Filler Fraction Effect on Creep Response of Crosslinked Polyester Matrix with Mineral Filler

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ABSTRACT: The effect of a particle marble filler on the creep response of a crosslinked polyester matrix before and after physical aging is described. Composites with various filler–polyester matrix percentages are prepared by applying mixing technology, curing at room temperature, and postcuring above the glass-transition temperature. Two groups of specimens of identical composition are studied. The first group is tested 1 month after preparation (relatively nonaged), whereas the second group is tested after 13 years of storage at stable room temperature and humidity, at current atmospheric pressure, and in the absence of direct light (aged). The two groups of specimens (aged and nonaged) are subjected to creep measurements. The modulus of elasticity and the creep compliance are determined, plotted against the filler volume fraction, and fit by empirical equations. A simple mechanical model is proposed to fit the compliance curves, and good agreement between the measured and predicted values is shown. The mechanical behavior of the composites is also described, using empirical equations that fit the relation between the composite/matrix ratio of the deformation characteristics and the filler volume fraction. A crucial matrix influence is proposed to fit the compliance curves, and good agreement between the measured and predicted values is shown. Experimentally established natural regularities can be used to predict the creep compliances of composites from a less demanding experimental program. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3329–3335, 2003

Key words: crosslinked polyesters; fillers; composites; creep; ageing

INTRODUCTION

Crosslinked polymers have a number of applications, including the production of composite materials. Composites consisting of a crosslinked polymer matrix and particulate fillers are used as structural materials, electric insulation materials, coatings, joint compositions, adhesives, putties, and so forth. They are also used as a matrix in more complex composite systems (polymer concrete; materials with fiber, mesh, or textile reinforcements; wood filler composites; etc.) The various applications of filled polymers are a consequence of the ability of a filler to change the structural, technological, and mechanical properties of polymers in a desired way. Fillers can also reduce costs.

The filler parameters influencing the structure and properties of a polymer matrix are chemical and mineralogical particle composition, size and size distribution, shape, particle effects, nature of the filler surface, surface pretreatment, and so forth. When optimizing the parameters of the filler, attention must be paid to synergistic effects and to indirect and frequently nonlinear effects on polymer structure and mobility.[1]

The modifying role of fillers and the properties of filled polymers have been the subject of many studies.[2–6] Oliver et al.[2] reveal very important differences between the cure kinetics of polyepoxy materials and those of composites. The presence of particulate fillers has a great influence on the main phase transitions. The influence of matrix viscoelastic softening on the loss of stiffness of filled polymers is emphasized in Meddad and Fisa.[3] The other main mechanism decreasing the stiffness of particulate composites is single particle debonding at large volume fractions of the filler.[4] The effects of the degree of loading, the nature of the filler surface, the pretreatment, and the content of the filler surface on the mechanical properties of particulate composites have been analyzed in several studies.[5–8] According to Gao and Tsou,[7] the approaches dealing with the effects of fillers on polymer behavior may be divided into three categories: kinetic, micromechanical, and empirical approaches. Curve fitting and optimization of the curve-fitting parameters of long-term creep test data were used in the present work. This can be referred to as an empirical

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approach. A variety of articles on filled polyesters have been based on this approach,[8–11] but long-term creep response and the influence of aging on it have not been studied simultaneously. Physical aging behavior as manifested by the creep response is attributed to a rather fundamental concept,[12] which works well in the linear viscoelastic region. The free volume hypothesis is supposedly correct, although exceptions do exist.[12,13] It appears that a good description of creep and aging behavior can indeed be obtained for individual polymers and composites, but there is no universal behavior covering a broad range of materials and loadings.

The aims of the present study are to experimentally determine the effect of the filler fraction on the inelastic and elastic deformations of the polyester matrix composite before and after long-term physical aging and to evaluate the obtained experimental data, which is exceptional in regard to the duration of both creep measurements and aging.

The role of the filler in altering the matrix deformation properties was evaluated on the basis of creep tests of composites with different filler–polyester matrix percentages. Two groups of specimens were subjected to creep measurements. The first group was tested 1 month after the preparation of specimens. The second group was tested after 13 years of storage at stable room temperature and humidity in the absence of direct light. As is well known, amorphous polymers below the glass-transition temperature are subjected to physical aging. A comparison of the test data of the two groups of specimens indicates that there is a significant difference between the materials and the effect of physical aging cannot be neglected, even at room temperature.

The creep response was investigated under compressive loading in the linear range. The deformation characteristics, modulus of elasticity, and creep compliance were determined from the creep test data. The effect of the filler volume fraction and the aging effect on the modulus of elasticity and the creep compliance allow a comparison of the influence of the above factors on the elastic and nonelastic deformation components.

EXPERIMENTAL

The unsaturated polyester resin Vinalkid 550 P (Orgachim Ltd.) was used. This resin is based on orthophthalic acid, maleic acid, and propylene glycol, which are dissolved in styrene. This resin is formulated to provide engineering materials that satisfy extremes of mechanical strength and thermal resistance, in addition to resistance to chemicals.

The marble filler used in the study was a by-product from marble block and plate fabrication. It is a polydisperse powder with particles in the size range of 2–30 μm. The specific surface (S_f) of the particles was 334 m^2/kg (according to Blaine's method). The basic minerals of the filler are calcite ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$).

Composites of different filler–polyester matrix contents of 29, 38, 45, and 55% (v/v) were prepared by a mixing technology. The cured unfilled polyester resin was also tested.

The materials were cured at room temperature for 24 h and postcured at 80°C for 6 h. Cyclohexanon peroxide was used as an initiator. The accelerator of the process was *co*-naphtenate. The concentration of both the initiator and the accelerator was 2 wt % of the unsaturated polyester resin weight.

Two groups of specimens of identical composition were studied, including unfilled polyester specimens. The first group was tested 1 month after preparation (nonaged materials), and the second group was tested after 13 years of storage at stable room temperature ($T = 20 \pm 1$°C), stable relative humidity ($W = 55 \pm 5$%), and an atmospheric pressure between 86 and 106 kPa in the absence of direct light (aged materials). The two groups of specimens were subjected to creep measurements at room temperature. Prismatic specimens ($4 \times 4 \times 12$ cm) were used. The creep response was measured with the use of a special compressive creep testing technique (small hydraulic presses). The strains were measured on both sides (a base of 30 mm) in the middle third of the height of the prismatic test specimens. The measurements were performed using mechanical strain meters (dial indicators) with graduating marks of 1 μm. Each creep test was performed using three–five identical specimens, and the average values were used in full generality.

The materials conserved for a long time under room conditions were rejuvenated in order to check the character of the occurring changes.[14] The specimens were thermally processed for 6 h at a temperature 10°C above the glass-transition temperature (T_g) and quenched to room temperature. Then they were subjected to creep loading under the same conditions. It was established that the obtained values of creep compliance coincided with those of the test specimens that had not been subjected to aging. In other words, the changes provoked in the materials conserved under room conditions for 13 years were reversible and resulted from physical aging.

From the creep test data we obtained the elastic strain (ϵ_e), corresponding to the constant stress (σ_0), and the inelastic (viscoelastic, creep) strain [$\epsilon_c(t)$] formed in time under σ_0. We determined the modulus of elasticity $E = \sigma_0/\epsilon_e$ (E_m for the matrix and E_c for the composites) and creep compliance $J(t) = \epsilon_c(t)/\sigma_0$ (J_m for the matrix and J_c for the composites).

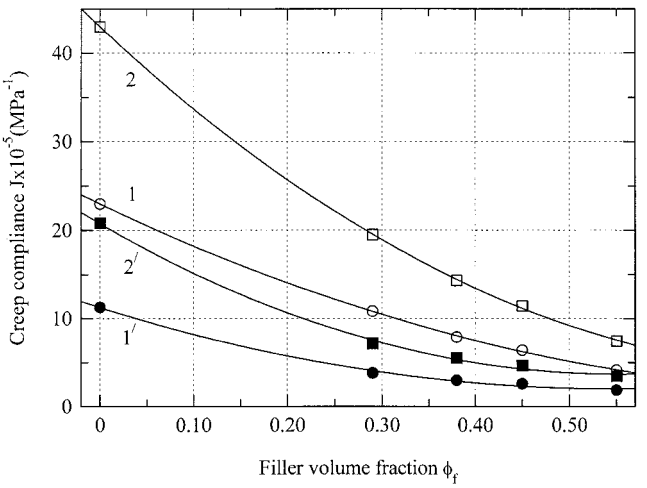

Figure 1 The changes in the creep compliance as a function of the filler volume fraction at constant creep time $t_1 = 1.44 \times 10^4$ min (curves 1, 1′) and $t_2 = 1.44 \times 10^5$ min (curves 2, 2′) before (curves 1, 2) and after physical aging (curves 1′, 2′).

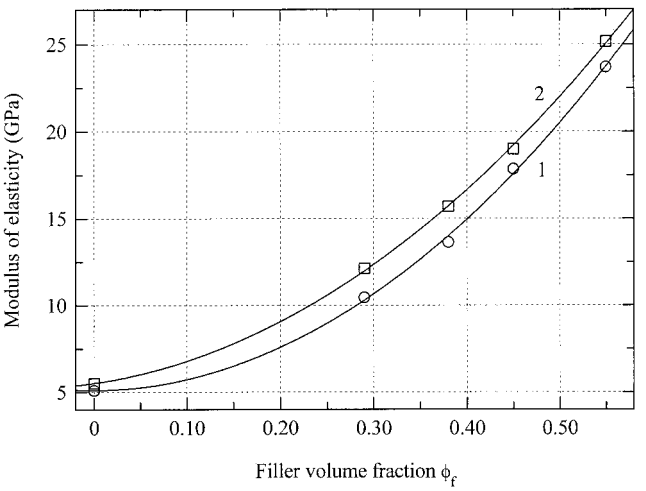

Figure 2 The modulus of elasticity values as a function of the filler volume fraction before (curve 1) and after (curve 2) physical aging.

RESULTS AND DISCUSSION

Changes in characteristics values

The changes in creep compliance are seen in Figure 1, which shows the creep compliance values of the two groups of materials for constant creep times $t_1 = 1.44 \times 10^4$ min (=10 days) and $t_2 = 1.44 \times 10^5$ min (=100 days). The relation $J = f(t_N, \phi_f, t_a)$ proceeds monotonously and can be very well fitted for an arbitrary creep time t_N by a second-power polynomial of the following type:

$$J(t_N, \phi_f, t_a) = R_1(t_N, \phi_f, t_a)$$

$$R_1(t_N, \phi_f, t_a) = C_1(t_N, t_a)\phi_f^2 + C_2(t_N, t_a)\phi_f + C_3(t_N, t_a)$$

$$N = 1, 2, \ldots n \quad (1)$$

The coefficients C_1, C_2, and C_3 were determined from the experimental data and are shown in Table I.

The values of the modulus of elasticity also increase nonlinearly with the increasing volume fraction of the filler. A similar effect is observed for nonaged materials, as well as for those subjected to physical aging. This is illustrated in Figure 2, where the dependence of the modulus values on the filler volumetric fraction

TABLE I
Values of Coefficients C_i Determined from Experimental Data

Materials	C_1	C_2	C_3	Standard Error	Max Deviation	r^2
			Fitting Eq. (1)			
Nonaged	30.2	−50.8	23.0	0.156	0.156	1.00
Aged (t = 10 days)	30.7	−33.7	11.3	0.297	0.271	0.997
Nonaged	63.1	−99.1	43.0	0.251	0.256	1.000
Aged (t = 100 days)	56.0	−61.8	20.8	0.426	0.376	0.998
			Fitting Eq. (2)			
Nonaged	61.3	0.125	5.11	0.338	0.356	1.000
Aged	50.7	7.59	5.52	0.200	0.208	1.000
			Fitting Eq. (4)			
Nonaged	1.470	−2.310	1.000	0.0048	0.0058	1.000
Aged (t = 100 days)	2.740	−3.000	0.997	0.0231	0.0207	0.998
			Fitting Eq. (6)			
Nonaged	12.000	0.048	1.000	0.0645	0.0678	0.999
Aged	9.280	1.340	1.000	0.0356	0.0376	1.000

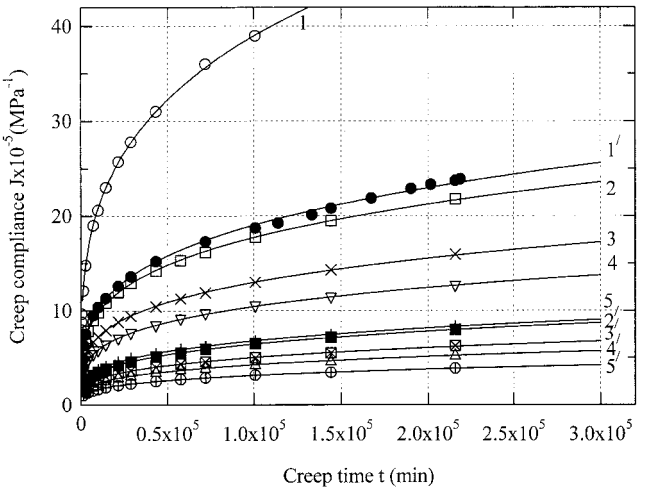

Figure 3 The creep compliance values predicted by eq. (3) (solid lines) and experimental data (symbols) for a polyester matrix (curves 1, 1′) and composites with filler volume fractions of 0.29 (curves 2, 2′), 0.38 (curves 3, 3′), 0.45 (curves 4, 4′), and 0.55 (curves 5, 5′) before (curves 1–5) and after physical aging (curves 1′–5′).

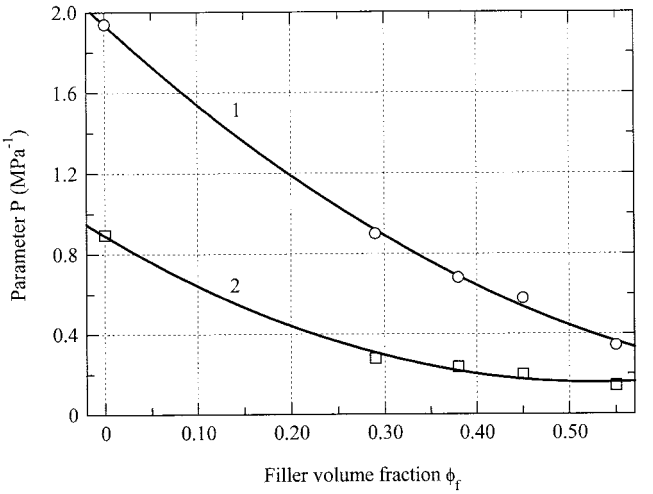

Figure 4 The parameter (P) values calculated by eq. (3) (symbols) and its second-order polynomial fit (solid lines) for the materials before (curve 1) and after (curve 2) physical aging vs. the filler volume fraction.

is plotted. It is seen that the values change monotonously and can be represented analogously as a function of the volumetric fraction in the form

$$E(\phi_f, t_a) = R_2(\phi_f, t_a)$$
$$R_2(\phi_f, t_a) = C_1(t_a)\phi_t^2 + C_2(t_a)\phi_t + C_3(t_a) \qquad (2)$$

The values of the C_i coefficients of eq. (2) are listed in Table I.

When comparing the values of the respective characteristics before and after aging (see Figs. 1, 2), it should be noted that aging exerts a much smaller effect on the values of the modulus of elasticity than on the creep compliance values.

Creep compliance fitting model

A simple time function whose parameters are supposed to depend on the filler volume fraction ϕ_f and the aging time t_a has been proposed[14] to describe the creep compliance curves:

$$J(t, \phi_f, t_a) = P(\phi_f, t_a)\exp[Q(\phi_f, t_a)\log(t)] \quad t \le t^*$$
$$J(t, \phi_f, t_a) = \Psi(\phi_f, t_a) \quad t \ge t^* \qquad (3)$$

where $P(\phi_f, t_a)$ (MPa^{-1}), $Q(\phi_f, t_a)$, and $\Psi(\phi_f, t_a)$ (MPa^{-1}) are free parameters (material constants) that may also depend on factors other than those indicated and have to be determined from experimental data and t^* is a time point defining a qualitative change during the long-term viscoelastic response of a material.

The good agreement between the measured creep compliance values and those predicted by eq. (3) for aged and nonaged materials with different filler volume fractions is shown in Figure 3.

Equation (3) defines in logarithmic coordinates a line with intercept log$P$ and slope 0.434Q. The P and Q parameter values obtained from the experimental data for the matrix and the composites are shown in Table II. It is evident that P depends on ϕ_f and on aging time t_a, while Q can be accepted (within the range of acceptable experimental error) to be practically independent of these factors [$\bar{Q}$ (nonaged) = 0.592 ± 0.008 (1.36%), $\bar{Q}$ (aged) = 0.620 ± 0.006 (0.91%)]. A comparison of the parameter values proves that P decreases

TABLE II
***P* and *Q* Parameter Values Determined from Experimental Data**

Filler Volume Fraction	Before Aging					After 13 Years Aging				
	P (MPa)	Q	Standard Error	Max Deviation	r^2	P (MPa)	Q	Standard Error	Max Deviation	r^2
0 (matrix)	1.940	0.598	0.124	0.287	1.000	0.856	0.621	0.245	0.468	0.998
0.29	0.900	0.596	0.075	0.129	1.000	0.281	0.627	0.027	0.062	1.000
0.38	0.681	0.590	0.058	0.098	1.000	0.223	0.615	0.037	0.078	1.000
0.45	0.578	0.579	0.046	0.079	1.000	0.200	0.613	0.048	0.069	0.999
0.55	0.342	0.598	0.034	0.046	1.000	0.139	0.622	0.039	0.115	0.999

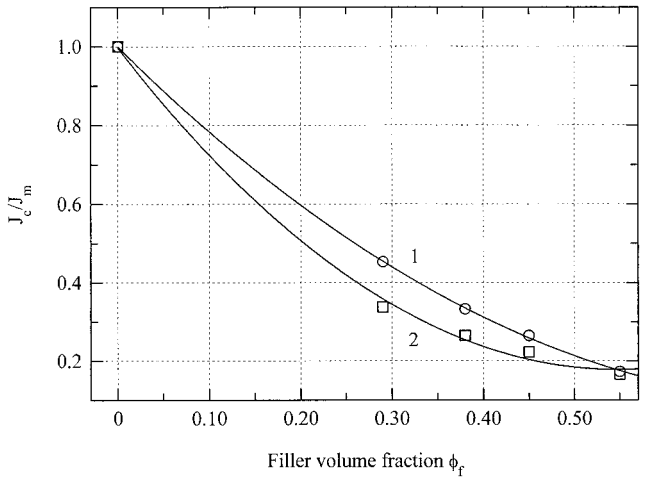

Figure 5 The experimental values of the ratio between the composite and matrix compliance (symbols) and its second-power polynomial fit (solid lines) before (curve 1) and after (curve 2) physical aging vs. filler volume fraction.

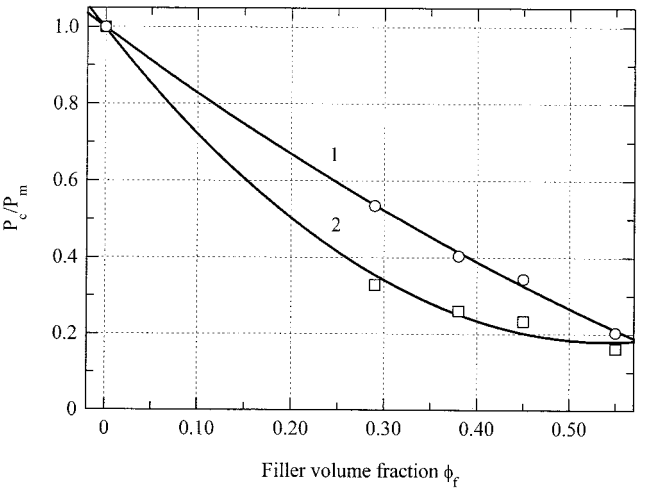

Figure 6 The P_c/P_m ratio values for nonaged (curve 1) and aged (curve 2) materials vs. the filler volume fraction.

with an increase in the filler volume fraction for both groups of materials, the P values of the physically aged materials being lower than those of the corresponding nonaged materials. The function $P(\phi_f, t_a)$ is monotonous and can be fitted by a second-power polynomial. The alteration of $P(\phi_f, t_a)$ after physical aging is described by a more slanting curve (Fig. 4, line 2), which indicates the fading influence of the filler volume fraction on the creep response.

Relations between filler volume fraction and mechanical characteristics of composites and matrix

The relations between the filler volume fraction and the mechanical characteristics of the composites and the matrix can also be established by fitting the experimentally determined ratios $J_c/J_m = f(\phi_f, t_a)$ and $E_c/E_m = f(\phi_f, t_a)$. The results show that the values of the ratio J_c/J_m change nonlinearly with the increasing volume fraction of the filler. The fitting function $J_c/J_m = f(\phi_f, t_a)$ for creep time $t = 1.44 \times 10^5$ min (=100 days) is presented in Figure 5. It is seen that with increasing filler volume fraction ϕ_f the ratio J_c/J_m decreases. The filler effect is stronger for lower concentrations of the filler. The changes inducted from physical aging lead to the conclusion that the J_c/J_m ratio is insignificantly dependent on aging. Then the compliance of the composites can be presented as a product of the matrix compliance and the second-power polynomial (R_3) describing the filler volume fraction effect:

$$J_c(t, \phi_f, t_a) = J_m(t, t_a)R_3(\phi_f) \quad (4)$$

The values of the C_i coefficients of eq. (4) are listed in Table I.

The assumption that parameter Q is a constant [not depending on ϕ_f and t_a, eq. (3)] enables us to find

$$R_3(\phi_f, t_a) = P_c(\phi_f, t_a)/P_m(t_a) \quad t \le t^* \quad (5)$$

The values of the P_c/P_m ratio versus ϕ_f for the two groups of materials are shown in Figure 6.

The experimental relationship $E_c/E_m = f(\phi_f, t_a)$ is plotted in Figure 7. Note that the E_c/E_m ratio increases with increasing ϕ_f, and the relationship in fact does not depend on the aging.

The E_c can be presented in an analogous way as a product of the E_m and the second-power polynomial (R_4) encompassing the influence of ϕ_f:

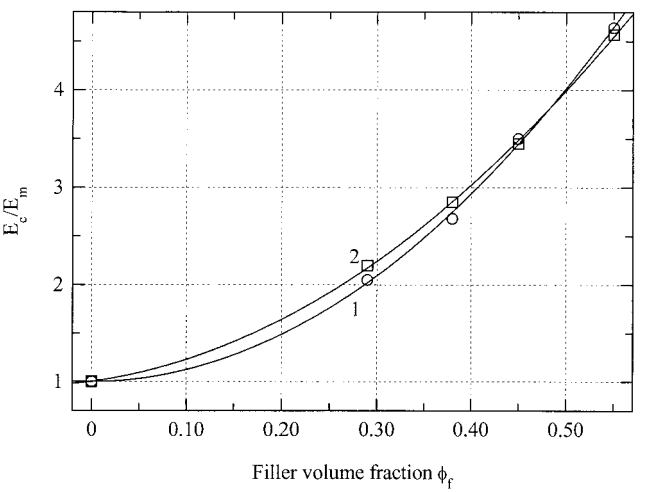

Figure 7 The experimental values of the ratio between the modulus of elasticity of the composites and the matrix (symbols) and its second-power polynomial fit (solid lines) before (curve 1) and after (curve 2) physical aging vs. the filler volume fraction.

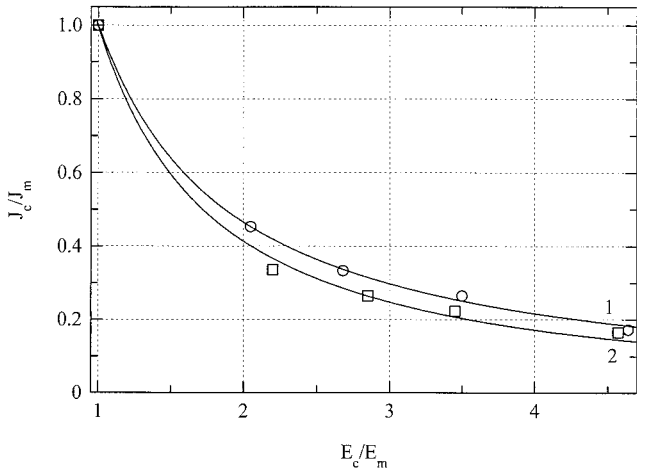

Figure 8 The experimental values of the ratio between the composite and matrix compliance (symbols) and its power function fit (solid lines) before (curve 1) and after (curve 2) physical aging vs. the ratio between the composite and matrix modulus of elasticity.

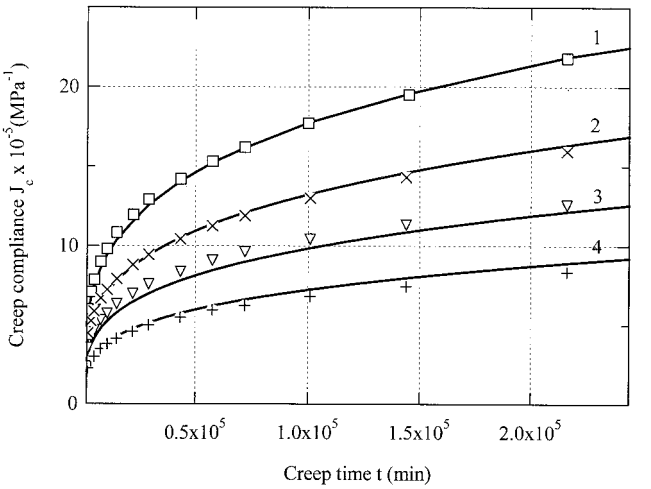

Figure 9 The creep compliance values predicted by eq. (8) (solid lines) and its experimental data (symbols) for nonaged composites with filler volume fractions of 0.29 (curve 1), 0.38 (curve 2), 0.45 (curve 3), and 0.55 (curve 4).

$$E_c(\phi_f, t_a) = E_m(t_a)R_4(\phi_f) \tag{6}$$

The values of the C_i coefficients of R_4 in eq. (6) are presented in Table I.

An attempt is made to relate the two ratios J_c/J_m and E_c/E_m between the inelastic and elastic characteristics of the composites and the matrix. As is shown in Figure 8, the influence of E_c/E_m ratio on the compliance ratio is greater for lower filler concentrations, and it gradually fades with increasing filler volume fraction. The curves for the nonaged (Fig. 8, curve 1) and aged materials (Fig. 8, curve 2) are situated sufficiently close to one another. This provides grounds to assume that aging exerts a negligible effect on the dependence $J_c/J_m = f(E_c/E_m)$.

Using eqs. (4) and (6), we can find

$$R_3(\phi_f) = D_1[R_4(\phi_f)]^{D_2}$$

$$J_c(t, \phi_f, t_a) = J_m(t, t_a)D_1[E_c(\phi_f, t_a)/E_m(t_a)]^{D_2} \tag{7}$$

The values of parameters D_1 and D_2 are given in Table III. It is evident that coefficient D_1 in eq. (7) can be omitted for this case. Consequently, the compliance of the composites can be presented as the product of the matrix compliance and an exponential member dependent on the ratio of the modulus of elasticity of a composite to the modulus of elasticity of the matrix:

$$J_c(t, \phi_f, t_a) = J_m(t, t_a)*[E_c(\phi_f, t_a)/E_m(t_a)]^{D_2} \tag{8}$$

Equation (8) enables us to predict the creep compliance of the composites from a less demanding experimental program, according to its extent. Figure 9 shows a comparison of the creep compliances of the composites calculated by means of eq. (8) (curves) and the experimental values (symbols) for nonaged materials (t_a = 1 month).

Comparing eqs. (4) and (8), we find a pilot condition

$$P_c(\phi_f, t_a)/P_m(t_a) \cong [E_c(\phi_f, t_a)/E_m(t_a)]^{D_2} \tag{9}$$

which should be valid for these composites within acceptable error. A comparison of the expressions in eq. (9) is favorable (see Table IV).

TABLE III
Values of Coefficients D_i Determined from Experimental Data

Materials	D_1	D_2	Standard Error	Max Deviation	r^2
Nonaged	1.000	−1.100	0.0129	0.0140	0.999
Aged	0.995	−1.270	0.0286	0.0306	0.997

CONCLUSIONS

The influence of a particulate marble filler on the creep response of a crosslinked polyester matrix before and after long-term physical aging has been studied. As could be expected, the values of the creep compliance decrease and the values of the modulus of elasticity increase with increasing filler volume fraction.

A simple two-parametric time function has been proposed to fit the experimental creep compliance data. One of the two parameters of the modeling function depends on the filler volume fraction and aging (aging time), but the other parameter does not depend on these factors. Good agreement between

TABLE IV
Values of Expressions in Eq. (9)

Filler Volume Fraction	Before Aging			After 13 Years Aging		
	(P_c/P_m)	$[E_c/E_m]^{D_2}$	Index	(P_c/P_m)	$[E_c/E_m]^{D_2}$	Index
0.29	0.464	0.453	1.024	0.328	0.366	0.896
0.38	0.351	0.339	1.035	0.261	0.264	0.989
0.45	0.272	0.252	1.080	0.234	0.207	1.116
0.55	0.177	0.185	0.950	0.180	0.162	1.116

measured and predicted creep compliance values has been proved using the model.

Empirical equations that fit the relationships between the filler volume fraction, the mechanical characteristics of the composites, and the matrix enable us to predict the creep response of composites with filler volume fractions other than those used in the experimental investigations.

Long-term room aging causes a decrease in the creep compliance of the matrix and the composites and an increase in the moduli of elasticity. However, the influence of aging on the relationship between the filler volume fraction and the ratios of the mechanical characteristics of the composites and the matrix is negligible. In accordance with this, an exponential equation has been proposed to fit the relation between the inelastic and elastic characteristics of the composite and the matrix. This equation can be used to predict the creep compliance of the composites using a less demanding experimental program.

References

1. Kausch, H. H.; Beguelin, Ph.; Fischer, M. Mech Compos 2000, 36, 305.
2. Oliver, P.; Ioualalen, K.; Cottu, J. P. J Appl Polym Sci 1997, 63, 745.
3. Meddad, A.; Fisa, B. J Appl Polym Sci 1997, 65, 2013.
4. Metzner, A. P. J Appl Polym Sci 2002, 85, 455.
5. Moustafa, A. B.; Faizalla, A.; Abd El Hady, B. M. J Appl Polym Sci 1998, 67, 637.
6. Liang, J. Z.; Li, R. K. Y. Polym Int 2000, 49, 170.
7. Gao, Z.; Tsou, A. H. J Polym Sci Part B Polym Phys 1999, 37, 155.
8. Marcovich, N. E.; Reboredo, M. M.; Aranguren, M. I. J Appl Polym Sci 1998, 70, 2121.
9. Sen, S.; Nugay, N. J Appl Polym Sci 2000, 77, 1128.
10. Mansour, S. H.; Abd-El-Messieh, S. L. J Appl Polym Sci 2002, 83, 1167.
11. Saroja Devi, M.; Murugesan, V.; Rengaraj, K.; Anand, P. J Appl Polym Sci 1998, 69, 1385.
12. Hutchinson, J. M. Prog Polym Sci 1995, 20, 703.
13. Robertson, C. G.; Monat, J. E.; Wilkes, G. L. J Polym Sci Part B Polym Phys 1999, 37, 1931.
14. Minster, J.; Hristova, J. In Proceedings of the 9th International Conference on Mechanics and Technology of Composite Materials, G. Zachariev, Ed., CLPCHM BAS Publisher, Sofia, Bulgaria; 2000; Vol. 9, p 300.