ELSEVIER

S0032-3861(96)00277-7

Polymer Vol. 37 No. 19, pp. 4251–4256, 1996

0032-3861/96/$15.00+0.00

Solid-supported wettable hydrogels prepared by ozone induced grafting

J. O. Karlsson and P. Gatenholm*
Department of Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden
(Received 4 October 1995; revised 31 January 1996)

Ozone-induced graft polymerization of hydrogel forming polymers on to polypropylene (PP) membranes and fibres was studied. A higher rate of water absorption and higher water content at equilibrium were found when diethylene glycol methacrylate (DEGMA) rather than 2-hydroxyethyl methacrylate (HEMA) was grafted on to microporous substrates. Ozone-induced grafting of HEMA and DEGMA on to polypropylene fibres resulted only in thin hydrogel layers that were evenly distributed on the fibre surfaces. Dynamic contact angle measurements of HEMA-grafted fibres using water as the test liquid showed a hysteresis typical of a polyHEMA gel. A higher wettability was obtained when DEGMA was grafted on to the PP fibres. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ozone; grafting; hydrogel)

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymer networks. When these polymers are exposed to water, they swell to equilibrium without dissolving. In the swollen state, hydrogels can contain a high percentage of water, while at the same time preserving their shape[1]. This property, and the fact that several hydrogels are biocompatible, make them the material of choice in several biomedical applications[2–4]. However, a high water content of hydrogels also leads to inferior mechanical properties[5], which prevent their use in many new applications, e.g. as artificial tissues and organs.

One way to improve the mechanical performance of hydrogels would be to reinforce them with fibres. Such solutions exist among biological species. A jellyfish, for example, has good mechanical strength at less than 1% organic content[6]. A collagen fibre network embedded in a mucoprotein hydrogel matrix[7] makes possible complicated movements without damaging the structure. In some cases, e.g. when preparing dialysis membranes, hydrogels have been fixed on to a solid support[8]. This can be performed by coating or by chemical modification of the solid material. Surface-induced grafting has been pointed out as a convenient method for preparing hydrogel-like surfaces on various substrates[9–11] and, during recent years, radiation has been extensively evaluated as a method for inducing surface grafting[12–16].

Polypropylene (PP) and polyethylene are chemically inert polymers with good mechanical and thermal properties. Their inert surface requires an activating pretreatment in order for them to be used as a solid support for hydrogels. Various techniques for the modification of PP by surface grafting have been reviewed in the literature[17]. A simple method of surface oxidation with ozone was used for grafting various monomers on to polyolefinic surfaces[18–21]. As a result of the ozone treatment, the substrates are oxidized and hydroperoxides are formed[22]. When exposed to heat, the hydroperoxides break into radicals that are able to initiate graft polymerization. By using this technique it is possible to create surfaces that are tailor-made for certain applications, e.g. in the field of biomedicals. The surface characteristics of a biomaterial represent a crucial property that affects its interactions with a biological environment, and is therefore responsible for the degree of biocompatibility. A few reports have described the surface properties of hydrogels grafted on to polyolefins[23,24].

In this study, various PP substrates were used for ozone-induced grafting. The monomers used were hydroxyalkyl methacrylates, forming hydrogels with different degrees of hydrophilicity. The effect of ozone treatment on the substrates was investigated by studying the hydroperoxide concentration and polymer degradation as a function of treatment time. Surface characterization of grafted and ungrafted substrates was carried out using scanning electron microscopy (SEM), electron spectroscopy for chemical analysis (e.s.c.a.) and dynamic contact angle measurements (DCA).

EXPERIMENTAL

Materials

PPs, without additives and in the form of fibres and microporous membranes, were used as substrates for ozone treatment and grafting. The fibres had a diameter of $\sim 20\,\mu m$ and were cut from a spunbond supplied by Fiber Web, Norrköping, Sweden. The membranes had a

* To whom correspondence should be addressed

pore size of 0.2 μm and were supplied by Enka Corporation, Germany. Both the membranes and the fibres were surface-purified by extraction before use. The solvents used were methylene chloride, acetone and water, in that order. The substrates were treated, 15 min in each solvent, in an ultrasonic bath. After extraction, the substrates were dried at 70°C for 2 h. The specific areas of membranes and fibres were determined by the BET method using nitrogen adsorption. Five measurements of each substrate were performed at relative pressures of nitrogen in the range 0.05–0.21. The equipment used was a Digisorb 2600 (Micromeritics).

The monomers used in the study were 2-hydroxyethyl methacrylate (HEMA) and diethylene glycol methacrylate (DEGMA). HEMA monomer was purchased from Fluka Chemicals AG and was vacuum-distilled prior to use. DEGMA was supplied by the Institute of Macromolecular Chemistry in Prague. The purity of the latter monomer was confirmed by g.c. analysis and was then used as received.

Ozone treatment

Ozone treatment of the PP substrates was carried out in a gas phase reactor at 32°C. The substrates, which were cut into pieces (1 × 2 cm), were kept in end-open glass tubes during the treatment. The equipment used for generating ozone was a Fischer Ozon 502 ozone generator, which produced an O_2/O_3 flow of 0.250 $m^3 h^{-1}$ 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 O_2/O_3 mixture at a temperature of 32°C was then blown into the reactor. The concentration of hydroperoxides formed on the PP substrates during ozone treatment was determined according to Carlsson and Wiles[25].

Size exclusion chromatography (s.e.c.)

S.e.c. was used to measure the degradation of PP as a consequence of ozone treatment. The analysis was performed using a Waters 150 cv with a RI detector. PP (1–3 $g l^{-1}$) was dissolved in trichlorobenzene for 16 h at 135°C. The solutions were filtered on a Waters metal filter (0.45 mm); 250 μl of each solution was then injected into the column. The evaluation was done using the Waters Expert Ease calculating program. The calculation was performed with narrow polystyrene and broad polyethylene standards.

Graft polymerization

Immediately after ozone treatment, the substrates were placed in a monomer solution. The solution was prepared by diluting 3.0 g of monomer in equal amounts (15 ml) of methanol and deionized water. The water contained 75 mg of dissolved ammonium ferrous 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 dried at 50°C for 2 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.

Scanning electron microscopy (SEM)

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.

Water uptake

The swelling kinetics of the grafted microporous substrates was studied by measuring the weight increase of samples immersed in deionized water. The equilibrium water uptake was investigated after 40 h in water.

Electron spectroscopy for chemical analysis (e.s.c.a.)

The surface chemistry of the grafted and ungrafted substrates was investigated with e.s.c.a.. A Perkin Elmer PHI 5500 equipped with a Mg $K\alpha$ X-ray source was used for the e.s.c.a. measurements. The area analysed had a diameter of 0.8 mm. The mean values, with corresponding standard deviations from at least six measurements, were calculated.

Dynamic contact angle analysis (DCA)

The instrument used for dynamic wettability measurements of the PP fibres was a Cahn 322 Dynamic Contact Angle Analyzer operating at a stage speed of 20 $\mu m s^{-1}$. Wettability measurements were performed in deionized water ($\gamma = 72.8$ mN m^{-1}). The fibre was dipped into the water and kept there for 5 min before carrying out receding measurements. Immediately after the measurements in water, each fibre perimeter was determined by using a liquid that provides complete wetting, hexadecane ($\gamma = 27.6$ mN m^{-1}). Since the test liquid completely wets out the fibre, the contact angle (θ) is zero and the fibre perimeter can thus be calculated by using equation (1). The new perimeter was used when calculating the advancing and receding contact angles of water. Results from measurements of 20 individual fibres were used to calculate the mean values and standard deviations of the contact angles:

$$P = F/(\gamma \cos\theta) \qquad (1)$$

where P is the perimeter (m), F is the force (mN) and γ is the surface tension of the test liquid (mN m^{-1}).

RESULTS AND DISCUSSION

Ozone-induced grafting on to membranes

Samples of PP membranes were ozonized for 60 min and then immediately immersed in monomer solutions composed of various hydrophilic monomers. After grafting, extraction and drying, the substrates were studied by SEM. Ungrafted and DEGMA-grafted microporous PPs are shown in *Figure 1*. It can be observed that a thick layer of polyDEGMA is evenly distributed on the PP surface as a result of the graft polymerization. The amount of grafting was established as 1319% in this case. For HEMA- and HEMA/DEGMA (3/1)-grafted membranes, the amount of grafting was 1446 and 1199%, respectively. The effects

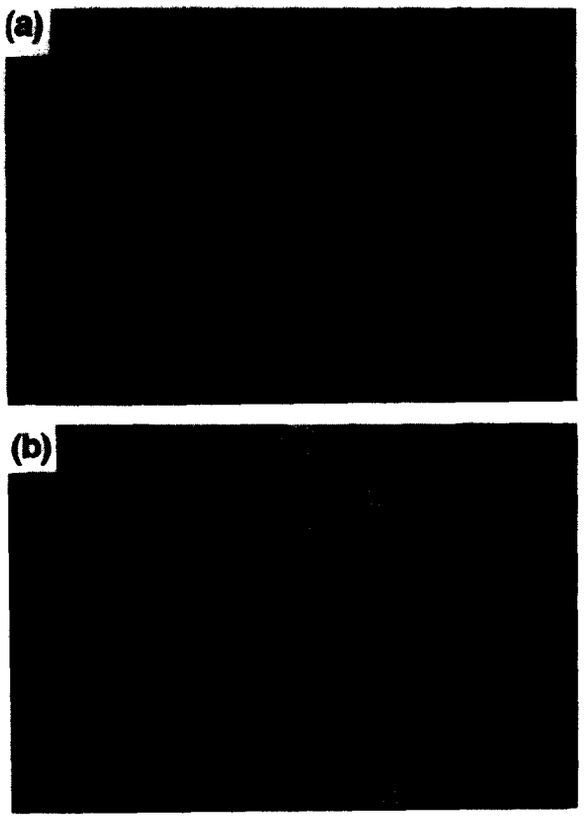

Figure 1 Scanning electron micrographs of polypropylene membrane: (a) untreated PP membrane; (b) PP membrane grafted with DEGMA. Magnification: 5000×

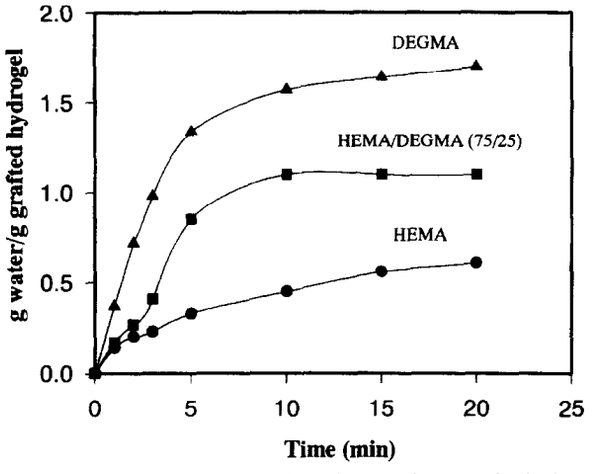

Figure 2 Water uptake as a function of immersion time for hydrogel grafted microporous PP

of ozonation and grafting time, as well as the effect of monomer concentration on the extent of grafting of HEMA on to microporous PP, have been studied previously[19]. Although the efficiency of the grafting process was similar for DEGMA and HEMA, the DEGMA-grafted material exhibit different water absorption properties. *Figure 2* illustrates water uptake as a function of immersion time for three polymer samples grafted in monomer solutions of various compositions. The water uptake of DEGMA-grafted membranes is more rapid than HEMA- and HEMA/DEGMA (3/1)-grafted membranes. As seen from the

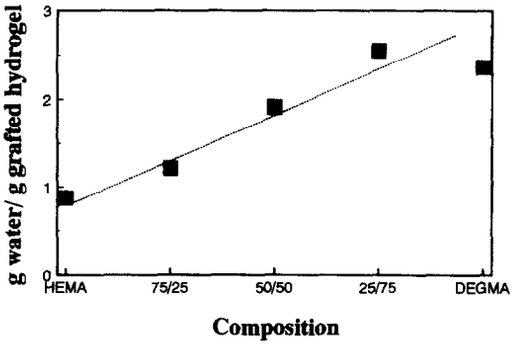

Figure 3 Equilibrium water uptake of grafted microporous PP. Immersion time: 40 h

slope of the water absorption curve, grafted polyHEMA has the lowest value of the rate constant. A similar relationship was observed for the equilibrium water uptake measured after immersion in water for 40 h, shown in *Figure 3*. It can be observed that the maximum absorption increases as a function of the DEGMA content of the monomer mixture. DEGMA-grafted membranes have an equilibrium water uptake of $2.4\,g\,g^{-1}$ grafted polymer, while HEMA/DEGMA (1/1) copolymer and polyHEMA have values of 1.9 and $0.9\,g\,g^{-1}$ grafted polymer, respectively. These values correlate very well with values measured for slightly crosslinked hydrogels of poly-HEMA and -DEGMA prepared without solid support[26].

Ozone-induced grafting on to fibres

The major intention of this study was to prepare hydrogels supported on fibres. When PP fibres were exposed to ozone for 75 min, followed by grafting of HEMA under the same conditions as applied for microporous substrates, we were not able to detect any weight gain. Untreated and treated fibres were therefore further investigated with SEM. It can be seen in the micrographs shown in *Figure 4* that the untreated fibre has a perfectly smooth surface, whereas a thin, evenly distributed coating can be observed on the treated fibre. The effect of ozonation time on the extent of grafting was, therefore, further determined using e.s.c.a.. All fibres were grafted in monomer solution for 60 min after ozone treatment for various periods of time. The results of the e.s.c.a. measurements are shown in *Figure 5*. The oxygen/carbon ratio increases from 0 to 0.26 after only a short ozonation time (15 min) prior to grafting. At extended ozone treatment, the O/C ratio increased almost linearly with the ozonation time. Furthermore, it can be observed that the scatter of the O/C ratio decreases as the ozonation time increases. This implies that the grafted layer becomes more homogeneously distributed on to the fibre surface. The fibres that were ozone-treated for 75 min before grafting have an O/C ratio of 0.40 ± 0.03. This value is in good agreement with the results reported by Morra *et al.*[27] and López *et al.*[28] for pure polyHEMA. We can thus say that the PP fibres are completely covered with polyHEMA after ozone treatment for 75 min and grafting for 60 min. The reason for the lower experimental O/C ratio as compared with the theoretical, which is equal to 0.5, is explained by the mobility of the hydroxyl group in polyHEMA. It is energetically more favourable to bury the polar hydroxyl

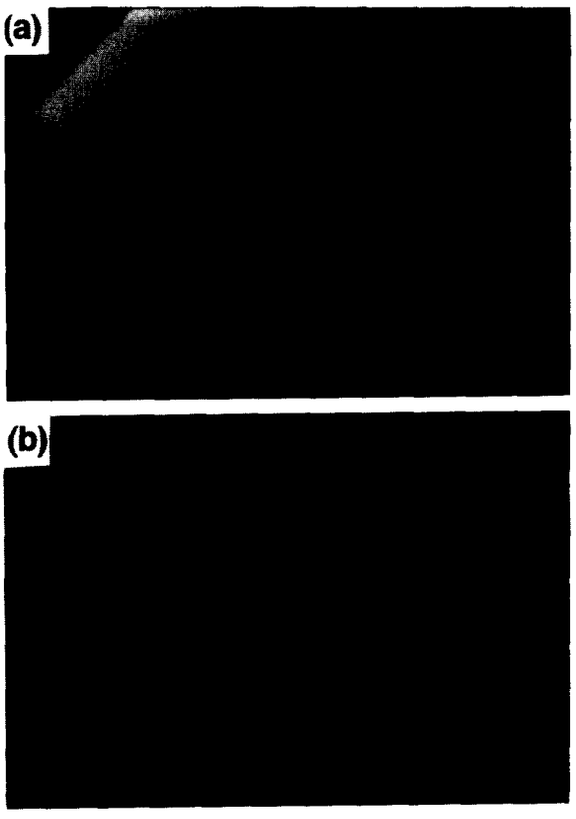

Figure 4 Scanning electron micrographs of PP fibres: (a) untreated PP fibre; (b) PP fibre grafted with HEMA. Magnification: 3000×

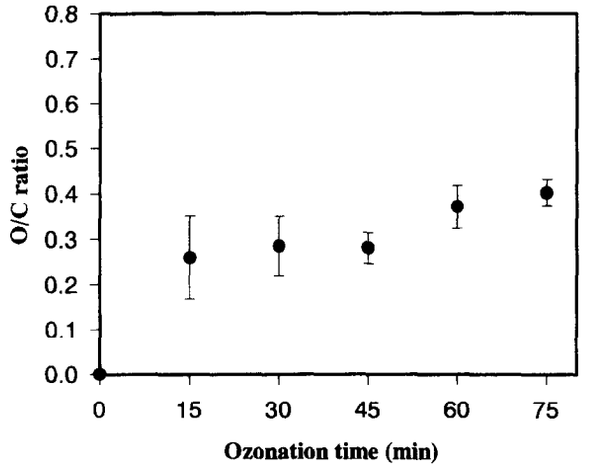

Figure 5 E.s.c.a. results for HEMA grafted polypropylene fibres. The fibres are grafted for 60 min after ozone treatment for various periods of time

group in the gel and expose the non-polar groups of the polymer to air. This behaviour of polyHEMA films was first discussed in detail by Holly and Refojo[29] and appears to be the same for polyHEMA prepared by ozone-induced graft polymerization on to fibres.

The PP fibres were also surface-modified by ozone-induced grafting of DEGMA. The ozonation time was 75 min and the grafting time 60 min. The O/C ratio measured by e.s.c.a. was 0.41 ± 0.03. As in the case of polyHEMA, the experimental value for polyDEGMA is lower than the theoretical one. We suggest that a

Table 1 Experimental and theoretical O/C ratios for poly-HEMA and -DEGMA grafted on to PP fibres

Coating	O/C (e.s.c.a.)	O/C (theoretical)
PolyHEMA	0.40 ± 0.03	0.50
PolyDEGMA	0.41 ± 0.03	0.50

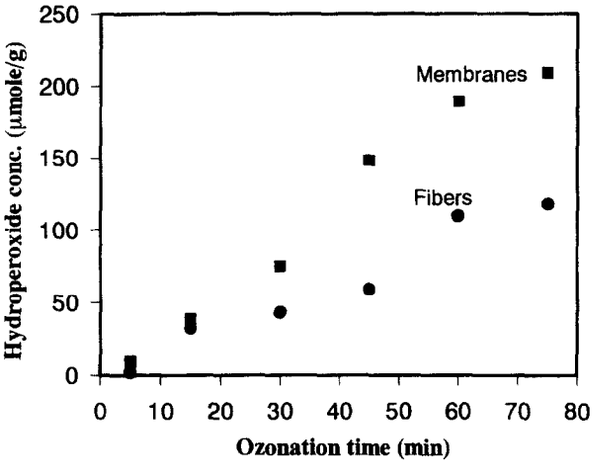

Figure 6 Hydroperoxide concentration as a function of ozonation time. Membranes compared with fibres

reorientation of polar groups, similar to that for polyHEMA, occurs on the surface of polyDEGMA. Theoretical and measured O/C ratios for both grafted hydrogels are presented in *Table 1*.

Hydroperoxide formation and PP degradation

During ozone treatment, the PP substrates are oxidized and hydroperoxides are formed[21,22,30,31]. When exposed to heat in the presence of a redox initiator, the hydroperoxides break into radicals. The alkoxyl radicals that are formed on the PP backbone are then able to initiate graft polymerization. The concentration of hydroperoxides formed on polypropylene membranes and fibres, as a function of ozonation time, is illustrated in *Figure 6*. It is observed that the concentration increases with extended ozone treatment time, and that more hydroperoxides per gram of polypropylene are formed on the membranes as compared with the fibres. This is explained by the large difference in surface area. The surface areas measured by BET were 0.72 and 29.32 $m^2 g^{-1}$ for fibres and membranes, respectively. The increased hydroperoxide concentration as a function of ozonation time correlates well with our earlier mentioned e.s.c.a. results. Extended ozone treatment at constant grafting time resulted in an increased O/C ratio. This is explained by an increased amount of polyHEMA grafted on to the fibres owing to an increased number of initiation sites.

A macromolecular degradation occurs during oxidation of polypropylene with the use of ozone. *Figure 7* illustrates the effect of ozone treatment on the molecular weight of membranes as compared with fibres. There is a great difference in degradation behaviour between these substrates as a result of the difference in accessible surface area. The drop in molecular weight is most significant for membranes during the first 5 min. Thereafter, M_w is almost constant. Compared to the membranes, the PP

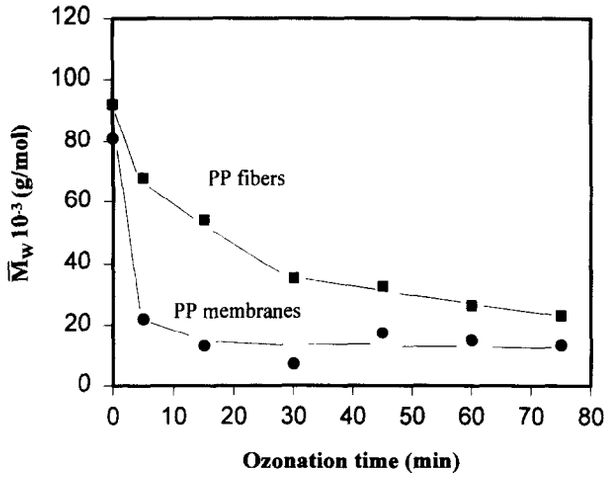

Figure 7 PP degradation during ozone treatment. Membranes compared with fibres

fibres are less sensitive for degradation during the first 30 min.

Wettability of fibres

The dynamic wettability of single fibres that were separated from PP spunbond was measured with a dynamic contact angle analyser. The properties of both grafted and ungrafted PP fibres were investigated. *Figure 8a* illustrates a typical wetting cycle of an untreated PP fibre. The forces registered during immersion and withdrawal are almost equal to each other, which results in a receding (θ_r) contact angle similar to the advancing (θ_a) contact angle. By applying equation (1), the calculated value of (θ_a) was $95 \pm 4°$ and (θ_r) was equal to $93 \pm 4°$. The wetting cycles of grafted PP fibres differ dramatically from the untreated ones. *Figure 8b* shows the result of a HEMA-grafted PP fibre. The calculated advancing contact angle is almost as high ($91 \pm 6°$) as for pure PP, whereas water almost completely wets out the fibre during withdrawal. This results in a receding contact angle close to zero. The behaviour of the wetting process of bulk-polymerized and u.v. grafted poly-HEMA has been discussed in the literature[24,28]. It is believed that, in air, the hydroxyl groups are oriented into the bulk of the polymer, since this is energetically more favourable. However, when water is spread on a poly-HEMA surface, the hydroxyl groups in the hydrogel/water interface are reoriented, which allows them the possibility to interact with water by hydrogen bonding. The mobility of the polar group can vary depending on the way the polymer has been produced. In our case, the PP fibres were covered with polyHEMA, which was produced by ozone-induced grafting. The hydroxyl groups in this layer are undoubtedly very mobile, since a pronounced hysteresis can be observed in the tensiograms.

Somewhat different wetting cycles were observed when DEGMA was grafted on to the fibres (*Figure 8c*). The force registered during immersion was higher than that demonstrated by HEMA-grafted fibres. The higher force is a result of a more wettable fibre surface, i.e. a lower advancing contact angle. The calculated θ_a was equal to $69 \pm 5°$. *Table 2* presents the contact angles of untreated and HEMA- and DEGMA-grafted PP fibres.

Another interesting observation made during the wettability measurements of DEGMA grafted PP fibres

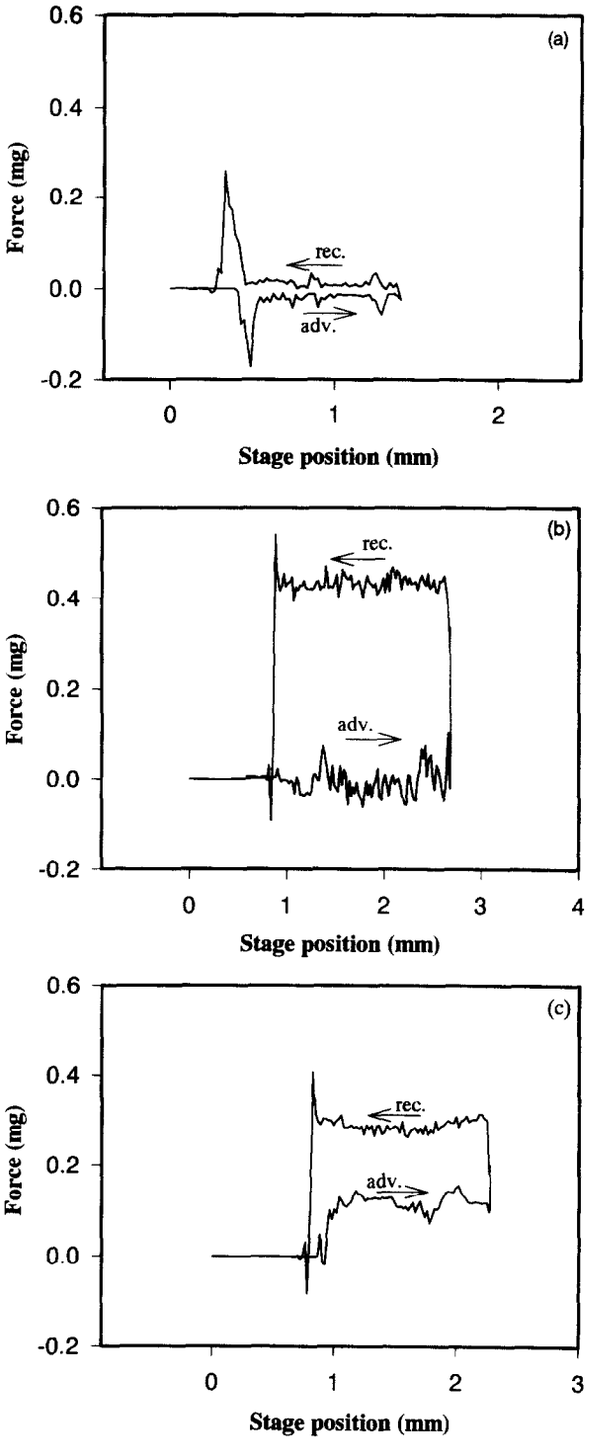

Figure 8 Wetting cycles of single fibres: (a) untreated PP fibre; (b) HEMA-grafted PP fibre; (c) DEGMA-grafted PP fibre

was the large scatter in the receding contact angle. However, in all measurements, the values of θ_r were higher than the one for HEMA-grafted fibres. The results indicate that the mobility of the hydrophilic groups in poly-DEGMA and polyHEMA is different. A study to clarify further the wetting properties of polyDEGMA graft polymerized on to fibres is underway in our laboratories.

CONCLUSIONS

A higher rate of water absorption and higher water content at equilibrium were found when DEGMA rather

Table 2 Advancing contact angles measured by DCA

Fibre	θ_a
Untreated PP	95 ± 4
HEMA-grafted PP	91 ± 6
DEGMA-grafted PP	69 ± 5

than HEMA was grafted on to microporous substrates. Ozone-induced grafting of HEMA and DEGMA on to PP fibres resulted in thin hydrogel layers that were evenly distributed on the fibre surfaces. It was observed that the amount of hydroperoxides formed on the fibres as a result of ozone treatment increased as a function of ozonation time. By using e.s.c.a., we found that 75 min of ozone treatment prior to a grafting process of 60 min was required to coat the fibres fully with grafted hydrogel. During the dynamic contact angle measurements, the HEMA-grafted fibres exhibited a hysteresis typical of HEMA hydrogel. When DEGMA was solid-supported on the fibres, however, a less pronounced hysteresis was found. The advancing contact angle for DEGMA-grafted fibres was also lower than that obtained for HEMA.

ACKNOWLEDGEMENTS

The authors are most grateful to Dr J. Michálek for assistance in the experimental work. The Bo Rydin Foundation is gratefully acknowledged for financial support.

REFERENCES

1 Colvin, J. R. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges and J. I. Kroschwitz), John Wiley, New York, 1985, Vol. 7, pp. 783–806
2 Wichterle, O. and Lim, D. *Nature* 1960, **185**, 117
3 Gombotz, W. R. and Hoffman, A. S. in 'Hydrogels in Medicine and Pharmacy' (Ed. N. A. Peppas), CRS Press, Boca Raton, FL, 1986, Vol. 1, p. 95
4 Kiraly, R. J. and Nose, Y. *Biomater. Med. Devices, Artif. Organs* 1974, **2**, 207
5 Ikada, Y. Molecular Symposium—36th Microsymposium on Macromolecules, 'High Swelling Gels' (Ed. J. Kahoveci), Prague 10–14 July, 1995. Hüthig and Wepf Verlag, Zug, Switzerland (in press)
6 Barnes, R. D. 'Invertebrate Zoology' 5th edn, Saunders College Publishing, Fort Worth, 1987
7 Chapman, G. in 'The Cnidaria and Their Evolution' (Ed. W. J. Rees), Academic Press, 1965
8 Fang, Y. and Shi, T. *J. Membr. Sci.* 1988, **39**, 1
9 Loh, F. C., Tan, K. L., Kang, E. T., Uyama Y. and Ikada, Y. *Polymer* 1995, **36**, 21
10 Lai, J. Y., Chen, M. H., Shuh, C. Y. and Hsu, K. Y. *J. Appl. Polym. Sci.* 1993, **49**, 1197
11 Takigami, S., Kimura, T. and Nakamura, Y. *Polymer* 1993, **34**, 604
12 Ratner, B. D. and Hoffman, A. S. *J. Appl. Polym. Sci.* 1974, **18**, 3183
13 Koul, V., Guha, S. K. and Choudhary, V. *Polym. Int.* 1993, **30**, 411
14 Abdel-Bary, E. M., Dessouki, A. M., El Nesr, E. M. and El Miligy, A. A. *Polym.-Plast. Technol. Eng.* 1995, **34**, 383
15 Poncin-Epaillard, F., Chevet, B. and Brosse, J.-C. *J. Appl. Polym. Sci.* 1994, **53**, 1291
16 Romero, M.-A. and Domard, A. *Polymer* 1994, **35**, 5342
17 Singh, R. P. *Prog. Polym. Sci.* 1992, **17**, 251
18 Fujimoto, K., Takebayashi, Y., Inoue, H. and Ikada, Y. *J. Polym. Sci., Polym. Chem. Edn* 1993, **31**, 1035
19 Gatenholm, P., Ashida, T., Nabeshima Y. and Hoffman, A. S. *ACS PMSE Preprints* 1992, **66**, 445
20 Citovický, P., Mikulásová, D., Chrástová, V., Mejzlik, J. and Majer, J. *Angew. Makromol. Chem.* 1983, **117**, 131
21 Dasgupta, S. *J. Appl. Polym. Sci.* 1990, **41**, 233
22 Yamauchi, J., Yamaoka, A., Ikemoto, K. and Matsui, T. *J. Appl. Polym. Sci.* 1991, **43**, 1197
23 Ratner, B. D., Weathersby, P. K., Hoffman, A. S., Kelly, M. A. and Scharpen, L. H. *J. Appl. Polym. Sci.* 1978, **22**, 643
24 Morra, M., Occhiello, E. and Garbassi, F. *Colloid Polym. Sci.* 1993, **271**, 696
25 Carlsson, D. J. and Wiles, D. M. *Macromolecules* 1969, **2**, 597
26 Gatenholm, P., Michálek, J. and Vacik, J. Molecular Symposium—36th Microsymposium on Macromolecules, 'High Swelling Gels' (Ed. J. Kahoveci), Prague 10–14 July, 1995. Hüthig and Wepf Verlag, Zug, Switzerland (in press)
27 Morra, M., Occhiello, E. and Garbassi, F. *J. Colloid Interface Sci.* 1992, **149**, 84
28 López, G. P., Castner, D. G. and Ratner, B. D. *Surf. Interface Anal.* 1991, **17**, 267
29 Holly, F. J. and Refojo, M. F. *J. Biomed. Mater. Res.* 1975, **9**, 315
30 Catoire, B., Verney, V., Hagege, R. and Michel, A. *Polymer* 1992, **33**, 2307
31 Yamauchi, J., Ikemoto, K. and Yamaoka, A. *Makromol. Chem.* 1977, **178**, 2483