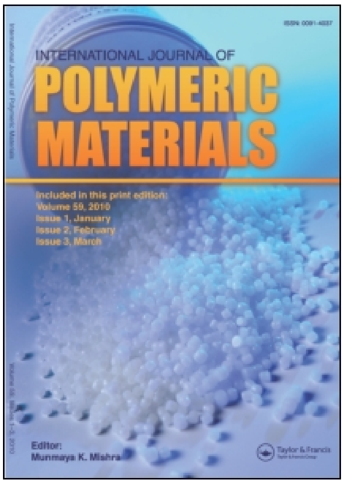

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Yielding Behavior of Particulate Reinforced Polyphenylene Oxide Polymers

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The mechanical behavior of particulate reinforced polyphenylene oxide composites is correlated in a simple fashion to the mechanical responses of the individual constituents. By use of time-temperature-composition superposition principles it is shown that experimental values of yield stress, deformation during creep and time-to-yield can be superposed to form master curves and that the shift factors are separable function of temperature, stress and composition.

Yield stress data are shown to conform to an equation of the form $\sigma_y = K_1 + K_2 \ln \dot{\epsilon} a_T$ while creep data fit a curve of the form $\epsilon_{\text{creep}} = A_0 \exp - [(Q/RT)] [\exp (\sigma/\sigma_c)] t^2$. The temperature shift factor for the data was given by $\ln a_T = (20{,}150/T) - 65.5$ and was independent of stress and composition. The yield stress of the composite σ_{yc} was related to the yield stress of the matrix σ_{yo} by $\sigma_{yc} = \sigma_{yo} (1 - 1.21\phi^{0.67})$. Finally, the creep data for the composites could be superposed to a single curve by using a stress parameter $\sigma_c = \sigma_{co} (1 - 1.21\phi^{0.61})$.

INTRODUCTION

At temperatures below the primary glass transition, most organic polymers exhibit either brittle or ductile failure, depending upon the load and temperature history imposed on the material. When ductile, these polymers are tough and resistant to impact and when brittle they are not. Polyblending with finely dispersed particles sometimes results in large increases in toughness, while polyblending with coarse rigid particles sometimes results in increased brittleness.

The measured tensile yield stress will depend on temperature and strain rate and it is well known that data can be shifted to form master curves.[1,2,3] To a good first order approximation the master curve obtained can be represented by the equation

$$\sigma_y = K_1 + K_2 \ln \dot{\epsilon} a_T \tag{1}$$

where σ_y is the tensile yield stress, K_1 and K_2 are constants which depend on the reference temperature chosen and on the specific polymer, $\dot{\epsilon}$ is the strain rate and a_T is the shift factor which is often a relatively simple function of temperature.

For polyphenylene oxide polymers the authors have shown[4] that experimental data can be represented by the following empirical equations:

$$\sigma_y \,(\text{psi}) = 11{,}400 + 270 \ln \dot{\epsilon} a_T \tag{2}$$

where $\dot{\epsilon}$ is the strain rate in min^{-1} and a_T is the temperature shift factor relative to a reference temperature of 34°C, and

$$\ln a_T = (20{,}150/T) - 65.5 \tag{3}$$

where T is in degrees Kelvin.

Following the suggestion of DiBenedetto and Trachte,[5] the total strain at the yield point ϵ_y can be expressed as the sum of two terms, a linear elastic (and recoverable) strain and a non-linear (and irrecoverable) strain. The elastic strain is calculated from the initial elasticity of the material σ/E_s, where E_s is the initial tangent modulus of elasticity. The irrecoverable strain is equated to the strain caused by the additional volume created by irreversible processes such as microcavitation and free volume formation:

$$\epsilon_y = \epsilon_s + \epsilon_p = (\sigma_y/E_s) + \epsilon_p \tag{4}$$

It was shown that the irreversible strain at the yield point was a linear function of temperature and independent of loading rate.[4,5] For polyphenylene oxide polymers its temperature dependence was expressed as follows:

$$\epsilon_p = 1.03 \times 10^{-4} (525 - T) \tag{5}$$

Under conditions of constant stress, a glassy amorphous polymer will exhibit creep. It has been shown that the total deformation as a function of time can be represented to a reasonable approximation by an equation of the following form:[4]

$$\epsilon(t) = (\sigma_o/E_s) + A_o\,[\exp - (Q/RT)]\,[\exp (\sigma/\sigma_c)]\, t^n \tag{6}$$

where $\epsilon(t)$ is the strain, σ_0/E_s is an instantaneous elastic (recoverable) deformation and the time dependent term on the right-hand side of Eq. (6) is due to non-recoverable deformation processes. (In crosslinked glasses this term must be replaced by a term for retarded elastic deformation.)

For the polyphenylene oxide polymers studied previously the best *empirical* representation can be obtained by curve fitting the experimental data to give:

$$[\epsilon(t) - (\sigma_0/E_s)] = 1.0 \times 10^{22} [\exp - (37{,}200/T)] [\exp (\sigma_0/160)]\, t^2 \qquad (7)$$

From Eqs. (4) to (7), one can equate the irrecoverable strain at the yield point ϵ_p with the left side of Eq. (7) to obtain the time required to initiate a general yield under constant stress:

$$t_y^2 = \frac{1.03 \times 10^{-26} (525 - T)}{[\exp - (37{,}200/T)] [\exp (\sigma_0/160)]} \qquad (8)$$

When a glassy polymer is mixed with a non-adhering particulate filler, the mechanical response of the composite is changed in a predictable way. The yield strength of the material has been shown to decrease in proportion to about the 2/3 power of the filler volume fraction[3,6] and the elastic modulus of the composite increases.[7] The creep rate decreases in proportion to the modulus increase when there is good adhesion between phases, but changes less predictably when the adhesion is poor. It has also been shown that time-temperature superpositioning can also be used for composites and that for some systems the required shift factors are independent of filler concentration.[8,9]

It is the purpose of this paper to show that the mechanical behavior of the particulate reinforced polyphenylenoxides can be simply correlated with the mechanical responses of the individual constituents.

EXPERIMENTAL

Composites of polyphenylene oxide and glass microspheres were prepared by dry-mixing the components, compression molding at 285°C and then slowly cooling the mold to room temperature. The polyphenylene oxide was General Electric's Grade 631-111 with a glass transition temperature of 210°C and a Poison's ratio of 0.35. It was supplied as a 20–400 mesh powder and was dried at 125°C and 29.9 inches of vacuum for 8–10 hours prior to compression molding. The glass microbeads were from Cataphote Company and had a size range of 1–30 microns, a density of 2.54 g/cc and a Poisson ratio of 0.25. Prior to use they were magnetically cleaned of iron particles present in the as-received material. The beads were used in an unsized condition with no surface treatment. Materials containing about 10%, 25% and

42% by volume filler were studied. All samples were annealed below T_g to minimize molding stresses. Standard ASTM tensile tests were carried out on an Instron testing machine at temperatures ranging from 34°C to 140°C and at strain rates of 0.00526 to 0.526 in/in-min. The yield point was defined as the maximum in the engineering tensile stress versus strain curve. This point was chosen because it was the closest point to the onset of cold drawing in the material that could be reproducibly measured. The "elastic strain" was measured from the initial tangent modulus, and the irrecoverable deformation was associated with non-linear portion of the stress-strain curve. The irreversible deformation versus time plots were obtained from creep-recovery experiments by keeping the materials at a constant load for a fixed period of time and then removing the load to permit recovery. The residual deformation at the end of recovery was considered irreversible. Time to yield was determined by observing the time required at a constant load to cause cold drawing of the specimen.

RESULTS AND DISCUSSION

A summary of the yield stress data at constant strain rate is shown in Figure 1. Time-temperature superpositioning at a reference temperature of 34°C was used to condense the data. The shift factor a_T for the abscissa was independent of filler concentration and identical to that for the unfilled polymer (Eq. 3).

All of the data in Figure 1 can be superimposed to a single curve by shifting along the ordinate by a factor of $(1 - 1.21\phi_f{}^{2/3})$, as illustrated in Figure 2.

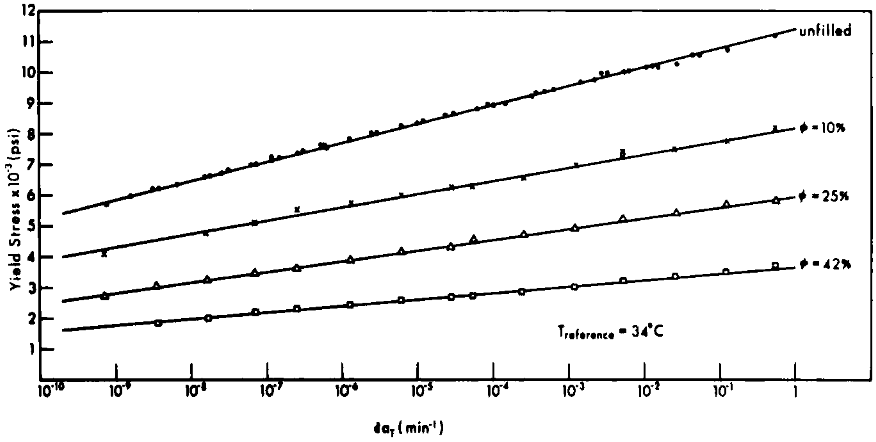

FIGURE 1 Effect of strain rate on yield stress for different concentrations of glass beads.

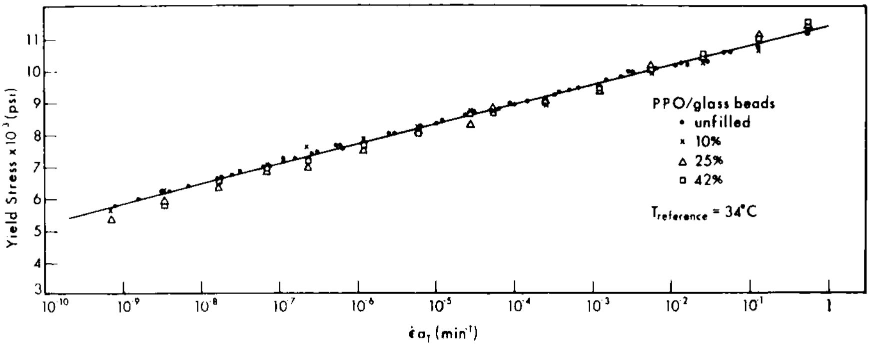

FIGURE 2 Reduced stress-strain data for particulate reinforced polyphenylene oxide composites (Eq. (9)).

Thus, at constant reduced rate of strain ($\dot{\epsilon}a_T$) the yield strength of the composite is given by:

$$(\sigma_{yc})_{\dot{\epsilon}a_T} = (\sigma_{yo})_{\dot{\epsilon}a_T}(1 - 1.21\phi_f{}^{2/3}) \tag{9}$$

where σ_{yo} is the yield strength of the unfilled material and is given by Eq. (2) and ϕ_f is the volume fraction of filler.

This result tends to confirm the simple model for the dependence of yield stress on volume fraction of non-adhering filler proposed by Nicolais and Narkis.[3] In this model, yielding is assumed to occur in the minimum cross section of the polymer phase which is perpendicular to the applied load. This minimum cross-section is shown by a simple geometric argument to be equal to $(1 - 1.21\phi^{2/3})$ for a composite containing spherical particles. Where there is no adhesion between phases, Eq. (9) will give the composite yield stress.

The creep behavior of the composites is summarized in Figures 3 to 6. The creep rates are considerably higher than in the unfilled matrix, indicating that the presence of filler has induced a large amount of irreversible damage and deformation. The process of irreversible deformation is a combination of nucleation of submicroscopic defects at stress inhomogenieties and their subsequent growth to macroscopic dimensions. This is quite apparent visually when one sees the general stress whitening of the composites and the growing opaqueness of the material under stress. The presence of non-adhering particulate filler provides additional sites for stress concentration and micro-cavitation and therefore increases the rate of nucleation of microdefects.

All of the data of Figures 3 and 4 are plotted on the single curve of Figure 7. The master curve conforms to the following equation:

$$\left(\epsilon(t) - \frac{\sigma_0}{E_c}\right) = 1.0 \times 10^{22}\left(\exp - \frac{37{,}200}{T}\right)\left(\exp \frac{\sigma_0}{160(1 - 1.21\phi^{0.61})}\right)t^2 \tag{10}$$

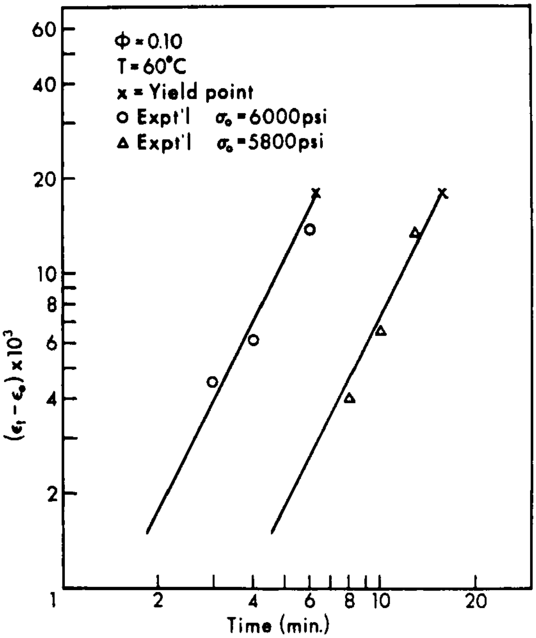

FIGURE 3 Non-recoverable deformation in creep ($\phi = 0.10$).

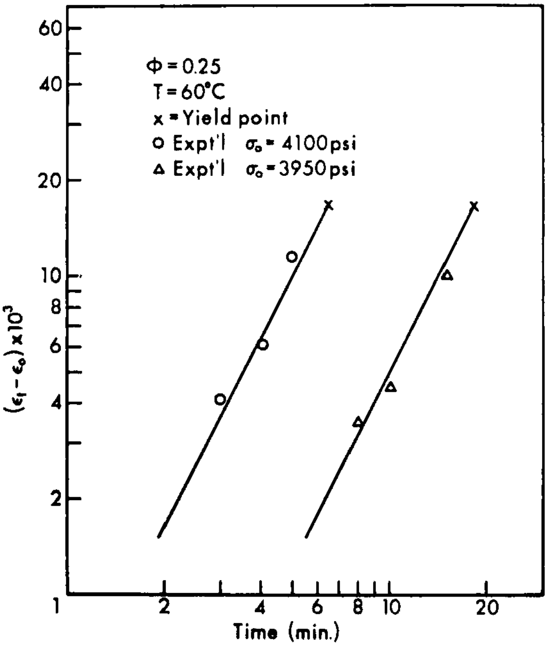

FIGURE 4 Non-recoverable deformation in creep ($\phi = 0.25$).

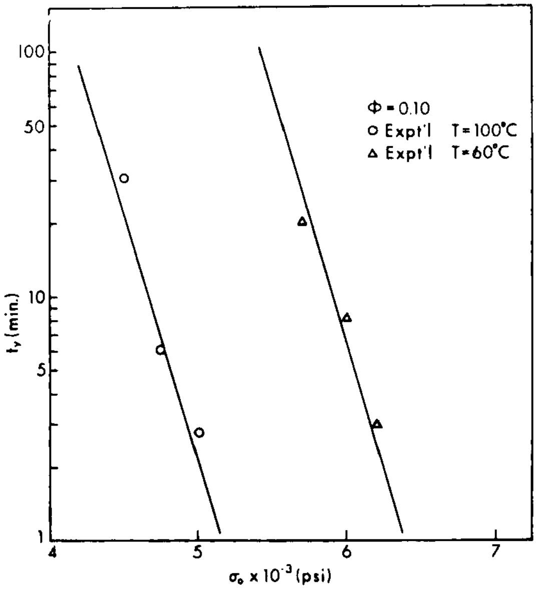

FIGURE 5 Time-to-yield under constant load ($\phi = 0.10$).

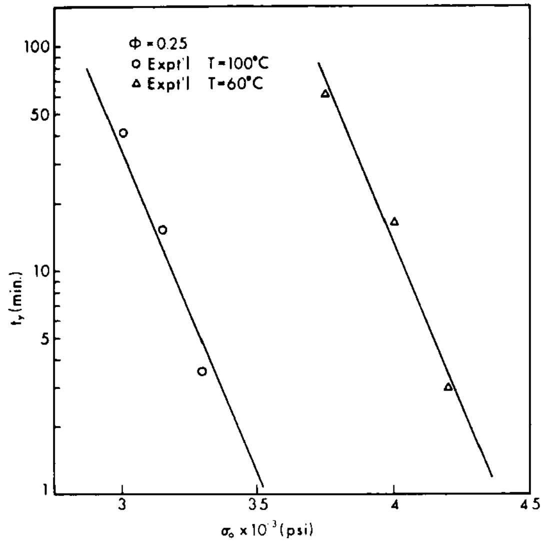

FIGURE 6 Time-to-yield under constant load ($\phi = 0.25$).

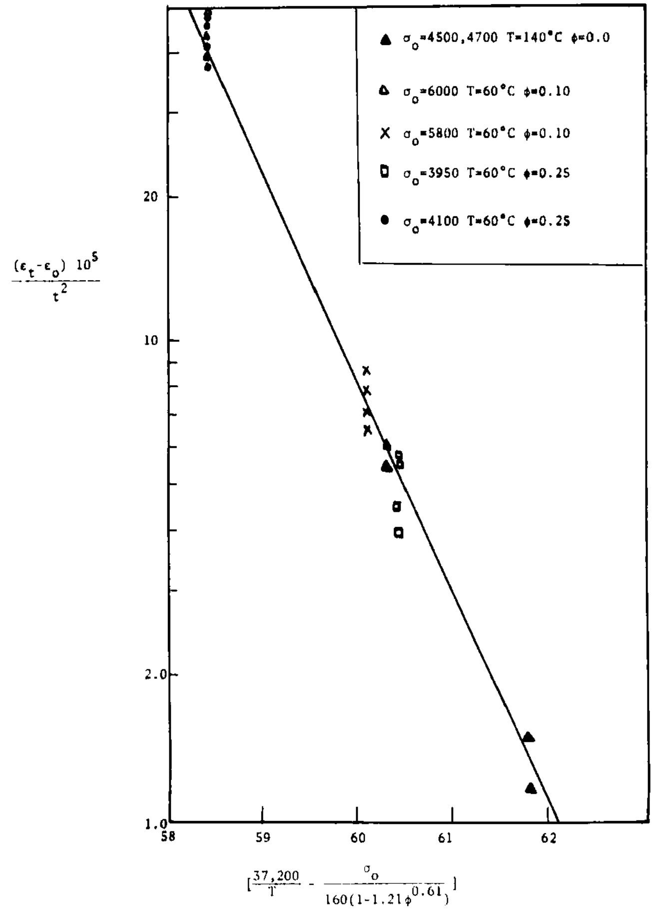

FIGURE 7 Master curve for non-recoverable deformation in creep of glass bead reinforced polyphenylene oxides.

The experimental values of time to yield are plotted in Figure 8 along with the predicted master curve:

$$\frac{t_y^2}{(525-T)} = \frac{1.03 \times 10^{-26}}{\exp-[(37{,}200/T)-(\sigma_0/160(1-1.21\phi^{0.61}))]} \tag{11}$$

Eq. (11) is obtained by combining Eqs. (10) and (5) and is analogous to Eq. (8). The experimental points lie somewhat above the predicted curve and tend to scatter. Since we could not measure reproducibly the strain at yield in the composites, it is not possible to say that Eq. (5) accurately represents the plastic deformation at the yield point. Furthermore, the temperature, stress and composition appear in a very lage exponential factor

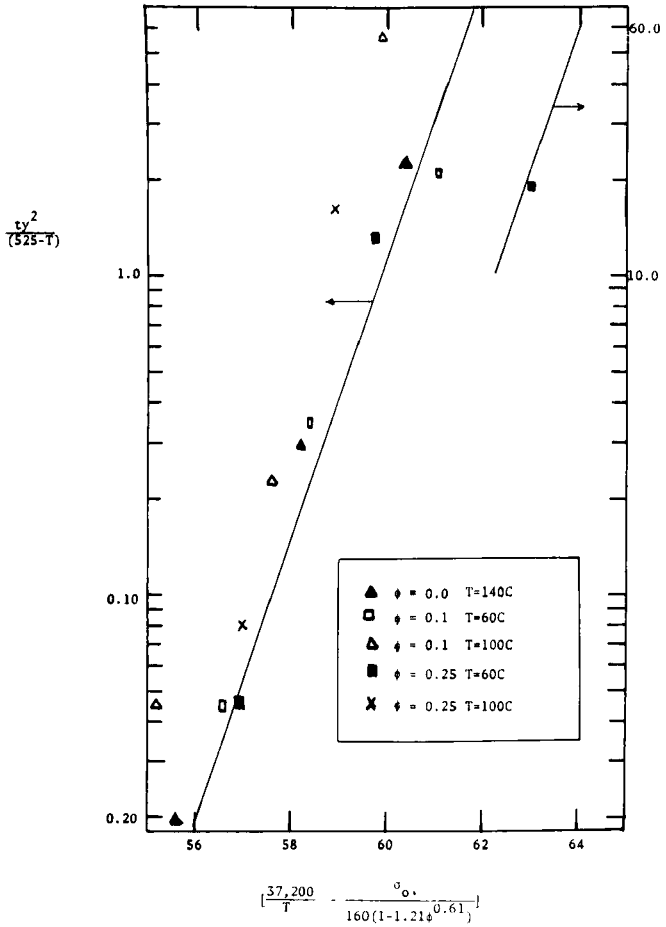

FIGURE 8 Master curve for time-to-yield under constant load for glass bead reinforced polyphenylene oxides.

which magnifies considerably small variations in these variables. For example, the temperature control in the oven on the Instron testing machine was no better than ± 1°K, which introduces an uncertainty in the predicted value of t_y^2 of roughly ± 30% at 373°K, the stress was measured to roughly ± 50 psia which introduces an additional uncertainty of the order of ± 60% and the composition variation from specimen to specimen was no worse than ± 1/2% which can also introduce an uncertainty of another ± 50%. Thus a scatter of ± 100 to 150% is certainly not unexpected.

Within the limitation of the very high sensitivity of the creep and yield behavior to the environmental variables, it is possible to superposition the composites data to a single master curve my modifying the exponential stress term to account for the volume fraction of filler. The empirical shift factor of $(1 - 1.21\phi^{0.61})$ is nearly the same as that used for shifting the yield stress data (i.e. $1 - 1.21\phi^{2/3}$) but probably has no theoretical significance. The shift factor for temperature appears to be identical to that of the matrix and independent of filler concentration.

The ability to add composition variables to superpositioning techniques greatly simplifies the correlation of composite properties and enables one to estimate behavior on the basis of limited data.

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