Physical Aging of Polymer Concrete During Creep

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ABSTRACT: The long-term creep of polymer concrete was predicted with the structural approach and with the phenomenological model of the creep of a polymer binder (polyester resin). The physical aging of polyester resin during the previous exposure of the composite at elevated temperatures and its subsequent creep was examined. The model accounted for the deceleration of relaxation processes in the polyester resin and its shrinkage. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3427–3431, 2003

Key words: polyesters; aging; structure

INTRODUCTION

The glassy state of a polymer is thermodynamically a nonequilibrium one. The transition to equilibrium, physical aging,[1] occurs in time and is exhibited as a change in polymer volume (density), its creep compliance, and so on.[1–3] The effect of aging [time (t_{ag}) and temperature (T_{ag}) of preliminary exposure] on the creep compliance of a polymer and a polymer-based composite at short-term tests has been described with the principle of analogies on t_{ag}.[1,4]

Physical aging is a thermally activated process, and temperatures of $T_{ag} = T_g - 10/20$°C, where T_g is the glass-transition temperature, are usually used for its acceleration. Therefore, it is quite often asserted that this process occurs at temperatures close to T_g. However, physical aging also takes place at lower temperatures. We found out[4] that long-term (~ 13 years) exposure of a cured polyester resin ($T_g \approx 70$°C) to laboratory conditions at $T_{ag} \approx 20$°C led also to a reduction of the resin's creep compliance according to the principle of analogies. Polyester resin filled with a diabase (polymer concrete) displayed the same effect. For the cured polyester resin, a binder based on the resin with a diabase filler volume content (c) of 0.28 and a polymer concrete with a c of 0.778, the reduction functions describing the changes of creep compliance with short-term tests on t_{ag} and T_{ag} coincided. That is, the aging of the polymer, polyester resin, in the block and in a composite was the same.

The creep compliance of polymer concrete in a conditionally initial state and after the preliminary exposure at $T_{ag} \approx 20$°C for 13 years was calculated with the structural models of a composite (a polymer filled with spherical particles).[5]

There are grounds to suggest that the physical aging of polymers also occurs during its creep: an account for the aging of cured polyester resin on its creep compliance[4] allowed us to refine the prediction of long-term creep on the basis of the time–temperature analogy (TTA) principle from the results of short-term creep tests at elevated temperatures. The physical aging of polymer composites during creep was not studied earlier. The exception is a study[6] in which the shrinkage due to physical aging during the creep of thermoplastic polyamide reinforced with carbon fibers was evaluated.

The purpose of this study was to estimate the compliance that accounted for the aging of polymer concrete during long-term creep.

Because of the relaxation nature of the physical aging of a polymer, its rate decreases in time. The effect of aging on creep depends on the material age at the moment of loading. Therefore, it is important to develop a model that takes into account the influence of preliminary aging on the aging during creep.

EXPERIMENTAL

Material and tests

The stated problems were solved with experimental data on long-term (~ 3 years) creep at a temperature (T) of $T_{ag} \approx 20$°C of a polymer concrete (brand PC-5, a Bulgarian polyester resin, Vinalkid 550P, filled with marble flour and marble aggregate; total $c = 0.741$) in the conditionally initial state and after preliminary exposure for $t_{ag} \approx 90$, 180, 300, and 500 days at $T_{ag} = 40$, 60, and 90°C. The results of the experiment for shorter creep time (until 0.3 years) were reported earlier.[4] Experimental data on long-term (~ 0.6 years)

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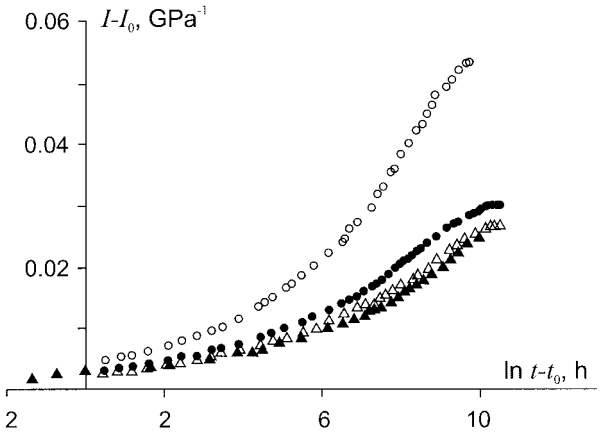

Figure 1 Experimental creep compliance curves of PC-5 at different ages: t_{ag} = (○) 0, (●) 225, (△) 315, and (▲) 510 days for T_{ag} = 60°C.

creep at $T = T_{ag} \approx 20$°C and short-term (~ 4 days) creep at T = 20, 30, 40, 50, and 60°C of a cured polyester resin in the conditionally initial state[4] were also used. All creep tests were carried out in compression when the operating stresses did not exceed the limit of linear viscoelasticity.

Experimental data

The results of the long-term creep tests of PC-5 in the conditionally initial state and after preliminary exposure at T_{ag} = 60°C for 225, 315, and 510 days (Fig. 1) showed that the plateau (horizontal asymptote) of creep compliance was reached after 2.5 years. Also, the horizontal asymptotes of creep compliance of PC-5 were different for different t_{ag}'s. An experimental description of this revealed the fact that it was not enough usage the principle of analogies on t_{ag}. It can be stipulated, perhaps, that the shrinkage of the polymer concrete was due to (a) a reduction in the porosity of the PC-5 structure under the action of constant compression stress and/or (b) the physical aging of the polyester resin in the PC-5. Thus, the compliance of polymer concrete might be considered as the sum

$$I = I_0 + I_{ve} + I_p + I_{sh} \tag{1}$$

where I_0 is instantaneous compliance, I_{ve} is the viscoelastic compliance conditioned by the creep of the polyester resin, I_p is the plastic compliance conditioned by the closing of the pores, and I_{sh} is the compliance conditioned by the shrinkage of the polyester resin due to physical aging.

Calculations

To describe the viscoelastic component of the creep compliance of the polyester resin, we used the phenomenological creep model of an aging material with a kernel in the form of exponent sum.[7] The integral equation, which is linear with regard to the stresses, gives the following expression:

$$I_{ve} = \sum_{i=1}^{n} b_i \left(1 - \exp\left(-\frac{1}{\tau_i}\int_{t_0}^{t} a_{ag}(s)\, ds\right)\right) \tag{2}$$

where τ_i, b_i ($i = 1 \cdots n$) is the spectrum of retardation times; $a_{ag}(s)$ is the reduction function characterizing the change in the spectrum due to aging; and $t_0 \equiv t_{ag}$ is the age of the material.

If the creep duration ($t - t_0$) is so small that the aging process during the creep can be neglected, $a_{ag}(s) \equiv a_{ag}(t_0)$, and eq. (2) is transformed as follows:

$$I_{ve} = \sum_{i=1}^{n} b_i \left(1 - \exp\left(-a_{ag}(t_0)\frac{(t - t_0)}{\tau_i}\right)\right) \tag{3}$$

We used this relation earlier[4] for the definition of the spectrum of retardation times of the polyester resin in the conditionally initial state ($t_0 = 0$, $a_{ag} = 1$) by the results of short-term creep tests at different temperatures on the basis of the TTA principle, $\tau_i = \tau_{0i}/a_T$, where a_T is a time–temperature reduction function. This experimentally obtained function can be approximated by the formula of Williams–Landel–Ferry (WLF):

$$\ln a_T = \frac{c_1(T - T_0)}{c_2 + T - T_0} \tag{4}$$

where T_0 = 20°C is a basic temperature, c_1 = 29.1, and c_2 = 108.7.

The calculation of the viscoelastic component of creep compliance of polymer concrete from the properties of the structural components was carried out on the basis of Kerner's model[8] and the generalized one.[9] For a two-component system with filler, aggregate, and binder, which may simulate in the first approach the considered PC-5 with a c of 0.741 and the Poisson ratio of the binder (ν_m) constant at 0.382, the calculation of the viscoelastic compliance of polymer concrete is reduced to the multiplication of the binder viscoelastic compliance by a constant value. In our case, for Kerner's model, this value was equal to 0.105; for the generalized model, the value was 0.142.

To describe the reduction function $a_{ag}(t_{ag})$, we used the following relation:[4]

$$\ln a_{ag} = -\alpha[1 - \exp(-kt_{ag})] \tag{5}$$

where

$$k = k_0 \exp\left(-\frac{\beta}{T_{ag}}\right) \quad (6)$$

The parameters $\alpha = 3$, $k_0 = 0.0243\ h^{-1}$, and $\beta = 1610\ K^{-1}$ were defined by the results of the short-term (~ 4 days) creep tests of PC-5 with the different t_{ag} and T_{ag} values.

The age t_0 (or t_{ag}), the material state with regard to the conditionally initial one ($t_0 = 0$), was determined by the reduction function $a_{ag}(t_{ag})$. This state was reached after a long time, $t_{0ag} = t_0$, at room temperature, T_{0ag}, or after time t_{1ag} at an elevated temperature, T_{1ag}. When we equated the values of the reduction function a_{ag} (or $\ln a_{ag}$) in eq. (5), we obtained

$$\exp\left(-\frac{\beta}{T_{1ag}}\right)t_{1ag} = \exp\left(-\frac{\beta}{T_{0ag}}\right)t_{0ag}$$

or

$$t_0 = t_{1ag}\exp\left(\beta\left(\frac{1}{T_{0ag}} - \frac{1}{T_{1ag}}\right)\right) \quad (7)$$

The effect of physical aging on the viscoelastic compliance of a material subjected to a constant stress (σ_0) at time t_0 is characterized by the reduction function $a_{ag}(t - t_0, T)$. The function $a_{ag}(t - t_0, 20)$, calculated by eq. (5) for $t_{ag} = (t - t_0) + t_0$ with allowance for eqs. (6) and (7) for $T_{0ag} = 20°C$ and $T_{1ag} = T_{ag} = 60°C$, are shown in Figure 2(a). The aging during creep was most intensive in the conditionally initial material, whereas it was the least intensive in the material preliminarily aged at $T_{ag} = 60°C$ for 500 days.

To separate the shrinkage strain from the viscoelastic strain during creep is complicated enough. Therefore, we used the approach of ref. 10, based on concept of free volume, according to which one of the reduction functions of a polymer is connected with change of its free volume (f):

$$\ln a = B\left(\frac{1}{f} - \frac{1}{f_0}\right)$$

In case of physical aging, the changes in free volume and specimen volume (V) coincide. For the function a_{ag}, we have

$$\ln a_{ag}(t - t_0, T) - \ln a_{ag}(t_0, T_{ag}) = \ln \frac{a_{ag}(t - t_0, T)}{a_{ag}(t_0, T_{ag})} \approx \frac{1}{f_0^2}\left(\frac{\Delta V}{V_0}\right)_m \quad (8)$$

where $(\Delta V/V_0)_m$ is the relative change in the binder volume due to aging during the creep, f_0 is the relative free volume of the binder at $T_{ag} = T = 20°C$ in the conditionally initial state. In the WLF eq. (4), $c_1 = (1/f_0)$, that is, $f_0 = 0.035$.

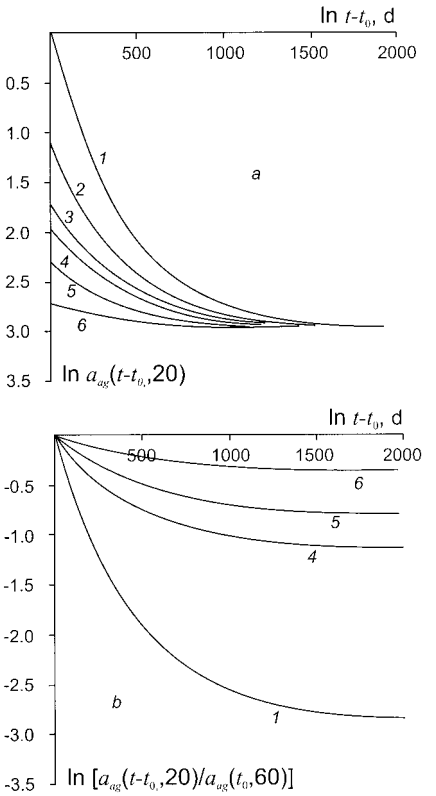

Figure 2 (a) Reduction function describing the change in the compliance of PC-5 during creep at 20°C and calculated by eq. (5) with allowance for eqs. (6) and (7) for $T_{ag} = 60°C$ and t_{ag} = (1) 0, (2) 90, (3) 180, (4) 225, (5) 315, and (6) 510 days. (b) Changes in the reduction function of PC-5 at different ages during creep [designations are the same as in Fig. 2(a)].

The relative change in the PC-5 volume was proportional to the change in the binder volume:

$$\left(\frac{\Delta V}{V_0}\right)_c = (1 - c)\left(\frac{\Delta V}{V_0}\right)_m \approx (1 - c)f_0^2 \ln \frac{a_{ag}(t - t_0, T)}{a_{ag}(t_0, T_{ag})}$$

where c is the total volume content of the filler and aggregate in the concrete; in our case, $1 - c = 0.259$.

The shrinkage strain (ε_{sh}) and the corresponding compliance (I_{sh}) are

$$I_{sh} = \frac{\varepsilon_{sh}}{\sigma_0} = \frac{1 - c}{3\sigma_0} f_0^2 \ln \frac{a_{ag}(t - t_0, T)}{a_{ag}(t_0, T_{ag})} \quad (9)$$

The dependencies of $\ln[a_{ag}(t - t_0, T)/a_{ag}(t_0, T_{ag})]$ on $t - t_0$ for PC-5 at different ages are shown in Figure 2(b).

RESULTS AND DISCUSSION

The results of the calculation of the viscoelastic compliance of PC-5 on the viscoelastic compliance of the

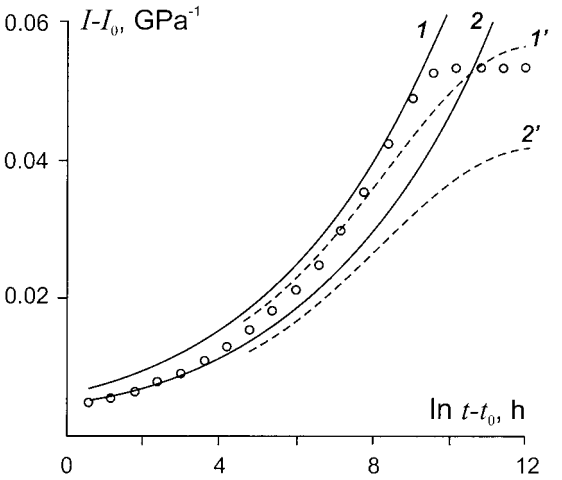

Figure 3 Creep compliance of PC-5 in the conditionally initial state: The points are experimental data, and the lines are the calculations based on Kerner's (2 and 2′) and the generalized (1 and 1′) models with the creep compliance of binder, the calculations based on the TTA principle (1 and 2), and the experimentally determined data (1′ and 2′).

binder (polyester resin),[4] determined from the short-term creep tests at different temperatures on the basis of the TTA principle and directly from the long-term creep test, are shown in Figure 3. The comparison of the calculation with the experimental data showed that

1. The application of the generalized model (Fig. 3, lines 1 and 1′) gave values of compliance that are higher than the experimental data already in the range of small values of time $t - t_0$:
2. The application of Kerner's model (Fig. 3, lines 2 and 2′) gave values of compliance that were practically coincident with the experimental ones in the range of small values of time, $\ln t - t_0 < 4.5$ ($t - t_0 < 90$ h), and that were much below the experimental ones at larger times $t - t_0$. The observed discrepancy of the calculation with the experiment (more intensive growth of experimental values of a creep compliance in time) can be stipulated by the shrinkage of PC-5.

An attempt to estimate the shrinkage of the polymer concrete due to pores closure was undertaken. The modification of the volume content of the pores during the creep of PC-5 was evaluated from the results of long-term creep tests of PC-5 and binder with the generalized structural model. The solution of the problem is specified in ref. 5. The Poisson ratios of PC-5 and binder were assumed to be constant during creep. The porosity of PC-5 increased during creep (see Fig. 4). This result was qualitatively in line with our previous results on the optimization of complex of structural parameters, pores, and interphase layers

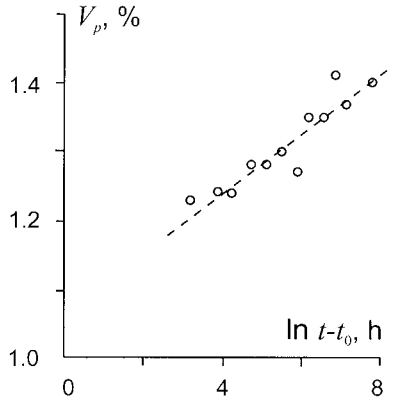

Figure 4 Values of the porosity of PC-5 calculated by the results of the creep tests of PC-5 and the binder with the generalized model of a composite.

included[5] in PC-5. So, we did not find any effect of pore closure.

The calculation results of the viscoelastic component of the creep compliance of PC-5 at different ages from the viscoelastic compliance of the binder at different ages described by eqs. (3), (5), and (6), on the basis of the Kernel's model, are shown by solid lines in Figure 5. For preliminarily aged PC-5, the calculated data practically coincided with the experimental creep compliance curves in the region $t - t_0 < 12{,}000$ h $= 500$ days and were above experimental ones at large $t - t_0$ values. For the conditionally initial material, the calculated curve deviated from the experimental one at much shorter $t - t_0$ times.

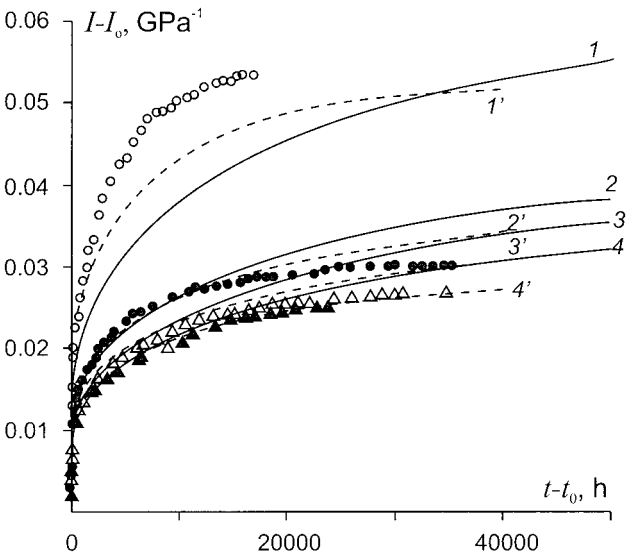

Figure 5 Creep compliance of PC-5 at different ages: t_{ag} = (○) 0, (●) 225, (△) 315, and (▲) 510 days at T_{ag} = 60°C: Points are experimental data, and solid lines are the calculation based on Kerner's model with the creep compliance of the binder and calculated by eq. (3), and the dashed lines are the calculations from eq. (1) with allowance for eqs. (4)–(6) and (9).

An attempt to account for the shrinkage of PC-5 due to the physical aging of the polyester resin was undertaken. The shrinkage strains and appropriate compliances were calculated with eq. (9) with the dependencies of $\ln [a_{ag}(t - t_0, T)/a_{ag}(t_0, T_{ag})] - (t - t_0)$ [Fig. 2(b)] of PC-5 at different ages. The calculation of the creep compliance of PC-5 was carried out as follows:

1. The viscoelastic compliances of the binder at different ages were calculated with eq. (2) with allowance for eqs. (5), (6), and (7):
2. The viscoelastic compliances of PC-5 at different ages were calculated with the Kerner's model:
3. The creep compliances of PC-5 at different ages were calculated as the sums of viscoelastic and shrinkage compliances.

A comparison of the calculation results with the experiment (see Fig. 5, dashed lines) showed that the use of this suggested approach allowed us to refine the prediction of the long-term creep of PC-5 both in the conditionally initial state and after preliminary exposure at elevated temperatures ($T_{ag} = 60°C$).

CONCLUSIONS

As a result of the investigation of the creep of the polymer concrete PC-5 at 20°C, we concluded that

The creep compliance of polymer concrete with different ages can be calculated from the creep compliance of the appropriate binder with the structural Kerner's model.

The application of the principle of analogies on aging time and temperature is enough for the estimation of the creep compliance of a polymer concrete at different ages for the range of small times of the creep.

For estimation of the creep compliance of a polymer concrete at different ages in the range of large times, it is necessary to take into account both the deceleration of relaxation processes and the shrinkage of the binder due to its physical aging.

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