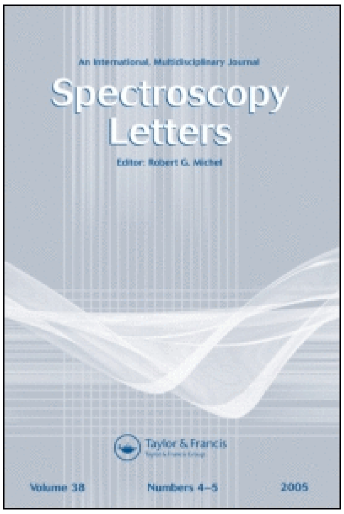
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Ultraviolet Spectroscopic Study of the Cellulose Functionalization with Silanes

M. U. de la Orden[a]; M. C. Matías[b]; C. González Sánchez[c]; J. Martínez Urreaga[b]
[a] Departamento de Química Orgánica I, E. U. Optica, Universidad Complutense de Madrid, Madrid, Spain [b] Departamento de Ingeniería, Química Industrial y del Medio Ambiente, E.T.S.I. Industrials Universidad Politécnica de Madrid, Madrid, Spain [c] Departamento de Ingeniería Química y Tecnología del Medio Ambiente, Universidad de Oviedo, Oviedo, Spain

To cite this Article de la Orden, M. U. , Matías, M. C. , Sánchez, C. González and Urreaga, J. Martínez(1999) 'Ultraviolet Spectroscopic Study of the Cellulose Functionalization with Silanes', Spectroscopy Letters, 32: 6, 993 — 1003

To link to this Article: DOI: 10.1080/00387019909350044

URL: http://dx.doi.org/10.1080/00387019909350044

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SPECTROSCOPY LETTERS, 32(6), 993–1003 (1999)

ULTRAVIOLET SPECTROSCOPIC STUDY OF THE CELLULOSE FUNCTIONALIZATION WITH SILANES

Keywords: Cellulose ; Silane Coupling Agents ; Diffuse Reflectance UV-VIS Spectroscopy ; Cellulose Reinforced Composites

Downloaded At: 03:18 30 January 2011

M.U. de la Orden[1], M. C. Matías[2], C. González Sánchez[3], J. Martínez Urreaga[2,*]

[1] Departamento de Química Orgánica I, E. U. Optica, Universidad Complutense de Madrid, Arcos de Jalón, S/N. 28037-Madrid, Spain.
[2] Departamento de Ingeniería Química Industrial y del Medio Ambiente, E.T.S.I. Industriales, Universidad Politécnica de Madrid, José Gutiérrez Abascal, 2. 28006- Madrid, Spain.
[3] Departamento de Ingeniería Química y Tecnología del Medio Ambiente, Universidad de Oviedo, Julián Clavería, S/N. 33071-Oviedo, Spain.

ABSTRACT

The reaction of a cellulosic material (Whatman no. 42 filter paper) with two silanes was studied by Diffuse Reflectance Ultraviolet-Visible Spectroscopy and

---

* To whom correspondence should be addressed.
FAX 34 91 3363009
e-mail jmartinez@iqi.etsii.upm.es

Copyright © 1999 by Marcel Dekker, Inc. www.dekker.com

Diffuse Reflectance Fourier Transform Infrared Spectroscopy. The silanes were 3-aminopropyltriethoxysilane (APS) and methyltrimethoxysilane (MS), a silane with a non-reactive organofunctional group. The use of organic peroxides was required in order to achieve an efficient cellulose modification with the silanes. The Diffuse Reflectance UV-VIS Spectroscopy can provide valuable information about the mechanism of the reactions between silanes and cellulose. The reaction between APS and cellulose involves not only the silanol groups of the silane, but also the amino groups. The spectra of APS-treated celluloses show an absorption band at 325 nm. This band was assigned to imines produced in the reaction of the amino groups of APS with the cellulose. This absorption band increased when APS-treated cellulose was cured at 120°C. The amino groups attached to the cellulose dissappeared in this process

Downloaded At: 03:18 30 January 2011

INTRODUCTION

Silane coupling agents have been extensively used in the last decades for the surface chemical modification of materials used as reinforcements for polymer-matrix composites, in order to improve compatibility between the polymer and the reinforcement[1-4]. The general formula of these silanes is $RSiX_3$, where X is an easily hydrolyzable group, such as $-O-CH_3$ or -Cl, and -R is the organofunctional group that should provide the desired compatibility with the matrix. Aminosilanes like APS (3-aminopropyltriethoxysilane) or AAPS (N-2-aminoethyl-3-aminopropyltrimethoxysilane) have been widely used in the functionalization of inorganic fillers and reinforcements, as glass fiber, mainly for epoxy-matrix composites[5-7]. Aminosilanes have also been used as coupling agents in composites made from cellulosic materials and thermoplastic matrices. Maldas et al.[8] used APS, in conjuction with maleic anhydride, as coupling agents in wood fiber-polystyrene composites, with good results.

The mechanism of the reaction between silane coupling agents and inorganic reinforcements, such as glass fiber, has been extensively studied employing several experimental techniques, such as Fourier Transform Infrared (FTIR) Spectroscopy, X-ray Photoelectron Spectroscopy (XPS), Thermal Analysis (TA) and others. The first step of the general mechanism is the hydrolysis of the silane to form silanol (Si-OH) groups. After hydrolysis, the coupling agent can develop either hydrogen or covalent (after curing) bonds with some hydroxyl groups of the reinforcement.

However, when more reactive reinforcements, such as cellulosic materials, are functionalized with a silane coupling agent, a more complex reaction process may be expected. For example, for cellulosic materials the functionalization process depends on the use of free-radical sources such as organic peroxides. Xanthos[9] reported that the performance of some cellulose reinforced composites was improved when a methacryloxysilane was used as a coupling agent in conjunction with organic peroxides. Beshay and Hoa[10] reported that radical sources were necessary to form covalent bonds between silane coupling agents and cellulosic materials.

On the other hand, when cellulosic materials react with silane coupling agents, besides the condensation between cellulose hydroxyl groups and silanol groups, other secondary reactions may occur between reactive groups of the cellulose and some silane organofunctional groups. These secondary reactions, as well as processes that could occur during the curing of treated materials, have been scarcely studied to the present.

We have studied in this work the reaction of a reference cellulosic material with two coupling agents, as well as the thermal curing of silane-treated materials. APS and MS (methyltrimethoxysilane), a silane having a non-reactive organofunctional group, were selected for the study of possible secondary reactions during the functionalization of cellulosic materials with silanes. Two experimental techniques were used : Diffuse Reflectance Fourier Transform Infrared (DRIFT) Spectroscopy and Diffuse Reflectance Ultraviolet Spectroscopy. This second technique has been scarcely used in this area to the present. However, it may provide some useful results, mainly for the rapid

Downloaded At: 03:18 30 January 2011

detection of secondary reactions taking place during the functionalization process.

MATERIALS AND METHODS

Materials

The cellulosic material used was Whatman no. 42 ashless filter paper. It is an almost pure cellulose, consisting of >99% cellulose. The only pretreatment was drying in air at 65°C for 18 h. MS was kindly supplied by Dow Corning Iberica S.A. (Barcelona, Spain). APS (Union Carbide) was also kindly supplied by Cristalería Española S.A. (Madrid, Spain). The two silanes were used as received. Benzoyl peroxide (Merck) and the solvents (Fluka) were used also without further purification.

Treatment with Silanes

1 g of cellulose was added to 20 ml of silane solutions in acetone-water (95/5, v/v). Silane concentration varied from 2 to 10% and benzoyl peroxide (when used) was 0.3% (based on the cellulose weight). The reaction mixture was kept under nitrogen atmosphere at 60°C for 2 h. After washing with the solvent, treated celluloses were oven-dried at 65°C for 18 h. Curing of treated samples was made at 120°C in air.

Spectroscopy

The DRIFT spectra before and after treatments were recorded with a Mattson 3020 FTIR Spectrometer, using a Specac diffuse reflectance accessory. Each spectrum was recorded at a resolution of 4 cm^{-1}, with a total of 90 scans. The Diffuse Reflectance UV spectra were obtained with a Shimadzu 2401 PC

Downloaded At: 03:18 30 January 2011

UV-VIS Spectrophotometer, using a Shimadzu diffuse reflectance accessory, at 200 nm.min^{-1}. All reflectance spectra were corrected according to the Kubelka-Munk function.

RESULTS AND DISCUSSION

We have studied the reaction of the cellulose with the two silane coupling agents, both in the presence and in the absence of benzoyl peroxide as a free radical source. Fig. 1 shows the diffuse reflectance UV-VIS spectrum of the untreated material, as well as the spectra corresponding to samples treated with 5% by weight of MS. Fig. 2 illustrates the spectra of APS-treated materials. From the comparison of the two figures we can deduce that the main effect of the use of inorganic peroxide in the cellulose treatments, was the appearance of a new absorption band centered at ca. 280 nm in the UV-VIS spectra of silane-treated celluloses.

An additional consequence of the cellulose treatment with the aminosilane was the appearance of a new absorption band centered at ca. 325 nm. This absorption was very weak when no peroxides were used in the treatment (Fig. 2). This result appears to indicate that the presence of free radicals is required in order to achieve a more efficient cellulose modification in the treatment with silanes. This result is in good agreement with those reported by Beshay and Hoa[10].

The absorption band at 325 nm was specific for the spectra of APS-treated materials. No similar bands were detected in the spectra of cellulose samples treated with MS, a silane with a non-reactive organofunctional group (Fig. 1). Hence, the band at 325 nm can not be explained by the general mechanism of cellulose modification with silanes, i.e., it can not be assigned to the condensation reaction between silanol groups of hydrolyzed silane and cellulose hydroxyl groups. Thus,the diffuse reflectance UV-VIS Spectroscopy revealed a

Downloaded At: 03:18 30 January 2011

Downloaded At: 03:18 30 January 2011

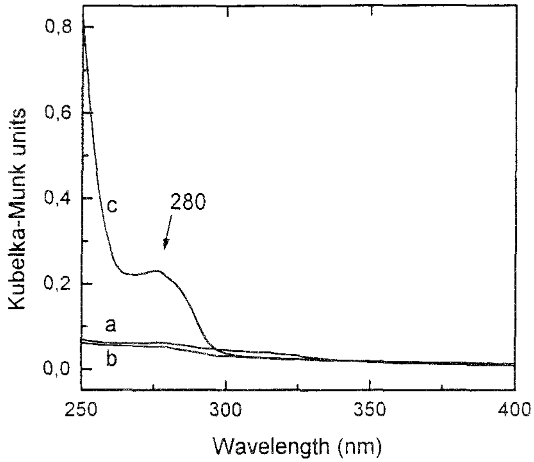


FIG. 1 Diffuse reflectance UV-VIS spectra of: (a) untreated cellulose, (b) cellulose treated with 5% MS, and (c) cellulose treated with 5% MS and 0.3% benzoyl peroxide (all % based on the cellulose weight).

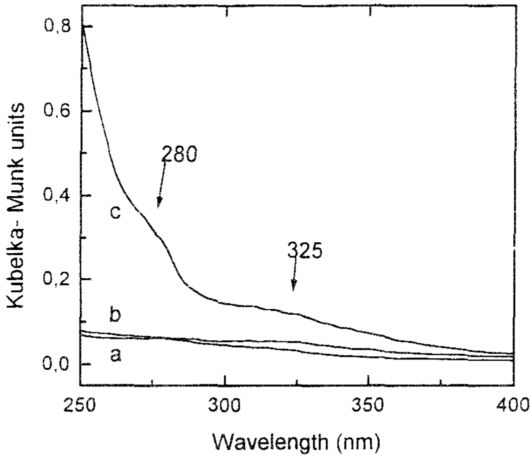


FIG. 2 Diffuse reflectance UV-VIS spectra of: (a) untreated cellulose, (b) cellulose treated with 5% APS, and (c) cellulose treated with 5% APS and 0.3% benzoyl peroxide.

Downloaded At: 03:18 30 January 2011

second cellulose modification mechanism involving the reactive amino groups of APS.

The absorption band at 325 nm was tentatively assigned to imines produced in the reaction between a fraction of the amino groups deposited onto the cellulose and some carbonyl groups existing in the cellulose. Besides the strong π-π^* absorption band at $\lambda < 200$ nm, imines present a weak n-π^* absorption band centered at ca. 300 nm[11] . This absorption maximum strongly depends on the nature of the substituents attached to the imine group. It is well known that amines react with carbonyl compounds to produce imines. Some carbonyl compounds may exist in the untreated cellulose and additional carbonyls may be produced during the cellulose treatment with silanes at 60°C.

Additional evidence of the formation of imines during the treatment of cellulose with APS was obtained from the study of the curing process for the treated materials. These modified materials are usually subjected to curing at temperatures higher than 100°C, and are often used at temperatures near 200°C, as in the melt blending of composites made from thermoplastic matrices and cellulosic reinforcements. The study of the curing process is interesting in order to detect chemical changes in the material at such temperatures.

Fig. 3 shows the diffuse reflectance UV-VIS spectra of cellulose samples treated with MS (5%) and benzoyl peroxide (0.3% based on the cellulose weight), before and after heating in air at 120°C for 60 min. No significant changes were detected in the spectrum, revealing that no significant chemical changes occur during heating of MS-treated celluloses. However, the absorption band at 325 nm clearly increased when cellulose samples treated with APS in the same conditions were cured at 120°C (Fig. 4). This increase was assigned to the formation of additional imine, involving the reaction of some amino groups remaining in the APS-treated cellulose with carbonyl groups generated in the cellulose heating process. Further evidence supporting this hypothesis was obtained from the infrared study of the curing process (Fig. 5). The DRIFT spectra of APS-treated celluloses show an absorption band at 1599 cm^{-1}, which

Downloaded At: 03:18 30 January 2011

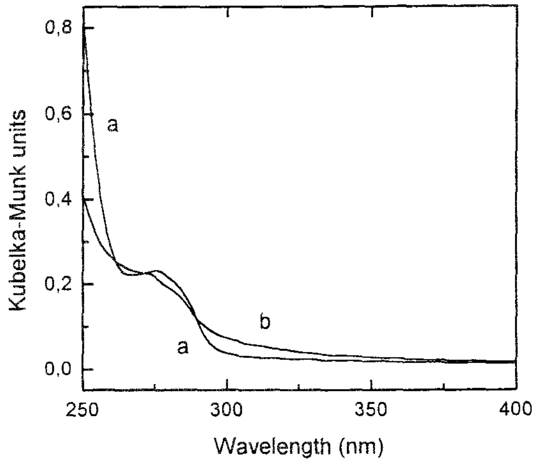


FIG. 3 Diffuse reflectance UV-VIS spectra of cellulose treated with 5% MS and 0.3% benzoyl peroxide before (a) and after (b) heating in air at 120°C for 60 min.

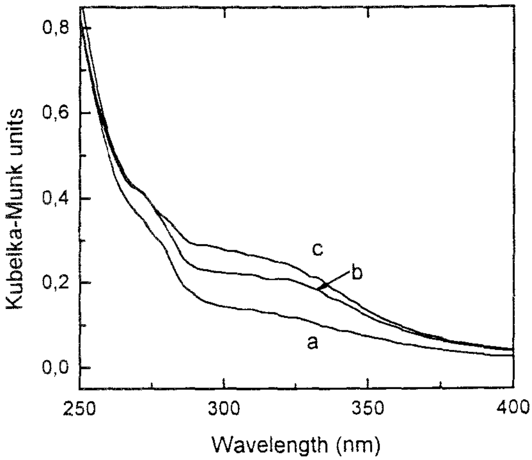


FIG. 4 Diffuse reflectance UV-VIS spectra of cellulose treated with 5% APS and 0.3% benzoyl peroxide before (a) and after heating in air at 120°C for 20 (b) and 60 min (c).

Downloaded At: 03:18 30 January 2011

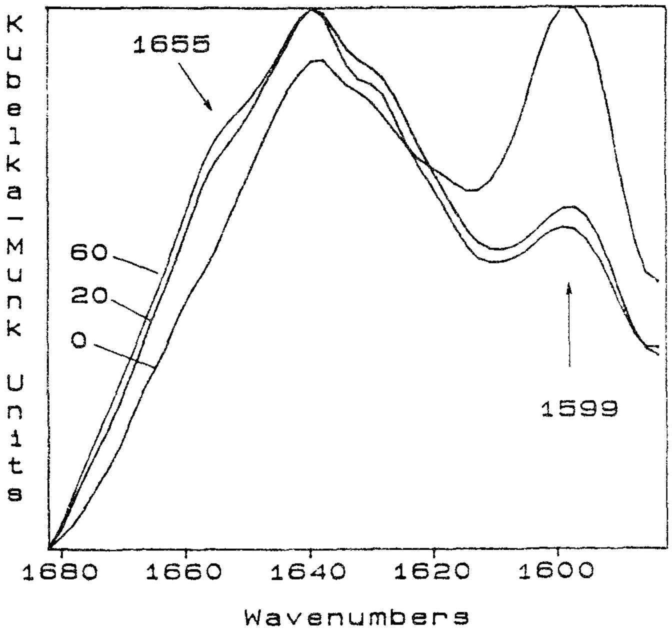


FIG. 5 DRIFT spectra of cellulose treated with 5% APS and 0.3% benzoyl peroxide before and after heating in air at 120°C for 20 and 60 min.

may be assigned to the amino groups deposited onto the cellulose (amine deformation band)[5]. The intensity of this band decreased when the material was heated at 120°C, revealing the disappearance of the amino groups in the curing process. Fig. 5 also shows that a weak band at 1655 cm^{-1} developed in this process. This absorption band was assigned to the imine groups produced in the curing of the material (C=N stretching vibrations)[12].

The results obtained in this work reveal that aminosilane coupling agents can react with cellulosic materials by two parallel mechanisms, one of them involving the reactive amino groups. Heating of aminosilane-treated celluloses can substantially alter the nature of the chemical functionalization of the cellulose. The diffuse reflectance UV-VIS spectroscopy can provide valuable information about the mechanisms of the reactions between cellulose and silane coupling agents, as well as about the chemical changes due to the heating of the treated materials.

ACKNOWLEDGMENTS

The authors are grateful for the partial financial support provided by the Universidad Complutense de Madrid (Project PR156/97-7158).

REFERENCES

1. E.P. Plueddemann. *Silane Coupling Agents.* 2nd ed. New York : Plenum, 1991.

2. Larena A., Matías M.C., Martínez Urreaga J. Thermal Degradation of Polysiloxane Coatings on E-Glass Fiber. A FTIR Study. Spectrosc. Lett. 1992 ; 25 : 1121.

3. Larena A., de la Orden M.U., Martínez Urreaga J. Thermal and Fourier Transform-Infrared Study of E-Glass Short-Fiber Functionalization with Methylvinyldichlorosilane and Vinyltrichlorosilane. J. Colloid Interface Sci. 1992 ; 149 : 34.

4. Maldas D., Kokta B.V. Interfacial Adhesion of Lignocellulosic Materials in Polymer Composites : an Overview. Composite Interfaces 1993 ; 1 : 87.

5. Chiang C.H., Koenig J.L. Fourier Transform Infrared Spectroscopic Study of the Adsorption of Multiple Amino Silane Coupling Agents on Glass Surfaces. J. Colloid Interface Sci. 1981 ; 83 : 361.

6. Culler S.R., Naviroj S., Ishida H., Koenig J.L. Analytical and Spectroscopic Investigation of the Interaction of CO_2 with Amine Functional Silane Coupling Agents on Glass Fibers. J. Colloid Interface Sci. 1983 ; 96 : 69.

7. Dibenedetto A.T., Lex P.J. Evaluation of Surface Treatments for Glass Fibers in Composite Materials. Polym. Eng. Sci. 1989 ; 29 : 543.

8. Maldas D., Kokta B.V., Daneault C. Influence of Coupling Agents and Treatments on the Mechanical Properties of Cellulose Fiber-Polystyrene Composites. J. Appl. Polym. Sci. 1989 ; 37 : 751.

Downloaded At: 03:18 30 January 2011

9. Xanthos M. Processing Conditions and Coupling Agents Effects in Polypropylene/Wood Flour Composites. Plast. Rubber Process. Appl. 1983 ; 3 : 223.

10. Beshay A., Hoa S.V. Improved Interface Bonding between Cellulosic Fillers and Thermoplastics. Sci. Eng. Compos. Mater. 1992 ; 2 : 85.

11. Olsen E.D.. *Métodos Opticos de Análisis.* Barcelona : Reverté, 1990.

12. Conley R.T.. *Espectroscopia Infrarroja.* Madrid : Alhambra, 1979.

Date Received: December 21, 1998
Date Accepted: July 1, 1999

Downloaded At: 03:18 30 January 2011