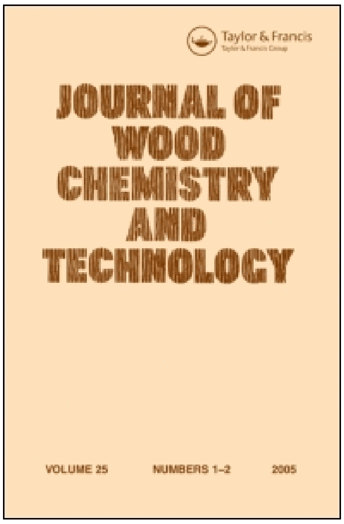

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Characterization of Poly (Methyl Acrylate) Grafted Bleached Sulfite Pulp Fibers using AFM, AEM, EDS and STEM

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Characterization of Poly (Methyl Acrylate) Grafted Bleached Sulfite Pulp Fibers using AFM, AEM, EDS and STEM

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Abstract: Sulfite pulp fibers were grafted by poly (methyl acrylate) at a low-consistency (1% pulp consistency) and medium-consistency (10% pulp consistency). It is of fundamental interest to determine the distribution of the polymer chains obtained at different fiber concentrations during grafting. In this study, modern analytical tools such as atomic force microscope (AFM), energy dispersive spectrometer (EDS), and scanning transmission electron microscope (STEM) were used for investigating the distribution of the polymer chains in the fiber matrix. AFM images in tapping mode showed that the fiber surface was covered with *in-situ* generated polymers. The X-ray mapping of Na in the cross-section of the hydrolyzed grafted fibers by using EDS in combination with Na line scans by STEM showed that the distribution of poly (methyl acrylate) was affected by the pulp consistency during grafting; at a medium-consistency condition the outer region of the fiber structure had a higher polymer concentration than the inner region. On the other hand, at a low-consistency condition, grafting occurred uniformly across the fiber wall structure.

Keywords: AEM, AFM, cellulose fibers, distribution of grafted polymer, EDS, grafting polymerization, PMA, pulp consistency, STEM

INTRODUCTION

The graft polymerization technique has been widely used for the surface modification of cellulose fibers. Grafting may take place at the surface of

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the cellulosic fibers, or at random within the fiber structure. From the view point of utilizing grafted fibers in various products, it is important to investigate the distribution of the grafted chains in the fiber matrix. The preparation of the modified material possessing new properties, requires in various cases different reaction conditions for the localization of the polymer produced.[1,2] For example, for the preparation of modified materials possessing resistance to water or oil penetration or increased resistance to wear it is sufficient to provide localized grafting on the surface of the fiber. However, to make material with other properties, such as non-flammability, resistance to micro-organism or to alter the dyeing properties of fibers, the internal grafting (volumetric grafting) would be preferred.

We studied the graft copolymerization of methyl acrylate onto pulp fibers based on the ceric-induced free radical method. In such a process, cellulose molecules in pulp fibers are oxidized by ceric, and subsequently with the formation of cellulose complexes, their further decomposition leads to the generation of free radicals onto the cellulosic backbone where grafting of vinylic monomers can occur; the details were given elsewhere.[3] We also found that the pulp fibers grafted by poly (methyl acrylate), PMA, at a low-consistency (1% pulp consistency) and medium-consistency (10% pulp consistency) during grafting exhibited different water absorbency after alkaline hydrolysis, despite the same grafting yield. The water retention value (WRV) was higher for samples obtained at a medium-consistency condition than at a low consistency condition.[4] There might be several reasons to account for such differences, for example, molecular mass distribution of the grafted polymer chains, their frequency, structure, and localization in the fiber wall. The morphology and distribution of grafted polymers in the microstructure of the pulp fibers can be investigated by means of AFM and analytical electron microscopy, AEM. In recent years, the application of AFM to the surface morphological studies of natural and synthetic polymers has grown rapidly. It has been used to study the topographical changes occurred in cellulose fibers,[5–16] synthetic fiber,[17,18] carbon fiber,[19] and various polymeric films,[20,21] from various methods including; grafting, irradiation, plasma treatments. The microscopic techniques have also been used to investigate the distribution of the grafted polymer in the fiber matrix.[22–25] In an earlier study, TEM has been used by Kaji[26] to examine the distribution of poly(acrylic acid) in grafted film; he found that without Mohr's salt the grafted poly(acrylic acid) layer is formed on the surface of the film, whereas in the presence of Mohr's salt the grafting layer consisting both of poly(acrylic acid) and polyethylene is formed on the inside of the surface. Recently, the importance of AEM was shown in great detail to obtain high resolution morphological images with chemical element distributions to localize the grafted polymers in cellulose fibers.[27] They found that grafting, followed by hydrolysis, caused extensive splits in the S_1 layer. Also, in these samples, there are numerous micro voids. The enhanced water absorbency of these fibers were attributed to the S_1 layer disruption, the presence of polymer within the S_2 wall, and the presence of a drastically altered and more accessible S_2 wall substructure.

The aim of this work was to characterize the distribution of the grafted polymer chains in the fiber matrix in order to explain the difference in the water retention value from grafting of pulp fibers under the low and medium-consistency conditions.

EXPERIMENTAL

The bleached sulfite pulp sample was kindly supplied by a mill in Eastern Canada. The pulp sample was refined in a PFI mill, and stored in a refrigerator at a 30% pulp consistency. In a typical experiment, never dried pulp in water was first disintegrated and filtered, and then transferred to a plastic bag (5.0 gm oven dried), which was diluted with deoxygenated and distilled water (acidified to pH 2 with nitric acid). The bag was fitted with a PTFE septum fitting in a polypropylene housing for use with a syringe. This allows the introduction of liquid material by injection with the help of a syringe, and the evacuation of oxygen/air in the bag. The graft copolymerization of PMA onto pulp fibers was carried out by first addition of methyl acrylate and then of ceric ammonium nitrate, CAN, to the pulp. Grafting was carried out at both low-consistency (1% pulp consistency) and medium-consistency (10% pulp consistency). Further details for the preparation of graft copolymer are given elsewhere.[3] The fibers analyzed in this study were grafted at different monomer/pulp (M/pulp) ratio as shown in Table 1. For STEM and EDS analysis, grafted fibers were hydrolyzed for 30 min in 2 wt% NaOH at 105° Celsius and then washed thoroughly with distilled-deionized water.[4]

Experiments were conducted on a JEOL 6400 scanning electron microscope operated at 10 kV on carbon coated specimen blocks.

Table 1. Various properties of fibers grafted at different M/pulp ratio

	1% Fiber consistency				10% Fiber consistency			
M/Pulp	G_y	$\overline{Mv}$	N_g	WRV	G_y	$\overline{Mv}$	N_g	WRV^a
1:1	82.6	3.1	0.27	18.1	80.7	2.9	0.28	24.9
2:1	173.5	4.2	0.41	42.4	166.3	4.3	0.38	47.5
3:1	250.8	4.76	0.52	56.4	250.1	4.6	0.55	75.2
4:1	340.0	5.56	0.61	56.9	273.0	4.0	0.68	91.2

Grafting: CAN charge = 3.5 wt% of pulp, Temp. = 25°C, Time = 4 h.

Hydrolysis condition: [NaOH]=3 wt%, Time = 2 h, Temp. = 105°C, Fiber concentration = 1% w/v.

[a] Determined by following the centrifugal technique.[28]

Initially all fiber samples were hydrated for 30 min in distilled-deionized water and then dehydrated by successive ethanol concentration (10%, 30%, 50%, 70%) up to pure ethanol. After that samples were infiltrated with spurr resin and then polymerized at 70°C for 2 days. Embedded blocks were trimmed with glass knives for fibers in cross-section suitable for Electron Probe analysis. The whole block mounted on brass stubs and carbon coated for conductivity in the Probe. To obtain the X-ray map for Na, experiments were conducted on JEOL 733 microprobe (energy dispersive spectrometer) with a Probe current of 30 nA.

For TEM analysis, thin sections of fibers (200–300 nm) were cut dry using an ultra microtome. The sections were mounted on nickel uncoated grids. The TEM analysis was performed on a JEOL 2011 STEM operated at 200 kV. Line scans were acquired in STEM mode with a probe size of 10 nm.

AFM experiments were performed in tapping mode by using a Bioscope system equipped with a Nanoscope IIIA controller (Digital Instruments/Veeco, Santa Barbara, CA, USA). A standard silicon cantilever with a resonance frequency of 250–400 kHz and nominal tip radius of around 10 nm (provided by the manufacturer) was used for the analysis. The tapping mode was operated at relatively slow scan frequencies 1–2 Hz capturing 512 samples per line. Dry fiber samples were mounted on a steel disc by using a double sided scotch tape.

RESULTS AND DISCUSSION

In an earlier study,[3] it was shown that the graft copolymerization of PMA onto softwood sulfite pulp fibers was successful. At both a low consistency and a medium consistency the conversion of monomer into the polymer was over 95%, with only small fraction of homopolymer formation. However, there were significant differences of the results obtained at 1 and 10% fiber consistency as shown in Table 1. The WRV of the grafted copolymers obtained at 1% fiber consistency level was lower than that at 10% fiber consistency. For samples obtained at 1% fiber consistency, the WRV increased up to M/pulp ratio 3:1 and then stopped increasing beyond the M/pulp ratio 3:1 in spite of the substantial increase in the grafting yield. However, for samples obtained at 10% fiber consistency condition, the WRV increased continuously with the increase of monomer concentration and there was a substantial increase in the WRV in spite of a small increment in grafting yield beyond M/pulp ratio 3:1. For both samples obtained at 1 and 10% fiber consistency, the molecular weight ($\overline{Mv}$) and the number of grafted chains (N_g) increased with the monomer concentration. However, for later sample the molecular weight of the grafted chains started to decrease beyond M/pulp ratio 3:1, whereas the number of grafted chains continued to increase. The decrease in molecular weight at 10% fiber consistency, we propose, is because the grafted polymer chains are confined to the surface, rather than diffuse into the cellulose matrix. Therefore, the rapidly forming grafted chains on the cellulose surface hinder the access of monomer units, resulting in the decreased molecular weight of the grafted chains. The difference in the distribution as well as orientation of the grafted polymer chains obtained at low- and medium-consistency conditions during grafting may be the cause for the difference in WRV results. In the following sections, we will provide evidence to support the hypothesis.

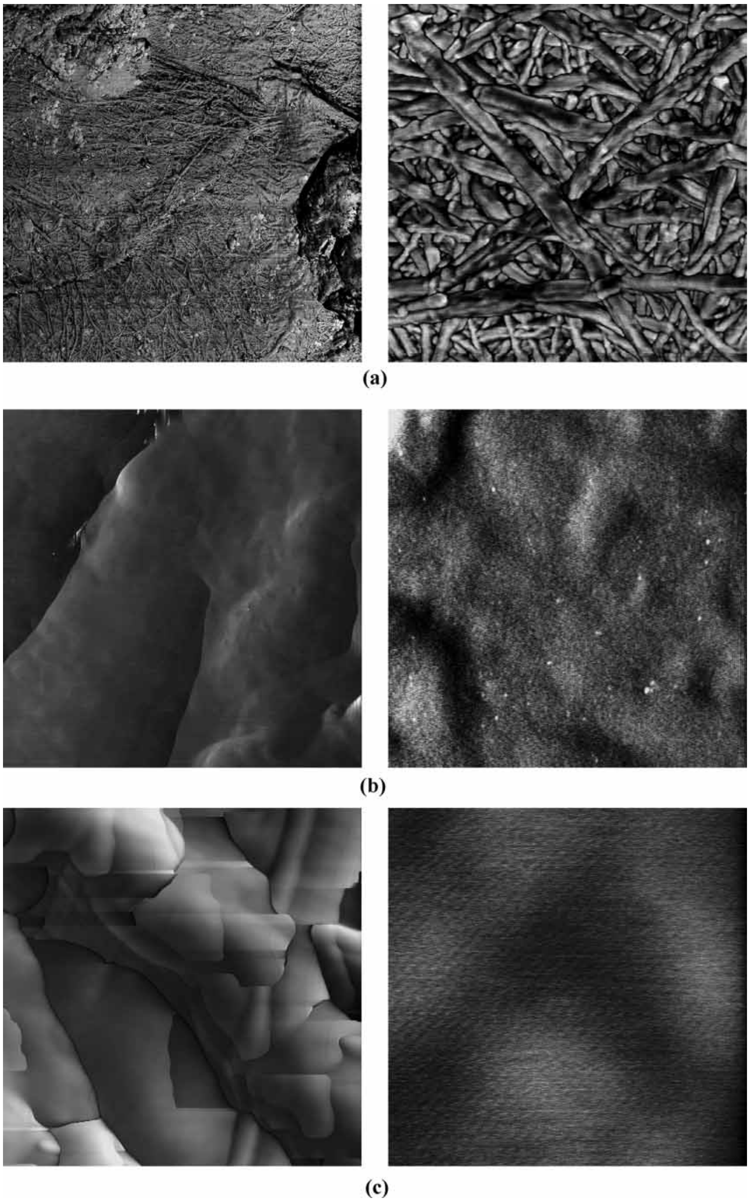
Surface Morphology by AFM

Detailed information on surface modification induced by the grafting at low- and medium-consistency was obtained based on AFM images in the tapping mode.[9,29] Figure 1 shows AFM images of the sulfite pulp fibers (a) and those grafted at low pulp consistency (b), and medium pulp consistency (c). Ungrafted pulp fibers in Figure 1(a), showed the random cellulose microfibrils, which can further be seen on the right for a smaller area (625 nm × 625 nm). The presence of microfibrils was in agreement with the literature results.[30,31] The grafted fiber surface was covered by the polymer as shown in Figures 1(b) and 1(c). Once grafted, the fiber surface was very smooth and the microfibrils present in Figure 1(a) were absent. In Figure 1(b) polymer coating appeared to be thick enough to planarize the surface compare to the Figure 1(c), which showed multiple polymer patches in spite of the low grafting yield as shown in Table 1. Therefore, these AFM images give an indication that the polymer concentration differs on the surface of the fibers grafted at 1 and 10% pulp consistency and needs to be confirmed further.

It was also noted that the AFM phase images of the samples with low grafting yield irrespective of the fiber consistency were found to have non-uniform coverage on a single fiber. In regions where the polymer coating exists, it conformed to the substrate that is, underlying fibrils.

AEM Analysis

We also determined the PMA distribution in the fiber matrix after alkaline hydrolysis by following the distribution of Na. During hydrolysis, ester group in the polymer gets converted into the Na carboxylate functionality. The X-ray mapping technique was applied based on the EDS technique to trace the concentration distribution of Na and the results are shown in Figure 2. The SEM images in Figures 2(a) and 2(b) show the cross-section of a hydrolyzed fiber grafted at low- and medium-consistency, respectively. Corresponding images on the right side show the Na map of the same fiber. From the top right image it was observed that Na concentration was uniformly distributed in the cross-section of the fiber wall. On the other


(a)

(b)

(c)

Figure 1. AFM phase images with image size and z-scale (a) ungrafted pulp fiber with area 5 μm × 5 μm; 36°, corresponding image on the right with area 625 nm × 625 nm; 24°; (b) fibers grafted at 1% fiber consistency and M/pulp ratio 4:1 with area 5 μm × 5 μm; 55.5°, corresponding image on the right with area 500 nm × 500 nm; 10°; (c) fibers grafted at 10% fiber consistency and M/pulp ratio 4:1with area 5 μm × 5 μm; 83.5°, corresponding image on the right with area 500 nm × 500 nm; 5°.

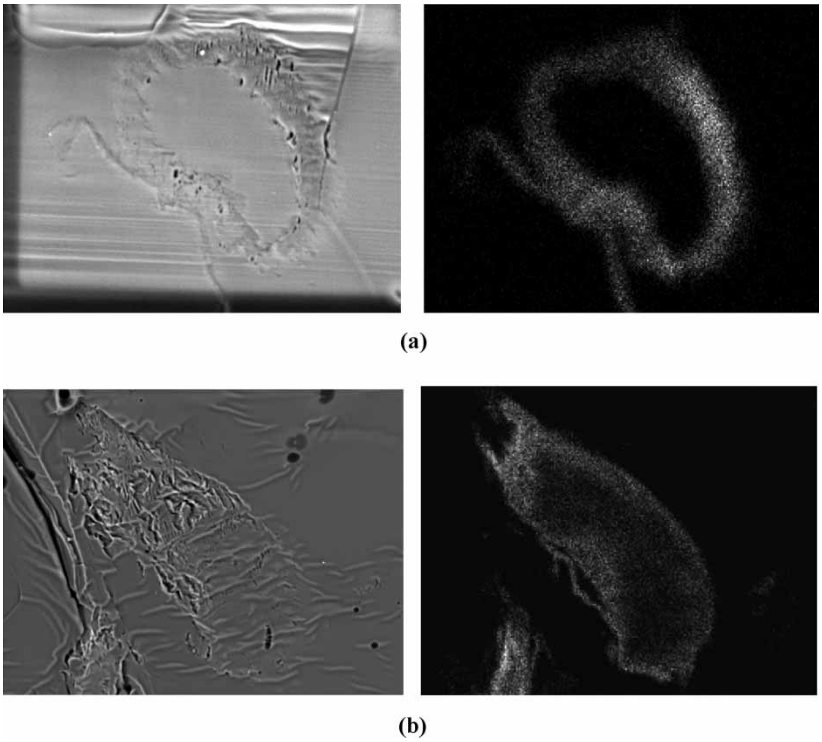
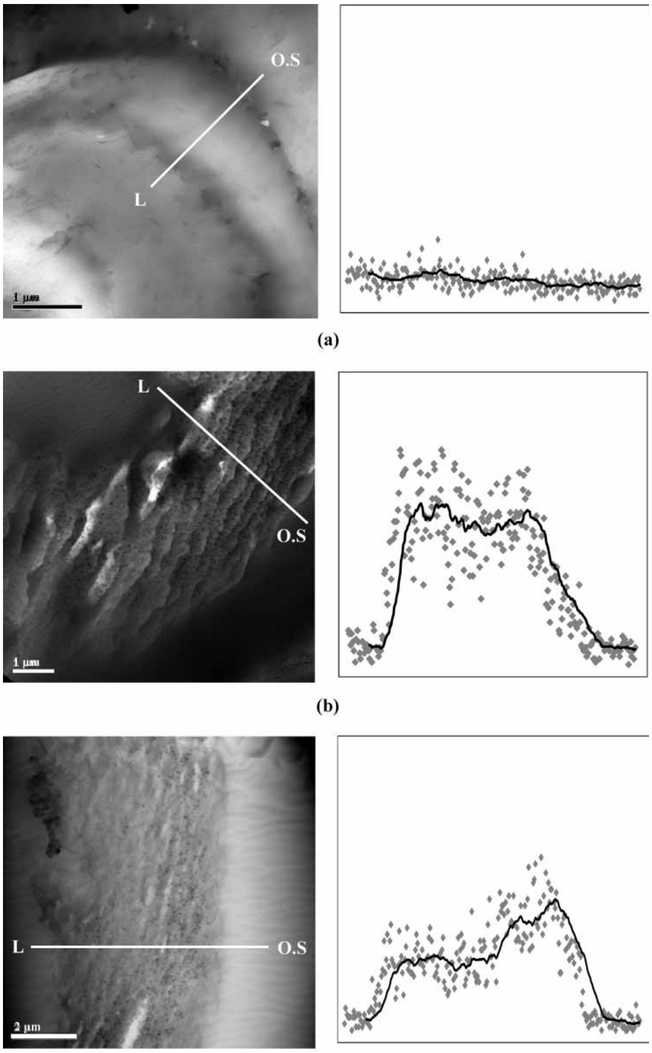


Figure 2. Cross-sectional view of hydrolyzed grafted fibers by SEM and EDS (a) SEM image of fibers grafted at 1% fiber consistency and M/pulp ratio 3:1 (magnification × 2000); corresponding X-ray map of Na on the right (magnification × 2000), (b) SEM image of fibers grafted at 10% fiber consistency and M/pulp ratio 3:1 (magnification × 800); corresponding X-ray map of Na on the right (magnification × 800).

hand, the bottom right image shows that the Na concentration was higher at the outer region of the wall than the inner region. To further support the aforementioned results, we conducted the Na line scans in STEM mode.

Figures 3(a), 3(b), and 3(c) show the STEM images on the left and corresponding Na line scans on the right. The Na detected by AEM represents the total carboxylate group (in the form of polymer) present in the fibers. In an earlier study,[27] it was shown that the "uncomplexed" Na remained in the hydrolyzed grafted fibers after thorough washing accounted for less than 10% of the total Na detected. Therefore, no further effort was made to determine the free Na present in our system. Figure 3(a) shows the STEM image of a hydrolyzed ungrafted pulp fiber. The Na counts along the line scans shown in the corresponding right image were similar to those in the background embedding plastic. STEM image of the hydrolyzed fibers grafted at low-consistency condition and M/pulp ratio 3:1 is shown in



(a)

(b)

(c)

Figure 3. AEM of the cross-section of ungrafted and grafted fibers after hydrolysis (a) TEM image of ungrafted fiber, corresponding Na line scans on the right; (b) TEM image of fibers grafted at 1% fiber consistency and M/pulp ratio 3:1, corresponding Na line scans on the right; (c) TEM image of fibers grafted at 10% fiber consistency and M/pulp ratio 3:1, and corresponding Na line scans on the right. Left figures: white Line drawn across the fiber wall (left to right) denotes the path along which discrete points were analyzed for Na. Each line represents 256 discrete points. L represents the line end toward the lumen, whereas O.S represents the line end toward the outer surface of the fiber wall. Right figures: Y-axis represents the intensity of Na X-ray counts and the vertical scale is 100 counts. A general trend of discrete points along the line drawn is shown by moving average of 20.

Figure 3(b). The line scan on the right image exhibits relatively uniform sodium (PMA) level throughout the fiber wall including the S_1, S_2, and S_3 layers. However, line scans corresponds to Figure 3(c) for the medium-consistency condition and M/pulp ratio 3:1 shows lower Na counts in the inner region of the fiber wall (toward lumen L) and relatively higher counts toward the outer surface (O.S) of the fiber wall.

At a low-consistency condition, methyl acrylate monomers readily diffuse into the fiber wall structure, thus, when the reaction starts, monomers that are inside the fiber wall get polymerized, resulting in a very uniform distribution of PMA inside the fibers. Inversely, at a medium-consistency condition, the monomers penetrate slowly into the fiber wall structure, thus, the monomer concentration is higher in the outer region of the fiber wall, whereas it is lower in the inner region. Such a difference leads to an uneven distribution of PMA inside the fiber wall. Therefore, it can be concluded that the fiber concentration during grafting has significant impact on the distribution of the grafted polymer throughout the fiber wall.

CONCLUSIONS

Based on the aforementioned investigations, it can be implied that the distribution of grafted chains differ, depending on the wood fiber concentration during grafting in a free radical system. When grafting took place at a medium-consistency condition (about 10% pulp consistency), the outer region of the fiber structure had a higher polymer concentration than the inner region. On the other hand, when grafting took place at a low-consistency condition (about 1% pulp consistency), the grafting occurred uniformly across the fiber wall structure. Therefore, the fiber concentration during grafting in a free radical system can be an important factor for the distribution of PMA grafted chains introduced into the wood cellulose fibers.

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