

ESCA Spectroscopy of Poly(methyl methacrylate) Grafted onto Wood Fibers

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SYNOPSIS

The incompatibility of hydrophilic wood fiber and hydrophobic polymers is the main difficulty with wood thermoplastic polymer composites. To overcome this issue, many researchers suggest grafting polymer onto wood fiber for improving the interfacial adhesion during mixing. A systematic ESCA study of chemi-thermo-mechanical pulp (CTMP) grafted fiber has been performed to provide chemical information about surface composition modification. The material analyzed included initial CTMP fiber, the pure polymer i.e., poly(methyl methacrylate) (PMMA) as reference material, and grafted fiber at different polymer loadings. Interest is focused on the carbon and oxygen spectra. Samples at high polymer loading or high grafting level have an O/C, C₁, C₂, C₄, O₁, and O₂ intensities much similar to those of the PMMA but a little different since some wood fiber sites have still not fixed the polymer. ESCA spectra provide information on about 1–5 nm depth. The ESCA technique allows the monitoring of grafting polymer onto wood fiber as a surface phenomenon.

INTRODUCTION

Use of cellulose, cellulose derivatives, and entire wood fibers from the pulping process as reinforcements and/or filler agents in thermoplastic composites offers the potential of manufacturing a new class of materials.^{1,2} Very little is known about wood fiber surface chemistry and its effects on the properties of the final product.

The first issue confronting the design of wood fiber thermoplastic composites is the incompatibility of phases due to the mixing of hydrophilic wood fibers with hydrophobic polymeric matrices.^{3–9} Wood fibers absorb water from humid atmosphere, and this results in a decrease in interfacial adhesion with a hydrophobic polymer matrix. The incorporation of some hydrophobic polymer onto fiber surface could markedly improve the interfacial adhesion that is

crucial in determining the performance of a composite.⁶

Many researchers suggested fiber surface modification either by grafting some specific polymer or using a coupling agent.^{4,9–16} In recent studies,^{6,7} infrared spectroscopy was used to analyze wood fibers modified by anionic grafting, cellulose treated with styrene, and modified textiles.^{3–5,17} This technique, however, also yields information about the bulk as well as the surface of modified wood fibers. The objective of the present study is to characterize only the chemical surface composition of grafted wood fibers by using electron spectroscopy for chemical analysis (ESCA). This technique allows quantitative determination of surface chemical composition and chemical bonding on a surface by measuring the chemical shift of the electron binding energies of the surface elements. The ESCA technique yields information about the chemical surface with a spatial resolution of a few millimeters in the system used and a depth resolution of about 5 nm depending on the take-off angle.^{18–20}

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ESCA involves the measurements of binding energies of the electrons photoejected by interaction of a molecule with a monoenergetic beam of soft X-rays. The most commonly used photon sources are $\text{MgK}_{\alpha_1\alpha_2}$ (1253.6 eV) and $\text{AlK}_{\alpha_1\alpha_2}$ (1486.6 eV). The sample-size requirements are minimal (about 15 mg). The time required to accumulate the spectrum of a sample is relatively short: It is about 300 s for a high-resolution spectrum of carbon or oxygen and about 600 s for the sulfur spectrum, due to its low signal-to-noise intensity ratio.

ESCA has already been employed for the characterization of wood,^{23,24} pulp wood fiber,^{21,25-29} textiles,^{17,30} cellulose,^{3-5,29,30,31} and polymers.^{22,32-36} This work presents ESCA spectra of poly(methyl methacrylate) (PMMA) grafted onto the chemi-thermo-mechanical pulp (CTMP) fiber, at different grafting levels, in the region of 0–1000 eV with a focus at 153–180 eV, 275–295 eV, and 525–545 eV, corresponding to sulfur (2p), carbon, and oxygen (1s) spectra. These spectra are compared to those of the initial CTMP wood fiber and pure polymer.

EXPERIMENTAL

Materials

Wood fibers used in this work were CTMP from Consolidated Bathurst and were made up of soft-wood and hardwood.

Methyl methacrylate (MMA) from Kodak, used as monomer, was purified by distillation after removing inhibitors with sodium hydroxide (2.5*N*) and stored in a dark bottle in a refrigerator at 4–5°C.

PMMA obtained from Polyscience was dissolved in acetone and 10 mL of a 10% weight solution pipetted in a Petri dish. The Petri dish was covered and the acetone evaporated over 48 h to obtain a thin film of PMMA ready for the ESCA analysis. All other chemical products were used as received. Sodium peroxide from Anachemia, carbon disulfide, ferrous ammonium sulfate (FAS), hydrogen peroxide, and Tween-80, all from Fisher Scientific, were ACS reagents. Potassium metabisulfite and acetone were obtained from Canlab and meet the specification of analytical reagents AR.

Fiber Treatment

Experimental procedures used for grafting monomer onto wood fibers were similar to those previously published.^{12,37} Without going into a detailed de-

scription of the grafting procedure, specific conditions were the following:

Pulp, 4.50 ± 0.10 g, (o.d.), corrected for its solubility (3.5%) in NaOH were alkali-treated in 300 mL of NaOH (0.75*N*) at 25°C for 45 min. Xanthation was performed for 2 h in CS_2 vapor in a desiccator at 25°C. The pulp was then washed with acidified distilled water (pH 4.5). Ion exchange was done for 2 min in 300 mL of 0.006% solution of FAS. The pulp was then filtered and washed with neutral distilled water (pH 6.5). Monomer and Tween-80 were added depending on the polymer loading desired.¹² After 15 min of impregnation, 5 mL of aqueous hydrogen peroxide (30%) were mixed in. The reaction time is about 20 h in a nitrogen atmosphere.

After 20 h, the grafting and polymerization reactions are quenched by adding 1% of potassium metabisulfite during 5 min and washing with distilled water. Acetone is used to remove the homopolymer by Soxhlet extraction for up to 8 h. The level of grafting or the polymer loading (PL) expressed as grafting percentage was determined gravimetrically after soxhlet extraction using the following equation¹⁶:

$$\text{PL}(\%) = 100 \times \frac{A - B}{B} \quad (1)$$

where *A* is the weight after polymerization, grafting, and extraction in grams; *B* is the initial pulp weight in grams; and PL is the polymer loading in percentage. The standard error on PL is about 3% according to balance error, loss during washing and filtering, and extraction steps. This value was estimated by blank tests.

ESCA SPECTROSCOPY

ESCA analysis of the fiber surfaces was performed using an ESCALAB MKII spectrometer fitted on a Microlab system from V.G. Scientific (base pressure $< 10^{-10}$ Torr) and equipped with a nonmonochromatized dual Mg—Al anode X-ray source.

Kinetic energy measurements were made using an hemispherical electrostatic analyzer with 150 mm radius working in a constant pass energy mode (20 eV). Under the experimental conditions employed, the gold $\text{Au}_{4f}(7/2)$ level at 84 eV, the $\text{Ag}_{3d}(5/2)$ level at 368.3 eV, and the $\text{Cu}_{2p}(3/2)$ level at 932.7 eV binding energies were used for spectrometer calibration.^{33,38} The silver level $\text{Ag}_{3d}(5/2)$ had a full

width at half-maximum (fwhm) of 1.2 ± 0.2 eV; this value was taken as the spectrometer resolution. Fibers were pressed into a steel cup with maximum care to avoid sample contamination, before being introduced in the working chamber. To avoid thermal and radiation deterioration, the sample and steel cup were kept at about 80 K with liquid nitrogen and at pressure of 10^{-8} Torr. Spectra were recorded using the Mg anode at 300 W with typical accumulation times of 600 s for the sulfur S_{2p} peak, 300–400 s for the carbon C_{1s} peak, and 200–300 s for the oxygen O_{1s} peak. To check that the fiber surface was stable with exposure time, repeated spectra acquisitions were performed. The suitable maximum exposure time was determined to be about 30 min. The spectrometer was operated in a computer-controlled scanning mode, and another computer with appropriate software was used for peak synthesis.^{19,21,29,38}

Data Treatment

Monochromatic X-rays impinge upon the sample, interact with the surface atoms of all elements contained in the sample, and eject core-level electrons from these atoms. With a take-off angle of 30° , only electrons originating from atoms lying within 10 nm of the surface have a high probability of escaping from the sample with a characteristic kinetic energy, E_k , given by the following formula:

$$E_k = E_x - (E_b + E_c + \Phi) \quad (2)$$

where E_x is the energy of the incident X-ray (1253.6 eV for Mg), E_b is the binding energy of the electron on its original shell (eV), and E_c is the energy lost in counteracting the potential associated with the steady charging of the surface. To obtain the absolute value of E_c , the oxygen 1s peak is set at 533.2 eV or the carbon C_{1s} at 285 eV as reference for cellulosic materials.^{19,21,25–27,29} Φ is the work function of the spectrometer.

The binding energy, E_b , is influenced by the nuclear charge, oxidation state, and formal charge of the atom from which the electron is ejected. Rearrangement of eq. (2) gives

$$E_b + E_c = E_x - (E_k + \Phi) \quad (3)$$

Then, E_k , the kinetic energy, is, respectively, 968.6 eV and 720.4 eV for the carbon and the oxygen ejected electrons from a sample as detected by a given spectrometer (ours) and a monochromatized Mg X-ray source.

The atomic ratio of oxygen and carbon at the surface region analyzed by ESCA can be estimated from their respective peak intensity by the following equation^{19,21,22,25–27,29}:

$$O/C = \frac{\sigma_c \cdot D_c \cdot \lambda_c \cdot I_O}{\sigma_o \cdot D_o \cdot \lambda_o \cdot I_C} \quad (4)$$

where σ refers to cross section for photoelectron generation; D , to the spectrometer transmission; λ , to the mean path of photoelectrons depending on their kinetic energy; and I , to the integrated surface of the peaks. Using Scofield's cross sections for the oxygen O_{1s} , carbon C_{1s} , and sulfur S_{2p} peaks,³⁹ corrected for angular asymmetry,⁴⁰ eq. (4) can be rewritten as

$$O/C = \frac{I_O}{2.85 \cdot I_C} \quad (5)$$

$$S/O = 1.487 \cdot \frac{I_S}{I_O} \quad (6)$$

From eqs. (5) and (6), calculation of various atomic ratios are straightforward from the peak areas.

In this study, the complex spectra structure was resolved by a curve-fitting technique. From a spectrum, several theoretical peaks with a fixed Gauss/Lorentz (G/L) ratio and fixed fwhm give a calculated envelope that fills in the experimental spectrum with an accepted area standard error of 2%. A good fit was obtained with an fwhm of 2.0 ± 0.2 eV and a G/L ratio of 60% for the components of the C_{1s} and O_{1s} peaks.

RESULTS

Table I is the classification of different carbon and oxygen component lines for woody and methacrylate materials as observed by the ESCA technique.^{22,25} This classification is based on carbon and oxygen binding energies references, respectively, at 285 eV for C_1 and 533.2 eV for O_2 .

Table II contains binding energy correction E_c for different samples when the cellulose oxygen peak O_2 is used as a reference at 533.2 eV as suggested by Dorris and Gray.^{25–27} This energy value corresponds to the most intense peak for the cellulose oxygen spectrum. The values of binding energy E_b of C_1 , C_2 , C_3 , C_4 , O_1 , and O_2 are, respectively, about 285 ± 0.4 eV, 286.5 ± 0.4 eV, 288 ± 0.4 eV, 289.5 ± 0.4 eV, 531.5 ± 0.4 eV, and 533.2 eV, in full agreement with those reported in the literature.^{21,23,27,28} The

Table I Classification of Carbon and Oxygen Peak Components: C_{1s} and O_{1s} ESCA Lines for Woody and Methacrylate Materials^{a-c}

Group	ΔE_b (eV)	Symbol	Carbon or Oxygen Atoms Bound to
Carbon			
I	0.0 ± 0.4	C ₁	C—C or/and C—H
II	1.5 ± 0.4	C ₂	C—O
III	3.0 ± 0.4	C ₃	C=O or/and O—C=O
IV	4.5 ± 0.4	C ₄	O—C=O
Oxygen from			
Cellulose	0.0 ± 0.4	O ₂	C—O
Methacrylate	0.0 ± 0.4	O ₂	<u>O</u> —C=O
Methacrylate	-1.5 ± 0.4	O ₁	O—C= <u>O</u>

Chemical shift (ΔE_b) is referenced to carbon C₁ at 285.0 eV and oxygen O₂ at 533.2 eV.

^a Ref. 27.

^b Ref. 22.

^c Refs. 41 and 42.

chemical shifts of C_{1s} components are relative to 285 eV, corresponding to the C₁ peak. These chemical shifts ΔE_b of C_{1s} components are displaced from the C₁ component by 1.50 ± 0.4 eV when a carbon

is bound to an oxygen by a single bond and, respectively, 3.0 ± 0.4 eV and 4.5 ± 0.4 eV, for double and triple bonds as observed in woody and methacrylate materials.^{22,23,41}

Table III shows the experimental atomic ratio O/C calculated from eq. (4) and representing the oxygen concentration divided by the carbon concentration at the surface region sensed by ESCA for the PMMA, CTMP, and grafted CTMP fiber versus PL. The various peak components of carbon spectra (C₁, C₂, C₃, C₄) and oxygen spectra (O₁, O₂) are expressed relative to total carbon and total oxygen peak area, respectively. Also, the ESCA spectrum at about 160–175 eV reveals a low-level S_{2p} signal for different samples.

DISCUSSION

As shown in Figure 1, grafting and polymerization reactions of some specific monomers to cellulose, cotton textiles, or wood fibers are well known.¹⁰ From this figure, several steps are involved: the alkali-treatment (1), the xanthation (1), the ion exchange (2), the free radical formation (3), and the grafting (4). In this work, after the free radical formation, wood fibers are considered as the woody reference.

Table II Experimental Corrected Energy E_c (eV), Corrected Binding Energies E_b (eV), and Chemical Shift ΔE_b (eV) for the Reference PMMA, CTMP Fiber, and Grafted Fiber at Different PL

Sample No.	PL (%)	E_c (eV)	E_b (eV)						ΔE_b (eV)				
			C ₁	C ₂	C ₃	C ₄	O ₁	O ₂	C ₁	C ₂	C ₃	C ₄	O ₁
1	CTMP	2.8	285.0	286.7	288.4	0	531.3	533.2	0.0	1.7	3.4	0	-1.9
2	FAS	3.3	285.1	286.7	288.2	0	531.4	533.2	0.1	1.8	3.2	0	-1.8
3	H ₂ O ₂	2.5	285.3	286.8	288.5	0	531.4	533.2	0.3	1.8	3.5	0	-1.8
4	5	3.4	285.2	286.7	288.4	289.0	531.6	533.2	0.2	1.7	3.4	4.0	-1.6
5	10	2.3	284.8	286.8	287.9	289.3	531.5	533.2	-0.2	1.8	2.9	4.3	-1.7
6	20	2.7	285.0	286.8	287.7	289.4	531.4	533.2	0.0	1.8	2.7	4.4	-1.8
7	25	3.5	285.0	286.5	288.1	288.9	531.6	533.2	0.0	1.5	3.1	3.9	-1.6
8	30	3.2	285.1	286.4	288.4	289.3	531.7	533.2	0.1	1.4	3.4	4.3	-1.5
9	40	2.8	285.3	286.2	287.8	289.2	531.6	533.2	0.3	1.2	2.8	4.2	-1.6
10	50	3.5	284.8	286.4	287.7	289.2	531.9	533.2	-0.2	1.4	2.7	4.2	-1.3
11	60	2.8	284.7	286.5	287.7	289.4	532.0	533.2	-0.3	1.5	2.7	4.4	-1.2
12	80	2.3	284.6	286.3	287.8	289.1	531.8	533.2	-0.4	1.3	2.8	4.1	-1.4
13	100	2.1	284.9	286.7	287.7	289.0	531.7	533.2	-0.1	1.7	2.7	4.0	-1.5
14	120	2.6	285.1	286.7	287.7	289.0	531.7	533.2	0.1	1.7	2.7	4.0	-1.5
15	140	3.0	285.1	286.2	287.8	289.0	531.8	533.2	0.1	1.2	2.8	4.0	-1.4
16	PMMA	2.5	285.4	286.3	287.9	288.9	531.6	533.2	0.4	1.3	2.9	3.9	-1.6

Chemical shift is referenced to carbon C₁ at 285.0 eV and Oxygen O₂ at 533.2 eV.

Table III Experimental Peak Intensity Ratio of PMMA, CTMP Fiber, and Grafted Fiber at Different PL

Sample No.	PL (%)	O _t /C _t	S _t /O _t	C ₁ /C _t	C ₂ /C _t	C ₃ /C _t	C ₄ /C _t	O ₁ /O _t	O ₂ /O _t	F _C	F _O
1	CTMP	0.37	0.15	0.60	0.34	0.06	0.00	0.15	0.85	—	—
2	FAS	0.48		0.48	0.44	0.08	0.00	0.12	0.88	—	—
3	H ₂ O ₂	0.58	0.10	0.32	0.62	0.06	0.00	0.10	0.90	1.00	1.00
4	5	0.56	0.06	0.34	0.60	0.06	0.00	0.12	0.88	0.97	0.95
5	10	0.55		0.36	0.55	0.05	0.04	0.12	0.88	0.82	0.95
6	20	0.54		0.39	0.50	0.05	0.06	0.17	0.83	0.71	0.83
7	25	0.52		0.41	0.48	0.04	0.06	0.20	0.80	0.67	0.75
8	30	0.50	0.04	0.44	0.46	0.04	0.07	0.18	0.82	0.63	0.80
9	40	0.48		0.48	0.41	0.04	0.08	0.24	0.76	0.53	0.65
10	50	0.47		0.51	0.37	0.04	0.09	0.26	0.74	0.47	0.60
11	60	0.46		0.53	0.35	0.04	0.10	0.26	0.74	0.40	0.60
12	80	0.44		0.55	0.31	0.04	0.12	0.30	0.70	0.30	0.50
13	100	0.42		0.56	0.29	0.00	0.15	0.36	0.64	0.22	0.35
14	120	0.41		0.57	0.27	0.0	0.16	0.38	0.62	0.17	0.30
15	140	0.41		0.58	0.26	0.0	0.16	0.40	0.60	0.16	0.25
16	PMMA	0.38		0.60	0.20	0.0	0.20	0.52	0.48	—	—

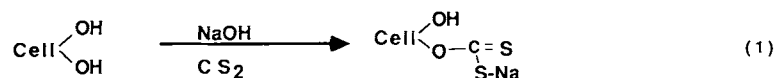
C₁ intensity ratio corresponds to C₁ area divided by the total carbon C_{1s} area (C₁/C_t). O_t/C_t and S_t/O_t intensity ratios calculated by eq. (4), with the correction factor for spectrometer, cross section, and molecular orbital of 2.85 and 2.29, respectively, for O/C and O/S.

Effect of Grafting

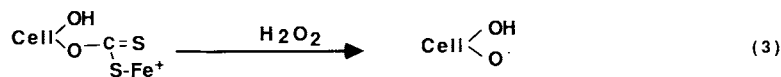
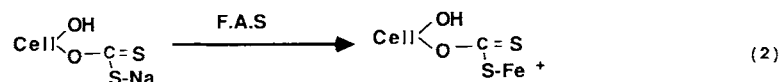
ESCA spectra of grafted wood fiber show sulfur, oxygen, and carbon spectra different from those of the H₂O₂-treated wood fiber and they become more similar to the PMMA spectra, as polymer loading or

grafting level increases (Figs. 2–4). The discussion will be focused on the intensity variation of S_{2p}, C_{1s}, and O_{1s} spectra of different samples after polymerization and grafting. The oxygen and carbon spectra of various samples are presented, respectively, in Figures 2 and 3. Although the peak intensity and

1. Alkali treatment and Xanthation



2. Free Radical formation



3. Grafting and polymerization

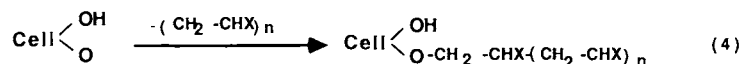


Figure 1 Grafting and polymerization reactions: (1) Thiocarbonated CTMP fiber results from an alkali and xanthation treatment; (2) CTMP fiber is ion exchanged (Na and Fe) by the action of ferrous ammonium sulfate on the xanthated pulp; (3) free radical formation follows the action of H₂O₂ on ion-exchanged CTMP fiber; (4) final CTMP grafted with polymer.

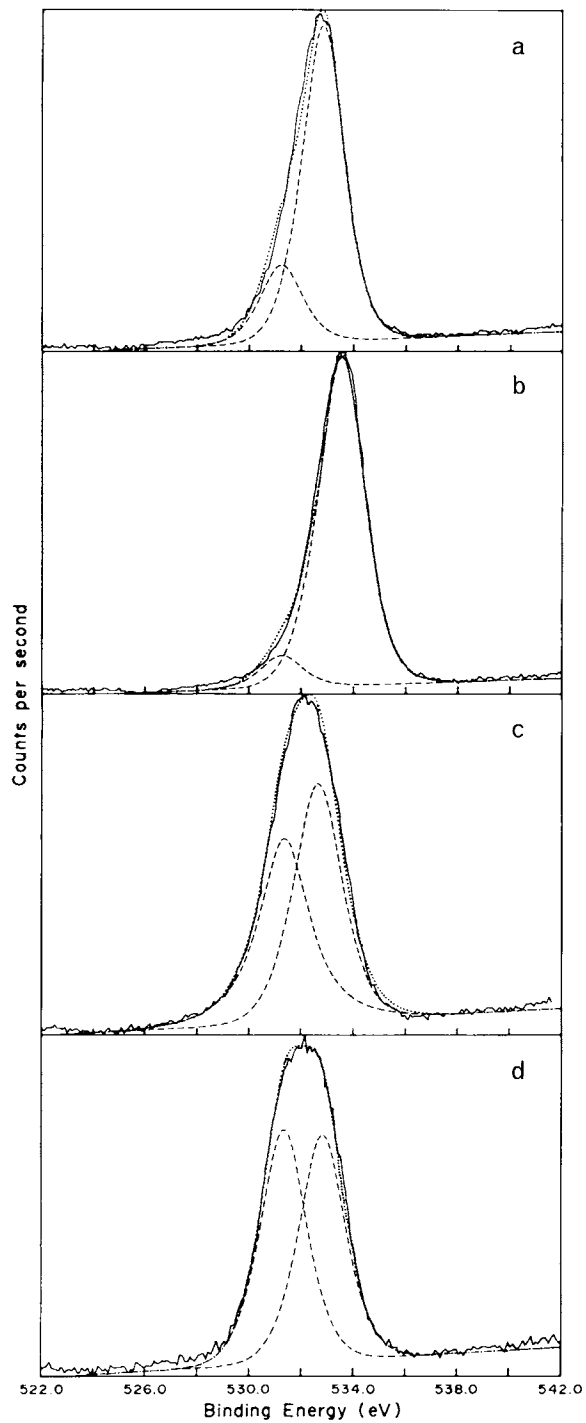


Figure 2 ESCA O_{1s} spectra as electron counts per second vs. binding energy expressed in (eV): experimental spectrum (—); total peak synthesis (· · · · ·), deconvoluted peaks (-----); (a) CTMP wood fiber; (b) H_2O_2 CTMP wood fiber treated; (c) CTMP wood fiber grafted at 100% PL; (d) PMMA.

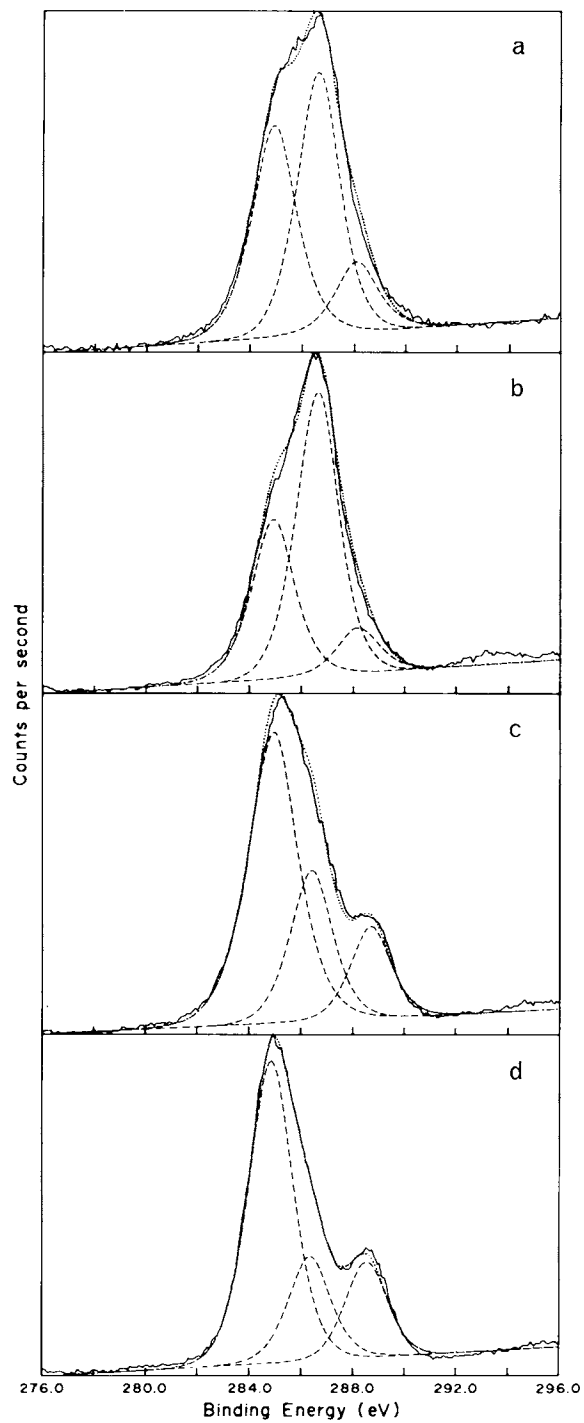


Figure 3 ESCA C_{1s} spectra as counts per second vs. binding energy expressed in electronvolts (eV): experimental spectrum (—); total peak synthesis (· · · · ·); deconvoluted peaks (-----); (a) CTMP wood fiber; (b) H_2O_2 CTMP wood fiber treated; (c) CTMP wood fiber grafted at 100% PL; (d) PMMA.

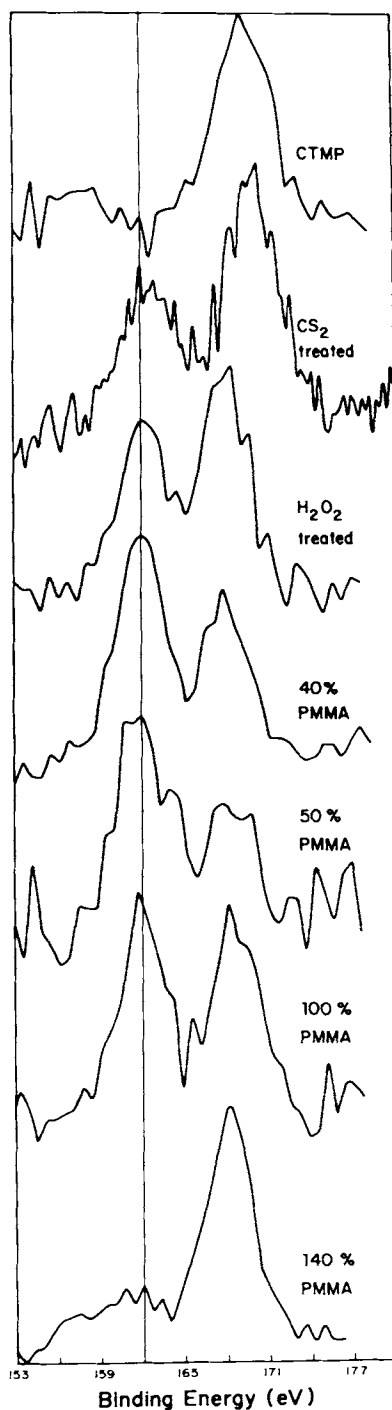


Figure 4 ESCA S_{2p} spectra as counts per second vs. binding energy expressed in electronvolts (eV) of (a) CTMP wood fiber; (b) CS_2 CTMP wood fiber; (c) H_2O_2 CTMP wood fiber treated; (d) CTMP wood fiber grafted at 40% PL; (e) CTMP wood fiber grafted at 50% PL; (f) CTMP wood fiber grafted at 100% PL; (g) CTMP wood fiber grafted at 140% PL.

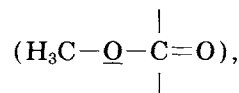
signal-to-noise ratio is rather low for the sulfur, Figure 4 shows the correspondent spectra.

S_{2p} Peak

Figure 4 presents S_{2p} spectra for various samples in the region of 160–180 eV. These spectra show two main peaks with binding energy of, respectively, 162 and 168 eV. The higher binding energy peak corresponds to sulfur S(VI) at the state of oxidation six and as sulfur in sulfate ester groups and is in agreement with those reported in the literature.²² The lower binding energy peak is assigned to sulfur S(II) at state of oxidation two. Chemical analysis according to CPPA technical section standard method G-28 gives a sulfonate content of 1.0% on CTMP fiber. This sulfur content according to the binding energy (168 eV) is from sulfate ester groups,²² originating from the bisulfite pulping process and/or from the ferrous ammonium sulfate remaining after the ion-exchange step during the grafting process. Figure 4 shows that the sulfur peak at 162 eV appears after the xanthation, confirming the carbon disulfide fixation by the initial CTMP wood fiber during the xanthation step as proposed by Krassig.^{11,12} Table III shows the calculated S/O atomic ratios obtained by eq. (6) with the largest value for the initial CTMP fiber. The S/O atomic ratio decreases with increasing PL, due to the absence of sulfur in PMMA. However, the S/O atomic ratio decreases down to an asymptotical value (0.011) where the PL level is at 140%, suggesting that some sulfur sites are still uncovered by the grafting and detected by ESCA.

O_{1s} Peak

The PMMA repeat unit shows two oxygens, one singly bound to a carbon and to a methyl group



and the other, double bound to a carbon. The PMMA oxygen O_{1s} spectrum presents two oxygen components. The first oxygen (O_1) component is located at 531.6 ± 0.4 eV, and the second (O_2), at 533.2 eV. The O_1 peak corresponds, then, to a negative chemical shift of 1.5 ± 0.4 eV relative to the O_2 peak. The O_1 peak is from an oxygen bound to carbon with a double bond or a ketonic oxygen as in an acrylate,

acetate, polyacrylic acid, polyalkylacrylate, polyalkylmethacrylate, and polycarbonate.^{22,41} The O_2 peak component with higher binding energy is from oxygen directly bonded to carbon in ester type linkages of the PMMA. For the PMMA, the relative atomic ratios of both species O_1 and O_2 are, respectively, 0.52 ± 0.2 and 0.48 ± 0.2 (Table III) and correspond to the theoretical value: 0.50 for O_1 and 0.50 for O_2 .

The O_{1s} binding energies of cellulosic materials are much less predictable although single-bound oxygen is generally assigned to higher binding energy, and doubly bonded oxygen, to the lower. O_{1s} peaks of woody materials are discussed very little in the literature.^{19,21} This is due to the great difficulty involved in predicting the O_{1s} chemical shifts and assigning them to specific moieties, compared to the C_{1s} peaks. This has been attributed to the electronegativity and the polarizability of substituents interacting directly or indirectly with the oxygen atom.^{21,42} Figure 2 shows the presence of two unequal intensity peaks, both separated by 1.5 ± 0.4 eV, and this is true for all oxygen spectra.

For CTMP fiber, O_1 is less intense than O_2 (Table III). The O_2 atomic ratio is about 100% for pure cellulose and 85% for the CTMP fiber.^{19,25} This difference is due to the presence of some extractives and sulfates on the CTMP fiber. These substances contain oxygen O_1 that reduces the O_2 atomic ratio with respect to the CTMP fiber value.

For the pretreated sample, that is, ion-exchanged and H_2O_2 -treated fiber, the O_1 atomic ratio is about 0.10. The decrease of the O_1 atomic ratio with the pretreatment suggests extraction, oxidation, or coverage of substances associated to the O_1 peak at the fiber surface. These results suggest that the effect of the pretreatment is an increased surface concentration of polysaccharides and a decrease of sulfur concentration at the sample surface.

For the grafted fiber at 140% PL, Figure 5 shows, as does Table III, the O_1 atomic ratio increasing up to 0.40. Moreover, this ratio asymptotically tends to the 0.50 value of PMMA. This confirms the evidence of the O_1 contribution from the PMMA. The O_T/C_T atomic ratio values also tend toward a limit as PL increases (Fig. 6).

C_{1s} Peaks

There is a general agreement on the assignment of components C_1 , C_2 , C_3 , and C_4 of spectrum C_{1s} of woody and methacrylate materials.^{22,23} The C_1 component corresponds to a carbon atom bound only to other carbon atoms and/or hydrogen atoms, i.e., the

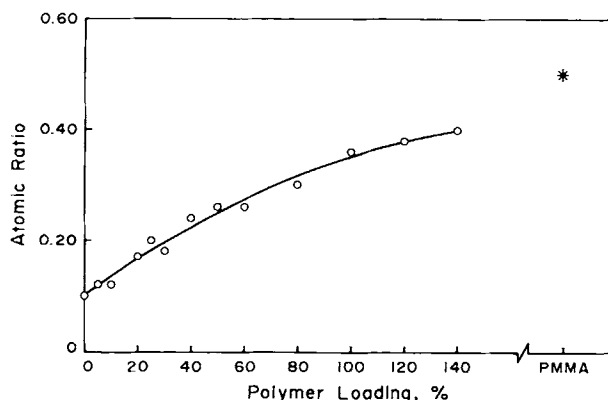


Figure 5 Atomic ratio of oxygen O_1 atomic ratio vs. polymer loading expressed in percentage (%).

nonoxidized carbon with a zero state of oxidation. This component arises mainly from the lignin constituent of wood and from extractives.^{23,25-27} The C_2 component is due to a carbon atom bound to a single noncarbonyl oxygen atom, i.e., a state of oxidation of one (Table I). The C_2 component arises from both the carbohydrate and lignin constituents of wood. The C_2 is the main component of cellulose carbon spectrum. The C_3 component represents a carbon atom bound to one carbonyl oxygen atom or two noncarbonyl oxygen atoms, i.e., in a state of oxidation of two (Table I). C_4 represents a carbon atom linked to a carbonyl oxygen and a noncarbonyl oxygen atom corresponding to an oxidation state of three.

Figure 3 shows that there are three peak components: C_1 , C_2 , and C_4 , in the PMMA C_{1s} spectrum (Table I). The main difference between wood fiber and PMMA is the presence of the C_4 carbon peak component and the absence of C_3 in PMMA.

Table III shows the fraction area of each peak's components, C_1/C_t , C_2/C_t , C_3/C_t , and C_4/C_t , as a function of PL. ESCA analysis of PMMA gives relative intensities of 0.60, 0.20, and 0.20, respectively, for C_1 , C_2 , and C_4 . This distribution is predicted by the elemental composition, and the particular C_3 component should, indeed, be absent in the PMMA carbon spectrum.

Reference wood fibers present a C_{1s} carbon spectrum with three components C_1 , C_2 , and C_3 . The C_4 representing carbon linked to a carbonyl and a noncarbonyl oxygen is absent, due to the low concentration of carboxylic groups at the wood fiber surface, which makes them undetectable by the ESCA technique (Fig. 3).

Pretreatment on CTMP wood fibers (alkali, xanthation, and ion exchange) modifies C_1 , C_2 , and C_3

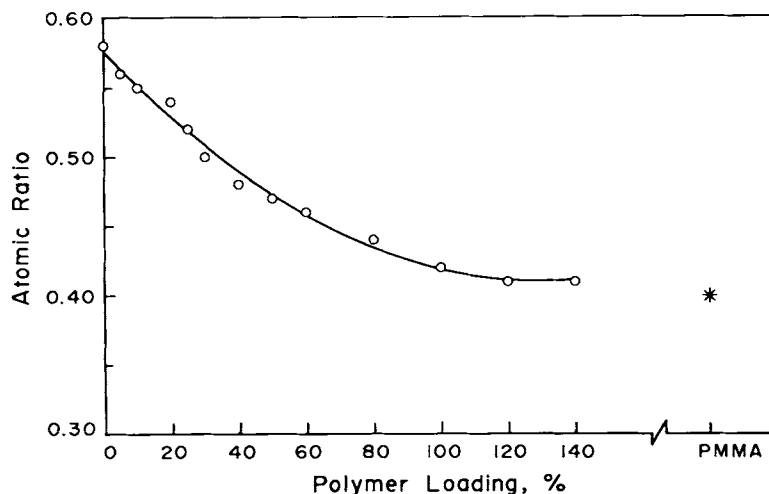


Figure 6 O_t/C_t atomic ratio calculated by Eq. (5) vs. PL expressed in percentage (%).

concentration on the fiber surface. The C_1 atomic ratio decreases from 0.60 to 0.32. Such carbon species are present in lignin and in extractives. The C_2 , present in cellulose, increases from 0.34 to 0.62, confirming the increasing surface concentration of polysaccharides due to the pretreatment with alkali and by H_2O_2 . C_3 is almost stable at 0.05 ± 0.02 atomic ratio.

Figure 7 illustrates the relation between the C_1/C_t atomic ratio and the PL. Grafting PMMA on wood fiber increases C_1 and C_4 surface concentrations because of the contribution of methylene, methyl, and carboxylic groups of PMMA, respectively. The curve presents a maximum value of the

C_1 atomic ratio near 0.58, asymptotical to the PMMA value of 0.60.

Figure 7 also shows that C_4 is detectable in PMMA grafted onto wood fiber samples at PL higher than 10%. As the PL increases, the atomic ratio of the C_4 component also increases up to a value of 0.16, close to the C_4 component value of pure PMMA (0.20).

C_1 and C_4 increase with PL, whereas C_2 and C_3 decrease. With C_3 absent in PMMA, the grafting process contributes to reduce the relative importance of C_3 on the grafted fiber surface. The relative importance of C_2 on the initial pretreated fiber surface is about 0.60 and on PMMA, about 0.20. After graft-

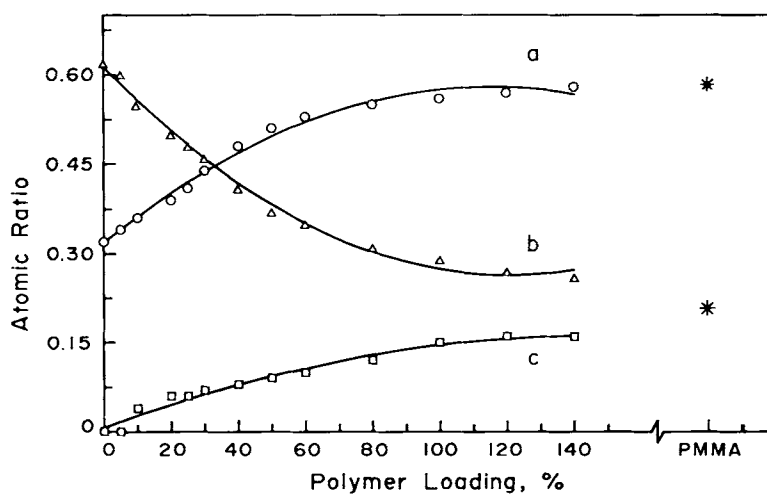


Figure 7 Atomic ratio of carbon C_{1s} spectrum and components vs. PL expressed in percentage (%): (a) (O) C_1/C_t atomic ratio representing the area of C_1 over the total carbon C_{1s} peak area; (b) (Δ) C_2/C_t atomic ratio; (c) (\square) C_4/C_t atomic ratio.

ing, the C_2 atomic ratio varies from 0.60 to 0.26 depending on the PL level, as illustrated in Figure 7. At a given PL level, the C_2 atomic ratio of a grafted sample originates from both contributions of wood fibers and polymer at the surface of a sample, because wood fibers and pure PMMA both contain such carbons. Knowing that PMMA has equal C_2 and C_4 atomic ratios (0.20) and that C_4 is absent in wood fiber, the C_2 wood fiber atomic ratio contribution F_C for a grafted sample could be calculated by the following expression:

$$F_C = \frac{C_2 - C_4}{C_2} \quad (7)$$

Table III shows value of F_C decreasing from 1.0 to 0.16 for the analyzed samples. The sample at the higher PL has a C_2 atomic ratio of 0.26, of which 16% is from the original CTMP wood fiber and 84% from the PMMA.

The O_1 atomic ratio should theoretically be 0.50 for the PMMA. It is 0.10 for the H_2O_2 -treated sample, and it increases from 0.10 to 0.52 with the PL for the grafted sample. The F_O , oxygen contribution from the wood fiber to the O_1 species, could be evaluated by the following equation:

$$F_O = \frac{0.50 - O_1}{0.40} \quad (8)$$

Samples at high PL have an O_1 atomic ratio of 0.40 and F_O of 0.25; the O_1 contribution from wood fiber, F_O , is about 25%, and then about 75% from the

polymer at PL of 140%. Table III also gives various F_O 's decreasing from 1.0 to 0.25, whereas F_C decreases down to 0.16. Figure 8 shows the very similar behavior of F_O and F_C when PL increases. The slight difference between both could be attributed to the presence of some oxygen bound to sulfur, in the form of sulfate on the grafted fiber surface as detected by ESCA. This also suggests that an oxydative phenomenon occurs during the grafting process.

The carbon C_{1s} analysis shows that the fiber surface, resulting after grafting PMMA to CTMP fiber at high PL, become more compatible to the PMMA surface with the C_{1s} component C_1 near to 0.58, C_2 to 0.26, C_3 to 0.00, and C_4 to 0.16. From the C_{1s} spectrum, the maximum grafting level that should modify wood fiber surface by radical polymerization and with MMA as monomer is about 100%, because C_1 and C_4 are almost constant from 100 to 140% of PL. This assumes, however, that the PMMA surface interaction in the grafted sample does not reach further than the depth characterized by the ESCA technique (5 nm).

O_{1s}/C_{1s} Interpretation

Table III presents atomic ratio O/C for different samples. The initial CTMP fiber shows an O/C atomic ratio of 0.40 compared to 0.33 for lignin, 0.10 for abietic acid (principal constituent of wood extractives), and 0.83 for pure cellulose.²⁵⁻²⁷ The CTMP fiber value of O/C suggests that its surface contains a considerable quantity of lignin and some extractives that lower its O/C value. A mild acetone

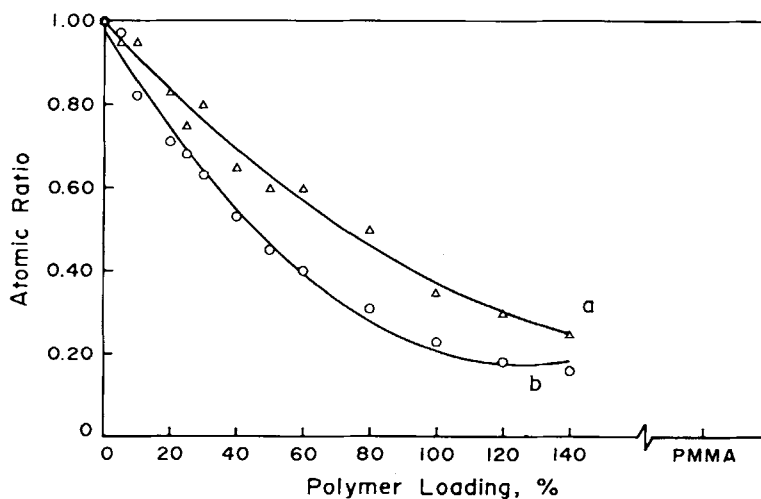


Figure 8 Wood fiber contribution calculated from Eqs. (7) and (8) vs. PL: (a) (O) F_C , carbon C_2 ; (b) (Δ) F_O , oxygen O_1 .

fiber extraction increases O/C from 0.40 to 0.51 for the TMP fiber²⁶ and from 0.37 to 0.53 for this CTMP fiber. This is consistent with extractive removal, since extractives are rich in C₁. After the H₂O₂ treatment, fibers show an O/C of 0.58, indicating that pretreatment considerably increases oxygen concentration and/or decreases carbon concentration on the fiber surface. The reason of this O/C increase is the solubilization of some hemicellulose during the alkali treatment and the extraction of some wood extractives both increasing the cellulose surface concentration on the external surface.

The PMMA macromolecule gives a theoretical O/C atomic ratio of 0.40. The C_{1s}/O_{1s} atomic ratio calculated using eq. (5) with the corresponding peak area in PMMA spectrum gives an experimental value of 0.38 ± 0.02, as in the literature.^{34,35} The slight difference between the measured and the calculated value is attributed to the surface contamination during manufacturing, microtoming, and handling the initial polymer.

Grafting of PMMA onto the wood fiber surface decreases the atomic ratio O/C as shown in Figure 6 and Table III. The atomic ratio at the PMMA surface should be 0.40 of oxygen and 0.60 of carbon so that grafting results in a decrease of the total oxygen surface concentration. The wood-grafted fiber O/C atomic ratio tends to 0.40 ± 0.2, close to the calculated value of the PMMA as PL tends toward high values.

ESCA analysis of sulfur, carbon, and oxygen spectra of grafted polymer onto wood fiber shows that it is a surface phenomena. The ESCA atomic ratios of CTMP wood-grafted fiber are asymptotically near those of the PMMA but a little different since some sites, possibly initial sulfate, have been not completely covered by the polymer.

CONCLUSIONS

ESCA analysis shows a progressive change in the chemical surface composition of wood-grafted fibers as a function of the PL.

- The C_{1s} spectra are the most useful tool for this purpose because of their high resolution and the C₁ and C₄ components modification following grafting.
- The atomic ratio O_{1s}/C_{1s} decreases with the PL increase because of the high carbon atom content (60%) compared to the oxygen atom content (40%) in the PMMA.
- ESCA S_{2p} spectra show two main peaks corresponding to sulfur at different oxidative states of two and six for the pretreated and the grafted samples. The presence of sulfur on the grafted sample suggests that grafting has not covered the entire external surface of the initial sample.
- ESCA analysis confirms that grafting polymer onto wood fibers modifies the surface composition of the wood fibers. By making an appropriate choice of the monomer to be grafted onto the wood fiber surface, it is then possible to tailor the chemical surface composition of the wood fiber surface for specific end uses in thermoplastic composites.

Further studies are underway to determine the adsorption energies and the surface area of such modified fibers.

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