Eucalyptus Kraft Pulp Fibers as an Alternative Reinforcement of Silicone Composites. I. Characterization and Chemical Modification of Eucalyptus Fibers with Organosilane Coupling Agent

S. U. A. REDONDO, E. RADOVANOVIC, M. C. GONÇALVES, I. V. P. YOSHIDA

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083-970, Campinas, São Paulo, Brasil

ABSTRACT: In this study, bleached *Eucalyptus* fibers obtained by a Kraft pulping process were characterized prior to and after chemical modification with a silane coupling agent, vinyltriethoxysilane, for use as an alternative additive in composites based on silicone. The presence of a silane coating on the fiber surface was observed by infrared, energy dispersive, and X-ray photoelectron spectroscopies. The morphology of the fibers was investigated by field emission scanning electron microscopy. The untreated fibers were ribbon-shaped and had a rough surface, due to the presence of fibrils. The coating reaction conducted in ethanol gave rise to loose fibrils and a more rough surface compared with those of untreated fibers. A smoother surface was observed when fibers were modified in tetrahydrofuran. The surface topography of the fibers was also examined by atomic force microscopy. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2573–2579, 2002

Key words: Eucalyptus fibers, surface modification, silane coupling agent

INTRODUCTION

In the last decade, there has been great demand for environmental friendly materials coming from renewable resources instead of petrochemical sources. Raw materials (biomass) are fundamentally important to sustainable development simply because they can be grown, and consequently are renewable, and can also participate in the ecological biodegradation/regeneration cycles, contrary to nonorganic and fossil materials.[1, 2]

In this sense, the use of cellulosic fibers as reinforcement elements for synthetic polymers is receiving special attention. These fibers offer a number of advantages, such as their renewable, nontoxic, and nonabrasive character, relative low cost, good mechanical properties, high stiffness, low density, and biodegradability.[3–5] Moreover, because of the several kinds of abundantly available vegetable sources, specific properties are dependent on the vegetable specimen chosen, such as wood, sisal, pineapple, coconut, etc.[5] However, the hydrophilic character of cellulosic fibers appears to be a disadvantage because of its incompatibility with hydrophobic polymeric matrices. This causes poor adhesion between fibers and matrix, making the dispersion of the fibers into polymeric matrices difficult and leading to composites of poor final properties.[3, 6] The bad dispersion of fibers results in their agglomeration into knotty masses, which is due to the strong hydrogen bonding. All these factors have limited the use of cellulosic fibers in several industrial applications.[6]

Chemical treatment of the fiber surface is often necessary to improve the adhesion at the fiber–

matrix interface, which increases the performance of these fibers as reinforcing elements.[7–12] Several organic coupling agents have been designed for specific applications, such as poly(styrene-*co*-maleic anhydride),[7] isocyanates,[8] and maleic-anhydride modified polypropylene,[9, 10] etc. Recently, silane coupling agents have also been widely used; for example, aminopropyltrimethoxysilane, methyltrimethoxysilane, and vinyltrimethoxysilane.[10–12]

We present here the characterization and chemical modification of the *Eucalyptus* fiber surface with vinyltriethoxysilane. The goal of this study is to analyze the microstructure and the thermal and morphological properties of these modified fibers prior to their incorporation into the silicone polymeric matrix.

EXPERIMENTAL

Materials

The cellulosic fibers used in this study, a mixture of *Eucalyptus grandis* and *saligna* bleached Kraft pulp fibers, with an average length of ~0.8 mm, were kindly supplied by "Companhia Suzano de Papel e Celulose" (Suzano, SP, Brazil). Vinyltriethoxysilane (VTES) and powdered microcrystalline cellulose, used as a reference material, were purchased from Aldrich (Milwaukee, WI) and used as received. Tetrahydrofuran (THF) and ethyl alcohol, purchased from Merck (Rio de Janeiro, RJ, Brazil), were dried and distilled prior to use.

Surface Treatment

The cellulosic fibers were dried in an oven under vacuum at 50 °C for 2 days prior to the surface modification reaction. Prior to the reaction, the VTES was pre-hydrolyzed in the presence of water and tin dibutyldiacetate, used as a catalyst, which promoted the self-condensation of the monomers. Two different solvents, THF and ethanol, were used in the reactions following specific procedures. When THF was used, the modification reaction was carried out by suspending the dry fibers in the solvent at room temperature, and the pre-hydrolyzed VTES was added. This mixture was then kept under an argon atmosphere and magnetically stirred for 7 days at room temperature.[8] When the modification reaction was performed in ethanol, the dry fibers were pretreated in a stirring blender with the solvent to

get a better dispersion and consequently to allow a higher surface area for the modification reaction. Afterwards, this suspension was transferred to the reaction flask, under argon atmosphere, and the pre-hydrolyzed VTES was added. The mixture was then stirred magnetically for 7 days at room temperature.

In both reactions, 20% (w/w) silane coupling agent, in relation to the amount of fibers, was added. To eliminate the unreacted silane, the modified fibers were subjected to 8 h of Soxhlet extraction using THF as a solvent. The fibers were then dried in a vacuum oven at 50 °C for 2 days.

Fiber Microstructure and Chemical Composition

Infrared spectra of the *Eucalyptus* fibers, before and after the modification reactions, were obtained in a Nicolet 520 spectrometer (Madison, WI), using diffuse reflectance (DRIFT) spectroscopy, with a resolution of 4 cm^{-1} in the range 4000–400 cm^{-1}. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a McPherson, model ESCA-36 spectrometer (Acton, MA), using AlK$_\alpha$ radiation. The presence of the silane on the fiber surface was confirmed by energy dispersive spectroscopy (EDS) using a scanning electron microscope, JEOL T-300 (Middleton, WI), operated at 15 kV.

Thermal Properties of Fibers

The thermal stability of fibers was analyzed in a TA 2950 thermobalance, TA Instruments (New Castle, DE), in the range 30–1000 °C, at a scanning rate of 20 °C/min under argon. Microcrystalline cellulose was used as a reference material.

Fiber Morphology

The dispersion of fibers before and after the modification reaction was observed by optical microscopy, using an Olympus SZ-BR Stereo microscope (Tokyo, Japan). The morphology of the fiber surface was investigated by field emission scanning electron microscopy (FESEM) with a JEOL JSM-6340F microscope (Tokyo, Japan) operated at 5 kV. The samples were prepared by coating of the fibers with a thin carbon and gold layer. The topographic images of the fiber surface were also analyzed by atomic force microscopy (AFM) on a Topometrix Discovery TMX 2010 instrument (Santa Clara, CA), by the noncontact mode technique. The *Eucalyptus* fibers were immobilized on stubs with adhesive tabs. A low resonance fre-

quency (LRF) pyramidal silicon cantilever, model 1660-00 from Thermomicroscope, was used. The images were processed only by flattening to remove background slope.

RESULTS AND DISCUSSION

The effective modification on the surface of *Eucalyptus* fibers is important for assessing their potential as an alternative reinforcing additive, prior to compounding with polymers. Two main aspects must be observed; they are, the introduction of hydrophobic character and, if possible, the introduction of reactive groups on the surface to allow the formation of covalent bonds between the fibers and the polymeric matrix. Thus, the analysis of unreacted and modified surface of the *Eucalyptus* fibers is a desirable procedure before the preparation of fiber–polymer composites.

VTES was the modifier agent selected because it leads to the incorporation of vinyl groups on the fiber surface and concomitantly increases the hydrophobic character of the fiber. A silicone matrix obtained by hydrosilylation cure reaction, between a siloxane polymer containing SiH bonds and another siloxane polymer containing carbon—carbon double bonds, can be used as the polymeric phase in composites, where the modified cellulosic fibers can act as a reinforcing element. In these cases, the vinyl groups present on the fiber surface can also be active centers for the hydrosilylation reaction in the fiber–matrix interface, allowing the formation of covalent bonds between the fiber surface and the silicone polymeric phase, which can improve the mechanical
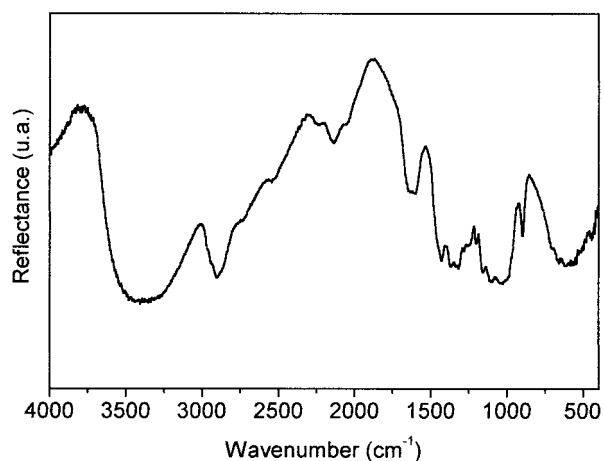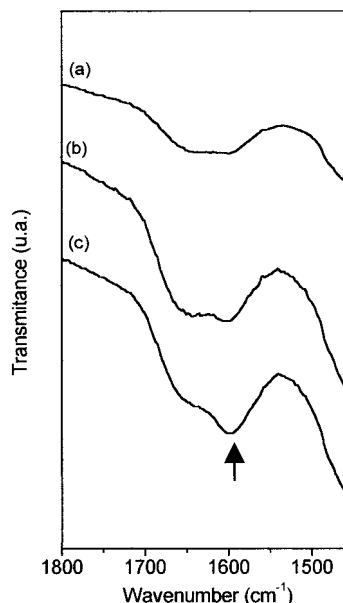

Figure 2 Expanded FTIR spectra (DRIFT) of (a) untreated fibers, (b) VTES/EtOH-treated fibers, and (c) VTES/THF-treated fibers.

properties of the composites. Because of the pre-hydrolysis of VTES, oligomeric species are the real modifier agent of the fiber surface. The formation of one of the possible oligomeric species involved in this process is described in Reaction 1, and the reaction between the fiber surface and the oligomer is illustrated in Reaction 2.
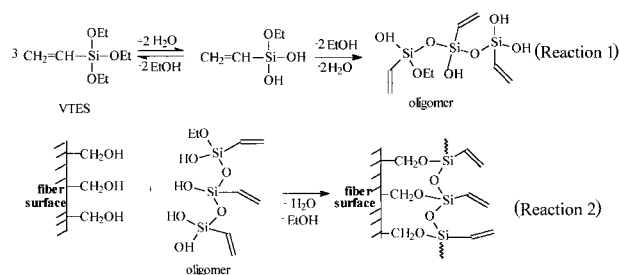
The bleached cellulosic fibers were characterized by DRIFT before chemical modification, and the spectrum obtained was characteristic of cellulosic materials, as seen in Figure 1.

The presence of OH groups from the cellulose chains could be detected by the strong and broad absorption in the 3750–3000 cm^{-1} range, characteristic of the O—H stretching. Because cellulose is a hydrophilic material, this band probably receives a strong contribution of adsorbed water, which showed another characteristic absorption at 1635 cm^{-1}.[13] On the other hand, absorptions corresponding to C—H aliphatic stretching were
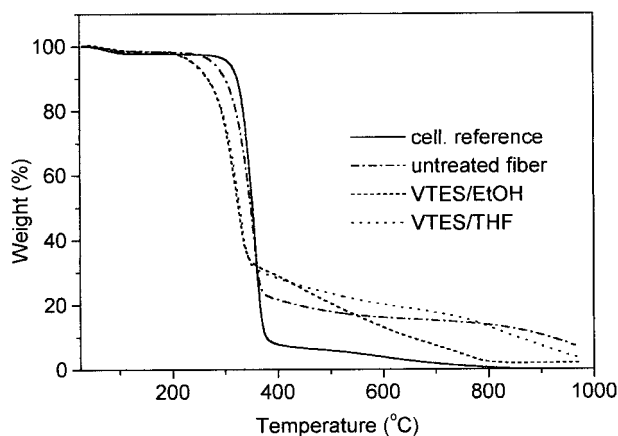

Figure 1 FTIR spectra (DRIFT) of untreated *Eucalyptus* fibers.

Figure 3 Thermogravimetric curves of untreated and modified fibers and cellulose reference material.

associated with the 3000–2840 cm^{-1} band. The broad absorptions at 1450 and 1360 cm^{-1} were associated to C—H deformation modes, whereas another broad absorption from 1200 to 1000 cm^{-1} corresponds to C—O stretching, CH_2 rocking, and C—H deformation modes.[13] Another characteristic band of untreated fibers, at ~890 cm^{-1}, could be assigned to the C—H β-D-glucopyranose ring deformation mode.[14]

The modified fibers showed DRIFT spectra similar to that for those untreated. The presence of VTES might be deduced from the absorption at ~1598 cm^{-1}, corresponding to C=C stretching of vinyl group, which appears as a discrete shoulder in the band centered at 1635 cm^{-1}, as can be seen in the amplified spectra shown in Figure 2.

The thermal degradation of *Eucalyptus* fibers, before and after the modification reactions, was examined by TGA (Figure 3). It is well known that the thermal degradation of cellulosic materials occurs through a complex process involving dehydration, depolymerization, oxidation, hydrolysis, cyclization, and charring.[15] Cordero et al.[16]

studied the degradation process of cellulose and showed that the main thermal decomposition occurred within a region ranging from 300 to 380 °C. Above this temperature, the weight loss became less significant. According to Statheropoulos et al.,[17] the main oxidative organic pyrolysis products of cellulose and extractives are carbon dioxide, aldehydes, ketones, acids, and alcohols.

For untreated fibers, a first stage of weight loss was observed in the range 52–128 °C, corresponding to 2% weight loss, which could be related to the desorption of moisture and/or volatile compounds present in the fibers.[17] A main decomposition step in the range 270–370 °C, showed a weight loss of 72 %, which could be attributed to the degradation of cellulose chains. Above this temperature, the degradation process occurs slowly until 1000 °C, with 7.6 wt % char residue. Similar behavior was observed for the cellulose reference material, for which no char residue at 1000 °C was detected. The presence of a higher char residue after the main decomposition process in the fibers, compared with cellulose reference material, could be attributed to the highly ordered structure present in the fibers. The modification of the fiber surface by the VTES did not change the thermal degradation profile significantly, but decreased its thermal stability. The initial temperature of the main decomposition process was 224 °C. The decrease of the initial temperature of this degradation process in the modified fibers is in agreement with technical literature.[18]

XPS can provide information about surface composition and consequently can confirm the modification of the fiber surface. Carbon atoms C_{1s} in wood materials have been classified[19] in four different categories based on their chemical shifts C_1 (C—C, C—H of hydrocarbon), C_2 (C—O), C_3 (C=O, O—C—O), and C_4 (O—C=O) at 285.0, 286.8, 288.4, and 289.8 eV, respectively. The XPS

Table I   XPS Results of Treated and VTES-Modified Fibers in Ethanol and THF Media

| Fiber Sample | Binding Energy (eV) | | | | | Atomic Ratio |
| | C_{1s} | | | O_{1s} | | |
	C_1	C_2	C_3	O_1	Si_{2p}	Si/C_{2+3}
Untreated	284.6	286.4	288.3	532.6	—	—
VTES/EtOH	284.6	286.5	288.1	532.6	102.2	0.02
VTES/THF	284.6	286.7	288.7	532.4	102.2	0.06

spectra of the *Eucalyptus* fibers showed three peaks, C_1, C_2, and C_3. The C_1 component arises from lignin and wood extractives, C_2 from both lignin and carbohydrate, and C_3 from cellulose.[20] In this research, the pulp fibers were bleached and the content of lignin was minimum. Thus, this C_{1s} peak was mainly attributed to hydrocarbon residues of the spectrometer.[21] In the case of silane treated fibers, the presence of silicon on the surface was detected from its characteristic emission peak at 102 eV, corresponding to Si_{2p}.[12] The binding energies of the C_{1s}, O_{1s}, and Si_{2p} components, and the values of silicon/carbon (Si/C) atomic ratios are presented in Table I.

The partially hydrolyzed VTES, used to modify the fiber surface, has SiOH and SiOEt reactive groups, which react with OH groups of cellulose fiber surface (as shown in Reaction 2) producing H_2O and EtOH as byproducts. In the presence of ethanol as a solvent, there was a competition reaction between this solvent and the C—OH of the fiber surface, which explains the lower Si/C atomic ratio observed in ethanol modified fibers. On the other hand, THF did not promote any parallel reaction, leading to the higher Si/C atomic ratio, corresponding to a thicker vinylsiloxane layer. Nevertheless, a better dispersion of fibers could be obtained in ethanol, which will be of great importance in the preparation of the composites with the polymeric matrix. Untreated fibers showed knotty mass agglomerates, as can be seen in the optical micrograph of Figure 4a. After the modification reaction, the VTES/EtOH fibers were loosened (Figure 4b), whereas the VTES/THF fibers stood together (Figure 4c) as observed for the untreated ones. When ethanol was used as the reaction solvent, the fibers were separated from each other because of the better ability of this solvent to solvate the fibers, avoiding the formation of part of the hydrogen bonds that hold them together, which led to a better fiber dispersion.

SEM with EDS was also employed to obtain information about the chemical modification of the fibers. The microprobe analysis of the fibers treated either in ethanol or THF showed that silicon was present in all the extension of the fiber surface (not shown).

The morphology of the fibers was investigated by FESEM (see Figure 5). Untreated fibers were ribbon shaped, presenting a rough and an uneven surface (Figure 5a) that is due to the presence of macrofibrils of ~400 nm in diameter. Fibers modified by VTES in ethanol (Figure 5b) showed an accentuated roughness, and the presence of loose
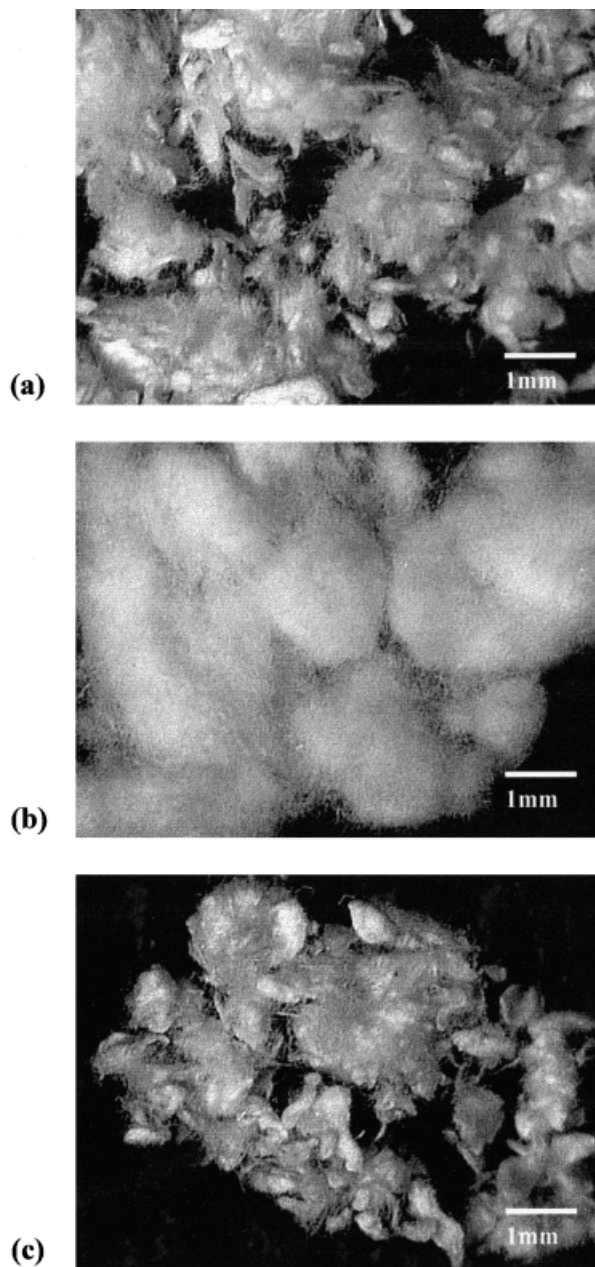

Figure 4 Optical micrographs of (a) untreated, (b) VTES/EtOH-, and (c) VTES/THF-modified fibers (magnification 10×).

fibrils, which were produced by the dispersion procedure in the blender, were observed at the surface. Nevertheless, the presence of these loose fibrils could enhance the adhesion by mechanical anchoring, when compounded with the polymer-forming matrix. The treatment performed in THF (Figure 5c), led to fibers with a smooth surface. In some regions of the fiber surface it was difficult to distinguish the individual macrofibrils, probably because of the thicker silane layer on the fiber surface.

AFM was also used to monitor the topography of the surface of the untreated and modified *Eucalyptus* fibers (Figure 6). Untreated fiber surface was characterized by an extensive series of low furrows and ridges, which were formed by bundles of macrofibrils arranged parallel to the longitudinal axis of the fiber, as can be seen in Figure 6a. The difference between the height of the nodules and the depth of the valleys decreased in the modified fibers (Figures 6b and 6c) compared with
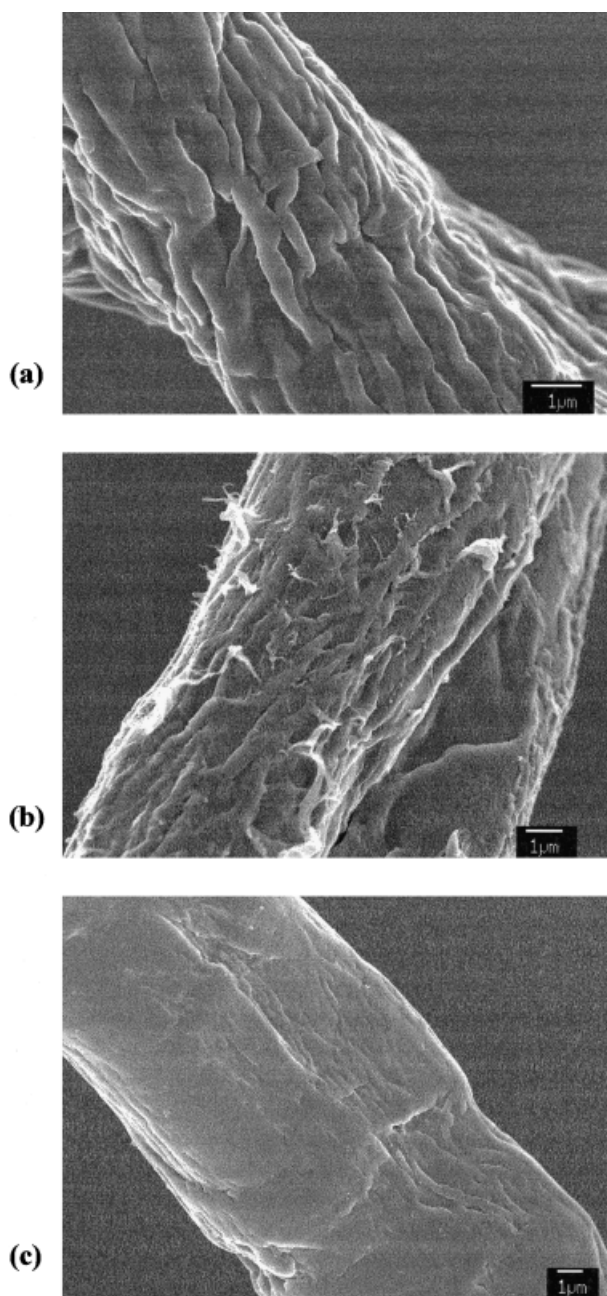

Figure 5   FESEM photomicrographs of (a) untreated, (b) VTES/EtOH-, and (c) VTES/THF-modified fibers.
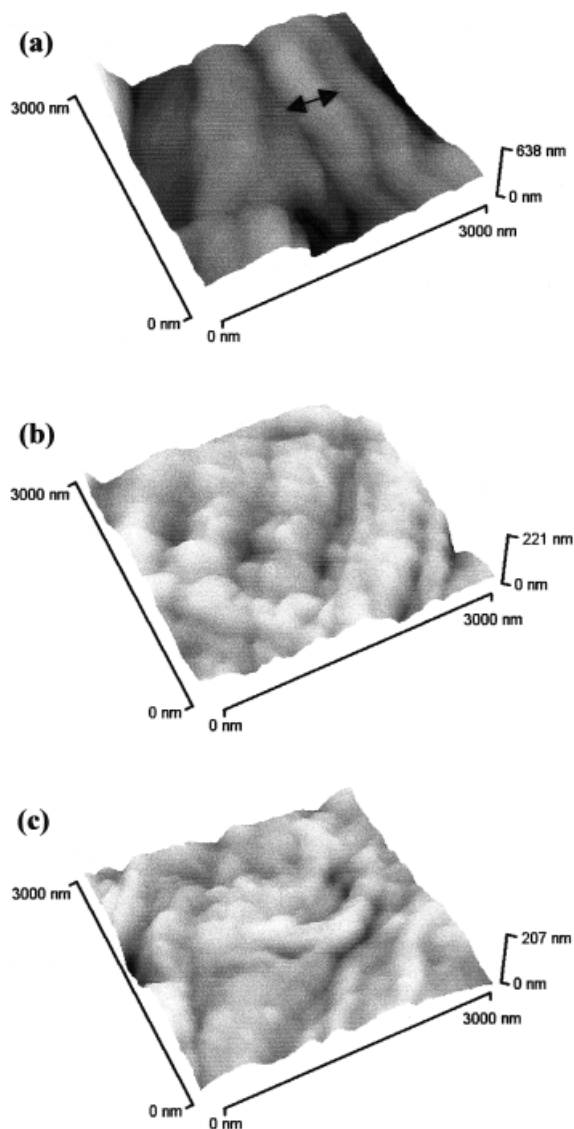

Figure 6   AFM images (3×3 μm) of (a) untreated, (b) VTES/EtOH-, and (c) VTES/THF-modified fibers. Macrofibril is indicated by a double-headed arrow.

the untreated ones, indicating the smoothing effect of the vinylsiloxane layer on the fiber surface.

CONCLUSIONS

Based on the observations presented in this study, it was concluded that the modification of *Eucalyptus* fiber surface with silane coupling agent can be conducted in both ethanol or THF solvents, the former being more efficient to break the knotty masses agglomerates. The thermal stability of the fibers showed a slight decrease after the modification procedure. The microscopic

investigation of the fibers indicated the coating effect of the silane coupling agent on the fiber surface morphology and on its topography. An important result was the introduction of functional reactive organic groups on the fiber surface, which can be used as chemical anchoring to the silicone-forming matrix by covalent bonds.

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