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STUDIES OF STRESS-STRAIN BEHAVIOR OF SAN/GLASS BEAD COMPOSITES ABOVE THE GLASS TRANSITION TEMPERATURE

BY

M. NARKIS
L. NICOLAIS

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23

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FOREWORD

The research reported herein was conducted by the staff of Monsanto/Washington University Association under the sponsorshio of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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STUDIES OF STRESS-STRAIN BEHAVIOR OF SAN/GLASS BEAD COMPOSITES ABOVE THE GLASS TRANSITION TEMPERATURE

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ABSTRACT

Relaxation and stress-strain behavior of SAN/glass bead composites is studied above the glass transition temperature. The strain imposed on the polymeric matrix of the composite is defined as $\varepsilon_p = \varepsilon_c/(1 - \phi^{1/3})$. Stress relaxation data for the filled polymer which is independent of strain can be calculated by multiplying the relaxation modulus (at a certain strain) by $(1 + \varepsilon_p)$. Stress-strain curves at constant strain rate and for different concentrations of the filler can be shifted to form a master curve independent of filler content if the tensile stress is plotted versus ε_p. The relaxation modulus increases with increasing the filler concentration and can be predicted by a modified Kerner equation at 110°C.

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**On leave from the Laboratorio di Ricerca su Tecnologia dei Polimeri e Reologia del C.N.R. Napoli, Italy.

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Introduction

In a recent publication [1] the behavior of SAN(styrene-acrylonitrile copolymer)/glass bead composites in the glassy region was described. The behavior of similar composites in the region above the glass transition temperature is discussed here. The quantitative analysis of stress-strain data for even unfilled polymers at high extensions is not straightforward. Obviously, it is much more complicated to analyze similar data for filled polymers. Smith [2] suggested a simple equation for calculation of strain in the continuous polymeric matrix as a function of the composite strain and the filler content. Essentially the same equation is used in this work and the significance of the strain in the polymer is shown by using a semi-empirical quantitative analysis.

Composites of a thermoplastic matrix and particulate fillers have been studied by several researchers above the glass transition temperature. Landel [3] studied the dynamic mechanical properties of PIB/glass bead composites. In his work, the temperature shift factors for the composites were nearly identical to those for the unfilled polymer. The Guth-Smallwood equation [4,5] was found appropriate for the prediction of the stiffness in the long-time region. The dewetting time in stress relaxation experiments for plasticized PVC/$CaCO_3$ composites has been shown to depend on the filler concentration, decreasing as the filler content is increased [6]. The effect of filler concentration on tensile properties of highly filled, cross-linked polyurethane rubber was also studied [7]. In this work the mechanical behavior at low extensions can be represented by a generalized Maxwell model and the modulus increase with increasing the filler content is satisfactorily described by an empirical modification of the Eilers equation [8].

Experimental

Preparation techniques for SAN(LUSTRAN A, Monsanto Co.)/glass bead composites were described in a previous paper [1]. Test specimens were 6 inch long strips, 1/2 inch wide and 0.1 inches thick. A gage of 2" was used in all tests.

Results and Discussion

It has been shown that the relaxation modulus of an unfilled polysulfone is time and strain dependent [9]. However, if strain is defined as $\ell_n(\ell/\ell_o)$ and a correction is made for the decrease of cross-sectional area, then the relaxation modulus is only time dependent at any given temperature. Other definitions must be used for filled polymers.

Smith [2] has shown by a simple theoretical analysis that

$$\varepsilon_c = \varepsilon_p\,(1 - 1.105\phi^{1/3}) \qquad (1)$$

where ϕ is the volume fraction of filler, ε_p is the strain in the polymer and ε_c is the strain imposed on the composite. The data obtained in the present work were analyzed by using the equation $\varepsilon_c = \varepsilon_p\ (1 - K\phi^{1/3})$ and the best fit was obtained for K equal to unity, thus the definition of strain in the polymer in the present work is as follows:

$$\varepsilon_p = \frac{\varepsilon_c}{1 - \phi^{1/3}} \tag{2}$$

The relaxation modulus for filled polymers depends on time and strain at a constant temperature. Analysis of experimental data shows that the ratio of two relaxation moduli (for a certain composite) at a common time but at different strains is practically independent of time within the range of strain and time that were studied. Therefore, stress relaxation curves for a filled polymer at different strains ε_c can be shifted along the modulus axis to a reference curve at a reference strain. This procedure has been used in the past for unfilled polymers [10].

Further analysis of the experimental data has shown that the above mentioned modular ratio is a function of the strains imposed on the polymer. This function can be described as follows

$$\frac{\left[E_{c\varepsilon}(t)\right]_2}{\left[E_{c\varepsilon}(t)\right]_1} = \frac{1 + (\varepsilon_p)_1}{1 + (\varepsilon_p)_2} \tag{3}$$

The term $(1 + \varepsilon_p)$ apparently accounts for the reduction in cross-sectional area of the polymer that is "isolated" from the composite.

In Table 1 calculated ε_p values, according to Equation (2), and $(1 + \varepsilon_p)$ values, to be used in Equation (3), are shown for two filler concentrations and for several levels of composite strain.

In Table 2 relaxation data for $\phi = 0.213$ and for three different strains are shown. The modular ratios are practically independent of time. The average experimental ratios are in good agreement with the predicted ratios as calculated with Equation (3). A similar conclusion can be drawn from Table 3 which summarizes experimental and calculated results for $\phi = 0.427$.

In light of this conclusion the relaxation modulus of the composite $E_c(t)$ independent of strain is defined as follows

$$E_c(t) = \left(1 + \frac{\varepsilon_c}{1 - \phi^{1/3}}\right) E_{c\varepsilon}(t) = \left(1 + \varepsilon_p\right) E_{c\varepsilon}(t) \quad . \qquad (4)$$

In Table 4 the stress relaxation modulus, independent of strain, is tabulated for experimental data at three different strains. For linearly viscoelastic bodies, stress-strain curves at a constant strain rate can be calculated from relaxation data [9,11] by using the following equation [12,13]:

$$f(t) = \dot{\varepsilon} \int_{-\infty}^{\ell nt} tE(t)\,d\ell nt \qquad (5)$$

Equation (5) was found appropriate for unfilled polysulfone and polycarbonate above their glass transition temperature if proper definitions of strain and strain rate are used [9]. In the present case, the relaxation data given in Table 4 is believed to be strain independent and one can try to use it for calculation of stress-strain curves. In order to extend the relaxation data given in Table 4 to the region of shorter times, which is necessary for the integration of Equation (5), stress relaxation data at 118°C were shifted to the reference curve at 127°C. The strain independent stress relaxation moduli in the time range from 0.025 to 1 min. is given in Table 5. By using the data given in Tables 4 and 5, the integral in Equation (5) can be evaluated. Calculated stress-strain curves at two strain rates are shown in Figure 1 along with the experimental curves. The calculated and experimental curves have similar shapes, however the agreement is not entirely satisfactory. Undoubtedly, additional comparison of calculated stress-strain curves according to Equation (5) with experimental curves is required for filled polymers.

In Figure 2 stress-strain curves for different concentrations of glass beads at a constant strain rate are shown. At a given strain, ε_c, the stress increases with increasing filler concentration. This is typical for filled polymers above their glass transition temperature. In Figure 3 the data of Figure 2 are replotted as the stress versus strain in the polymer. Analysis of these curves shows that the ratio of two stresses for different glass bead concentrations, but at a common ε_p, is independent of ε_p. According to this result the curves can be shifted along the stress axis to produce a master curve. In Figure 3 the stress-strain curves are also shifted to the curve for the unfilled SAN and are in a good agreement with the experimental points for the unfilled polymer. The shift factors a_c are 1.0, 1.3, 1.95 and 4.5 for 0.0, 0.213, 0.427 and 0.536 volume fraction of glass beads respectively. Attempts to predict the values of a_c have been unsuccessful so far.

The effect of glass bead concentration on the relaxation modulus was studied at 110°C, which is close to the transition temperature of the filled polymer . In Figure 4 the relaxation modulus at 110°C is plotted versus time for different concentrations of glass beads. The modulus at a certain time increases with increasing the filler content as predicted by Kerner [14]. A good agreement between the experimental and calculated relative moduli was obtained by a modified Kerner equation which was recently suggested by Lewis and Nielsen [15]. The modified Kerner equation was confirmed for the relative storage modulus in shear of epoxy/glass bead composites by these authors.

Assuming that $E_c/E_p \doteq G_c/G_p$, the modified Kerner equation can be written as follows

$$\frac{E_c}{E_p} = \frac{1 + AB\phi}{1 - B\psi\phi} \qquad (6)$$

where

$$A = \frac{7 - 5\nu_p}{8 - 10\nu_p} = 1.5 \qquad\qquad B = \frac{G_g/G_p - 1}{G_g/G_p + A} \doteq 1$$

and

$$\psi = \left[1 + \left(\frac{1 - \phi_m}{\phi_m^2}\right)\phi\right] \tag{7}$$

or

$$\psi\phi = 1 - \exp\left(\frac{-\phi}{1 - \phi/\phi_m}\right) \tag{8}$$

The function ψ is the modification of Lewis and Nielsen which accounts for the maximum packing fraction ϕ_m. Poisson's ratio for the polymer ν_p above its glass transition is equal to 0.5. The ratio of the modulus of glass beads G_g to the modulus of the rubbery polymer G_p is very large compared to unity, thus $B \doteq 1$. ϕ_m is equal to 0.64.

Equation (8) was used for the epoxy/glass bead composites while for the SAN/glass bead composites Equation (7) is found to be more satisfactory. In Figure 4 calculated $E_p(t)$ values from data on filled SAN is shown to be in a good agreement with the experimental relaxation modulus for the unfilled polymer. At 127°C the modular ratio is found to be time dependent which cannot be predicted by any of the theoretical reinforcement equations.

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Table 1: Calculated ε_p values for two filler concentrations and different composite strains, ε_c.

	$\phi = 0.213$ $1 - \phi^{1/3} = 0.403$		$\phi = 0.427$ $1 - \phi^{1/3} = 0.247$	
ε_c	ε_p	$1 + \varepsilon_p$	ε_p	$1 + \varepsilon_p$
0.05	-	-	0.202	1.202
0.10	0.248	1.248	0.404	1.404
0.20	0.496	1.496	0.808	1.808
0.30	0.744	1.744	-	-

Table 2: The effect of strain on relaxation modulus, $E_\varepsilon(t)$ at 127°C. Modulus units are (dynes/cm^2)10^{-6}. $\phi = 0.213$.

Min.	$E_{0.1}(t)$	$E_{0.2}(t)$	$E_{0.3}(t)$	$\frac{E_{0.1}(t)}{E_{0.2}(t)}$	$\frac{E_{0.1}(t)}{E_{0.3}(t)}$	$\frac{E_{0.2}(t)}{E_{0.3}(t)}$
1	7.10	6.05	5.75	1.17	1.23	1.05
2	5.50	4.65	4.15	1.18	1.32	1.12
3	4.60	3.90	3.30	1.18	1.40	1.18
5	3.65	3.10	2.65	1.18	1.37	1.17
10	2.55	2.15	1.80	1.19	1.41	1.19
20	1.60	1.40	1.15	1.14	1.39	1.22
40	1.07	0.90	0.77	1.19	1.39	1.17
		<u>Average</u>		1.18	1.36	1.16
		<u>Predicted (Eq. 3)</u>		1.20	1.40	1.17

Table 3: The effect of strain on relaxation modulus $E_\varepsilon(t)$ at 127°C. Modulus units are (dynes/cm^2) x 10^{-6}. $\phi = 0.427$.

Min.	$E_{0.05}(t)$	$E_{0.1}(t)$	$E_{0.2}(t)$	$\frac{E_{0.05}(t)}{E_{0.1}(t)}$	$\frac{E_{0.05}(t)}{E_{0.2}(t)}$	$\frac{E_{0.1}(t)}{E_{0.2}(t)}$
1	17.9	15.6	11.0	1.15	1.62	1.42
2	11.7	10.0	7.50	1.17	1.55	1.33
3	9.60	8.06	5.95	1.19	1.62	1.36
5	7.20	6.03	4.55	1.19	1.58	1.32
10	4.40	3.74	2.83	1.17	1.55	1.32
20	2.60	2.24	1.76	1.16	1.48	1.28
40	1.45	1.28	1.00	1.13	1.45	1.28
		Average		1.17	1.57	1.33
		Predicted (Eq.3)		1.17	1.51	1.29

Table 4: Strain independent modulus calculated from relaxation data at different strains at 127°C. $\phi = 0.217$. Modulus units are (dynes/cm^2) x 10^{-6}.

Min.	$1.248 \times E_{0.1}(t)$	$1.496E_{0.2}(t)$	$1.744E_{0.3}(t)$
1	8.85	9.05	10.0
2	6.85	6.95	7.20
3	5.75	5.85	5.75
5	4.55	4.65	4.62
10	3.18	3.21	3.14
20	2.00	2.10	2.00
40	1.33	1.35	1.34

Table 5: $E_c(t)$ as a function of time at 127°C. $\phi = 0.213$.
Units are $(\text{dynes/cm}^2) \times 10^{-6}$

Min.	0.025	0.05	0.1	0.15	0.25	0.5	0.75	1
$E_c(t)$	22.4	18.8	15.8	14.2	12.5	10.3	9.13	8.85

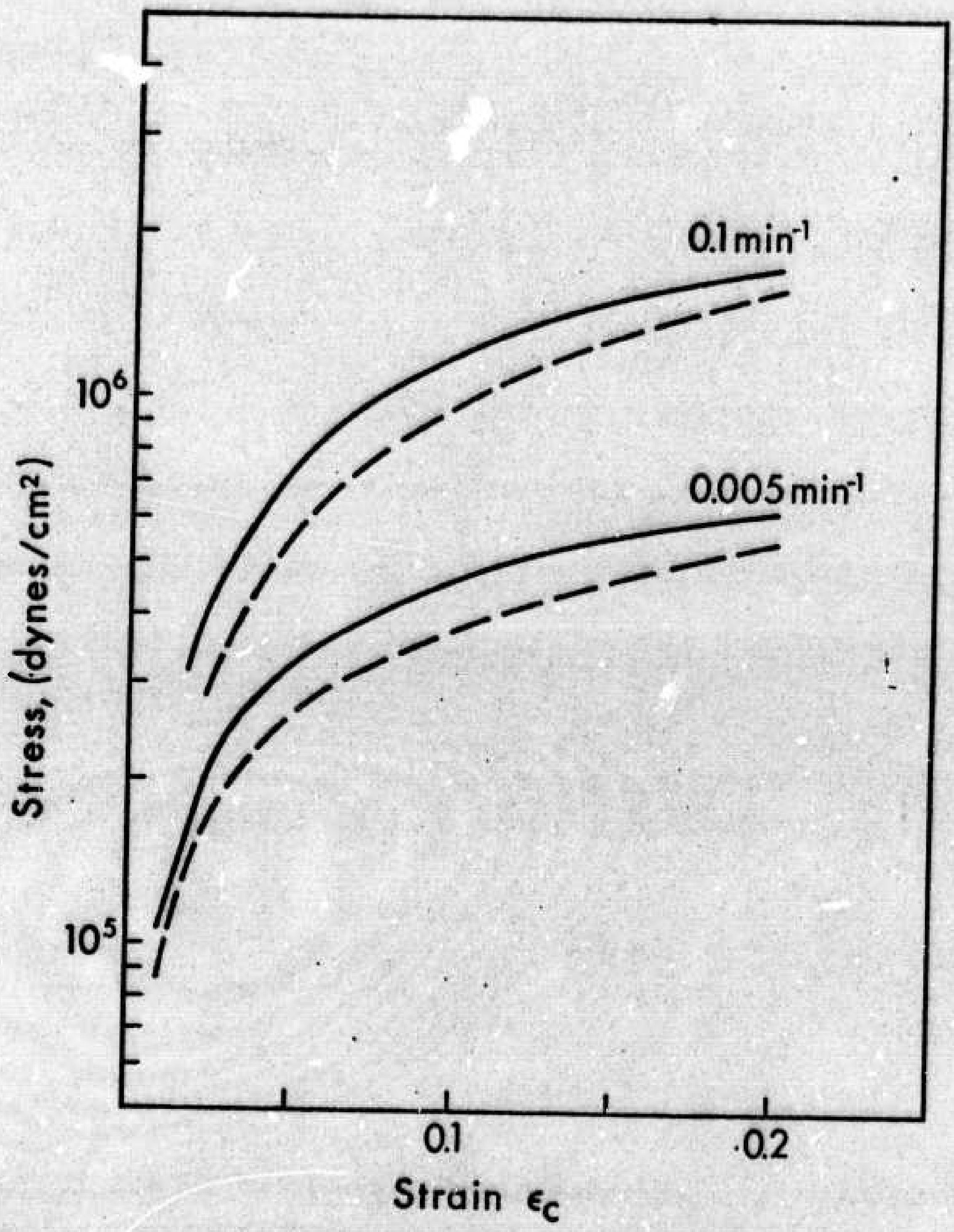
List of Figures

Figure 1: Comparison of experimental stress-strain curves with calculated curves according to Equation (5) for $\phi = 0.213$ and a temperature of 127°C.___experimental---calculated.

Figure 2: Stress vs. composite strain for different concentrations of glass beads. $\varepsilon_c = 0.005$ min^{-1} and temperature equals 127°C.

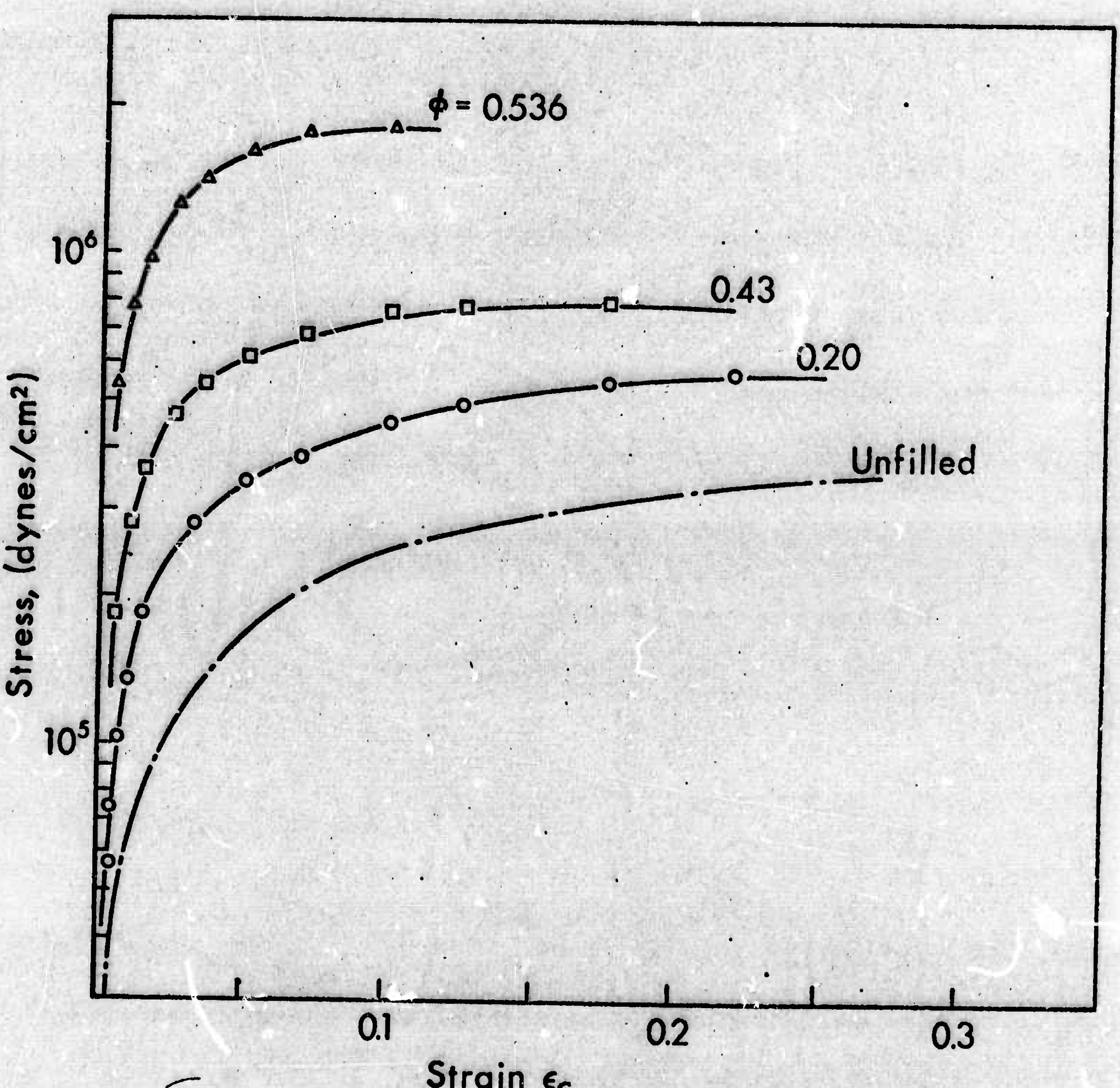
Figure 3: Stress vs. polymer strain for different concentrations of glass beads. $\varepsilon_c = 0.005$ min^{-1} and temperature equals 127°C.

Figure 4: Relaxation moduli at 110°C versus time for different concentrations of glass beads. Data for unfilled SAN are also compared with calculated values by using the modified Kerner equation. ● is data for unfilled polymer.



0.1 min^{-1}
0.005 min^{-1}
10^6
10^5
Stress, (dynes/cm^2)
0.1
0.2
Strain ϵ_c

Figure 1



φ = 0.536
0.43
0.20
Unfilled
10^6
10^5
Stress, (dynes/cm²)
0.1
0.2
0.3
Strain ϵ_c

Figure 2

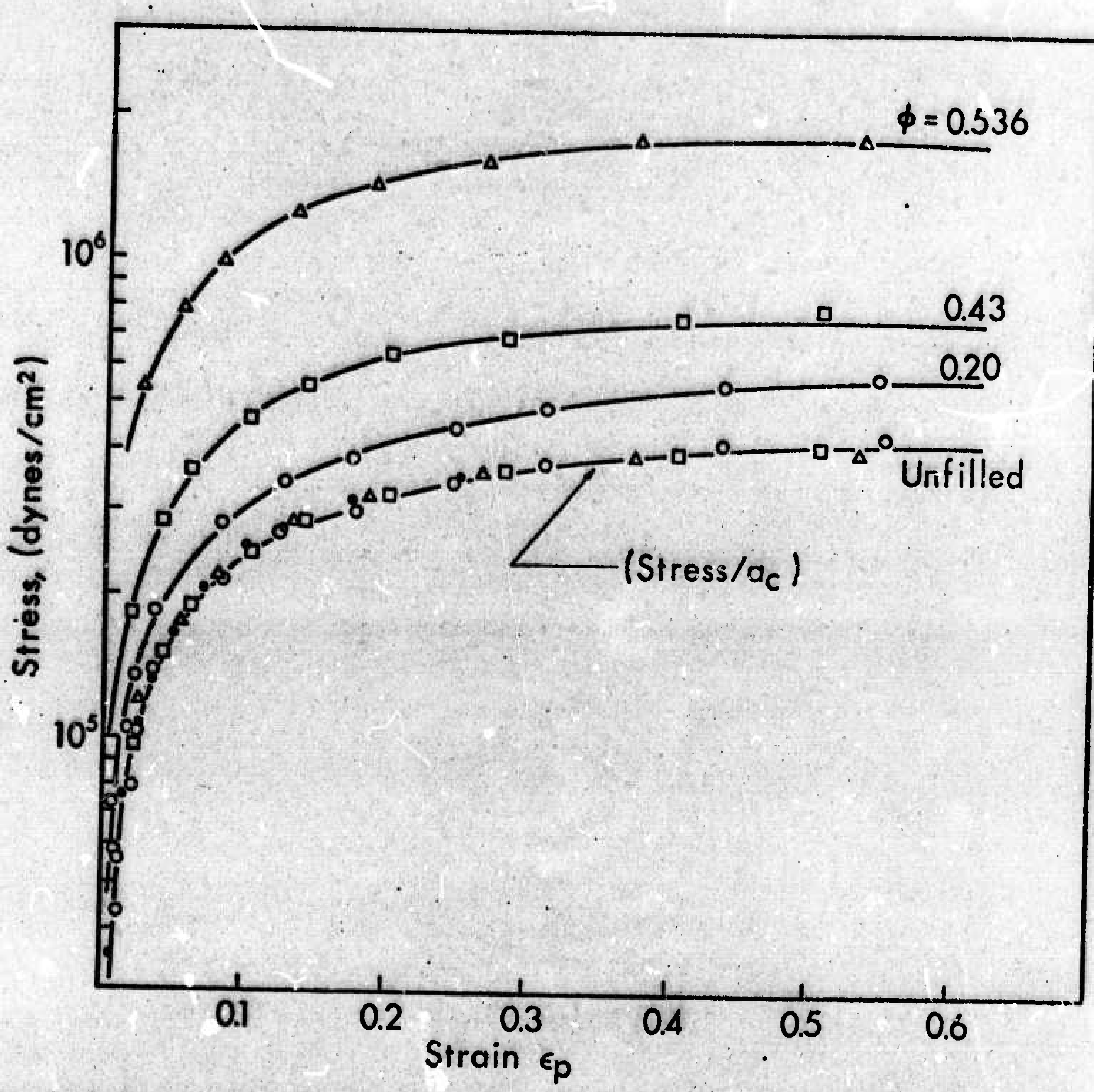

$\phi = 0.536$
0.43
0.20
Unfilled
(Stress/a_c)
10^6
10^5
Stress, (dynes/cm^2)
0.1
0.2
0.3
0.4
0.5
0.6
Strain ϵ_p

Figure 3

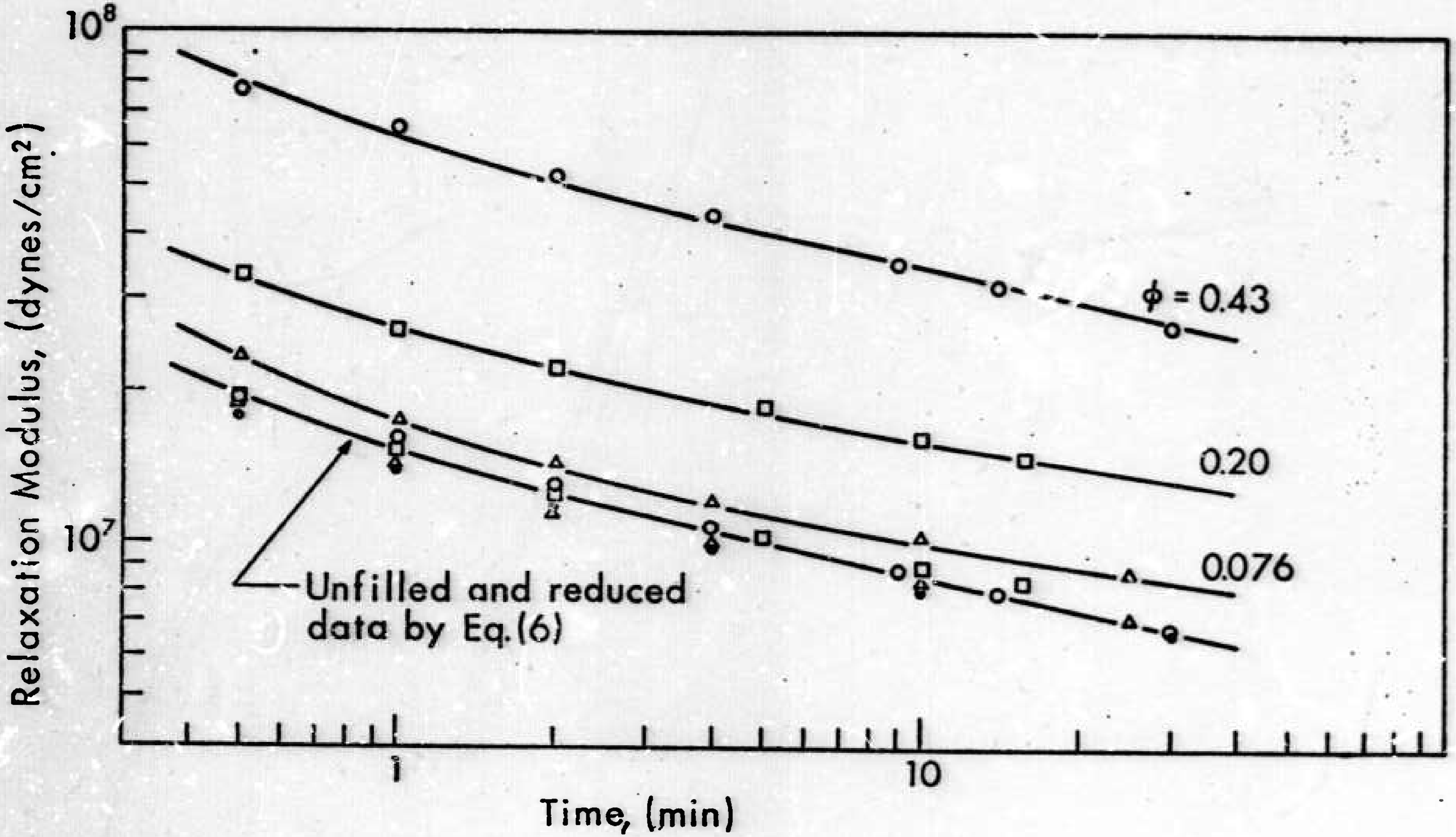

10^8
10^7
Relaxation Modulus, (dynes/cm²)
Time, (min)
1
10
ϕ = 0.43
0.20
0.076
Unfilled and reduced data by Eq.(6)

Figure 4

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13. ABSTRACT

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