A Constitutive Equation for Creep in Polymer Concretes and Their Resin Binders

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Synopsis

We present here a method for superposing creep measurements on polymer concrete (PC), taken at different temperatures, imposed stresses, and resin contents, onto master curves, which describe the respective responses of various PC systems and their resin binders, to compressive, tensile, and flexural loads. This treatment is extended to systems reinforced with chopped glass fiber and montmorillonite (MMT). The general applicability of this superposition is tested with creep measurements by other investigators under tensile, compressive, and flexural loads. The results make it possible to predict the long-term creep behavior of unfilled as well as reinforced glassy polymer systems at different temperatures and load conditions from limited, short-term data. Success of the multiple superposition suggests a generalized constitutive equation, which describes the creep compliance of these systems as a product of separable functions of each parameter in the form of shift factors for temperature (a_T), stress (a_σ), resin content (a_v), fiber reinforcement (a_F), and MMT reinforcement (a_M): $J(PC) = J_r a_T a_\sigma a_v a_F a_M t^m$, where J_r is an appropriately chosen reference creep compliance. The time exponent m does not depend on the chemical nature of the polymer matrix.

INTRODUCTION

Recent advances in polymer concrete (PC) technology have produced systems that are used increasingly in large, load-bearing structures (beams, floor panels, pipe) where long-term response to static loads (creep) is an important design parameter.[1-4] Consequently, we embarked on a study, aimed at developing techniques for predicting the long-term creep behavior of various PC systems at different temperatures and load conditions from limited, short-term data.

In a previous paper, dealing specifically with flexural creep measurements on polyester PC,[5] we presented a method whereby creep strain data obtained at different temperatures, stress levels, and resin contents were successfully superposed to give a single master curve of creep compliance vs. time at a chosen reference state. This superposition method is extended here to include epoxy and acrylic PC systems and their unfilled resin binders; PC systems with additional reinforcement (chopped glass fibers for strength, montmorillonite for cure shrinkage control); and loading modes in tension and compression as well as flexure. In an effort to test the general applicability of this

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TABLE I

Composition of PC Systems

Unsaturated polyester/styrene resin base	
Resin: Dion Iso-6315 (Koppers Co.)	97.3 wt %
Initiator: methyl ethyl ketone peroxide (MEKPO)	1.5 wt %
Promoter: cobalt naphthenate (CN)	0.2 wt %
Coupling agent: 3 methacryloxy-propyltrimethoxysilane	1.0 wt %
Epoxy–polyamide resin base	
Epon 828 (Shell Chemical)	65 wt %
Versamid 140 (General Mills)	35 wt %
Mineral aggregate and filler	
Silica sand, 8–100 mesh in particle size	

method, we have used it to treat (in addition to our own data) creep measurements reported by other investigators, some of which extend to very long times (10^4 h).

EXPERIMENTAL

PC systems based on unsaturated polyester/styrene and polyamide-cured epoxy resin were formulated as shown in Table I. Two different aggregate size distributions were used, resulting in different resin contents: the "fine sand" system containing 22 wt % resin (volume fraction 0.44) and the "distributed aggregate" system with 15 wt % resin (volume fraction 0.30). Details of the preparation techniques are discussed elsewhere.[5] In addition to the basic PC systems, special systems containing chopped glass fiber (E glass, 10^{-3} cm diameter × 1.2 cm long, 3 wt % of the total system), as well as PC formulations with the mineral montmorillonite (MMT) dispersed in the resin to control cure shrinkage[6,7] were also prepared.

Flexural creep measurements were obtained on bar-shaped specimens measuring 1.6 × 1.6 × 16 cm using a three-point loading mode in an apparatus that records continuously the deflection under dead-weight loads in a controlled-temperature environment. The experiments covered a temperature range from −5 to +70°C, stress levels from 5 to 21 MN/m², and relatively short time periods ($\leq$ 160 h). The flexural strengths of PC specimens in the temperature range of the creep experiments were also measured using an Instron Testing Machine at a crosshead speed of 0.2 cm/min, with specimens of the same dimensions as in the creep experiments.

RESULTS

Stable Creep vs. Creep Rupture

In a creep experiment the total strain (ϵ_{tot}) shown by the specimen at any time (t) can be divided into two components: the elastic strain, (ϵ_{el}), which represents the instantaneous response to the imposed load, and the time-dependent creep strain (ϵ_{cr}). We extracted the elastic strain from total strain measurements by extrapolating to very low times ($t = 10^{-2}$ h). Figures 1(a) and 1(b) show typical plots of $\epsilon_{cr}(= \epsilon_{tot} - \epsilon_{el})$ vs. time for polyester and
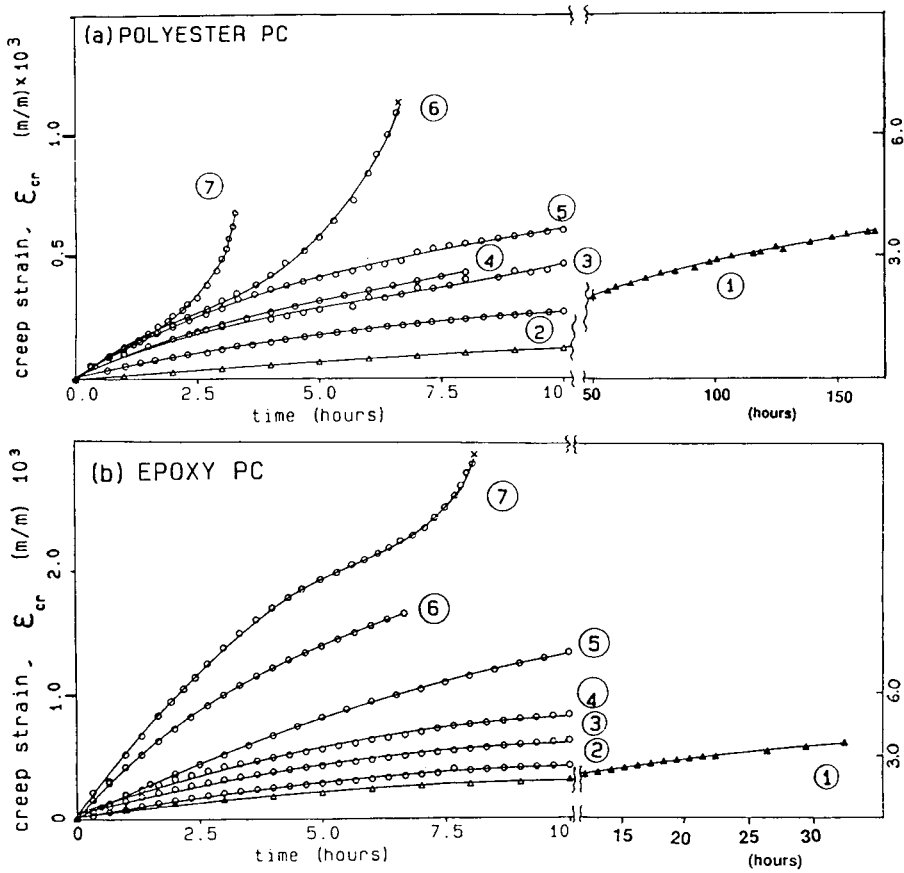
Fig. 1. Plots of creep strain vs. time for polyester PC (a) and epoxy PC (b) at different temperatures $T(C°)$, stress levels $\sigma(MN/m^2)$, and resin contents v, respectively, of the PC formulation: (a): (1) 22, 9.40, 0.30; (2) 25, 9.43, 0.30; (3) 48, 9.43, 0.30; (4) 25, 9.43, 0.41; (5) 25, 11.2, 0.30; (6) 25, 14.8, 0.30; (7) 25, 15.4, 0.41; (b): (1) 22, 11.5, 0.30; (2) 22, 11.8, 0.30; (3) 41, 11.8, 0.30; (4) 22, 10.9, 0.41; (5) 22, 11.8, 0.41; (6) 50, 11.8, 0.30; (7) 46, 11.0, 0.41.

epoxy-based PC systems with different resin contents, loaded in flexure, at different temperature and stress levels. Two modes of creep behavior are observed in both types of systems. At low and moderate loads the slopes of the creep strain curves decrease monotonically with time ($\partial^2\epsilon_{cr}/\partial t^2 < 0$), a characteristic of stable creep behavior. At high loads there comes a point when ($\partial^2\epsilon_{cr}/\partial t^2$) changes sign and the specimen creeps to failure (creep rupture).

Temperature / Stress / Resin-Content Superposition

Our creep data, as well as measurements by other investigators,[8-12] show that, within the stable creep domain, the isochronal creep strain increases with increasing temperature (T), stress (σ), and resin content (v). By dividing creep strain by the corresponding applied stress, we obtain the creep compliance (J), which we shall use as a measure of creep behavior.
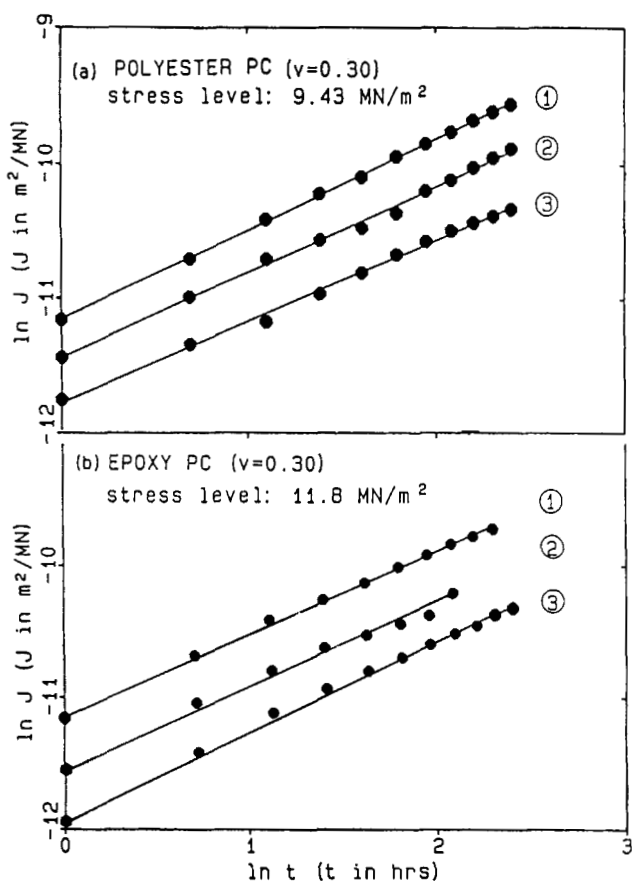
Fig. 2.   Logarithmic plots of creep compliance (J) vs. time for polyester PC (a) and epoxy PC (b) with the same resin content and applied stress levels, measured at three different temperatures (°C): (a): (1) 48; (2) 25; (3) 5; (b): (1) 50; (2) 41; (3) 22.

Figures 2(a) and 2(b) show logarithmic plots of the time dependence of J for polyester and epoxy PC systems. Three sets of data are shown for each system, obtained at different temperatures from specimens of a given resin content ($v = 0.30$), subjected to the same stress level ($\sigma = 9.43$ and 11.8 MN/m², respectively, for polyester and epoxy PC). Each point is the average value of J obtained from three different specimens at $t = 1, 2, \ldots, 10$ h and the solid lines are least square fits to the data points. The plots are linear, parallel, and have the same slope of 0.6 for both resin systems. This allows the J vs. t measurements obtained at different temperatures to be superposed on a single curve by the use of a temperature-shift factor, $a_T = [J(T)/J_r]_{t, \sigma, v}$ so that

$$[J(T)]_{\sigma, v} = a_T J_r t^m \tag{1}$$

J_r is the reference creep compliance of a PC system with the same resin content (v), measured at the same stress (σ), a chosen reference temperature, and $t = 1$ h. We have chosen the volume fraction of resin $v(=$ resin
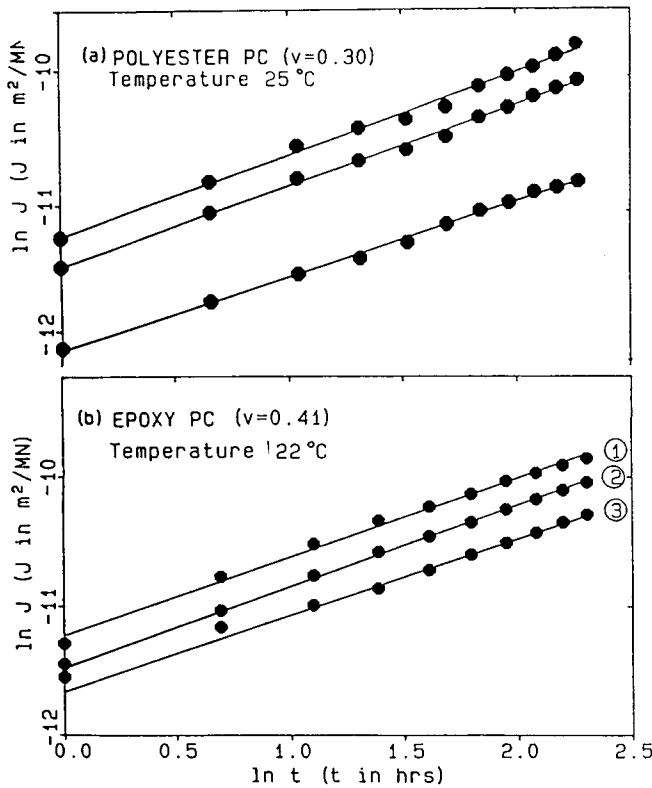
Fig. 3. Logarithmic plots of creep compliance (J) vs. time for polyester PC (a) and epoxy PC (b) at the same resin content and temperature, measured at three different stress levels (MN/m^2): (a): (1) 11.2; (2) 9.43; (3) 7.12; (b): (1) 11.9; (2) 10.9; (3) 9.20.

volume/total PC volume) as a measure of the resin content in a given PC system.

Figures 3(a) and 3(b) show the dependence of flexural creep compliance on applied stress. The linear and parallel logarithmic plots of J vs. t at different stress levels (with T and v constant) indicate that these measurements can be superposed on a single curve of J vs. t by the use of a stress-shift factor, $a_\sigma = [J_\sigma/J_r]_{t, T, v}$ so that

$$[J(\sigma)]_{T, v} = a_\sigma J_r t^m \tag{2}$$

J_r is the reference creep compliance of a PC system with the same v, measured at the same temperature (T), a chosen reference stress, and $t = 1$ h.

The effect of resin content on flexural creep compliance is shown in Figures 4(a) and 4(b). The linear and parallel logarithmic plots allow yet another superposition of J vs. t data at different resin contents, using a resin-content shift factor, $a_v = [J(v)/J_r]_{t, T, \sigma}$ so that

$$[J(v)]_{T, \sigma} = a_v J_r t^m \tag{3}$$

J_r is the reference creep compliance of a PC system with a chosen reference resin content, measured at the same T and σ, and at $t = 1$ h.
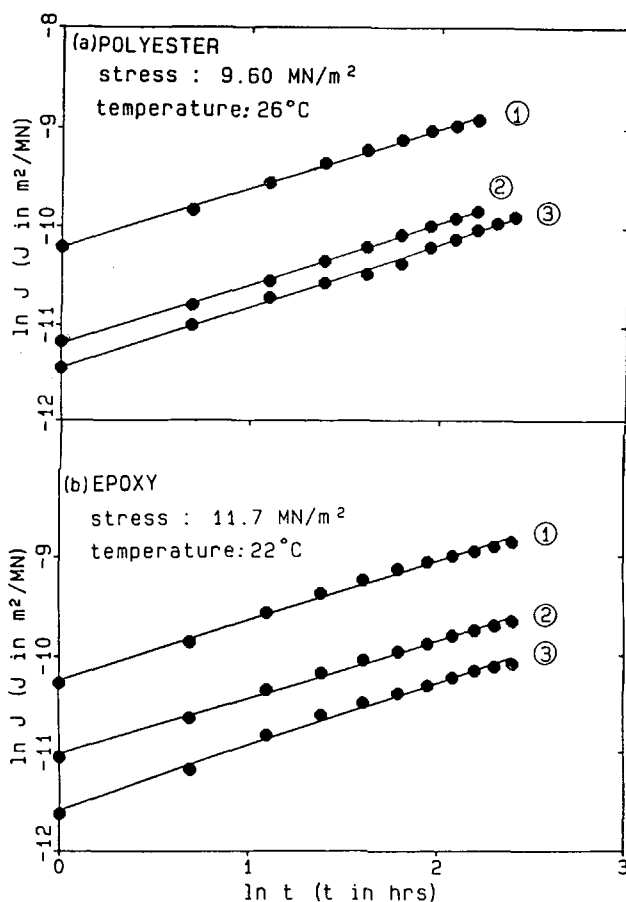
Fig. 4.   Logarithmic plots of creep compliance (J) vs. time for polyester (a) and epoxy (b) formulations with different resin contents measured at the same temperature and applied stress: (1) unfilled resin (v = 1.0); (2) PC (v = 0.41); (3) PC (v = 0.30).

Equations (1), (2), and (3) indicate that it is possible to superpose flexural creep data of PC systems with different resin contents taken at different temperatures and stress levels, onto a single master curve of creep compliance (J_r) vs. time at a chosen reference state by use of the appropriate shift factors:

$$J(t, T, \sigma, v) = J_r a_T a_\sigma a_v t^m \tag{4}$$

This triple superposition is shown in Figure 5 for the polyester and epoxy PC systems used in this study. It is noteworthy that the time exponent m has the same value of 0.6 in both PC systems, despite their different polymer matrices. It should also be noted that, while the experimental measurements were limited to time periods of only 10 h, the superposition process expands the data over a range of 90 h. The reliability of superposition was verified by conducting for each PC system an independent creep experiment at the respective reference values of v, T, and σ for a period of 160 h. The data are shown in Figure 6.
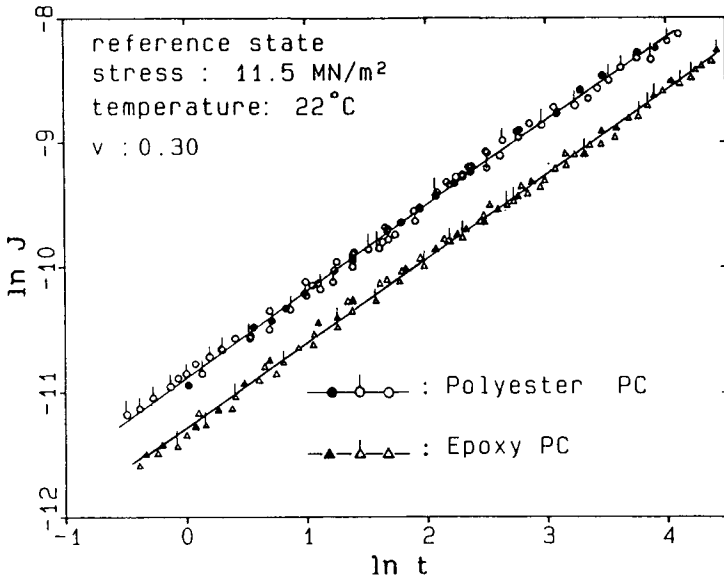
Fig. 5. Superposition of creep compliance data, taken at different temperatures, imposed stresses, and resin contents onto a single master curve for flexural creep: ($-\bullet- \mathrm{O} - \mathrm{O} -$) polyester PC; ($-\blacktriangle - \triangle - \triangle -$) epoxy PC.
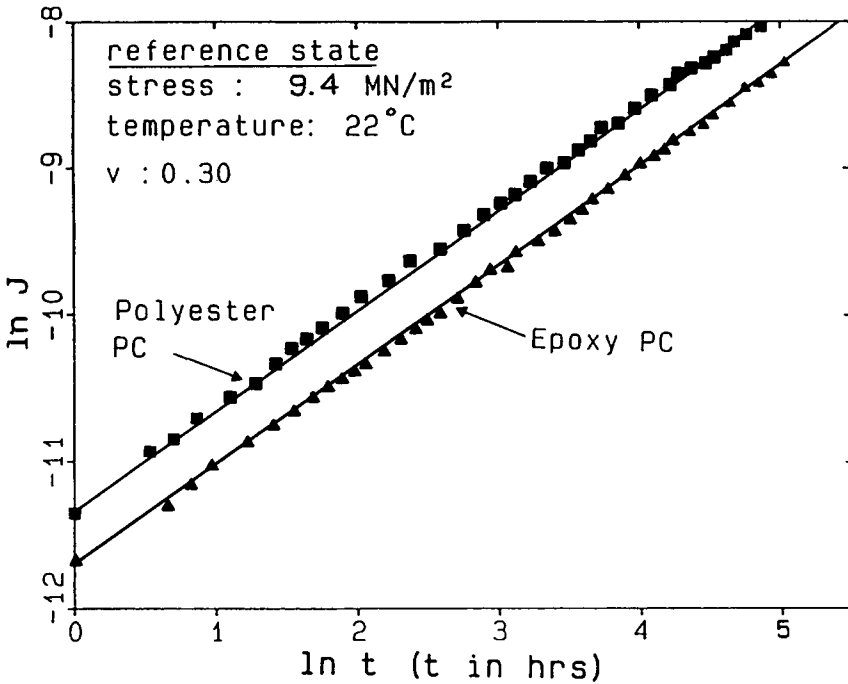
Fig. 6. Verification of the master curve by means of independent experimental data: ($\blacksquare$ $\blacktriangle$) actual experiment; ($-$) master curves.

Extension of Superposition to Reinforced Systems

Use of chopped glass fiber reinforcement in unsaturated polyester PC produced a 20% decrease in creep strain, compared to the ordinary (unreinforced) PC at the same T, σ, and v. Dispersion into the resin of the mineral montmorillonite (MMT) to produce zero-shrinkage PC systems gave an additional 25% decrease. Montmorillonite (MMT) enhances the strength and creep resistance of thermosetting resins and their corresponding PC systems by counteracting cure shrinkage, thereby eliminating setting stresses.[6,7] However, neither additive affected the shape of the ϵ_{cr} vs. t curves. This allowed us to apply superposition to the reinforced PC systems and to relate the creep compliances J_F (for glass-fiber-reinforced PC) and J_{M-F} (for MMT/fiber PC) to the creep compliances $J(t, T, \sigma, v)$ of the corresponding unreinforced PC systems, given by eq. (4):

$$J_F = a_F J(t, T, \sigma, v), \qquad \text{where } a_F = 0.8 \tag{5}$$

$$J_{M-F} = a_F a_M J(t, T, \sigma, v), \qquad \text{where } a_M = 0.75 \tag{6}$$

The shift factors a_F and a_M equal the ratios of the (short-term) tensile strengths of the corresponding ordinary and reinforced PC systems. The master curves obtained by applying these shift factors are shown in Figure 7.

Extension of Superposition to Compressive and Tensile Creep

The successful superposition of our flexural creep data has encouraged us to apply this method to creep measurements obtained previously by other
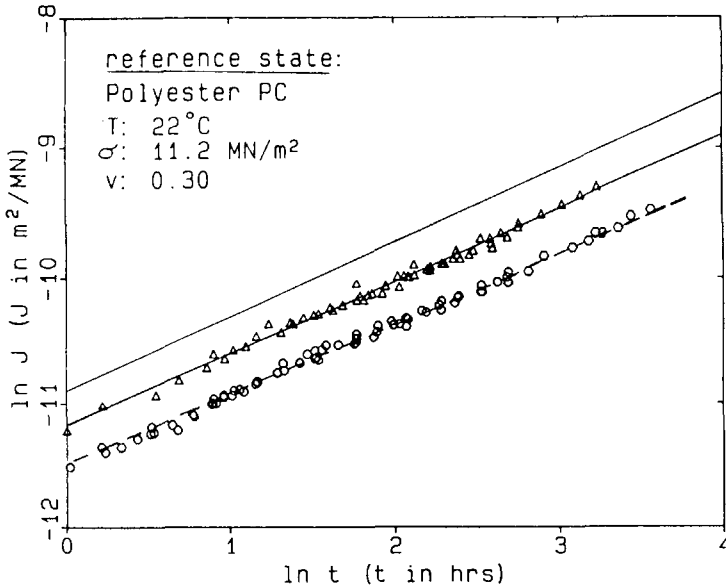

Fig. 7. Master curves for flexural creep of polyester PC systems reinforced with chopped glass fiber and fiber/MMT: (—) ordinary PC; (△) fiber PC; (○) fiber MMT PC.
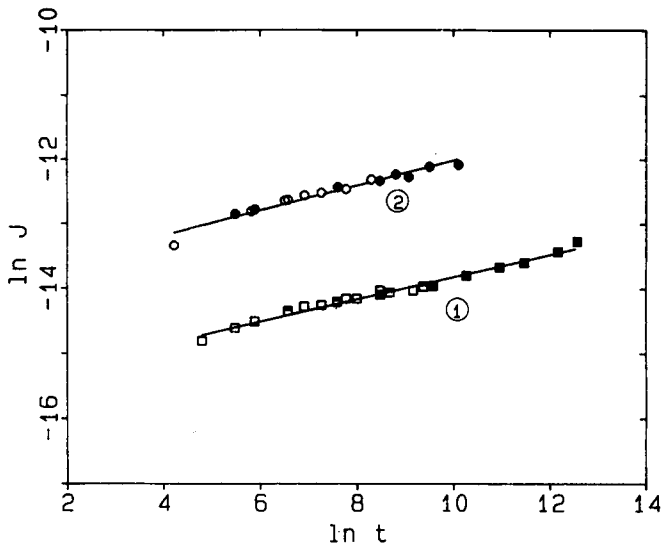
Fig. 8. Master curves for compressive creep compliance of polyester (1) and acrylic (MMA) (2) PC systems obtained by stress superposition of data by other investigators. Temperature 22°C; stress 19.6 MN/m².

investigators. Helal[8] had conducted in 1978 compressive creep experiments on large specimens of polyester PC (15.2 cm diameter cylinders by 30.5 cm long) for periods up to 1 year at ambient temperature and stresses of 21.1, 32.0, and 38.0 MN/m². Logarithmic plots of these three sets of creep compliance vs. time gave straight and (nearly) parallel lines with a common slope of 0.20 ± 0.017. We also applied stress superposition to compressive creep data of Hsu[9] taken on large acrylic concrete beams at stresses of 20 and 27 MN/m². The logarithmic plots of the two sets of data had a common slope of 0.21 ± 0.019. Figure 8 shows master curves obtained from stress superposition of the Helal and Hsu measurements at a common T and σ.

Ogorkiewitz[11] and Turner[12] have published extensive creep measurements for unfilled PMMA in tension. These cover stress-to-strength ratios from 0.06 to 0.94 and times up to 1 year. After extracting the elastic strains (from the total strains at 10^{-2} h) we applied stress superposition to these measurements. The logarithmic plots of creep compliances from both sets of data fell on a single master curve, as shown in Figure 9. It is noteworthy that the slope of these tensile creep compliances vs. time is 0.20, the same as the compressive creep plots of Figure 8.

Critical Stress-to-Strength Ratios

The time exponent m in the creep compliance equation provides a means for distinguishing between the domains of stable creep ($m < 1$) and creep rupture ($m > 1$). In order to explore the transition from stable to catastrophic creep, we measured the ultimate flexural strengths (s) of the PC systems in this study at the values of T and v used in the creep experiments and plotted the exponent m against stress-to-strength ratio (σ/s), as shown in Figure 10. At low σ/s ratios all PC systems and their resin matrices show stable
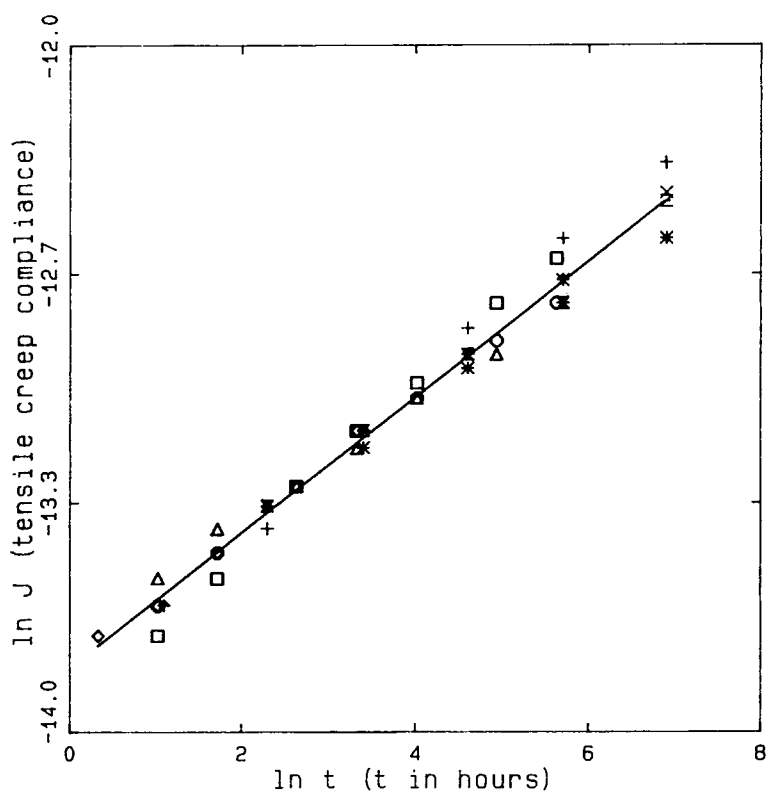
Fig. 9. Master curve for tensile creep compliance of unfilled poly(methyl methacrylate) obtained by stress superposition of data by other investigators: (□, ○, △, ◇) data from Ref. 12; (t, x, 4, z, Y, ×) data from Ref. 11.
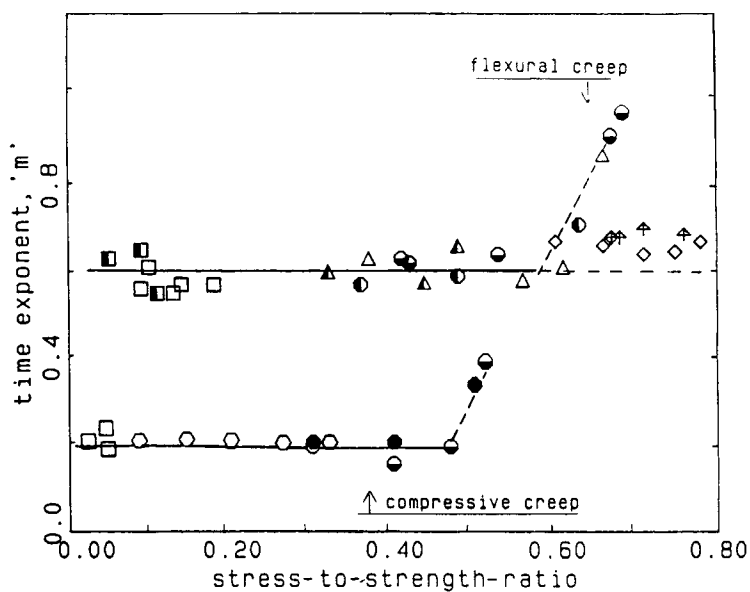

Fig. 10. Plot of the time exponent m in flexural and compressive creep vs. stress-to-strength ratio for polyester, epoxy, and acrylic PC systems and their resin binders: (◗, ◖, ●) PC ($v = 0.30$); (△, ▲) PC ($v = 0.41$); (○, □, ▮) resin ($v = 1.0$); (◇) fiber PC; (↑) fiber/MMT PC.

creep ($m = 0.6$ in flexure, 0.2 in compression). In unreinforced PC systems the stable creep domain extends to σ/s ratios of ca. 0.55 in flexure and 0.45 in compression. As the imposed loads increase beyond these σ/s ratios, the PC systems show a progressive tendency to shift into catastrophic creep. At σ/s ratios exceeding 0.6 in flexure and 0.5 in compression, all unreinforced PC systems go quickly to creep rupture. The use of glass fiber reinforcement (with or without MMT) extends the stable creep domains to σ/s values, approaching 0.8. This is not unexpected since the fibers tend to prevent local stress concentrations and inhibit crack formation and propagation.

DISCUSSION

The practical significance of this multiple superposition method is that it makes it possible to estimate the long-term creep behavior of PC systems based on different resins, over a range of temperatures, stress levels, resin contents, and in the presence of reinforcing agents, from limited data taken within very short time periods in a small number of systems. In constructing the master curves shown in Figure 5, we deliberately limited the data used to 10 points from each experiment, taken at 1 h intervals over a period of only 10 h. The superposition process gave master curves covering a range of 90 h, which were verified by independent creep measurements over 160 h, as shown in Figure 6. Use of stress superposition on literature data from experiments extending over 1-year periods gave master curves, covering periods of 3.4 and 31 years. Since the logarithmic plots of these curves are linear, they could have been established with the same accuracy from short-term experiments. In principle, it is possible to establish the entire master curve of a completely new PC system from a minimum number of six 10-h-long creep experiments (two for each of the three parameters T, σ, and v). This master curve can be extended to reinforced PC systems by obtaining the ratio of strengths between the parent and reinforced PC from stress/strain curves at the same loading mode as the creep measurements.

The success of this multiparameter superposition of creep compliances in PC systems is due to the fact that creep in these materials originates in a single component, the macromolecular matrix. This has been verified by the successful incorporation of creep data from the pure (unfilled) polymer ($v = 1$) into the master curves. The parameters considered in this study (temperature, imposed stress, resin content, particulate or fiber reinforcement) affect the overall system only to the extent that they modify the creep behavior of the polymer network. These parameters do not change the shape of the ϵ_{cr} vs. t curve, i.e., the nature of the macromolecular relaxation processes that produce creep strain, but only affect the rate of these relaxation processes. Consequently, the creep compliance of the composite can be described as a product of separable functions of each parameter in the form of shift factors:

$$J(\mathrm{PC}) = J_r a_T a_\sigma a_v a_F a_M t^m \tag{7}$$

We offer eq. (7) as a generalized creep equation for PC systems within the stable creep domain. Data from systems, based on three different resins

(polyester, epoxy, acrylic) show the time exponent m to be independent of the polymer matrix.

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