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Preparation and characterization of cellulose-supported HEMA hydrogels

J. O. Karlsson and P. Gatenholm*
Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden
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Cellulose fibre-supported hydrogels of HEMA were prepared by means of an ozone-induced graft polymerization process. The effect of various process parameters during ozone treatment on the ability to form hydroperoxides on the cellulose fibres was studied. Ozonation of water-swollen cellulose fibres with a humidified, saturated ozone/oxygen mixture resulted in a significant increase in hydroperoxide formation. The hydroperoxidized cellulose initiated graft polymerization of HEMA mostly in the pores of cellulose, leaving the surface incompletely covered, as detected by ESCA and AFM. The addition of a bifunctional crosslinking monomer, DEGDMA, not only increased the amount of add-on, but also 'led-out' the graft polymerization process from the pores onto the surface and then into the symmetrical spheres. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Hydrogels are crosslinked polymeric networks that exhibit the ability to swell in water without dissolving. Owing to their biocompatibility, special surface properties and high water content, hydrogels have been the material of choice in many biomedical applications[1]. The high water content also leads to low mechanical strength, however, which in some cases limits the field of applications. The mechanical performance of hydrogels can be improved by increasing the crosslink density, forming interpenetrated networks or inducing crystallization[2]. Another approach is to fix the hydrogels onto a stronger support. Ratner *et al.*, for instance, grafted 2-hydroxyethyl methacrylate (HEMA) and acrylamide onto polyethylene and silicone rubber[3]. The use of natural polymers as a support material for hydrogels has recently been investigated and this concept will certainly be of great interest in future research. Graft polymerization of N-vinyl pyrrolidone onto woollen substrates was performed by Guthrie *et al.*[4]. Among other substrates used are starch[5] and pineapple leaf fibres[6]. Cellulose is particularly suitable as support material for hydrogels due to its renewability, good mechanical performance and ability to be formed into structures with various geometries. Cellulose-supported HEMA (2-hydroxyethyl methacrylate) hydrogels have been prepared by using photo-initiated graft polymerization[7–10]. Other recent studies have dealt with γ-ray and chemical initiation of graft polymerization[11–13]. Some of these techniques have disadvantages. These include the high price of the equipment, difficulties in controlling the grafting process and difficulties in avoiding homopolymerization. This has resulted in limited industrial applications of the graft polymerization technology.

We have successfully used an inexpensive technique, ozone-induced graft polymerization, for the preparation of solid-supported hydrogels onto PP membranes and fibres[14,15]. Ozone has also been used as an activation step before the grafting of acrylic monomers and methacrylic monomers onto cellulose[16], although the concept was never developed. Since ozone is currently a promising delignification and bleaching reagent for the pulp industry[17,18], an investigation of ozone treatment as an activation step for graft polymerization is of interest, as it opens the opportunity for using existing equipment. In recent studies[19], various cellulosic materials, such as cellulose membranes, wood pulp fibres, cotton linters and regenerated cellulose, have been investigated with regard to their ability to form hydroperoxides during ozone treatment. Further work has shown that the hydroperoxide formation on polyethylene surfaces was more effective than that on cellulose surfaces. Furthermore, it has been shown that the surface area of the substrate has a major effect on the amount of hydroperoxides formed. The hydroperoxides can decompose to form radicals, which can initiate graft polymerization. We have earlier shown that the hydroperoxide concentration affects the ability to graft onto PP[14]. Several authors have reported that swelling the cellulose fibres enlarges the pores and capillaries, resulting in increased grafting efficiency[20,21]. Another method for improving the graft polymerization is with the addition of a bifunctional monomer[23,23].

The aim of this study was to prepare polyHEMA hydrogels supported onto cellulose fibres. An ozone pretreatment was used to form hydroperoxides on the cellulose substrates before the graft polymerization was performed. This study describes the effect of ozone

* To whom correspondence should be addressed

treatment conditions on hydroperoxide formation and graft polymerization of HEMA onto cellulose. A discussion is also included of the role of a bifunctional monomer in the monomer mixture used for grafting. The modified fibre surfaces were investigated with ESCA, AFM and SEM.

EXPERIMENTAL

Materials

The cellulose fibre used in this study was a Munktell filter paper No. 5 made from pure cotton linters produced by STORA Filter Products, Grycksbo, Sweden. The monomers were 2-hydroxylethyl methacrylate (HEMA) and diethyleneglycol dimethacrylate (DEGDMA). The HEMA monomer as purchased from Fluka Chem. AG. (Switzerland) were vacuum-distilled prior to use. DEGDMA was supplied by Institute of Macromolecular Chemistry in Prague.

Ozone treatment

The treatment of the cellulose fibres was carried out in a gas phase reactor. The equipment used for generating ozone was a Fischer Ozon 502 ozone generator, which produced an oxygen/ozone flow of $0.250\,m^3\,h^{-1}$ from pure oxygen gas. The ozone concentration was $25\,g\,m^{-3}$. The oxygen/ozone mixture was blown into the reactor, where the fibres were kept in end-open glass tubes. The concentration of hydroperoxides formed on the cellulose substrates using ozone treatment was determined according to Carlsson and Wiles[24]. The decrease in DP (degree of polymerization) as a consequence of ozone treatment was measured by capillary viscosimetry using a standard procedure Scan-C 15:62[19].

Graft polymerization

Immediately after ozone treatment, the substrates were placed in the relevant monomer solution. The solution was prepared by diluting 3.0 g of monomer in equal amounts ($15\,cm^3$) of methanol and deionized water. The water contained 75 mg of dissolved Fe(II) ammonium sulfate hexahydrate salt, which forms a redox initiator. The pH of the solution was set to 3.0.

The grafting process was performed in a nitrogen atmosphere, in sealed glass ampoules, for 60 min. 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 methanol overnight, to remove monomer residuals and vacuum dried at 50°C for 15 h before they were weighed. The amount of grafting was expressed as

$$\text{grafting amount } (\%) = 100(w_2 - w_1)/w_1 \qquad (1)$$

where w_1 and w_2 represent the weight of the dry substrates, before and after grafting, respectively.

Surface characterization

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 an Mg $K\alpha$ X-ray source was used for the ESCA measurements. The area analysed had a diameter of 0.8 mm. The surface morphology was examined using the Digital Instruments NanoScope III Atomic Force Microscope (AFM) fitted with a NanoScope III Controller with Phase Extender Module and Dimension 3000 Large Sample AFM with type G scanner. A standard silicon tip was used for the analysis, which was performed in air. Furthermore, 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.

RESULTS AND DISCUSSION

Ozone treatment of cellulose

The effect of the conditions used in the ozonation process on the formation of hydroperoxides on cellulose was first investigated. The lower curve in *Figure 1* shows the effect of ozone treatment time on the hydroperoxide concentration. In this case, dry cellulose fibres were treated with a dry gas stream. A concentration of $10\,\mu mol\,g^{-1}$ was reached after 225 min of ozone treatment.

To increase the reactivity of our cellulose material, the cellulose fibres were preswelled in water. The fibres were, however, completely dried after as little as 15 min of treatment with the dry ozone/oxygen mixture. An ozonation apparatus was therefore designed in which preswollen cellulose fibres were treated with a gas stream that was passed through a bottle of water. The temperature in both the bottle and the reactor was adjusted to maintain a moisture-saturated atmosphere in the reactor during the treatment. The process is shown schematically in *Figure 2*. The change in ozonation conditions significantly increased the effectiveness of hydroperoxide formation. The results are illustrated in *Figure 1*, where the upper curve represents the hydroperoxide concentration as a function of ozonation time at 32°C by a humidified ozone/oxygen mixture. It can be observed that the hydroperoxide concentration reaches a plateau after about 90 min of ozone treatment.

Ozone treatment of cellulose is an oxidation process in which the hydroperoxide formation is one of the reactions that takes place. When the cellulose is oxidized, the chains usually break down as a result of opening and cleavage of the monomeric rings, which leads to a decreased molecular mass[25,26]. Extensive chain scission would undoubtedly affect the mechanical strength of the cellulose fibres and thus reduce their ability to perform as a hydrogel support. The molecular weight reduction was

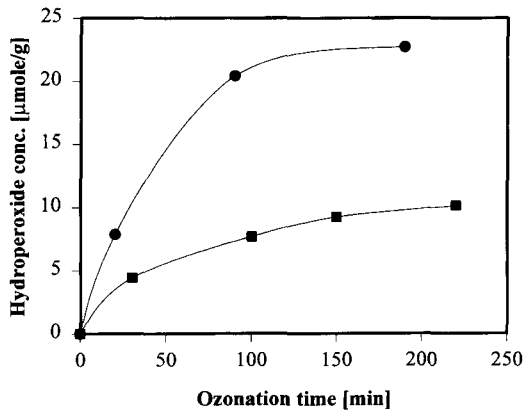

Figure 1 Hydroperoxide formation as a function of ozonation time. Dry fibres and dry ozone/oxygen mixture (squares) compared with preswelled fibres and humidified ozone/oxygen mixture (circles)

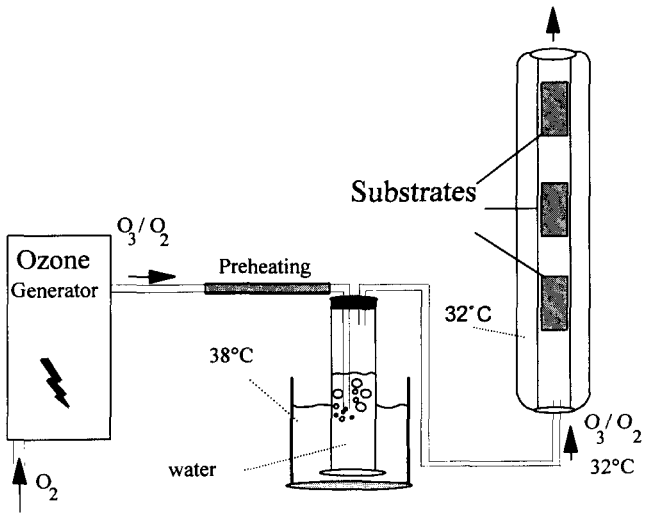

Figure 2 Schematic illustration of the ozonation process

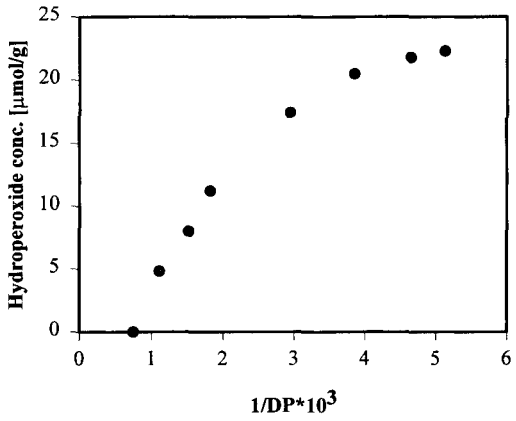

Figure 3 Hydroperoxide concentration vs. 1/DP

therefore investigated, and the effect of ozonation time on degree of polymerization recorded. *Figure 3* illustrates the relationship between the hydroperoxide concentration and the reciprocal degree of polymerization (DP). From the standpoint of hydroperoxide formation in relation to cellulose degradation, it is seen that the optimal ozonation time is reached when $\sim 20\,\mu$mol hydroperoxides g^{-1} have been formed, which corresponds to approximately 90 min of ozone treatment. An extended ozone treatment results chiefly in increased degradation of the cellulose.

Graft polymerization and surface composition

Thermal decomposition of the hydroperoxides in the presence of a redox initiator yields macromolecular radicals capable of initiating a graft polymerization. The cellulose fibres were ozone-treated for 90 min. After this treatment, the fibres were transferred into a polymerization tube containing a monomer mixture composed of HEMA, methanol and water (with Fe^{2+}). After 60 min of reaction, the cellulose samples were removed, extracted and dried. The graft add-on was established gravimetrically to be 50%. The surface composition of untreated and HEMA-grafted cellulose was investigated with ESCA. *Figure 4a* shows a C1*s* ESCA peak of an untreated cellulose substrate. This peak can be decovoluted into three peaks,

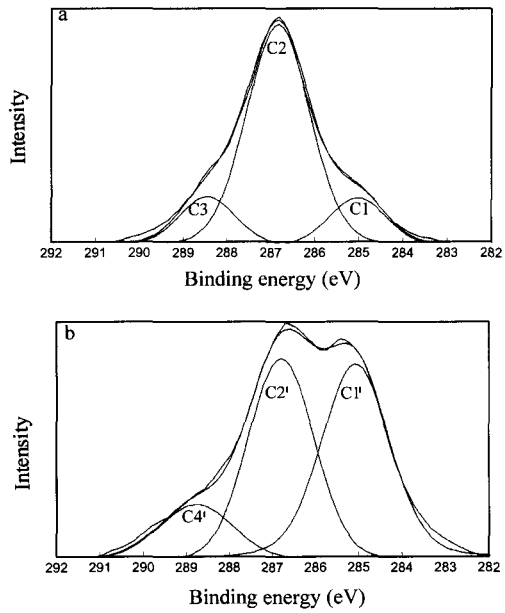

Figure 4 ESCA C1*s* peak of: (a) untreated cellulose, C1 (C–C–C), C2 (C–C–O), C3 (O–C–O); (b) cellulose with 50% graft polymerized HEMA, C1′ (C–C–C), C2′ (C-C–O), C4′ (O–C=O)

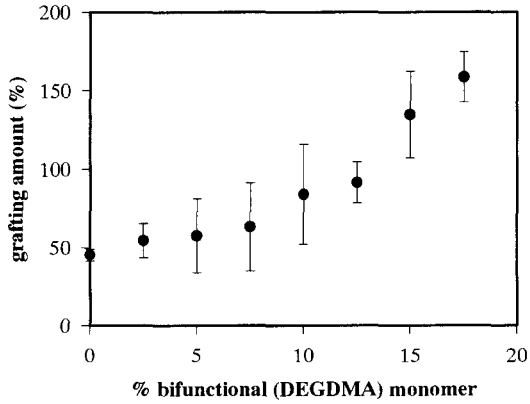

Figure 5 Grafting amount (%) as a function of DEGDMA content in the monomer mixture

C1–C3, as suggested in earlier papers[27,28]. The C1*s* peak of the grafted cellulose can also be deconvoluted into three main peaks C1′, C2′ and C4′. The position of these peaks corresponds to a pure HEMA spectrum[29]. The intensity of C2′ and the tailoring of C4′ suggest, however, that C2 and C3 from cellulose contributes to the C1*s* spectra of the grafted sample, which means that the surface is not completely covered with P(HEMA).

Various amounts of bifunctional monomer (DEGDMA), normally used as a crosslinker for hydrogels, were added to the monomer mixture used for graft polymerization. The addition of DEGDMA significantly affected the amount of grafting. *Figure 5* shows a very strong effect in terms of an increased amount of grafting by the addition of DEGDMA. However, at 20 wt% of DEGDMA, homopolymer appeared in some of the polymerization tubes. We have therefore chosen to not calculate any mean value for this monomer composition. A similar graft polymerization enhancement effect, although at a lower level, was previously observed when bifunctional monomers were added to u.v. and photo-induced graft polymerization of HEMA onto

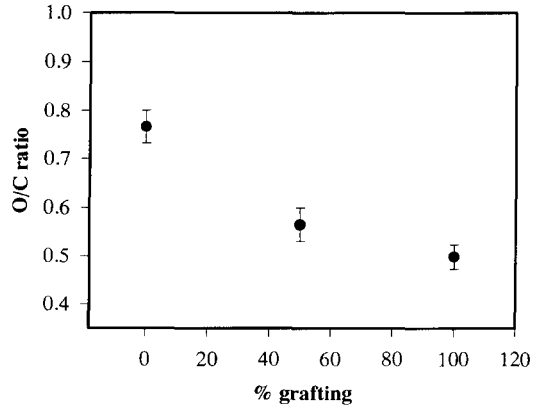

Figure 6 O/C ratio measured by ESCA as a function of grafting amount (%)

cotton[8,9]. The enhancement of grafting was proposed mainly to occur through the branching of the grafted chains. We propose that a similar mechanism is responsible for enhanced graft polymerization in the current system.

Additional ESCA analyses were performed in order to localize the grafted hydrogels for samples showing the increased grafting yield. *Figure 6* shows the O/C ratio for untreated cellulose and for cellulose grafted with 50% and 100% HEMA, respectively. The hydrogel with this composition has a theoretical O/C ratio of 0.5, although the values of HEMA reported in the literature are always slightly lower because of the reorientation of functional groups. Whereas cellulose grafted with 50% HEMA does not seem to completely cover the surface, the 100% grafted sample shows a value that agrees well with HEMA. This indicates that the graft polymerization starts in the pores and that at least 100% grafting is required to form a surface-supported hydrogel that covers the cellulose fibre substrate.

Surface morphology

The surface morphology of the grafted cellulose was investigated with AFM in the tapping mode. *Figure 7a* shows a 1-μm field of a cellulose substrate that was ozone-treated for 90 min. The microstructure of well-ordered parallel arrays of fibrils, characteristic of cotton linters can be clearly observed. The ozone-treated samples are slightly rougher than the untreated sample. *Figure 7b* shows one of the investigated spots of 50% grafted samples. The surface had a much smoother appearance than that of the ozonated sample. The grafting process appears to coat the cellulose fibre. Nevertheless, the phase images of the grafted samples showed some evidence of material variations from spot to spot, suggesting that the coating did not completely cover the substrate. In regions where the coating is very thin, it may conform to the substrate, allowing us to perceive the underlying fibrils. In other areas, the coating appeared to be thick enough to planarize the surface, hiding the fibrils. The grafted samples appeared to have some fine bumps that were associated with the coating because their spatial distribution was different from what we saw on the untreated fibres. The AFM representation of the 100% grafted sample, shown in *Figure 7c*, had more of these bumps than did the 50% grafted sample.

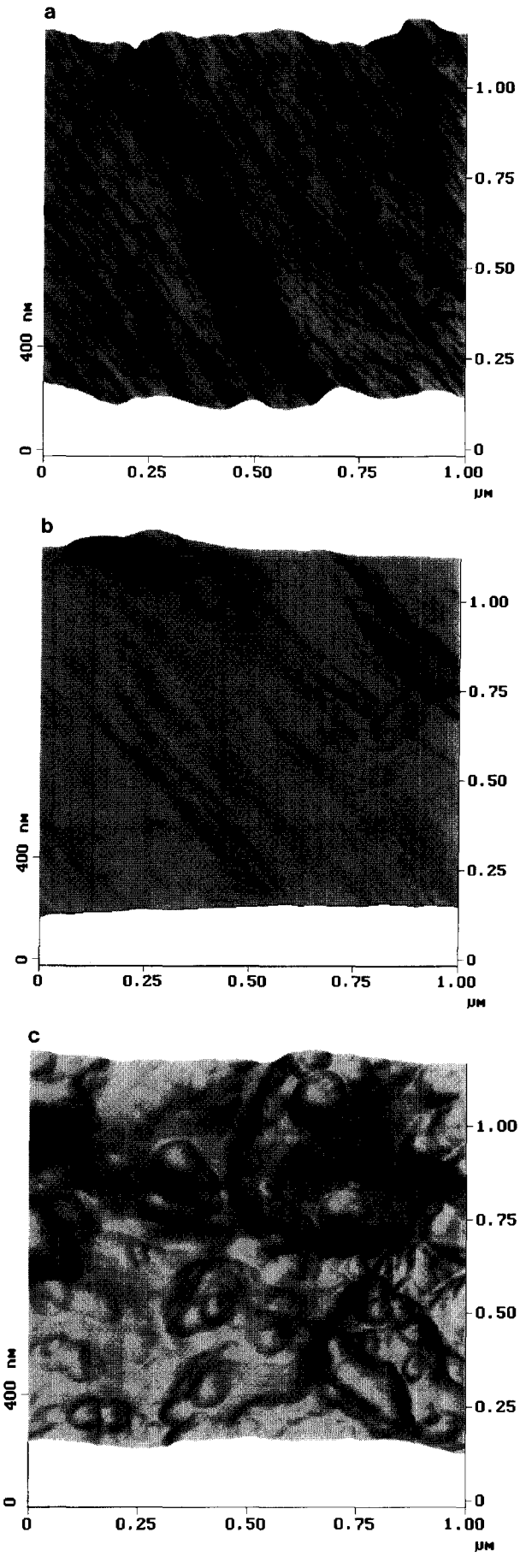

Figure 7 AFM micrographs of cellulose samples: (a) ozone-treated cellulose; (b) cellulose grafted with 50% HEMA; (c) cellulose grafted with 100% HEMA

The fibres were also investigated with SEM. *Figure 8a* shows an electron micrograph of untreated cotton linter cellulose with its characteristic, well-arranged fibrils. *Figure 8b* shows a micrograph of a 300% grafted sample. The fibre was grafted in a monomer mixture containing 20% of DEGDMA. No homopolymerization was observed in the polymerization tube. The bumps that were identified with AFM are enhanced at this amount of grafting and can clearly be seen as spheres on the fibre surface.

CONCLUSIONS

The formation of hydroperoxides as a result of the ozone treatment was increased by treating preswelled fibres with a humidified ozone/oxygen mixture. Optimal hydroperoxide formation, in relation to cellulose degradation, was found by measuring the DP as a function of ozonation time. Graft polymerization onto the ozone-treated fibres started chiefly in the pores of the cellulose, while the surface did not become completely covered. The grafting yield and surface coverage was significantly increased by adding a bifunctional monomer. In addition to a fine coating of fibrils, the development of bumps of the grafted polymer into spheres was seen when the amount of grafting was increased. The use of a bifunctional monomer not only significantly increased the amount of grafting amount but also 'led out' the polymerization from the pores onto the surface and, thus, appears to offer a method for controlling the localization of the grafted hydrogel.

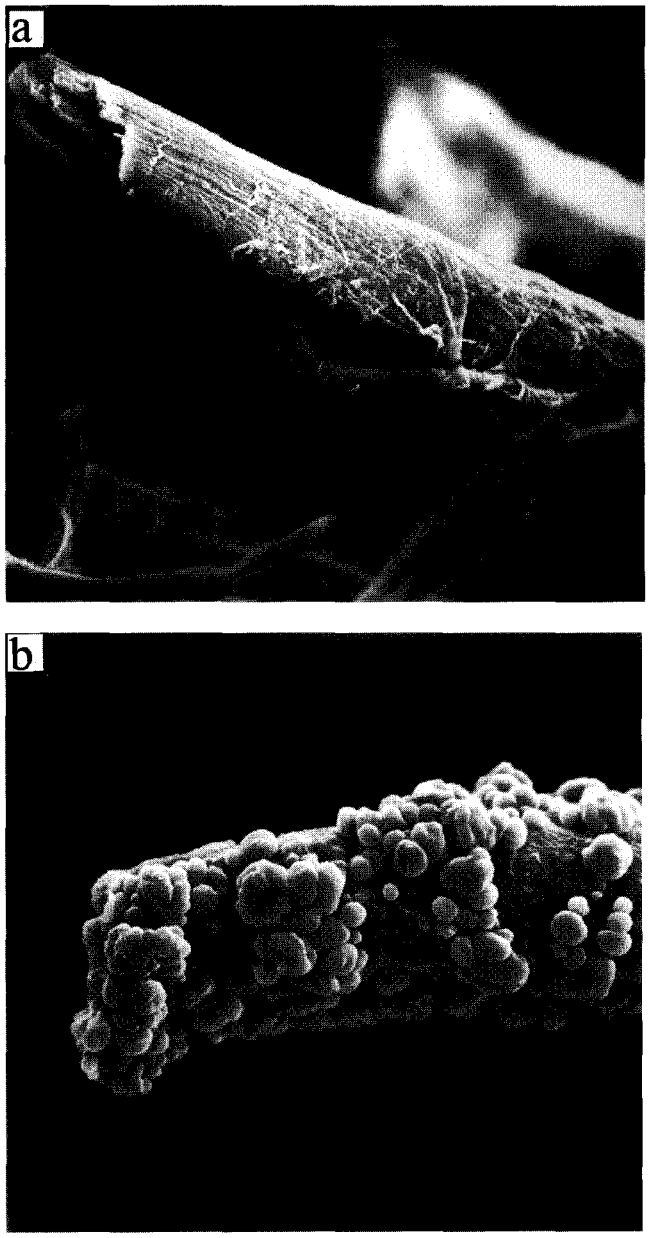

Figure 8 SEMs of cellulose fibres: (a) untreated fibre; (b) fibre grafted with 300% HEMA

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REFERENCES

1. Wichterle, O. and Lim, D., *Nature*, 1960, **185,** 117.
2. Peppas, N. A., *Hydrogels in Medicine and Pharmacy*, Vol. 1. CRC Press, Boca Raton, 1986.
3. Ratner, B. D., Weathersby, P. K., Hoffman, A. S., Kelly, M. A. and Scharpen, L. H., *J. Appl. Polym. Sci.*, 1978, **22,** 643.
4. Barker, P., Guthrie, J. T., Davis, M. J., Godfrey, A. and Green, P. N., *J. Appl. Polym. Sci.*, 1981, **26,** 521.
5. Trimnell, D., Fanta, G. F. and Salch, J. H., *J. Appl. Polym. Sci.*, 1996, **60,** 285.
6. Mohanty, A. K., Parija, S. and Misra, M., *J. Appl. Polym. Sci.*, 1996, **60,** 931.
7. Shukla, S. R., Gopala Rao, G. V. and Athalye, A. R., *J. Appl. Polym. Sci.*, 1991, **42,** 2163.
8. Shukla, S. R. and Athalye, A. R., *J. Appl. Polym. Sci.*, 1993, **48,** 1877.
9. Shukla, S. R. and Athalye, A. R., *J. Appl. Polym. Sci.*, 1994, **51,** 1499.
10. Da Silva, M. A., Gil, M. H., Lapa, E. and Guthrie, J. T., *J. Appl. Polym. Sci.*, 1987, **34,** 871.
11. Zahran, A. H., Williams, J. L. and Stannett, V. T., *J. Appl. Polym. Sci.*, 1980, **25,** 535.
12. Abdel Hafiz, S. A., El-Rafie, M. H., Hassan, S. M. and Hebeish, A., *J. Appl. Polym. Sci.*, 1995, **55,** 997.
13. Ghosh, P., Dev, D. and Samanta, A. K., *J. Appl. Polym. Sci.*, 1995, **58,** 1727.
14. Karlsson, J. O. and Gatenholm, P., *Polymer*, 1996, **37,** 4251.
15. Gatenholm, P., Ashida, T. and Hoffman, A. S., *J. Polym. Sci., Chem. Ed.* (in press).
16. Simionescu, C. I. and Oprea, S., *J. Polym. Sci.: Part C*, 1972, **37,** 251.
17. Sun, Y. and Argyropoulos, D. S., *Holzforschung*, 1996, **50,** 175.
18. Eriksson, T. and Gierer, J., *J. Wood. Chem. Technol.*, 1985, **5,** 53.
19. Hedenberg, P. and Gatenholm, P., *J. Appl. Polym. Sci.*, 1996, **60,** 2377.
20. Shukla, S. R. and Athalye, A. R., *J. Appl. Polym. Sci.*, 1992, **44,** 435.
21. Kubota, H., Murata, Y. and Ogiwara, Y., *J. Polym. Sci. Polym. Chem. Ed.*, 1973, **11,** 485.
22. Davis, N. P. and Garnett, J. L., *J. Polym. Sci. C*, 1976, **55,** 287.
23. Pascual, B., Castellano, I., Vazques, B., Gurruchaga, M. and Goñi, I., *Polymer*, 1996, **37,** 1005.
24. Carlsson, D. J. and Wiles, D. M., *Macromolecules*, 1969, **2,** 597.
25. Hebeish, A. and Guthrie, J. T., *The Chemistry and Technology of Cellulosic Copolymers*. Springer-Verlag, Berlin, 1981.
26. Katai, A. A. and Schuerch, C., *J. Polym. Sci. A*, 1966, **4,** 2683.
27. Dorris, G. M. and Gray, D. G., *Cellul. Chem. Technol.*, 1978, **12,** 9.
28. Gray, D. G., *Cellul. Chem. Technol.*, 1978, **12,** 735.
29. Beamson, G. and Briggs, D., *High Resolution XPS of Organic Polymers, The Scienta ESCA300 Database*. John Wiley & Sons Ltd, Chichester, 1992.