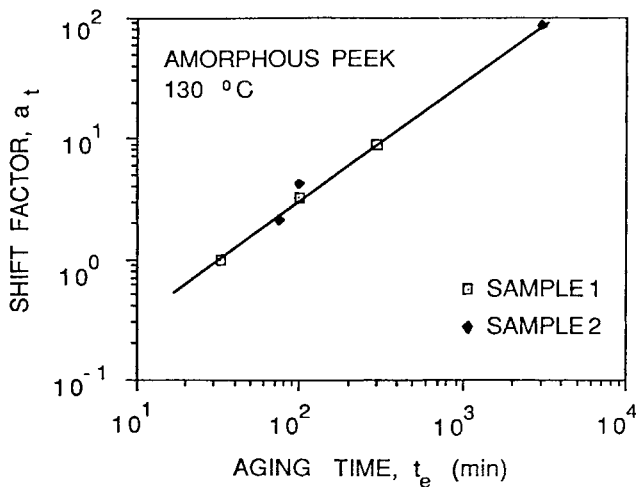


Fig. 7. Shift factor versus aging time for amorphous PEEK at 130°C.

The resulting plots of  $a_t$  vs.  $t_e$  are reported in Figures 7 and 8 for both amorphous and crystalline sample, respectively, at the same level of undercooling of 15°C, i.e., at a temperature of 130 and 140°C, respectively. The experimental data are plotted in the log-log graph and are well fitted by straight lines whose slope is the shift rate. The values are close to 1 for the amorphous sample and 0.5 for the semicrystalline sample. As previously discussed, the presence of chains constrained by the crystalline phase makes the overall system less sensitive to the aging as indicated by the lower values of the shift rate.

The same procedure has also been used for both amorphous and semicrystalline samples undercooled 5 and 25°C. The dependence of the shift rate, on the undercooling level, calculated according to the generally accepted definition ( $T_g - T$ ), is reported in Figure 9. The shift rates at temperatures of 130

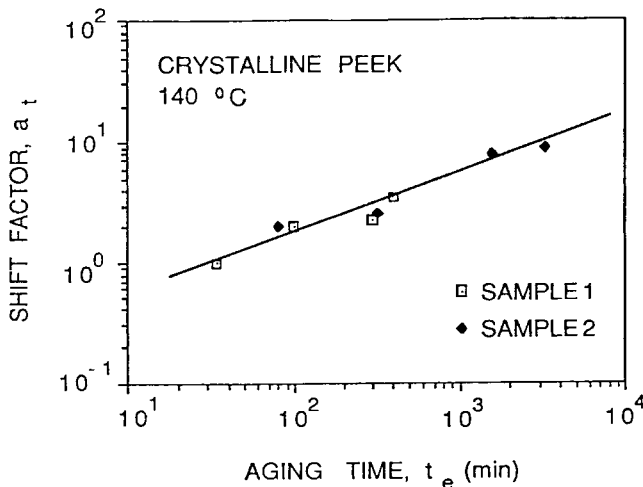


Fig. 8. Shift factor versus aging time for crystalline PEEK at 140°C.

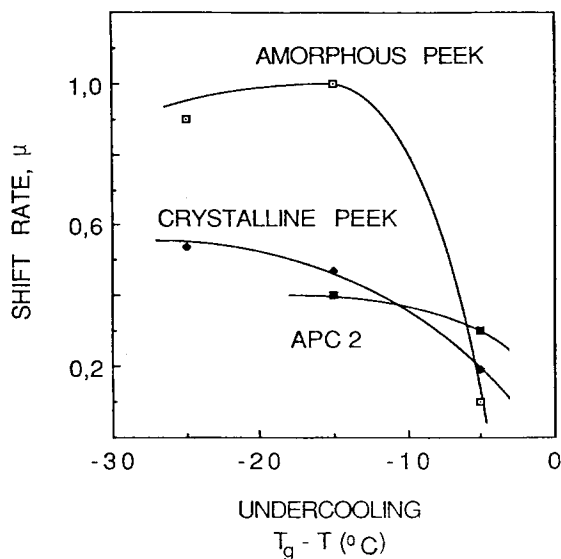


Fig. 9. Shift rate versus degree of undercooling ( $T_g - T$ ) for the amorphous and crystalline PEEK and APC2.

and 140°C, for the APC2 sample with fibers oriented at 90° have also been reported in Figure 9. For this system, undercooling of 15 and 5°C from the corresponding  $T_g$  have been investigated. Chain mobility constraints are also present in the carbon fiber composites, and they cannot only be attributed to the presence of the fillers but, even in this case, to the epitaxial crystals nucleated and grown from the fiber surfaces. Fibers are, in fact, surrounded and masked by highly crystalline regions. Nonetheless, the presence of the fibers, also in completely amorphous materials, has been described to induce a local increase of the glass transition associated to the local stress distribution.

The shift rates of the three systems decrease on approaching  $T_g$ . However, while the curve of the amorphous sample is steep, it becomes progressively flatter for the crystalline sample and for the APC2, respectively. This behavior reflects the broadening of the glass transition already discussed in the dynamic measurements of Figure 1.

At large undercooling the following sequence for the shift ratio has been thus observed

$$1 = \mu_{\text{amorphous}} > \mu_{\text{crystalline}} > \mu_{\text{APC2}} \quad (10)$$

as a consequence of the fact that the process becomes less self-retarding with increasing the amount of fillers. It has been noted that, at small undercooling, the sequence is reversed. This can be probably attributed either to the fact that the process is closer to equilibrium with decreasing the amount of the inclusions and also to the broadening of the glass transition region. Undercoolings, as previously indicated, were calculated from the  $T_g$ , which is defined as the midpoint of the glass transition, even if the shift rate is zero (fastest relaxation) only at the end of the glass transition region ( $T_f$ ). A more convenient definition should hence evaluate the undercoolings from the  $T_f$ .

The same trend can be observed in the results of Ogale and McCullough<sup>6</sup> for amorphous and crystalline PEEK, but with different values of the shift rates.

### CONCLUSIONS

A viscoelastic analysis has been performed on aged samples of amorphous and crystalline PEEK and of the PEEK-based composite APC2.

The results have been basically discussed using the theory proposed by Struik. The shift ratio has been analyzed as a function of the undercooling  $T_g - T$  for the three systems. The crucial effect of constraint due to the crystalline phase and/or the fibers has been discussed and related to the experimental results. An increase of the amount of the inclusions resulted in a lower sensitivity of the material to the physical aging.

An analytical shift procedure, based on the Findley expression of the creep compliance, has been implemented.

As a future goal, the analysis of the possible dependence of the shift rate on the aging time should be performed, especially in the systems where the shift rate is always lower than unity.

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