On the Dynamic Mechanical Behavior of Poly(ethyl Methacrylate) Reinforced with Kevlar Fibers

J. L. GÓMEZ RIBELLES, J. MAÑÓ SEBASTIÀ, R. MARTÍ SOLER, M. MONLEÓN PRADAS,* A. RIBES GREUS, and J. J. SUAY ANTÓN

Laboratory of Thermodynamics and Physical Chemistry, ETSII, Universidad Politécnica de Valencia, P.O. Box 22012, 46071 Valencia, Spain

SYNOPSIS

The dynamic mechanical relaxation spectra of a series of composites with a matrix of poly(ethyl methacrylate) reinforced with continuous Kevlar fibers present several characteristics that have been proposed in the literature regarding polymer composites as a proof of the existence of an interphase between the polymeric matrix and the filler with mechanical properties different from both: The α-relaxation, associated with the glass transition of the matrix, is shifted in the temperature axis, and a peak appears in the tan δ vs. temperature plot, which was not present either in the matrix or in the fiber relaxation spectra. Nevertheless, a simple block model which does not include the existence of such an interphase is able to reproduce not only the dependence of the loss tangent and storage modulus with the fiber content, but also the shift of the α-relaxation and the presence of the new α' peak in the composites.

INTRODUCTION

The mechanical behavior of polymer composites depends strongly on the adhesion between the polymeric matrix and the filler. The layer of polymer which is in contact with the filler may have mechanical properties different from those of the rest of the matrix because of the interaction with the filler surface via mere mechanical immobilization of the chains, electrostatic forces, or chemical bonds or because of the presence of internal stresses, voids, or microcracks in the interlayer. The properties of the interface may have an important role in determining the mechanical behaviour of the composite.

Dynamic mechanical relaxation spectrum analysis as a technique related to the mobility of the polymer chain segments has been used in studies on composite materials for the characterization of the properties of the interface (Refs. 1–6; Ref. 7, Chap. IV). The α-relaxation of the polymeric matrix associated with its glass transition shows up also in the composites, but shifts in its temperature both towards higher or lower temperatures have been found experimentally.[1,5,8] The usual interpretation of this fact relates this shift to the properties of the interface between filler and matrix, and even to the appearance of qualitatively new behavior: A different mobility of the matrix chain segments forming the interlayer in contact with the filler would lead to the existence of an *interphase* with properties different from the rest of the matrix. Several models have been developed on the basis of a three-phase material which predict the shift of the α-relaxation towards higher or lower temperatures, depending on the values of the modulus of the interphase (Refs. 8 and 9 and literature cited there).

Several composites with Kevlar fiber as reinforcing material exhibit a new relaxation peak at temperatures higher than the α-relaxation, a peak which has been related to the glass transition of a hypothetical interphase consisting of matrix chains aligned at the surface of contact with the fibers as an effect of the polar interaction between the amide groups of the PPTA molecule and the polar groups of the matrix.[2,3]

In this study we analyze the dynamic mechanical behavior of poly(ethyl methacrylate) (PEMA) with continuous poly(p-phenylene terephthalamide) (PPTA) fiber reinforcement in composite bars with several fiber contents. The results are discussed with the aid of the simple two-phase block model which, nevertheless, is able to reproduce the main features of the experimental results.

MATERIALS AND METHODS

The matrix polymer was prepared as follows: monomer from Fluka, previously distilled and with a 0.03% in weight azo-bis-isobutyronitrile as initiator, was bulk polymerized between glass plates at 333 K for 2 h and kept another 24 h at 343 K in order to achieve a complete polymerization. The polymer was then dissolved in tetrahydrofuran, washed in ethanol, and again dissolved in toluene. The solution was poured into a mold where the fibers were kept fixed and arranged in parallel in the form of continuous bundles. After evaporation of the solvent at ambient, the composite samples were cut to sizes adequate to the measuring apparatus and stored in the vacuum oven at 383 K until no further change in their weight was observed.

The source of poly(*para*-phenylene terephthalamide) fibers was commercial Kevlar-49 (DuPont).

A set of samples with different fiber contents was prepared. The fiber volume fraction of each sample was obtained from its fiber weight fraction, and this last magnitude was determined from a thermogravimetric analysis of a representative piece cut from each sample. A DuPont 951 thermogravimetric analyzer was employed for this purpose. The thermogravimetry of the Kelvar fiber, carried out at the rate of 20 K/min in a nitrogen atmosphere, shows that the fiber loses approximately 25% of its weight between 843 and 873 K, and does not present any significant loss of weight below 823 K. By contrast, a sample of PEMA loses 100% of its weight below 773 K. Thus, the weight fraction of PEMA in a composite specimen can be determined through the weight loss of the sample between room temperature and 773 K. The density values accepted for the conversion of weight to volume fractions were 1.20 g/cm^3 for PEMA and 1.45 g/cm^3 for PPTA. The results reported here correspond to samples with fiber volume fractions of 0.03, 0.09, 0.12, 0.18, 0.21, 0.37, and 0.41. Typical values for the dimensions of the samples prepared ranged from 0.12 to 0.23 mm (thickness) and from 5 to 6 mm (width).

The mechanical spectrometry was performed in a Polymer Laboratories dynamic mechanical thermal analyzer, in the "double cantilever" flexure measuring mode, with a sample free length of 1 mm. The quality of the experimental results in the high temperature region demands such small values of the free length because of the small thickness of the composite samples. A maximum strain amplitude of about 3% obtains with this free length. Measuring scans were performed between 298 and 453 K at a heating rate of 1 K/min for frequencies of 0.3, 1, 3, 10, and 30 Hz. In order to minimize the possibility of slippage, the samples were clamped with a sheet of fine grain sandpaper between the faces of the clamp and the sample. A bundle of Kevlar fibers was also tested with this technique; it was kept fixed in the apparatus frame by gluing its ends with epoxy.

The PL-DMTA software converts the measured force/displacement ratio in data of storage and loss moduli through a "geometric constant" of the sample. The value of the storage modulus depends multiplicatively on the value of this factor, but tan δ is independent of it. Because of the very small free length used in this study and, additionally, because of the difficulty of assigning a single well-defined thickness value in samples where this magnitude is not homogeneous, some uncertainty was unavoidable in the calculated values of the geometry factor, uncertainty which, as said, carries over to the absolute magnitude of log E', but not to tan δ.

RESULTS

PEMA presents a mechanical relaxation (called the α-relaxation) in the range of temperatures between 303 and 423 K. The corresponding maximum in the loss tangent, tan δ, appears at 378 K (1 Hz), as shown in Figure 1. This relaxation process is attributed to the cooperative rearrangements of the main chains of the polymer and, thus, it is directly related to the glass transition of the polymer. In addition, as is well known, methacrylate polymers present a secondary relaxation (the β-relaxation) due to the rotation of the carboxile group around its bond with the main chain (Refs. 10 and 11). In the temperature range of the present study the β-relaxation of PEMA does not appear as a maximum of tan $\delta(T)$, but its overlapping with the low temperature side of the α-relaxation is responsible for the high values of tan δ between 303 and 333 K as well as for the smooth drop of E' (the real part of the complex modulus) when the temperature increases, and it explains also the shape of the curve of log $E''(T)$,
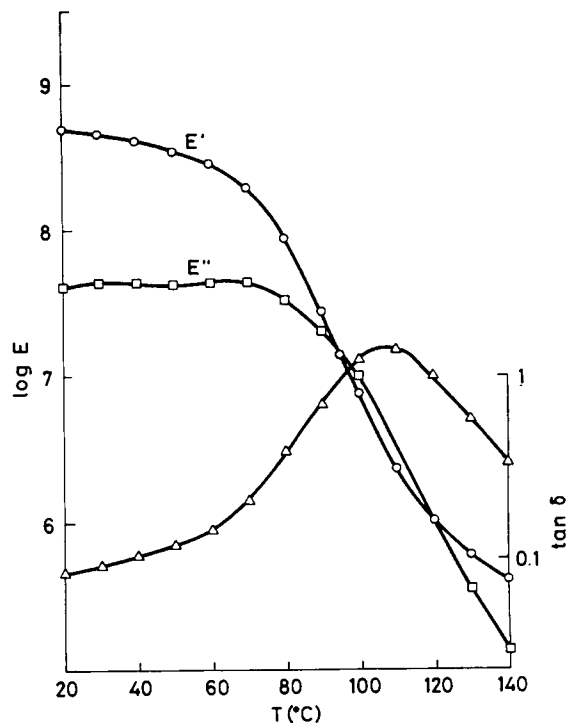
Figure 1 Temperature dependence of the storage and loss moduli and the loss tangent of PEMA for 1 Hz.

where the α peak is less apparent than usual in other amorphous polymers (Fig. 1).

The measurements done on the pure PPTA sample showed a flat course of tan δ in the temperature zone here analyzed, with a value of 0.02. Thus, there is no relaxation of PPTA in this temperature interval (compare also with Ref. 12). For the reasons stated above it was not possible to assert a reliable value for the magnitude of log E', which nevertheless could be seen to be constant in the experimental temperature range. The model calculations introduced in the next section were based on the average value of the published data (e.g., Ref. 13),

$$E' = 1.2 \times 10^{11} \text{ Pa}$$

The effect of the reinforcing fiber on the mechanical relaxation spectrum can be seen in Figure 2 for a composite sample with a volume fraction of fibers of ϕ = 0.41. The value of tan δ at the maximum of the α relaxation decreases, and the temperature of the maximum shifts towards lower temperatures (this shift can be seen better in Fig. 3, where the curves of tan δ as a function of temperature are shown for a series of composites with different fiber content). A new peak, which will be called hereafter α', appears around 408 K (1 Hz). The value of the

storage modulus, E', increases, but is always far below the one of the Kevlar fiber (1.2×10^{11} Pa).

Both the temperature and height of the α maximum depend monotonously on the fiber content (see Figs. 3 and 10), whereas the temperature of the α' maximum is almost independent of the fiber content and its height shows a more irregular behavior (Fig. 11).

The dependence on frequency of both relaxations can be seen in Figure 4 for a composite with an intermediate value of ϕ. When the frequency increases both peaks tend to overlap, what explains the increase of the value of tan δ at the maximum of both relaxations. An Arrhenius diagram (Fig. 5) shows the position of both maxima as a function of the frequency. The slope of this relation is higher for the α' than for the α-relaxation.

DISCUSSION

We focus our attention on three features exhibited by the experimental results which merit discussion: the dependence of the magnitudes of log E' and tan δ on the composition of the samples, the temperature
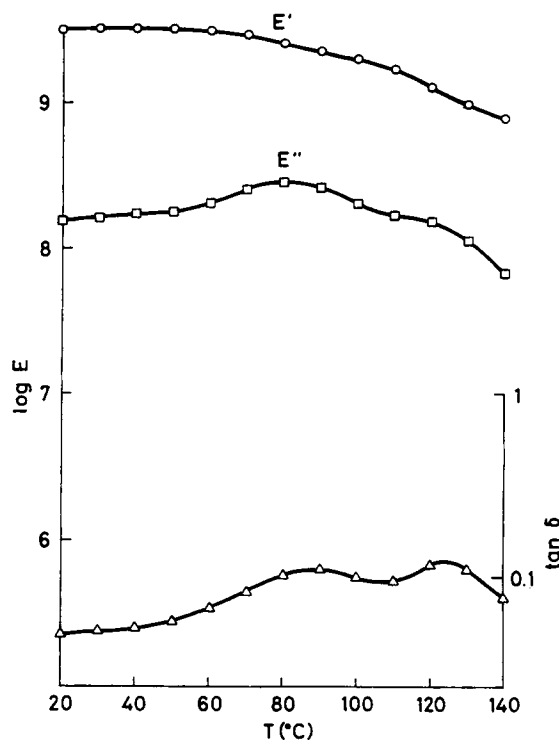
Figure 2 Temperature dependence of the storage and loss moduli and the loss tangent of a PEMA/Kevlar fiber composite with ϕ = 0.41.
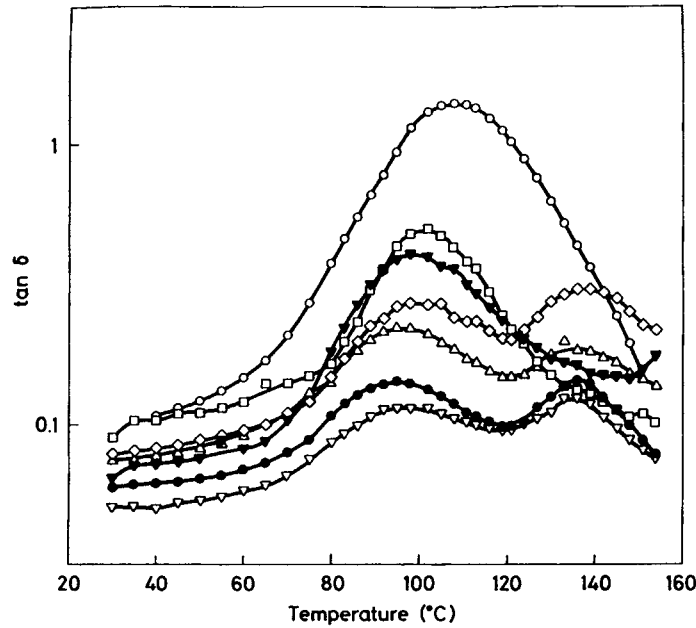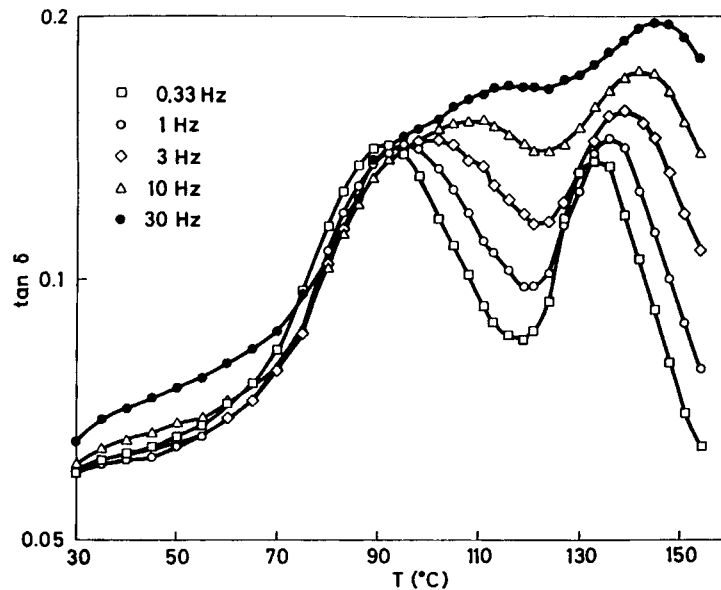
Figure 3 Temperature dependence of the loss tangent of a series of PEMA/Kevlar fiber composites. (O) pure PEMA; fiber fraction ϕ equal to: (□) 0.03; (▼) 0.09; (◇) 0.12; (△) 0.18; (●) 0.21; (▽) 0.41.

shift of the α peak, and the appearance of the new peak, α'.

A common means to relate the properties of a composite to those of its pure components is to compare the experimental results with the behavior predicted by some model body, in which the overall properties are related to the properties of the phases in a known way. This circumstance is met, for example, in the much used block model of Takayanagi.[14] On its basis, the simple *rule of mixtures* can be deduced for a two block parallel arrangement:

$$E_c^* = \phi E_f^* + (1 - \phi)E_m^* \tag{1}$$

Figure 4 Temperature dependence of the loss tangent of a PEMA/Kevlar composite with $\phi = 0.21$ and different frequencies (Hz): (□) 0.33; (O) 1; (◇) 3; (△) 10; (●) 30.
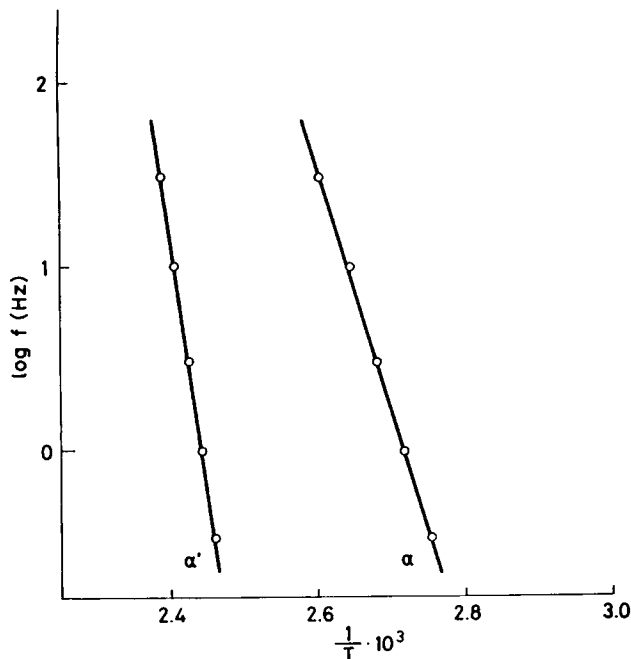
Figure 5 Arrhenius diagram showing the position of the α and α' maxima in a composite with $\phi = 0.21$.

6(c)]. If E_m^*, E_f^*, and E_c^* stand, respectively, for the complex moduli of the matrix, the fiber, and the composite, the equation that governs the behavior of such a triblock arrangement, with ϕ the fiber volume fraction and λ the volume fraction of the matrix in series [i.e., $\lambda(1 - \phi) \equiv \xi$ is the total volume fraction in series], is

$$\frac{1}{E_c^*} = \frac{1 - \xi}{\psi E_f^* + (1 - \psi)E_m^*} + \frac{\xi}{E_m^*} \qquad (2)$$

from which

$$E_c' = \frac{\begin{array}{c}(M'E_m' - M''E_m'')(\xi M' + \bar{\xi}E_m') \\ + (M''E_m' + M'E_m'')(\xi M'' + \bar{\xi}E_m'')\end{array}}{(\xi M' + \bar{\xi}E_m')^2 + (\xi M'' + \bar{\xi}E_m'')^2} \qquad (3)$$

$$\tan \delta_c = \frac{\begin{array}{c}(M''E_m' + M'E_m'')(\xi M' + \bar{\xi}E_m') \\ - (M'E_m' - M''E_m'')(\xi M'' + \bar{\xi}E_m'')\end{array}}{\begin{array}{c}(M'E_m' - M''E_m'')(\xi M' + \bar{\xi}E_m') \\ + (M''E_m' + M'E_m'')(\xi M'' + \bar{\xi}E_m'')\end{array}} \qquad (4)$$

where E_m^*, E_f^*, and E_c^* denote the complex moduli of the matrix, the fiber, and the composite, respectively, and ϕ is the fiber volume fraction in the composite body.

It is very infrequent, nevertheless, that the experimental behavior follows (1). There are several factors which can explain such deviations. Equation (1) is deduced under conditions which demand the same strain of the matrix and fiber in the clamped cross sections of the sample [see Fig. 6(b)]. It is very difficult to have these conditions in actual experimental settings: Usually only the surface of the samples can be clamped, so that the strain is not homogeneous in the cross section [Fig. 6(a)]. This "skin effect" (Ref. 15, p. 401) explains a lower apparent storage modulus and a higher loss tangent. Other factors which can cause the real behavior to deviate from (1) are the misalignment of the fibers in the composite bars (leading to a distribution of unequally loaded fibers), and eventually the lack of perfect adhesion between matrix and reinforcement.

The additional strain actually obtained as a consequence of this "skin effect" can be taken into account in the block model by adding to it a certain amount of material in series; misalignment effects, lack of perfect adhesion, and other possible causes of lessened reinforcement efficiency can be summarized through a "coefficient of efficiency," K, attached to the properties of the reinforcement [Fig.
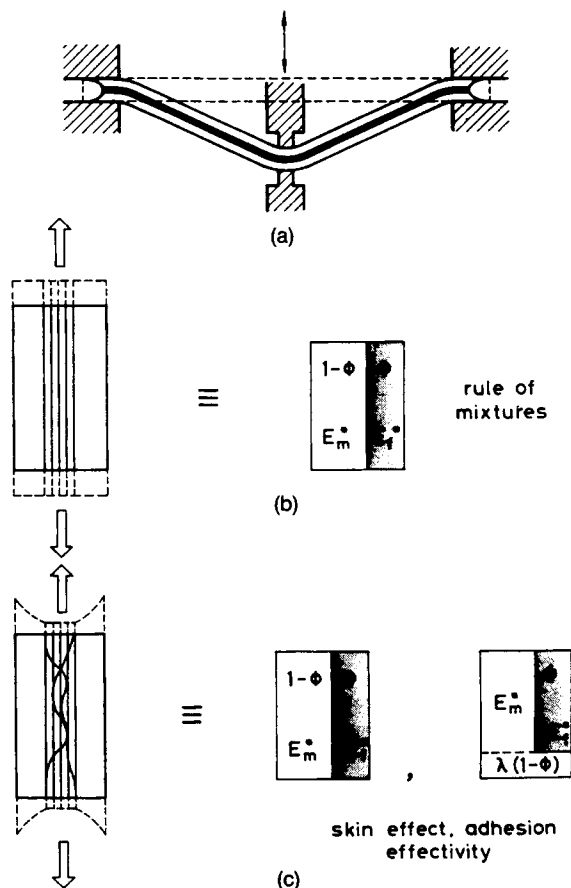

Figure 6 Scheme of block models and the situations intended to be modeled.

where

$$M' = \psi E'_f + \bar{\psi} E'_m, \qquad M'' = \psi E''_f + \bar{\psi} E''_m$$

$$\psi = \frac{\phi}{1 - \xi}, \qquad \xi = \lambda(1 - \phi)$$

and

$$\bar{\xi} = 1 - \xi, \qquad \bar{\psi} = 1 - \psi$$

Here, E'_f and E''_f must be replaced by KE'_f and KE''_f if an efficiency coefficient different from 1 is to be considered. These will be the equations employed in the sequel, whenever it comes to compare the experimental behavior with the model behavior; the computer calculations have been performed introducing in (3) and (4) the experimental values of E^*_m, and the constants

$$E'_f = 1.2 \times 10^{11} \text{ Pa}, \qquad \tan \delta_f = 0.02$$

The displacement of the main peak in the temperature axis with varying reinforcement concentration has been related to the properties of the interface between matrix and filler, and even to the presence of a genuine interphase. An increase in the temperature of the relaxation is attributed to segmental immobilization of matrix chains at the filler's surface, and is thus indicative of good adhesion (e.g., Ref. 1). Reciprocally, a shift of the main peak towards lower temperatures is thought of as an indication of bad adhesion. The same conclusions are reached on the basis of a three-phase model, including an interphase besides the two phases of matrix and filler[8]: strong bonds between matrix and filler increase T_g, whereas weak bonds tend to decrease T_g.

It is interesting to remark, however, that this feature can also be explained without recourse to molecular considerations, as a macroscopical thermomechanical gross effect of the presence of a nonrelaxing phase (the filler) alongside a relaxing phase (the matrix).

Consider, for example, the situation corresponding to eq. (2) with $\lambda = 0$ [that is, the case leading to eq. (1)]. From the general relationship

$$\tan \delta = E''/E'$$

it follows that

$$\log \tan \delta = \log E'' - \log E'$$

so that if $T_{\max}$ denotes the temperature at which $\tan \delta$ attains a maximum,

$$\frac{d \log E''}{dT}(T_{\max}) = \frac{d \log E'}{dT}(T_{\max}) \qquad (5)$$

Now, assuming (1) to apply, and E^*_f to be a constant function of temperature in the range of temperatures considered, it follows from (1) that

$$\frac{d \log E'_c}{dT} = \frac{(1 - \phi) E'_m}{E'_c} \frac{d \log E'_m}{dT} \qquad (6)$$

$$\frac{d \log E''_c}{dT} = \frac{(1 - \phi) E''_m}{E''_c} \frac{d \log E''_m}{dT} \qquad (7)$$

so that

$$\frac{d \log \tan \delta_c}{dT} = \frac{(1 - \phi) E''_m}{E''_c} \cdot \frac{d \log E''_m}{dT}$$
$$- \frac{(1 - \phi) E'_m}{E'_c} \cdot \frac{d \log E'_m}{dT} \qquad (8)$$

When this last relationship is applied for the temperature $T_{\max,m}$ where $\tan \delta_m$ of the matrix reaches a maximum and (5) is taken into account, it follows that

$$\frac{d \log \tan \delta_c}{dT} = (1 - \phi) \frac{d \log E'_m}{dT} \left(\frac{E''_m}{E''_c} - \frac{E'_m}{E'_c} \right)$$
$$= \frac{(1 - \phi) E'_m}{E'_c} \frac{d \log E'_m}{dT}$$
$$\times \left(\frac{\tan \delta_m}{\tan \delta_c} - 1 \right) \qquad (9)$$

In this equation the argument of all functions is $T_{\max,m}$, which has been omitted for simplicity. Now, whenever

$$\tan \delta_m(T_{\max,m}) > \tan \delta_c(T_{\max,m})$$

which will be the situation if the filler is more rigid than the matrix, all factors in the right member of (9) are positive numbers, except the term

$$\frac{d \log E'_m}{dT}$$

which is negative. Thus

$$\frac{d \log \tan \delta_c}{dT}(T_{\max,m}) < 0$$

from which it follows that

$$\frac{d\tan\delta_c}{dT}\,(T_{max,m}) < 0$$

This means that at $T_{max,m}$ tan δ_c has already gone through its maximum, that is,

$$T_{max,c} < T_{max,m}$$

A computer simulation confirms this fact: Figure 7 shows the shift towards lower temperatures predicted by the model [eq. (4) with $\lambda = 0$] when ϕ increases.

The shift towards higher temperatures of the maximum of the α peak can also be got from the model as a consequence of the presence of certain material in series ($\lambda \neq 0$) (Fig. 8). Thus, shifts in the temperature of the relaxations with varying amounts of filler phase can in principle be explained merely as gross effects of the presence of a nonrelaxing phase, bearing no clear direct relation to the properties of the interface between matrix and filler, not to say to those of a hypothetical interphase.

The appearance of a new peak, not present either in the pure matrix or in the fiber polymer, seems to be indicative of qualitatively new properties of the material, attributable in principle of the formation of an interphase. So it has been done by Kodama and Karino.[2,3] These authors have found the appearance of a new α' peak in dynamic mechanical spectra of composite systems with Kevlar-49 as reinforcing fiber and various matrices having polar groups, poly(methyl methacrylate) among them. From data of Fourier transform spectroscopy they conclude a polar interaction between the amide group of Kevlar and the carbonyl group of PMMA, probably due to the formation of hydrogen bonds. The new peak would thus correspond to the relaxation behavior of a new phase, the interphase, formed by a certain amount of the matrix in the neighborhood of the fiber surfaces, with motions of the chains more impeded because of these additional interactions. Other researchers have also found modifications of other matrices in the vicinity of Kevlar fibers that can be interpreted as interphases.[16,4] Poly(ethyl methacrylate) is in no way different from PMMA in this respect, and so the new α' peak found in the present work should be interpreted as the main relaxation of the matrix crust around the fibers. The value of the apparent activation energy of the α' peak found by us, greater than that of the α-relaxation, would be in line with this hypothesis.

There is, however, an alternative explanation. Figure 9 shows the behavior predicted by the model,
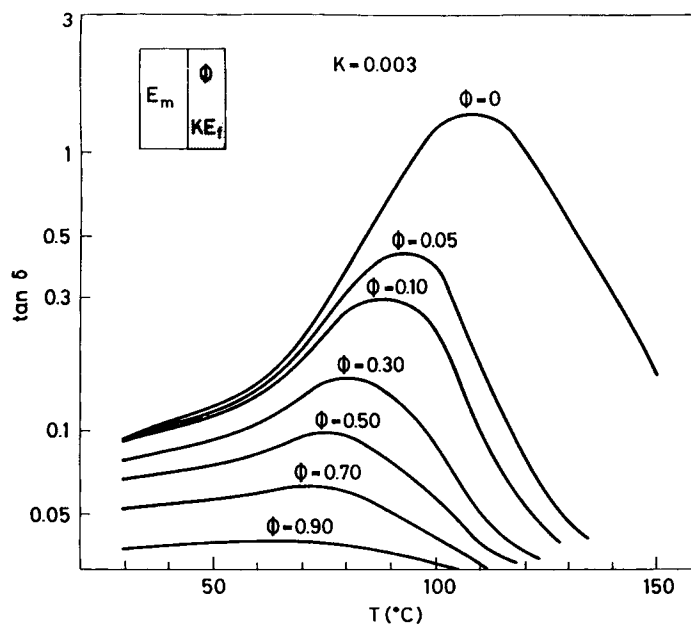
Figure 7 Temperature dependence of the loss tangent for different fiber contents (shown on the graph) predicted by the block model depicted in the figure [eq. (2) with $K = 0.003$ and $\lambda = 0$]. The shift of the α maximum towards lower temperatures is predicted by this model.
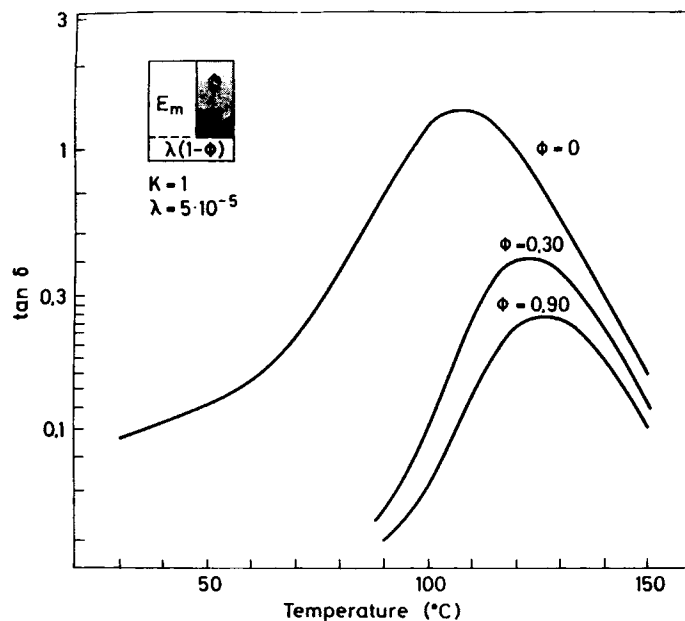
Figure 8 The same as in Figure 7, this time with $K = 1$ and $\lambda = 5 \times 10^{-5}$, and the fiber contents shown on the graph. A shift of the α maximum towards higher temperatures is predicted.

eq. (4), when certain pairs $K \neq 1$ and $\lambda \neq 0$ are considered: There appears the α' peak! If the three-block model of Figure 6 is an adequate description of the experimental setting, then the appearance of

the new peak is a necessary feature of the thermo-mechanical behavior of the *two*-phase system: again, as happened with the shift in temperature of the α peak, a gross effect with no connection with inter-
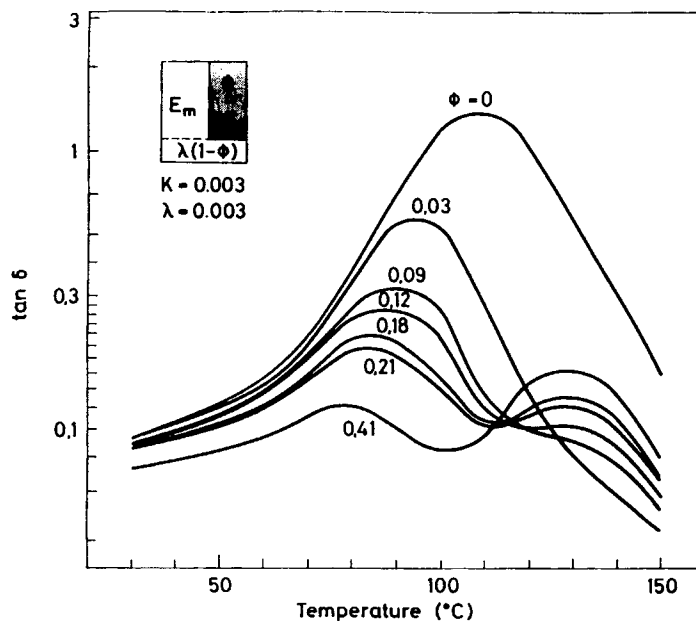
Figure 9 Computer simulation corresponding to the triblock model, eq. (2), of the tan $\delta(T)$ curves of a series of composites with the same fiber content as the experimental samples, and $\lambda = 0.003$, $K = 0.003$. This figure is to be compared with the experimental results shown in Figure 2.
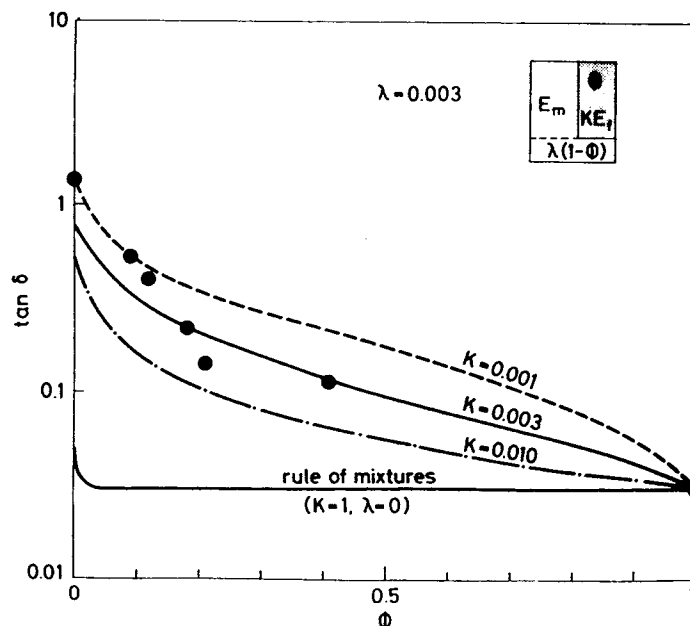
Figure 10 Maximum intensity of tan δ in the α peak as a function of the fiber volume fraction: experimental results ($\bullet$) and computer predictions with $\lambda = 0.003$ kept fixed and different values of K.

phases. The model is able to pick up qualitatively the following features of the behavior observed experimentally: the decrease in the intensity of the α-relaxation and its shift towards lower temperatures when ϕ increases; the appearance of the new peak at higher temperatures; the constancy of the temperature of this peak with varying fiber volume fractions ϕ. From a quantitative point of view, the shift

in T_α predicted seems to be somewhat greater than that observed; the position of the α' peak deviates some 4 or 5° from the one observed; as for the intensity of the α-relaxation, Figure 10 shows the good agreement which can be achieved between experimental results and the model predictions; the fit of the intensity of the α' peak is not as good, but still reasonable (Fig. 11). Finally, Figure 12 presents the
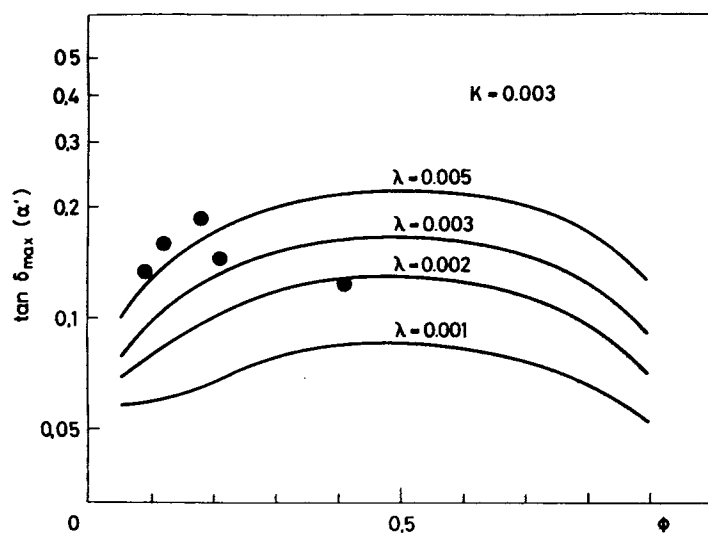
Figure 11 As in Figure 10, but for the α' peak.
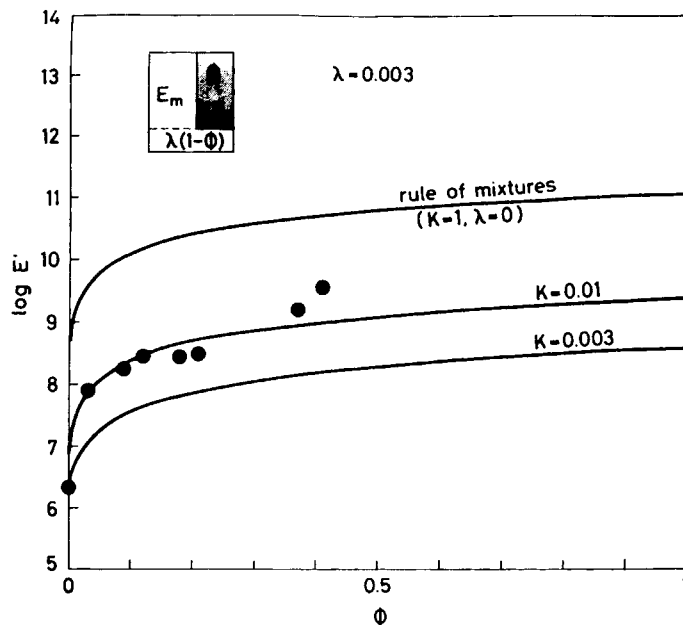
Figure 12 Storage modulus at 413 K (1 Hz) as a function of the fiber volume fraction. Experimental results (●) and values predicted by the model with the parameters shown on the figure.

dependence of the isothermal storage modulus on the fiber content. The values of the parameters K and λ which seem to fit well the loss factor give here a lower prediction. Nevertheless, the following caution must be borne in mind when referring to data of the storage modulus: In dynamic mechanical measurements their absolute value is not as reliable as that of tan δ because they depend upon the value of the geometric factor of the sample, which is subject to the errors commented in a preceding section, and which do not affect the value of tan δ.

The hypothesis just presented is supported further by results of ours on PMMA/Kevlar composites[17]: with samples prepared in exactly the same way as the ones for the present work the model (2) is able to reproduce the observed behavior with the same values of the parameters K and λ as here. In this case, however, eq. (4) does not predict the appearance of the new α' peak, which is precisely what happens actually: There is no second peak for this type of samples. In the case of PMMA/PPTA the model predicts the appearance of a second peak for much higher values of λ. This would correspond to samples with a more important "skin effect." Now, this is what can be expected for samples made with *short cut* instead of *continuous and aligned* fiber. If this were so, it would explain why the second peak

appears in Refs. 2 and 3, but does not appear in Ref. 17.

CONCLUSIONS

The dynamic mechanical spectrum of the composite system PEMA(matrix)/Kevlar (fiber) exhibits certain challenging features: namely, the shift in temperature of the main relaxation of the matrix, and the appearance of a new peak. According to the literature, they can be explained as effects arising from specific interactions in the interface matrix/fiber. Conflicting with this view there is an alternative explanation, which can deliver the features mentioned as consequences of the overall behavior in a two-phase system, whose phases have viscoelastic transitions in separate temperature intervals. A similar argument was employed in Ref. 18, where the author warned against the interpretation of certain peaks obtained with the torsion braid technique as molecular transitions. Thus it seems that the interpretation of dynamic mechanical spectra must be done with special care whenever the material is not uniform and homogeneous, and that, in any case, a single experimental technique cannot settle these and related questions.

REFERENCES

1. K. Iisaka and K. Shibayama, *J. Appl. Polym. Sci.*, **22**, 1321–1330 (1978).
2. M. Kodama and I. Karino, *J. Appl. Polym. Sci.*, **32**, 5057–5069 (1986).
3. M. Kodama and I. Karino, *J. Appl. Polym. Sci.*, **32**, 5345–5355 (1986).
4. F. Kumamaru, T. Oono, T. Kajiyama, and M. Takayanagi, *Polym. Compos.*, **4**, 141–148 (1983).
5. S. A. Paipetis, *Colloid Polym. Sci.*, **258**, 42–50 (1980).
6. P. Theocaris, G. Spathis, and B. Kefalas, *Colloid Polym. Sci.*, **260**, 837–841 (1982).
7. T. Murayama, *Dynamic Mechanical Analysis of Polymeric Materials*, Elsevier, Amsterdam, 1978.
8. P. Theocaris and G. Spathis, *J. Appl. Polym. Sci.*, **27**, 3019–3025 (1982).
9. P. Theocaris and G. Papanicolau, *Colloid Polym. Sci.*, **258**, 1044–1055 (1980).
10. J. Heijboer, *Ann. N.Y. Acad. Sci.*, **279**, 104–116 (1976).
11. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymers*, Wiley, New York, 1967.
12. T. Kunugi, H. Watanabe, and M. Hashimoto, *J. Appl. Polym. Sci.*, **24**, 1039–1051 (1979).
13. M. Takayanagi, T. Kajiyama, and T. Katayose, *J. Appl. Polym. Sci.*, **27**, 3903–3917 (1982).
14. M. Takayanagi, *Mem. Fac. Eng. Kyushu Univ.* **XXIII**(1), 41–96 (1963).
15. L. Nielsen, *Mechanical Properties of Polymers and Composites*, Dekker New York, 1974, Vol. 2.
16. F. Kumamaru, T. Oono, T. Kajiyama, K. Suehiro, and M. Takayanagi, *Polym. Compos.*, **4**, 135–140 (1983).
17. R. Díaz Calleja, J. L. Gómez Ribelles, M. Monleón Pradas, A. Ribes Greus, and F. Romero Colomer, to appear in *Polymer Composites*.
18. L. E. Nielsen, *Polym. Eng. Sci.*, **17**, 713–714 (1977).