

# Functionalization of Polyester PET Fibers

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## SYNOPSIS

In order to promote chemical linkage between polyester PET fibers and thermoplastic or elastomer matrices, a diazide derivative has been synthesized and reacted with the free hydroxyl groups of the fibers. The completion of the reaction was controlled by means of IR spectroscopy and chemical analysis, and fiber characterization was carried out by thermogravimetric and DSC techniques. The obtained results permit the determination of the suitability of the synthesized diazide to functionalize PET fibers that could be used as reinforcing fibers for polymer matrices composites. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Almost any organic textile fiber can be incorporated into a composite structure, but because of their relatively low stiffness, most of these fibers are used as reinforcements with even lower stiffness matrix materials, such as rubbers and thermoplastics.<sup>1</sup> So, as has been previously shown, increases of about 300 and 260% in LDPE tensile modulus have been obtained with the incorporation of 40% by weight of polyester PET and polyamide short fibers, respectively.<sup>2,3</sup>

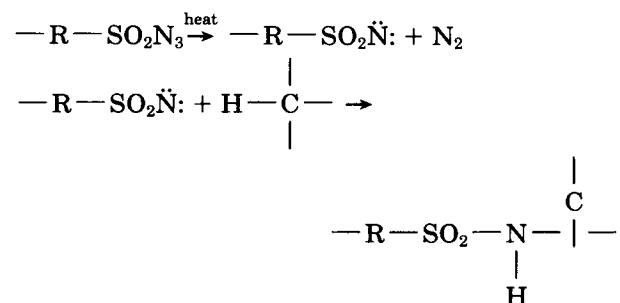
On the other hand, in the rubber industry, there are specific properties in short fiber composites that cannot be duplicated by cord construction. Some examples of these are across-the-thickness, flexural and compression stiffening, reduced molding shrinkage, improved tear and abrasion resistance, damping characteristics, and solvent resistance. In fact, these effects have been observed in previous experiences carried out in our laboratories.<sup>4</sup> These properties have been utilized in some commercial examples: belts, hoses, diaphragms, gaskets, and energy managements, for example. Good dispersion of the short fibers within the rubber matrix is of prime consideration for obtaining maximum performance in these applications. Therefore, fibers pretreated for improved mixing, as well as bonding to the polymer phase, are preferred.

In order to improve the physical performance of mineral filled or reinforced polymers, titanate and

silane coupling agents have been used.<sup>5</sup> These agents are bifunctional molecules, containing alkoxy silane moieties capable of reacting with the surface silanol groups of an inorganic filler, and an organofunctional group that reacts, or at least strongly interacts, with the polymer matrix.

However, the unique chemistry of azidosilane coupling agents allows for covalent attachment to any available carbon–hydrogen bond, thus offering considerably more versatility to the end user. Treatment of mica, glass microspheres, milled glass fibers, and commercial chopped fiberglass with azidosilane coupling agents<sup>6,7</sup> has shown to improve significantly the mechanical properties of these fillers/reinforcements filled polyolefines. This reinforcing effect occurs in polyolefines without the vis-breaking or crosslinking side reactions common to peroxide grafting systems. The nitrene insertion reaction also applies to numerous other polymers containing the C–H bond, such as nylons and polyesters.

The azide decomposes to yield a highly reactive singlet nitrene intermediate, which inserts into any available carbon–hydrogen bond.<sup>8,9</sup> The reaction between sulfonyl azide and polymer is accomplished as follows:



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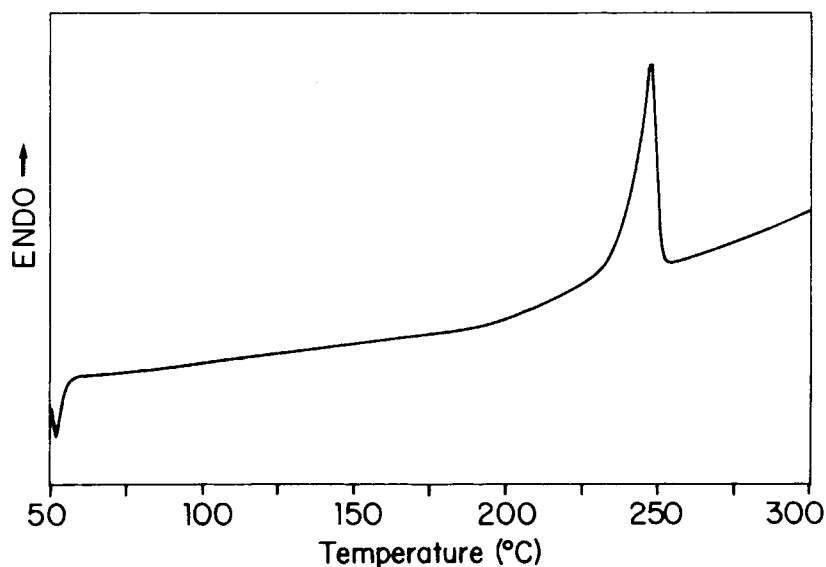


Figure 1 DSC of the polyester PET fiber.

The thermal decomposition behavior of sulfonyl azides has been widely studied and it has been shown that, at ambient temperature, the half-life of the azido group is on the order of four hundred years, so that normal filler treatment will not prematurely activate the molecule.<sup>10</sup> However, under typical plastic compounding conditions (e.g., 200–210°C, with a 3 min extruder residence time for mica/PP), 95% of the azido silane groups have reacted. Likewise, the use of diazides as crosslinking agents in dienic<sup>11</sup> and saturated<sup>12</sup> elastomers has also been investigated, and it has been shown that the reaction rate of the crosslinking process is affected by the chemical nature of the polymers, basically by its degree of unsaturation.

The primary goal of this study is to pretreat polyester PET fibers with a previously synthesized sulfonyl-carbonyl diazide, which reacts with the free hydroxy groups of the poly(ethyleneterephthalate) fibers through the isocyanate groups, originated by the Curtius transposition of the carbonyl-azide ones.<sup>13</sup> After the reaction with the fiber has taken place, the resulting product is stable and can be stored without detrimental effects.

The chemical structure of the azide compound makes it readily detectable by analytical techniques, infrared spectroscopy being the most important one. The azide group has a strong absorbance in a relatively uncluttered region of the infrared spectrum (approximately 2105  $\text{cm}^{-1}$ ); one can readily monitor its presence on the fibers, even at low addition levels, by using a spectral subtraction approach.

Because of its particularly effective reactivity with polyolefins, the focus of future work will be on filled thermoplastics and elastomers.

## EXPERIMENTAL

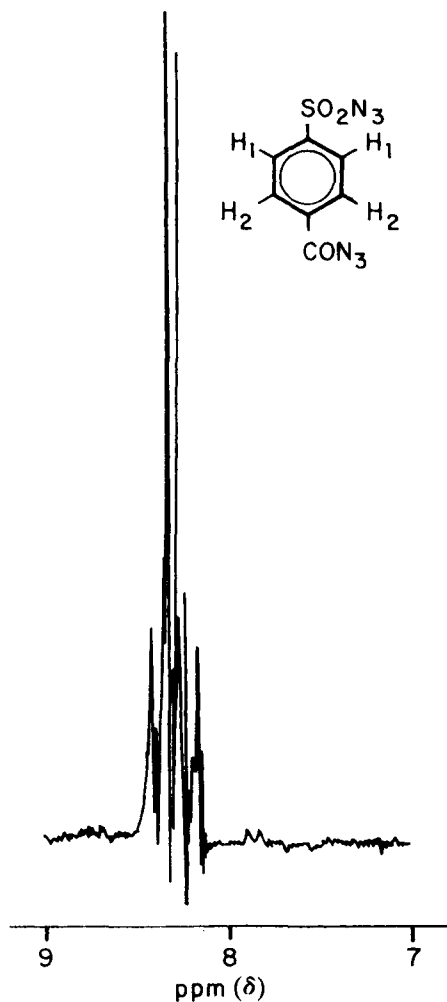
### Materials

Textile short polyester PET fibers, delivered by Velutex-Flock S.A., whose DSC and technical characteristics are shown in Figure 1 and Table I, respectively, were used. The acid number of the PET was negligible and its hydroxyl number was 77.3, as calculated by acetylation of the fibers and titration of the solution with sodium hydroxide 0.1 N. From this result, the mol wt of the polyethyleneterephthalate fibers was deduced to be 14,300.

*p*-Chlorosulfonyl Benzoic acid, delivered by Aldrich-Chemie, was used as a raw material to obtain the diazide derivative.

Table I Technical Characteristics of Polyester PET Fibers Measured at 20°C and 65 Relative Humidity

Density	1.38 $\text{g}/\text{cm}^3$
Melt Temperature	250/260°C
Tensile Strength	2.9/3.7 dN/dtex
Strain to Break	85/105%



**Figure 2** NMR spectrum of the sulfonyl-carbonyl diazide of the benzoic acid.

### Synthesis of the *p*-Sulphonyl-Carbonyl Diazide of the Benzoic Acid

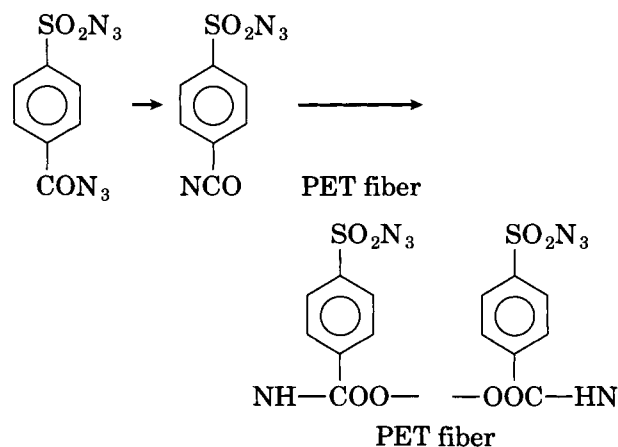
The sulphonyl-carbonyl diazide of the benzoic acid was synthesized following a previously described

procedure.<sup>14</sup> Briefly, the *p*-chlorosulfonyl benzoic acid was reacted with sodium azide to obtain the *p*-sulfonyl azide of the benzoic acid. This product was treated with thionyl chloride in order to obtain the *p*-chloro-sulfonyl azide of the benzoic acid chloride. Finally, through the reaction of this chloride acid with sodium azide, the sulfonyl-carbonyl diazide of the benzoic acid was obtained.

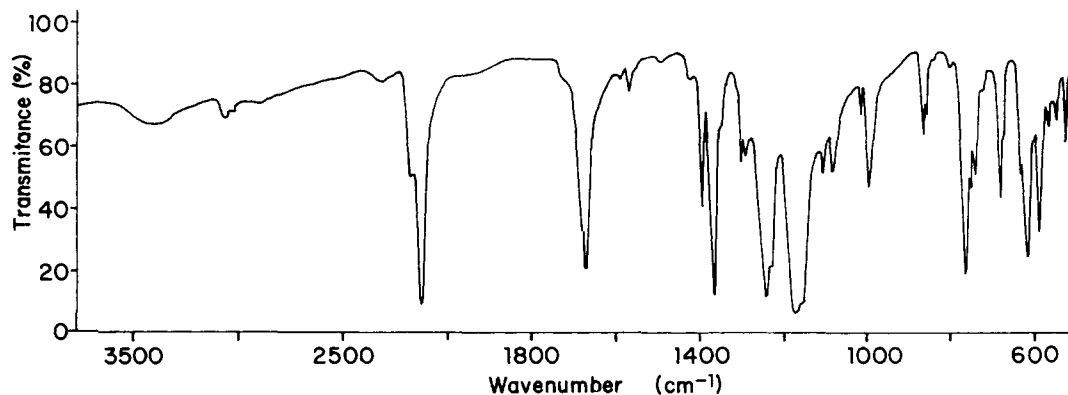
### Chemical Treatment of Polyester PET Fibers

The reaction between the previously obtained sulfonyl-carbonyl diazide derivative and the polyester PET fibers was carried out at 80°C, in benzene and in total absence of humidity. Under these conditions, the carbonyl azide group underwent a Curtius transposition to a isocyanate group, which immediately reacted with the end hydroxyl groups of the PET fibers. So, we can attach aromatic rings, with a sulfonyl azide group in the para position, to the fibers.

The scheme of reaction can be represented as follows:



Briefly, the process can be described as follows: 0.6 g of *p*-sulfonyl-carbonyl diazide of benzoic acid



**Figure 3** Infrared spectrum of the sulfonyl-carbonyl diazide of the benzoic acid.

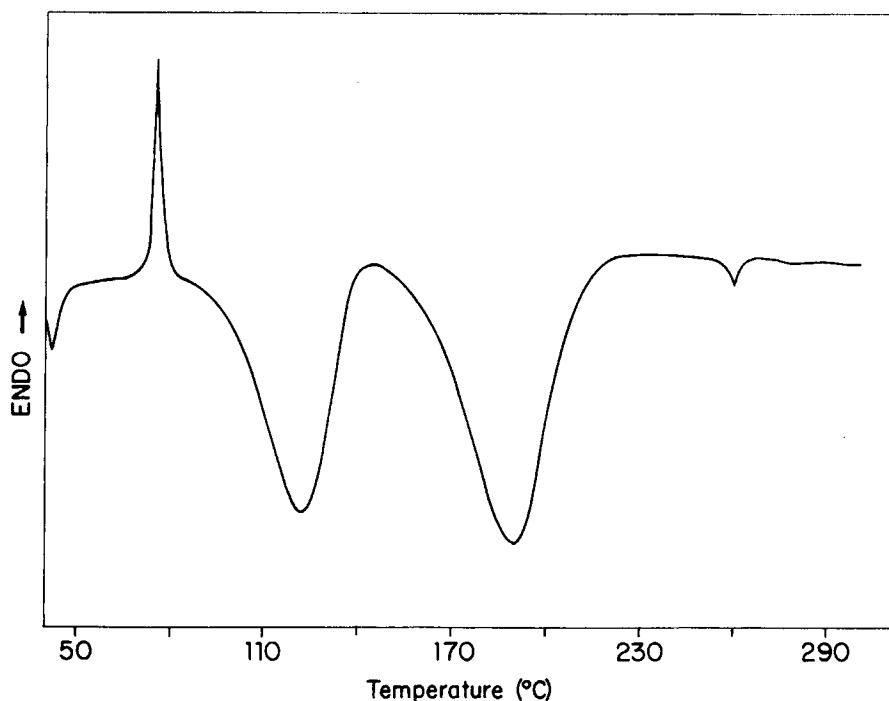


Figure 4 DSC of the sulfonyl-carbonyl diazide of the benzoic acid.

are dissolved in 300 mL of dry benzene, using a double-wall reactor, which was entirely isolated from the outside to avoid any contact with humidity. 30 g of dry short PET fibers were added while stirring. The reaction was performed at 80°C. The process was followed by sampling the reactant solution, taking aliquot parts at every 15 min. The decrease of the absorption band at 2105  $\text{cm}^{-1}$  in the IR spectra, corresponding to the azide groups, was used to control the reaction progress. The reaction was completed at about 4 h. Then the fibers were filtered off and dried in an oven at 60°C.

#### Characterization Procedures

IR studies were carried out on a Perkin-Elmer, model 457, using KBr pellets or a 0.1 thickness NaCl cell for solid and liquid samples, respectively.

The NMR spectra were obtained on a Varian apparatus, model EM-390 90 MHz, using TMS as reference.

DSC curves were obtained on a Perkin-Elmer DSC 7 apparatus, with samples of about 10 mg, at a heating rate of 10°C/min, in an inert gas atmosphere.

Thermogravimetric measurements were carried out on a Perkin-Elmer TA system 4, following a

special procedure that permits the detection of small weight losses.

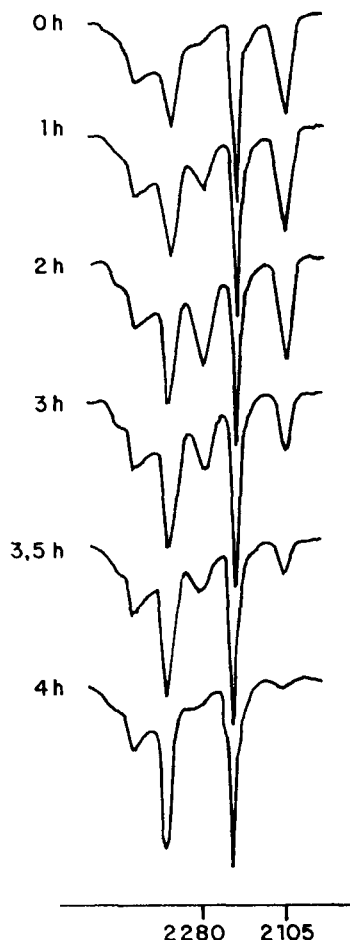
The carbon, hydrogen, and nitrogen contents were measured in a Perkin-Elmer 240 CHNO.

## RESULTS AND DISCUSSION

The sulfonyl-carbonyl diazide of the benzoic acid was characterized by NMR and IR spectroscopy, DSC, and chemical analysis, as shown in Figures 2 to 4, and Table II. As can be seen in Figure 3, the NMR spectrum shows the bands at 8.33 and 8.28 ppm corresponding to the H1 and H2 hydrogens of the diazide derivative. On the other hand, the band at approximately 2105  $\text{cm}^{-1}$  with a small shoulder, in the IR spectrum corresponds to the azide groups

Table II Chemical Analysis of the *p*-Sulfonyl Carbonyl Diazide of the Benzoic Acid

	Theoretical	Experimental
C (%)	33.33	33.60
H (%)	1.58	1.80
N (%)	33.33	33.04



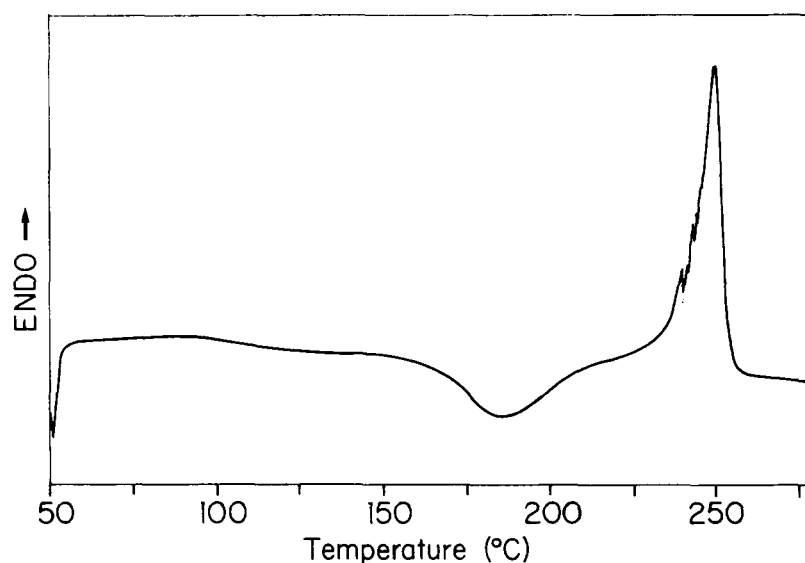
**Figure 5** Infrared spectra of the solution as a function of the reaction time. (Bands at 2280 and 2105  $\text{cm}^{-1}$  correspond to the isocyanate and azide groups, respectively.)

and, finally, the DSC curve shows the melting point of the diazide derivative at about 80°C and the exothermic peaks corresponding to the decomposition of the carbonyl and sulfonyl azide groups that appear at 125 and 185°C, respectively. The yield of the reaction was about 95% and the product was kept at low temperature until being used.

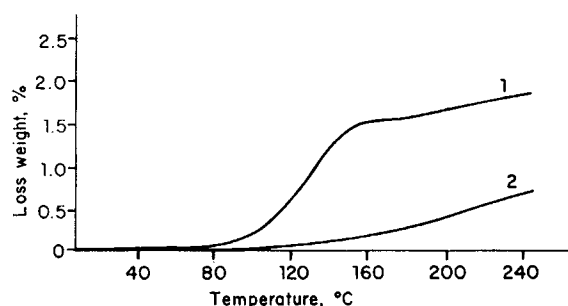
The progress of the reaction between the diazide compound and the PET fibers was followed by IR spectroscopy, as is shown in Figure 5, where the infrared spectra of the solution as a function of reaction time is graphically represented. As it can be seen, the band at 2105  $\text{cm}^{-1}$ , corresponding to the azide groups, is continuously decreasing, while the band at 2280  $\text{cm}^{-1}$ , which corresponds to the isocyanate group, initially increases as the Curtius transposition takes place, and later on decreases again as the reaction with the fiber is progressing.

When the reaction is completed, as is determined from the IR spectra (about 4 h), the fibers were separated by filtration and characterized by chemical analysis, DSC, and thermogravimetric techniques.

The hydroxyl number of the modified PET fibers was negligible, which means that all the hydroxyl groups of the fibers have reacted with the diazide derivative. From Figure 6, a depression in the DSC curve of the modified fiber can be observed at about 185°C, which corresponds to the decomposition of the sulfonyl azide group that is present in the PET fibers. This temperature must be taken into account to prepare composite materials based on polyolefin matrices in order to achieve a chemical linkage between the modified PET fibers and the polymer ma-



**Figure 6** DSC curve of the modified PET fiber.



**Figure 7** Thermograms of the modified (1) and unmodified (2) PET fiber.

trix. So, an increase in the physical and mechanical properties of these composites can be expected.

The thermogravimetric curve of the modified fiber (Fig. 7) shows that almost all the diazide has been incorporated to the PET fibers.

## CONCLUSIONS

From the above results it is deduced that:

- The *p*-sulfonyl carbonyl diazide of the benzoic acid is a suitable reactive to functionalize PET fibers through the introduction of reactive azide groups in the fiber surface.
- The reaction between the diazide derivative and the PET fibers takes place through the isocyanate groups coming from the Curtius transposition of the carbonyl azide groups, in a relatively short time (about 4 h), and can be easily controlled by the IR spectra of the reactant solution.
- The functionalization of the PET fibers has been confirmed by means of DSC and TGA techniques.
- Obviously, the functionalized fibers may have a great influence on the mechanical and rheological properties of polymer composites. This is the goal of our present studies and will be the subject of future communications.

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