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The effects of extensional creep and creep recovery on the dynamic properties of an unfilled and filled crosslinked polyester resin

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Changes in the dynamic properties of unfilled and filled cured polyester resins during extensional creep were measured with the aid of a modified torsion pendulum. Glass beads were used as filler. The decrease in the real shear modulus during creep is attributed mainly to a debonding process. Dewetting–rewetting processes reflected by modulus changes, were discussed on the basis of a theory of Takahashi *et al.* Voigt–Kelvin rheological models were used to characterize the modulus and the creep compliance recoveries after load release.

1. Introduction

In a previous paper [1] the dynamic properties of filled and unfilled cured epoxy resins measured during extensional creep were discussed. Results of similar experiments performed with the same experimental set-up on an unfilled and filled cured polyester resin are reported and discussed in this paper. A new approach to the analysis of the shear modulus changes occurring during creep is presented and a possible correlation between the modulus changes and dewetting–rewetting phenomena in filled specimens is also considered. This study may add to the understanding of the wetting–dewetting phenomena in composite materials through investigation of changes occuring in the dynamic properties of the system.

2. Experimental details

2.1. Materials

The resin used in this work was an unsaturated maleic-type polyester dissolved in styrene, Crystic 189, a product of Makhteshim, Beer-Sheva. Curing was initiated by methylethylketone peroxide (manufactured by Fluka), and a 6% solution of cobalt naphthenate in dimethylphthalate served as a promoter for the curing process. Weight percentages of resin : initiator : promotor were 97.8 : 2.0 : 0.2, respectively. All the ingredients were mixed, degassed in a vacuum chamber for 10 min and cast into a mould. The filled mould was heated for 3 h at 60° C, then for an additional 3 h at 80° C and then cooled slowly in the oven to room temperature. The volume fraction of glass beads in the samples was 0.43. Details about the glass beads, mould and torsion pendulum were reported previously [1].

2.2. The testing procedure

The specimen was clamped into the torsion pendulum and its initial real (G_0') and imaginary (G_0'') shear moduli were calculated after measurement of the free oscillation frequency (ω) and damping (Δ). A load imposed on the specimen caused an extensional deformation with a certain amount of creep. After application of the load, several measurements of the frequency and the damping were made and the new dynamic moduli (G', G'') were calculated. The specimen was under the action of load for 30 min, then the load was removed and the dynamic properties of the sample were measured again during the relaxation process. The elongation of the specimen was recorded by means of a linear variable differential

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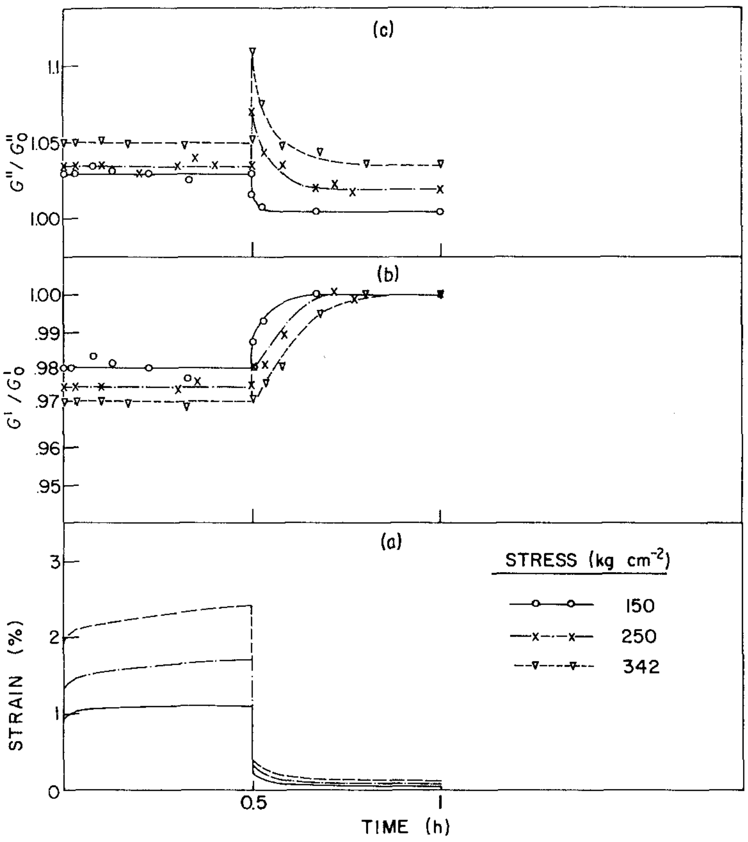


Figure 1 Changes in dynamical mechanical properties and strain in unfilled polyester specimens due to the action of load and after load release.

transformer (LVDT). The experiments were performed at room temperature (about 20° C).

3. Results and discussion

3.1. Unfilled specimens

Data of the experiments with unfilled polyester specimens performed on three stress levels, 150, 250 and 342 kg cm^{-2}, are shown in Fig. 1. The deformation, the relative real (G'/G'_0) and the relative imaginary, (G''/G''_0) moduli appear in Figs. 1a, b and c, respectively. The values of G'_0 and G''_0 were 6.32×10^6 and 3.17×10^5 kg cm^{-2}, respectively. The changes in the moduli were very small in the case of the unfilled specimens and even in the sample subjected to the highest stress, changes of only 3% in the real modulus and 5% in the imaginary modulus, occurred.

In all the experiments elastic, retarded elastic and residual strains were observed. Immediately after the load application a drop in the real modulus occurred; the drop was higher with the increase of stress. Also the loss modulus increased with the loading of the sample. In earlier experiments, with epoxy specimens [1], the loss modulus dropped in most cases when the load was applied and the only exception was the experiment in which the specimen was highly stressed and consequently also highly deformed. However, one must note, that the absolute deformations obtained in the experiments with polyester specimens were considerably higher than those observed in the experiments with the epoxy specimens.

In the experiments of Lifshitz and Rotem [2], a rise in the loss modulus occurred at the beginning of a tension test, yet in their experiments, the imposed deformation rate was high in comparison with the deformation rates in the creep tests in our previous work [1]. Based on the overall data it may be assumed, that a rise in mechanical losses may occur if the specimen is stressed at:

1. a high strain rate, or to
2. a large deformation.

After the load release the real modulus regained its initial value and this recovery was time dependent: 10 min to full recovery when the load was 150 kg cm^{-2} and 20 min in the 342 kg cm^{-2} test. A sharp rise in the loss modulus occurred when the load was removed and this sharp rise is due, perhaps, to the high momentary negative strain rate with the load release. After the sharp rise,

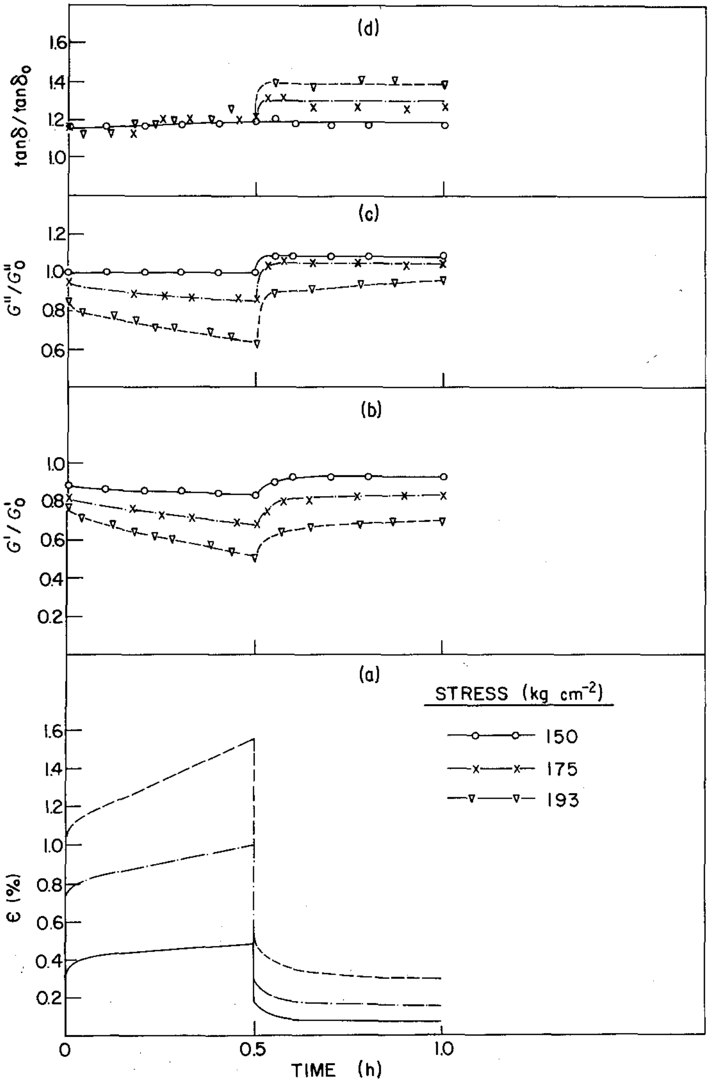


Figure 2 Changes in dynamic mechanical properties and strain due to the action of load and after load release in filled polyester specimens.

a continuous decrease in the modulus took place, but in no case was the initial value of the loss modulus reached. The difference between the original modulus and the one after recovery increased with increasing residual deformation in the specimen. It is interesting to note, that in spite of the residual deformation, the real modulus fully recovered to its initial value. It seems, therefore, that the loss modulus is much more affected by the residual strain than the real modulus.

3.2. Filled specimens

The results of the experiments carried out with filled specimens are shown in Fig. 2; the values of G'_0 and G''_0 were 1.12×10^7 and 5.35×10^5 kg cm^{-2}, respectively. Due to the large changes in G' and G'' it was possible to plot the change of tan δ during the experiments. In the case of the unfilled specimens it was impossible to draw this type of relationship because of the large relative errors resulting from the measurement of small changes in the values of G' and G''.

The loading of the specimens initiated a process of debonding between the filler and matrix which could be observed without the aid of the microscope, as whitening of the samples. The specimen which was transluscent prior to stressing, became totally opaque at the end of the debonding process. The debonding process was much more pronounced in the case of the filled polyester than in the case of filled epoxy samples.

After load release the whitening of the sample did not disappear completely, thus indicating the presence of residual debonding.

Large residual strains were obtained in exper-

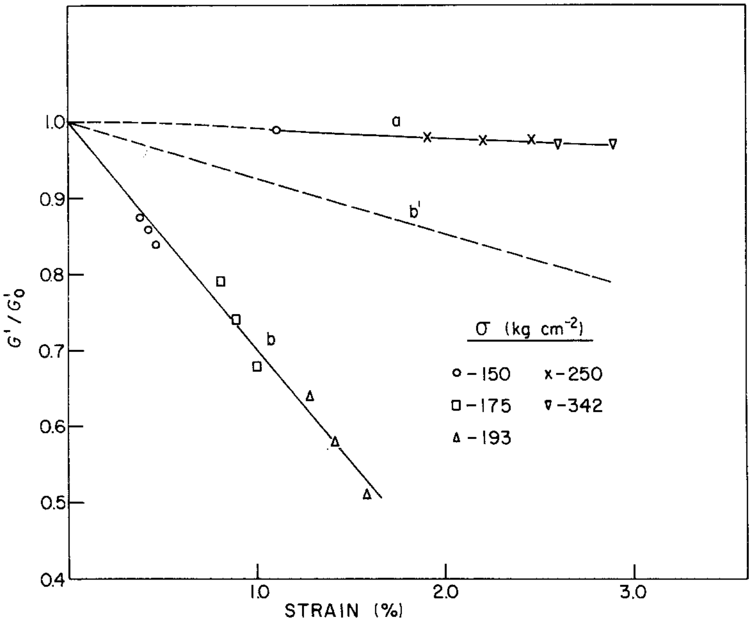


Figure 3 The real shear modulus as a function of axial strain during load action on polyester specimens: curve a, unfilled, curve b, filled and curve b′, filled, after transformation according to Bueche's [3] approach.

iments with filled polyester specimens when compared with residual strains in the unfilled specimens (Fig. 2). This is most probably due to a debonding between the phases in the glass bead filled material, a phenomenon which is only partially reversible as realized after stress release.

The application of load causes an immediate deformation and an increase in strain during the time that load is maintained (creep). Both the immediate strain and the strain rate, while the load is maintained, increase with the magnitude of the applied stress. Until the moment of unloading, the real modulus behaves in a similar way to that of the deformation modulus, yet it has a negative sign: the real modulus decreases while the strain increases. When the load is released an immediate drop occurs in the strain value, followed by a gradual decrease in the strain. No immediate recovery in the real modulus was observed, but only a gradual change took place. Half an hour after unloading, the residual deformation and partially recovered real modulus were measured.

Considering the results in Fig. 1b and Fig. 2b, it appears that the decrease in the real modulus in the filled specimens is mainly due to separation between the phases in the filled material and not to processes occurring in the matrix alone. This is probably true, because even when the highest stress ($342\,\mathrm{kg\,cm^{-2}}$) was applied to the pure matrix, the change in the real modulus was only a minor one (3%), whereas in the experiment performed with a filled specimen even under the smallest stress ($150\,\mathrm{kg\,cm^{-2}}$), the decrease in the real modulus was about 19% while the specimen was much less deformed (0.4% compared to more than 2% in the unfilled specimen). An interesting picture is obtained by replotting the experimental data shown in Figs. 1 and 2 and presenting them as G'/G'_0 against the strain, Fig. 3. Curve b′ is a reconstruction of curve b, based on the G'/G_0 values of the original curve but after transforming the strain values to amplified strains in the matrix, according to Bueche's approach [3]. The amplified strain value in the matrix is calculated by multiplication of the strain in the composite by a factor $1/(1-\phi^{1/3})$, where ϕ is the volume fraction of the filler; in our case this factor was 4.08. The use of Mullins and Tobin [4] strain amplification factor $(1 + 2.5\phi + 14.1\phi^2)$ leads to somewhat higher strain values, due to a higher calculated factor, 4.68, but in order to preserve the clarity of the figure this data was not shown in Fig. 3.

The initial part of curve b from Fig. 3 and a plot of G'/G'_0 against strain during the recovery process after load release, are shown in Fig. 4. The difference between the slopes of the curves is considerable: − 29.4 as compared with − 96.1. This difference can be explained by assuming that while the load is applied, the strain in the specimen results from the deformation of the matrix and from debonding. The deformation of the matrix only causes a small decrease in G'/G'_0 (as may be seen from Fig. 1); the change

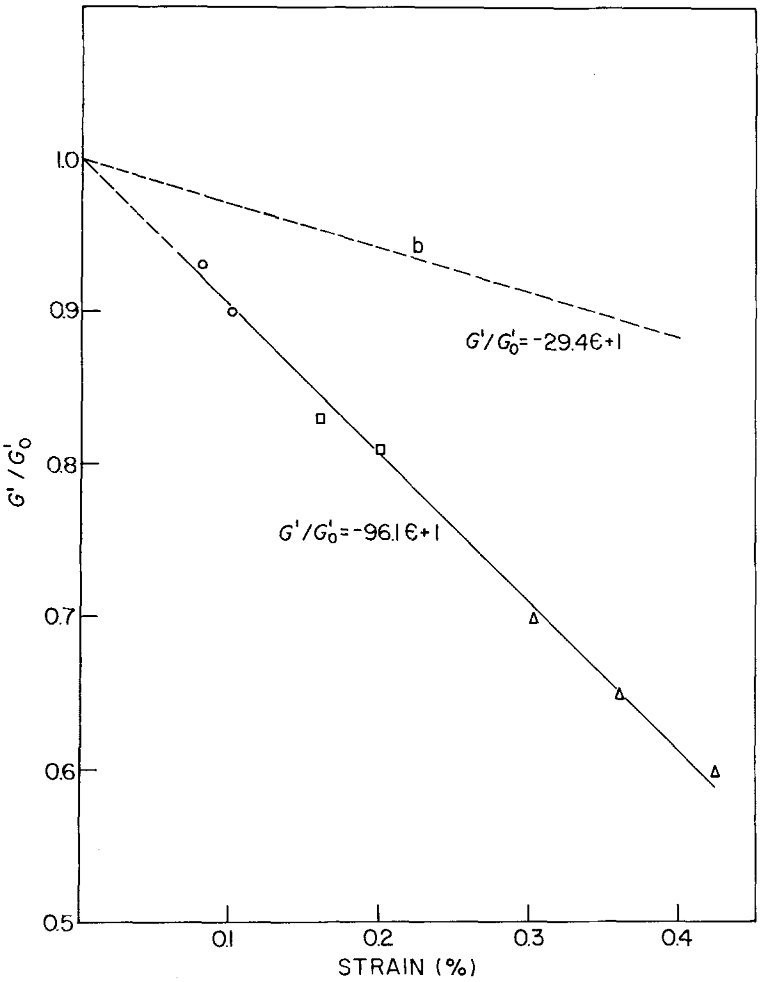


Figure 4 Effect of the residual axial deformation on the real shear modulus of filled polyester specimens after load release (full line) and a section of line b from Fig. 3 (dotted line).

in G'/G'_0 over a large deformation results in the low value slope -29.4. However, after the load release, an immediate decrease in the deformation (mainly due to the fast dimensional recovery of the matrix, Fig. 1) occurs without a significant rise in G'/G'_0. This change is followed by a gradual and slow dimensional recovery, which is assumed to be due to a rewetting process and which has a large effect on G'/G'_0. This process of recovery in G'/G'_0 over a small change in deformation is the reason for the high slope of -96.1 in the recovery of the filled samples.

3.3. Recovery of strain and of real modulus

The similarity between the recoveries of deformation and real modulus (Figs. 2a and b) of the filled polyester specimens, is shown in Fig. 5. In this figure the non-recovered portion of the real modulus was plotted against the residual strain at the end of the experiment and a simple linear relation between the two variables was found, as indicated in the figure. It is interesting to note that for 0.1% of residual strain a 10% change in the original modulus was obtained.

The relation found between the non-recovered real modulus and the residual strain stimulated a study of a possible relation between the time dependent recoveries of the two variables. In order to investigate this possibility it was assumed that both recoveries of the strain and the real modulus behave according to a rheological model which consists of a Voigt–Kelvin element connected in series to a dashpot. The Voigt–Kelvin element represents the time dependent recoveries of both the strain and the real modulus, whereas the dashpot stands for the residual strain and the non-recovered real modulus.

According to the suggested model, the strain $\epsilon(t)$ of a specimen, relaxing from a load which acted on the specimen during a period of time, t_1,

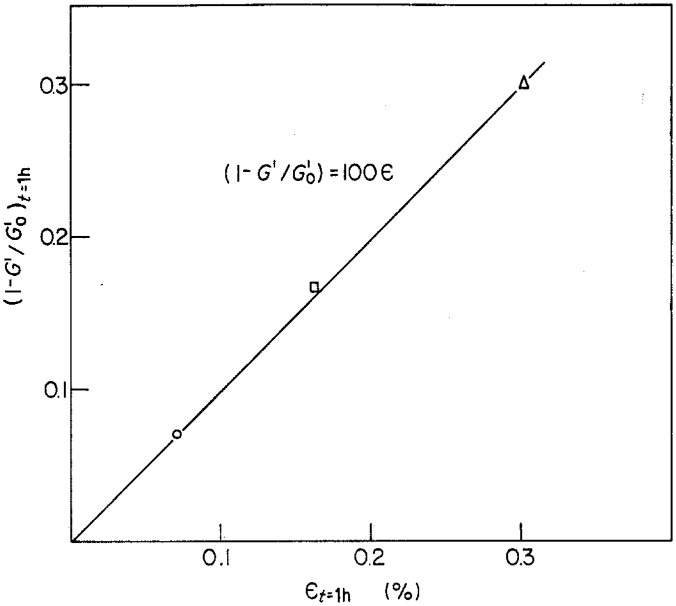


Figure 5 The extent of non-recovery in the real shear modulus of filled polyester specimens as a function of residual axial strain at the end of the experiments.

is given by:

$$\epsilon(t) = \frac{\sigma}{G}\exp\left(-\frac{t}{\tau}\right) + \frac{\sigma t_1}{\eta_r} \tag{1}$$

where σ is the stress, G is the elastic modulus of the spring in the Voigt–Kelvin element, τ is the retardation time of the Voigt–Kelvin element ($\tau = \eta/G$, η being the viscosity of the liquid in the dashpot) and η_r is the viscosity of the liquid in the dashpot connected in series to the Voigt–Kelvin element.

Equation 1 can be rewritten in terms of compliance $J(t)$ in order to avoid the dependence of ϵ on stress:

$$J(t) = \frac{\epsilon(t)}{\sigma} = \frac{1}{G}\exp\left(-\frac{t}{\tau}\right) + \frac{t_1}{\eta_r}. \tag{2}$$

Equation 2 leads to the following relationship:

$$\ln\left[J(t) - \frac{t_1}{\eta_r}\right] = \ln\frac{1}{G} - \frac{t}{\tau}. \tag{3}$$

By using Equation 3 it was possible to determine the constants of the rheological model from the experimental data. The same equation was used to evaluate the constants of the rheological model for the recovery of the real modulus. For this reason the creep compliance $J(t)$ in Equation 3 was replaced by the reduced relative real modulus $(1/\sigma)(G'/G'_0)$.

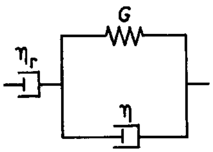
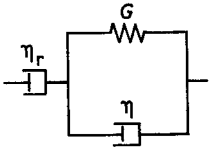
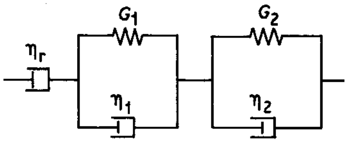
The rheological models and the values of their constants for each stress are shown in Table I for both the creep compliance and the reduced relative real modulus. It was found that in the case of lower stresses (150 and 175 kg cm^{-2}), the suggested rheological model of a Voigt–Kelvin element in series with a dashpot characterizes well the recoveries of both properties, whereas in the case of the highest stress of 193 kg cm^{-2} it was necessary to add another Voigt–Kelvin element in order to describe with more accuracy the recoveries. From Figs. 2a and b it could be expected that the time dependent recoveries of the strain and of the real modulus would be similar and indeed, data in Table I show that the recoveries are alike: they are characterized by the same rheological models with approximately the same time constants. The values of G, η and η_r are lower by approximately two orders of magnitude in the case of creep compliance, due to the difference of two orders of magnitude in the scales of Figs. 2a and b (note: ϵ in Fig. 2b is expressed in % whereas G'/G'_0 is presented as a simple fraction).

3.4. Analysis of dewetting–rewetting phenomena

Takahashi *et al.* [5] developed formulas for the calculation of the elastic modulus of filled polymers as a function of the elastic moduli of the composite constituents and the filler volume fraction. Three cases of matrix–filler interaction were considered: (a) perfect adhesion, (b) free slippage, (c) dewetted zones in the poles of filler particles due to the stretching of the composite material.

The analysis of Takahashi *et al.* [5] was used to determine the extent of dewetting during creep and creep recovery. It was assumed that the

TABLE I Rheological constants of shear modulus and compliance recoveries

	Stress (kg cm^{-2})														
	150				175				193						
															
	η_r	η	G	$\tau = \frac{\eta}{G}$	η_r	η	G	$\tau = \frac{\eta}{G}$	η_r	η_1	G_1	$\tau_1 = \frac{\eta_1}{G_1}$	η_2	G_2	$\tau_2 = \frac{\eta_2}{G_2}$
Real modulus	3.85	0.225	1.49	150	1.85	0.169	1.14	148	1.16	0.166	4.26	38.9	0.388	1.34	290
Creep compliance	360	16.1	144	112	197	16.7	129	130	115	18.7	415	45	35.3	111	317

Units: $\eta = 10^9$ poise, $G = 10^9$ dyne cm^{-2}, τ = sec.

formulas derived originally for Young's modulus hold also for the shear modulus. The authors found it useless to modify the formulas from Young's to shear modulus by the use of the Poisson's ratio because the latter is extremely dependent on dewetting [6]. It should be noted also that the theory of Takahashi *et al.* was developed assuming no filler interaction. In this study, where 43% volume bead content was used, filler particles may interact.

The determination of the extent of dewetting in the material using the theory of Takahashi *et al.* [5] was as follows: in every state the material was assumed (similar to the assumption made by Sato and Furukawa [7]) to consist of a portion of material giving perfect adhesion and of a portion, ϕ_d, in which all the filler particles are debonded from the matrix.

The ratio between the modulus of the composite (G') and the modulus of the matrix (G'_m) in every state is:

$$\frac{G'}{G'_m} = \phi_d B + (1-\phi_d)A \qquad A > 1 > B \quad (4)$$

where A is the moduli ratio G'/G'_m calculated according to the perfect adhesion case and B is the moduli ratio in the debonded state.

Substitution of the elastic moduli of the polyester–glass system ($E_m = 1.81 \times 10^4\ \text{kg cm}^{-2}$, $\nu_m = 0.435$, $E_f = 7.4 \times 10^5\ \text{kg cm}^{-2}$, $\nu_f = 0.22$; E and ν are Young's modulus and Poisson's ratio, respectively; subscripts m and f denote the matrix and filler, respectively) into the formulas of Takahashi *et al.* [5] gave the following values of $A = 1.93$ and $B = 0.467$. Since the initial value of G'/G'_m is 1.774 and not 1.93, it seems, according to the analysis, that a certain portion ($\phi_d = 11\%$) of the material is debonded prior to the application of load. This may be caused by air bubbles entrapped in the filler–matrix interphase during the specimen preparation or to other factors, like humidity, filler surface impurities, etc., which prevent filler–matrix adhesion. The decrease in the real modulus during creep is mainly due to the growth of the debonded fraction, ϕ_d.

It is interesting to investigate the change of ϕ_d with strain while the specimen is under load and after load release. In order to find the correlation between ϕ_d and the strain ϵ, the curve b in Fig. 3 was expressed by the following relationship:

$$\frac{G'}{G'_0} = -29.4\epsilon + 1 \qquad (5)$$

The left side of Equation 4 can be rearranged in the following way:

$$\frac{G'}{G'_m} = \frac{G'}{G'_m}\frac{G'}{G'_0} \simeq \frac{G'_0}{G'_{0m}}\frac{G'}{G'_0} = 1.774\frac{G'}{G'_0}$$

$$= 1.93(1-\phi_d) + 0.467\phi_d$$

$$= 1.93 - 1.463\phi_d \qquad (6)$$

The correlation between ϕ_d and ϵ as derived from Equations 5 and 6 is:

$$\phi_d = 0.107 + 35.7\epsilon \qquad (7)$$

Alternatively, $(1-\phi_d)$, the fraction in which the two phases do perfectly adhere to each other, is expressed by:

$$1 - \phi_d = 0.893 - 35.7\epsilon \qquad (8)$$

The same treatment applied for the recovery process, yields by use of the relation obtained from Fig. 4:

$$\frac{G'}{G'_0} = -96.1\epsilon + 1 \qquad (9)$$

the equation:

$$1 - \phi_d = 0.893 - 117\epsilon. \qquad (10)$$

4. Conclusions

1. It was shown using Bueche's approach [3], that the decrease in the real modulus during the deformation of filled polyester samples is mainly due to an interfacial phenomenon, i.e. debonding (or dewetting).

2. The recoveries of the real modulus and of the creep compliance in filled specimens, after the load release, are both characterized by the same rheological models with approximately the same time constants, τ. As for the other constants, G, η and η_r, these related to the creep compliance recovery were found to be greater by two orders of magnitude than those of the real modulus recovery.

3. Implementing the model suggested by Takahashi *et al.* [5] it is possible to analyse the state of adhesion between the phases in the filled specimens during the load action and after load release. Two correlations describing the relationship between the state of adhesion and strain were found. One relation is appropriate for the state of load action and the other for the recovery process after load release.

References

1. D. KATZ, Y. SMOOHA and A. I. ISAYEV, *J. Mater. Sci.* **15** (1980) 1167.
2. J. M. LIFSHITZ and A. ROTEM, *J. Comp. Mater.* **3** (1969) 412.
3. F. BUECHE, *J. Appl. Polym. Sci.* **4** (1960) 107.
4. L. MULLINS and N. R. TOBIN, *ibid.* **9** (1965) 2993.
5. K. TAKAHASHI, M. IKEDA, K. HARAKAWA and K. TANAKA, *J. Polym. Sci. Phys. Ed.* **16** (1978) 415.
6. T. L. SMITH, *Trans. Soc. Rheol.* **3** (1959) 113.
7. Y. SATO and J. FURUKAWA, *J. Rubber Chem. Tech.* **36** (1963) 1981.

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