Effect of a Diazide as Adhesive Agent in Elastomeric Matrix–Short Polyamide Fibers Composite

LUIS IBARRA* and CARMINA JORDÁ

Instituto de Ciencia y Tecnología de Polímeros, C.S.I.C., Juan de la Cierva 3, 28006 Madrid, Spain

SYNOPSIS

The effect of a diazide, chemically bonded to short polyamide fibers, has been investigated in order to establish if the diazide acts effectively as a bond bridge between the elastomeric matrix and the fibers. Composite properties, such as green strength, solvent swelling, tensile and tear strength, and elongation at break, which clearly manifest the existence of a strong interface, have been measured in comparison with those obtained in a similar composite with a conventional adhesive system. Likewise, the temperature dependence of tan δ showed a dispersion peak in the temperature range 30–90°C, which corresponds to the addition of the two relaxations related to the fiber and the interface. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The properties of elastomeric matrix–short fiber composites depend on three parameters: the dispersion of the fibers in the matrix, their orientation, and the existence of bonds between the matrix and the reinforcement, which, most favorably, should consist of true covalent bonds.[1]

One of the advantages that these composites have, as compared with those reinforced with continuous filament, is that they can be prepared without using special techniques in the same way as a conventional rubber compound, although the dispersion of the fibers and their orientation cannot be acted on directly, since these are determined by the normal methods of preparation for these materials.[2,3]

The resistance of the matrix–fiber interface is ultimately responsible for the properties of these materials; for this reason, the primary goal of the research is to obtain a strong interface. An adhesive system, commonly of the phenyl–formaldehyde type,[4] which acts positively with most of these materials, is generally incorporated in order to increase the resistance of the interface. It should be reiterated, however, that the ideal system would be one that would yield true covalent bonds between the elastomeric matrix and the fiber, by the use of reagents capable of bonding to both phases. Consequently, we prepared and used as crosslinking agents with elastomers both saturated and nonsaturated rubbers,[5,6] derived from diazide, with the capacity to react through the azide group, $-N_3$, with double bonds and/or carbon atoms of a polymeric chain.

Accordingly, the purpose of this work was to create an interface, formed by covalent bonds between the matrix and the fiber, which could advantageously replace the conventional adhesive systems, using the reactivity of the derivatives of diazide, which would act as bond bridges between both phases.

This first stage of the research attempts to show that the incorporation of diazide, after reacting with the polymeric fiber, is capable of creating matrix–fiber bonds.

EXPERIMENTAL

Preparation of the Diazide and Modification of the Fiber

A 6,6 nylon fiber was selected as the synthetic fiber, which was approximately 6 mm in length with a diameter of 60 μm and a specific weight of 1.14, supplied by the firm Velutex Floc.


The 1,4 carboxy–sulphonyl–diazide was used as a derivative of diazide, which was previously prepared according to the methods carried out in this laboratory,[7] on the basis of commercial products that used the following reaction scheme:

$$SO_2Cl \xrightarrow{N_3Na} SO_2N_3 \xrightarrow{Cl_2SO} SO_2N_3 \xrightarrow{N_3Na} SO_2N_3$$
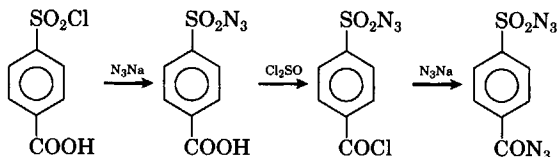
The intermediate and the final products were characterized by the usual techniques (e.g., elemental analysis, IR, and RMN spectroscopy).

The modification of the fiber took place in a reactor, in which the amount of fiber to be modified was introduced with a certain proportion of azide (2% by weight for fiber), in an appropriate solvent (predried benzene). The reaction mass was stirred for 3 h at a temperature of 80°C. When the azide was heated in the benzenic solution, it was transformed into the corresponding isocyanate, according to the Curtius transposition reaction[8]:
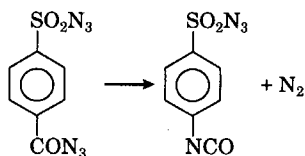
The isocyanate reacted with the fiber, preferably through the terminal groups[9]; in this way the sulfonyl–azide group would be free to bond with the elastomeric matrix.

Table I Formulation of the Composites

	A	B	C	D
SBR 1500			100	
Zinc Oxide			3	
Stearic Acid			2	
Black N-330 (HAF)			30	
Accelerant CBQ			1	
Sulfur			2	
Silica, Ultrasil VN-3	—	—	5	—
Resorcine	—	—	2.5	—
Cohedur A[a]	—	—	1.6	—
Polyamide Fiber	—	17.1	17.1	17.3

[a] Formaldehyde donor, supplied by Bayer.

Table II Green Strength (kg/cm^2) and Orientation

Sample	L[a]	T[a]	Orientation (%)
A	2.63	2.86	—
B	13.01	3.47	80.3
C	30.32	4.60	87.75
D	25.9	5.48	83.69

[a] L and T represent the longitudinal or preferred and transverse sections, respectively.

After the reaction time, the fibers were isolated, repeatedly washed with the solvent, and dried until totally eliminated.

Preparation of Composite Materials

The composite materials were prepared in a laboratory two roll mix (12 inches long, friction ratio 1 : 1.14). The fiber was incorporated at the end of the mixing process, taking care to of maintain the direction of compound flow; this guaranteed better orientation of the fibers, which, was never unidirectional, though for the most part it followed the direction of the flow.

Table I shows the ingredients of the recipe used. Compound C is the reference or control compound, as it incorporates a conventional adhesive system with a known effect.[10]

Measurement of Properties

Curing properties were measured on a rotorless rehometer, Monsanto Model MDR 2000E, at a vulcanization temperature of 150°C.

Green strength was determined using rectangular test pieces with the approximate dimensions of 25 × 150 × 2 mm, on an Instron model 1026, at a stretching rate of 500%/min. The samples were precured on a vulcanization press at 120°C for 2 min.

The longitudinal swelling values were determined after an immersion period of 48 h in n-heptane at 30°C.

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

The dynamic properties, the storage and loss moduli, as well as the loss factor, tan δ, were determined on a parallepipedic sample, approximately 16 × 4 × 16 mm in size, on a Metravib Viscoanalyser

Table III   Vulcanization Parameters

Sample	T_{min} (dN m)	T_{max} (dN m)	ΔT (dN m)	t_{90} (min)	t_{s2} (min)
A	1.49	17.98	16.5	18.74	5.74
B	2.45	25.74	23.29	19.03	4.68
C	3.31	31.51	28.20	39.40	2.89
D	2.94	28.10	25.15	18.25	4.78

with varying deformation amplitude, frequency, and temperature.

RESULTS AND DISCUSSION

Green Strength

When green strength of these composites was measured, a characteristic property of these materials was observed, which was anisotropy. Anisotropy is a result of, to a certain extent, the orientation of the fibers in the matrix. The fibers act to raise the green strength of the material, mainly following direction of flow or longitudinal direction of the fiber. This measurement, with the green strength obtained in a transverse or perpendicular direction to the preferred direction of the fibers and the green strength of the unreinforced matrix, provides an orientation factor, represented by the improvement ratio of this property.[11]

Table II shows the values obtained from the different samples. In all cases of material with fiber, the anisotropy of this property is obvious, as is the increase in the green strength, particularly in compound C and D, which have a conventional adhesive system and an azide-modified fiber, respectively.

Moreover, the orientation of the fibers, calculated as an improvement ratio, exceeds 80% in all samples, which is generally considered a high orientation, though it is not unidirectional, as indicated above.

Vulcanization

Table III shows the vulcanization parameters, measured by a Monsanto Rheometer. It is possible to deduce a logical increase in the viscosity of the compound when the fibers are incorporated, represented by the T_{min} value, which is greater in the compound having conventional adhesive, C, and in the compound that has the fiber modified with azide, D. These samples show higher values of increase of the torque, measured by ΔT, which implies a higher crosslinking density.

There is a great difference in vulcanization time between compound C and the remaining compounds. The conventional adhesive system substantially enlarges the vulcanization time, as shown in previous studies,[12] but if the fiber used is modified with azide, this prolongation does not occur, being unchanged

Table IV   Tensile and Tear Strength

Sample	Direction	Stress at 100% (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Tear Strength (N)
A	L	1.66	16.67	430	29.7
	T	1.76	16.4	416	26.6
B	L	9.82	10.55	140	77.95
	T	4.36	10.44	342	48.94
C	L	—	12.55	76	136.4
	T	4.26	9.33	358	59.86
D	L	—	10.6	88	92.21
	T	4.13	9.99	324	47.92
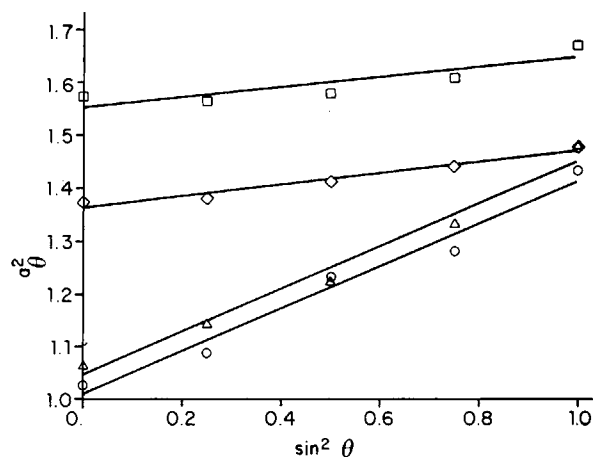
Figure 1 Swelling variation as a function of the angle of measurement θ. ($\square$) Compound without fiber, ($\lozenge$) Composite without adhesive system, (O) Composite with conventional adhesive, ($\triangle$) Composite with diazide modified fiber.

the unreinforced matrix before the critical volume of the fiber has been reached, at which point the tensile strength begins to increase.

The results of Table IV show, first, the existence of anisotropy of these properties as a constant in this type of material, which is a consequence of the preferred orientation of the fibers in the direction of the flow at the time of its preparation in the mixer.

Second, a reduction in the elongation at break of the materials with fiber is observed, particularly in C and D compounds, which show reductions of about 40% of the value attained in compound B without any type of adhesive. This, combined with an increase in the tear strength of these compounds, confirms the idea that there is a matrix–fiber resistant interface in these materials, which for sample D is a test that the diazide is acting in accordance with the project.

and even less than for the compound without fiber, A, which could be explained as an activation of the vulcanization by the azide group present in the fibers.

The presence of the azide provides safer compounds, with less "scorch" tendency or premature vulcanization, measured by t_{s2} time, than those with a conventional adhesive.

Tensile and Tear Strength

If there is good adhesion between the matrix and the fibers, the following aspects should be observed: (a) a rise in the moduli or stress at a particular deformation, (b) a drastic reduction in elongation at break, (c) a rise in tear strength. With respect to the tensile strength, its value does not generally indicate anything in particular, since the variation of this property depends on the loading and type of fiber and the nature of the matrix,[13] although one should not be surprised at values even lower than

Swelling in Solvents

The swelling measurements in a solvent, in addition to determining the crosslinking density, provide information on the resistance of the interface, the degree of dispersion of the fibers, and their direction in the elastomeric matrix.[14]

In fact, a strong adhesion between both phases would cause a restriction in the swelling of the matrix, resulting, if the adhesion is perfect, in swelling ratios (swollen length/original length) near to unity (total restriction). Moreover, if the orientation of the fibers is high, upon an increase in the measurement angle in relation to the direction of preferred orientation of the fibers, the swelling values will progressively increase, so that at an angle of 90%, perpendicular to the direction of orientation of the fibers, the swelling must be equal or very near to the matrix without fiber. In short, the values of the swelling ratio at 0° allow a greater or lesser adhesion between the matrix and the fiber to be deduced, and with the increase of the slope, a greater orientation of the fibers.

Table V   Swelling in n-Heptane

Sample	a_L	a_T	Slope	v_r	$\nu \times 10^4$
A	1.235	1.260	0.0165	0.456	5.66
B	1.172	1.207	0.0818	0.454	5.54
C	1.005	1.189	0.4028	0.493	7.57
D	1.023	1.205	0.4052	0.477	6.69

Table VI   Dynamic Glass Transition Temperatures as a Function of the Vibration Frequency (Hz)

Sample	7.8	15.6	31.2	62.5	125	250
B	−47	−43	−40.6	−39	−35.8	−33.4
C	−43.7	−42.3	−41.6	−38.8	−37.4	−35.3
D	−45.9	−44.5	−42.4	−40.3	−38.45	−36.4

Figure 1 shows the variations in the dimensional swelling ratio in terms of the angle of orientation of the fibers, θ, in accordance with eq. (1),

$$a_\theta^2 = (a_T^2 - a_L^2)\sin^2\theta + a_L^2 \qquad (1)$$

which is generally accepted for these materials[15]; Table V shows the values calculated, using this representation, of a_L, a_T, and the slope, together with the values of v_r, or fraction in volume of swollen rubber in equilibrium, calculated with eq. (2)

$$v_r = 1 - v_{nm}/a_L a_T a_z - v_{nm} \qquad (2)$$

where v_{nm} is the fraction in volume of the components of the compounds not affected by swelling (zinc oxide, filler, fiber, etc.) and a_L, a_T, and a_z are the dimensional ratios for length, transverse, and thickness, respectively.

The crosslinking density, shown in the last column of Table V, was calculated using eq. (3),

$$\nu \, (\text{mol/cc}) = - \frac{(\ln(1 - v_r) + v_r + \mu v_r}{V_1(v_r^{1/3} - v_r/2)} \qquad (3)$$

in which v_r is the fraction in volume of swollen rubber, V_1 is the molar volume of the solvent, and μ is the Huggins polymer–solvent interaction parameter.

The a_L values in C and D compounds, near to unity, indicate a practically total restriction of the swelling, due to the existence of a strong interface.

The values of the slopes, in C and D samples, which are practically equal, show a similar restriction of swelling caused by the presence of an adhesive agent. They have an identical orientation as well.

The a_T values of all samples show that, perpendicular to the preferred orientation, the swelling is independent of the presence of fibers and the values are near to those of the matrix.

When the crosslinking density is measured, higher values are obtained for compounds C and D. Evidently, the crosslinking is caused only by the

presence of vulcanizing agents—accelerators and sulphur—, which are common for all prepared materials and should supply the same value for crosslinking density. This assumption operates for compounds A and B, but not for C and D, in which the bonds existing between the phases are regarded, for the purpose of swelling, as crosslinks. For this reason, the differences between the crosslinking density of the latter samples and the previous ones shows the extent of the matrix-fiber bonds.

Dynamic Properties

The presence of links between the matrix and the fibers decreases the mobility of the polymeric chains and, thus, a higher dynamic glass transition temperature is obtained. The relaxation spectrum, a variation of the tan δ with the temperature, yields a maximum at low temperatures corresponding to the glass transition of the elastomeric matrix.

Some authors,[16] working on composite materials with polyester fibers, have observed a transition at a high temperature of about 135°C, corresponding
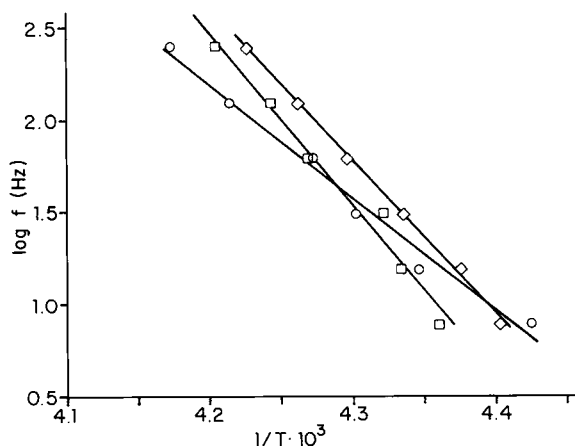

Figure 2   Variation of maximum damping temperature with the oscillation frequency. (○) Without adhesive system, (□) With conventional adhesive system, (◇) With diazide modified fiber.

to the polyester fiber, and a new relaxation at about 90°C, attributed to the matrix–fiber interface. When these studies are transferred to composite materials with polyamide fiber, the fiber transition is observed at lower temperatures than for polyester, but not for the relaxation corresponding to the interface, probably due to the fact that the maximum is hidden by the α'-dispersion of the fiber.

The measurements of the dynamic properties of these materials tend to show the following two phenomena, which are evidence of the existence of an interface of matrix–fiber bond: the glass transition temperature is shifted to higher temperatures, and the presence of a relaxation is corresponding to the interface.

Table VI shows the maximum temperature corresponding to the principal relaxation of the matrix in the prepared composite materials for the different vibration frequencies at which the test was made.

These temperatures are related to the apparent activation energies of the relaxation process using eq. (4). This equation, for the different materials, is shown in Figure 2.

$$\log f = \log f_0 + \Delta H / 2.303 RT \qquad (4)$$

Table VII expresses the calculated values of the energy, together with the dynamic glass transition temperature, calculated for a frequency of 5 Hz.

As observed, the transition temperature moves to higher values and the activation energy increases, attributed to the presence of a strong interface,[17] which again confirms the existence of bonds between the fiber and the matrix as a result of the conventional adhesive in sample C and the azide bonded to the fiber in D.

Figure 3 represents the variation of the loss factor, tan δ, with the temperature between 30 and 90°C. In sample B, without adhesive, there is a slight increase of tan δ above 60°C, which can be associated with the relaxation of the fiber. The loss factor falls at higher temperatures. In the curves for samples C and D, the increase of tan δ is greater, which, in our
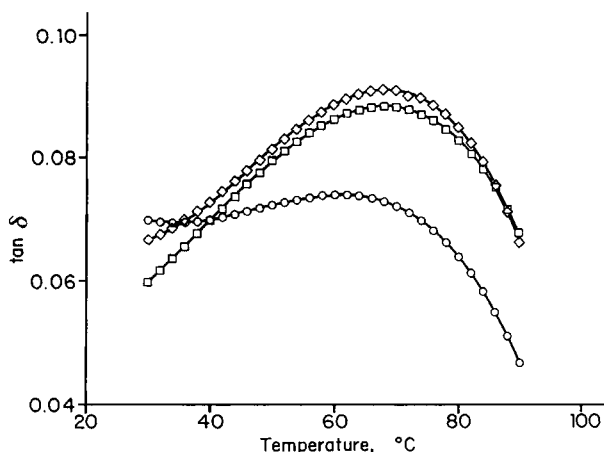
Figure 3 Variation of tan δ with the temperature, in the range 20–90°C. Symbols are as in Figure 2.

opinion, can only be due to the addition of the two relaxations related to the fiber and the interface, which would appear at close temperatures with the latter masked by the first. Behavior in these two cases is similar, but differs from the sample without adhesive; while the only difference between all of them is the presence of a bonding agent, conventional in one and azide in the other.

CONCLUSIONS

The research work described confirms the stated hypotheses. The results indicate that the fibers are modified by their reaction with the azide, producing a composite material with a set of properties similar to the material prepared with conventional adhesive.

This study will serve to set future lines of action with respect to the use of diazides as agents for creating polymeric–fiber interfaces in composite materials reinforced with short fibers.

REFERENCES

1. L. A. Goettler, in *Handbook of Elastomers. New Developments and Technology*, Marcel Dekker, New York, 1988, p. 215.
2. S. R. Moghe, *Rubber Chem. Technol.*, **49**(5), 1160 (1976).

Table VII Transition Temperature and Activation Energy of the Relaxation Process

Sample	$T_{g,d}$	ΔH (kJ/mol)
B	−53.5	118.2
C	−48.9	180.9
D	−51.4	160.2

3. L. A. Goettler and K. S. Shen, *Rubber Chem. Technol.,* **56**(3), 619 (1983).
4. T. S. Solomon, *Rubber Chem. Technol.,* **58**(3), 561 (1985).
5. J. L. de Benito, L. Ibarra, and L. González, *Kauts Gummi Kunstst.,* **43**(8), 697 (1990).
6. J. L. de Benito, L. Ibarra, and L. González, *Kauts Gummi Kunstst.,* **43**(2), 146 (1990).
7. J. L. de Benito, Doctoral Thesis, Universidad Complutense de Madrid, Spain, 1991.
8. T. Curtius, *Chem. Ber.,* **23**, 3023 (1890); P. A. S. Smith, *Org. React.,* **3**, 337 (1946).
9. E. Perry and J. Savory, *J. Appl. Polym. Sci.,* **11**, 2473 (1967).
10. L. Ibarra and C. Chamorro, *J. Appl. Polym. Sci.,* **43**, 1805 (1991).
11. A. P. Foldi, *Rubber Chem. Technol.,* **49**(2), 379 (1976).
12. L. Ibarra and C. Chamorro, *Polym. Composites,* **10**(4), 256 (1989).
13. J. E. O'Connor, *Rubber Chem. Technol.,* **50**(5), 945 (1977).
14. M. Ashida, *International Polym. Sci. Tech.,* **12**(8), 47 (1985).
15. A. Y. Coran, K. Boustany, and P. Hamed, *J. Appl. Polym. Sci.,* **15**, 2471 (1971).
16. T. Noguchi and S. Mashimo, *J. Appl. Polym. Sci.,* **29**, 661 (1984).
17. M. Ashida, T. Noguchi, and S. Mashimo, *J. Appl. Polym. Sci.,* **30**, 104 (1985).