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### **FTIR Study on Chemical Modification of E-Glass Short Fiber with Tert-Butyldiphenylchlorosilane**

A. Larena<sup>a</sup>; J. Martinez Urreaga<sup>a</sup>; M. U. de la Orden<sup>b</sup>

<sup>a</sup> Dpto. Ing. Química Ind., E.T.S.I. Industriales, MADRID <sup>b</sup> Dpto. Química Orgánica, I, E.U. de Optica U., MADRID

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FTIR STUDY ON CHEMICAL MODIFICATION OF E-GLASS  
SHORT FIBER WITH TERT-BUTYLDIPHENYLCHLOROSILANE

Key words; FTIR Spectroscopy; Chemical Modification;  
E-Glass Fiber; Tert-butyldiphenylchloro-  
silane.

A. Larena, J. Martínez Urreaga

Dpto. Ing. Química Ind., E.T.S.I. Industriales,  
U. Politécnica de Madrid, 28006-MADRID.

M.U. de la Orden.

Dpto. Química Orgánica I, E.U. de Optica,  
U. Complutense de Madrid, 28031-MADRID.

ABSTRACT

The reaction of E-glass short fibers with tert-butyldiphenylchlorosilane (TBDPCS) and trimethylchlorosilane (TMCS) was studied by FTIR spectroscopy in water and in toluene. Fiber coating obtained from TMCS in aqueous solution contained siloxane bonds, by which the trimethylsilyl group was attached to

the glass surface. Coatings obtained from TBDPCS, however, consisted of silane and silanol, and no siloxane bonds were observed. This may be attributed to the effect of steric hindrance in the reaction.

## INTRODUCTION

Glass fibers are commonly used in reinforced plastics because they are inexpensive and improve some material properties (e.g. impact strength and rigidity in thermoplastics).<sup>1-4</sup> Usually, coupling agents are applied to the fibers in their manufacture to improve fiber-matrix adhesion, one of the major factors governing the processing and properties of composite materials.

These coupling agents are mostly silanes of general formula  $\text{RSiX}_3$ , where R is an organofunctional group and X is a group such as -OR or -Cl.

These silanes, as well as monofunctional silanes ( $\text{R}_3\text{SiX}$ ), are also used in the organic functionalization of silicas for high performance liquid chromatography.<sup>5,6</sup>

The reaction of silanes with glass fibers depends on the nature of the silane, the surface characteristics of the fiber, and the reaction conditions. To

study the influence that the organic substituents at the silicon atom have on this reaction, we used Fourier Transform Infrared (FTIR) Spectroscopy to study the reaction of E-glass short fibers with TBDPCS, a silane with high steric hindrance. The results given by TBDPCS were compared with those given by TMCS.

Solutions in water and in toluene were used as reaction media, and also was studied the effect of pyridine as a silanization catalyst in toluene.<sup>7</sup>

#### EXPERIMENTAL

Glass fiber was treated with 0.5-10 % (v/v) solutions of silanes in either water (pH 3.3, stirring for 1h at room temperature) or toluene (4h at reflux temperature). When pyridine was used, its concentration was 5% by volume. Treated fiber was filtered under vacuum and washed with solvent fractions for 5min, after which it was dried at room temperature for 24h.

TBDPCS, TMCS (Sigma), toluene and anhydrous pyridine (Merck) were used as received. Doubly distilled (in glass) water was used. E-glass fiber (average length 180 m, average diameter 10 m) was supplied

by Cristalería Española, and was heat-cleaned at 500°C for 4h.

FTIR spectra (90 scans,  $2\text{cm}^{-1}$  resolution) were recorded on a Nicolet 20 SXC spectrophotometer in transmission mode. Solid samples were analyzed in spectroscopy grade KBr pellets. Liquid samples were analyzed in cells with CsI windows.

Thermograms were recorded on a Mettler Thermoanalyzer-2 thermobalance, at a heating rate of 5°C/min. Gas (dry air or dry nitrogen) flow rate was 100ml/min.

## RESULTS AND DISCUSSION

### A.- SILANE HYDROLYSIS

Si-Cl bond hydrolysis is generally accepted as an intermediate step in the attachment by siloxane bonds of these chlorosilanes to glass surfaces. Hydrolysis was studied by FTIR spectroscopy in water and toluene solutions of TMCS and TBDPCS.

TMCS was hydrolyzed to form hexamethyldisiloxane (HDMSO, absorption band at  $1050\text{cm}^{-1}$ ) by reaction with water. Pyridine catalyzed this reaction in toluene. However, no hydrolysis was observed for TBDPCS at room temperature. In refluxing toluene, pyridine catalyzed TBDPCS hydrolysis with silanol formation

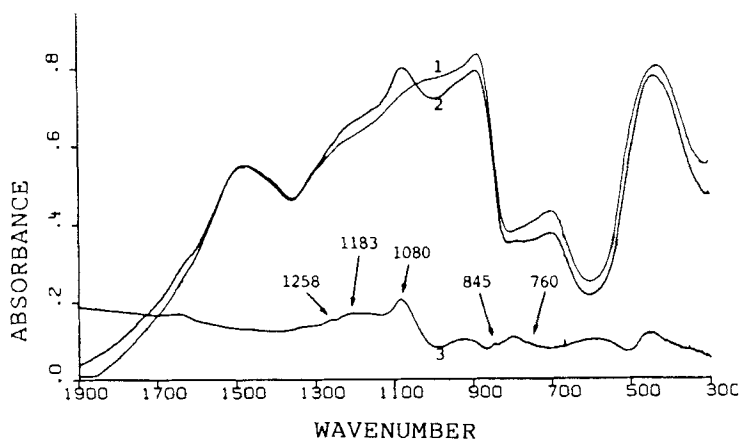


FIG.1.- FTIR spectra of: E-glass short fibers (1); E-glass fibers treated with aqueous TMCS (2). 3: Difference spectrum.

(band at  $1067\text{cm}^{-1}$ ), but no disiloxane formation was observed. Steric hindrance could explain this different behaviour of TBDPCS.

## B.- GLASS COATINGS

### B.1.- Aqueous Solution

The FTIR spectra of fibers treated with aqueous TMCS (10%, v/v) showed the existence of a coating (difference spectrum, Fig.1) containing the trimethylsilyl group (characteristic bands at 760, 845, and  $1258\text{ cm}^{-1}$ ). The broad bands at 1080 and  $1183\text{cm}^{-1}$  seem to indicate that this coating is attached to the fiber by siloxane bonds of the  $\text{Si}_{\text{silane}}-\text{O}-\text{Si}_{\text{glass}}$

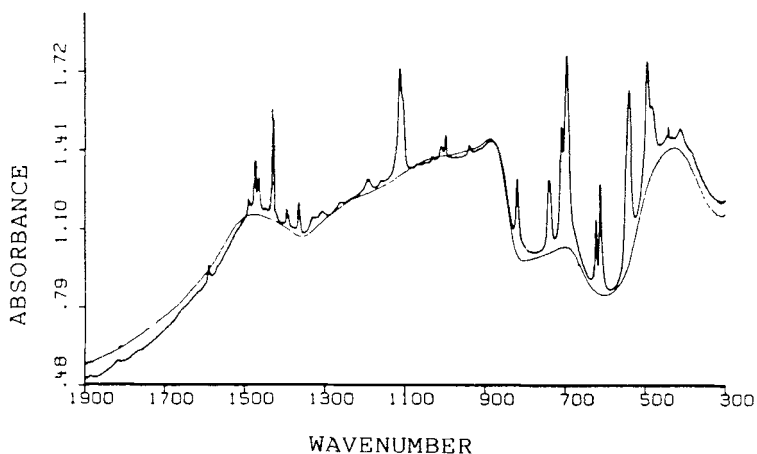


FIG.2.- FTIR spectra of E-glass fibers treated with aqueous TBDPCS and untreated fibers (baseline)

type. The same attachment was previously observed in fibers treated with chloromethyldimethylchlorosilane.<sup>8</sup>

The bands at 455, 800, 920 and 1650  $\text{cm}^{-1}$  were attributed to the slight leaching (by HCl formed as a consequence of silane hydrolysis) of soluble oxides from the glass surface. Such leaching would generate reactive hydroxyl groups at the fiber surface.<sup>8</sup>

On the other hand, the FTIR spectrum of fibers treated with aqueous TBDPCS (Fig.2) shows the silane characteristics bands, indicating that these fibers

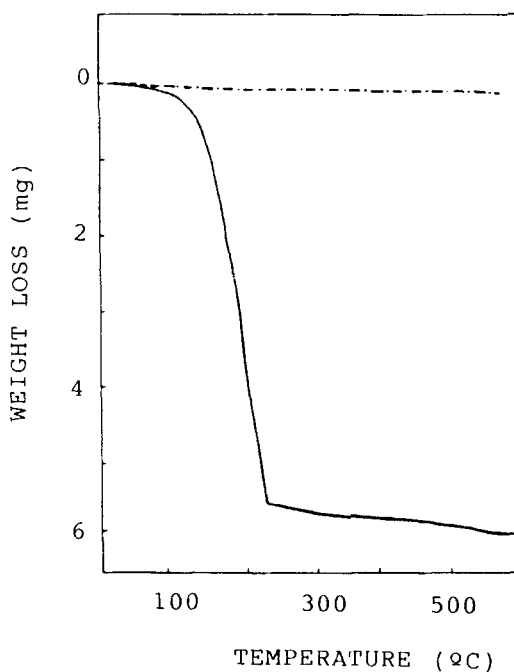


FIG.3.- Thermograms of: E-glass fibers treated with aqueous TBDPCS (1); Treated fibers washed with THF (2). Initially: 40mg. Gas: dry air.

contain a substantial amount of silane. A small absorption peak at  $1067\text{ cm}^{-1}$  is also noted. This band seems to indicate the presence of a small amount of silanol, which may facilitate the adsorption of silane onto the fiber. However, no siloxane bonds were observed in this coating, suggesting that steric hindrance plays a major role in these reactions.

Consequently, the coating is only physically adsorbed and may be removed by heating at low tempera-



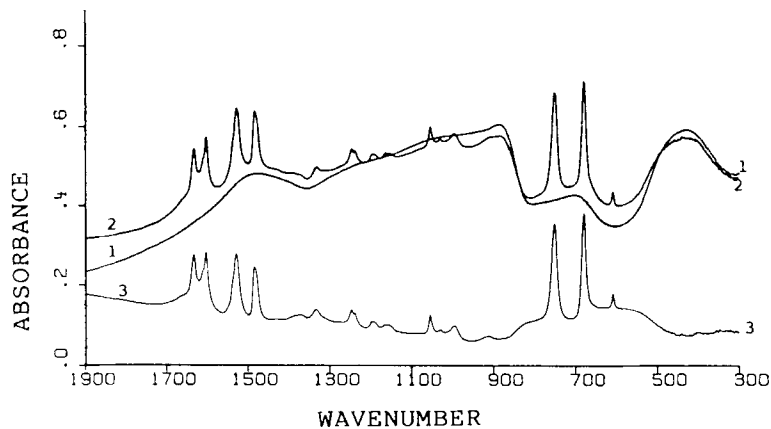
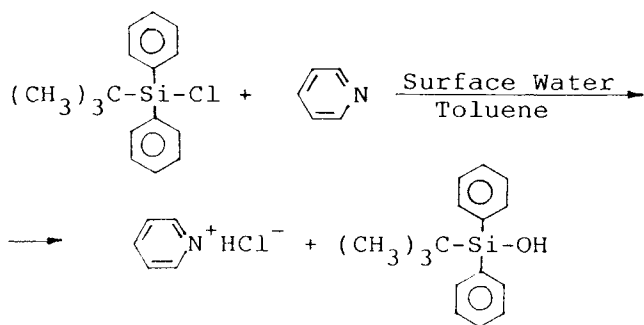


FIG.4.- FTIR spectra of: E-glass fibers (1); E-glass fibers treated with TMCS and pyridine in toluene (2). 3: Difference spectrum.



Scheme 1

tures, as shown by thermogravimetric analysis, or by washing with a solvent such as THF (Fig.3).

## B.2.- Toluene

Glass fibers were unaltered by treatment with TBDPCS or TMCS in refluxing toluene in the absence of pyridine. These silanes were not hydrolyzed under these conditions.

Fiber treated in refluxing toluene with TMCS (10%, v/v) and pyridine contained an average of 10% by weight of pyridinium chloride (identified by comparing the FTIR spectrum of the coating (Fig.4) with that of homemade pyridinium chloride).

The coating obtained by pyridine-catalyzed reaction with TBDPCS (10%, v/v) apparently contained silane and silanol, in addition to pyridinium chloride (Scheme 1).

The smaller amount of coating (1% by weight) obtained from TBDPCS could be caused by slower hydrolysis of TBDPCS due to steric hindrance.

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