Preparation of Antimicrobial Sutures by Preirradiation Grafting of Acrylonitrile onto Polypropylene Monofilament. III. Hydrolysis of the Grafted Suture

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ABSTRACT: Polypropylene-*grafted*-polyacrylonitrile (PP-*g*-PAN) sutures were prepared by graft polymerization of acrylonitrile onto polypropylene (PP) monofilament using a preirradiation method. The grafted PP monofilaments were subsequently hydrolyzed to introduce carboxyl groups for antimicrobial drug immobilization. The maximum conversion of nitrile groups into carboxyl groups was limited to about 62% and produced sutures with carboxyl content ranging from 0.042 to 0.25 mmol/g. The physical characteristics of sutures were evaluated by FTIR, X-ray diffraction, differential scanning calorimetry, and X-ray photoelectron spectroscopy. In general, the hydrolysis did not cause any significant variation in crystalline structure. The mechanical strength was affected in all the grafted sutures. The tensile strength of sutures was investigated as a function of the degree of grafting. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2509–2516, 2004

Key words: polypropylene (PP); acrylonitrile; suture; radiation; graft polymers

INTRODUCTION

Polymers are chiefly used as construction materials in the field of medical technology,[1–5] a significant application of which is polymeric biomaterials in surgical sutures. Surgical observation shows that bacterial invasion occurs at the site of wounds and is quite frequent. Currently available sutures do not have antimicrobial characteristics and, thus, it is necessary to modify these sutures in such a way that they not only retain inherent mechanical properties but also exhibit antimicrobial activity for prolonged periods, thus preventing bacterial infections in postoperative wounds. Considerable efforts have been made by different researchers to make antimicrobial polymers.[6–12] This can be accomplished either by the addition of an antimicrobial agent to the polymer chips before extrusion[6–8] or by coating a polymer with an antimicrobial agent.[9–12]

In recent years, active drugs have been linked as side substitutents to a polymeric or oligomeric structure by means of cleavable bonds. Release of the drug occurs without significantly affecting the molecular weight of the polymer. This method of obtaining macromolecular drugs involves the preparation of polymeric carriers with chemical functional groups, which are able to react selectively with the suitable groups present in the drug molecule. Radiation-induced graft polymerization of vinyl monomers has proved to be an effective method to introduce functional groups onto the polymer.[13–18] The attractive feature of radiation grafting is that it combines the desirable properties of two polymeric matrices. We recently reported the grafting of acrylonitrile onto polypropylene (PP) sutures by a preirradiation method.[19] The grafting introduces certain changes in the physiochemical characteristics as a function of the degree of grafting.[20] The grafted sutures were subsequently hydrolyzed to obtain carboxylic groups for antimicrobial drug immobilization. This article presents results of the investigation of hydrolysis of polypropylene-*grafted*-polyacrylonitrile (PP-*g*-PAN) sutures and characterization of the resultant sutures.

EXPERIMENTAL

Materials

Polypropylene (PP) used for this study was manufactured by the Indian Petrochemical Corporation Ltd. (IPCL, New Delhi, India). The monofilament was prepared by melt spinning of PP (melt flow index = 3) at 230°C under nitrogen atmosphere using an extruder. Acrylonitrile monomer was received from GS Chemicals (India) and was purified by distillation under vacuum. Dimethyl formamide (DMF) was received from Merck (Darmstadt, Germany); sodium hydrox-

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ide and hydrochloric acid were received from Qualigen (Mumbai, India).

Grafting reaction

The preparation of polyacrylonitrile grafted polypropylene sutures, with different degrees of grafting, was carried out by a preirradiation technique using a Co^{60} γ-ray source (900 Ci) as reported earlier.[19] The monofilament was exposed to a desired dose of gamma radiation. Grafting was carried out in glass ampoules (2×10 cm^2) containing the monofilament and required amount of the monomer, under an inert atmosphere. After a desired period, the grafted suture was removed and Soxhlet extracted with DMF to remove any adhering homopolymer. The grafted suture was dried and weighed. The degree of grafting into the suture was calculated according to the following equation:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where W_0 and W_g are the weight of the ungrafted and grafted sutures, respectively.

Hydrolysis

Hydrolysis of the grafted sutures was carried out by using different concentrations of sodium hydroxide, at different temperatures, in a thermostated water bath for different time intervals. Subsequently, the sutures were removed and washed thoroughly with double-distilled water. These sutures were placed in 2% hydrochloric acid for 2 h to transform carboxyl groups into the proton form. Finally, sutures were washed with distilled water several times until washings were free any traces of acidity.

Carboxyl content

Sutures were placed in 0.5*M* KCl solution for 6 h at ambient temperature. The solution was titrated against 0.05*M* sodium hydroxide solution using phenolphthalein indicator. The carboxyl content was represented as the mmol/g of the dry monofilament.[21]

FTIR spectroscopy

FTIR spectroscopy studies on sutures were carried out on a Spectrum-BX FTIR system (Perkin Elmer Cetus Instruments, Norwalk, CT). Sutures were vacuum dried at 50°C before FTIR measurements.

X-ray diffraction

X-ray diffraction (XRD) patterns of the grafted and ungrafted sutures were recorded in the 2θ range of 10–35°, on a Philips (Eindhoven, The Netherlands) X-ray diffractometer, equipped with a scintillation counter. Cu–K_α radiation (wavelength, 1.54 Å; filament current, 30 mA; voltage, 40 kV) was used for the generation of X rays.

Differential scanning calorimetry (DSC)

DSC studies on samples were carried out using Perkin–Elmer DSC-7 system. Vacuum-dried samples were loaded into the DSC system and the thermogram was run in the temperature range 50–180°C, under a nitrogen atmosphere at the heating rate of 10°C/min. The sample was maintained at 180°C and then cooled to 80°C. The heat of fusion (ΔH_f) was obtained from the area under the melting thermograms. Crystallinity in the suture was obtained from the following expression:

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_{f\,(\text{crys})}} \times 100 \quad (2)$$

where ΔH_f is the heat of fusion of the sample and $\Delta H_{f\,(\text{crys})}$ is the heat of fusion of 100% crystalline PP and was taken as 163 J/g.[22]

Mechanical properties

The tensile properties of sutures were measured, using an Instron (Canton, MA) tensile tester. All the experiments were carried out using the following specifications: gauge length, 100 mm; crosshead speed, 10mm/min; full scale load, 500 N.

X-ray photoelectron spectroscopy (XPS)

XPS measurements were made using on a PHI 5500 (Philips), equipped with hemispherical analyzer and a nonchromatized Mg–K_α X-ray source with pass energy of 125.6 eV. The analysis was carried out under UHV (10^{-9} Torr) over an area of 0.12 mm^2. Spectra were taken at an angle of 45°.

RESULTS AND DISCUSSION

Influence of hydrolysis conditions

The variation in the carboxyl content with the reaction time, under various sodium hydroxide concentrations, is presented in Figure 1. It can be seen from the results that both the initial rates of hydrolysis and final carboxyl content increase with increasing sodium hydroxide concentration. The carboxyl content reached

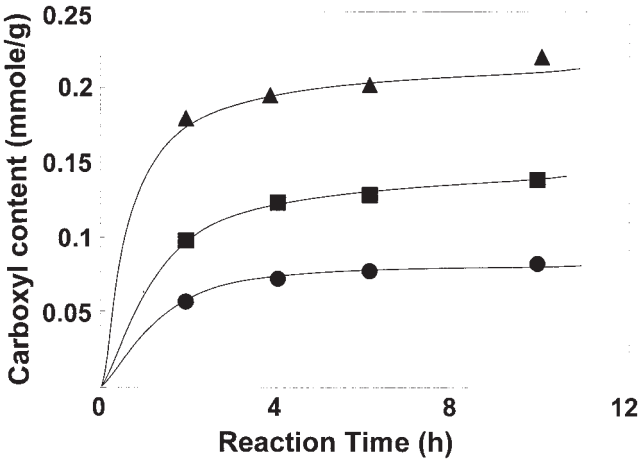


Figure 1 Variation in the carboxyl content with the reaction time for different sodium hydroxide concentrations: (a) ● 5%, (b) ■ 10%, (c) ▲ 20%. Degree of grafting, 5%; reaction temperature, 50°C.

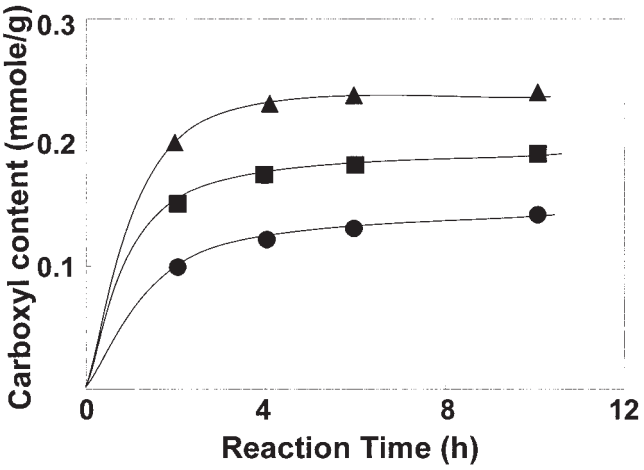
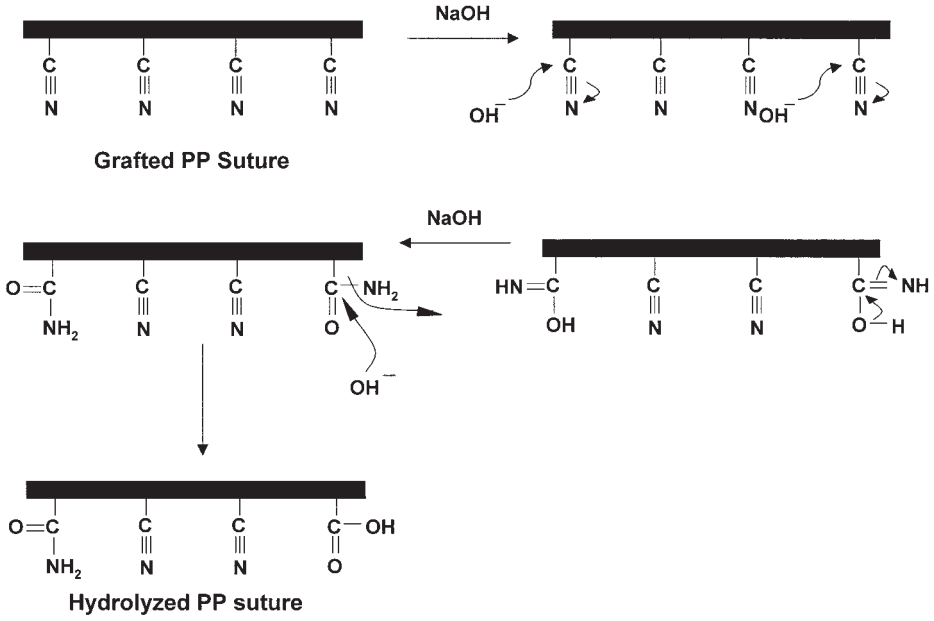


Figure 2 Variation in the carboxyl content with the reaction time for different reaction temperatures: (a) ● 50°C, (b) ■ 60°C, (c) ▲ 70°C. Degree of grafting, 5%; sodium hydroxide, 10%.

saturation within 4 h of the reaction. The maximum conversion of nitrile groups into carboxyl groups was limited to about 62% after 6 h of hydrolysis. This is may be because of the electrostatic repulsion between COO^- groups and the hydroxyl ions (OH^-) catalyzing the reaction.[23] It is important to mention that this conversion amounts to the incorporation of carboxyl groups in the range of 0.042 to 0.25 mmol/g for all grafted sutures. The reactions involved in the hydrolysis of the grafted suture is given in Scheme 1.[24]

The variation in the carboxyl content with reaction temperature is presented in Figure 2. The carboxyl content increases with increasing reaction temperature. The reaction rate, as observed from the slopes of the initial conversion, shows an increase with increasing temperature. This might be attributable to the fact that, at high temperature, the diffusion of the sodium hydroxide within the matrix is facilitated or may be at high temperature activation energy required for the conversion of nitrile groups to carboxylic groups at a lower temperature, which results in an increase in the final carboxyl content. The variation of the carboxyl content with the degree of grafting is presented in Figure 3. A maximum carboxyl content of 0.25 mmol/g was achieved for the graft level of 8%.



Scheme 1 Proposed mechanism of hydrolysis of PP-*g*-PAN suture.

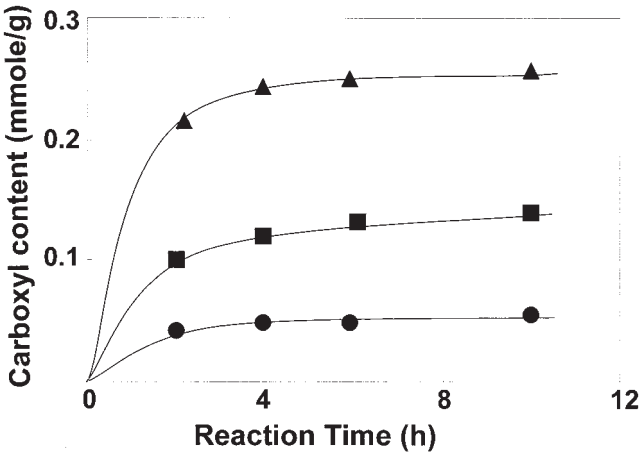


Figure 3 Variation in the carboxyl content with the reaction time for different degrees of grafting: (a) ● 2%, (b) ■ 5%, (c) ▲ 8%. Reaction temperature, 50°C; sodium hydroxide, 10%.

FTIR spectroscopy

FTIR spectra of PP-*g*-PAN sutures, before and after hydrolysis, are presented in Figure 4. The two spectra show significant variation between the regions 2200–2250 and 1600–1800 cm^{-1}. The characteristic peak of the nitrile group (2245 cm^{-1}) diminished in the grafted sutures along with the origin of additional peaks in the hydrolyzed sutures. The origin of an additional band at 1715 cm^{-1} (–C═O stretching) confirms the conversion of nitrile groups and the presence of carboxyl groups during hydrolysis of the suture.

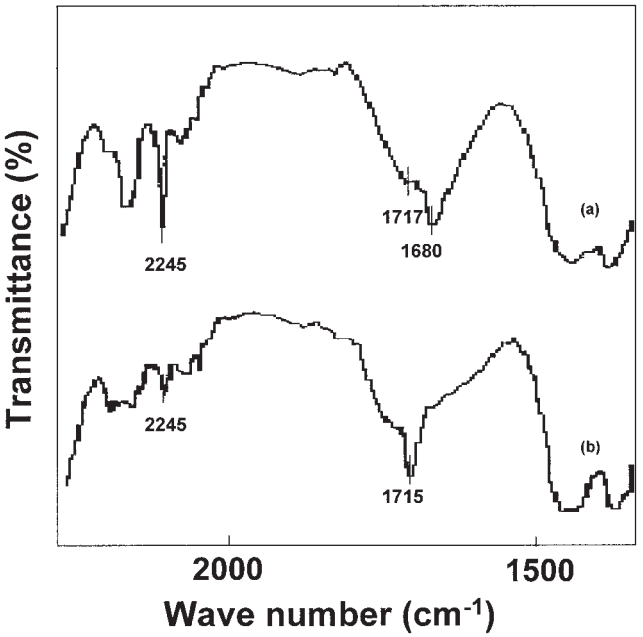


Figure 4 FTIR spectra of (a) 5% PP-*g*-PAN monofilament and (b) hydrolyzed PP-*g*-PAN monofilament.

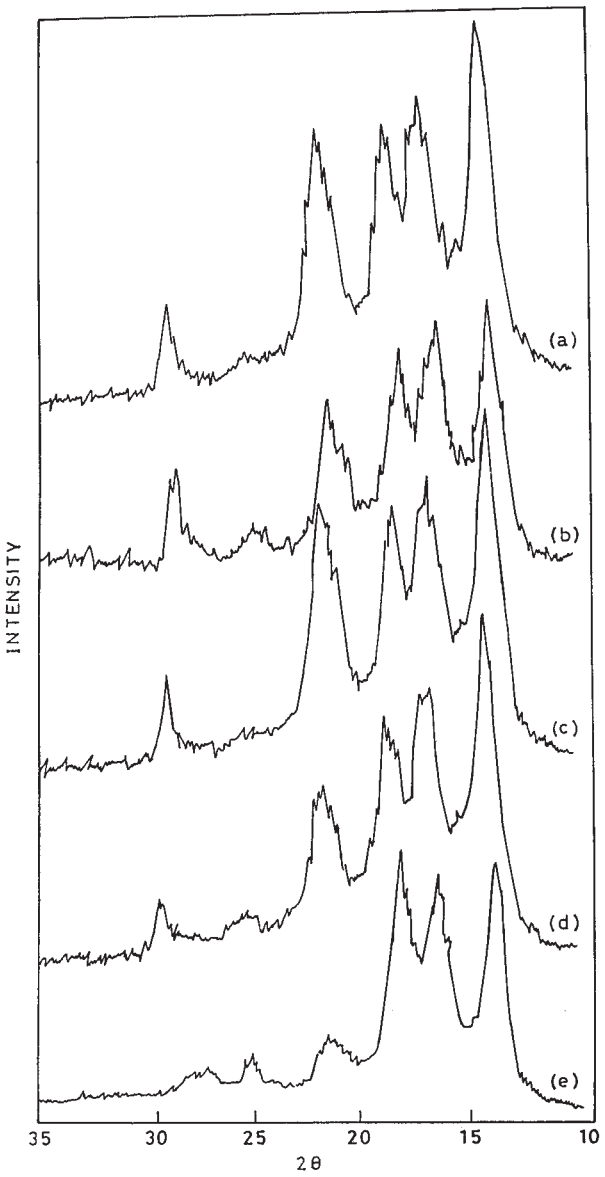


Figure 5 X-ray diffraction patterns of (a) ungrafted PP monofilament, (b) exposed PP monofilament, (c) 2% hydrolyzed PP-*g*-PAN monofilament, (d) 5% hydrolyzed PP-*g*-PAN monofilament, and (e) 8% hydrolyzed PP-*g*-PAN monofilament. Degree of grafting, 5%; reaction temperature, 50°C; sodium hydroxide, 10%.

X-ray analysis

The X-ray patterns of virgin PP and hydrolyzed PP-*g*-PAN sutures are presented in Figure 5. Crystalline reflections of the unmodified, gamma-ray–exposed, and hydrolyzed PP sutures occur at identical angles and no additional peak was observed in the range of 10–35°. The intensity of the peaks decreases in the γ-irradiated suture [Fig. 5(b)], which is an indication of the diminishing crystallinity during irradiation of the sample.[20] We reported in our earlier studies that the crystallinity of the PP monofilament diminishes, probably as a result of the introduction of defects into

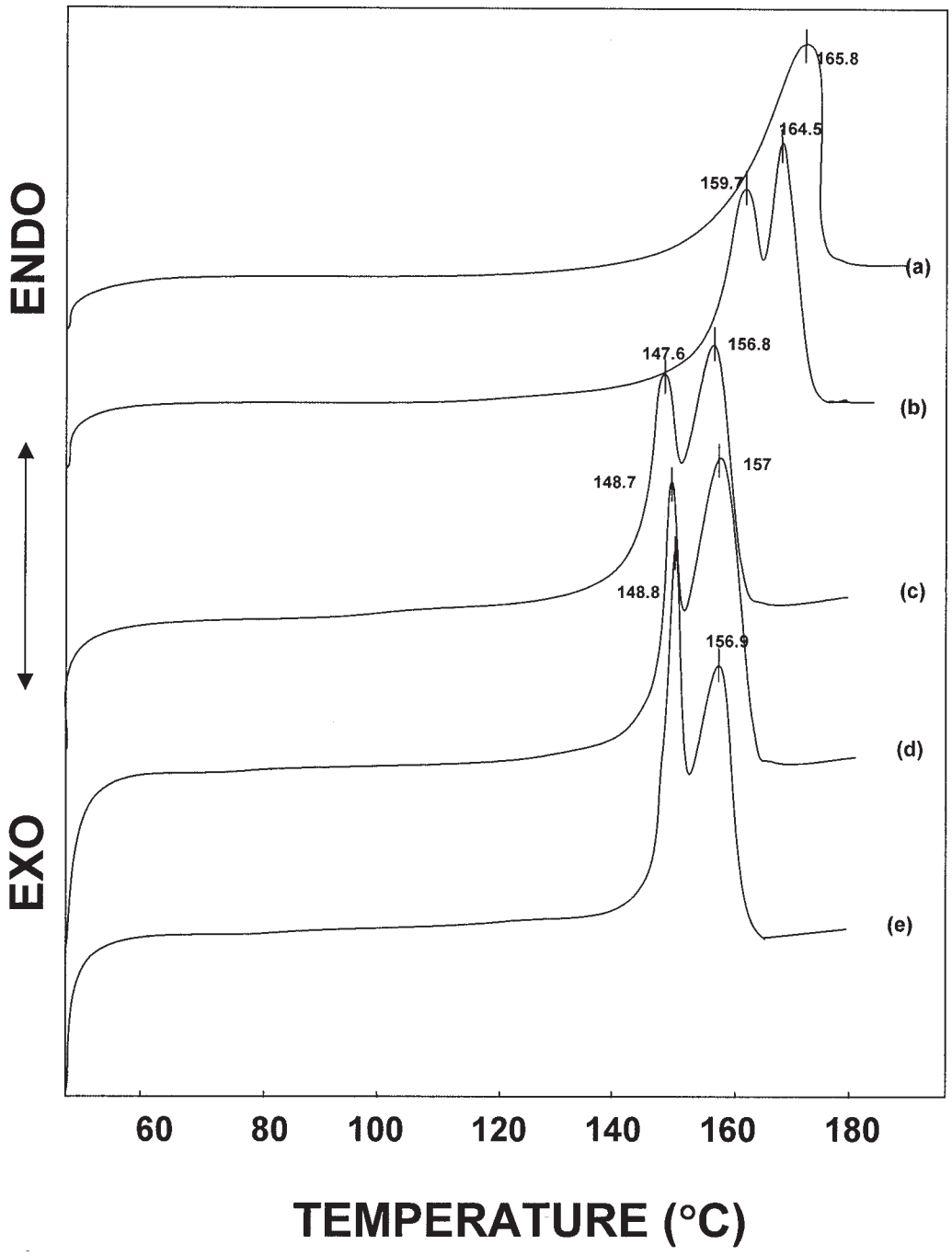


Figure 6 DSC thermograms of (a) ungrafted PP monofilament, (b) exposed PP monofilament, (c) 2% hydrolyzed PP-*g*-PAN monofilament, (d) 5% hydrolyzed PP-*g*-PAN monofilament, and (e) 8% hydrolyzed PP-*g*-PAN monofilament. Degree of grafting, 5%; reaction temperature, 50°C; sodium hydroxide, 10%.

the crystalline regions of the suture by radiation. The grafting does not lead to any appreciable loss in the crystallinity as it changes from 55 to 54.1%, for the 5% graft level, as observed in our earlier studies.[20] The subsequent hydrolysis of the suture leads to a decrease in crystallinity, from 54.1 to 53.5%, on hydrolysis of the 5% grafted suture. This suggests that hydrolysis does not lead to an appreciable change in the inherent crystalline regions in the grafted sutures and is confined to the grafted polyacrylonitrile domains in the amorphous region.

DSC analysis

The DSC thermograms of virgin PP and hydrolyzed PP-*g*-PAN sutures are presented in Figure 6. The dual

TABLE I
Variation in Percentage Crystallinity with Grafting and Hydrolysis of Grafted Sutures

Percentage grafting	Percentage crystallinity	
	DSC	XRD
Original PP	62.5	62
Exposed PP	56.9	55
Hydrolyzed (2%)	57.8	53.6
Hydrolyzed (5%)	57.3	53.5
Hydrolyzed (8%)	55.7	52.1

mode of melting originates in exposed, grafted, and hydrolyzed sample.[20] This may be attributable to the scission of the chains and subsequent reorganization into crystallites. Crystallinity of the PP suture, as calculated from the eq. (2), decreased with grafting and on subsequent hydrolysis (Table I). The crystallinity of the virgin PP is 62.5%, whereas the hydrolyzed suture, with 5% graft levels, shows 57.3% crystallinity. Even with the increase in grafting, the crystallinity decreases only slightly. The slight decrease in crystallinity may therefore be a reflection of the dilution of the inherent crystallinity resulting from incorporation of the PAN-grafted chains.[20] These observations reinforce the X-ray diffraction results and suggest that hydrolysis does not deteriorate the inherent crystallinity of the suture.

Mechanical properties

Variation of the tensile strength and elongation of samples is given in Figure 7. Both the tenacity and elongation are significantly affected in the hydrolyzed sample. The tenacity of the grafted suture is always much higher, which thus substantially decreased in

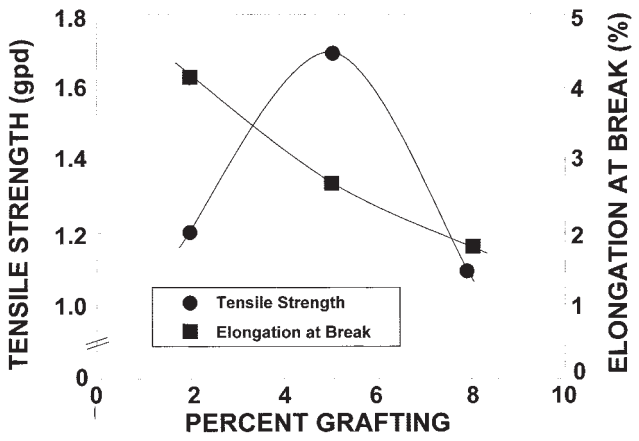


Figure 7 Variation of the tensile strength and elongation at break with the degree of grafting in hydrolyzed PP-*g*-PAN monofilament. Reaction temperature, 50°C; sodium hydroxide, 10%.

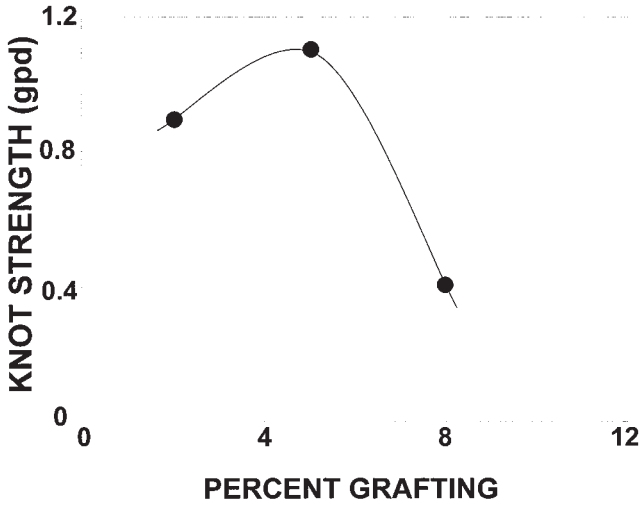


Figure 8 Variation of the knot strength with the degree of grafting in hydrolyzed PP-*g*-PAN monofilament. Reaction temperature, 50°C; sodium hydroxide, 10%.

hydrolyzed samples.[20] The tenacity of the 5% grafted monofilament was 2.4 gpd,[20] which reduced to 1.8 gpd on hydrolysis. This is evident from the fact that the decrease in tenacity on hydrolysis may be explained by the disorientation of chains.

The tensile strength of the hydrolyzed suture improves with increasing graft levels, up to 5%, and then tends to decrease. It may be because, at lower graft levels, PAN microstructures are incorporated within the voids and in the amorphous region of the monofilament and act as fillers, and exert a reinforcing effect within the suture matrix, thereby enhancing the tensile strength of the suture.[25] With further increases in grafting, the grafted domains are pushed apart and the integral structure of the suture is affected, leading to the decrease in tensile strength. On the other hand, the elongation of the suture decreases with increasing graft levels. This may be explained by the fact that the graft chains are linked to the polypropylene backbone, thus reducing the mobility of the chains and lowering the elongation. The knot strength of the hydrolyzed suture (Fig. 8) also shows a trend similar to that of the tensile strength. The strength improves slightly, but deteriorates rapidly beyond the 5% graft level. These studies reflect the diminishing compatibility of the grafted component with the base PP matrix.

XPS analysis

Changes in the chemical structure of the surface-modified PP sutures, with grafting of acrylonitrile followed by hydrolysis, are given in Figure 9. The spectrum of the ungrafted suture [Fig. 9(a)] shows peaks for carbon and oxygen at 285 and 532 eV, respectively. The presence of a peak for oxygen in the ungrafted suture

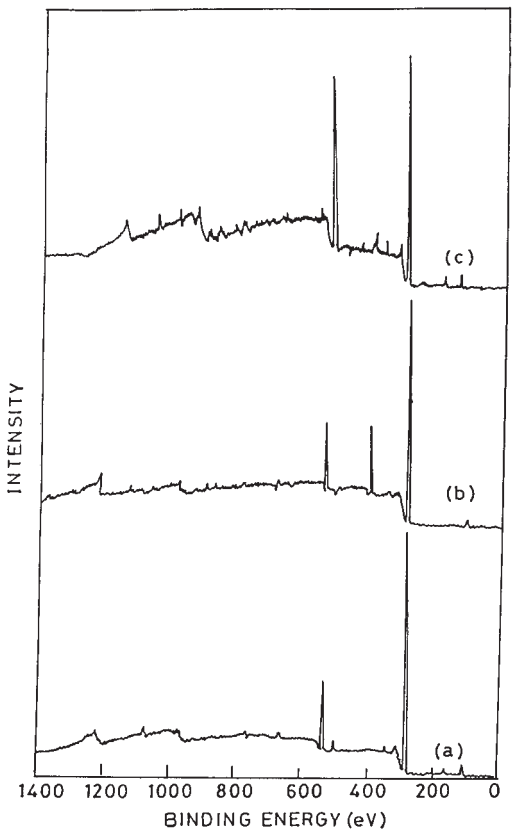


Figure 9 XPS spectra of (a) original PP monofilament, (b) 8% PP-*g*-PAN monofilament, and (c) hydrolyzed PP-*g*-PAN monofilament. Reaction temperature, 50°C; sodium hydroxide, 10%.

may be attributable to oxidative degradation of PP during gamma irradiation. An additional peak appeared in the spectrum of the grafted suture [Fig. 9(b)] at 400 eV, which corresponds to the binding energy of nitrogen. This confirms the successful grafting of acrylonitrile onto the PP suture. It is evident from the spectrum [Fig. 9(c)] that the intensity of the peak at 532 eV, which is based on oxygen, was dramatically enhanced in the hydrolyzed sample. This is explained by the conversion of nitrile groups to carboxylic groups on hydrolysis. The original suture shows an oxygen content of 14.2% in spite of its paraffin nature. This may be a result of the creation of oxygen-containing groups during the processing of polymer chips into monofilament. Irradiation of the monofilament under oxygen enhances the oxygen content to 30.9%, which should arise as a result of the formation of peroxides and hydroperoxides in the monofilament matrix. As the degree of grafting increases, the oxygen content decreases and the nitrogen content increases. Hydrolysis of the grafted suture leads to the transformation of the nitrile groups into carboxyl groups and is reflected in a decrease in oxygen content and a loss in nitrogen content. The oxygen content is enhanced from 7.5 to 31.2% in the hydrolyzed sample, whereas the nitrogen content decreased from 8.2 to 1.6% in the 8% grafted suture (Table II). This further suggests the conversion of nitrile groups into carboxylic groups.

CONCLUSION

The graft polymerization of acrylonitrile onto PP sutures, and subsequent hydrolysis, is an effective way to introduce carboxyl groups into the monofilament. The transformation of nitrile groups into carboxylic groups is strongly governed by reaction conditions such as sodium hydroxide concentration and reaction temperature. It is observed that a reaction time of 4 h is sufficient to achieve maximum carboxylic groups into the sutures. This approach produces a suture with carboxyl functionality of about 0.25 mmol/g, which is certainly high enough for subsequent antimicrobial drug immobilization. The XPS confirms the occurrence of a hydrolysis reaction. No significant variation in crystalline regions occurs on hydrolysis of the grafted sutures, which indicates that the grafting reaction remains confined to the amorphous region of the polypropylene suture. The hydrolysis leads to considerable loss in mechanical strength of the grafted suture. The mechanical strength of the resultant suture, although low, was still retained to a large extent. The tetracycline drug immobilization and release behavior will be reported in a future publication.[26]

TABLE II
Variation in Percentage of Carbon, Oxygen, and Nitrogen in PP, PP-*g*-PAN Suture, and Hydrolyzed PP-*g*-PAN Suture

Percentage grafting	Carbon content (%)	Oxygen content (%)	Nitrogen content (%)
Original PP	73.3	14.2	0.1
Exposed PP	68.1	30.9	0.9
PP-*g*-PAN (2%) (nonhydrolyzed)	76.9	22.0	1.0
PP-*g*-PAN (5%) (nonhydrolyzed)	79.8	17.8	2.3
PP-*g*-PAN (8%) (nonhydrolyzed)	80.4	7.5	8.2
Hydrolyzed PP-*g*-PAN (2%)	67.2	20.6	2.1
Hydrolyzed PP-*g*-PAN (5%)	83.8	23.4	1.8
Hydrolyzed PP-*g*-PAN (8%)	67.1	31.2	1.6

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