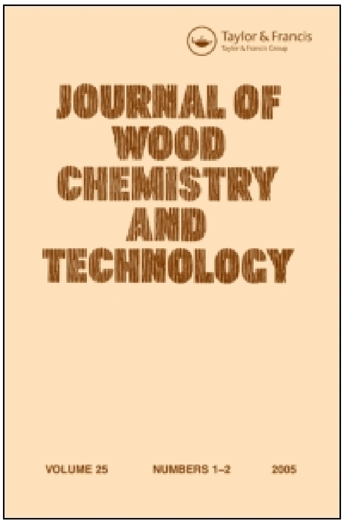


Journal of Wood Chemistry and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Infrared Study of Grafted CTMP Fibers

A. O. Barry[a]; P. D. Kamdem[a]; B. Riedl[a]; S. C. Kaliaguine[b]
[a] Département des Sciences du Bois, Centre de recherche en science et en ingéniérie des macromolécules, Université Laval, Ste-Foy, Québec [b] Département de Génie Chimique, Université Laval, Ste-Foy, Québec

To cite this Article Barry, A. O. , Kamdem, P. D. , Riedl, B. and Kaliaguine, S. C.(1989) 'Infrared Study of Grafted CTMP Fibers', Journal of Wood Chemistry and Technology, 9: 3, 341 — 364
To link to this Article: DOI: 10.1080/02773818908050304
URL: http://dx.doi.org/10.1080/02773818908050304

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 9(3), 341-364 (1989)

INFRARED STUDY OF GRAFTED CTMP FIBERS

A.O. Barry, P.D. Kamdem and B. Riedl
Département des Sciences du Bois
Centre de recherche en science et en ingéniérie
des macromolécules,
Université Laval,
Ste-Foy, Québec, G1K 7P4

and

S.C. Kaliaguine
Département de Génie Chimique, Université Laval,
Ste-Foy, Québec, G1K 7P4

ABSTRACT

Graft-copolymerization of methyl methacrylate (MMA) and acrylonitrile (AN) onto CTMP fibers using Fe^{2+}-H_2O_2 redox system was investigated. The proof of grafting was performed by means of FT-IR and gravimetric methods. Analyses of IR spectra of samples after mercerization, xanthation, ion exchange and of samples with different polymer loadings, together with chemical reactions were performed. The variation of the characteristic IR band absorption intensity of MMA (the C=O groups stretching at 1731 cm^{-1}) and of AN (the nitrile stretching at 2244 cm^{-1}) vs the percent of grafting can be used as calibration curves for quantitative determination. It appears also from the IR spectra analyses, that some of the mechanisms suggested for graft-copolymerization are of very small significance.

INTRODUCTION

Wood can be considered as a polymeric composite made up of three essential polymers: cellulose, hemicelluloses and lignin. These polymers are responsible for most of the physical and chemical properties exhibited by wood and wood products. Wood can also be considered as substrate for further chemical composite formations. One of the major disadvantages of products made from wood or wood fibers or pulp is their tendency to absorb water from humid atmosphere. Water uptake leads to swelling and dimensional instability of the product for exterior use. Thus, the high hygroscopicity of wood fibers remains in some cases a problem. If a small portion of an inexpensive polymer could be incorporated into or onto the fiber surface, the water-resistance as well as strength properties could be therefore markedly improved. Such surface chemical modification of the fiber by graft coplymerization has been extensively performed and reported in the literature. However, despite numerous reports and mechanisms suggested[1], no systematic study of samples after each step of grafting in conjunction with the suggested mechanisms has been reported. In view of this, a systematic infrared study of chemithermomechanical pulp (CTMP) samples grafted with methylmethacrylate (MMA) or acrylonitrile (AN) monomers by copolymerization was undertaken .

Infrared spectroscopy has been extensively used in polymer[2,3] cellulose[4,5], lignin[6,7], characterization as well as in the confirmation of pulp grafting[8-11]. The potential of infrared analsys in studying wood and pulp components was further enhanced by the advent of Fourier Transform Infrared Spectroscopy (FTIR). Increased sensitivity and signal averaging ability of FTIR instruments permits generation of useful spectra from samples. The advent of software which allows mathematical manipulation of the spectral data is also very important. As a result of data processing ability, advantage can be taken from the improved signal-to-noise ratio available from FTIR, yielding greater spectral sensitivity.

One of the most widely used spectral processing techniques, beyond simple computation of transmission or absorbance spectra, is the digital subtraction of absorbance spectra in order to reveal or to emphasize subtle differences between two compounds. In order to follow the surface chemical modification of grafted CTMP fibers, the use of this technique will be implemented.

EXPERIMENTAL

Materials

Methylmethacrylate (MMA) and acrylonitrile (AN), were purified by distillation after removing inhibitors with sodium hydroxide (2.5N). The distilled monomers were stored in a refrigerator (5°C) in dark bottles. All others chemical products were used as received. The chemithermomechanical pulp (CTMP) was made up of soft-wood (50% spruce and 50% of balsam fir) with 0.3% of sulfonate content.

Graft-copolymerization

The procedure for the graft copolymerization of the CTMP fibers is the same as that described by Kokta et al.[12]. Without going in detail in the description of the grafting procedure, one can detail the pulp conditionning before grafting as follows: 4.50±0.01g of pulp (o.d.) corrected for its solubility (3.5%) in the NaOH solution was used in each experiment; an alkali treatment of the pulp was accomplished in 300ml of NaOH solution (0.75N) and (0.50N) for the MMA and AN monomers respectively, at ambient temperature for 45 min.; this was followed by xanthation of the mercerized pulp for two hours over CS_2 vapour in a dessicator. The pulp was then washed with pH(4.5) adjusted distilled water. This was followed by ion exchange for 2 min. in 300 ml of ferrous ammonium sulfate (F.A.S.) solution (0.006% for MMA and 0.004% for AN). The pulp was then filtered off and washed with neutral (pH=6.5) distilled water.

For a complete description of the grafting procedure, one can refer to Kokta et al.[12]. The level of grafting (or polymer loading), expressed as percent of grafting, was determined gravimetrically after soxhlet extraction of homopolymer for up to 16 hours with acetone and N,N-dimethylformamide for the PMMA and the PAN, respectively. The others grafting parameters (the total conversion and the grafting efficiency) will not be discussed here.

Spectroscopy

Infrared spectra were recorded in absorbance units with the KBr pellet technique with an FTS-60 Digilab spectrometer. The spectrometer was equipped with a nitrogen cooled-source, a computer control (IRIS) and a DTGS detector.

The spectral recording conditions are as follows: frequency range: 400 to 4000 cm^{-1} , $2cm^{-1}$ of resolution, 300 scans of coadding with a triangular apodization. The samples were measured in potassium bromide disks as milled fibers. The technique of disk prepration was described in a previous paper[13].

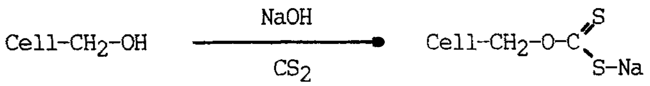
The ability to subtract two absorbance spectra opened a new whole area for the transmission study of solids[14]. Indeed, if the spectrum of a bulk sample can be obtained as well as the one of the same sample after surface modification, the spectral subtraction technique can be used to remove the contributions of the bulk phase[14]. The spectra subtraction was accomplished with the spectrometer manufacturer›s software, based on a least-squares algorithm derived from the criterion of minimization of the sum of squared differences between the spectra to be subtracted.

RESULTS AND DISCUSSION

Results will be discussed following the different steps of the grafting procedure in accordance with the following grafting reaction mechanisms reported in the literature[15,16].

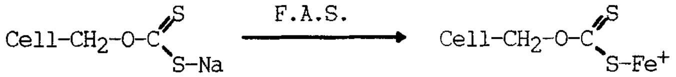
Reaction mechanism of the (Fe^{2+}-H_2O_2) redox grafting process

1- Mercerization and Xanthation



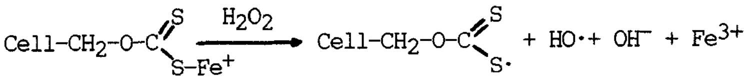
$$\text{Cell-CH}_2\text{-OH} \xrightarrow[CS_2]{NaOH} \text{Cell-CH}_2\text{-O-C}\begin{matrix}\nearrow\!\!\!\!\!/ S\\ \searrow S\text{-Na}\end{matrix} \qquad [1]$$

2- Ion Exchange



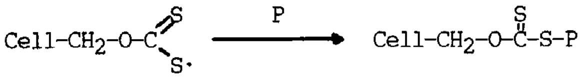
$$\text{Cell-CH}_2\text{-O-C}\begin{matrix}\nearrow\!\!\!\!\!/ S\\ \searrow S\text{-Na}\end{matrix} \xrightarrow{F.A.S.} \text{Cell-CH}_2\text{-O-C}\begin{matrix}\nearrow\!\!\!\!\!/ S\\ \searrow S\text{-Fe}^+\end{matrix} \qquad [2]$$

3- Action of H_2O_2



$$\text{Cell-CH}_2\text{-O-C}\begin{matrix}\nearrow\!\!\!\!\!/ S\\ \searrow S\text{-Fe}^+\end{matrix} \xrightarrow{H_2O_2} \text{Cell-CH}_2\text{-O-C}\begin{matrix}\nearrow\!\!\!\!\!/ S\\ \searrow S\cdot\end{matrix} + HO\cdot + OH^- + Fe^{3+} \qquad [3]$$

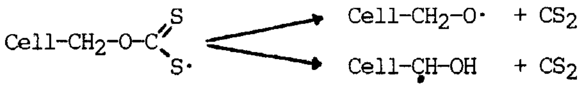
4- If the xanthate radical can react with polymer (P),one may observe a direct addition as follows:



$$\mathrm{Cell{-}CH_2{-}O{-}C({=}S){-}S\cdot} \xrightarrow{P} \mathrm{Cell{-}CH_2{-}O{-}C({=}S){-}S{-}P} \qquad [4]$$

or,

5- Radical transfer



$$\mathrm{Cell{-}CH_2{-}O{-}C({=}S){-}S\cdot} \longrightarrow \mathrm{Cell{-}CH_2{-}O\cdot} + \mathrm{CS_2} \qquad [5a]$$

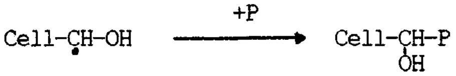
$$\mathrm{Cell{-}CH_2{-}O{-}C({=}S){-}S\cdot} \longrightarrow \mathrm{Cell{-}\dot{C}H{-}OH} + \mathrm{CS_2} \qquad [5b]$$

followed by

6- grafting

6a- $\mathrm{Cell{-}CH_2{-}O\cdot} \xrightarrow{+\,P} \mathrm{Cell{-}CH_2{-}O{-}P}$ [6a]

6b-



$$\mathrm{Cell{-}\dot{C}H{-}OH} \xrightarrow{+P} \mathrm{Cell{-}CH(OH){-}P} \qquad [6b]$$

It appears from the mechanism suggested that three compounds can be encountered from Eq. 4, 6a, and 6b in addition to the homopolymer formation.

The discussion will also be presented in accordance with results obtained after alki treatment, xanthation, ion exchange, and after completion of grafting.

Effect of alkali treatment of the pulp

In figure 1 infrared spectra of the untreated CTMP control (1a), the alkali treated (1b), the xanthated CTMP (1c) and ion exchanged (1d) samples are illustrated. Obviously, there are many differences between the spectrum of the mercerized (1b) and that of the control (1a). There is no discernable band at 1731 cm^{-1} in

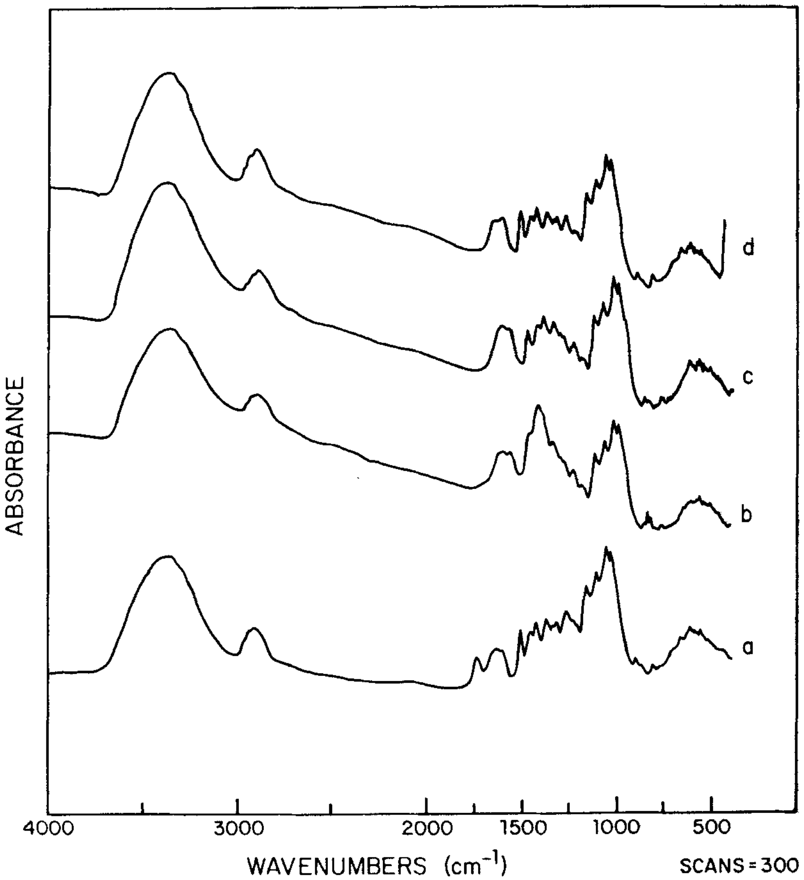


Figure 1. a- Infrared spectrum of untreated CTMP sample (control).

b- Infrared spectrum of a mercerized CTMP sample.

c- Infrared spectrum of a xanthated CTMP sample.

d- Infrared spectrum of sample after ion exchange (F.A.S.).

fig.1b, absorption bands intensities between 1490 and 1317 cm^{-1} are drastically increased after mercerization, and new bands are observed at 881, 869 and 836 cm^{-1} in fig.1b.

One of the effect of the alkali treatment is the disappearance of the band at 1731 cm^{-1} associated to the C=O carboxyl groups vibration[17]. The disappearance of this band in the infrared spectrum must be assessed with some caution, since salt formation may take place, shifting the carboxyl band from 1731 cm^{-1} to the 1600 cm^{-1} region. In this region it may be obscured by a broad band arising from the C=O stretching vibration of the α-keto carbonyl[17,18] at 1660-1655 cm^{-1}, also by a band arising from OH stretching vibration of the adsorbed water[19] at 1650 cm^{-1} [19] and by bands arising from lignin skeletal benzene ring vibration[17] at 1605-1590 cm^{-1}. The removal of this band may be accounted for by deacetylation of the galactoglucomannans present in the softwood fraction and of the hardwood (20% of the furnish) xylan and formation of the sodium salt of uronic acid residues[20]. The absence of any detectable band at 1731 cm^{-1} in the mild acid washed of the alkali treated sample spectrum (not shown), suggests a partial elimination of the carboxyl groups, leaving the cellulose more accessible on the fiber surface[20,21].

Most of the bands at 1458-1452,1435,1376,1341 and 1319 cm^{-1} are related to cellulose C-OH stretching vibration as suggested by Tsuboi[19], who found that the intensities of the 1452 and 1336 cm^{-1} bands do diminish on deuteration. One of the consequence of the alkali CTMP treatment is to render cellulose more accessible, and this increase of cellulose accessibility is responsible for the increase of the degree of grafting due to a better diffusion of the grafting mixture through cellulose and other pulp compounds[22]. The new not yet assigned bands observed in the mecerized sample spectrum, will be discussed in the following next section.

Effect of pulp xanthation on IR spectrum

The infrared spectrum of the xanthated pulp is shown in fig.1c. One can first see a net decrease of the 1458-1452 cm^{-1} band due to the OH in-plane bending mode and a disappearance of the bands located at 881, 869 and 836 cm^{-1} after xanthation. Thus, one can tentatively assign these bands to OH hydroxyl vibration in accordance with the xanthation mechanism (equation 1). Careful examination of the xanthated sample spectrum (fig.1c), reveals some new bands with very weak intensity at 1292, 1225 and 1002 cm^{-1}. However, although one canot assess with certainty that these bands arise from the C-S, C=S or CSS- links stretching vibration, results obtained from ESCA (electron spectroscopy for chemical analysis) analysis reveal very clearly a higher sulfur content in the xanthated pulp than in the CTMP control (the ESCA results will be discussed in a following paper).

Effect of ion exchange on IR spectrum of the xanthated sample

In figure 1d the spectrum of the sample recorded after the ferrous ammonium sulfate (F. A. S.) reaction with the xanthated sample is also illustrated. The aim of the reaction being to exchange sodium ions with ferrous ions, little change in the IR spectrum is expected if we refer to Eq. 2. However, a comparison between figures 1d and 1c reveals some differences in the shape as well as in the absorption intensity of bands lying in the 1500-1200 cm^{-1} region. The shape of the spectrum 1d, being a result of two successive reactions i.e. a mild acid wash followed by an ion exchange, looks very similar to that of the untreated sample, probably a consequence of the acid washing. Spectrum 1d does not show however any band at 1731cm^{-1} even after the acid wash, confirming an elimination of wood components responsible for this stretching vibration. Differences observed between spectra 1d and 1c suggest also that the ion exchange mechanism as suggested in Eq. 2, represents the overall equation for a more sophisticated mechanism.

Effect of graft copolymerization of MMA on CTMP infrared spectrum

Figures 2a, b, and c present infrared spectra of the untreated CTMP control, the poly(methylmethacrylate) (PMMA) and the 100% grafted CTMP samples, respectively. Table 1 contains a list of assignments of the various bands observed in this work with appropriate references. For the purpose of comparison,table 1 lists also bands of PMMA from the literature. The discussion related to band assignments is well documented in the literature[5,7,18,20,23]. Thus, we will focus our discussion in the variation of bands distribution before and after grafting.

The proof of grafting obtained by gravimetric method is confirmed by the IR spectrum presented in fig.2c with characteristic bands of PMMA[24] at 1731, 840 and 752 cm^{-1} which were not present in the spectrum of the fully conditioned pulp

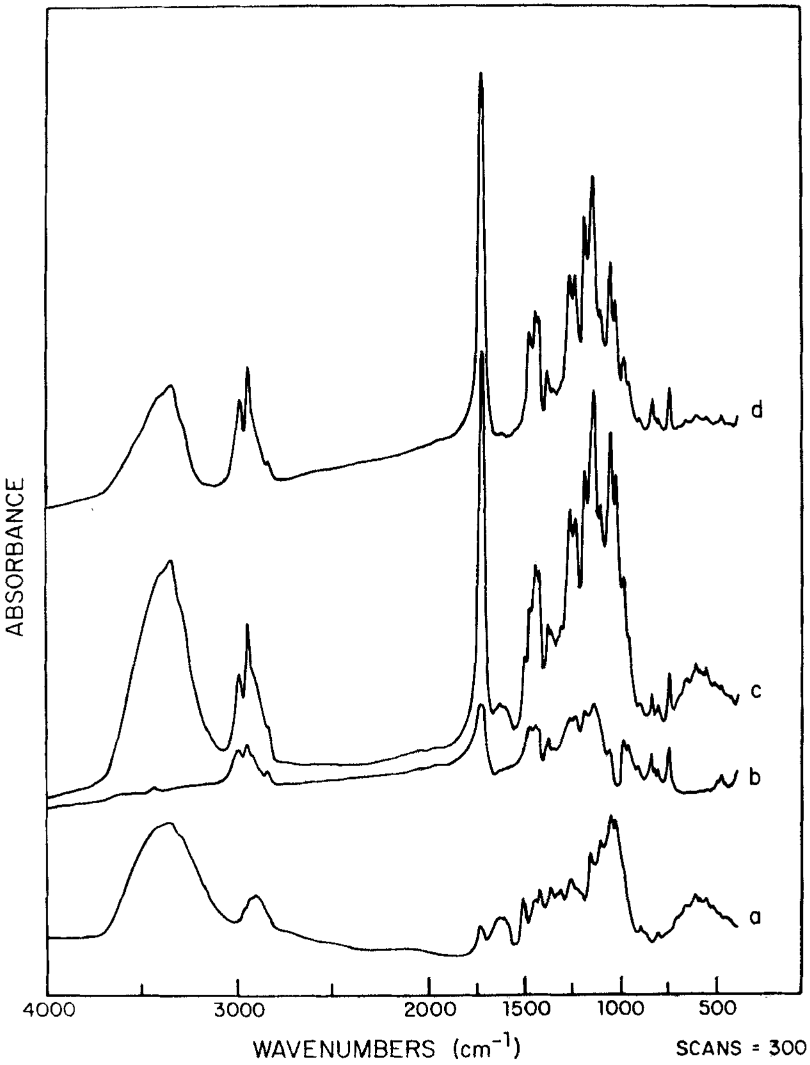


Figure 2. Infrared spectrum of :

a- The untreated CTMP control.

b- The poly(methylmethacrylate) (PMMA).

c- The 100% CTMP -PMMA grafted sample.

d- Difference spectrum of (100% grafted sample spectrum - CTMP control spectrum).

Table 1: Assignments of the IR absorption bands of grafted, ungrafted CTMP fibers and of PMMA

CTMP (pure) (1) cm^{-1}	100% Grafted CTMP (2) cm^{-1}	(2 - 1) cm^{-1}	PMMA (this work) cm^{-1}	PMMA (literature) cm^{-1}	Assignments of the bands discussed	References
3700-3000	3700-3000	3700-3000	----	----	OH hydrogen bonded stretching	17,28
----	2995	2998	2998	2996	$(O)CH_3$ and $(C)CH_3$ stretching	29
----	2951	2951	2953	2952	CH_2, $(C)CH_3$ and $(O)CH_3$ stretching	29
2933	2933	----	----	----	CH_2 antisymmetric stretch.	28
----	2920	2920	2920	2920	OCH_3 and	
2904	2904	----	----	----	C-H stretching	19,29
----	2847	2840	2844	2844	$(O)CH_3$ stretching	29
1733	1731	1731	1730	1732	C=O stretching	29
1651	1650	----	----	----	absorbed water	19,30
1607	1607	----	----	----	C=C benzene ring	17
1511	1507	----	----	----	stretching (lignin)	17
----	1484	1485	1487	1483	$(C)CH_3$ stretching	29
1462	----	----	----	----		
1453	1451	1451	1451	1450	CH_2,$(C)CH_3$,$O(CH_3)$ stretch.	29
----	1436	1437	1437	1438	$(O)CH_3$ stretching	29
1426	1426	----	----	----	CH_2 scisson vibration in cellulose	17
----	1387	1388	1389	1388	$(C)CH_3$, $(O)CH_3$ stretching	29
1372	1370	1369	1366	1368	CH_2 twisting or wagging	25
1336	1334	----	----	----	C-O-H stretching holocellulose	25

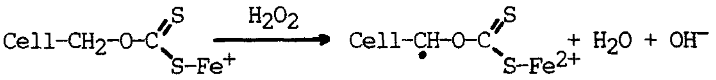
1318	1317	----	----	----	CH_2 wagging in holocellulose	17
1267	1272	1272	1273	1270	bands associated	
1234	1244	1243	1244	1242	with ester groups	
1209	1209	----	----	----	vibration of PMMA	29
----	1195	1195	1195	1194		
1162	----	----	----	----		
----	1151	1151	1147	1150	PMMA ester groups vibration	29
1112	1112	1112	----	----	Glucose ring stretching	25
1060	1060	1060	1063	1063	C-O and C-C stretching	29
1035	1035	1035	----	----	C-O stretching in holocel.	29,31
----	991	990	990	990	(O)CH_3 rocking coupled with C-O-C stretch.	29
----	968	966	965	967	(C)CH_3 rocking	29
----	910	910	913	915		
895	895	----	----	----	Anomeric carbon group frequency in cell.and xylan	32
----	842	844	841	842	CH_2 rocking	29
----	826	826	827	827	C-O-C stretching	29
810	810	810	810	810		
----	750	751	750	752	skeletal C-C stretching	29
----	484	484	484	484	C-CO-O out-of-plane deform.	29

(fig.1d) before grafting initiation. The spectrum of the CTMP control (fig.2a) exhibit some C=O band absorption at 1731cm^{-1}. The infrared spectrum presented in fig.2d is obtained by subtracting the spectrum of the ungrafted (2a) from that of the 100% grafted (2c) samples. Table 1 gives a list of bands observed in this resulting spectrum under the third column(2-1). Comparison of figures 2b and 2d or of results presented in table 1 under columns (2-1), 3 and 4, reveals that these two spectra are made up of almost the same bands, the difference being in their intensity. This result suggests that the surface of the grafted fiber is covered by the polymer in a large portion. The mechanism of cellulose grafting suggested (Eq. 4, 6a and 6b), which is probably valid for other wood components such as lignin or hemicelluloses, can help to understand this result. Indeed , the wood compound radical is formed by an hydrogen atom abstraction from an OH hydroxyl. Thus, there is probably no rupture or modification of the cellulose ring during a grafting process using a Fe^{2+}-H_2O_2 redox system.

The small but positive band related to hydrogen bonded hydroxyl at 3349 cm^{-1} observed in the difference spectrum can be a consequence of the higher accessibility of cellulose after mercerization or to a higher moisture content. But the positive band at 1112 cm^{-1} due to the glucose ring stretching vibration [25] in the difference spectrum supports the first hypothesis. Because there are no discernable positive or negative bands in the difference spectrum at 1600 cm^{-1} and at 1500 cm^{-1} associated to lignin[17], one can conclude that there is no detectable elimination nor degradation of lignin. This means that, contrarily to the ceric ion which oxidizes lignin during grafting[26], and contributes to a decrease of bands associated to lignin, ferrous ion does not.

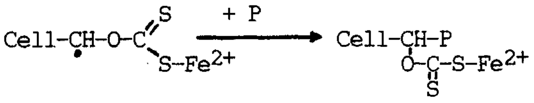
The absence of bands in the difference spectrum (fig.2) assignable to C-S, C=S or C-S-C stretching vibration[27], suggests that Eq. 4 in the grafting mechanism with formation of Cell-CH_2-O-C(S)S-P does not hold. This conclusion is supported by ESCA analyses of the grafted and ungrafted samples (to be published), showing less sulfur content in the grafted sample than in the ungrafted sample. This result is also in accordance with that of Teichman et al.[15], who state that the linking of polymer chain, via thiocarbonate groups as shown in Eq. 4, takes place to a very small degree, if at all.

From equation 3, they also report the possibility of radical formation on carbon atom via the following mechanism:



$$\mathrm{Cell{-}CH_2{-}O{-}C({=}S){-}S{-}Fe^{+}} \xrightarrow{H_2O_2} \mathrm{Cell{-}\dot{C}H{-}O{-}C({=}S){-}S{-}Fe^{2+}} + H_2O + OH^- \qquad [7]$$

leading to a C-C atoms link polymerization, as follows:



$$\mathrm{Cell{-}\dot{C}H{-}O{-}C({=}S){-}S{-}Fe^{2+}} \xrightarrow{+\,P} \mathrm{Cell{-}CH(P){-}O{-}C({=}S){-}S{-}Fe^{2+}} \qquad [8]$$

Results from ESCA and from SIMS (secondary ion mass spectroscopy) about iron content in the grafted samples, may help to elucidate this part of the mechanism.

Use of a characteristic infrared band to follow the increase of the grafting level

The grafting levels, evaluated by the gravimetric method are: 5, 10, 25, 30, 50 and 100% with an error of 2%. To illustrate the effect of increasing the grafting amount on the surface chemical composition of the fibers, we chose to follow the variation of the more intense and characteristic band of the PMMA at 1731 cm^{-1} due to the C=O stretching vibration. A net increase of the intensity of this band as the percent of grafting increases, in accordance with Beer's law is observed. To support this statement, plots of the infrared band area and of the Log (I_2/I_1) of the band as a function of the percentage of grafting are shown in figures 4a and 4b, respectively. The band area was evaluated using software data processing while the values of I_2/I_1 where obtained as shown in fig.4a from the ratio of the transmission percentages (100-percent of absorption) at the botton and the top respectively of the vertical dotted line[28]. These figures reveal, in general, the existence of a linear relationship between the C=O band intensity and the percentage of grafting. Although the lines would be expected to go through the orgin if we refer to the conditioned sample (fig.1d), both have a finite intercept, even after subtracting the untreated CTMP C=O band absorption value as illustrated in fig.4a. As suggested by Higgins[28], the scatter of the results around Beer's law curve arises mainly from errors of the amount of polymer loading rather than spectroscopic causes. But, these finite intercepts may be also a consequence of a side reaction of peroxide with the pulp. Indeed, it is established

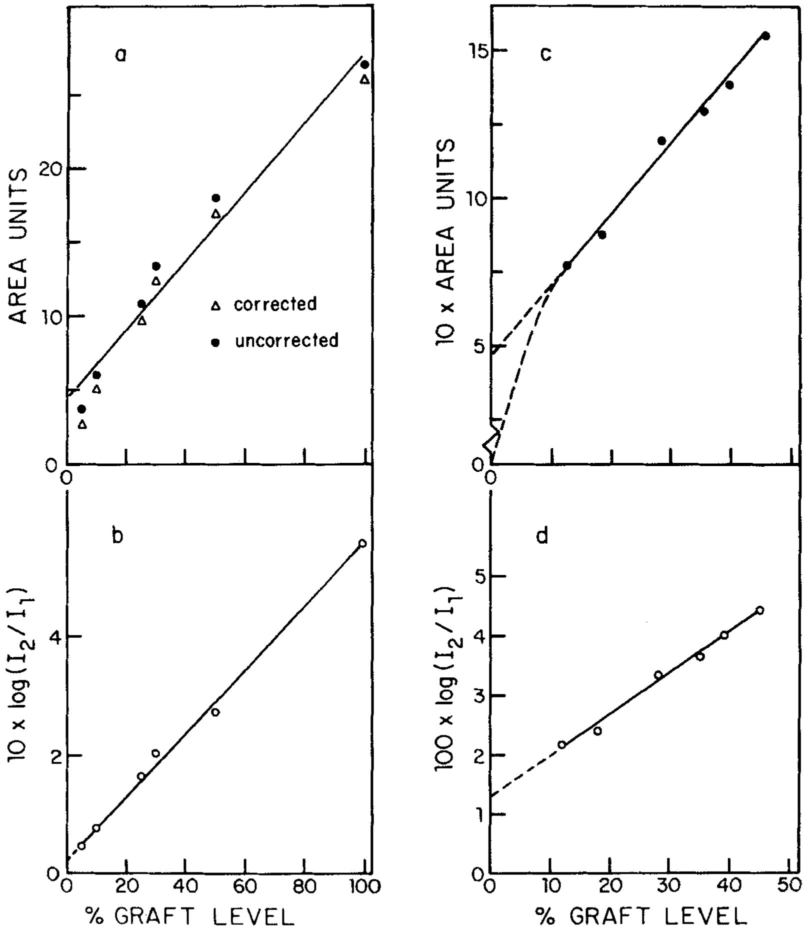


Figure 3. C=O and CN bands areas and intensities (fig.3a and 3b) and (fig.3c and 3d) respectively, vs the percentage of grafting.

that oxidation can occur when peroxide is reacted whith the pulp. The occurence of this reaction is supported by the appearance of a very weak but well defined absorption band at 1731 cm^{-1} in the spectrum (not shown) of a CTMP sample reacted with the peroxide in the absence of the monomer. Thus, if this reaction of oxidation can occur between the pulp and the peroxide, specially when the concentration of the monomer is low, it will contribute to an over estimation of the 1731cm^{-1} band absorption intensity, leading to the finite intercepts observed. However, one can use these lines as calibration curves to determine unknown grafting levels, except bellow 5 to 10% where it would not recommended to use these curves.

In order to verify that the finite intercepts observed are not a consequence of the C=O wood components contribution and/or a consequence of the pulp oxidation by the peroxide, a second type of monomer was grafted onto the CTMP fibers. The choice of acrylonitrile monomer was based on the fact that it has a characteristic nitrile (CN) group which is absent in the spectrum of the untreated CTMP sample (fig.1a) and is not affected in its intensity by the oxidation of the pulp by the peroxide during the grafting process.

A typical infared spectrum of a CTMP sample which was graft-copolymerized with acrylonitrile (AN) is shown in fig.5b and, for comparison, the spectrum of the untreated CTMP sample used in the AN grafting experiments in fig.5a. The formation of graft copolymer of AN can easily be detected by the presence of the

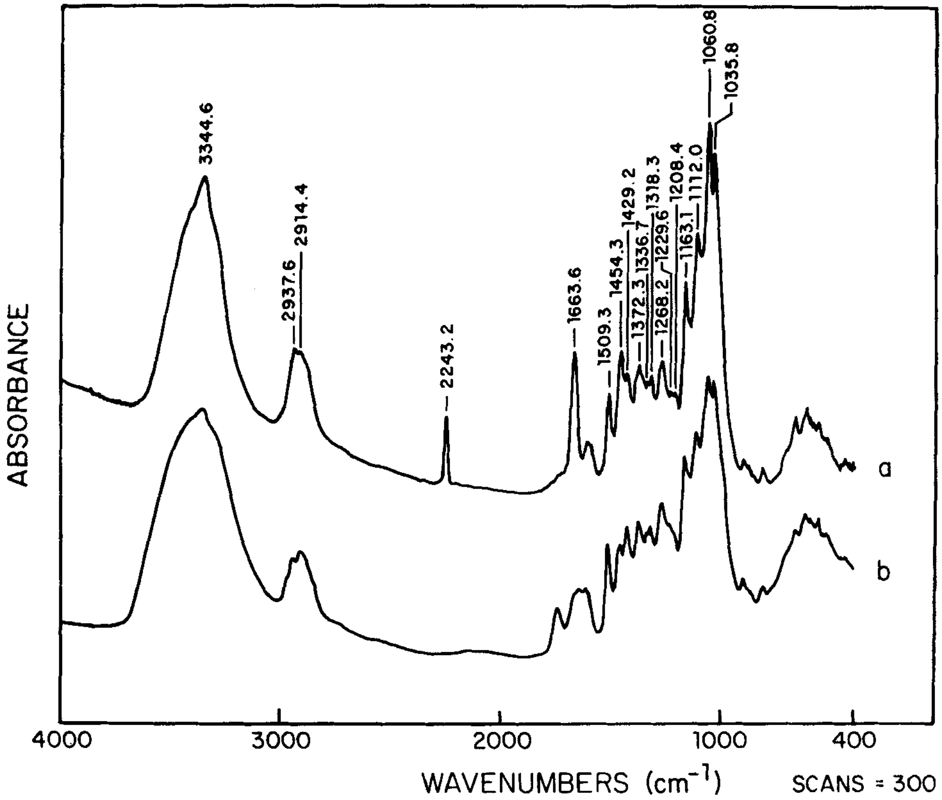


Figure 4. Infrared spectrum of:

a- The untreated CTMP control.

b- The 45% CTMP-PAN grafted sample.

distinctive and characteristic nitrile absorption band at 2244 cm^{-1}. The CH_2 deformation vibration, another characteristic band of acrylonitrile[29], appears at 1454 cm^{-1} as well as the CH_2 deformation vibration of wood components. Thus, the nitrile absorption band will serve as a control of pulp grafting.

The spectral data processing was exactly the same as in the case of samples grafted with MMA.

The grafting percentages determined by the gravimetric method are: 12, 18, 28, 35, 39 and 45%. The variation of the band absorption intensity at 2244 cm^{-1} as a function of the percent of grafting is similar to that observed previously in the case of MMA, it increases in intensity with the increase of the grafting level. In fig. 4c and 4d the nitrile band area and intensity, Log I_2/I_1, are illustrated as a function of the percent of grafting. As in the case of MMA, both curves have finite intercepts. Thus, the finite intercepts observed in fig. 4a and 4b are due not to wood components contribution but rather to overestimation in the grafting percentage evaluation. Indeed, the percentage of grafting determined gravimetrically is calculated as follows:

$$(\%)\ \text{grafting} = [(A-B)/B]*100 \qquad [9]$$

where A corresponds to the weight of the product after graft-copolymerization and extraction, and B the original weight of the sample. The grafting percentage determined in this manner did not take into account neither the adsorbed metallic ions, nor the residual homopolymer after extraction. The ion adsorption, also reported by Lin et al.[26] in the case of ceric ion, confirmed by results from ESCA analysis of the grafted samples, as well as the residual homopolymer in the extracted sample may increase the value of A and thus, the percent of grafting. It is suggested in the literature that a more precise percent of grafting can be obtained if the grafted sample is extracted before being dried, the homoplymer as well as the adsorbed metallic ions being more easily extracted (26).

CONCLUSIONS

The results of the Infrared study of the graft-copolymerization of methyl methacrylate (MMA) and of acrylonitrile (AN) onto chemithermomechanical (CTMP) fibers can be summarized as follows:

1- Infrared spectra of CTMP samples recorded after mercerization, xanthation and ion exchange reveal very well the effect of these processes on the fiber chemical history. The mercerization has the most important effect on the sample spectrum by a net increase of absorption bands intensity due to hydroxyl groups at 1452,881,869 and at 836 cm^{-1}. This result confirms the swelling of the pulp and the higher accessibility of cellulose. Some new bands observed after xanthation at 1292,1225 and at 1002 cm^{-1} are tentatively associated to carbon-sulfur atoms links vibrations.

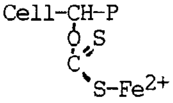
2- The appearance of characteristic bands at 1731,840 and 752 cm^{-1}, and on the other hand, of the nitrile band at 2244 cm^{-1}, are proof of grafting of MMA and AN, respectively.

3- The spectral subtraction illustrates very well the effect of grafting on the surface chemistry of the fibers by the positive bands in the difference spectra being almost entirely due to the grafted polymer.

4- At over 5 to 10% of polymer loading, the MMA and AN IR characteristic band absorption intensity at 1731 and 2244 cm^{-1} respectively, can be used as calibration curves for quantitative determination.

5- The finite intercept of the characteristic band intensity or band area vs the percent of grafting, may be an indication of the presence of residual homopolymer and adsorbed metallic ions in the extracted samples.

6- The absence of any discernable positive band in the IR difference spectrum associated to CS links, is an indication that the graft-copolymerization mechanism leading to the formation of



is accomplished with a very slow rate, if at all.

ACKNOWLEDGEMENT

We thank the National Sciences and Engineering Research Council and the Ministère de l'emploi et de l'immigration du Canada for research grants and Consolidated Bathurst for the pulp supply.

References

1- K. Dimov and P. Pavlov, J. Polym. Sci., 7, 2775 (1969).

2- S.C. Lin, B.J. Bulkin, and E.M. pearce, J. Polym. Sci.: Polym. Chem. Ed., 17, 3121 (1979).

3- D.J. Jenkin, Appl. Polym. Symp., 28, 1309 (1976).

4- F.G. Hurtubise, Tappi, 45 (6), 460 (1962).

5- C.Y. Liang and R.H. Marchessault, J. Polym. Sci., 39, 269 (1959).

6- H.I. Bolker and N.G. Sommerville, Pulp and Paper Magaz. Canada, T187 (1963).

7- A.J. Michell, A.J. Watson and H.G. Higgins, Tappi, 48(9), 520 (1965).

8- A.E. Nabila and F.E. Samira, J. Appl. Polym. Sci., 30, 2171 (1988).

9- B.V. Kokta, P.Lepoutre and J.L. Valade , Tappi, 55 (3), 370 (1972).

10- P. Zadorecki and P. Flodin, J. Polym. Sci., 30, 2419 (1985).

11- A. Lagos and J. Reyes, J. Polym. Sci.: Polym. Chem. Ed., 26, 985 (1988).

12- B.V. Kokta and J.L. Valade, Tappi, 55, 336 (1972).

13- A.O. Barry, Z. Koran and R.S. Kaliaguine, submitted for publication.

14- S.R. Culler, H. Ishida and J.L. Koenig, Ann. Rev. Mater. Sci., 13, 387 (1983).

15- H.E. Teichmann, W.J. Brickman, R.V. Faessinger, C.G. Mayer and H.A. Grassig, Tappi, 57 (7), 61 (1974).

16- H.A. Grassig, J. Macromol. Sci. Chem., A10, 759 (1976).

17- S. Kolboe and O. Ellefsen, Tappi, 45 (2), 163 (1962).

18- C.Y. Liang, K.H. Bassett, E.A. Mcginnes and R.H. Marchessault, Tappi, 43 (12), 1017 (1962).

19- M. Tsuboi, J. Polym. Sci., 25, 159 (1957).

20- A.J. Michell, A.J. Watson and H.G. Higgins, Tappi, 48 (9), 520 (1965)

21- S. Rydholm, Tappi, 7, 11 (1970).

22- A.Kobayashi,R.B. Phillips, W. Brown and V.T. Stannett, Tappi, 54 (2), 215 (1971).

23- S.K. Dirlikov and J.L. Koenig, Appl. Spectroscopy, 33 (6), 551 and 555 (1979).

24- A. Lagos and J. Reyes, J.Polym. Sci. :Part A: Polym. Chem., 26, 985 (1988).

25- C.Y. Liang and R.H. Marchessault, J. Polym. Sci., 37, 385 (1959).

26- K.C. Lin, Y.S. Wu, T.H. Tan and T.L. Tai, J.Am. Chem. Soc., 233 (1982).

27- R.T.O Connor, E.F. Dupre and E.R. MacCall, An. Chem., 29 (7), 998 (1957).

28- L.J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd Ed., London, Methuen, 1958.

29- K.D. Stoil and J.L. Koenig, Appl. Spectrosc., 33 (6), 551 and 555 (1979).

30- R.H. Marchessault, in Proc. IUPAC Wood chem. Symp., Montreal, 1961, London, Buttherworths, 1962.

31- R.J. Yamadera, Polym.Sci., 50 (153), 54(1961).

32- K. Nakanishi, Infrared Absorption Spectroscopy-Practical; Holden-Day, San Francisco, C A. 1962.