Highly Dispersed Titanium(IV) Oxide on α-Cellulose Surface: An XPS, SEM, and XRD Study

LINDOMAR R. DAMASCENO DA SILVA,[1] YOSHITAKA GUSHIKEM,[1,*] MARIA DO CARMO GONÇALVES,[1] UBIRAJARA P. RODRIGUES FILHO,[1] and SANDRA C. DE CASTRO[2]

[1]Instituto de Química, Unicamp, CP 6154, and [2]Instituto de Física Gleb Wathagin, Unicamp, CP 6165, 13083-970 Campinas, SP, Brazil

SYNOPSIS

Interaction of titanium chloride with a cellulose surface and the decurrent modifications introduced on its morphology were studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The chemical analysis of the surface was carried by X-ray photoelectron spectroscopy (XPS) and changes in the crystallinity upon chemical treatment was determined by the X-ray diffraction (XRD) technique. Interaction of titanium with cellulose occurs only at the surface and a decrease of its crystallinity was observed with the amount of metal oxide incorporated into the solid matrix. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Cellulose is the main constituent of cellular walls of superior plants and constitute about 50% of the total existent biomass.[1-3] The structural characteristics are intimately related with its physical and chemical properties.[4-8] Particularly, the physical properties of cellulose are determined by the presence of hydroxyl and methoxyl groups involved in intra- and intermolecular hydrogen bonding.[9] Ivanova et al.[10] studied by FTIR technique the hydrogen bonding in cellulose and identified two types of intramolecular hydrogen bonding, O_2—H$\cdots$O$_6^I$ and O_3^I—H$\cdots$O$_5$, and one intermolecular hydrogen bonding, O_6^I—H$\cdots$O$_3^{II}$. The hydroxyl groups involved in these hydrogen bonds are mainly responsible for the reactivity of cellulose with organic or inorganic reagents.[11]

The crystallinity of polymeric materials are characteristically associated with intermolecular interactions in the structure of the solid. In the case of cellulose, the crystallinity of the biopolymer results from the intermolecular hydrogen bonding with average energies of about 15 kcal mol^{-1}. Breaking of these bonds when cellulose is submitted to a chem-

ical reaction is mainly responsible for the changes in crystallinity.[2]

In this work, the results obtained from treatment of cellulose with titanium chloride are reported. This strong Lewis acid can react with a basic center and in particular with hydroxyl groups liberating HCl_{gas} and forming O—Ti bonds[11-15] when an aprotic solvent is used as the reactional medium. Change of morphology and crystallinity of cellulose were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD) and the structure change on the surface by X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Preparation of Cellulose–Titanium(IV) Oxide Composite

Four preparations were carried out. In three preparations, about 5 g of cellulose (Sigma 99.5%) were immersed in 250 cm^3 of purified CCl_4 and then a variable volume between 0.25 and 1.5 cm^3 of $TiCl_4$ was added. The mixture was stirred under nitrogen atmosphere for 5 h at 343 K. The mixture was filtered under nitrogen atmosphere in a Schlenk apparatus, washed with CCl_4, and then the solvent and trapped HCl were eliminated under vacuum. The chemically modified cellulose was immersed in dry ethanol and then NH_3 gas was passed in the
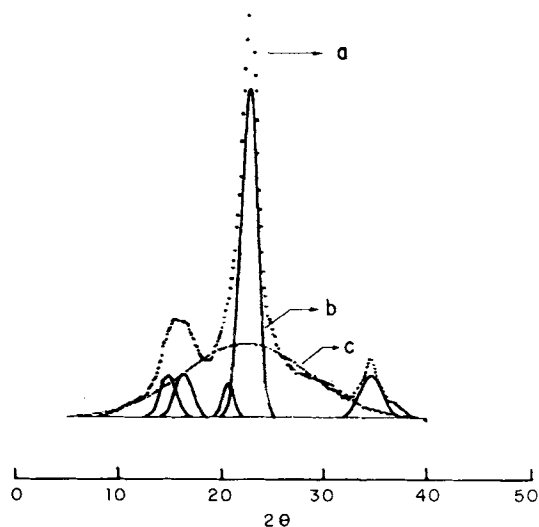
Figure 1 X-ray diffraction peaks for Cel/TiO₂ 10% w/ w. (a) observed diffractograms; (b) Gaussian resolved peaks corresponding to the crystalline phase; (c) Gaussian resolved peak corresponding to the amorphous phase.

mixture. The resulting solid was filtered in air, washed with a mixture of ethanol/water (50% v/ v) and pure water. The material was dried at 353 K under vacuum for 4 h.

Characterization

The quantity of the incorporated oxide was determined calcinating 0.2 g of sample at 1173 K in air for 2 h and weighing the residue.

XPS measurements were carried out using a McPherson-36 spectrometer, using an aluminum anode (Al_{κ_α} = 1486.6 eV) and a pressure of 2×10^{-7} Torr. The atomic ratios were estimated integrating the area under the peaks and using the corresponding Scofield cross section for each atom.[16] The binding energies of the atoms were calibrated against carbon 1s binding energy of 284.6 eV to hydrocarbons.[17]
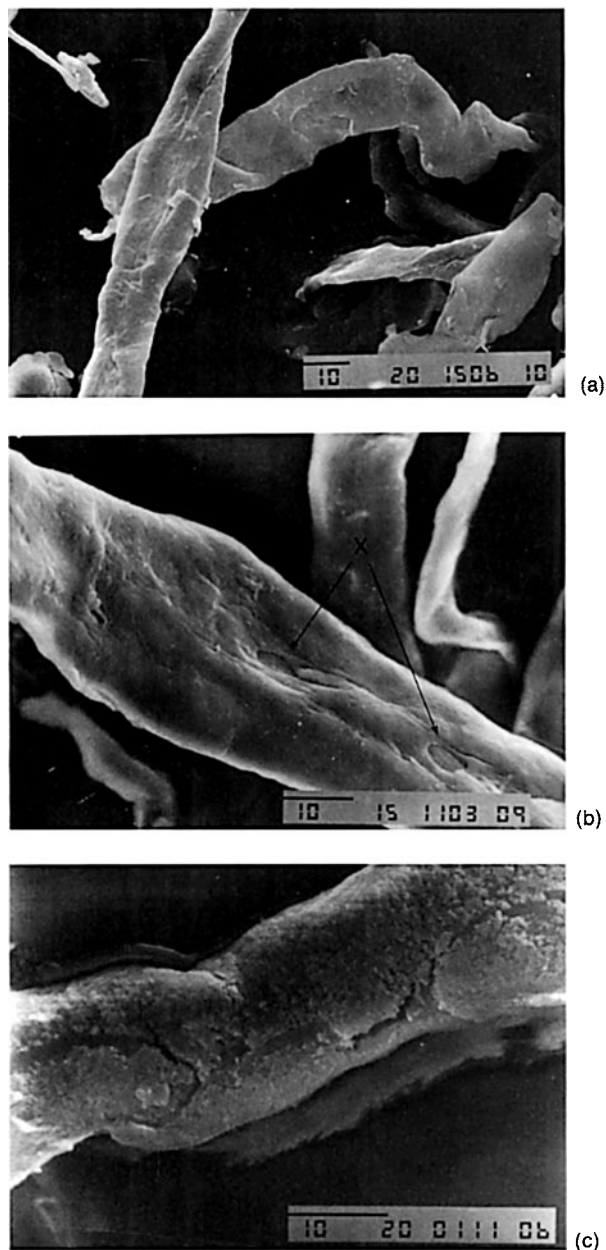
Figure 2 SEM of Cel/TiO₂. (a) α-cellulose (1500×); (b) Cel/TiO₂ 1.2% w/w (1500×); (c) Cel/TiO₂ 10% w/w (1500×); X indicates cavities.

Table I Quantity of Titanium Incorporated on Cellulose Surface

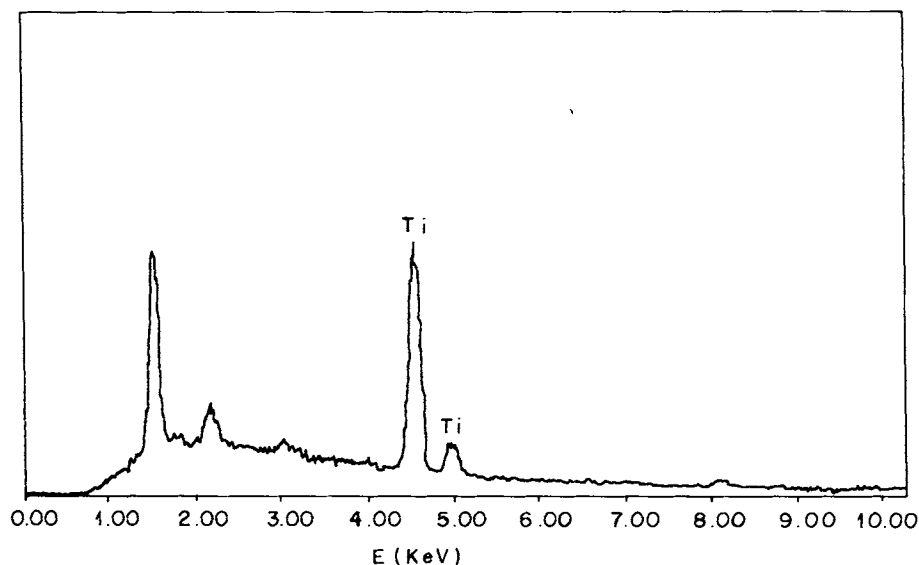| Samples	w (g)	Ti Added (mmol)	Ti Incorporated (mmol g⁻¹) (% w/w)	S_{BET} (m² g⁻¹)
Cel	—	—	—	1.9
Cel-1	5.0	0.45	0.16 (34.4)	2.5
Cel-2	5.0	0.91	0.89 (97.6)	19.0
Cel-3	5.0	1.80	1.25 (69.0)	25.0
Cel-4	20.0	3.60	0.88 (24.2)	46.0

Figure 3   EDS spectrum obtained from Cel/TiO$_2$ 10% w/w.

To obtain the morphology of cellulose and the composite surfaces, the samples were dispersed on a brass support and fixed with a double face 3M™ tape. The material was then coated with gold/palladium alloy using the sputtering technique with the Sputter Low Voltage LVC76 from Plasma Science Inc. The scanning electron microscope (JEOL JSM T-300) was connected to a secondary electron image (SEI) and X-ray energy dispersive (EDS) (from Northern) detectors were used.

The X-ray diffraction patterns were obtained using a Shimadzu XD-3A diffractometer. The following conditions were used to obtain the spectra: radiation of Cu$_{K_\alpha}$ ($\lambda = 0.154$ nm), tension of 30 kV, current of 20 mA, and scan rate of 1° min^{-1}. Deconvolution of diffraction peaks were carried out as shown in Figure 1. The crystalline region of the sample is represented by the narrower peaks and the amorphous region presents the broad peak (halo). The crystallinity of cellulose and the composites were obtained by fitting the calculated peaks to the observed ones using the function[18-20]: $f(2\theta)$ $= \Sigma Gi(2\theta) + AM(2\theta) + B(2\theta)$ where $Gi(2\theta)$ is the Gaussian distribution function for peaks corresponding to the crystalline phase, $AM(2\theta)$ is the Gaussian distribution function of the corresponding amorphous phase, and $B(2\theta)$ is the baseline function.

RESULTS AND DISCUSSION

As stated above, the reactivity of cellulose is due to the hydroxyl groups attached to the glycosidic ring.

The reaction liberates HCl$_{(g)}$ and forms an intermediate chemically modified cellulose in which the metal is bonded to the matrix through the oxygen atom, —O—TiCl$_{4-n}$. Further hydrolysis of the material liberates more HCl$_{(g)}$ and in its final form, the metal remains only as hydrated metal oxide represented as Cel/TiO$_2$. In this treatment the cellulose matrix is submitted to a surface degradation whose extension will depend on the quantity of TiCl$_4$ used.

The quantity of titanium incorporated into the matrix increases as the amount of TiCl$_4$ is increased, but the reaction yield does not present a linear correlation with the molar ratio of TiCl$_4$ and the quantity of cellulose used in the reaction as can be seen in Table I.

Images of the composite cellulose-hydrated metal oxide by SEM are shown in Figure 2. The α-cellulose used in this work is morphologically observed as twisted fibers of different sizes [Fig. 2(A)]. The image of cellulose having 1.2% w/w of titanium oxide [Fig. 2(B)] shows that some regions present cavities (marked X) originated from a degradative acid attack.[8] However, when the quantity of TiCl$_4$ was increased eightfold, formation of a dense layer of hydrated oxide formed by hydrolysis is observed [Fig. 2(C)]. The deposited oxide is amorphous because the specific surface area, S_{BET}, increased from 1.9 m^2 g^{-1} (see Table I) in pure cellulose to 46 m^2 g^{-1} for the composite having 15.5% w/w of oxide. This fact was further confirmed by XRD that indicated an amorphous oxide species on the surface. EDS analysis of the coated fibers shows emission lines of Ti $\kappa\alpha$ and Ti $\kappa\beta$ X-ray at 4.52 and 4.93 keV, respectively, as shown in Figure 3. The X-ray image map-
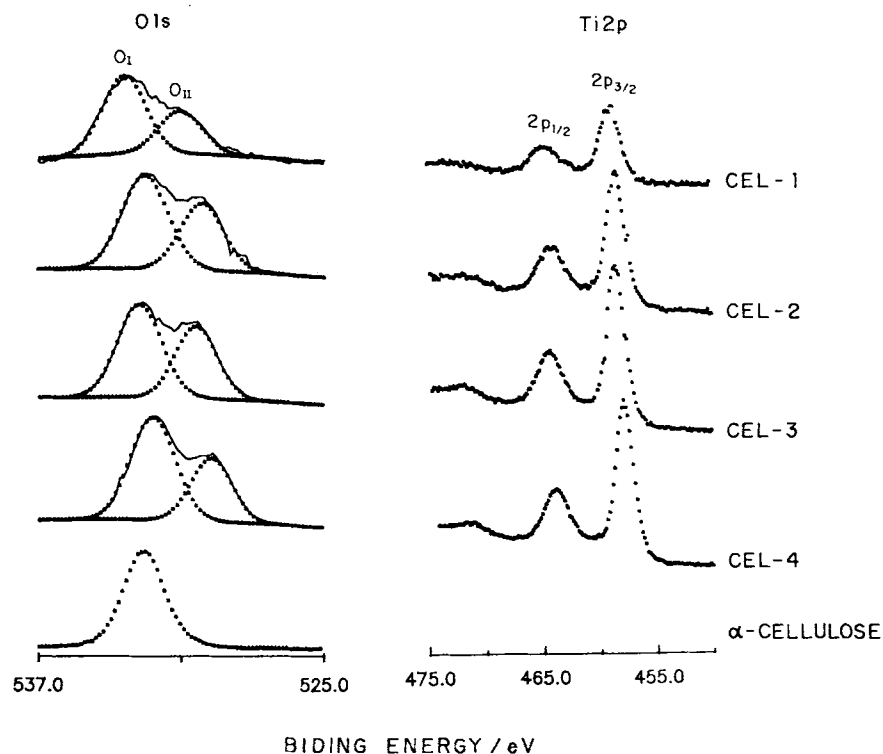
Figure 4 XPS spectra of α cellulose and Cel/TiO₂.

ping (not shown) indicates that the metal oxide is uniformly dispersed over the cellulose fiber surfaces.

In Figure 4, the oxygen Ols binding energy of untreated cellulose (hereafter designated as O_I) in the XPS spectrum is observed at 532.1 eV. Cellulose having incorporated TiO_2 presents in addition to the O_I peak, another one (hereafter designated as O_{II}) at 530.5 eV corresponding to the binding energy of oxygen bonded to the titanium atom. This last peak appears as a shoulder in Cel-1 (TiO_2 1.2% w/w) and its intensity increases as the amount of oxide increases to 15.5% in Cel-4. The position of this peak is similar to that observed for $TiO_{2(anatase)}$ for which the oxygen binding energy is observed at 530.5 eV.[17] Titanium $2p_{3/2}$ and $2p_{1/2}$ binding energies are

observed at about 458.5 and 464.3 eV, respectively, and do not differ as the amount of oxide increases. For TiO_2 in anatase or rutile form and in $MTiO_3(M^{2+} = Ca, Sr, Ba, and Pb)$ Ti $2p_{3/2}$ binding energies are found between 459.0 and 458.6 eV.[21] The atomic ratio O_{II}/Ti (Table II) is 4.1 for the Cel-1 sample and for the other samples (Cel-1, Cel-3, and Cel-4) the ratio is nearly 3.

Although various methods for determining the crystallinity of cellulose obtained from sources such as cotton, rayon, and wool are known,[6,22-25] the XRD technique is the most widely used.[24] The crystallinity of the samples was determined from the XRD patterns shown in Figure 1. The integrated area under the peaks corresponding to the crystalline phase of

Table II XPS Data for Treated Cellulose

Samples	TiO₂ (%)	Ti $2p_{3/2}$[a] (eV)	Atomic Ratio	
			O_I/Ti	O_{II}/Ti
Cel-1	1.2	458.5 ± 0.3	3.8	4.1
Cel-2	7.0	458.6 ± 0.3	4.7	3.1
Cel-3	10.0	458.8 ± 0.3	4.2	3.0
Cel-4	15.5	458.0 ± 0.3	5.3	2.9

[a] Binding energy.

Table III Crystallinity Degree of Treated and Untreated Cellulose

Samples	Crystallinity Degree (%)
α-Cellulose	49 ± 3
Cel-1	50 ± 3
Cel-2	49 ± 3
Cel-3	40 ± 3
Cel-4	33 ± 3

cellulose (these areas were obtained by Gaussian deconvolution as stated above) were divided by the total area. The results presented in Table III clearly show that increasing the oxide loading on the matrix decreases the crystallinity.

CONCLUSIONS

In the coating process of the cellulose surface by $TiCl_4$, interaction of the metal with the surface is presumably by oxygen to metal bonding at the interface of both phases as was suggested by vibrational spectroscopy data.[26,27] Increasing the metal loading on the surface, the metal oxides cover all of the surface of the fiber and the atomic ratio O_{II}/Ti $\cong 3$ for quantity of loading $\geq 7.0\%$. Therefore, it appears that hydrated oxides that cover the surface are coordinatively unsaturated because this atomic ratio should be 4.1 as shown by XPS measurements carried out for bulk phase TiO_2. This bulk phase was obtained by calcinating the composite Cel/TiO_2 in air at 973 K.

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