Evaluation and Modeling of the High-Temperature Short-Term Creep Performance of Selected Glass-Filled Semicrystalline and Liquid Crystalline Polymers

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ABSTRACT: The creep performance of a material is one of the main criteria currently used to assess the long-term performance of thermoplastic composites. In a wide number of applications, including electrical connectors and various automotive applications, dimensional stability at elevated temperatures (i.e., short-term creep performance) is an essential design requirement. In many of these applications the material can be exposed to elevated temperatures and high applied stresses as part of the fabrication process or in the end-use application. The elevated temperature creep behavior of 30%, and 40% glass-filled syndiotactic polystyrene, 30% glass-filled poly(butylene terephthalate), 30% glass-filled poly(phenylene sulfide), and a 30% glass-filled liquid crystalline polymer has been evaluated. The creep behavior for each of the materials has been modeled using the formulation proposed by Findley, Kholsa, and Petersen (FKP). The FKP model was found to provide a good description of the creep performance of these glass-filled materials. The parameters in the FKP model were evaluated for each of the materials as a function of temperature and applied stress. Comparison of the predicted short-term creep behavior using the FKP model with experimental data has shown that the predicted creep behavior is within ±10% of the measured value over the temperature and applied stress ranges examined. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 1177–1183, 1998

Key words: syndiotactic polystyrene; elevated-temperature creep; FKP model; semicrystalline polymers

INTRODUCTION

The creep performance of a material is one of the main criteria currently used to assess the long-term performance of thermoplastic composites. In a wide number of applications, including electrical connectors and various automotive applications, dimensional stability at elevated temperatures (i.e., short-term creep performance) is an essential design requirement. In many of these applications the material can be exposed to elevated temperatures and high applied stresses as part of the fabrication process or in the end-use application. Therefore, a complete characterization of the creep performance of materials used in such areas is of primary importance in assessing

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the reliability of the fabricated part. The creep behavior of polymeric materials can be improved greatly by the addition of glass fibers.[1–9] To a first approximation, in analogy to particulate-filled systems, the creep strain of a glass-filled material relative to that of the unfilled material is given by the ratio of the Young's modulus of the unfilled system relative to that of the filled system.[10,11] This relationship is based on the assumption that the addition of the rigid filler does not change the retardation time spectrum of the polymer. The relationship has been found to hold for some systems such as particulate-filled polyethylene.[10] At high elongation, at high filler levels, or at long times, dewetting (or adhesive failure) between the matrix and filler can occur. Once this occurs the creep rate can increase dramatically and the simple relationship discussed above is no longer valid.[12–15]

Numerous models have been proposed to describe the creep behavior of polymeric materials and glass-filled composites. Lederman proposed the following equation and used it to describe the creep of bakelite at constant stress:

$$\varepsilon = \varepsilon^0 + A \log t + Bt \tag{1}$$

where ε^0, A, and B are functions of stress, temperature, and the material, respectively.[16] A number of investigations have utilized mechanical models employed in viscoelasticity theory.[17–20] Findley, Kholsa, and Petersen (FKP) proposed an empirical relationship for creep behavior which has been found to describe the creep behavior of rigid polymeric materials over a wide range of temperatures.[21–23] The FKP model can be expressed as

$$\varepsilon = \varepsilon^0 + \varepsilon^+ t^n \tag{2}$$

where ε is the total creep strain, ε^0 is the strain at zero time or strain offset, ε^+ is strain prefactor, and n is the power law exponent. In general, ε^0, ε^+, and n are all material-dependent. For a number of materials, ε^0 and ε^+ have been found to be functions of the applied stress and temperature. Lai and Findley found n to be independent of both stress and temperature and generally less than 1.[24]

The FKP model can be modified to describe the nonlinear creep behavior of materials by introducing a hyperbolic sine function of the applied stress:

$$\varepsilon = \varepsilon^0 \sinh\left(\frac{\sigma}{\sigma^0}\right) + \varepsilon^+ t^n \sinh\left(\frac{\sigma}{\sigma^+}\right) \tag{3}$$

where ε^0, ε^+, σ^0, and σ^+ are functions of temperature and material, respectively. The hyperbolic sine function can be attributed to the rate process activation theories and describes the influence of stress on the thermal activation of deformational processes.[25,26] The hyperbolic sine function has also been found to describe the stress dependence of the creep in some filled semicrystalline materials.[10,11,27] In these examples the term σ^+ was found to be independent of filler concentration if the fillers were particulates, and dependent on filler concentration if the fillers were glass fibers. The influence of stress on the thermal activation of deformational processes can also be accounted for in the FKP model by assuming that both ε^+ and n are dependent on both the applied stress and temperature as

$$\varepsilon^+ = \varepsilon_0^+ \exp\left[\frac{-(E_a - \alpha\sigma)}{RT}\right] \tag{4}$$

$$n = n_0 \exp\left[\frac{-(E_a^* - \alpha^*\sigma)}{RT}\right] \tag{5}$$

where E_a and E_a^* are the activation energies for the creep process, α and α^* are the stress dependence of the creep process, ε_0^+ and n_0 are pre-exponential factors, R is the gas constant, T is the temperature, and σ is the applied stress. By combining eqs. (2), (4), and (5), a description of the effects of stress and temperature on the creep behavior of a material can be formulated.

In the work reported herein, the short-term high-temperature creep behaviors of several glass-filled semicrystalline materials have been investigated. Using the experimental data, a model has been developed and validated which allows the creep performance of the resins studied here to be predicted accurately at a specified temperature and applied stress.

EXPERIMENTAL

Materials

The materials used in this study included 30% and 40% glass-filled syndiotactic polystyrene (GF-sPS) obtained from Dow Chemical Company (Midland, MI); a 30% glass-filled poly(butylene terephthalate) (GF-PBT), designated as Valox 420SEO and obtained from General Electric Corporation; a 30% glass-filled liquid crystalline polymer (GF-LCP), designated as Vectra E130 and

Table I Selected Physical Properties of the Materials Studied

Material Type	sPS	sPS	PBT	PPS	LCP
Glass Reinforcement (%)	30	40	30	40	30
Specific gravity (g/cm^3)	1.41	1.51	1.62	1.65	1.61
Melting point (°C)	270	270	217	280	—
Tensile strength (MPa)	103	108	117	141	207
Flexural strength (MPa)	154	165	165	193	255
Flexural modulus (GPa)	10.4	13.1	7.8	13.1	14.5
Notched Izod (J/m)	85	100	64	80	149
HDTUL (°C)					
at 0.46 MPa (66 psi)	263	262	215	> 260	> 260
at 1.82 MPa (264 psi)	240	239	204	> 260	254

obtained from Hoescht Celanese Corporation; and a 40% glass-filled poly(phenylene sulfide) (GF-PPS), designated as Ryton R4 and obtained from Phillips Petroleum. The materials were used as received. Basic physical properties of the materials are listed in Table I.

Sample Fabrication

Injection-molding was conducted using a Mannsman Demag 100-ton injection-molding machine fitted with a 6.0-oz. nonvented barrel. A standard Demag screw design with a sliding-ring check device was used throughout the study. The mold was configured with a cold sprue bushing and generous runner system and was set up to produce ASTM type 1 tensile bars and a 2.0-inch diameter disk during each shot. Mold temperature was controlled using an Advantage Temptender® 500 single-zone hot-oil temperature controller. Processing conditions for each material are summarized in Table II.

Characterization of Creep Behavior

The creep behavior of the materials was evaluated using a Rheometrics RSAII solids analyzer equipped with a high-temperature oven. The experiments were conducted using three-point bend fixtures with a constant span of 48 mm. The samples were placed onto the bottom support and the top fixture was adjusted to just make contact with the sample. The oven was set to the desired temperature and the sample was allowed to equilibrate for 10 min. After this time a slight compressional force of 100 Pa was placed on the sample to ensure contact. This initial load is much less than the loads used in the actual creep experiments. The creep experiment was initiated by applying a stress then following the resulting creep strain for 600 s, over which 500 measurements of the strain were taken. All the experiments reported herein were conducted in a dry nitrogen environment.

In order to investigate the effect of temperature as well as applied stress on the creep behavior of each of the materials, two sets of experiments were conducted. First, the applied stress was held constant at 1.59 MPa (230 psi) and the creep behavior was measured at 175, 200, 225, 250, and 260°C. Next, the temperature was held constant (usually at 250°C) and the creep behavior was measured at applied stresses of 0.86 MPa (125 psi), 1.03 MPa (150 psi), 1.38 MPa (200 psi), 1.59 MPa (230 psi), and 1.72 MPa (250 psi). For GF-PBT, due to the lower crystalline melting temperature (T_m) of the PBT, direct creep measurements could not be made at 250°C. Therefore, the creep

Table II Injection-Molding Conditions for the Materials Studied

Material	Target Melt Temperature (°C)	Mold Temperature (°C)	Drying Temperature (°C)	Drying Time (h)
30% GF-sPS	322	150	N/A	0
40% GF-sPS	322	150	N/A	0
GF-PBT	270	80	225	110
GF-LCP	330	150	110	8
GF-PPS	330	150	110	8

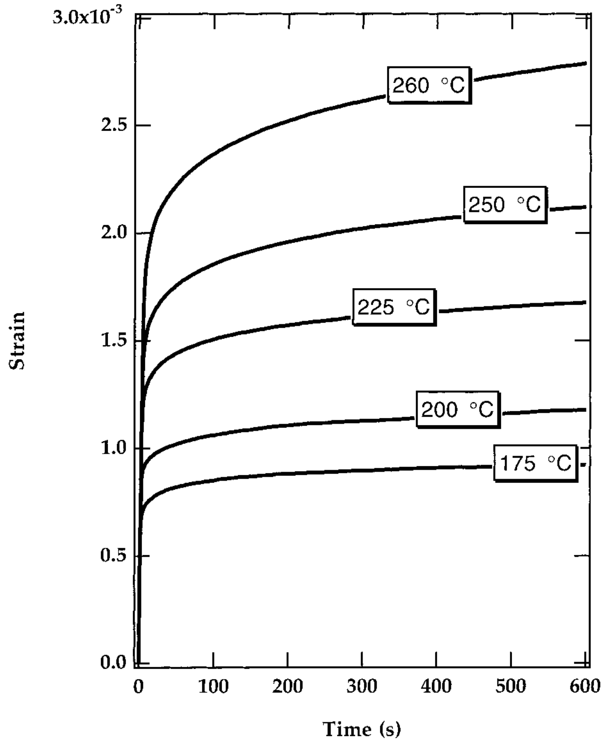

Figure 1 The creep behavior of 30% GF-sPS as a function of temperature at an applied stress level of 1.59 MPa.

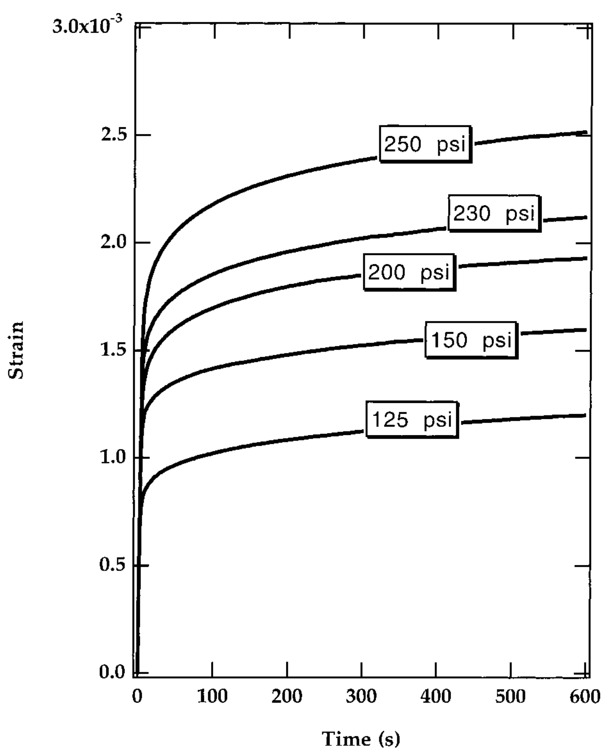

Figure 2 The creep behavior of 30% GF-sPS as a function of stress level at 250°C.

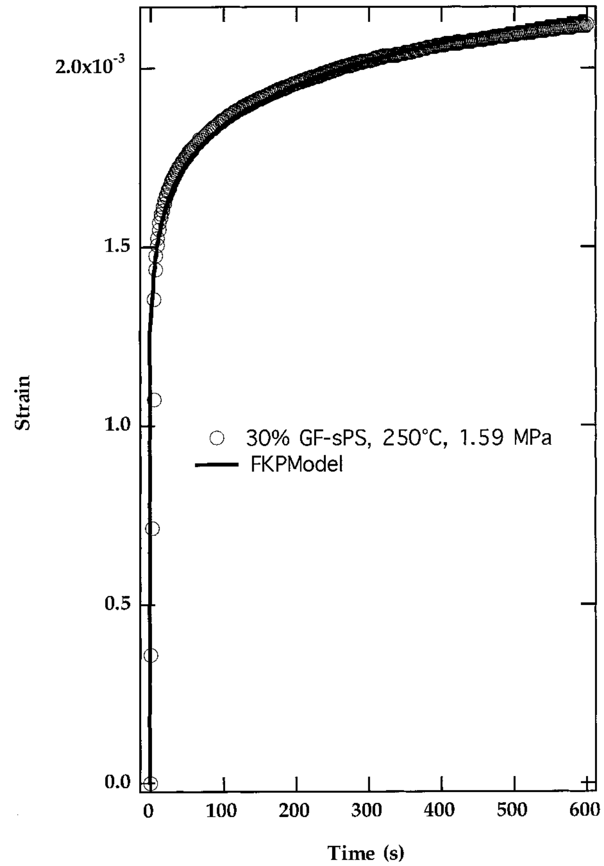

Figure 3 The fit of the FKP model to the experimental creep data for 30% GF-sPS at an applied load of 1.59 MPa and 250°C.

behavior was evaluated at temperatures of 110, 125, 150, 175, and 200°C. The dependence of applied stress for GF-PBT was evaluated over the same stress range as above, but was conducted at 200°C. Replicate runs of five specimens were conducted for each material and at each experimental condition. The creep curves reported herein are the average response of the five replicate experiments. For all of the materials, the relative standard deviation of the various experiments was less than ±10%.

RESULTS AND DISCUSSION

Evaluation of Model Parameters

The creep behavior of all of the glass-filled materials exhibited a strong dependence on both the temperature and the applied stress. The temperature and stress dependence of the creep behavior of 30% GF-sPS is illustrated in Figures 1 and 2, respectively. For each of the materials studied in

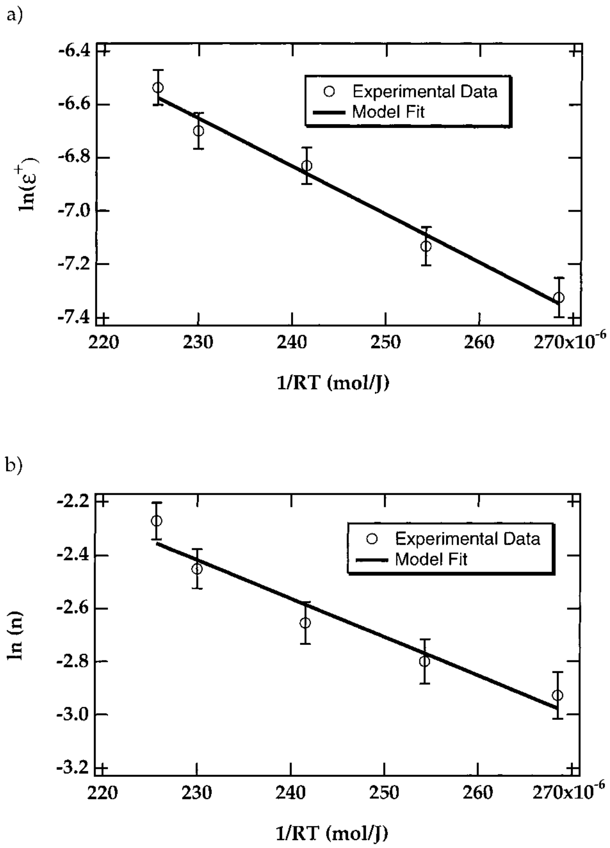

Figure 4 Analysis of the parameters (a) ε_0^+, and $(E_a - \alpha)$; and (b) n_0, $(E_a^* - \alpha^*)$ in the FKP model for 30% GF-sPS.

this work, the experimental creep data—with varying applied stress at constant temperature as well as varying temperature at constant applied stress were fit to the FKP model [eq. (3)] with $\varepsilon^0 = 0$. An example of the model fit to the experimental data for 30% GF-sPS is illustrated in Figure 3. From these fits the dependence of n and ε^+ on applied stress and temperature were obtained. Using eqs. (4) and (5) and the data for each material with fixed temperature and varying applied stress and with fixed applied stress and varying temperature, the values of n_0, ε_0^+, E_a, E_a^*, α, and α^* can then be obtained in a straightforward manner. One of the data sets, typically that with fixed applied stress and varying temperature, was used to evaluate n_0, ε_0^+, and the quantities $(E_a - \alpha)$ and $(E_a^* - \alpha^*)$. The second data set was then used to evaluate E_a, E_a^*, α, and α^* using the previously determined values of n_0 and ε_0^+. Representative curves for the data fits for 30% GF-sPS are illustrated in Figures 4 and 5. The error bars represented in the figures are the ± one standard deviation errors associated with fitting the model parameters to the experimental data. Reversing the order of the data-fitting routine yielded identical results for the fitting parameters. The results of the analyses for the materials studied, along with the ± one-standard-deviation error bars associated with the evaluation, are summarized in Table III.

From the data in Table III it is evident that both the constants in the FKP model were found to be dependent on temperature as well as applied stress level for all the glass-filled materials studied. This is in accordance with earlier findings in the literature, which found dependence on the applied stress for some of the parameters in the modified FKP model [eq. (3)] when glass fibers were used as the filler.[10,11,27] Also from the data in Table III for 30 and 40% GF-sPS, it is evident that the addition of higher levels of glass causes a decrease in the front factors (ε_0^+, and n_0) but does not cause any significant change in either of the activation energies (E_a and E_a^*).

Validation of Creep Model Predictions

In order to investigate the validity of the elevated-temperature short-term creep predictions, creep

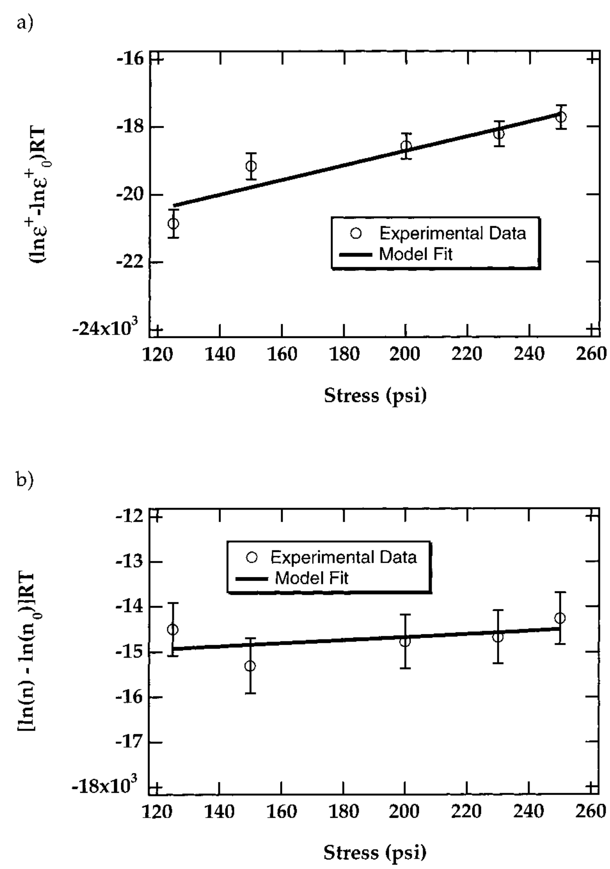

Figure 5 Analysis of the parameters (a) E_a and α, and (b) E_a^* and α^* in the FKP model for 30% GF-sPS.

Table III Summary of the Creep Parameters for the Materials Studied

Material	ε_0^+	$E_a\left(\frac{kJ}{mol}\right)$	$\alpha\left(\frac{kJ}{mol-MPa}\right)$	n_0	$E_a^*\left(\frac{kJ}{mol}\right)$	$\alpha^*\left(\frac{kJ}{mol-MPa}\right)$
30% GF-sPS	0.082 ± 0.006	23.0 ± 1.6	3.12 ± 0.13	2.52 ± 0.13	15.4 ± 0.16	0.49 ± 0.03
40% GF-sPS	0.055 ± 0.004	21.4 ± 1.8	2.93 ± 0.25	1.00 ± 0.068	11.5 ± 0.9	0.74 ± 0.05
GF-LCP	0.00076 ± 0.00008	5.6 ± 0.4	1.97 ± 0.17	2.49 ± 0.30 $(10)^3$	44.0 ± 3.8	1.22 ± 0.13
GF-PPS	0.0046 ± 0.0005	14.8 ± 1.1	3.49 ± 0.13	6.94 ± 0.8	20.0 ± 1.2	0.0 ± 0.03
GF-PBT	0.0075 ± 0.0006	12.4 ± 1.0	2.94 ± 0.28	2.39 ± 0.33 $(10)^4$	50.6 ± 5.3	0.74 ± 0.09

data was obtained on the various materials at temperatures and applied stresses not used to calculate the model parameters. The model was then used to predict the creep behavior at the same conditions and the predicted data was compared to the actual experimental measurements. In all cases the predicted values and the experimental data agreed to better than ±10%. An example of this comparison is illustrated in Figure 6 for 30% GF-sPS. From these experiments we feel that the creep models provide a reliable prediction of the creep behavior of GF-sPS as well as GF-LCP, GF-PPS, and GF-PBT over a wide variety of temperatures and applied stress levels. The calculated creep performance of the materials subjected to an applied stress of 2.1 MPa at 200°C is illustrated in Figure 7. From the data presented in the figure it is evident that the addition of higher levels of glass to sPS has a slight effect in reducing the creep behavior of the material. This result can also be seen by examination of the model parameters for 30 and 40% GF-sPS summarized in Table III. It is also evident that GF-PPS exhibits less creep than does 40% GF-sPS, despite the fact that both materials possess the same level of glass fibers and have similar T_m. This could be due to additional unknown additives in the GF-PPS material used in this study. The material with the lowest creep at these conditions is GF-LCP whereas GF-PBT displays the greatest amount

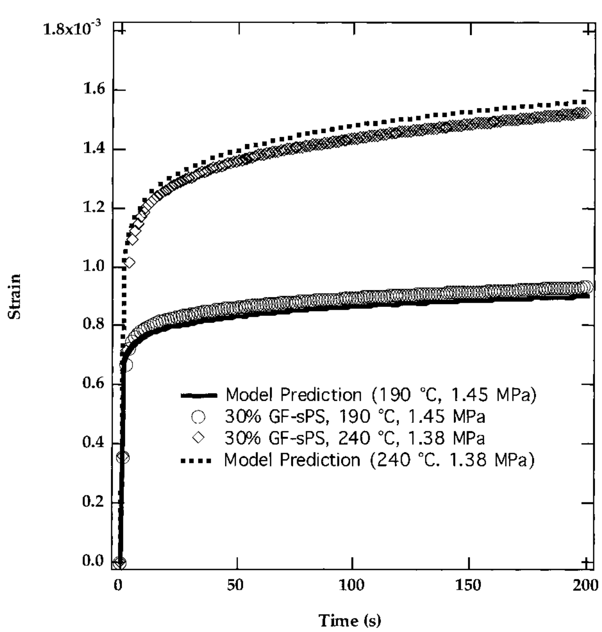

Figure 6 Comparison of the model predictions with experimental data for 30% GF-sPS at 190°C, 1.45 MPa, and 240°C, 1.38 MPa. Model predictions agree within ±10% with the experimental data.

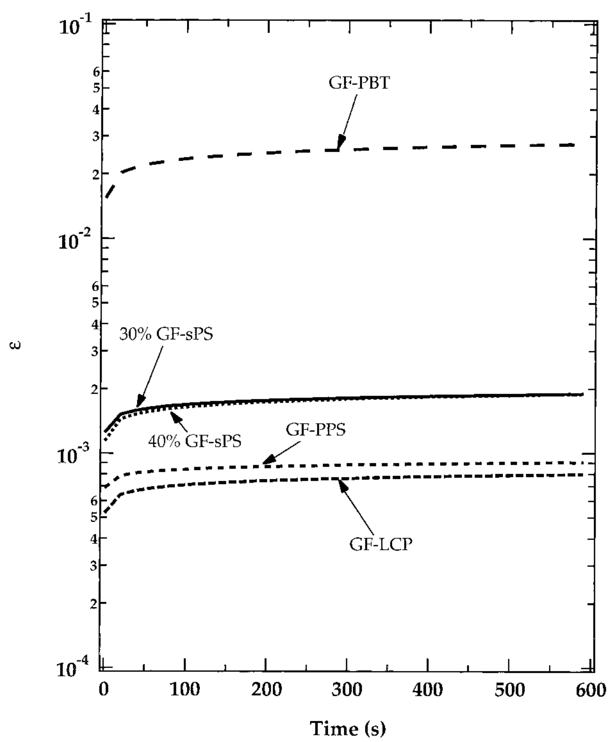

Figure 7 Predicted creep performance using FKP model for 30% GF-sPS, 40% GF-sPS, GF-PPS, GF-PBT, and GF-LCP at 2.1 MPa of applied stress and 200°C.

of creep, probably due to its lower crystalline T_m relative to sPS or PPS (217°C vs. 270°C for sPS and 280°C for PPS).

CONCLUSIONS

The elevated-temperature short-term creep performance of 30 and 40% GF-sPS, 30% GF-PBT, 30% GF-LCP, and 40% GF-PPS has been evaluated. The creep behavior for each of the materials has been modeled using the FKP formulation. The FKP model was found to provide a good description of the creep performance of these glass-filled materials. The parameters in the FKP model were evaluated for each of the materials as functions of temperature and applied stress. Comparison of the predicted creep behavior using the FKP model with experimental data has shown that the predicted creep behavior is within ±10% of the measured value over the temperature and applied stress ranges examined.

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