Grafting of Poly(methyl acrylate) onto Sulfite Pulp Fibers and Its Effect on Water Absorbance

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ABSTRACT: To prepare super water absorbent hydrogels of wood cellulose fibers, poly(methyl acrylate) (PMA) was copolymerized onto softwood sulfite pulp fibers using free radical initiator followed by alkaline hydrolysis. Ceric ammonium nitrate (CAN) was used as the free radical initiator. Effects of various parameters such as fiber concentration, monomer/pulp (M/pulp) ratio, CAN concentration, and reaction time on the grafting yield and on other grafting parameters were investigated. The graft conversion was the same from low to medium fiber concentration. The amount of initiator required was found to be independent of fiber concentration to achieve maximum grafting yield. Different fiber fractions (classified based on their length) have no effect on the grafting yield.

The evidence of graft copolymerization was determined by using ATR-IR spectroscopy. The X-ray diffraction (XRD) analysis shows that grafting takes place both in amorphous and crystalline regions of cellulose fibers and the decrease in crystallinity of the grafted fibers with an increase in grafting yield was confirmed. The surface morphology of the PMA-g-cellulose was characterized by scanning electron microscopy (SEM). The water retention value of the hydrolyzed grafted pulp was determined based on a centrifugation technique. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3195–3203, 2007

Key words: fibers; graft copolymers; hydrogels; FTIR; swelling

INTRODUCTION

Cellulose is cheap, renewable, biodegradable, and is the most abundant organic raw material in the world. Modification of cellulose by graft copolymerization is the most attractive technique to chemically change the cellulose chains by grafting functional polymers so that different properties can be imparted to the initial material.[1] Graft copolymerization of different monomers onto cellulosic or lignocellulosic materials has been used to enhance their properties including elasticity,[2] water absorbency,[3] ion-exchange capabilities,[4] thermal resistance,[5] and resistance to microbiological attack.[6]

Two methods have been developed for synthesizing cellulose absorbents for water; one is the cross-linking of water soluble cellulose derivatives e.g., carboxymethyl cellulose and the other is the grafting of hydrophilic vinyl based monomers (e.g., acrylic acid, methacrylic acid etc.) onto cellulosic materials. In the second method, water absorbents are prepared by grafting vinyl polymer[3,7–9]onto cellulosic materials followed by post hydrolysis and decrystallization.[10] Research for the second method is more advanced, because cellulose is particularly suitable as support material for hydrogels due to its renewability, good mechanical strength, and processability. These wood fiber-based hydrogels could be used specifically in towel papers to improve their absorbency as well as their wet and dry tensile strength.[9] Other applications could be in diapers and sanitary napkins.

In the graft copolymerization of vinyl monomers onto cellulose, free radical methods have received the most attention. Free radicals are formed on the cellulose molecules either by chemical means or by irradiation. Among these grafting methods, the direct oxidation of cellulose by ceric ion has gained considerable importance because of its high grafting efficiency compared with other known redox systems. It produces a complex with cellulose, which decomposes to generate free radicals onto the cellulosic backbone where grafting of vinylic monomers can occur.[11,12]

Various vinylic monomers such as acrylonitrile,[3] acrylic acid,[10] methyl acrylate[4] etc. have been used so far to improve the water absorbency of the cellulosic fibers. However, because of the increasing environmental concern acrylonitrile is no longer in use as it is a carcinogen. Acrylic acid has also been studied by various researchers for cellulose graft copolymer to improve the water absorbency, but its grafting efficiency is very low with CAN. Recently,[9] a compa-

rable study of all the important monomers with respect to their grafting yield and water absorbency has been given and methyl acrylate was found to be effective in terms of both grafting yield and water absorbency.

In the present work, we tried to examine closely the effect of reaction variables w.r t. the fiber concentration on the grafting yield and on other grafting parameters during grafting of methyl acrylate onto pulp fibers. Following the grafting, fibers were hydrolyzed in aqueous NaOH solution to achieve super water absorbency.

EXPERIMENTAL

Materials

Bleached softwood sulfite pulp fibers were kindly supplied by Fraser Papers Edmundston mill in New Brunswick, Canada. Methyl acrylate (MA) monomer (99%), ceric ammonium nitrate (CAN) initiator and hydroquinone were obtained from Sigma-Aldrich (Canada) and used as received. Nitric acid, sulfuric acid (reagent grade) and acetone (ACS grade) were obtained from Fisher Scientific Canada. Distilled deionized water has been used in all the experiments unless otherwise mentioned.

Fiber classification

Fiber classification was performed in a Bauer-McNett classifier according to *TAPPI Standard Methods* T 233 cm-82 and the length of the classified fibers was determined using a *Fiber Quality Analyzer* from Op Test Equipment Inc.

Graft copolymerization

The graft copolymerization of PMA onto pulp fibers was carried out by the addition of MA and then of CAN to the pulp. Sulfite pulp fibers were selected because of the lowest crystallinity among the wood pulp fibers, which favor the grafting reaction.[13,14] Grafting was carried out at low to medium consistency level (1–12% wt/wt) in a plastic bag. The bag was fitted with a PTFE septum fitting in a polypropylene housing for use with a syringe. This allows the introduction and evacuation of oxygen/air in the bag and liquid material can be injected with the help of syringe.

Never dried pulp in water was filtered to 30–32% consistency and transferred into the plastic bag (5.0 g oven dry) and then it was sealed. The deoxygenated and distilled water (acidified to pH 2 with nitric acid) was used for dilution. Nitrogen gas was introduced into the plastic bag and the mixture was kneaded for 5 min, and then the bag was evacuated (fresh N_2 was added during evacuation to remove the oxygen present in the cellulose fibers). This process was repeated 4–5 times and then the required amount of monomer was added by syringe and the mixture in plastic bag was mixed by hands for 15 min. Thereafter, the CAN solution (2–9 wt % of the oven dry pulp) freshly prepared in deoxygenated water acidified to pH 2, was added to the reaction mixture and again shaken for 15 min. After shaking, the bag was placed in a constant temperature water bath at 25°C for 4 h. After 4 h the polymerization reaction was stopped by the addition of hydroquinone and then washed several times with water and then with acetone and dried under vacuum at 60°C overnight. Finally, the removal of homopolymers from the grafted samples was carried out in soxhlet extraction unit for 24 h, using acetone as a solvent. The grafted product was then dried in a vacuum oven at 60°C for 12 h.

Hydrolysis of cell-g-PMA

The alkaline hydrolysis was done by boiling grafted fibers in a 3% NaOH solution for 2 h with magnetic stirring. After hydrolysis fibers were washed thoroughly with water.

Determination of molecular weight of grafted chains

The grafted polymer chains were isolated from backbone polymer by treatment with 72% sulfuric acid following the process described by Flaque and Montserrat.[15]

An Ubbelhode viscosimeter was used for intrinsic viscosity [η] measurement and Mark-Houwing equation was applied to calculate the viscosimetric average molecular weight. The molecular weight of the isolated polymer was determined using the following relationship for Poly (methyl acrylate) in acetone at 25°C.[16]

$$[\eta] = 5.5 \times 10^{-5} [\overline{M}v]^{0.77}$$

ATR-IR analysis

Attenuated total reflectance (ATR) spectra were recorded at ambient condition for blank sulfite pulp and methyl acrylate graft copolymer samples that had been acetone extracted. Air dried samples were ground in a Wiley mill and then screened to get a fine powder that was used for ATR. A Thermo Spectra Tech ZnSe horizontal ATR cell was used.
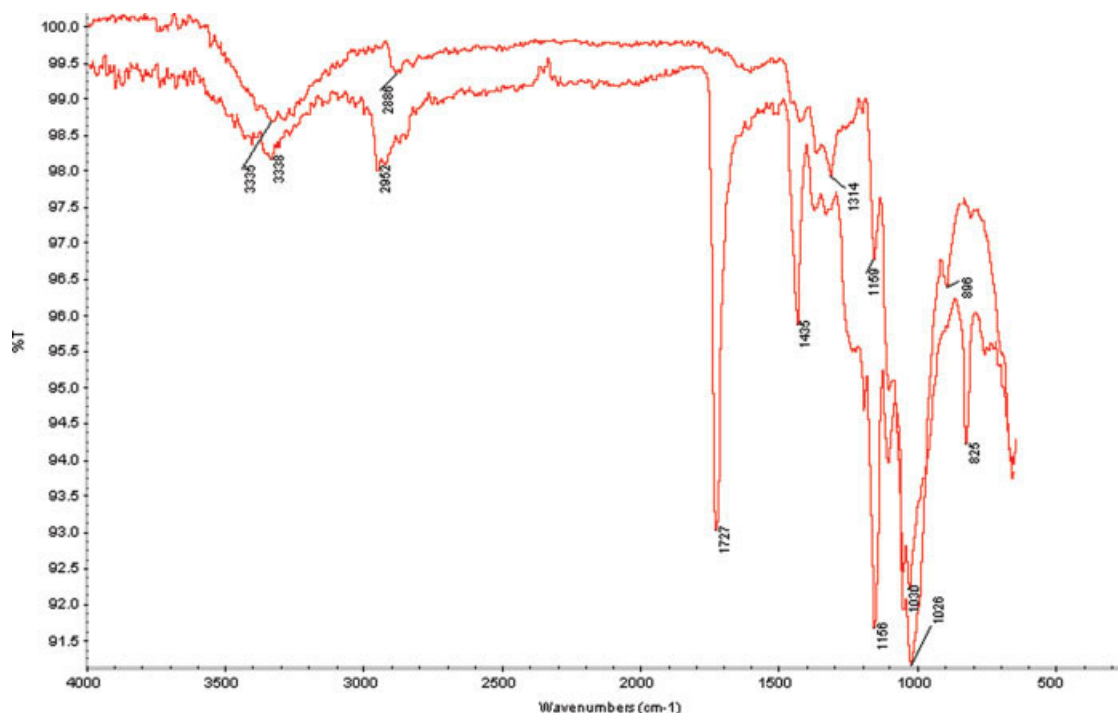
Figure 1 IR spectra of (a) Sulfite pulp (b) PMA grafted sulfite pulp. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

SEM analysis

Surface morphology of the original cellulose and grafted fibers were characterized with a JEOL 6400 scanning electron microscope, operated at 7 KV. Fibers were secured to the specimen stubs with double-sided scotch tape. The samples were coated with gold using an Edwards S150A sputter coater.

XRD analysis

Dried grafted fibers were ground in a Wiley mill so as to pass through a 50 mesh screen and then pressed into pellets.[17] X-ray diffraction was recorded with a Bruker X-ray diffraction machine, in the angular range 5–60° with a scan step size 0.02°. The CuK radiation was monochromatized from anode at 40 KV and 30 mA, with a wavelength of 1.54 Å.

Definition of various grafting parameters

The following grafting parameters were calculated as described in detail previously:[18]

Percent monomer conversion (C_t): weight percent of monomer converted into the polymer.

Percent grafting yield (G_y): weight percent of the grafted polymer with respect to initial weight of cellulose.

Percent grafting efficiency (G_e): weight percent of the grafted polymer with respect to total polymer formed.

Percent graft conversion (C_g): weight percent of monomer converted into the graft polymer.

Percent homopolymer conversion (C_h): weight percent of monomer converted into the homopolymer.

Number of grafted chains (N_g): number of moles of synthetic polymer chains grafted to cellulose, calculated as the ratio of weight of grafted polymer and molecular weight of the grafted chains.

$$\text{Grafting rate } (R_g) = \frac{1000w}{vtm}$$

where w is the graft polymer weight, v is the volume of reaction mixture, t is the time of reaction (in seconds), and m is the molecular weight of the monomer.

Water absorbency

The water absorbency of hydrolyzed grafted fibers was measured in terms of water retention value (WRV) by following the centrifugal technique (at 900G for 30 min).[8]

$$\text{WRV(g/g)} = \frac{W_2 - W_1}{W_1}$$

where W_2 and W_1 are the weight of wet and completely dry samples, respectively.

TABLE I
Effect of Fiber Concentration on Grafting Yield and on
Other Grafting Parameters

FC[a]	C_t	G_y	G_e	C_g	C_h
1	96.4	173.5	89.4	86.7	9.6
2	96.1	174.5	90.7	87.2	8.9
4	95.7	165.2	86.2	82.6	13.2
6	95.6	164.6	85.1	82.3	14.3
8	95.5	164.0	85.8	82.0	13.5
10	94.7	166.3	86.2	83.1	13.6
12	94.0	133.9	71.1	66.9	27.1

Grafting: M/pulp ratio 2 : 1, CAN charge = 3.5 wt % of pulp, Time = 4.0 h, Temp = 25°C.
[a] Fiber Concentration (FC) = wt/wt %.

TABLE II
Effect of CAN Charge on Grafting Parameters

	1% Fiber concentration			10% Fiber concentration		
CAN Charge	C_t	C_g	C_h	C_t	C_g	C_h
2.0	61.7	54.6	7.1	70.2	54.1	16.1
2.7	80.5	71.7	8.8	91.0	72.7	18.2
3.5	93.5	83.6	9.9	96.3	83.3	12.9
5.0	93.6	83.8	9.6	93.5	79.7	13.7
6.5	94.0	84.2	9.8	92.9	78.5	14.3
9.0	95.0	83.4	10.1	92.7	79.1	13.6

CAN Charge—wt % of oven dry pulp.

RESULTS AND DISCUSSION

Evidence of grafting by ATR-IR spectra

The grafting was confirmed by comparing the IR spectrum of pulp fibers with that of the grafted product and the results obtained are shown in Figure 1. In both spectra, a broad absorption band in the 3100–3500 cm^{-1} region corresponds to the O—H stretching vibrations of cellulose, absorbed water, hemicellulose.[19] In spectra (a), additional characteristic weak absorption band at 2826 cm^{-1} and very strong peak at 1026 cm^{-1} appeared due to the C—H stretching and bending, respectively.[20] IR spectrum (b) of purified PMA-g-cellulose in Figure 1 showed new characteristic sharp and strong absorption band at 1727 cm^{-1}, corresponds to the carbonyl group (C=O) group in PMA.[21] Absorption bands at 825 cm^{-1} and 1156 cm^{-1} were due to the C—H stretching vibration and C—O—C vibrations, respectively, in PMA molecules.[19] These results confirm the grafting of methyl acrylate on cellulose.

Effect of fiber concentration on grafting yield

Results are shown in Table I for the effect of fiber concentration (abbreviated as FC in the following

discussion) on various grafting parameters. The monomer conversion (C_t) was unaffected from 1 to 12% FC. However, the grafting yield (G_y), grafting efficiency (G_e) and graft conversion (C_g) were relatively higher at 1 and 2% FC in accordance with the low homopolymer formation and then remained constant up to 10% FC. Decrease in grafting yield (G_y) at 12% FC was due to increased homopolymer formation. At 12% FC, a low grafting yield in spite of the same monomer conversion (C_t) might be due to the poor mixing of the reaction mixture. Lepoutre et al.,[22] in their study of grafting of acrylonitrile on wood pulp fibers found that the rate of graft conversion and level-off value increase with increasing the fiber concentration up to 4% during grafting. However, in our case the level-off value was independent of fiber concentration up to 10%.

The low homopolymer formation at 1 and 2% FC than at 4–10% FC was due to the fact that at higher fiber concentration (4–10%), growing homopolymer macroradicals were relatively immobile and close to each other, favoring the homopolymer formation.

Effect of ceric ion charge

The CAN charge was varied from 2 to 9 wt % of oven dried pulp used and the results are shown in Figure 2. The grafting yield (G_y) first increased sig-
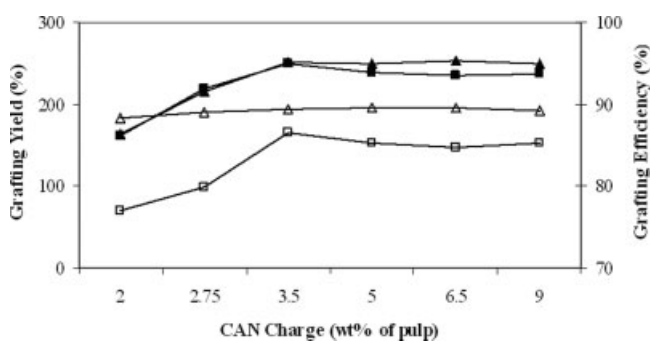

Figure 2 Effect of initiator concentration on grafting yield and grafting efficiency for M/pulp ratio 3 : 1, Time = 4.0 h, Temp = 25°C; Grafting yield at (■) 10% FC, (▲) 1% FC; Grafting efficiency at (□) 10% FC, (△) 1% FC.
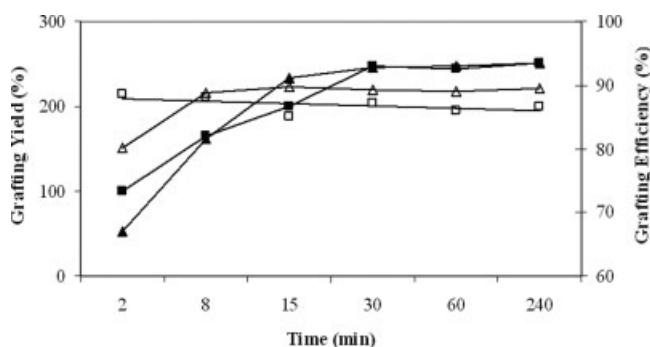

Figure 3 Effect of reaction time on grafting yield and grafting efficiency for M/pulp ratio 3 : 1, CAN charge = 3.5 wt % of pulp, Temp = 25°C; Grafting yield at (■) 10% FC, (▲) 1% FC; Grafting efficiency at (□) 10% FC, (△) 1% FC.

TABLE III
Effect of Reaction Time on Grafting Parameters

Time	1% Fiber concentration						10% Fiber concentration					
	C_t	C_g	C_h	$R_g \times 10^4$	$\overline{Mv} \times 10^{-5}$	N_g	C_t	C_g	C_h	$R_g \times 10^4$	$\overline{Mv} \times 10^{-5}$	N_g
2	21.7	17.4	4.3	5.1	2.65	0.20	37.4	33.0	4.3	106.0	2.85	0.35
8	60.9	54.0	6.8	4.0	4.15	0.39	62.2	54.8	7.4	44.2	3.73	0.44
15	87.0	78.0	8.9	3.0	4.67	0.50	78.8	66.6	11.9	28.7	3.90	0.51
30	91.4	81.6	9.7	1.6	4.76	0.52	94.2	82.2	12.0	17.7	4.60	0.54
60	94.8	82.4	10.1	0.8	–	–	94.4	81.1	13.2	8.6	–	–
240	94.2	83.6	10.6	0.2	–	–	96.3	83.3	12.9	2.2	–	–

R_g, mole/L-sec; time, min; N_g, mmoles/100 g cellulose.

nificantly to a maximum and then leveled-off. The initial increases in grafting yield with the increase in the CAN charge could be due to the increased catalyst consumption that resulted in the formation of complex between CAN and cellulose and produce more radical sites which lead to the formation of graft copolymer. The grafting yield was similar at 1 and 10% FC. The monomer conversion (C_t) and graft conversion (C_g), shown in Table II also followed the same trend as the grafting yield. However, the grafting efficiency (G_e) followed different trend for 1 and 10% FC with respect to the CAN charge. At 1% FC, the grafting efficiency was consistently higher than that at 10% FC and it did not vary for different CAN charges whereas at 10% FC, it first increased with CAN charge and then remained constant. The constant grafting efficiency at 1% FC means that CAN was mainly used for the generation of free radicals on the cellulose backbone, which were responsible for the initiation of graft copolymerization. However, for 10% FC the initial low grafting efficiency at low CAN charge might be due to the competition between grafting and homopolymer formation. It was also noted that the homopolymer formation (C_h) was higher at 10% than at 1% FC.

Effect of reaction time

The graft copolymerization was carried out at different time intervals keeping all other conditions constant. As shown in Figure 3, irrespective of the fiber concentration, the grafting yield reached to the maximum in 30 min and thereafter leveled-off. Initially the grafting efficiency (G_e) was lower for 1% FC and reached the maximum level in 8 min and then remained constant. However, the grafting efficiency for 10% FC remained almost constant. Other grafting parameters (C_t, C_g, and C_h) also followed the same trend as grafting yield irrespective of the fiber concentration as shown in Table III. In an earlier study, Ogiwara et al.[23] mentioned about the different stages of ceric ion consumption on cellulose fibers that corresponds to initial rapid adsorption of ceric ions on cellulose followed by slow oxidation of cellulose to create radical sites of different reactivity. Following

the adsorption, the first oxidation stage was very fast and then it took place slowly. The increase in grafting yield with time indicated that CAN retained its activity for a period of time and continuously formed active sites on the cellulose backbone to induce the graft polymerization. The leveling-off might be due to the depletion of the reactants.

Initial trends of increasing grafting yield up to 30 min reaction time were different for 1 and 10% FC as depicted in Figure 3. For 2 min reaction time, the grafting yield was higher for 10% FC and increased continuously up to 30 min and then level-off. However, the grafting yield increased at a faster rate from 2 to 15 min for 1% FC. The initial higher grafting yield at 10% FC was due to the higher grafting rate (R_g) as shown in Table III, which was due to the fast formation of radical sites on cellulose fiber backbone by the initiator. As the grafting reaction proceeds further, the slower increase in the grafting yield at 10% FC might be due to the resistance provided by the rapidly growing polymer chains on the surface of fibers for the diffusion of ceric ions and monomer.

We also determined the grafting frequency (number of grafted chains N_g) and molecular weight of the grafted polymers, and the results are shown in Table III. For 2 min reaction time, the number of grafted chains was much higher for 10% FC. In addi-
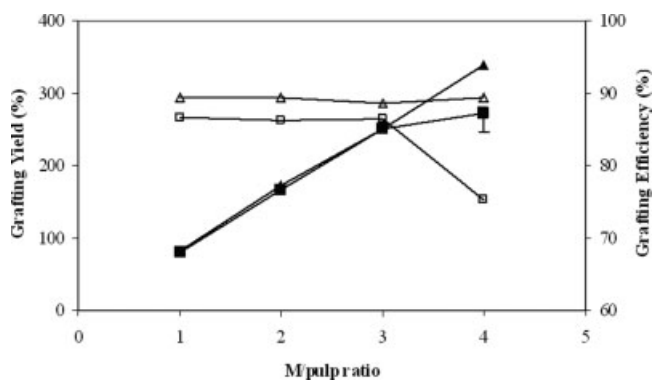

Figure 4 Effect of M/pulp ratio on grafting yield and grafting efficiency for, CAN charge = 3.5 wt % of pulp, Temp = 25°C, Time = 4.0 h; Grafting yield at (■) 10% FC, (▲) 1% FC; Grafting efficiency at (□) 10% FC, (△) 1% FC.

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TABLE IV
Effect of Monomer Concentration on Grafting Parameters

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M/pulp	1% Fiber concentration					10% Fiber concentration				
	C_t	C_g	C_h	$\overline{Mv}\times10^{-5}$	N_g	C_t	C_g	C_h	$\overline{Mv}\times10^{-5}$	N_g
1 : 1	92.3	82.6	9.7	3.1	0.27	93.2	80.7	12.4	2.9	0.28
2 : 1	96.4	86.7	9.6	4.2	0.41	96.2	83.1	13.1	4.3	0.39
3 : 1	94.2	83.6	10.6	4.76	0.52	96.3	83.3	12.9	4.6	0.55
4 : 1	95.0	85.0	10.0	5.56	0.61	90.0	67.7	22.2	4.0	0.68

tion to that, beyond 2 min reaction time the molecular weight and the number of grafted chains increased continuously and then reached the maximum level in 30 min. Furthermore, the final value of the molecular weight and the number of grafted chains were almost same for 1 and 10% FC samples.

Effect of monomer concentration

The effect of monomer/pulp weight ratio (M/pulp ratio) on the grafting yield and grafting efficiency, as well as on other grafting parameters is depicted in Figure 4 and Table IV. The grafting yield increased with increase of M/pulp ratio from 1 : 1 to 4 : 1. It increased linearly from M/pulp ratio 1 : 1 to 3 : 1 irrespective of the fiber concentration during grafting, but this increase deviated from linearity for 10% FC beyond M/pulp ratio 3 : 1. The linear increasing trend of grafting yield at 1 and 10% FC may be associated with the higher monomer concentration for the immobile cellulose macroradicals. However, for M/pulp ratio beyond 3 : 1, the decrease in grafting yield at 10% FC was due to the increased homopolymer formation (C_h) as shown in Table IV. The grafting efficiency in Figure 4 is also in accordance with the grafting yield trends.

Table IV shows that for 1% FC the number of grafted chains and the molecular weight increase with the monomer concentration. The same trends were observed for 10% FC up to M/pulp ratio 3 : 1. However, the molecular weight of the grafted chains starts to decrease beyond M/pulp ratio 3 : 1, whereas the number of grafted chains still increases. The decrease in molecular weight might be related to the fact that grafted polymer chains were confined to the surface rather than to the cellulose matrix. Therefore, rapidly forming grafted chains on the cellulose surface hinders the access of monomer units, thus resulting in the decreased molecular weight of the grafted chains.

X-ray diffraction analysis

Cellulose is composed of both crystalline (ordered) and amorphous (disordered) regions. Changes in the fine structure of cellulose as a result of grafting have been discussed before.[14] We determined the crystallinity of wood cellulose fibers and fibers grafted with poly (methyl acrylate) to see the changes in the

fine structure of cellulose as a result of grafting at medium consistency level. As shown in Figure 5 the degree of crystallinity of cellulose decreased as the grafting yield increased (with increase in M/pulp ratio), indicating that the growth of grafted chains occured in both the ordered region and the amorphous region of cellulose.

SEM analysis

Scanning electron microscope images of untreated and grafted fibers are shown in Figure 6. Figure 6(a) revealed that fiber surface was very rough and that of the original cellulose fibers showed microfibrils, cracks and pitches. Grafted fibers were relatively smooth and round for the M/pulp ratio 2 : 1 as depicted in Figure 6(b,c) but some pitches as shown in Figure 6(b) and fibrils in Figure 6(c) were still evident. At M/pulp ratio of 4 : 1 [Fig. 6(d)] the fiber surface was very smooth and completely covered with the polymer layer, and all the cracks disappeared. However some of the microfibrils underneath the polymer layer can be seen, indicating that the polymer layer was very thin. Therefore SEM images provide the evidence that a considerable amount of PMA was grafted onto pulp fibers.

Effect of fiber length on grafting parameters

Pulp fibers of different length may behave differently during grafting. To see this effect, fibers were
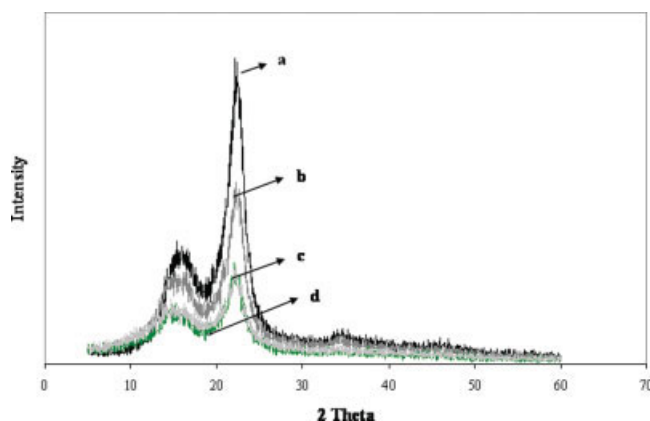

Figure 5 X-ray diffractograms of (a) blank sulfite pulp fibers; for 10% FC; (b) grafted fibers correspond to M/pulp ratio 1 : 1, (c) grafted fibers correspond to M/pulp ratio 2 : 1, (d) grafted fibers correspond to M/pulp ratio 3 : 1.
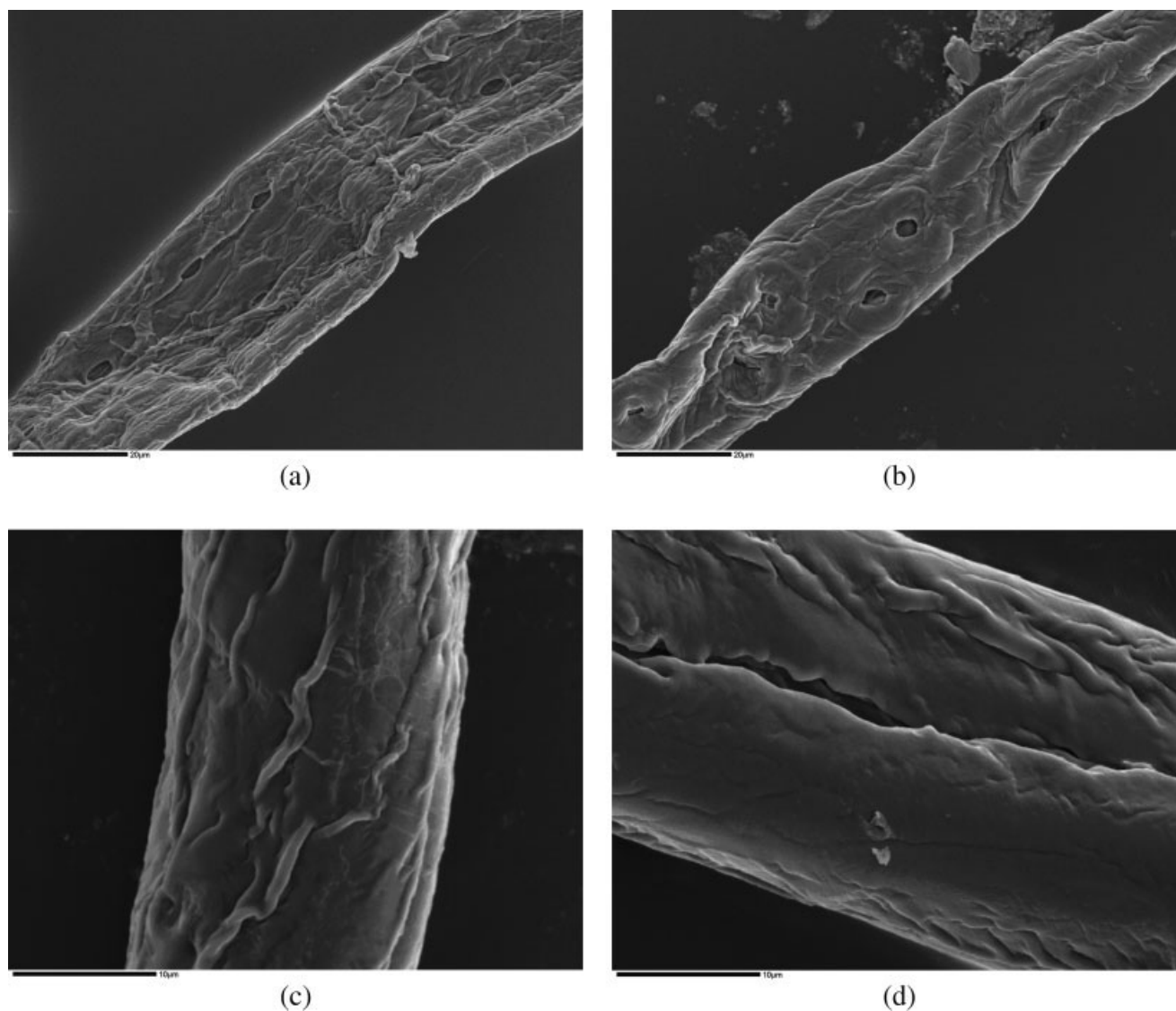
Figure 6 SEM images of the original and grafted fibers (at 10% FC); (a) Blank sulfite pulp fibers, magnification 1200; (b) Grafted fibers for M/pulp ratio 2 : 1, magnification 1200; (c) Grafted fibers for M/pulp ratio 2 : 1, magnification 3000; (d) Grafted fibers for M/pulp ratio 4 : 1, magnification 3000.

fractionated and subsequently grafted. Table V shows that for the untreated pulp the shorter fibers have higher water retention value (WRV).

The grafting yield results were essentially the same for different fractions, suggesting that the fiber length does not affect the grafting results. The WRV of these grafted fibers were significantly higher than the unfractionated sulfite pulp fibers, but the effect of different fractions on the WRV results followed the same trend. Therefore, these results supported the conclusion that the grafting behavior would be similar for pulp fibers with different fiber length and that the WRV is predominantly controlled by the grafted chains.

Effect of fiber concentration during hydrolysis

The WRV of the hydrolyzed grafted fibers are shown in Table VI. During the hydrolysis, methyl group in

TABLE V
Fiber Fractionation and Its Effect on Grafting Yield and WRV

Fiber type	Screen size	Length[b]	WRV[c]	G_y	WRV[d]
UF SP[a]	–	0.85 ± 0.03	2.89	166.3	42.2
SP #1	R14	2.33 ± 0.03	2.92	161.8	43.3
SP #2	P14/R28	2.02 ± 0.02	3.55	157.9	41.7
SP #3	P28/R48	1.30 ± 0.03	4.21	158.2	45.8
SP #4	P48/R100	0.71 ± 0.007	4.63	159.7	46.7

Grafting : M/pulp ratio 2 : 1, CAN charge = 3.5 wt % of pulp, Time = 4.0 h.
Hydrolysis condition: [NaOH] = 3.0% wt/wt, Time = 2.0 h, Temp = 105°C, FC = 2% (w/v).
[a] represents the unfractionated (UF) sulfite pulp (SP).
[b] Arithmatic mean length in mm.
[c] Control ungrafted fibers were soaked in water for 2.0 h to determine the WRV.
[d] Water retention value of the grafted fibers.

| M/Pulp | G_y | WRV | |
		2% (w/v)	1% (w/v)
1 : 1	80.7	21.9	24.9
2 : 1	166.3	42.2	47.5
3 : 1	250.1	70.0	75.2
4 : 1	272.5	80.0	91.2

All grafted samples are at 10% FC during grafting. Hydrolysis condition: [NaOH] = 3% wt/wt, Time = 2.0 h, Temp = 105°C.

| M/pulp | 1% Fiber concentration | | 10% Fiber concentration | |
	G_y	WRV	G_y	WRV
1 : 1	82.6	18.1	80.7	24.9
2 : 1	173.5	42.4	166.3	47.5
3 : 1	250.8	56.4	250.1	75.2
4 : 1	340.0	56.9	272.5	91.2

Hydrolysis condition: [NaOH] = 3% wt/wt, Time = 2.0 h, temp = 105°C, FC = 1% w/v.

the methyl acrylate is replaced by the sodium ion and provides an osmotic force that leads to the super water absorbency. WRV was found to be influenced by the fiber concentration during hydrolysis and it was higher at 1% than that at 2% FC. At a higher fiber concentration, neighboring fibers may interfere with the hydrolysis and the swelling behavior of the grafted chains. Results in Table VI further showed that the effect of the fiber concentration during hydrolysis on the WRV was more pronounced for samples with higher M/pulp ratio. For higher M/pulp ratio, grafted polymer chains were of higher molecular weight, thus, the negative effect of neighboring grafted fibers on their hydrolysis and their swelling behavior would be more extensive. The WRV increased linearly with the grafting yield.

It was further noticed that during the hydrolysis sufficient agitation is required to prevent the clustering of fibers that affects the fiber packing during filtration and centrifugation and consequently the WRV.

Effect of fiber concentration during grafting on WRV

To gain insight into the behavior of the properties of the graft copolymers obtained at different fiber concentration during grafting, the alkaline hydrolysis was done for different M/pulp ratio samples and the WRV results are shown in Table VII. Surprisingly, in spite of having almost the same grafting yield the WRV of the graft copolymers at 1% FC was much lower than that of graft copolymer at 10% FC. It was also observed that WRV for 10% FC samples increased continuously with the increase of monomer concentration during grafting. However, for 1% FC samples WRV increased up to M/pulp ratio 3 : 1 and then stopped increasing beyond M/pulp ratio 3 : 1 in spite of the substantial increase in the grafting yield. We propose that the difference in the distribution as well as orientation of the grafted chains obtained at 1 and 10% FC during grafting may be the cause for the difference in WRV results.

CONCLUSIONS

The graft copolymerization of PMA onto softwood sulfite pulp fibers was successfully carried out using ceric ammonium nitrate as an initiator. Grafting from low to medium fiber consistency was very effective and more than 95% conversion of monomer into the polymer was achieved with only small fraction of homopolymer formation. Graft conversion increases at the same rate, from low to medium fiber consistency, with increase in the initiator concentration and then level-off. The optimum CAN charge was 3.5 wt % of the pulp, which generated the maximum grafting yield.

From low to medium fiber consistency, grafting yield results were same upto a certain monomer concentration and thereafter it followed different trends. For the same grafting yield results up to M/pulp ratio 3 : 1, the molecular weight of the grafted chains were almost the same. However, some discrepancy exists beyond M/pulp ratio 3 : 1.

Grafting at high fiber concentration efficiently destroyed the regular packing of the original cellulose chains and took place throughout the cross section of the fibers. The WRV of the fractionated grafted fibers were found to be predominantly controlled by the grafted chains. In addition, a lower concentration of grafted fibers during alkaline hydrolysis leads to a higher WRV.

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