

Reinforcement of EPDM Matrices with Carbon and Polyester Fibers—Mechanical and Dynamic Properties

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Synopsis

This paper reports on the study of the mechanical and dynamic properties of composites with an EPDM matrix and short fiber, either polyester or carbon, at three different fiber concentrations. In general, the properties prove to be dependent on fiber concentrations and type, in particular on the final ratio fiber length/diameter. This ratio ranges for carbon fiber over 35–45 and for polyester over 135–175, thus placing the former near the lower limit of acceptability. Evidence is supplied of the existence of adhesion between the matrix and the fiber, in the form of measurements of the swelling and dynamic properties, especially through variation of relative damping and the displacement of the dynamic glass transition temperature towards higher ranges. Composites present a marked property anisotropy.

INTRODUCTION

The reinforcement of elastomers with short or discontinuous fibers combines the rigidity of the fiber with the elasticity of rubber, the resulting composites being of great interest in many applications. They present the additional benefit that the fiber is incorporated as one of the ingredients of the recipe, with the sole caveat that during the mixing process the direction of cylinder rotation is to be maintained in order to achieve maximum uniformity of fiber orientation in the matrix.

Several authors^{1–3} agree in pointing out three factors to be taken into account, in order to achieve adequate reinforcement, although it can never attain the levels reached with continuous fibers. These factors are the following: preservation of highly uniform fiber orientation in the matrix, preservation of an appropriate length/diameter ratio, and establishment of the strongest possible bond between the fiber and the matrix.

Although the length/diameter ratio can be measured directly, none of the other factors can be assessed by direct methods. Hence indirect methods must be relied upon, among which green strength measurements⁴ should be mentioned as an aid to determine fiber orientation, swelling measurements⁵ providing data about fiber orientation and the adhesion of both phases, as well as viscoelastic property measurements, likewise suited for interface evaluation in composites.

Many diverse systems have been studied⁶ with the aim of increasing fiber adhesion to the matrix while maintaining the length/diameter ratio as one of the main factors in reinforcement. The most widely used among these systems is the dry three components procedure—silica, phenol, and formaldehyde—

apart from the immersion method, in which the fiber is impregnated with RFL. Due to the greater ease in composite preparation, in this research the dry system was opted for as the method of choice.

In previous research,⁷ this adhesive system had been used in a modified version in the following way: the silica was replaced by the filler itself (natural magnesium silicate) which has the same or higher surface activity as silica, with satisfactory adhesion and other properties. The properties of short fiber composites depend both on fiber type and matrix configuration,⁸⁻¹⁰ as was demonstrated in previous research.^{11,12}

This research follows the general lines of previous work: composites with an elastomeric matrix, in this case ethylene-propylene-diene rubber filled with a semireinforcing mineral and strengthened with short fibers. The purpose of reinforcing with short fibers was to achieve a high level of properties starting from a base material with medium properties. Two fiber types were chosen, carbon and polyester, and an adhesive system consisting of the filler itself and phenol-formaldehyde.

Carbon fibers suffer a drastic rupture during material preparation,¹¹ which allows for the assumption that, even if there exists adhesion between both phases, the properties obtained will not be enhanced, as is the case with polyester fiber which undergoes a degradation which cooperates in the preservation of a good length/diameter ratio.

Special attention was given to the dynamic properties of composite as a means to determine matrix-fiber interaction.

EXPERIMENTAL

All composites were obtained by means of a laboratory two-roll mill (12-in. length, friction rate 1:1.14). The fiber was added as supplied, without treatment, at the end of the compounding process.

It can be assumed¹³ that all possible fiber orientation is achieved during the first mill pass, making additional passes almost unnecessary. It should be mentioned that milled samples were rolled along the mill direction before each pass and then sent through the mill.

The carbon fiber used, Sigrafil C, was supplied by Sigrí Elektrographit GmbH with density 1.75, length 6 mm, and diameter 7 μm . The polyester fiber, poly(ethylene terephthalate) (PET), was supplied by Velutex Floc SA with the respective characteristics of density 1.38, length 5 mm, and diameter 18 μm .

The curing properties were measured on an oscillating disk rheometer, Monsanto Model 750, at a vulcanization temperature of 150°C, 1° arc, 100 cpm.

Green strength was determined using rectangular samples with the approximate dimensions of 25 \times 150 \times 2 mm on an Instron Model 1026 at a stretching rate of 500%/min. The samples are precured on a vulcanization press at 120°C for 2 min.⁴

The longitudinal swelling values are determined after a 24 h immersion period in *n*-heptane at 30°C.

The physical properties are established according to national standards (UNE). Tear strength was measured on a Delft-type sample.

TABLE I
Recipes and Curing Properties

	1	2	3	4	5	6	7
EPDM 6463				100			
ZnO				5			
Stearic acid				1.25			
Filler, magnesium silicate				65			
Tri(ethanol amine)				3.25			
Accelerant				3			
Sulphur				1.5			
Resorcine	—	2.5	2.5	2.5	2.5	2.5	2.5
Cohedur A ^a	—	2.5	2.5	2.5	2.5	2.5	2.5
Carbon fiber	—	17.58	26.4	35.16	—	—	—
PET fiber	—	—	—	—	13.8	20.7	27.6
Monsanto rheometer, 150°C, 1° arc, 100 cpm							
Couple max (dN m)	49	46.8	51.8	57	59	59	66.5
Couple min (dN m)	22	16.9	19	23	18.5	19	24.7
ΔT	27	29.9	32.8	34	40.5	40	41.9
t_{90} (min)	35	55	56	60	40.5	40	42

^a Formaldehyde donor supplied by Bayer.

The dynamic properties, the storage and loss moduli as well as the loss factor, $\tan \delta$, were determined on a parallelepipedic sample of dimensions of approximately $16 \times 4 \times 16$ mm on a Metravib viscoanalyzer, varying deformation amplitude, frequency, and temperature.

The recipe used is indicated in Table I. These different fiber portions were tested corresponding to 10, 15, and 20 volumes per 100 parts in weight of rubber.

RESULTS AND DISCUSSION

Vulcanization

Table I compiles, apart from the experimental recipes, the results obtained from curing. In general terms, longer vulcanization times (t_{90}) are observed for composites as compared to the fiber-free control, as a consequence of the addition of the adhesive system which favors the creation of fiber-matrix bonds. Along the same lines, the greater couple increments (ΔT) have to be pointed out, indicative of a higher network density. This latter fact is exclusively attributable to the increase in matrix-fiber bonds, which can be computed in terms of network density.

Green Strength

Green strength measurements provide information about fiber orientation in the matrix. The extent of this orientation can be determined by comparison of physical properties in the intended orientation (L) and in the perpendicular (T) direction. From the differences between the green strength in the L and T directions, expressed as ratios of improvement over the unreinforced control, the extent of orientation can be estimated.⁴ To this purpose and in conformity

TABLE II
Green Strength and Fiber Orientation

Fiber dir.	Fiber volume			
	0	10	15	20
Carbon				
L		11.26	17.06	22.8
Green strength (kg/cm ²)	7.4			
T		5.15	7.00	8.82
Orientation (%)		68.8	70.9	72.1
Polyester				
L		13.1	16.8	20
Green strength (kg/cm ²)	7.4			
T		6.5	7.62	13.5
Orientation (%)		66.8	68.8	59.7

with the experimental conditions, green strength was measured longitudinally (L) to flow direction as well as transversally (T). The data obtained, together with the inferred data related to fiber orientation, are listed in Table II.

For both composites longitudinal green strength is greater than the control and increases proportionate to the fiber level, and is better than that obtained transversally. In principle, the anisotropy conferred by the fiber is at stake here.

At equal fiber volume, the longitudinal green strength values of both composites are very similar, as well as theoretical fiber orientation.

The smaller size of carbon fibers facilitates fiber orientation, even at high fiber concentrations, which does not occur with PET, which at higher concentrations seems to have increasing orientation difficulties.

Swelling

Swelling data provide information about fiber orientation and fiber-matrix adhesion, in the sense that the lower the longitudinal swelling ratio, the greater the adhesion coefficient, as the fiber constrains solvent-induced swelling. The greater the slope of the straight line obtained when plotting α_θ^2 against $\sin^2 \theta$ (where θ is the measurement angle with regard to the flow direction of the mix), the greater the degree of fiber orientation. Table III lists

TABLE III
Swelling Ratio and Swelling Variation Slopes with Measurement Angle

Fiber vol	α_L^a		Slope	
	Carbon	PET	Carbon	PET
10	1.059	1.06	0.203	0.197
15	1.03	1.02	0.250	0.183
20	1.023	1.00	0.268	0.163

^a α_L of the matrix = 1.48.

TABLE IV
Mechanical Properties of Composites

Properties	Fiber content						
	0	10		15		20	
		C	PET	C	PET	C	PET
Shore A hard	70.4	85	79.7	90	83.8	93.4	86
<i>a) Longitudinal measurements</i>							
Stress (MPa) at strain of							
10%	0.52	2.31	2.6	2.84	5.34	4.08	5.67
20%	0.91	3.41	3.76	4.52	6.63	5.05	6.88
50%	1.51	4.04	4.44	4.60	7.17	5.42	7.56
100%	2.23	4.89	5.42	5.25	7.33	5.70	8.07
Tensile strength (MPa)	6.57	7.29	7.6	7.01	8.28	7.29	8.1
Elongation (%)	574	228	193.7	205	227	197	122
Tear strength (N)	29.7	51.3	61.34	53.1	70	58.7	83.7
<i>b) Transversal measurements</i>							
Stress (MPa) at strain of							
10%	—	0.86	1.53	1.01	1.22	1.04	1.65
20%	—	1.65	2.45	1.83	2.49	1.86	2.72
50%	—	2.60	3.26	2.63	3.73	2.81	3.52
100%	—	3.6	4.22	3.58	5.03	3.54	4.32
Tensile strength (MPa)	—	6.41	7.66	5.77	6.31	5.36	6.98
Elongation (%)	—	276	254	211	195	201	233
Tear strength (N)	—	41.7	54	36.5	45.9	35.8	47.3

the values obtained from the longitudinal swelling ratios measured and the respective slopes.

The swelling ratio, for the same fiber type, diminishes inversely to fiber concentration. In any case, it is far below the value obtained for the fiber-free matrix, which evidences the existence of strong bonds between the two phases, with values coming close to unity or total restriction. The slopes show the same trend for each fiber type as that observed when measuring green strength for fiber orientation determination.

Mechanical Properties

Table IV indicates the data obtained from mechanical property measurements in both directions: longitudinally and transversally.

Regarding Shore A hardness, the greater stiffness of carbon fibers as compared to PET is clearly reflected in the table: at any fiber concentration carbon fiber composites (EPDM-C) prove to possess the greater hardness.

As was to be expected, a substantial increase in stress at constant strain is produced, in particular in the lower deformation range, with increments proportionate to fiber content. Tensile strength is likewise increased, although less spectacularly. Tear strength, however shows a remarkable increase, whereas elongation at break diminishes.

All these modifications of mechanical properties, which are common to both fiber types and which increase with greater fiber portions, are more marked in polyester-reinforced composites (EPDM-PET), due to the fact that PET

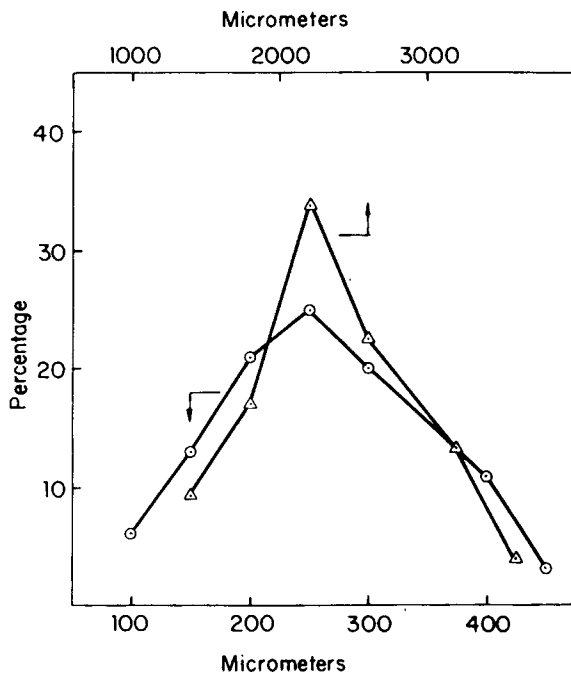


Fig. 1. Distribution of fiber lengths after processing: (\odot) carbon fiber; (Δ) polyester fiber.

fibers after mixing maintain the minimally necessary length/diameter ratio, which is not the case with carbon fibers.

Figure 1 represents fiber size distribution in the composite after mixing. Taking into account the original dimensions of fibers used, carbon fiber yields an L/D ratio in the range 30–45 (length 200–300 μm). It is further considered that for successful reinforcement the L/D coefficient should fall between 40 and 200¹⁴; it becomes obvious that carbon fiber, at best, is at the lower limit of acceptability. Hence the properties of composites reinforced with this fiber will not comply with potential requirements or expectations.

Last but not least, it should be pointed out that, similar to observations during green strength measurements, the mechanical properties showed a marked anisotropy.

Dynamic Properties

Measurements of storage moduli, E' , and loss moduli, E'' , as well as the loss factor $\tan \delta$, were carried out as a function of deformation range, frequency, and temperature.

Figure 2 represents storage modulus variation with deformation amplitude, under the conditions indicated in the figure. Due to fiber stiffness a modulus increment is produced, which increases with fiber content.

For larger fiber level, 20 volumes, the greater stiffness of carbon fiber gives rise to higher modulus values. The consequential diminution, however, in the higher deformation range, is greater due to the smaller size of carbon fibers.

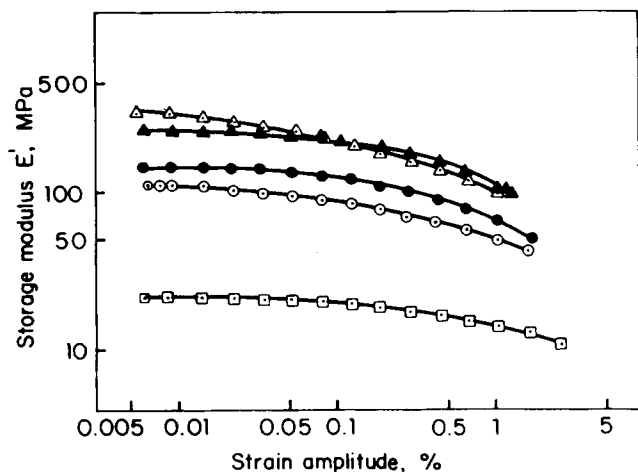


Fig. 2. Variation of storage modulus E' as a function of deformation amplitude. Tension compression test; longitudinal direction; frequency 11 Hz; temperature 30°C. (□) Fiber-free; (○) EPDM-C 10 volumes; (△) EPDM-C 20 volumes; (●) EPDM-PET 10 volumes; (▲) EPDM-PET 20 volumes.

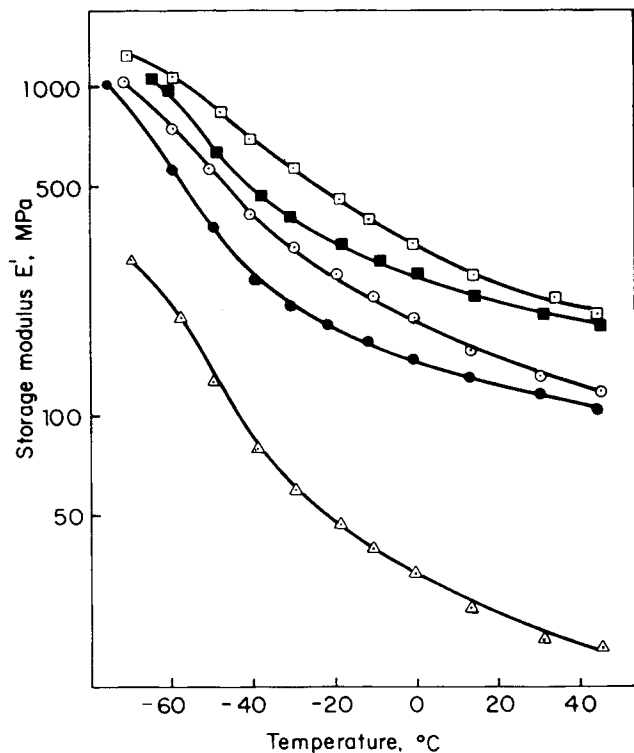


Fig. 3. Variation of storage modulus as a function of temperature. Tension compression test; longitudinal direction; frequency 7.8 Hz; dynamic strain 0.015%. (△) Fiber-free; (○) EPDM-C 10 volumes; (□) EPDM-C 15 volumes; (●) EPDM-PET 10 volumes; (■) EPDM-PET 15 volumes.

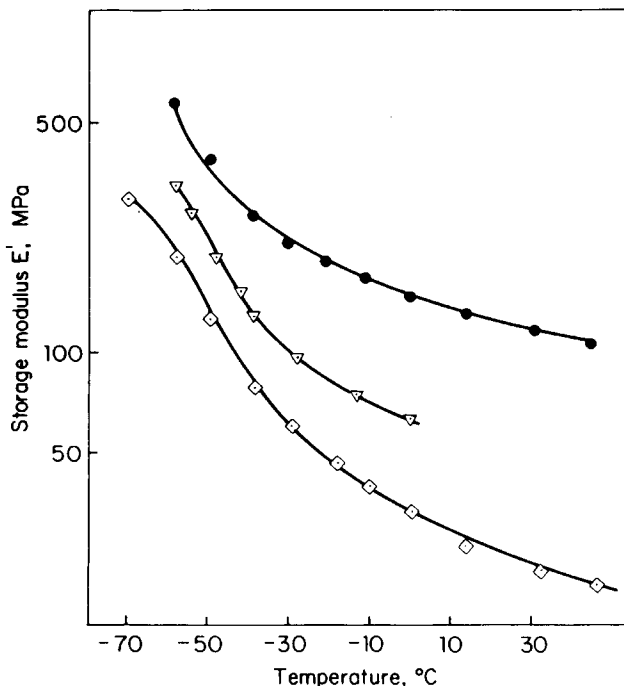


Fig. 4. Variation of storage modulus as a function of temperature, experimental material EPDM-PET 10 volumes. Conditions as in Figure 3: (●) longitudinal; (▽) transversal measurement; (◇) fiber-free.

The linear response zone of the modulus is narrowed and even disappears in EPDM-C composites as a function of fiber concentration increase. Modulus reduction in the higher deformation range is more pronounced as a consequence of gradual phase separation.

Storage modulus E' variation with temperature is shown in Figure 3. Apart from modulus increase with fiber content and a decrease as a function of rising temperature, the graphs are observed to change their shape: They become less sensitive to temperature changes. In the case of carbon fiber, response to temperature variation being more marked, the slope of the curve is larger; once again, the deterioration suffered by the carbon fibers during processing has a bearing on the behavior of the end product.

For the same fiber concentration, the moduli of EPDM-C composites are greater than these corresponding to EPDM-PET composites, due to the greater stiffness of carbon fiber.

The anisotropy of these properties is shown in Figure 4. The graph representing modulus variation as a function of temperature in transversal measurement is positioned between the control curve (fiber-free material) and that corresponding to longitudinal measurements. Transversal measurement follows the trend of the fiber-free sample.

Damping or loss factor $\tan \delta$ variation with temperature presents, within the experimental range, a single peak which corresponds to the main relaxation process in the elastomeric matrix, i.e., dynamic glass transition as represented in Figure 5.

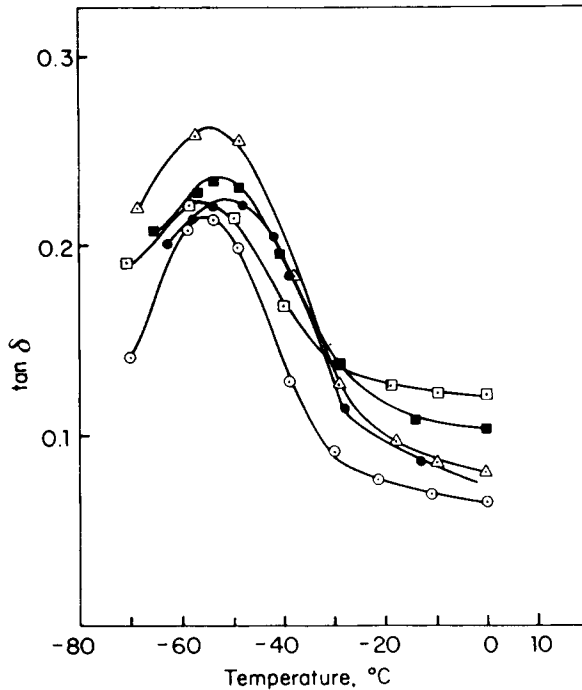


Fig. 5. Variation of $\tan \delta$ with temperature. EPDM with 10 volumes of fiber. Conditions as in Figure 3: (Δ) without fiber; (\square) EPDM-C longitudinal measurement; (\blacksquare) EPDM-C transversal measurement; (\circ) EPDM-PET longitudinal; (\bullet) EPDM-PET transversal.

Although the curves are similar, there exist considerable differences among them. The composites, independent of fiber type, present a relaxation spectrum with an expanded transition zone. The intensity of maximum damping is dependent on fiber orientation; transversally, it is higher than longitudinally. The temperature at which this peak occurs is displaced towards higher ranges in the presence of fiber. This shift is dependent on fiber orientation (control, -58.6 ; EPDM-C (L), -57.2 ; EPDM-C (T), -54.4 ; EPDM-PET (L), -56.64 ; EPDM-PET (T), -51.5°C).

Figure 6 shows the relationship between the relative damping values $(\tan \delta_{\max})_c / (\tan \delta_{\max})_m$ plotted against fiber content.^{15,16} Similar to other composites,¹⁷ the transversal peak value decreases with fiber level increase and can be expressed in terms of the following equation:

$$\tan \delta_c = \tan \delta_m - aV_f$$

where the subscripts c and m stand for composite and matrix, respectively, and V_f is the fiber portion volume, a representing a fiber type depending coefficient. Hence the following expression is legitimate:

$$(\tan \delta_{\max})_c / (\tan \delta_{\max})_m = 1 - bV_f$$

where b stands for the matrix-dependent coefficient. The value of b in this equation allows one to estimate the degree of fiber-matrix interaction. If the

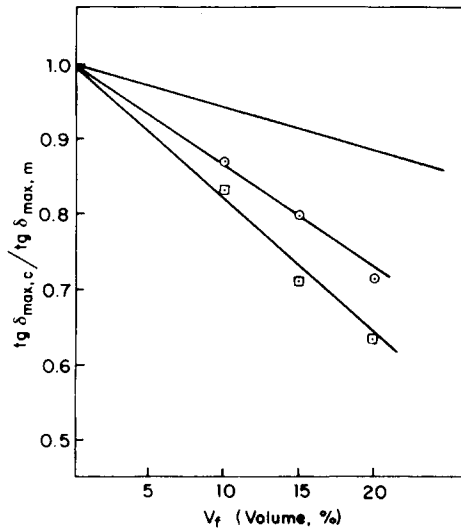


Fig. 6. Relative damping as a function of fiber content: (○) EPDM-C; (◻) EPDM-PET.

damping effect was exclusively due to the matrix, relative damping would be approximately equal to the volume fraction of fiber incorporated to the matrix^{18,19} and would diminish with the straight line without markings in Figure 6. The relative damping values for composites deviate from this line as a function of fiber type. From the slopes of these graphs, a b value is derived in such a way that the more distance it is from 1.0, the stronger the interaction between the two phases.

On the other hand, the temperature of the $\tan \delta$ peak is displaced in higher ranges as a function of higher vibration frequencies. Figure 7 shows the

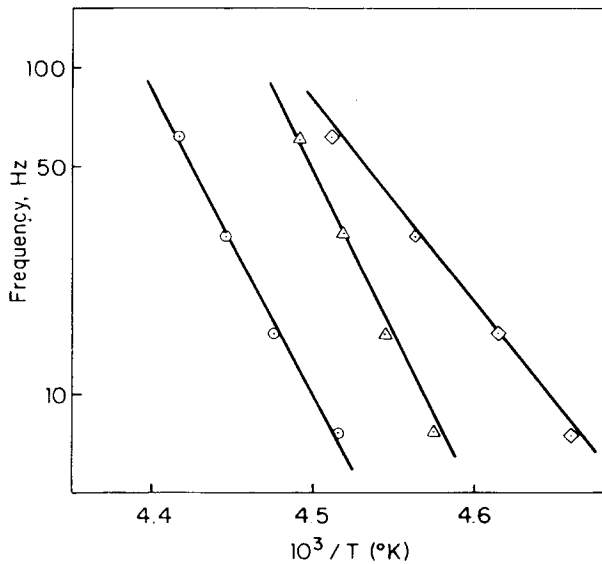


Fig. 7. Frequency maximum $\tan \delta$ -temperature relationship for: (◊) fiber-free; (Δ) EPDM-C 10 volumes; (○) EPDM-PET 10 volumes.

TABLE V
Activation Energies (kJ/mol) and Interaction Factor of Composites

Fiber volume	EPDM—C	EPDM—PET
0		117
10	182.6	174.2
15	196.7	200.3
20	205.7	207.2
<i>b</i>	2.43	3.02

relationships between frequency and $\tan \delta$ peak temperature for the total material indicated in the figure. Similar determinations were performed for the rest of the series. Starting out from the linear relationship

$$\log f = \log f_0 - H/2.303RT$$

the activation energy of the main dispersion in each sample can be determined. These values, together with the computed value of coefficient *b*, are compiled in Table V.

The activation energy increases with regard to the value computed for the matrix allow for the assumption¹⁶ that the mobility of the matrix in the composite is inhibited due to the fiber-matrix adhesion, which is logically enhanced as a function of increasing fiber content. The zones of strong interaction, however, are smaller in EPDM—C composites with respectively lower *b* values as a consequence of fiber rupture.

CONCLUSIONS

Reinforcement of EPDM matrices with short polyester or carbon fiber depends upon both type and concentration. If the fiber breaks during incorporation into the elastomeric matrix so that the final length/diameter ratio is below the required limit, the material also presents a lower overall score in its set of properties. By the same token, composites with polyester fiber, at any fiber content, show better properties than carbon fiber.

Fiber-matrix adhesion, for which experimental evidence was supplied, in itself is not sufficient to achieve a substantial improvement, unless it is accompanied by a good *L/D* ratio.

In general terms, reinforcement with fiber, within the experimental conditions, causes an increase in green strength, stress at constant strain, especially in the low deformation range, as well as tear strength, whereas at the same time elongation at break is diminished, and, as a consequence of phase adhesion, practically total inhibition of solvent swelling is achieved.

These composites distinguish themselves from the matrix by having a higher storage modulus, due to fiber stiffness, although the linear response zone decreases or disappears during deformation, reduction rates being higher in the higher deformation range. Modulus variation with temperature is dependent on fiber type, EPDM—PET being less sensitive against temperature changes than EPDM—C.

Fiber size has logically an impact on matrix-fiber interactions, while matrix immobilization and the consequential displacement of the damping peak

towards higher temperature ranges are not a function of fiber type but exclusively of the matrix.

As a consequence of high fiber orientation, the composites present a considerable degree of property anisotropy.

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