

Swelling behavior of stimuli-responsive cellulose fibers

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Environmental scanning electron microscopy (ESEM) and dynamic contact angle (DCA) measurements showed to be a powerful combination for investigating the swelling behavior of stimuli-responsive cellulose fibers in various environments. The stimuli-responsive fibers were prepared by ozone-induced graft polymerization of acrylic acid onto regenerated cellulose fibers. Atomic force microscopy (AFM) in the tapping mode showed that a smooth polyacrylic acid layer covered the fiber surfaces. X-ray mapping of sodium atoms by EPMA/EDS (electron probe micro analyzer/energy dispersive spectrometer) analysis showed that NaOH-treated grafted polyacrylic acid was evenly distributed, not only at the surface but also in the cross-section of the fiber. By using ESEM, it was possible to vary the humidity around the fibers in a controlled manner and to study a controlled fiber swelling at high magnification. It was observed that the fiber swelling was dependent on the degree of crosslinking of the cellulose-supported hydrogel. Dynamic contact angle measurements using the Wilhelmy plate technique proved to be another technique for studying the swelling behavior of the grafted single fibers. A pH-sensitive swelling, with a perimeter increase from 122 μm at pH 2 to 228 μm at pH 5, was established for the acrylic acid-grafted rayon fibers. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Most natural biopolymers are able to interact with large volumes of liquids in their native environment. Biomaterials such as tissues carry biological fluids, and wood fibers are responsible for the transportation of substantial quantities of water in the trees¹. Biomaterials are usually constructed with highly crystalline fibers, which provide strength and stiffness. When the cellulose fibers are separated from wood, the strength and stiffness of the individual fibers are retained. The ability of the fibers to interact with water, however, is dramatically decreased. During the separation from wood, the lumen of the fiber is collapsed upon drying, which reduces the water transport capability. The inherent water swelling properties of single cellulose fibers are also rather limited. This is due to the restricted chain mobility because of the highly crystalline structure, the order of cellulose crystallites as well as inter and intra molecular interactions². Despite these facts, wood pulp fibers are used as the major component in most of absorption products.

The cellulose fibers separated from wood are short, which prevents the formation of webs such as nonwoven and other advanced structures. A typical tracheid derived from softwood is below 4 mm while a hardwood fiber is about 1 mm³. One way to take advantage of the cellulose backbone, which originates from a renewable and common source, and to obtain long fibers is to chemically modify and dissolve the cellulose and then spin the solution into fibers. The fibers can then be converted back (regenerated) into cellulose⁴. The swelling properties of

such regenerated cellulose fibers, generically known as rayon fibers, are however just slightly higher than for native fibers.

Attempts to improve the properties of cellulose and its derivatives have been reported in the literature. Increased absorbing properties of rayon fibers have been obtained for example by the incorporation of hydrophilic polymers into the fiber during the viscose process^{5,6}. Several authors have also performed surface modification by graft polymerization in order to control enzyme immobilization, dyeability, water interaction and swelling properties^{7–19}. We recently used ozone-induced graft polymerization of 2-hydroxyethyl methacrylate and acrylic acid onto various substrates such as polypropylene and native cellulose fibers^{20–23}. The cellulose fiber modification resulted in dramatically improved absorption properties as detected by measuring the weight increase of fiber networks immersed in liquids.

Most scientists have focused on increasing the grafting yield by varying and optimizing process parameters. Very few authors have investigated the properties of the material as a function of morphology of the grafted layer. In this study, by the addition of crosslinker into the monomer mixture, a controlled and reversible swelling of the fibers was obtained. We present new tools for studying the swelling behavior of grafted cellulose fibers. This knowledge can be used to prepare “tailor-made” grafted cellulose fibers with controlled and environmentally responsive swelling.

Measuring the absorption properties of fiber networks gives a complex result, composed of fiber swelling and absorption of liquid in capillaries between fibers. When modifying cellulose fibers, it is of chief interest to find out the effect of chemical modification on the swelling behavior of the single fibers. Cellulose fibers that have been grafted

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with acrylic acid absorb large amounts of liquid in a short period of time. A typical swelling process is takes less than one second and is thus difficult to study in detail with optical microscope. Environmental scanning electron microscopy (ESEM) is a technique that allows the investigation of polymers in a number of novel and previously inaccessible situations^{24–26}. The humidity in the ESEM sample chamber can be accurately controlled, and various degrees of swelling can therefore be studied. Another method suitable for evaluation of wetting characteristics and absorption properties of single fibers is dynamic contact angle (DCA) analysis by means of the Wilhelmy plate technique^{27–29}. In this study modern analytical tools such as atomic force microscopy (AFM) and X-ray mapping of sodium atoms by electron probe micro analyzer/energy dispersive spectrometer (EPMA/EDS) analysis were used to characterize the grafted fibers. This study has focused on the swelling of pH-responsive single cellulose fibers by the use of ESEM and DCA analysis. The pH-responsive cellulose fibers were prepared by ozone-induced graft polymerization of acrylic acid onto rayon fibers.

EXPERIMENTAL

Materials

The regenerated cellulose fibers used were supplied by Svenska Rayon AB, Sweden. The fibers had an average fiber length of 40 mm and a specific gravity of 1.59 g cm⁻³. Prior to use, the fibers were cleaned in boiling water for 12 h and then soxhlet-extracted with dichloromethane for a further 12 h. The monomers used in the study were acrylic acid (AA) and ethyleneglycol dimethacrylate (EDMA). The monomers, purchased from Fluka Chem. AG, Switzerland, were vacuum-distilled prior to use.

Graft polymerization of acrylic acid onto rayon fibers

Ozone was used to create hydroperoxides on the rayon fibers. Before the ozone treatment, the fibers were stored for a week in an environment with 100% humidity. The equipment used for generating ozone was a Fischer Ozon 502 ozone generator, which produced an oxygen/ozone flow of 0.250 m³ h⁻¹ from pure oxygen gas. The ozone concentration was 25 g m⁻³. The gas current was preheated and humidified before reaching the reactor. A saturated gas mixture at a temperature of 32 °C was then blown into the reactor, where the fibers were kept in end-open glass tubes. The fibers were ozone-treated for 90 min. Immediately after the treatment, the substrates were placed in a monomer solution prepared by diluting 6.0 g of monomer in 14 g of deionized water. The water contained 20 mg of dissolved Fe(II) ammonium sulfate hexahydrate salt (Mohr's salt), which forms a redox initiator. The pH of the solution was set to 1.5. The grafting process was performed for 60 min in a nitrogen atmosphere, in sealed glass ampoules. During the graft polymerization, the ampoules were shaken in a water bath at 50 °C. The polymerization was interrupted by opening the ampoules and immersing the substrates in water. The grafted substrates were extracted in water overnight to remove monomer residuals. After the extraction, the water was vacuum-filtrated from the fibers, which were then vacuum-dried at 50 °C for 15 h before being weighed. The extent of grafting was expressed as the percentage increase in weight according to:

$$\text{grafting amount (\%)} = 100(w_2 - w_1)/w_1$$

where w_1 and w_2 represent the weight of the dry substrates

before and after grafting, respectively. For neutralization of the grafted polyacrylic acid, 0.0125 M NaOH was used.

Atomic force microscopy (AFM)

AFM in the tapping mode was used to investigate fiber surfaces. The equipment used was a Digital Instrument Dimension 3000 Large Sample AFM with a type G scanner. The measurements were performed in air with a standard silicon tip.

Fourier-transform infrared (FTIR) spectroscopy

IR absorption was measured with a Perkin-Elmer 2000 FT-IR. Measurements were performed with the KBr technique on untreated, grafted and NaOH-treated grafted fibers.

Electron microscopy

The distribution of sodium atoms as a result of NaOH treatment was determined by X-ray mapping with the EPMA/EDS technique using a JEOL JXA-8600 electron probe combined with a Tracer Northern series II spectrometer. The surfaces were coated with a carbon layer before the analysis. ESEM was used to investigate the swelling properties of the fibers. Deionized water was used for the measurements. The equipment was an ElectroScan-ESEM model E3 with a Lanthanum hexaboride (LaB₆) filament. A standard Peltier stage was used to achieve temperature control. The swelling test was performed by mounting the fibers on Copper tape and placing this on the Peltier stage. The chamber pressure was lowered to 4 torr (532 Pa) at room temperature. After flooding twice, the temperature was decreased to 6 °C. To accomplish wetting, the chamber pressure was increased to 5 torr (665 Pa). Micrographs were taken during the swelling process.

Swelling by wetting measurements

The swelling properties of grafted single fibers were also measured by the Wilhelmy plate technique. The instrument used was a Cahn 322 DCA analyzer operating at a stage speed of 20 μm s⁻¹. The measurements were performed by using buffer solutions with various pH values as test liquids. The buffer solutions were prepared according to the literature³⁰, and the ionic strength was justified to 0.15 M in each solution by adding the required amount of sodium chloride salt. The surface tension of the buffer solutions were measured according to the Cahn Instruction Manual³¹. After the swelling measurements, the dry perimeter of each fiber was determined by using a test liquid, hexadecane ($\gamma = 27.6 \text{ m Nm}^{-1}$), which provides complete wetting without swelling the fiber.

RESULTS

Preparation of grafted fibers

Ozone-induced graft polymerization of acrylic acid was carried out on rayon cellulose fibers. After grafting, extraction and drying, the fibers were weighed and the grafting amount was calculated. The amount of grafted polyacrylic acid obtained on the regenerated fibers was 150%. However, when 3% of the acrylic acid monomer used for grafting was replaced with a bifunctional monomer, ethyleneglycol dimethacrylate (EDMA), the grafting amount increased to 200%. The increased grafting amount when adding EDMA is in agreement with results that we recently reported on graft polymerization under the same conditions on cotton and sulphate pulp fibers²³. The grafting

amount was higher, however, when rayon fibers were used as substrates for grafting. This is probably an effect of the less crystalline structure of rayon fibers. The crystallinity of rayon is approximately 30%, while cotton is 65–85% crystalline. As a consequence, the rayon fibers have a higher equilibrium moisture regain, 10–14% at 65% RH and 21 °C, compared to 7–8% for cotton⁴. This may result in a better transportation of monomers and a higher degree of accessibility for graft polymerization in the rayon cellulose fibers.

Fiber morphology

The surfaces of the fibers were investigated with AFM in the tapping mode. *Figure 1a* shows an untreated rayon fiber. The fiber has a characteristic parallel folding along the fiber axis that is formed during the regenerating step. The size of

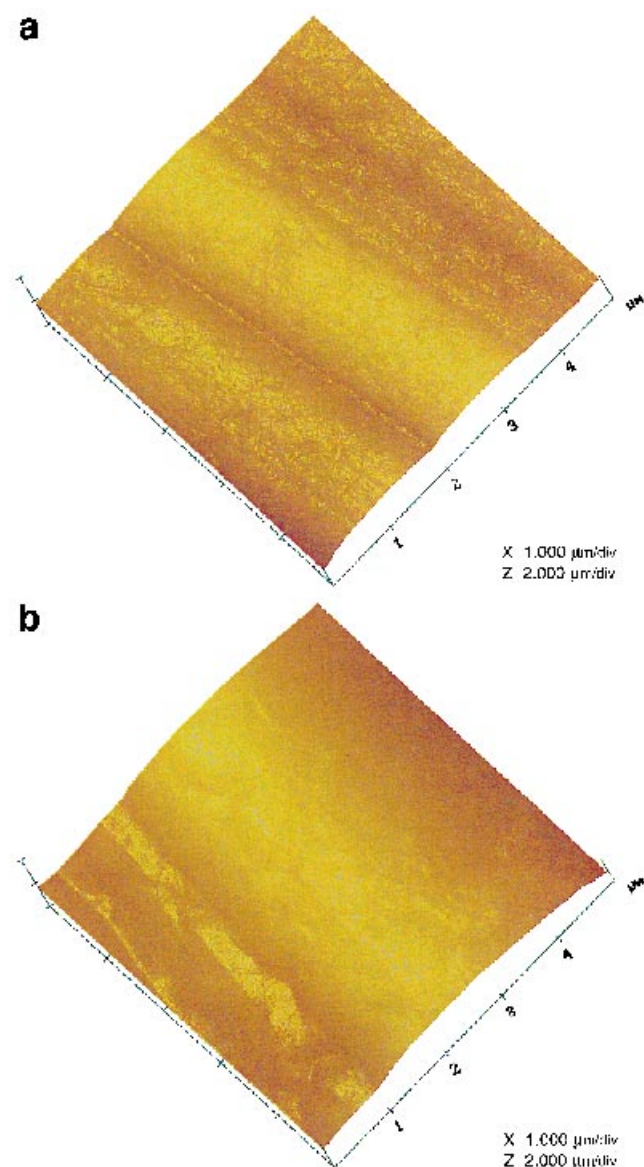


Figure 1 AFM images of rayon fibers: (a) untreated rayon fiber; (b) rayon fiber grafted with acrylic acid and 3% EDMA

the folds varied between two and four microns. A certain roughness, in the magnitude of tenths of micrometers, can also be observed on the surface of the untreated fiber. *Figure 1b* shows a fiber grafted with acrylic acid and 3% EDMA. The roughness of the surface has disappeared, and the fiber has become smoother as a result of the graft polymerization process. The characteristic parallel folding of the regenerated fiber is however preserved which indicates that grafted layer is very thin in the dry state. Such thin layers are hard to detect by SEM whereas AFM seems to be a suitable technique to use.

When using polyacrylic acid for absorbing purposes, the carboxylic acid group is always partially neutralized in order to reach a high swelling capacity^{32,33}. In this study, the neutralized form of the grafted polyacrylic acid was prepared by treating the grafted fibers with 0.0125 M NaOH. *Figure 2* shows IR absorption spectra for untreated, grafted and grafted and neutralized rayon fibers. The grafted fiber (*b*) shows a peak at 1735 cm^{-1} which is not present for the untreated fiber (*a*). This peak is characteristic for carbonyl stretch in a carboxylic acid dimer. For the neutralized fibers (*c*), additional peaks appear at 1585 cm^{-1} and 1414 cm^{-1} . These peaks are from the carbonyl stretch in carboxylate groups. The presence of carboxylate groups confirms that neutralization of the grafted polyacrylic acid has occurred.

The effect of NaOH treatment on the sodium content was investigated by the EPMA/EDS technique. *Figure 3a–b* shows sodium X-ray mapping diagrams of untreated and NaOH-treated grafted fiber. Only a slight trace of sodium atoms was detected for the untreated fiber. However, in *Figure 3b*, which shows the X-ray mapping diagram of grafted and neutralized fiber, a sharp sodium peak was obtained as a result of the neutralization. This is in accordance with the IR results, which showed the formation of carboxylate ions. The introduction of sodium atoms as a result of the NaOH treatment also made it possible to determine the localization of the grafted polyacrylic acid with the X-ray mapping technique. The SEM image in *Figure 4a* shows a cross-section of a grafted neutralized

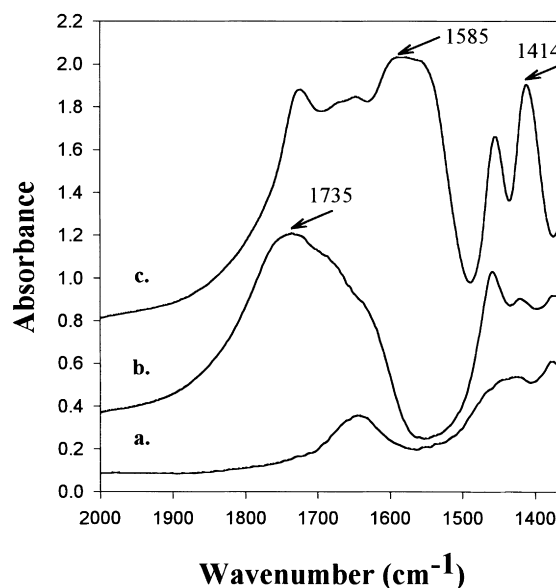


Figure 2 IR absorption spectra of rayon fibers: (a) untreated fiber; (b) fiber grafted with acrylic acid and 3% EDMA; (c) fiber grafted with acrylic acid and 3% EDMA and thereafter treated with NaOH

fiber. Figure 4b shows the mapping image of the same fiber. In this image, it is easy to see that a neutralized grafted polymer is present on the fiber surface. It can furthermore be observed that a significant amount of sodium atoms is

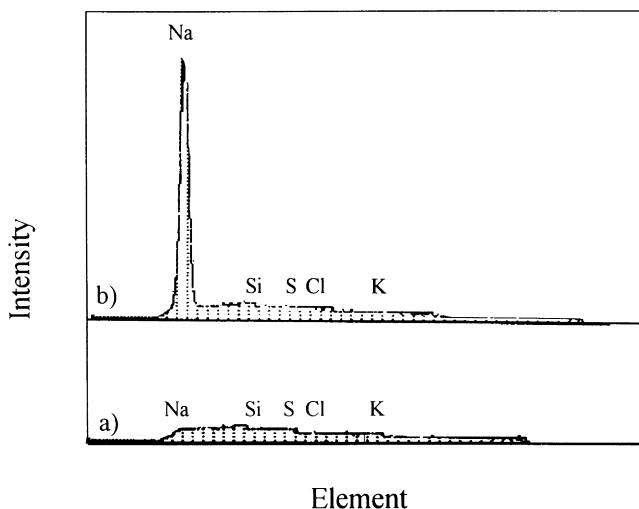


Figure 3 X-ray mapping diagrams: (a) untreated rayon fiber; (b) rayon fiber grafted with acrylic acid and 3% EDMA and thereafter treated with NaOH

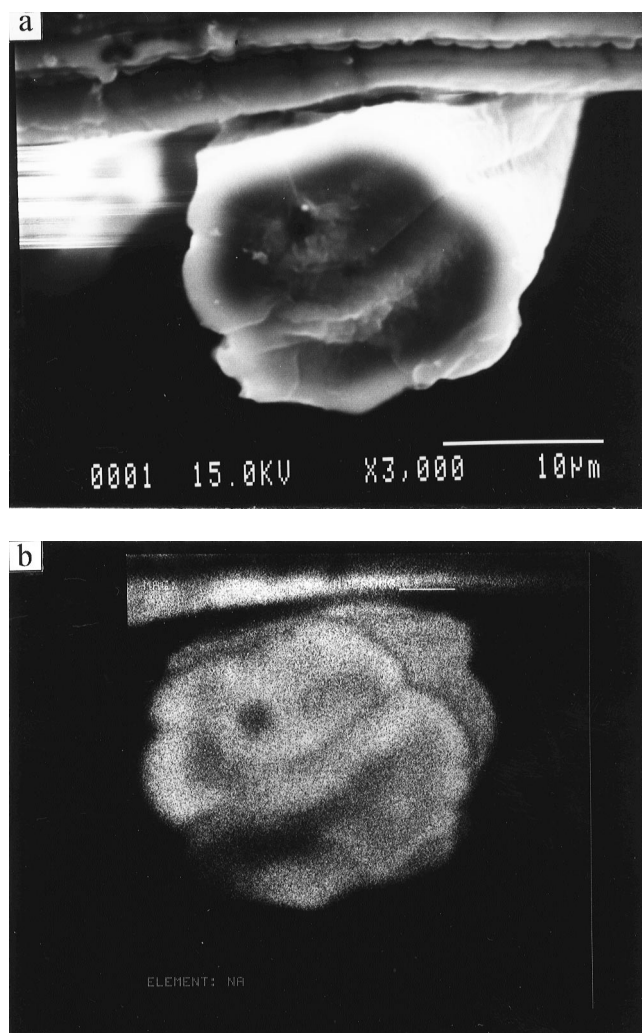


Figure 4 (a) SEM image (cross-section) of a rayon fiber grafted with acrylic acid and 3% EDMA, magnification $\times 3000$; (b) X-ray mapping image of Na atoms, magnification $\times 3000$. Same cross-section as shown in a

present in the cross-section of the fiber. This proves that graft polymerization of acrylic acid occurs both on the surface and in the pores of the regenerated cellulose fibers.

Swelling of single fibers studied by ESEM

The swelling behavior of untreated and grafted fibers was investigated using ESEM. The test liquid used in the ESEM measurements was deionized water. Figure 5a–b shows the hydration of an untreated rayon fiber. It can be seen that the fiber dimension does not change during the hydration process and that the diameter remains almost constant. In Figure 6a–b, swelling of an acrylic-acid grafted rayon fiber can be seen. The grafted fiber, which is in the neutralized state, was prepared with 3% crosslinker in the monomer solution. Comparing the dry fiber in Figure 6a and the maximally swelled fiber in Figure 6b, it can be observed that the diameter has increased about twice, from $23 \mu\text{m}$ in the dry state to about $46 \mu\text{m}$ in the swelled state. The swelling and subsequent drying of a fiber that was grafted in a monomer mixture without bifunctional monomer EDMA

Table 1 Surface energy of the buffer solutions used for swelling measurements

	pH2	pH4	pH5	pH8	pH11
$\gamma(\text{m Nm}^{-1})$	72	61	61	72	63

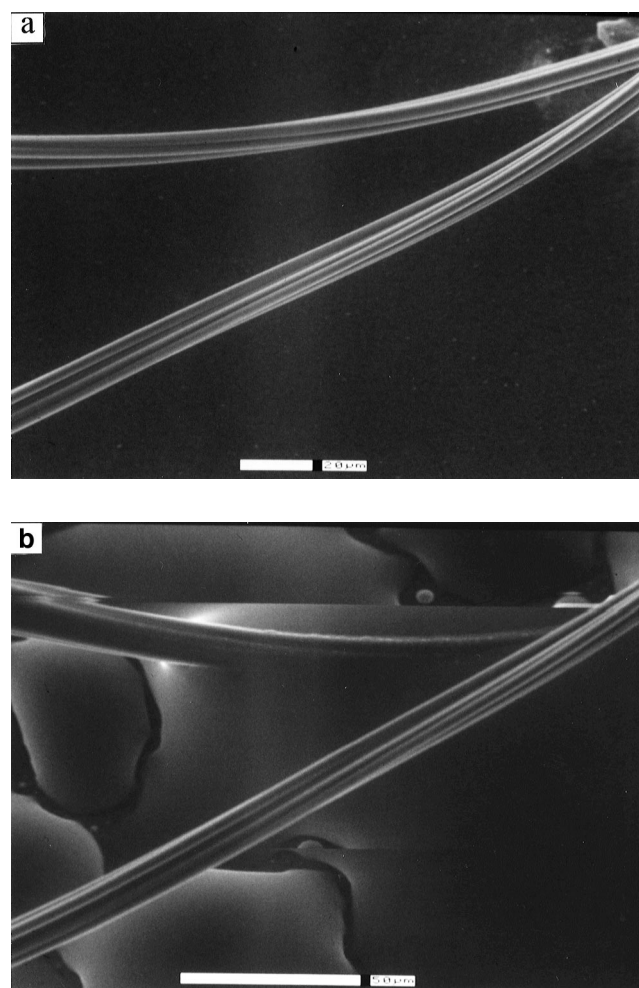


Figure 5 ESEM images of an untreated rayon fiber, magnification $\times 500$: (a) dry fiber; (b) fully swelled fiber

was also studied and is shown in *Figure 7*. The diameter has in this case increased from roughly $26\ \mu\text{m}$ (*Figure 7a*) to $62\ \mu\text{m}$ (*Figure 7b*). It can also be observed that the swelling in water is not completely reversible as the fiber after drying, as seen in *Figure 7c*, does not have the same appearance as before swelling. We observed similar results for non-crosslinked grafted polyacrylic acid during NaOH treatment, while a crosslinked grafted layer resulted in a reversible swelling²³.

pH-sensitive swelling of single fibers

Dynamic contact angle measurements were used to determine the perimeter of the grafted fibers in both the swelled and the dry state. Measurements of the swelled perimeter as a function of pH were performed by using different buffer solutions as test liquids, with a constant ionic strength. Because of the very high concentration of carboxyl and carboxylate groups in the grafted polymer, it can be assumed that the test liquids completely wet out the fiber in receding, i.e. the receding contact angle, Θ_R , is equal to zero and $\cos \Theta$ in equation (1) is equal to 1. The perimeter, p (μm), can easily be calculated by dividing the mean value of the force, F (μN), which is registered during the wetting cycle with the surface tension, γ (m Nm^{-1}), of the test liquids. The surface tensions of all buffer solutions used as test liquids were measured according to the literature³¹ and are listed in *Table 1*.

$$p = F/(\gamma \cos \Theta) \quad (1)$$

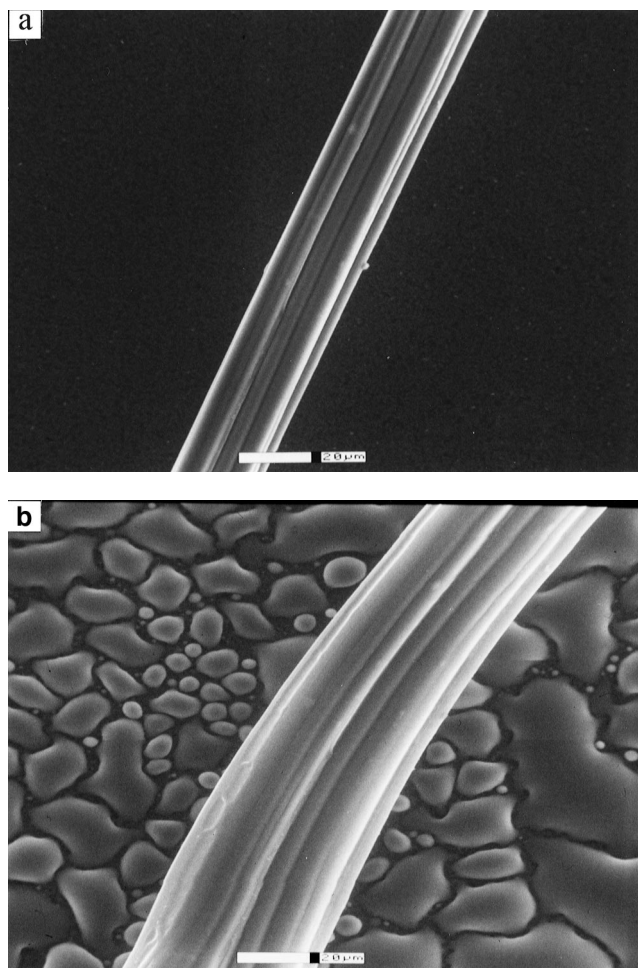


Figure 6 ESEM images of a rayon fiber grafted with acrylic acid and 3% EDMA, magnification $\times 500$: (a) dry fiber; (b) fully swelled fiber

In *Figure 8*, two wetting cycles of a NaOH-treated grafted fiber (3% EDMA) can be observed. The same fiber was used for both measurements, while the test liquid was changed from a buffer solution with a pH of 2 (*Figure 8a*) to a buffer solution with a pH of 5 (*Figure 8b*). The fiber was dipped vertically into the buffer solution and kept there for four minutes before the receding force was measured. As can be seen in *Figure 8a*, the mean receding force registered at pH 2 is $8.8\ \mu\text{N}$, which corresponds to a fiber perimeter of $122\ \mu\text{m}$. When the fiber was dipped in a solution with pH 5, the registered mean receding force was $13.9\ \mu\text{N}$, as can be

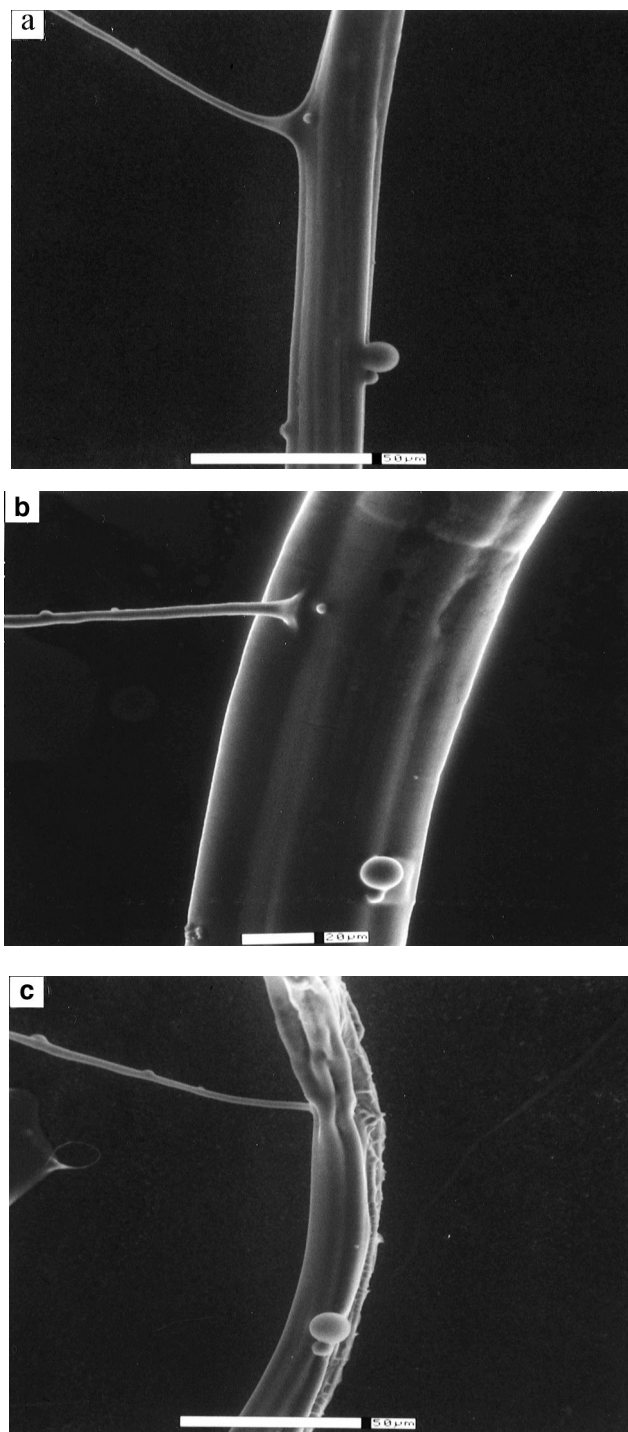


Figure 7 ESEM images of a rayon fiber grafted with acrylic acid (without crosslinker), magnification $\times 500$: (a) dry fiber; (b) fully swelled fiber; (c) fiber which has been dried in the chamber after the wetting measurements

seen in Figure 8b. This means that an increased swelling of the grafted fiber is obtained at a higher pH. The perimeter calculated for the relevant fiber at pH 5 is equal to 228 μm . The dry perimeter was determined to be 80 μm by using hexadecane ($\gamma = 27.6 \text{ m Nm}^{-1}$), which is a fully wetting but non-swelling test liquid.

In Figure 9, the perimeter determined at different pH values is plotted versus pH. It can be observed that the perimeter increases dramatically between pH 4 and pH 5 and then maintains a rather constant value. The sharp perimeter increase is a result of the pKa of the acrylic acid. Above pKa, dissociation of acid groups that were not neutralized during the NaOH treatment can occur. A high swelling capacity of the grafted hydrogel is obtained owing both to repulsion of the charged polymer chains and the presence of free counterions (Na^+) in the gel, which caused a high osmotic pressure and thereby a driving force for swelling. We have reported before the similar absorption behavior for networks composed of acrylic acid-grafted

wood pulp fibers. The Wilhelmy plate technique, however, offers the opportunity to study and quantify the swelling properties of single grafted fibers. The measurements of single fiber swelling eliminate information of adsorption of liquid between fibers, which always occurs in fiber networks, and thus accurate values of the swelling capacity of single fibers can be obtained.

CONCLUSIONS

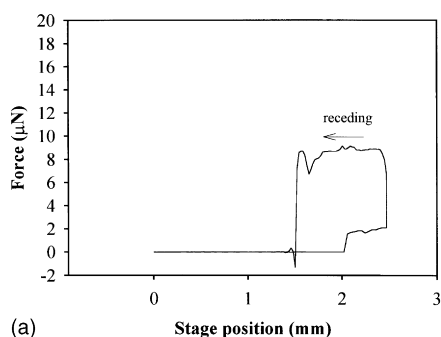
Rayon fibers with a pH-responsive swelling behavior were prepared by ozone-induced graft polymerization of acrylic acid. AFM showed that a thin coating covered the fiber surface as a result of the graft polymerization process. Grafted and neutralized polyacrylic acid were detected with X-ray mapping of Na atoms, both on the fiber surface and in the cross-section of the rayon fibers. The combination of ESEM with the Wilhelmy plate technique proved to be a very powerful tool for characterization of the swelling process of single stimuli-responsive cellulose fibers. Using ESEM, it was possible to study various degrees of swelling in a controlled manner. The Wilhelmy plate technique has been shown to be very useful for calculating the perimeter swelling of single fibers in various environments. Knowledge gained in this study can be utilized to tailor-make future generation of grafted fibers.

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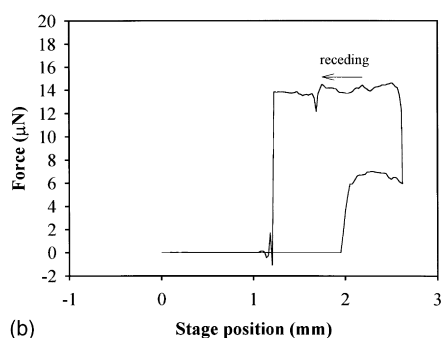
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(a)



(b)

Figure 8 Wetting cycles of a NaOH-treated grafted (acrylic acid with 3% EDMA) rayon fiber: (a) buffer solution with pH 2 used as test liquid, receding force used for calculation of the swelled perimeter; (b) buffer solution with pH 5 used as test liquid, receding force used for calculation of the swelled perimeter

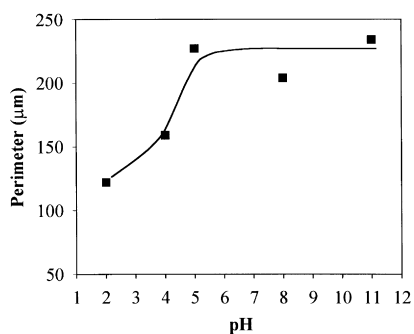


Figure 9 Swelled perimeter determined with the Wilhelmy plate technique at various pH. Same fiber used for all measurements

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