ELSEVIER

Polymer 40 (1999) 379–387

polymer

Cellulose fibre-supported pH-sensitive hydrogels

J. O. Karlsson, P. Gatenholm*

Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Received 21 March 1997; accepted 12 March 1998

Abstract

pH-sensitive cellulose fibre-supported hydrogels were prepared by ozone-induced graft polymerization of acrylic acid using cotton linters and wood pulp fibre substrates. An average amount of grafting of 60% was achieved on to the ozonized wood pulp fibres after only 1 min of graft polymerization. Grafted polyacrylic acid completely covered the cellulose fibre surfaces, as determined with electron spectroscopy for chemical analysis (ESCA) and scanning electron microscopy (SEM). The X-ray mapping of neutralized grafted fibres showed that polyacrylic acid was present not only at the surface but was also homogeneously distributed within the pores of the fibres. Exposure of the grafted fibres to alkali and subsequent drying resulted in a irreversible deformation of the fibre-supported hydrogel. A fibre-supported hydrogel which exhibited a reversible swelling and deswelling was prepared by an addition of a bifunctional monomer, ethyleneglycol dimethacrylate (EDMA), to the monomer solution used for grafting. Such muscle-like expanding and contraction was also stimulated by pH changes in the environment.

Keywords: Ozone; Grafting; Cellulose

1. Introduction

Stimuli-responsive hydrogels are crosslinked hydrophilic polymeric networks that exhibit various swelling properties depending on environmental variables such as pH, temperature, ionic strength and electric current [1–11]. Such hydrogels are utilized by the human body [12,13], for example where the muscle function is controlled by gels that are expanded and contracted as a result of electrical nerve signals. Synthetic stimuli-responsive hydrogels have been prepared as they are interesting model systems for biological functions [14]. Furthermore, several applications in recent years have been found in the field of drug delivery and molecular separation [15,16]. The best known temperature-sensitive hydrogel is poly *N*-isopropylacrylamide (poly-NIPAAm), and several authors have reported successful attempts to use this polymer in separation processes [17–19]. Another well-studied stimuli-responsive hydrogel is crosslinked polyacrylic acid. The presence of carboxylic acid groups results in a pH-sensitive behaviour. A high degree of swelling is obtained in basic solutions owing to both the osmotic pressure and electrostatic repulsion between the polymer backbones, while the polymer network collapses in acidic solutions, which results in a low swelling capacity [20,21]. The hydrophilicity and the high swelling capacity of neutralized polyacrylic acid has made it possible to use this polymer as a superabsorbing material and, furthermore, the carboxylic functionality leads to good ion-exchange properties [22–24]. Owing to the broad functionality that hydrogel-forming polymers can exhibit, new applications of these materials are continuously being found. A limiting factor for several applications, however, is the poor mechanical properties which are a consequence of the high water content of the hydrogels [25].

Contrary to hydrogels, polymeric fibres are materials that exhibit very good mechanical performance as a result of a high degree of orientation and crystallinity [26]. According to origin, the fibres can be classified as either natural or synthetic. Among the natural fibres, the most abundant are cellulose fibres. The cellulose fibres are built up of several layers or cell walls, and both amorphous and crystalline regions coexist in each layer [27]. The fibre architecture provides both flexibility and good mechanical properties. This and the fact that cellulose is a renewable polymer make it of great interest to investigate the possibility of upgrading such fibres and thereby extending the field of applications.

Although the chemical composition of the cellulose polymer, with large amounts of hydroxyl groups, should make it hydrophilic, the swelling properties of a cellulose fibre are rather poor as a consequence of the presence of

* Corresponding author.

0032-3861/98/$ - see front matter
PII: S0032-3861(98)00243-2

crystalline regions which restrict the mobility of the polymer chains. Despite the limited swelling capacity, networks of cellulose fibres are used as absorption cores in numerous hygienic products. To improve the absorption properties of the cellulose fibre network, granules of superabsorbing polymers such as neutralized polyacrylic acid are usually added. However, an external addition of superabsorbing polymers in the form of granules or powder to the cellulose network is not the ultimate technical solution, and widespread research is ongoing to find new and better alternatives. Depositing superabsorbing particles on to fibres or fibre spinning of superabsorbing polymers are among the procedures proposed [28,29]. Another interesting method is to 'build up' an absorbing polymer around a fibre by initiating a graft polymerization on to a cellulose fibre surface [30]. Such a method requires an activation step in order to create reactive groups for initiation. We have successfully used ozone treatment, resulting in the formation of hydroperoxides, for the activation of both polypropylene and cellulose substrates prior to graft polymerization of 2-hydroxyethyl methacrylate (HEMA) and diethyleneglycol methacrylate (DEGMA) [31–33]. The aim of this study has been to prepare pH-sensitive cellulose fibre-supported hydrogels and to characterize their surface and swelling properties.

2. Experimental

2.1. Materials

The cellulose fibres used were a standard sulfate fluff pulp (single fibres), EC 0.1, made from selected wood of softwood and Munktell filter paper No. 5 made from pure cotton linters. The pulp was manufactured by STORA Cell (Sweden) and the filter paper by STORA Filter Products, Grycksbo (Sweden). 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. A reference polyacrylic acid surface (refAA) was prepared by cold pressing polyacrylic acid powder. The polymer was manufactured by Scientific Polymer Products and had a weight average molecular weight of 450 000 g/mol.

2.2. Ozone treatment and graft polymerization

Before ozone treatment, the cellulose fibres were stored for a week in an environment with 100% humidity. The treatment of the cellulose fibres was then carried out in a gas phase reactor at 32°C. The equipment used for generating ozone was a Fischer Ozon 502 ozone generator, which produced an oxygen/ozone flow of 0.250 m^3/h from pure oxygen gas. The ozone concentration was 25 g/m^3. Before reaching the reactor, the gas current was preheated and humidified. A saturated gas mixture at a temperature of 32°C was then blown into the reactor, where the fibres were kept in end-open glass tubes. The concentration of hydroperoxides formed on the cellulose substrates as a consequence of the ozone treatment was determined according to Carlsson and Wiles [34]. Immediately after ozone treatment, the substrates were placed in the monomer solution. The solution was 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 (Mohrs salt), which forms a redox initiator. The pH of the solution was set to 1.5. The grafting process was performed 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 fibres, which then were vacuum dried at 50°C for 15 h before they were 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.

2.3. Characterization

Scanning electron microscopy (SEM) was used to study the substrates before and after grafting. The surfaces were coated with gold before the analysis, which was performed with a Zeiss DSM 940A operated at 10 kV. The distribution of sodium atoms as a result of the neutralization was determined by X-ray mapping with the EPMA/EDS technique (Electron Probe Micro Analyzer/Energy Dispersive Spectrometer) using a JEOL JXA-8600 electron probe combined with a Tracer Northern series II spectrometer. The surfaces were in this case coated with a carbon layer. The surface chemistry of the grafted and ungrafted filter papers was investigated by electron spectroscopy for chemical analysis (ESCA). A Perkin Elmer PHI 5500 equipped with a Mg Kα X-ray source was used for the ESCA measurements. The area analysed had a diameter of 0.8 mm. The swelling capacity of the grafted fibres in the neutralized form was measured by immersing the fibres in buffer solutions with various pH values. The solutions were prepared according to the literature [35]. The ionic strength was justified to 0.15 M in each solution by adding the required amount of sodium chloride salt. The buffer solution was vacuum filtrated from the fibres, and the equilibrium uptake of the fibres was expressed as gram of absorbed buffer solution per gram of grafted hydrogel.

3. Results and discussion

3.1. Acrylic acid grafted on to cotton linters

Cotton linters were ozone-treated for 90 min, which resulted in the formation of 20 μmol hydroperoxides per gram linters as determined with the iodometric method. After the ozone treatment, the fibres were immediately transferred to the acrylic acid solution and grafted for 3 h. The fibres were then extracted and dried, and the amount of grafting was established to be 80%. In a recent study of grafting of HEMA on to cotton linters, the fibre surface

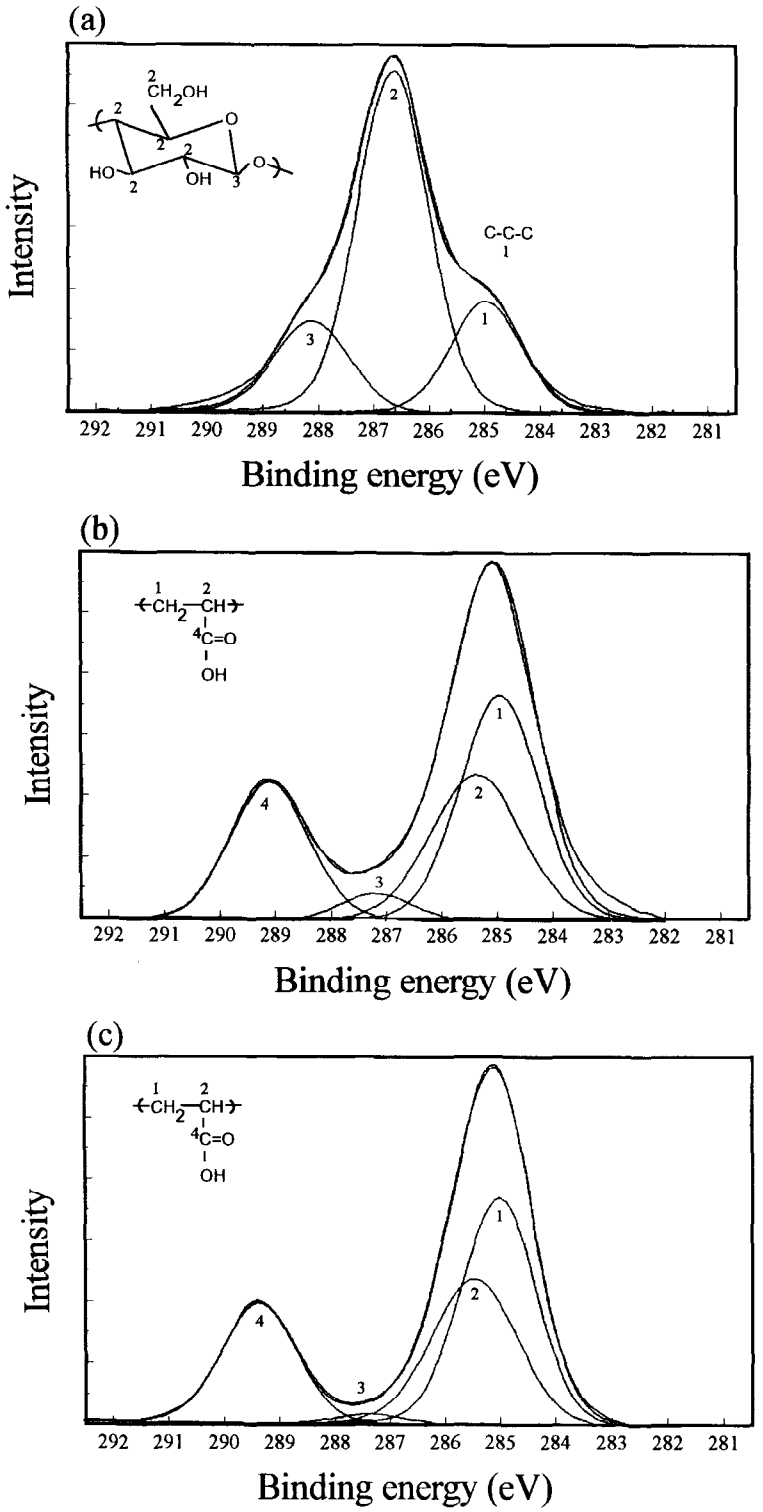

Fig. 1. Typical ESCA C1s peaks: (a) untreated cotton linters, (b) acrylic acid grafted cotton linters, (c) cold pressed polyacrylic acid powder (refAA).

was completely covered first at a grafting yield exceeding 100% [32]. To determine the surface coverage of fibres grafted with polyacrylic acid, ESCA was used. The chemical composition of untreated cotton linters, grafted cotton linters and cold pressed polyacrylic acid powder was investigated. The cold pressed polyacrylic acid powder was used as a reference surface (refAA). For all samples, carbon and oxygen peaks were detected in the survey spectra. The carbon and oxygen content in the surface of untreated linters was determined to be 60 ± 1% and 40 ± 1%, respectively. The corresponding values for grafted linters were 66 ± 3% and 34 ± 3%, respectively, which also was in agreement with the values obtained for the refAA surface. Although the values are close to the ones obtained for untreated fibres, a distinct difference can be observed when comparing the shapes of the deconvoluted C1s peaks shown in Fig. 1. In all cases the C1s peaks have been shifted in order to have peak 1 at a binding energy of 285.0 eV. The C1s peak of untreated cellulose, shown in Fig. 1(a), was deconvoluted into three peaks as suggested in the literature [36,37]. The C1s peak for the grafted fibres, shown in Fig. 1(b), was deconvoluted starting from polyacrylic acid, according to Beamson and Briggs [38]. The shape of this peak is in good agreement with the C1s peak of the refAA surface shown in Fig. 1(c), indicating that the cotton linters are covered with the grafted polymer. Peak 3 which appears in both Fig. 1(b) and (c) cannot directly be assigned to any carbon in the polyacrylic acid structure. The area of these two peaks corresponds to 4.5% and 1.9% of the total C1s peak, respectively. This indicates that at least 97.4% of the cellulose fibre surface is covered with acrylic acid.

3.2. Acrylic acid grafted on to wood cellulose

The major intention of this study was to prepare polyacrylic acid supported on to single wood pulp fibres. One of the drawbacks of graft polymerization is generally the long time required for the reaction. The majority of authors have achieved high grafting yield after hours of polymerization and an increased time generally results in increased grafting yield [39–42]. A study to elucidate the time dependence of grafting was therefore undertaken using single sulfate pulp fibres as substrates. For all experiments the ozonation time was fixed to 90 min while the polymerization time was varied. Fig. 2 illustrates the amount of grafted polyacrylic acid (PAA) determined gravimetrically as a function of grafting time. Surprisingly, we found that, after only 1 min of polymerization, a grafting of 60 ± 20% was achieved. Extended grafting time to 3 h did not contribute to a further weight increase, and the amount of grafting thus remained constant. The grafting amount on to sulfate pulp fibres, which is a highly bleached cellulose, was comparable with the one obtained for cotton linters. This can be

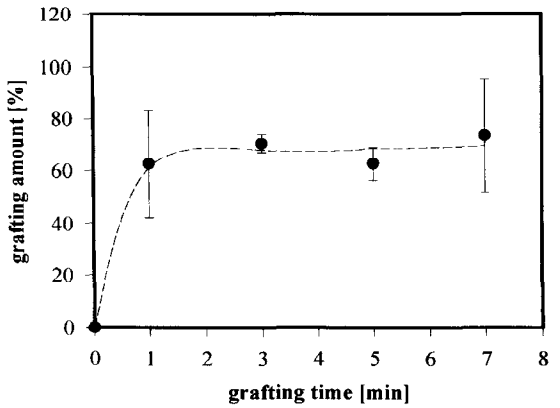

Fig. 2. Grafting amount (%) of polyacrylic acid (PAA) as a function of grafting time.

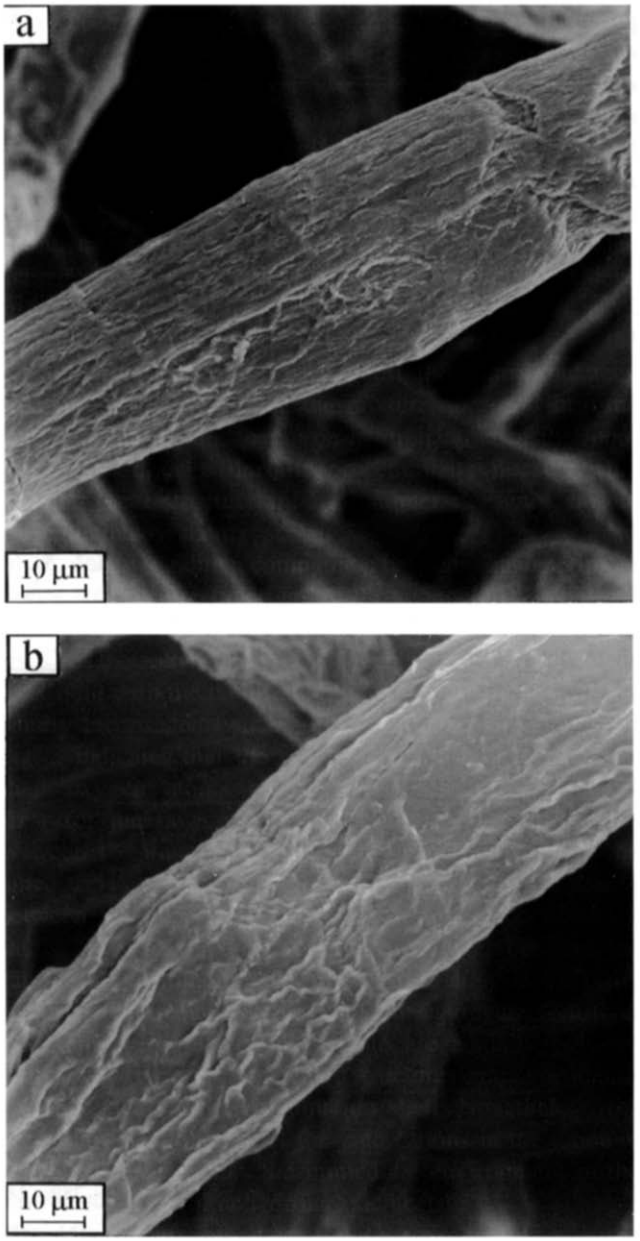

Fig. 3. Scanning electron micrographs: (a) untreated wood pulp fibre, (b) acrylic acid grafted wood pulp fibre.

expected because of the chemical and morphological similarities between these two substrates.

The grafted fibres were studied by SEM. Untreated and AA-grafted pulp fibres are shown in Fig. 3. The untreated fibre in Fig. 3(a) has a surface composed of fibrils, which is characteristic for a wood pulp fibre. A layer of the grafted polymer can be observed on the AA-grafted fibre shown in Fig. 3(b). The SEM micrographs in combination with the ESCA results suggest that a homogeneous coating of the cellulose fibre takes place.

3.3. Neutralization of grafted fibres

When used for absorbing purposes, polyacrylic acid is always partially neutralized to obtain a high swelling capacity [22,23]. The grafted pulp fibres prepared in this study were therefore treated with 0.0125 M NaOH. The neutralization of the carboxylic acid moiety resulted in an introduction of sodium counter-ions, which also gave us the opportunity to determine the localization of the grafted acrylic acid using an X-ray mapping technique. Fig. 4(a) shows a cross-section of an unneutralized AA-grafted pulp fibre, and Fig. 4(b) shows the mapping result of the corresponding cross-section. As expected, no sodium atoms were detected in this case. A significant difference was obtained for the NaOH-treated fibres, which are shown in Fig. 4(c–d). Fig. 4(c) illustrates a SEM micrograph and in the mapping image of the same fibre, shown in Fig. 4(d), it can clearly be observed that a large amount of sodium atoms has been detected in the polyacrylic acid layer along the fibre surface. Furthermore, it is interesting to note that sodium atoms are also detected in the fractured

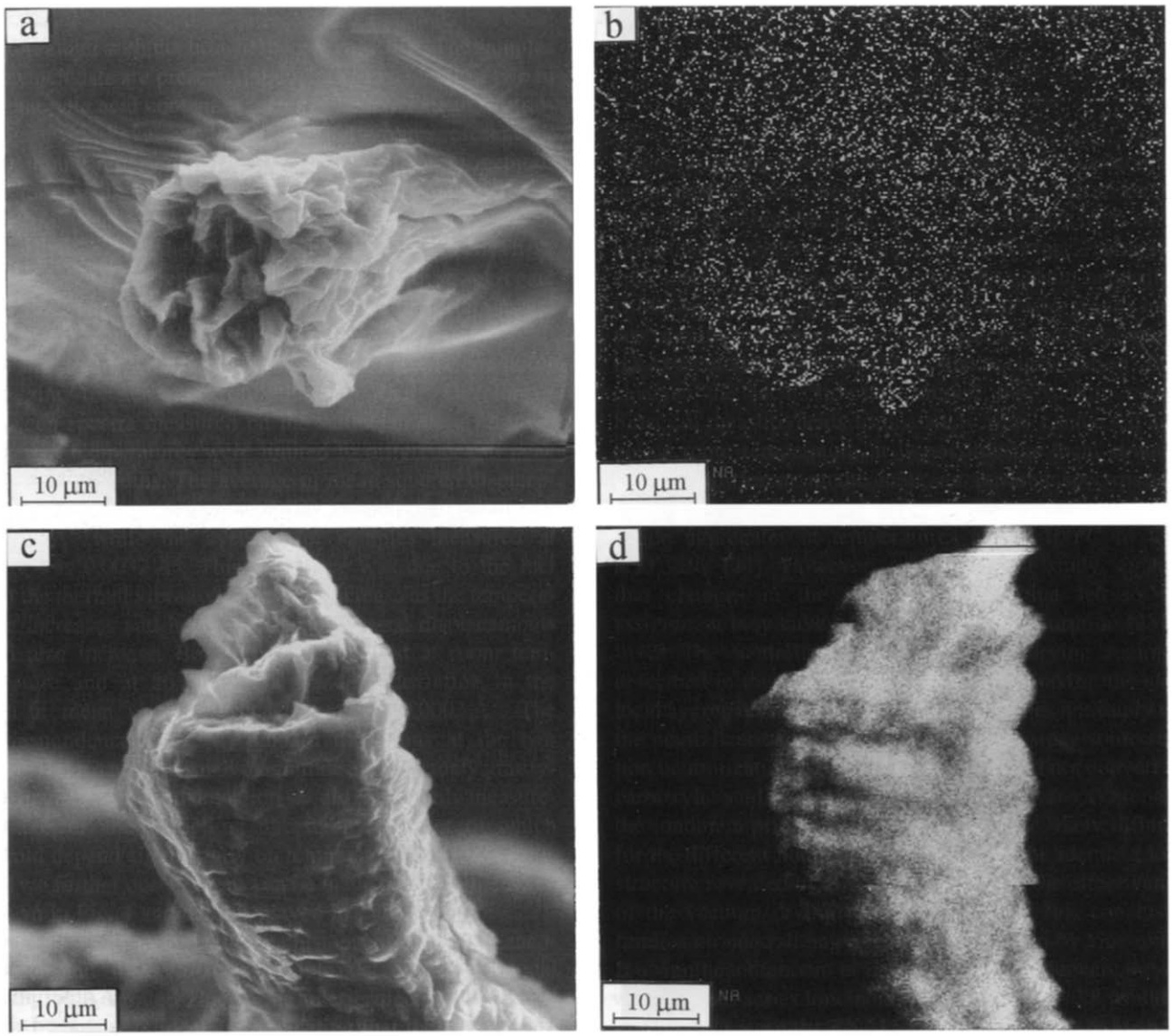

Fig. 4. SEM and X-ray mapping micrographs of acrylic acid grafted fibres: (a) unneutralized grafted fibres, (b) X-ray mapping of Na atoms (same cross-section as shown in Fig. 4(a)), (c) neutralized grafted fibre, (d) X-ray mapping of Na atoms (same cross-section as shown in Fig. 4(c)).

cross-section. This implies that neutralized acid groups are present and that the graft polymerization occurs not only on the fibre surface but also within the internal pores of the fibre. This is in good agreement with our earlier suggestions of the localization of graft polymerized HEMA [32]. The surface coating seems, however, to be more homogeneous when AA is grafted on to the fibres. X-ray mapping results of ungrafted cellulose fibres treated with NaOH under the same conditions as above showed no trace of sodium atoms.

3.4. Fibre networks

Networks of the grafted fibres were formed by filtration of the fibre suspension and subsequent vacuum drying. The effect of neutralization on the network appearance was studied with SEM. The network formed from fibres that were not neutralized is composed of individual grafted fibres, as can be seen in Fig. 5(a). Fig. 5(b) shows a network formed from alkali-exposed fibres. Polyacrylic acid has formed bridges between the fibres, and it is impossible in some areas to distinguish the single fibres. It seems to be likely that linear brush-like polyacrylic acid chains are attached to the cellulose backbones as a result of the graft polymerization. The treatment in sodium hydroxide results in a substantial swelling of the grafted polymer chain because of the high pH. During the drying process, the expanded hydrogel does not contract into the original shape, and a deformed structure is therefore obtained.

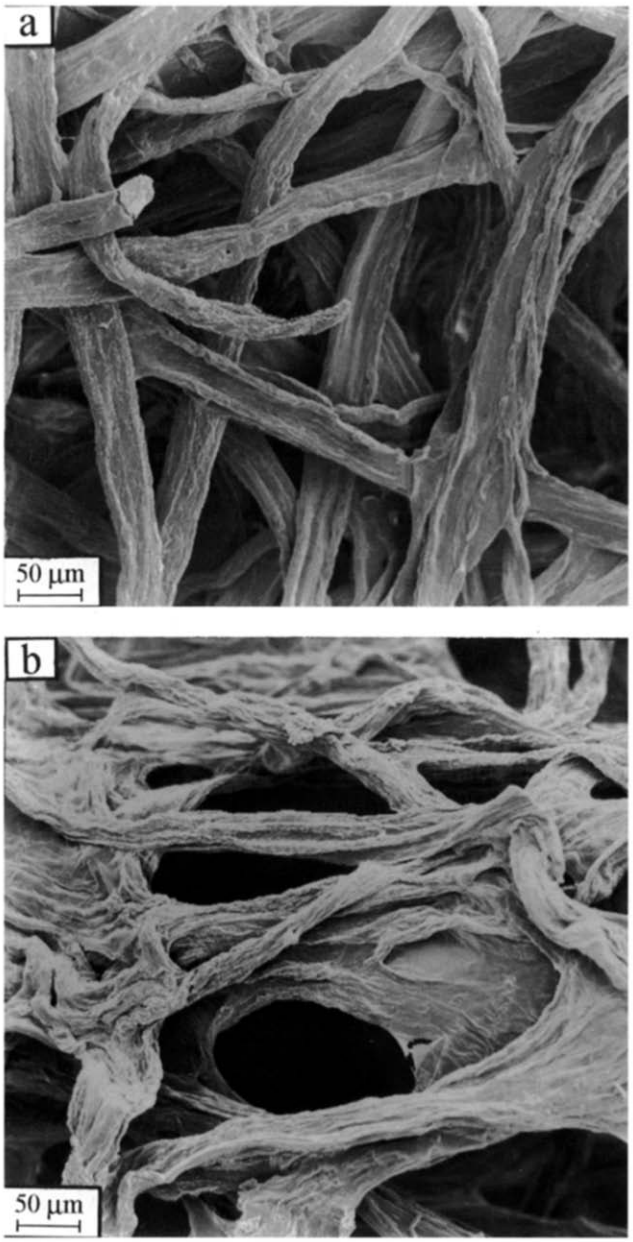

Fig. 5. Networks formed from grafted fibres: (a) fibres that have not been neutralized before network formation, (b) fibres that have been neutralized before network formation.

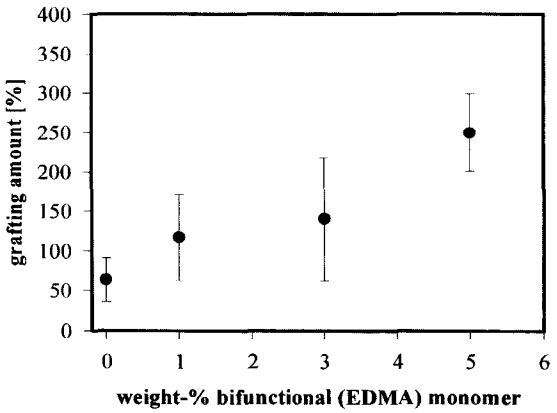

Fig. 6. Grafting amount as a function of weight% AA which has been replaced with EDMA.

The swelling behaviour of hydrogels can be controlled by changing the degree of crosslinking. Attempts to obtain crosslinked grafted polyacrylic chains around the pulp fibres was made by replacing various amounts of the acrylic acid monomer with a bifunctional monomer, ethyleneglycol dimethacrylate (EDMA), which is a typical crosslinker for hydrogels. By increasing the amount of bifunctional monomer in the monomer mixture, it was seen that the grafting amount dramatically increased. Fig. 6 shows the grafting amount as a function of EDMA concentration in the monomer mixture. The amount of grafting clearly increases with the concentration of EDMA in the monomer mixture and, when 5% of the AA monomer was replaced, the amount of grafting was about 250%. At higher EDMA concentrations, 9% and 13%, homopolymer started to appear in the monomer mixture. In this case it was impossible to separate the grafted fibres and therefore difficult to establish the exact amount of grafting.

The single fibres grafted in a mixture of acrylic acid and bifunctional monomers were treated with sodium hydroxide, filtrated and dried according to earlier description. The appearance of the networks formed was studied with SEM. For comparison the appearance of fibres that were grafted only with acrylic acid before (Fig. 7(a)) and after neutralization (Fig. 7(b)) are shown. The network shown in

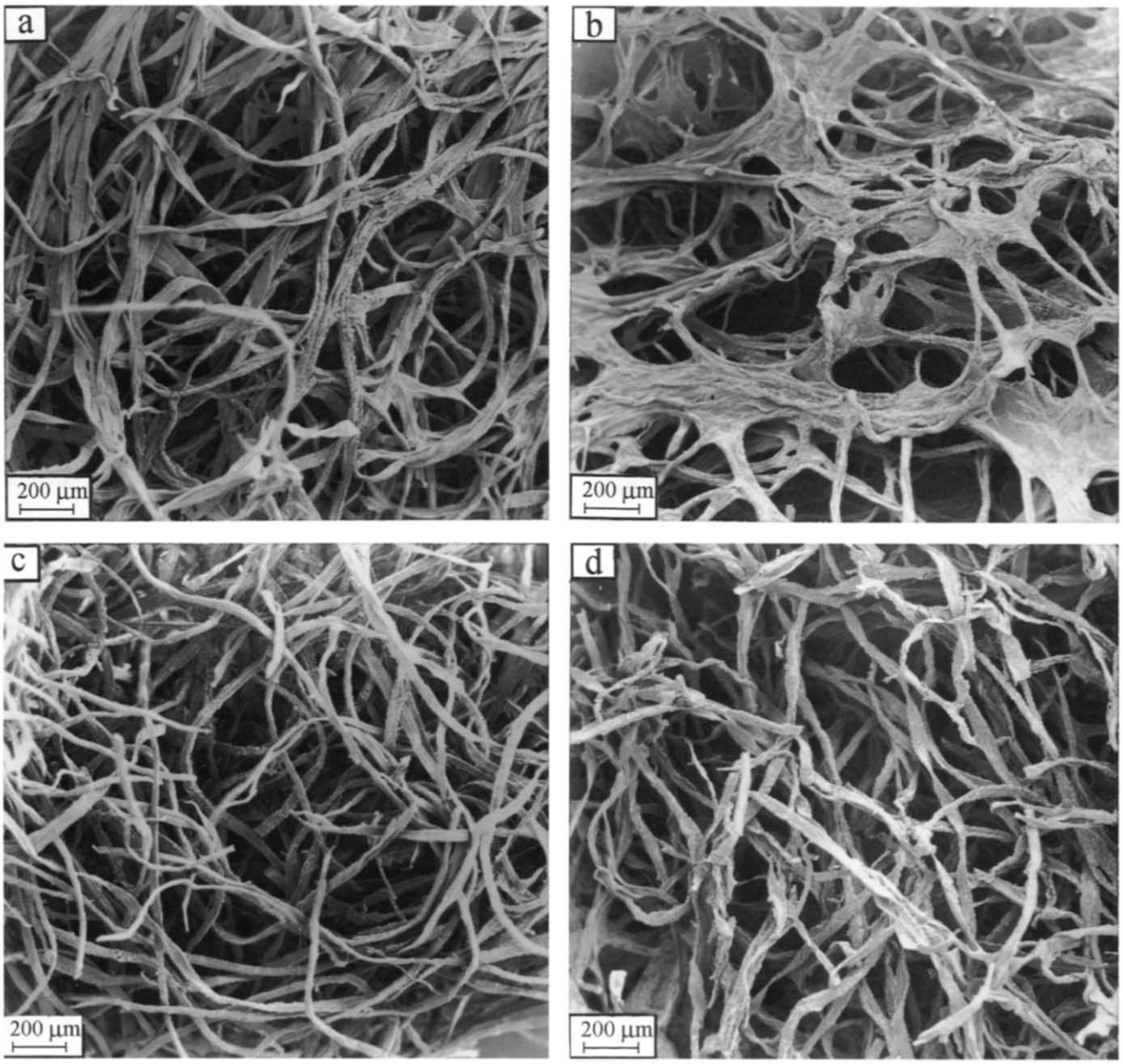

Fig. 7. Networks formed from fibres which have been grafted with and without the presence of bifunctional monomer. Unneutralized fibres compared with neutralized: (a) fibres grafted with only AA, unneutralized state, (b) fibres grafted with only AA, neutalized state, (c) fibres grafted with AA/EDMA (97/3, by weight), unneutralized state, (d) fibres grafted with AA/EDMA (97/3, by weight), neutralized state.

Fig. 7(c) consists of fibres that are grafted in a monomer mixture where 3 wt% acrylic acid was replaced with EDMA. Corresponding fibres in the neutralized state can be observed in Fig. 7(d). Contrary to the fibres that were grafted without EDMA, shown in Fig. 7(b), no fibre–hydrogel deformation was observed. Instead, the network looks similar to the one not exposed to alkali. A graft co-polymerization of AA and EDMA apparently resulted in a cross-linked polymer network with good mechanical properties and a reversible swelling behaviour in the NaOH solution. For fibres grafted in a monomer solution containing 1% EDMA, the fibre–hydrogel deformation was reduced, although the network was similar in some areas to the one shown in Fig. 7(b).

3.5. Swelling properties

The swelling behaviour of the pulp fibres grafted in a monomer mixture containing acrylic acid and 3% EDMA was measured by immersing networks of the neutralized fibres in buffer solutions with various pH. Before the measurements, the ionic strength was justified to 0.15 M in each solution. Fig. 8 illustrates the swelling capacity of the fibres as a function of pH. It can be observed that

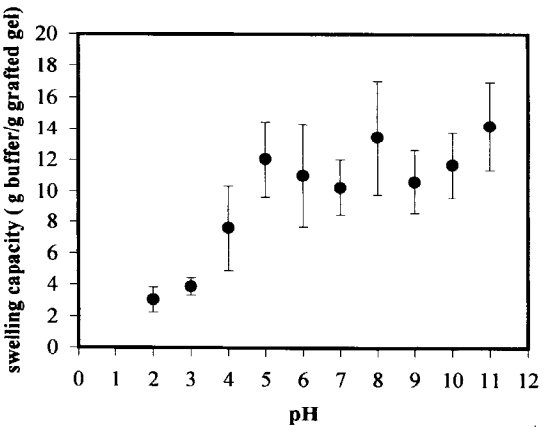

Fig. 8. Swelling capacity as a function of pH of fibres grafted with AA/EDMA (97/3, by weight).

stimuli-responsive properties of the modified pulp fibres were obtained as a result of the grafting process. When the fibres are immersed in buffer solutions with low pH, the ionization of the carboxylic acid groups is suppressed. The carboxylic acid groups that were preionized during the neutralization step are furthermore plausibly protonated to some extent, which decreases the electrostatic repulsion between the polymer backbones. These two factors result in a collapsed polymer network with a rather limited swelling capacity. A transition in the swelling capacity can be observed between pH 4 and pH 5 owing to the pK_a of the grafted polyacrylic acid. At this pH, dissociation of acid groups that were not preionized during the NaOH treatment can occur. Both the repulsion of the charged polymer chains and the presence of free counter-ions in the gel, which causes a high osmotic swelling pressure, contribute to the improved swelling capacity. The pK_a of the solid-supported polyacrylic acid agrees with values of polyacrylic acid reported in the literature [24]. At higher pH values, the swelling capacity is almost constant. The cellulose fibre-supported polyacrylic acid furthermore exhibited a good reversibility upon swelling and deswelling.

4. Conclusions

pH-sensitive cellulose fibre-supported hydrogels were prepared by ozone-induced graft polymerization of acrylic acid using cotton linters and wood pulp fibre substrates. As much as 60% grafting was achieved after only 1 min of graft polymerization on to the pulp fibres. The surface of the fibres was homogeneously covered, as seen with ESCA and SEM. X-ray mapping results showed that neutralized polyacrylic acid also was distributed into the pores of the fibres. The fibre-supported hydrogel was irreversibly deformed upon swelling in alkali and subsequent drying. An addition of a bifunctional monomer, ethyleneglycol dimethacrylate, into the monomer mixture used for grafting significantly increased the amount of grafting and resulted in a fibre-supported hydrogel which swelled reversibly in alkali. Such fibres also exhibited a stimuli-responsive swelling behaviour depending on the pH level in the environment.

Acknowledgements

The Bo Rydin Foundation is gratefully acknowledged for financial support. The authors are most grateful to Malin Andersson for her assistance in the experimental work.

References

[1] Tanaka T. Phys Rev Lett 1978;40:820.
[2] Hooper H, Baker J, Blanch H, Prausnitz J. Macromolecules 1990;23:1096.
[3] Baker J, Stephens D, Blanch H, Prausnitz J. Macromolecules 1992;25:1955.
[4] Moe S, Skjåk-Bræk G, Elgsaeter A, Smidsrød O. Macromolecules 1993;26:3589.
[5] Lee YM, Kim SH, Cho CS. J Appl Polym Sci 1996;62:301.
[6] Siegel R, Firestone B. Macromolecules 1988;21:3254.
[7] Kwon IC, Bae YH, Kim SW. Nature 1991;354:291.
[8] Brannon-Peppas L, Peppas NA. Chem Eng Sci 1991;46:715.
[9] Brannon-Peppas L, Peppas NA. J Control Rel 1991;16:319.
[10] Kost J, Horbett TA, Ratner BD, Singh M. J Biomed Mater Res 1985;19:1117.
[11] Dong LC, Hoffman AS. J Control Rel 1991;15:141.
[12] Tanaka T. In Harland RS, Prudhomme RK, editors. Polyelectrolyte gels. Washington, DC: ACS, 1992:1.
[13] Kramer O. Biological and synthetical polymer networks. London: Elsevier Applied Science, 1988.
[14] Gombotz W, Hoffman AS. In: NA Peppas, editor. Hydrogels in medicine and pharmacy, vol. 1. Fundamentals. Boca Raton, FL: CRC Press, 1986:95–126.
[15] Kim SW, Bae YH. In: Himmelstein K, Amidon GL, editors. Drug diffusion and transport processes in pharmaceutical systems. Marcel Dekker, 1993.
[16] Vacik J, Kopecek J. J Appl Polym Sci 1975;19:3029.
[17] Brazel CS, Peppas NA. Macromolecules 1995;28:8016.
[18] Sassi AP, Shaw AJ, Han SM, Blanch HW, Prausnitz JM. Polymer 1996;37:2151.
[19] Feil H. Ph.D. thesis, University of Twente, Enschede, The Netherlands, 1994.
[20] Brønstedt H, Kopecek J. In: Harland RS, Prudhomme RK, editors. Polyelectrolyte gels. Washington, DC: ACS, 1992:285.
[21] Ricka J, Tanaka T. Macromolecules 1984;17:2916.
[22] Buchholz F. In: Buchholz F, Peppas NA, editors. Superabsorbent polymers. Washington, DC: ACS, 1994:27.
[23] Lee W-F, Wu R-J. J Appl Polym Sci 1996;62:1099.
[24] Nemec J, Bauer W. In: Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI, editors. Encyclopedia of polymer science and engineering, vol. 1. New York: Wiley, 1985:211–234.
[25] Cha W, Hyon S-H, Oka M, Ikada Y. In: Kahoveci J, editor. Molecular symposia, 36th microsymposium on macromolecules, high swelling gels, Prague 10–14 July 1995. Zug, Switzerland: Hüthig and Wepf Verlag, 1996;109:115–127.
[26] Rebenfeld L. In Mark HF, Bikales NM, Overberger CG, Menges G, Kroschwitz JI, editors. Encyclopedia of polymer science and engineering, vol. 6. New York: Wiley, 1985:647–733.
[27] Sjöström E. Wood chemistry, fundamentals and applications. San Diego, CA: Academic Press, 1981.

[28] Reid AR. US Patent No. 4,128,692, 1978.
[29] Akers P. Superabsorbent staple yarns for sealing purposes, Techtextil Symposium 1993, Lecture No: 217, 1.
[30] Hebeish A, Guthrie JT. The chemistry and technology of cellulosic copolymers. Berlin: Springer-Verlag, 1981.
[31] Karlsson JO, Gatenholm P. Polymer 1996;37:4251.
[32] Karlsson JO, Gatenholm P. Polymer1997;38(18):4727–4731.
[33] Karlsson JO, Michálek J, Gatenholm P. In: BD Ratner, DG Castner, editors. Surface modification of polymeric biomaterials. New York: Plenum Press, 1997:79.
[34] Carlsson DJ, Wiles DM. Macromolecules 1969;2:597.
[35] Robinson RA. In: Weast R, Melvin J, editors. CRC handbook of chemistry and physics, 62nd ed. Boca Raton, FL: CRC Press, 1981–1982:D-125.
[36] Dorris GM, Gray DG. Cellul Chem Technol 1978;12:9.
[37] Gray DG. Cellul Chem Technol 1978;12:735.
[38] Beamson G, Briggs D. High resolution XPS of organic polymers, the Scienta ESCA 300 Database. Chichester, UK: Wiley, 1992.
[39] Abdel Hafiz SA, El-Rafie MH, Hassan SM, Hebeish A. J Appl Polym Sci 1995;55:997.
[40] Nho YC, Jin J-H. J Appl Polym Sci 1997;63:1101.
[41] Neimo L, Sihtola H, Harva O, Sivola A. Paperi ja Puu 1967;8:509.
[42] Okieimen EF, Ebhoaye JE. J Appl Polym Sci 1986;31:1275.