Preparation of Antimicrobial Sutures by Preirradiation Grafting of Acrylonitrile onto Polypropylene Monofilament. II. Mechanical, Physical, and Thermal Characteristics

Rachna Jain,[1,2] Bhuvanesh Gupta,[1] Nishat Anjum,[1] Nilesh Revagade,[1] Harpal Singh[2]

[1]*Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India*
[2]*Centre for Biomedical Engineering, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India*

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ABSTRACT: Polypropylene-*g*-polyacrylonitrile sutures were prepared by graft polymerization of acrylonitrile onto polypropylene monofilament by preirradiation method. Sutures with various graft levels were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Density, Birefriengence, X-ray Diffraction, Scanning Electron Microscopy (SEM), and Differential Scanning Calorimetry (DSC). Mechanical properties of the unmodified and grafted sutures were also evaluated. The physical characteristics of sutures were markedly affected by the graft levels. Density of the polypropylene sutures increased with an increased in the degree of grafting. The heat of fusion and heat of crystallization decreased with the increase in the degree of grafting. X-ray diffraction also revealed decrease in crystallinity with the increase in the graft levels. Tenacity of the monofilament improved, whereas the elongation at break decreased in grafted samples. Scanning electron microscopy showed significant variation in surface morphology in the grafted samples. J Appl Polym Sci 93: 1224–1229, 2004

Key words: poly(propylene) PP; radiation; graft polymerization

INTRODUCTION

Polymers, both synthetic and natural, are widely used as implantable and nonimplantable devices. Because these polymers are used in a physiological-rich environment, they are vulnerable to infection by variety of microbes. The polymers do not possess inherent antimicrobial nature and need to be modified. The present work is in the direction of incorporating antimicrobial agents onto such polymers/polymeric devices, so that they acquire ability to kill as well as inhibit the growth and metabolism of microbes. The graft copolymerization of vinyl and acrylic monomers offers an attractive way to modify polymers for biomedical applications.[1–7] Radiation-induced grafting has generated considerable interest in the modification of polymers for specific applications.[8–10] The advantage of radiation grafting is that the resultant material not only retains most of its original characteristics but also acquires additional properties of the grafted moiety. However, the structure of the suture may undergo considerable changes during the modification process depending on the nature and the amount of monomer being grafted. These changes may be in terms of mechanical strength, thermal stability, and crystallinity. In our previous investigation, we have reported that the grafting of methacrylic acid onto polypropylene (PP) results in an improvement in the mechanical properties.[11] Similarly, Tyagi et al.[12] have shown that grafting of 2-hydroxyethylmethacrylate (HEMA) results in an improvement in the tensile strength but for a low degree of grafting. However, higher graft levels bring a drastic deterioration in the tensile strength. Grafting also causes considerable changes in the thermal properties. Lodesova[13] have shown that the thermal decomposition temperature of polypropylene films grafted with acrylamide monomer increased and reached from 298–423°C. Similarly, improvement in the melting behavior of the PP fiber was reported for grafting of vinylpyrrolidone, acrylonitrile, acrylamide, and acrylic acid.[14] A multistep degradation behavior was reported when hydrophilic monomers are present as the grafted components in a copolymer.[14–16]

The grafting of hydrophilic monomers, such as HEMA, acrylic acid, and acrylamide to produce surface with hydrogel properties has been reported by several workers.[17–22] These materials offer a system where a drug may be immobilized. Recently, we have carried out the grafting of acrylonitrile on PP suture by using preirradiation technique.[23] The present investigation is aimed at the evaluation of the structural changes in PP suture during the course of grafting.

Correspondence to: B. Gupta (bgupta@textile.iitd.ernet.in).

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EXPERIMENTAL

Material

Polypropylene (PP) used for this study was manufactured by IPCL, India. The monofilament was prepared by melt spinning of PP (MFI 3) at 230°C under nitrogen atmosphere. Acrylonitrile monomer was received from GS Chemicals, India, and was purified by distillation under vacuum.

Grafting reaction

The preparation of polyacrylonitrile-grafted polypropylene sutures with different degrees of grafting was carried out by a preirradiation method using a Co^{60} γ-rays source (900 Curies) as reported earlier.[23] Grafting was carried out in glass ampoules of 2×10 cm^2 size containing the monofilament and the 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 fiber was calculated according to the following equation.

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

where W_o and W_g are the weights of the ungrafted and grafted monofilaments, respectively.

Fourier transform infrared spectroscopy

FTIR spectroscopy studies on samples were carried out on a Perkin-Elmer Spectrum-BX FTIR system. The presence of grafts in the modified sutures were ascertained by monitoring the peak at 2242 cm^{-1}. FTIR of the samples were recorded in the transmission mode.

Diameter measurement

The diameter of the suture was measured by using a Projectina microscope. An average of 10 values was reported for all samples.

Density measurement

Density measurements of original PP and grafted sutures were carried out using a Davenport density gradient column. The column was prepared by using isopropanol (d, 0.79 g/cm^3) and diethyleneglycol (d, 1.115 g/cm^3).

Birefringence

Birefringence measurements were carried out on a polarizing microscope (Vickers Instrument). Two different principle refractive indices were taken as parallel (η_{11}) and perpendicular ($\eta_\perp$) to the fiber axis. The refractive index ($\Delta\eta$) was obtained by the following expression.

$$\Delta\eta = \eta_{11} - \eta_\perp \quad (2)$$

X-ray diffraction

X-ray diffraction (XRD) patterns of the grafted and ungrafted samples were recorded in the 2θ range of 10–35° on a Phillips X-ray diffractometer equipped with a scintillation counter. CuKα 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 on a Perkin-Elmer DSC-7 system. Vacuum-dried samples were loaded, and the thermograms were run in the temperature range of 50–180°C under nitrogen atmosphere at a heating rate of 10°C/min. The samples were retained at 180°C and then cooled to 80°C. The heat of fusion (ΔH_f) and the heat of crystallization (ΔH_c) were obtained from the area under the melting and cooling thermograms.

The crystallinity in suture was obtained by the following expression:

$$\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_{f(\text{crys})}} \times 100 \quad (3)$$

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.[24]

Mechanical properties

The tensile properties of polypropylene graft copolymer monofilament (PP-*g*-AN) were determined using an Instron tensile tester. All the experiments were carried out using following specifications: gauge length 100 mm: crosshead speed 10 mm/min; full scale load 500 *N*. Tenacity and elongation at break of the samples were determined from the stress strain curve.

Scanning electron microscope

The surface characteristics of unmodified and grafted monofilaments were studied using STEREOSCAN 360 (Cambridge Scientific Industries Ltd.), scanning elec-

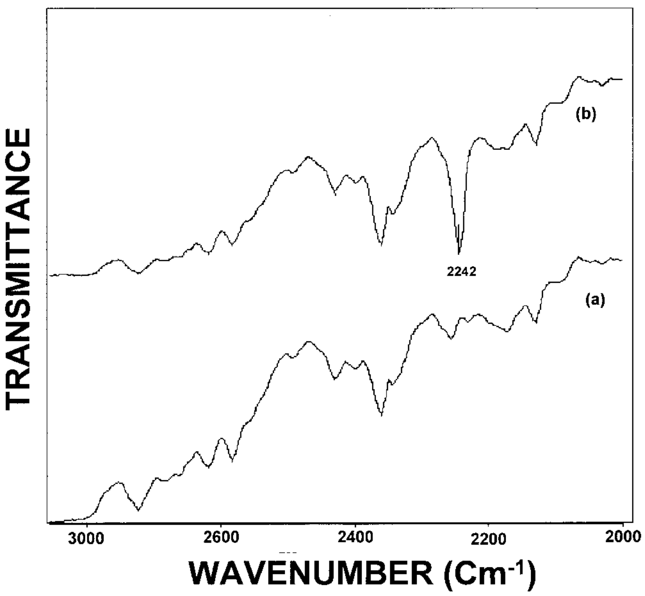

Figure 1 FTIR of (a) ungrafted PP fiber and (b) PP-*g*-PAN monofilament.

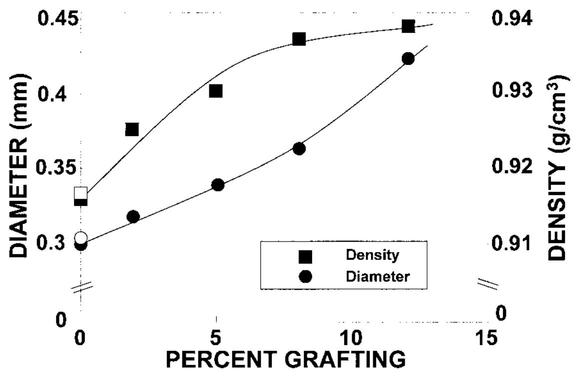

Figure 2 Variation of diameter and density with the degree of grafting in PP-*g*-PAN monofilament.

tron microscope, after coating them with silver. A thick layer of silver metal is used to provide conduction.

RESULTS AND DISCUSSION

The grafting of acrylonitrile onto polypropylene has been found to alter the inherent physical properties of the suture. A significant variation in the density, diameter, birefringence, crystallinity, and tensile properties has been observed as a function of the degree of grafting.

The presence of the grafts in the PP monofilament was confirmed by FTIR measurements, as shown in Figure 1. The results show the presence of a peak at 2242 cm^{-1} in the grafted monofilament, while the ungrafted monofilament does not show any peak in this range. This peak is the characteristic of the nitrile group, which confirms the presence of polyacrylonitrile grafts in the modified monofilament.[3]

Diameter and density of the original PP suture and grafted sutures as a function of degree of grafting is presented in Figure 2. Both the diameter and density increases with an increase in the degree of grafting. The density of the virgin PP was measured to be 0.915 g/cm^3, which increased to 0.936 g/cm^3 for a graft level of 12%. The open circle and rectangle shows the value for γ-irradiated monofilament. The increase in density may be due to the higher density of a PAN component present within the suture. Compared to a linear increase in diameter, density increases fast at lower graft levels. These results indicate that the grafting takes place both on the surface as well as in the bulk of the monofilament. Because the grafting process proceeds by the progressive diffusion of monomer within the bulk of the monofilament matrix, a large fraction of polyacrylonitrile (PAN) is incorporated within the voids in the amorphous region, and a sharp increase in the density is observed for initial graft levels. With an increase in the grafting, the size of the PAN chains increased, which ultimately results in pushing apart of molecular chains of the PP backbone. Similar observation was also reported for grafting of 2-hydroxymethacrylate on PP fibers.[12]

Birefringence of original PP and grafted PP sutures as a function of degree of grafting is presented in Figure 3. Birefringence decreases with an increase in the degree of grafting in the monofilament. The decrease in the birefringence with an increase in grafting is due to disorientation of the chain with the incorporation of the PAN moiety.

The X-ray patterns of sutures with different degrees of grafting are shown in Figure 4. Crystalline reflection for unmodified and grafted PP sutures occurs at identical angles. No additional diffraction peak was observed for grafted samples, which shows PAN is

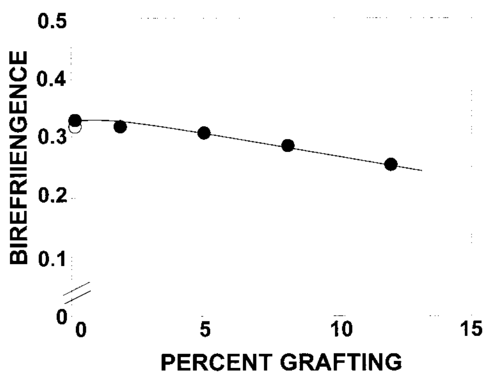

Figure 3 Variation of birefriengence with the degree of grafting in PP-*g*-PAN monofilament.

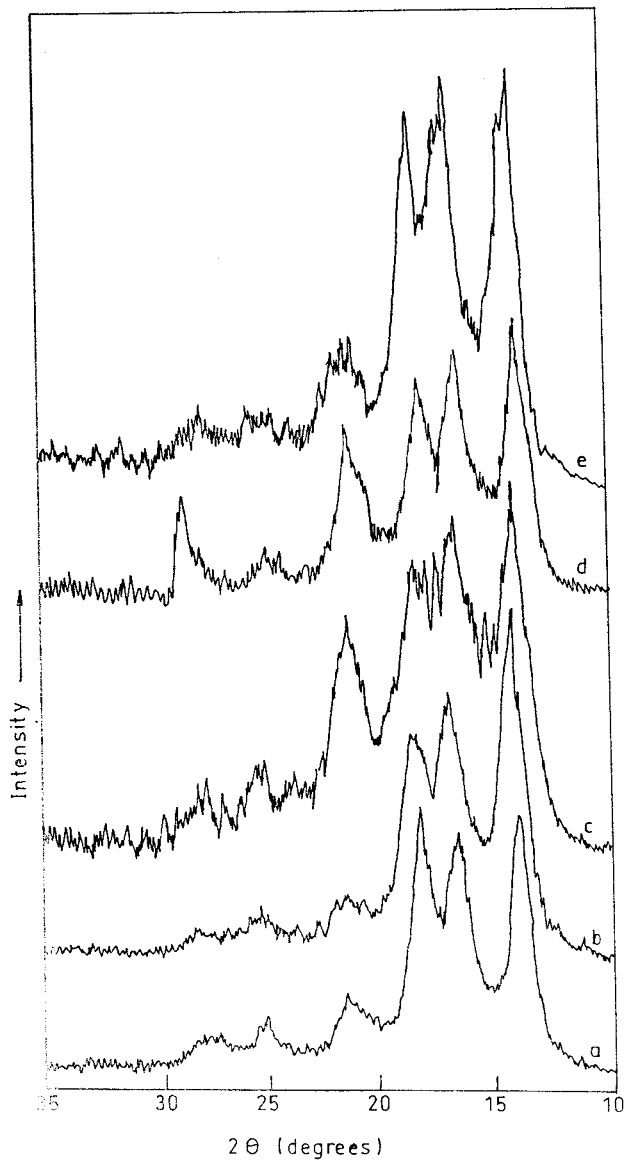

Figure 4 X-ray diffraction patterns of PP-*g*-PAN monofilament with different degree of grafting: (a) 8%, (b) 5%, (c) 2%, ungrafted PP monofilament (d), and exposed PP monofilament (e).

TABLE I
Variation in Percent Crystallinity with Different Degrees of Grafting

Percent grafting	Percent crystallinity (DSC)	Percent crystallinity (XRD)
Unexposed	62.5	62
Exposed	56.9	55
2	61.07	58.5
5	59.33	54.1
8	59.6	51.3
12	57.6	—

present as an amorphous moiety. However, the intensity of the crystalline peak decreases with an increase in grafting. Variation in the percent crystallinity with degrees of grafting is presented in Table I. The result shows a decrease in the crystallinity with an increase in grafting. These observations are well supported by DSC investigations on the samples.

DSC thermograms of the ungrafted and grafted PP sutures are presented in Figure 5. Thermograms of the unmodified and grafted sutures show distinct variation in the shape and area. The unmodified suture showed a peak at 165.8°C, which was transformed to a dual melting thermogram in the exposed sample. The subsequent grafting of exposed sample led to further shifting of peaks from 165.8 to 152.5°C. This suggests that considerable crystalline reorganization has been taken place during the process of irradiation of the PP monofilament. The original peak of the suture diminished with an increase in the grafting, and almost disappears at a graft level of 12%. However, the peak at 152.5°C became prominent in the 12% grafted sample. The origin of additional peak at 152.5°C is the indication of destruction and reorganization of the crystallites within the monofilament. The variation in the heat of fusion and heat of crystallization as a function of degree of grafting is presented in Figure 6. It is important to see that the heat of fusion decreases fast in the exposed samples (open circle), suggesting a significant crystalline deterioration in PP suture. The subsequent grafting on this exposed PP monofilament further leads to a loss in the heat of fusion. A decrease in the heat of fusion of samples is because of addition of polyacrylonitrile chains within the noncrystalline region of the suture and thus thereby interferes with the crystallinity. Crystallinity

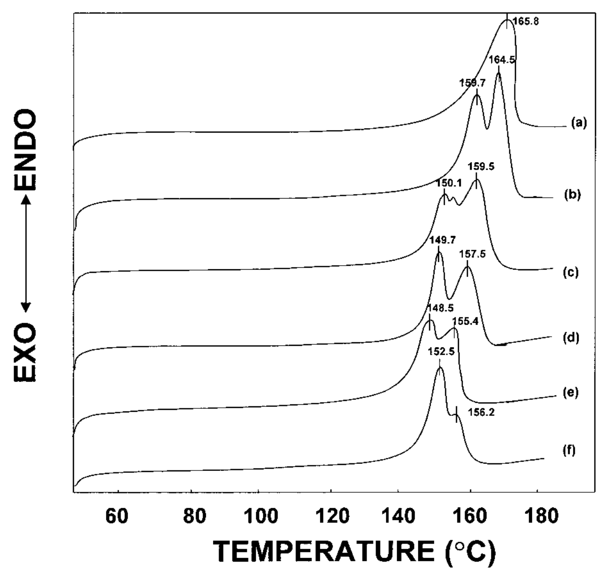

Figure 5 DSC thermograms of original PP (a) exposed PP (b) and PP-g-PAN monofilaments with different degrees of grafting: (c) 2%, (d) 5%, (e) 8%, and (f) 12%.

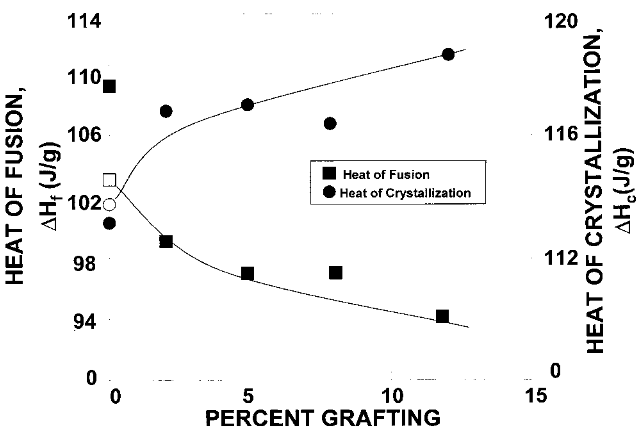

Figure 6 Variation of the heat of fusion and the heat of crystallization with the degree of grafting in PP-*g*-PAN monofilament.

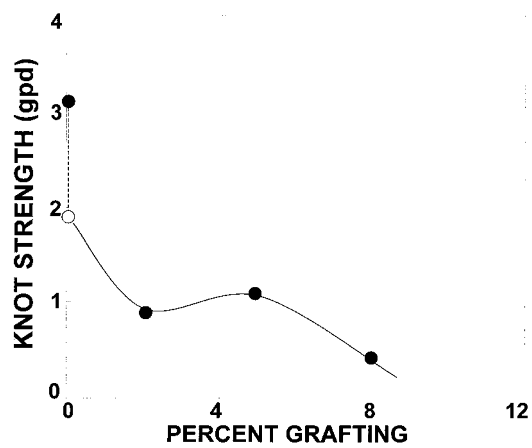

Figure 8 Variation of the knot strength with the degree of grafting in PP-*g*-PAN monofilament.

of the PP suture as calculated from the eq. (3) decreases with the increase in the degree of grafting (Table I). A similar decrease in crystallinity is also obtained from X-ray diffraction.

The variation of tenacity and elongation of samples is given in Figure 7. Tenacity and elongation are significantly reduced by the exposure of the monofilament by γ-radiation (as shown by open circles and squares). However, tenacity improves with the increase in the graft levels up to 5% and then tends to decrease. It seems that at lower graft levels microstructures that are formed act as a filler and exert a reinforcing effect in the system, thereby enhancing the tensile strength of the suture. However, with further grafting, the compactness of the chains were effected and pushed apart the molecular chains. As a result, mechanical strength decreases despite the reinforcement effect. Similar results have also been observed in case of polypropylene–methacrylic system.[11] The knot strength of the grafted suture (Fig. 8) also shows a trend similar to the tensile strength. The strength improves a bit but deteriorates after the 5% graft levels, and probably the compatibility between the PAN and the PP base matrix diminishes with the increase in the degree of grafting.

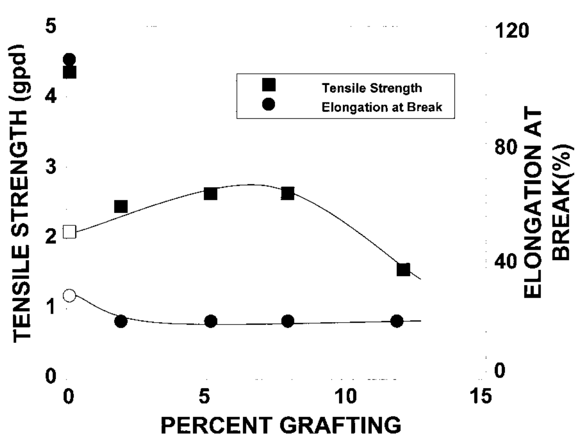

Figure 7 Variation of the tensile strength and elongation at break with the degree of grafting in PP-*g*-PAN monofilament.

The SEM photographs of the ungrafted and grafted PP monofilament were presented in Figure 9. The unmodified and modified PP monofilament shows distinct variation in the surface. The unmodified sutures has a smooth surface, whereas, in the case of grafted sutures, the surface becomes rough. Moreover, roughness of the surface increases with the increase in the degree of grafting.

CONCLUSION

The graft polymerization of acrylonitrile onto PP leads to a considerable change in physical and mechanical properties of the sutures. DSC thermograms of ungrafted and grafted monofilaments show distinct variation. The unmodified suture shows a peak at 165.8°C, which transformed to a dual peak in both the exposed and grafted samples. This may be due to the reorganization of crystals that has been taking place during the process of irradiation. Both the heat of fusion and crystallinity decreases with an increase in grafting because of the addition of a polyacrylonitrile chain within the noncrystalline region. Grafting of the PP monofilament with acrylonitrile leads to an increase in tenacity up to a graft level of 5% and then decreases sharply. The increase in tenacity is because of the reinforcing effect of the polyacrylonitrile grafts. The polypropylene sutures were further modified by alkaline hydrolysis so that a fraction of nitrile groups are transformed into carboxylic groups for subsequent drug immobilization to make them antimicrobial.[25,26]

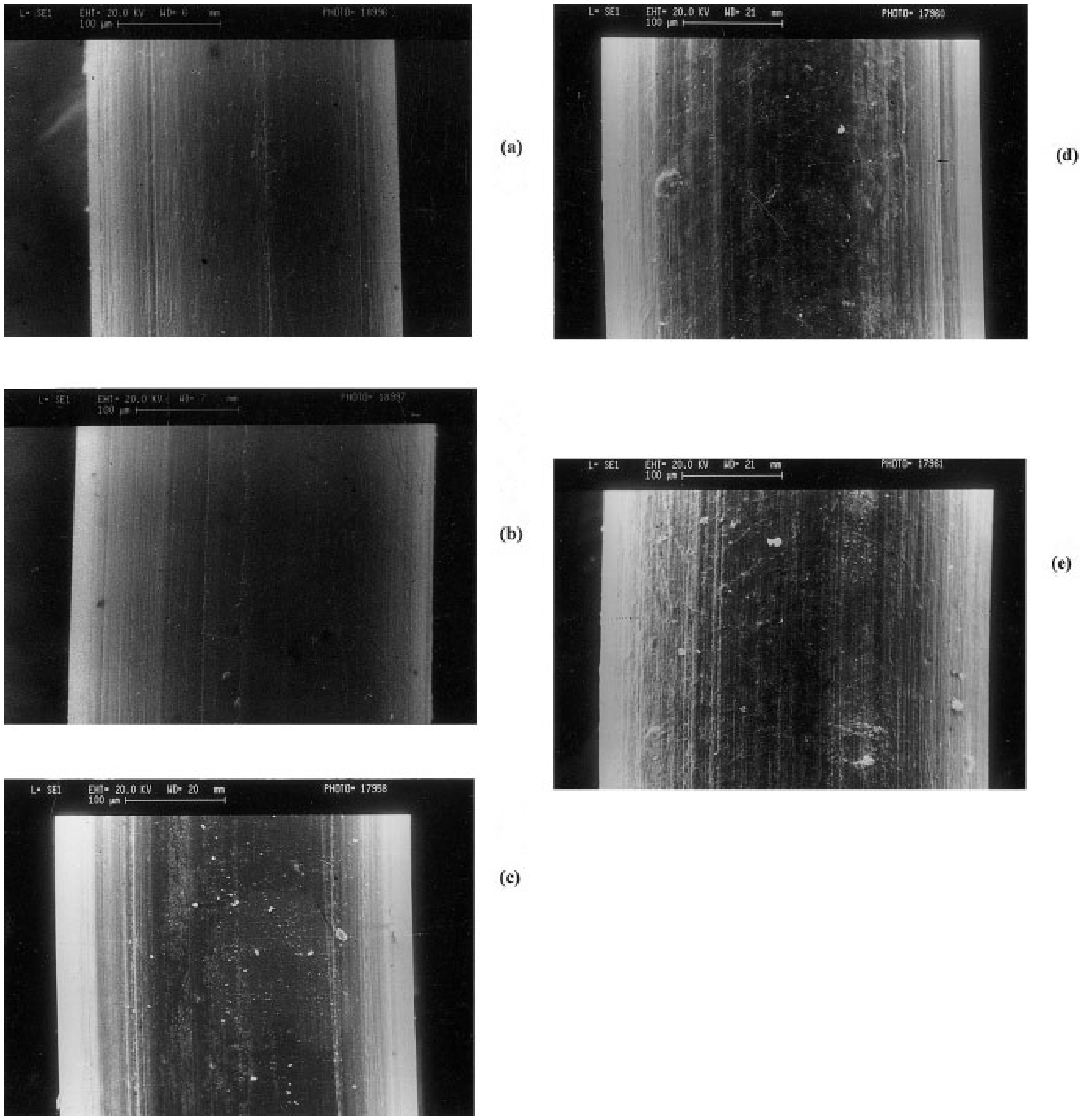

Figure 9 SEM photographs of original PP monofilament (a) and PP-*g*-PAN monofilaments with different degrees of grafting: (b) 2%, (c) 5%, (d) 8%, and (e) 12%.

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