

# The Effect of a Diazide as Adhesion Agent on Composite Materials Consisting of an Elastomeric Matrix and Short Polyester Fiber

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## SYNOPSIS

This research reports on the effect of a diazide, i.e., 1,4-carboxybenzenesulfonyl diazide, which had been incorporated onto fiber by a chemical reaction, on the formation of an interphase between the elastomeric SBR matrix and polyester fiber. The existence of the interphase becomes manifest not only in the variation of the mechanical properties, but especially through swelling measurements and dynamic properties. The effect of the new system based on diazide is similar to that obtained from a conventional adhesive system, but presents certain benefits, such as a shorter curing time due to absence of resin, enhanced tensile strength, and the formation of a more flexible interphase, which entails lesser heat generation due to mechanical energy loss. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The existence of a strong matrix–fiber interphase is of vital importance in the study of composites consisting of an elastomeric matrix and short or discontinuous fiber, if a set of useful properties is to be obtained. In practice, this interphase is achieved by the incorporation of conventional adhesive systems based on phenol–formaldehyde resins, the most favorable case being accomplished with the building up of covalent links between the phases. To this purpose, although not exactly with elastomeric matrices, silane derivatives containing an azide function in their molecules have been used,<sup>1</sup> in such a way that in the transformation process the silane group is bonded to the glass fiber employed and the azide group reacts with the polyethylene chain.

In recent research in our laboratory, azide derivatives have been utilized as cross-linking agents with elastomers having either a dienic nature or low or no unsaturation,<sup>2,3</sup> as well as for surface modification of inorganic fillers to enhance their reinforcing effects in rubber compounds.<sup>4</sup> Furthermore, the reactivity of the azide group has been used in the modification of short discontinuous polyamide fiber<sup>5</sup>

with such good results that it is considered to be an alternative to conventional adhesive systems for interphase formation.

According to previous research,<sup>6</sup> short polyester fibers (PET) yield the best results in SBR matrices when an adhesive system based on resorcinol and formaldehyde was incorporated into the rubber compound.

The main goal of the present study was to use a diazide derivative, such as 1,4 carboxybenzenesulfonyl diazide as a bonding agent between the fiber and the elastomeric matrix, making use of the reactivity of the azide group,  $-\text{N}_3$ . In fact, the synthesized diazide derivative reacts with free hydroxyl groups of the PET fibers through the isocyanate group originated by Curtius transposition of the carbonyl azide ones,  $-\text{CON}_3$ ,<sup>7</sup> resulting in sulfonyl azide functionalized fibers.

The modified or treated fibers are added to the elastomeric matrix. At the vulcanization temperature, the sulfonyl azide group,  $-\text{SO}_2\text{N}_3$ , decomposes, building up a nitrene group, which can react with the elastomeric chain, in such a manner that, finally, a chemical bond between the matrix and the fiber is formed.

If the above-mentioned mechanism takes place, the resulting composite material must present a series of enhanced properties in comparison to an ad-

hesive-free fiber-filled composite, especially with respect to swelling in solvents, stress at low strain, elongation at break, and tear strength. Similarly, some properties would be governed by the existence of an interphase formed by covalent links between the matrix and the fiber instead of a conventional adhesive system based on resorcinol-formaldehyde.

In this work, the results obtained from a composite with modified fibers are compared to those from two composites prepared with and without a conventional adhesive system and, finally, to those from a fiber-free composite, with the aim of elucidating whether the azide acts as a linkage agent between the phases and of assessing the potential improvements obtained over the features known for the conventional adhesive system.

## EXPERIMENTAL

### A. Treatment of the Fibers

Fiber modification implies a preliminary operation, such as the synthesis of the diazide. 1,4-Carboxybenzene sulfonyl diazide was used, following the preparation and characterization methods developed in our laboratory.<sup>8</sup> The details concerning fiber treatment and the characterization of the modified product will soon be published in this journal.<sup>9</sup> It must be noticed that under the reaction conditions used the carbonyl azide group undergoes a Curtius transposition, giving rise to the respective isocyanate, which reacts with the free OH terminal groups of the polyester fiber. The completion of the reaction was followed by IR spectroscopy, and, finally, the modified PET fibers were characterized by chemical analysis of the free OH groups that theoretically should have completely disappeared, as was shown. The fiber used is a polyester fiber (PET) supplied by Velutex Floc S.A., having a length of 6 mm, approximate diameter of 18  $\mu\text{m}$ , and specific gravity of 1.38.

### B. Composite Preparation

All the compounds were prepared in a 12 in. two-roll mix with a friction ratio of 1 : 1.4, under the same conditions, fibers being added at the end of the compounding process and always keeping the same rolling direction to promote fiber orientation. Compounds were finally sheeted, again in the rolling direction, into slabs of approximate 2 mm thickness.

The recipes of the different composites are the following:

	A	B	C	D
SBR 1502	100	100	100	100
Zinc oxide	3	3	3	3
Stearic acid	2	2	2	2
N-330 black (HAF)	30	30	30	30
CBS accelerator	1	1	1	1
Sulfur	2	2	2	2
Silica, Ultrasil VN3	—	5	—	—
Resorcinol	—	2.5	—	—
Cohedur A <sup>a</sup>	—	1.6	—	—
PET fiber <sup>b</sup>	—	20.7	—	20.7
Modified PET fiber <sup>c</sup>	—	—	20.7	—

<sup>a</sup> Formaldehyde donor supplied by Bayer AG.

<sup>b</sup> 15 volumes. As delivered by the supplier.

<sup>c</sup> Sulfonyl azide functionalized fiber.

Curing characteristics were measured with a rotorless Monsanto rheometer, Model MDR 2000E, at 150°C. All the compounds were vulcanized at their respective  $t_{97}$  in a press heated by a thermofluid.

### C. Properties Measurement

Green strength of the material was determined on rectangular test pieces, of 25  $\times$  150  $\times$  2 mm, using an Instron dynamometer, Model 1026, at a deformation rate of 500%/min, taking the value of the yield point as the green strength value. The test piece to be examined was subjected to press precuring for 2 min at 120°C.

The physical properties were measured according to national standards (UNE). Tear strength was determined on a Delft-type test piece.

The dynamic properties, the storage modulus,  $E'$ , and the loss factor,  $\tan \delta$ , were determined on parallelepipedic test pieces of dimensions of approximately 16  $\times$  4  $\times$  16 mm in a Metravib Viscoanalyzer. The sample shape and type used allow for property measurements by applying dynamic strain longitudinal and perpendicular to the direction of preferential fiber orientation. The swelling tests were carried out in *n*-heptane during an immersion period of 48 h at 30°C.

## RESULTS AND DISCUSSION

### A. Green Properties

Curing and green strength values are shown in Table I. From the data contained in that table, it is noteworthy that the presence of fibers generates an increase in viscosity, as measured from the minimum

**Table I Curing and Green Properties of Composites**

	A	B	C	D
<u>Curing at 150°C, Monsanto rheometer</u>				
$M_L$ (dN m)	1.50	3.50	3.4	2.05
$M_H$ (dN m)	18.00	25.70	27.5	20.07
$\Delta M$ (dN m)	16.50	22.20	24.1	18.02
$t_{97}$ (min)	18.75	47.25	20.0	19.50
$t_{\Delta 2}$ (min)	5.75	4.60	6.0	6.60
<u>Green strength (kg/cm<sup>2</sup>)</u>				
Direction L	2.63	24.50	31.4	19.9
Direction T	2.83	7.47	6.6	6.8

torque value,  $M_L$ , from a rheogram, and an increase in maximum torque,  $M_H$ , indicative of the enhanced stiffness of the fiber-reinforced materials, especially in  $\langle B \rangle$  and  $\langle C \rangle$  composites.

The maximum–minimum torque differential, expressed in Table I as the  $\Delta M$  value, points toward a greater cross-linking density in the fiber-reinforced  $\langle B \rangle$  and  $\langle C \rangle$  composites, which indicates that PET-fiber treatment with the diazide derivative generates links between the fibers and the matrix.

Sample  $\langle B \rangle$  needs a longer vulcanization time, expressed as  $t_{97}$ —or the time required to accomplish 97% of cross-links at the curing temperature—because this conventional adhesive system substantially extends vulcanization time, as shown by previous studies.<sup>10</sup> Sample  $\langle D \rangle$ , which corresponds to adhesive-free composite, has a curing time similar

to that of the elastomeric matrix, sample  $\langle A \rangle$ . Sample  $\langle C \rangle$  has a shorter  $t_{97}$ , which means an improvement in the comparative study of both matrix–fiber adhesive systems.

The fibers act in raising the green strength of the material, mainly following direction of flow, or longitudinal direction of the fibers, particularly in  $\langle B \rangle$  and  $\langle C \rangle$  composites, which have a conventional adhesive system and azide-modified fiber, respectively. As was to be expected, green strength varies with the direction of the measurement.

## B. Mechanical Properties

Table II compiles the stress–strain, tensile strength, elongation at break, and tear strength data of the four composites under study. The composite con-

**Table II Mechanical Properties of the Composites**

	Composite						
	A	B		C		D	
	Direction						
		L	T	L	T	L	T
Stress (MPa) at strain of							
10%	0.32	4.1	1.39	3.47	0.56	2.7	1.6
20%	0.7	6.88	3.02	6.93	1.69	6.2	3.7
30%	0.85	9.21	3.72	9.6	2.31	7.7	5
40%	1.0	9.47	4.20	11.8	2.74	8.6	5.9
50%	1.1	9.58	4.44	—	2.97	8.7	6.3
Tensile strength (MPa)	16.7	10.5	7.9	12.5	8.85	10.06	8.5
Elongation at break (%)	430	77.5	306	47	386	246	302.5
Tear strength (N)	29.7	82.8	54.3	78.1	47.9	46.6	32.8

*L* and *T* stand for the longitudinal or transverse direction of the measurements as referred to the preferential orientation of the fibers.

taining the modified fiber possesses qualities that may be considered typical of these materials with short fiber linked to the elastomeric matrix: a higher tear strength value and a drastic decrease in elongation at break, as well as a higher value of stress at constant deformation as compared to adhesive-free composite, sample <D>. In addition, these properties present anisotropy, as shown by the difference between the longitudinal (*L*) and transverse (*T*) measurements with respect to preferential fiber orientation inside the matrix. Overall, sample <C> values show a similar behavior as to that of sample <B>.

Tensile strength is not an exceptional property of these composite materials and its variation with fiber addition depends on the type of polymeric matrix and the fiber level. However, a higher value for modified fiber composite in comparison to the other fiber-loaded composites is observed, which can be considered as an improvement of the adhesion to the matrix through the azide derivative.

### C. Solvent Swelling

Another characteristic that may likewise be considered proper for materials with links between the elastomeric matrix and the reinforcing fibers is the inhibition of matrix swelling under the effects of solvents,<sup>11</sup> as well as an increase in cross-linking density.<sup>12</sup> To confirm the phase-bonding behavior of the azide derivative, the test materials were subjected to swelling in solvent according to the conditions indicated in the Experimental part. The respective data are compiled in Table III.

To compare the different materials, a parameter  $V_R$  (Ref. 11) is utilized, defined as

$$V_R = (V_I - V_F)/V_I$$

where  $V_I$  is the initial volume fraction of rubber obtained from the ratio between the total sample volume and the rubber portion present in it. Once swollen to equilibrium, and assuming that the rubber

portion does not vary between the dry and swollen samples, the volume fraction of rubber in the swollen sample,  $V_F$ , is obtained from the ratio between the volume of the swollen sample and the volume of rubber in it. Hence, in a system with a strong interphase, there would be a greater constraint on swelling and, consequently,  $V_R$  would show a relatively lower value. On the contrary, if phase adhesion is not adequate,  $V_R$  would be relatively higher.

In light of these results, the  $V_R$  values, which are lower in <B> and <C> composites, may be taken as conclusive evidence that there exists a significant inhibition of matrix swelling, due to the bonds with the fibers triggered by the resin and the azide, respectively. Constrained matrix swelling is likewise reflected in the  $a_L$  values<sup>13</sup> approaching 1, i.e., the dimensional swelling ratio in the preferential fiber orientation.

In addition, the cross-linking density,  $\nu$  (mol/cc), as calculated from the  $\nu_r$  values resulting from weighing the swollen and dry samples and corrected in the portion corresponding to the components unaffected by swelling and subsequent application of the Flory–Rehner equation,<sup>14</sup> is higher in samples <B> and <C> than in the adhesive-free composite, sample <D>. In this latter case, the  $V_R$  value is similar to that of the fiber-free polymeric matrix, due to the fact that phase bonding is computed as cross-links. From the swelling measurements, it can be concluded that the azide derivative acts as a bridging agent between the fibers and the polymeric matrix.

### D. Dynamic Properties

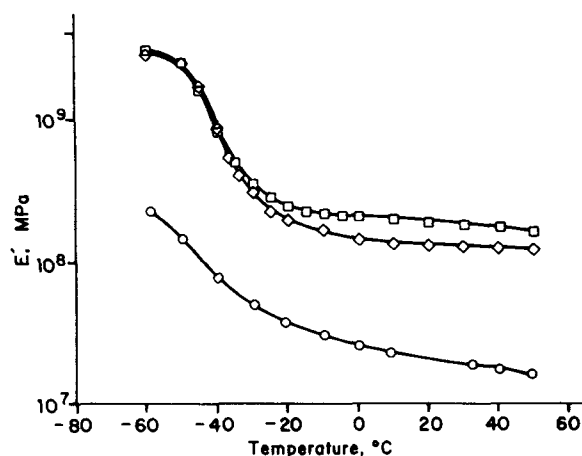
The strength of the interphase modifies the viscoelastic properties of the matrix. Figures 1 and 2 show the variation of the storage modulus  $E'$  and those of the loss factor  $\tan \delta$ , respectively, as a function of temperature.

The modulus, at any temperature, is greater in the fiber-filled composites and presents a more significant drop in the transition zone, i.e., the transition zone is narrower than in the elastomeric matrix. At low temperatures, the graphs of the fiber-containing composites practically overlap and only become differentiated above  $-10^\circ\text{C}$ .

The variation of the loss factor  $\tan \delta$  with temperature shows, for the experimental temperature range, the same spectrum in all cases: a single maximum damping peak corresponding to the main relaxation of the elastomeric matrix. In the fiber-filled materials, however, this peak is shifted to higher temperatures as a consequence of an immobilization of the polymeric matrix in the vicinity of the fiber,

**Table III Swelling Inhibition and Cross-linking Density**

Composite	$V_R$	$a_L$	$\nu \times 10^4$ (mol/cc)
A	0.5174	1.235	5.66
B	0.4667	1.02	6.27
C	0.4510	1.02	6.49
D	0.5238	1.208	5.59

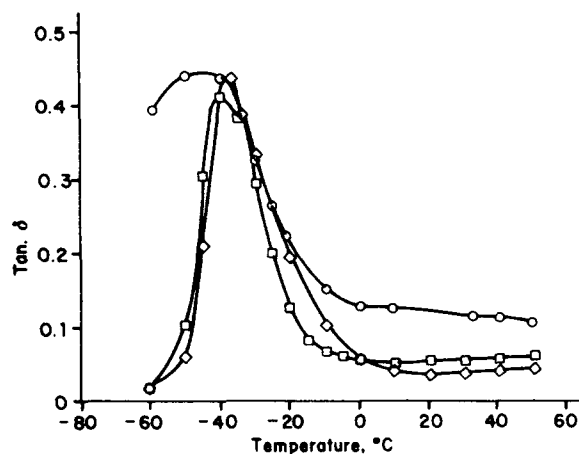


**Figure 1** Variation of storage modulus,  $E'$ , as a function of temperature. Frequency, 7.8 Hz. Longitudinal to fiber direction. (O) Elastomeric matrix; (□) composite reinforced with fiber and resin; (◇) composite reinforced with azide-modified fiber.

due to the presence of links between both phases, the higher shifts being observed for the composite containing the modified fiber. In the elastic zone of the spectrum, the values of the loss factor are lower in the fiber-filled materials, the lowest value being obtained for the azide-treated sample.

The maximum damping temperature can be determined from these curves as a function of the vibration frequency, and, subsequently, the value of the apparent activation energy of the relaxation process may be obtained. Table IV shows all these values, together with the dynamic glass transition temperature,  $T_{g,d}$ . As can be concluded from the values of Table IV, there exists a shift of the peaks toward higher temperature ranges, as well as an energy increase, which indicates the existence of interfacial energy between the matrix and the modified fiber.<sup>15</sup>

The presence of adhesive systems or links between the phases modifies the behavior of these materials *vis à vis* heat generation,<sup>16</sup> which is measured in terms of mechanical energy losses. The loss factor values represented in Figure 2 might suggest that, due to lesser damping, heat generation should be



**Figure 2** Variation of the loss factor  $\tan \delta$  with temperature. Conditions and symbols as in Figure 1.

lower. When representing hysteresis variation measured as

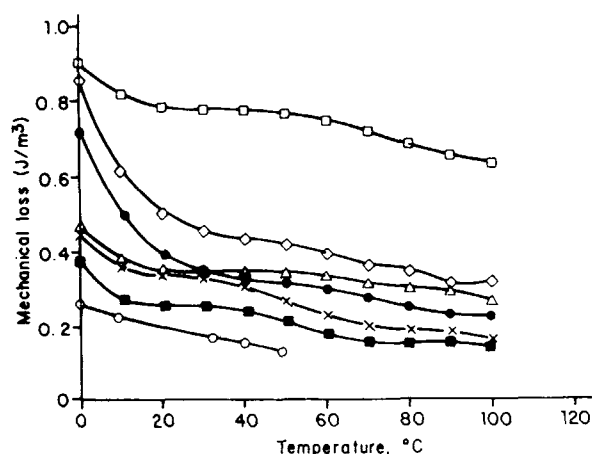
$$H = (\pi/4)(\text{DSA}/100)^2 E' \tan \delta$$

where DSA is the double-strain amplitude or peak-to-peak strain expressed in % of the nonstrained dimension, a configuration such as shown in Figure 3 is obtained, which represents hysteresis variations as a function of temperature for all the prepared composites.

This allows us to assert that at any temperature the presence of fibers increases the mechanical energy loss by cycle. In fact, when there exist links between the phases, a shear effect is generated in the interphase that increases mechanical energy loss. When the interfacial link is lacking, sample <D>, the value of the energy loss is likewise higher than that of rubber matrix, due to that the fiber ends act as stress raisers, contributing to mechanical energy loss.<sup>17</sup> Moreover, there exists a highly significant difference between composites <B> and <C>, so that when a conventional adhesive system is employed, where adhesion is achieved by means of resins, which confers greater stiffness and rigidity to the interphase and, hence, results in a higher modulus (Fig. 4), heat generation is also higher than when an azide

**Table IV** Maximum Damping Temperature,  $T_{g,d}$ , and Activation Energy

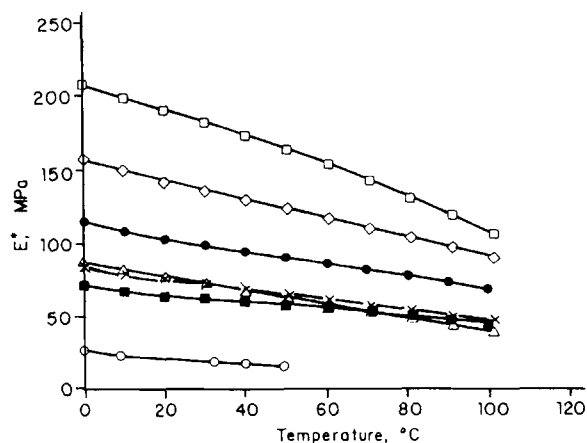
	7.8 Hz	15.6 Hz	31.2 Hz	62.5 Hz	$T_{g,d}$	$\Delta E$ (kJ/mol)
A	-47.9	-46.2	-43.8	-42.6	-53.5	118.2
B	-39.5	-38.5	-36.5	-35.0	-43.8	213.7
C	-37.3	-35.0	-34.7	-32.0	-42.0	213.2



**Figure 3** Variation of mechanical energy loss with temperature. Frequency 7.8 Hz; DSA = 0.3%. (○) Elastomeric matrix. Composite reinforced with fiber and resin: strain applied (□) longitudinally ( $L$ ) and ( $\Delta$ ) transversely ( $T$ ). Composite filled with modified fiber: strain applied ( $\diamond$ ) longitudinally ( $L$ ) and ( $X$ ) transversely ( $T$ ). Composite filled with fiber without adhesive system; strain applied ( $\bullet$ ) longitudinally ( $L$ ) and ( $\blacksquare$ ) transversely ( $T$ ).

derivative is used as a phase-bonding agent, which yields a more flexible interphase. The differences in the stiffness of the interphase, through which the tensions between the matrix and the fibers are transmitted, account for the divergent values in the mechanical energy loss or heat generation.

The greater elasticity of the interphase can explain the higher tensile strength in terms of the azide-induced matrix-fiber links being less strain-sensitive and, hence, of lesser polymer-fiber friction in the interphase. Energy loss diminishes with temperature increase, the decrease being more signifi-



**Figure 4** Variation of the complex modulus  $E^*$  with temperature. Symbols as in Figure 3.

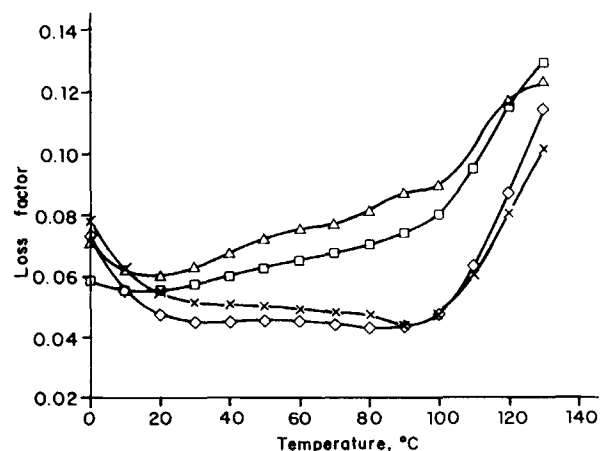
cant in the modified fiber composite, which presents a similar pattern to that of the adhesive-free fiber-filled composite.

Figure 3 suggests that mechanical energy loss depends on the direction of the strain. When it is perpendicular ( $T$ ) to the preferential fiber orientation, the energy losses, although still greater than that of the fiber-free elastomeric matrix, are relatively lower than when the deformation is applied parallel to fiber direction ( $L$ ). But, also, in this latter case, the value is lower for the modified fiber composite, the differences becoming greater with increasing temperatures. The adhesive-free composite provides less mechanical energy loss.

When the modulus is measured perpendicular to fiber orientation (Fig. 4), all the fiber-filled composites yield very similar values, due to the fact that in this direction interphase does not play a decisive role, although all the filled samples show higher values than does the elastomeric matrix.

It can be said that the existence of covalent bonds between the modified fiber and the matrix contributes to palliate the negative effect on heat generation (Fig. 3) and, thus, should reduce loss in fatigue strength from the addition of short fibers inside the rubber matrices. Therefore, composites of the experimental type  $\langle C \rangle$  may be considered to open up new horizons for interesting applications.

Figure 5 represents the variation of loss factor  $\tan \delta$  as a function of temperature for both  $\langle B \rangle$  and  $\langle C \rangle$  composites, measured in both directions, lon-



**Figure 5** Variation of  $\tan \delta$  with temperature in the range 0–130°C in fiber-filled composites as a function of strain direction. Frequency, 7.8 Hz; DSA = 0.3%. Composite with conventional adhesive system: (□) strain applied longitudinally and ( $\Delta$ ) transversely. Modified fiber composites: strain applied ( $\diamond$ ) longitudinally and ( $X$ ) transversely.

gitudinally ( $L$ ) and transversely ( $T$ ). For a temperature range around room temperature, the figure shows the elastic behavior zone of the composites.

Although the shape of the curves is different, the global response of both composites is very similar. Thus, in both materials, the  $\tan \delta$  values measured transversely are higher than those obtained from longitudinal measurements, indicative of the absence of interphase interference in the transverse direction. At high temperatures, an increase in  $\tan \delta$  is generated due to the relaxation peak of the polyester fiber whose transition temperature moves around 130°C. In the 20–80°C range, an alteration of the  $\tan \delta$  values is produced, indicative of a minor transition attributable to the interphase and in a similar zone, as demonstrated in previous work.<sup>5</sup> The difference in the intensity of this transition probably derives from the different natures of the conventional system and the azide-induced links.

## CONCLUSIONS

According to previous work, PET fibers were treated with 1,4-carboxybenzenesulfonyl diazide under certain reaction conditions, giving rise to a sulfonyl azide-modified fiber, which can yield covalent bonds with an SBR matrix, during vulcanization through the free  $-\text{SO}_2\text{N}_3$  group. This fiber treatment may be considered novel.

The existence of these bonds has been shown by inhibited matrix swelling measurements, which translates into higher cross-linking densities, as well as an increase of stress at constant deformation with a drastic reduction of elongation at break and a high tear strength. In addition, it has been demonstrated, by dynamic properties determination, that the relaxation process requires a higher apparent activation energy than does the elastomeric matrix as a consequence of the existence of these matrix-fiber bonds. Owing to the immobilization of the elastomeric chains, the transition temperature is shifted to higher values.

This new system gives rise to composites with a series of properties that are basically similar to those obtained with conventional adhesive systems, yet it provides certain benefits, such as a shorter curing

time approaching that of the fiber-free elastomeric matrix and lower heat generation, which is measured in terms of mechanical energy loss and is assumed to derive from the greater elasticity of the interphase generated. Briefly, it is adequate to consider the new system based on diazide derivatives as an alternative to conventional adhesive ones in composite materials due to the great reactivity of the azide group.

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