Retardation Spectra for the Existence of Interphase in Fiber Composites

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Synopsis

Retardation spectra, derived from dynamic measurements of extension compliances along three decades on the logarithmic scale of frequencies in standard specimens prepared from a fiber-reinforced composite with their fibers parallel to the longitudinal axis of the specimens, have revealed the structure of the matrix material of the composite. The experimental results were used to prove that the physicochemical rearrangements in the vicinity of the inclusions, consisting of restrained development of the macromolecules and especially their side chains due to the presence of the other phase, concentration of voids and dirt, shrinkage stresses developed during curing and creating microcracks (radial as well as along the interface), are activated by the existence of high stress gradients and eventually stress singularities due to the strong adhesion developed between phases.

INTRODUCTION

The first attempt to describe theoretically the mechanical properties of composite materials considered the thin layer around inclusions (fibers or particles) to be reduced to a perfect mathematical surface without any thickness, where stresses and displacements were assumed to be continuous without any kind of irregularity, according to the theory of elasticity.[1] However, substantial discrepancies between the results of carefully executed experiments and the results of this ideal model led to the introduction of the concept of *interphase*, as a separate third phase between the inclusions and the matrix, created during the casting and curing process of the matrix around the inclusions, which was concentrating all the physicochemical irregularities of the matrix material during these processes, as well as any stress gradient and stress singularity, due to the geometry and the quality of the surface of the inclusions and the voids concentrated along their boundaries.[2-4]

The first model introduced considered the interphase as a thin cylindrical layer surrounding any fiber or as a thin, approximately spherical layer surrounding any particle, whose properties depended on the mechanical properties of the constituents of the composite, as well as on the quality of adhesion of the phases.[2,3]

This single-cylinder model was further extended by assuming that the interphase consisted of an infinite number of concentric thin layers (cylinders or spheres) around the inclusion (fiber or particle). By allowing each cylinder progressively different mechanical properties, by changing from those of the inclusion to those of the matrix, a better model was introduced.[5]

Ever since, the concept of interphase was proved to yield satisfactory results, since it was shown experimentally that the mechanical behavior of the composite

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could not merely derive as depending only on the mechanical behavior of its individual constituents. It was necessary to introduce a separate phase.

The nature of this phase could depend mainly on the stress field developed at a thin layer around the inclusion and/or, at the other extreme case, it could extend further into the bulk around the inclusion, as a physicochemical disturbance.

The extent of these two mechanisms is expected to change for different kinds of inclusions and matrices according to the chemical affinity, the nature of the surfaces, the geometry, etc., of the constituents.

Thus, when encountering a composite, the question is raised of what is the nature and the extent of the interlayer region, according to the above discussion.

To answer this question for each particular case, it is necessary to describe the polymeric constituents of the particular composite at the molecular level, so that the actual response of the structure of the composite can reveal the answer. It is well known that the molecular network structure of a polymer determines its mechanical response and inversely mechanical-response experiments have been used extensively to yield information about the network structure of the constituent polymers in a composite.

Dynamic response experiments were judged to be the more suitable for this kind of investigation of the network structure of the composite. In order to avoid as much as possible viscoelastic effects, which may mask somehow the behavior of the model for the study of the network structure of the polymer, we chose to execute our tests very close to the rubbery region of viscoelastic behavior of the matrix material. By measuring the dynamic storage and loss compliances in a convenient experimental arrangement at a range of frequencies extending to three decades in the logarithmic scale of frequency, it was possible to evaluate the retardation spectra of the composite under different types of adhesion between phases. A comparison of retardation spectra for composite and equivalent simple specimens, made of the material of the matrix, showed that the junction motions of the polymeric network in the long-range motion zone are activated due to physicochemical rearrangements in the vicinity of the boundaries of inclusions.

EXPERIMENTAL

In order to study the cause of development of the interphase layer, a series of three types of experiments was executed. All specimens had the same dimensions; they were standard cylindrical tensile specimens convenient for dynamic testing in Dynastat and Dynalizer apparatuses. The dimensions of the specimens are indicated in Figure 1. The first series of specimens contained a central cylindrical core consisting of a steel wire of a diameter $d_c = 0.00008$ m. The lateral surface of the core was smooth and thoroughly cleaned before casting the surrounding matrix. The matrix material was prepared from an epoxy polymer plasticized with 15% of Thiokol LP3 polysulfide. The addition of plasticizer resulted in a reduction of the rubbery-plateau temperature to be attained by the experimental setup.

The second series of specimens were identical with the first, the only exception being that, before casting the matrix, the lateral surfaces of the core bars were

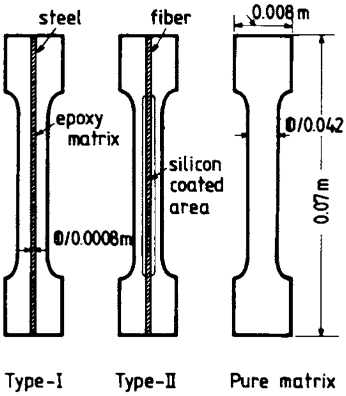

Fig. 1. Types and dimensions of specimens used for the experiments.

covered with a thin silicon layer to hinder any adhesion between inclusion and matrix. The third series were simple cylindrical specimens without core bars, made of the same material as the matrices of the two previous series.

This arrangement was found to be the most effective, since it was not possible to control, otherwise, the quality of bonding in a quantitative way between inclusion and matrix. During the preparation of the specimens care was taken to construct all of them under identical conditions of polymerization (temperature level, consistence of materials, time of degassing, etc.).

After identical procedures of curing, all the specimens were subjected to a sinusoidal mode of loading of a maximum amplitude of 1 N of prescribed and constant maximum amplitude at a temperature of 110°C, applied by Dynastat and Dynalizer apparatuses. The specimens were mounted between a long upper rod of high modulus of elasticity, which was connected in series with a load cell and a shorter lower rod, coupled together with the displacement transducer. By passing a servocontrolled electric current through the coil of the transducer, each specimen was subjected to a sinusoidal load of prescribed amplitude and frequency. The frequency range selected in our tests was varying between $\omega_{\min} = 0.1$ to $\omega_{\max} = 200$ Hz for all specimens.

By raising the temperature of experiments at a convenient level it was possible to activate short-range and long-range motions of network in their transition. This region was previously established[6] to be the transition zone to the rubbery plateau and the rubbery plateau where the bead-spring model was proved to be valid, which predicts a square-root law for the retardation spectra. Then, this region was selected for our tests, in order that the retardation spectra in dynamic behavior obey such a square-root law.

The storage and loss moduli $E'(\omega)$ and $E''(\omega)$ were determined for all three types of specimens along the whole frequency range of the tests. From them the respective instantaneous values of the compliances $D'(\omega)$ and $D''(\omega)$ were evaluated by using simple formulas of dynamic linear viscoelasticity.

Since the contribution of the fiber (core-steel bar) was always elastic, it may be readily eliminated by subtracting its contribution from the moduli of both types of composites. The remaining part will correspond to the viscoelastic part of the composite.

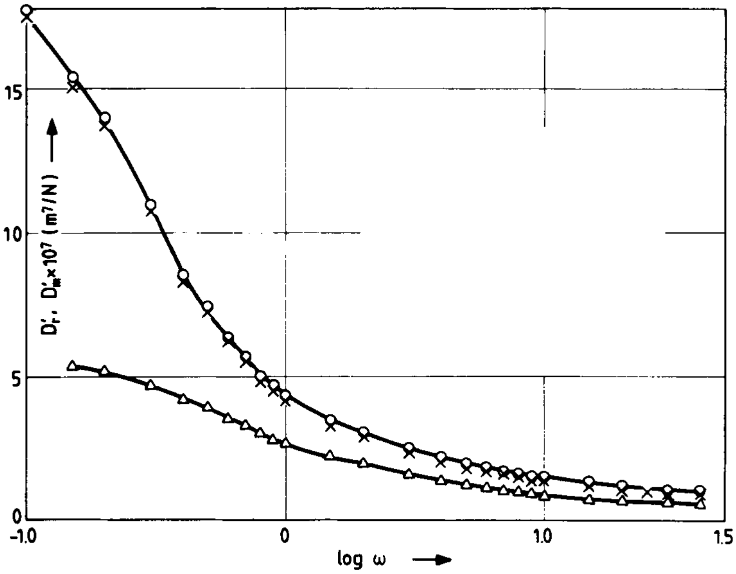

Fig. 2. The variation of the storage compliances D'_m, for type-III specimens (○), and $D'_r(\omega)$ vs. frequency for the remaining phase of the composites of type I (△) and type II (X), when the contribution of the elastic fiber is excluded.

If the contribution of the elastic storage modulus $v_fE'_f$ (or, respectively, the compliance) of the fiber is deducted from the modulus (or compliance) of the composite E'_c the remaining part yields the contribution of the part $v_mE'_m$or $v_mE''_m$ of the matrix material. Here E' and E'' are the storage and loss components of the dynamic modulus (or D', D'' for the respective compliances) and the subscripts f, m, and c correspond to fiber, matrix, and the composite, respectively, whereas v's express the respective volume fractions of each phase.

The effective compliances for each component of the composite were derived by using the well-known relations

$$D'(\omega) = \frac{E'(\omega)}{E'^2(\omega) + E''^2(\omega)} \quad \text{and} \quad D''(\omega) = \frac{E''(\omega)}{E'^2(\omega) + E''^2(\omega)} \tag{1}$$

Figure 2 presents the storage compliance $D'_r(\omega)$ vs. frequency for the remaining phase of the composite, when the contribution of the elastic fiber is excluded. This quantity has been derived by applying relation (1.1). Similarly, Figure 3 presents the respective loss compliance $D''_r(\omega)$ vs. frequency as derived from relation (1.2). In both figures these quantities were plotted for type-I and type-II composites, whereas for type-III specimens the plotted curves correspond simply their storage or loss compliances.

RESULTS AND DISCUSSION

The retardation spectra (first approximations) of a substance in the frequency range ω, in the case when the polymer is assumed as linear viscoelastic, are expressed by[6]

$$L(1/\omega) \simeq -dD'(\omega)/d(\ln \omega) \tag{2}$$

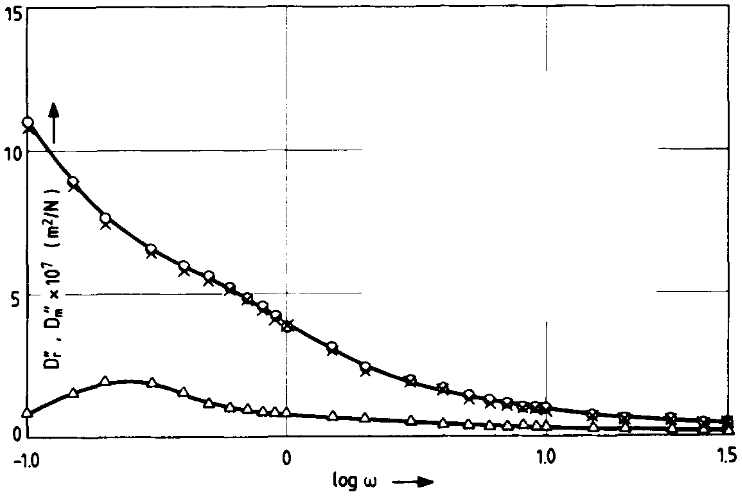

Fig. 3. The variation of the loss compliances D''_m(type III) (O) and $D''_r(\omega)$ type I (△), Type II (X) vs. frequency.

where $L(1/\omega)$ expresses the first approximation of the retardation spectrum and $D'(\omega)$ the storage compliance in extension of the material as function of the frequency ω.

The first approximations of retardation spectra $L(1/\omega)$ for the types I and II of composites and the type III of pure matrix material are plotted vs. frequency in Figure 4.

In order to evaluate the experimental results of Figure 4 a simple bead-spring model, introduced by Gross and Fuoss,[7] was applied, extended to be convenient for dynamic response and modified to take into consideration long-range motions of the junctions of the network.[8]

This model has some slight differences from other theoretical models discussed in Ref. 6. However, a more refined approximation was judged to be not necessary for our purposes, and therefore these refinements were not introduced here.

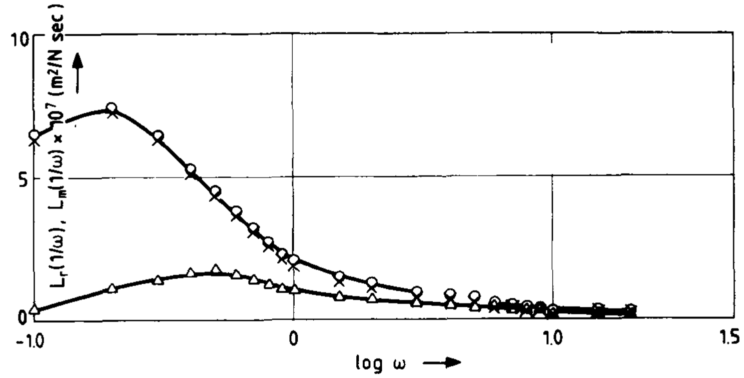

Fig. 4. The retardation spectrum, for the three types of specimens with respect to the logarithm of frequency: (△) $L_r(1/\omega)$ (type I); (X) $L_v(1/\omega)$ (type II); (O) $L_m(1/\omega)$ (matrix polymer).

If ν is the number of macromolecules per unit volume and β an integer expressing the number of macromolecules joined together per each junction point of the network, the retardation time for long-range motions, due to the junction motion, is given by

$$\tau_p = \tau_1 \beta^{2p} \tag{3}$$

where τ_1 expresses the retardation time of the first mode and τ_p the retardation time of the p^{th} mode of vibration.

Then, the retardation time for a single Voight element τ_p is given by

$$\tau_p = \tau_1 / p^2 \tag{4}$$

and the expression for the storage compliance $D'(\omega)$ is given by

$$D'(\omega) = \frac{1}{3\nu kT}\left(\int p^{-2}\frac{1}{1+\omega^2\tau_1 p^{-2}}\,dp + \int \beta^{-p}\frac{1}{1+\omega^2\tau_1\beta^{2p}}\,dp\right) \tag{5}$$

where k and T are Boltzmann's constant and the absolute temperature, respectively.

For low frequencies, $\omega < 1$, the first right-hand term of eq. (5) becomes negligible. Then, from eqs. (2) and (5) we derive

$$L\left(\frac{1}{\omega_p}\right) \simeq \frac{1}{3\nu kT}\frac{\tau_1^{1/2}}{\ln\beta^2}\tau_p^{-1/2} \tag{6}$$

where

$$1/\omega_p = \tau_p = \tau_1\beta^{2p} \tag{7}$$

Introducing the quantity A given by

$$A = \frac{1}{3\nu kT}\frac{\tau_1^{1/2}}{\ln\beta^2} \tag{8}$$

and using Eqs. (6)–(8), we obtain

$$\log L(1/\omega_p) = \log A + \frac{1}{2}\log(\omega_p), \quad \omega_p < 1 \tag{9}$$

For high frequencies with $\omega > 1$ the second term in Eq. (5) becomes negligible and in this case we have from Eqs. (2) and (5) that

$$\mathrm{L}(1/\omega_p) \simeq (1/6\nu kT)\,\tau_1^{-1/2}\tau_p^{1/2} \tag{10}$$

where

$$(1/\omega_p) = \tau_p = \tau_1 p^{-2} \tag{11}$$

Assuming that

$$(1/6\nu kT)\,\tau_1^{-1/2} = B \tag{12}$$

we may derive from Eqs. (9)–(11) that

$$\log L(1/\omega_p) = \log B - \frac{1}{2}\log(\omega_p), \quad \omega_p > 1 \tag{13}$$

Equations (9) and (13) indicate the behavior of the retardation spectra for low ($\omega < 1$) and high ($\omega > 1$) frequencies, respectively.

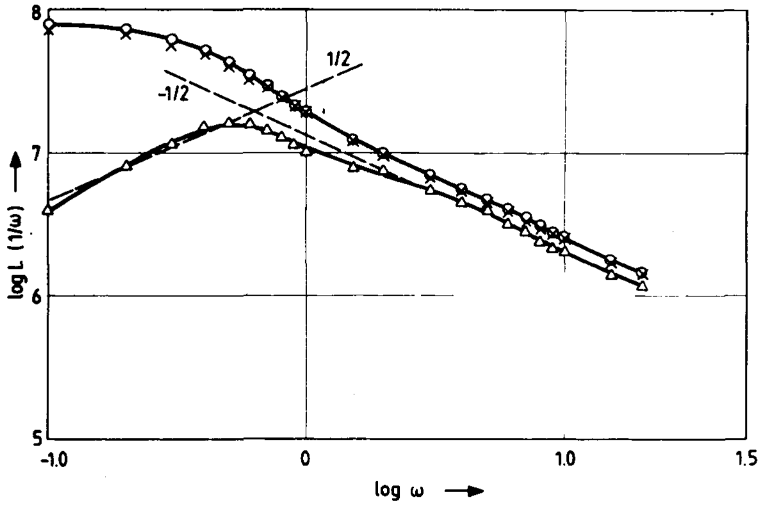

Fig. 5. The logarithm of the retardation spectrum for the three types of specimens vs. the logarithm of frequency: (△) log $L_r(1/\omega)$ (type I); (X) log $L_r(1/\omega)$ (type II); (O) log $L_m(1/\omega)$ (matrix polymer).

The following results may be derived from the spectra plotted in Figure 4.

(i) The retardation spectra of the polymeric phases of type-II composite and the pure matrix specimens are almost identical. This means that the physicochemical characteristics, that is, the degree of crosslinking (ν) and the effect of junction motion, expressed by the parameter β, are identical for both spectra. Hence, the structure of the polymeric phase of the composite as an average does not deviate from the structure expected for the polymer itself.

Moreover, the imposed separation between phases in the type-II specimens has a result to relieve the stresses between phases, and, therefore, in this type of composite, the two constituents do not in principle interact and there are no stress concentrations or singularities due to the interaction of phases. Therefore, a comparison between the type-II composite and the type-III matrix–polymer does not yield a decisive answer, which one of the two contributions is the cause of the development of the interphase.

(ii) The retardation spectrum of type-I composite deviates from that of the matrix–polymer spectrum at the low range of frequencies, whereas it tends to become identical with the other spectra, as the frequency ω is increasing (for $\omega > 1$).

The deviations observed between spectra in low frequencies in Figure 4 are explained in the plots of the spectra of Figure 5, where the quantities log $L(1/\omega)$ vs. log ω were plotted for all three types of specimens in an expanded ordinate scale. It is clear from this figure that the retardation spectra of all specimens have a slope equal to $-\frac{1}{2}$ for frequencies ω larger than unity. This is expected from eq. (13) describing the simple model, which yields the retardation spectrum for the first term of eq. (5) ($\omega > 1$). According to the Gross–Fuoss model,[7] as adapted in this paper, this term, related to high frequencies ω, corresponds to short-range motions of the chains of the macromolecule. But Figure 5 implies that the short-range motions ($\omega > 1$) of the chains and therefore the physicochemical structure of the polymer for all types of specimens are almost identical.

(iii) On the other hand, for $\omega \leq 1$ the first approximation of the retardation spectrum log $L(1/\omega)$ shows a significant difference between the type-I specimens (with good adhesion between phases) and the type-II and -III specimens (poor adhesion or matrix–polymer specimens). Indeed, while the slope of the spectra for types II and III are almost $\frac{1}{2}$ the slopes for the spectra of type I are equal to $-\frac{1}{2}$.

This part of the spectra is approximated by the Eq. (9) which yields a slope for log $L(1/\omega)$ equal to $\frac{1}{2}$. The retardation spectrum of eq. (9) is derived from the second term of eq. (5), which corresponds to low frequencies ($\omega < 1$) and therefore is describing long-range motions of the junction points of the polymeric network. Hence, it can be inferred from the above discussion that in the polymeric phase of type-I specimens only the long-range motions, due to the motion of the network junctions, play a predominant role in this range of frequencies ($\omega < 1$).

(iv) The fact that the contribution of the network-junctions motion is predominant and controls the process only in type-I composites, as compared to the two other types of specimens, may be explained by the following mechanism. The existence of stress concentrations, and in some places stress singularities at the separating surface of the fiber from the matrix, because of a substantial frictional adhesion for this type of composites only, forces the network junctions of the matrix polymer to follow the motions of the fiber and thus to play a significant contribution to the specific values of spectra of the matrix at low frequencies. However, for high frequencies, this effect is diminished progressively and substantially because only short-range motions of chains are significant at this range of frequencies.

CONCLUSIONS

A comparison of the first approximations of retardation spectra for three types of models representing either good or poor adhesion between a unique fiber centered along the axis of the cylindrical polymeric specimens, or pure-matrix polymeric specimens yielded the following conclusions:

(i) Substantial differences were observed in the storage and loss compliances, as they have derived from dynamic tensile tests, between the two types of composite specimens with good and bad adhesion between the unique fiber and the surrounding matrix.

These results support the idea that a third term in the law of mixtures must be assumed which is related to the "good" or "bad" adhesion.

(ii) By calculating the retardation spectra from the dynamic compliances along a rather wide range of variation of frequencies close to the rubbery plateau of the polymers, it was derived that only in the low range of frequencies there exists a substantial difference between the respective spectra. A reasonable explanation of these discrepancies is that only the long-range motion of the polymer network (low frequencies) is affected from the existence of the fiber reinforcement.

(iii) The differences observed between the retardation spectra in storage and loss tensile compliances cannot arise from a different physicochemical structure of the matrix, since matrices in plain polymeric specimens behave identically with their respective counterparts of composites where the adhesion between fiber and matrix is loose. Moreover, if this difference existed, then the discrepancies observed in the low-range of frequencies and therefore in the long-range motion of the polymer network should extend along the whole spectrum of frequencies. But in our experiments the short-range motions, corresponding to high frequencies, are almost identical and independent of the quality of adhesion. Therefore, these differences cannot be attributed to different physicochemical structure of the matrix material as a bulk and the existence of an interphase layer playing the role of a regulator of the junction motions of the polymeric network is the only alternate sound explanation.

Finally, it may be concluded, from the above discussion, that deviations observed in storage and loss compliances, although indicative, are not sufficient to completely explain the mechanism of deformation of the composite. Retardation spectrum analysis is further necessary to reveal the nature of the interphase developed between inclusion and the matrix in each particular composite.

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