Development of Antimicrobial Polypropylene Sutures by Graft Polymerization. I. Influence of Grafting Conditions and Characterization

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ABSTRACT: Modification of polypropylene monofilament was carried out by the graft polymerization of 1-vinylimidazole (VIm) using simultaneous radiation grafting method. The effect of radiation dose, monomer concentration, and the grafting medium on the degree of grafting was evaluated. It was observed that the presence of organics as additives in the reaction medium had significant influence on the graft levels. These grafted sutures were characterized using several techniques, such as infrared spectroscopy (IR), X-ray diffraction, and differential scanning calorimetry (DSC). It was found that the grafts are confined to the amorphous region of the monofilament and the crystalline regions remain intact. The surface morphology of sutures was evaluated by scanning electron microscopy. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3895–3901, 2006

Key words: polypropylene; 1-vinylimidazole; suture; radiation grafting

INTRODUCTION

Recent developments in medical textile industry have diversified with the new materials for biomedical technology. The advancement in medical procedures requires innovations in the products that offer desired biological behavior and performance in specific applications. This requires perfect knowledge of textiles and biosciences to produce appropriate material. One of the classical applications of textiles is in the form of sutures, wound care materials, and surgical systems. It is observed that tissues become more susceptible to infection if sutures are used to stitch the injury site. Therefore, it becomes necessary to modify sutures in such a way that it could offer antimicrobial nature besides retaining its inherent physical properties. Many studies have been carried out to make polypropylene antimicrobial.[1–3] Radiation grafting is one of the ways to introduce desirable properties into polypropylene and has been reported by several researchers earlier.[4–12] The attractive feature of radiation grafting is that the size of the grafted component can easily be controlled by proper selection of radiation conditions.[13–14] This approach requires the grafting of an appropriate monomer containing functional sites where a drug may be immobilized. It is this drug that is released into the surrounding tissue and offers antimicrobial atmosphere at the wound site.

Grafting of 1-vinylimidazole (VIm) can be one of the appropriate options to make polypropylene functional for different applications.[15–19] Han et al.[15] carried out plasma-induced grafting of VIm onto low-density polyethylene films so that lamination of the modified films with copper foils could be achieved. On the other hand, the research group of Chapiro[16] investigated the kinetics of grafting of VIm into polyethylene by preirradiation grafting method, and a comparative analysis vis-à-vis grafting onto FEP films was carried out. Polypropylene has also been modified by photografting of VIm, but antimicrobial property of such modified materials have not been reported yet.[20–21] It was observed that the photografting of pure VIm onto polypropylene could not be initiated. However, a combination of VIm with other monomers led to a reasonable graft levels.

We have been working on the development of antimicrobial sutures by radiation grafting of 2-hydroxyethylmetharylate and acrylonitrile monomers onto polypropylene monofilaments.[22–25] The acrylonitrile grafted suture was subsequently hydrolyzed to transform nitrile groups into carboxyl groups.[25] However, significant deterioration in the mechanical properties and knot strength proceeds because of the grafting process. We have extended our work to the grafting of VIm so that a suture with desired mechanical strength may be produced. In the present investigation, we have carried out the grafting of VIm onto polypro-

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pylene monofilament by simultaneous radiation grafting method. The influence of reaction parameters on the degree of grafting has been investigated. The structural evaluation of the grafted sutures as a function of the degree of grafting has also been undertaken.

EXPERIMENTAL

Materials

Commercial grade, isotactic polypropylene of MFI 20, supplied by Reliance Industries, India, was used for the present study. The 1-vinylimidazole monomer supplied by Fluka was purified by distillation under vacuum. Distilled water was used wherever needed. Acetone and methanol were supplied by Merck, India.

Preparation of monofilament suture

The monofilament suture was produced by melt spinning of the polymer on a BETOL spinning machine followed by two-stage sequential drawing. The feed zone, compressing zone and metering zone of the extruder were maintained at 180, 190, and 200°C. The temperature of die, housing the spinneret was maintained at 230°C. The extruded filament was quenched immediately by ice-cooled water kept 2 cm below the spinneret's level. The drawing was carried out at 110°C to a draw ratio of 1:4 to get the monofilament of required characteristics.

Irradiation unit

A Co^{60} source (900 Curies), supplied by Bhabha Atomic Research Centre, India, was used for irradiations of samples. The source had a dose rate of 0.2 kGy/h and all irradiations were carried out at ambient temperature (30°C ± 2°C).

Grafting reaction

Grafting was carried out by simultaneous irradiation method in glass ampoules of 11.5 × 2.8 cm^2 size. The monofilament suture was placed in an ampoule containing the required amount of the monomer solution. Nitrogen was purged into the ampoule to remove air from the grafting solution. Subsequently, ampoule was placed in gamma chamber and was taken out after a desired period. The polyvinylimidazole (PVIm) homopolymer adhering to the suture was removed by extraction with acetone. Finally, the filament was dried in an air oven and weighed. The degree of grafting into the filament was calculated according to the following equation.

$$\text{Degree of grafting} = [(W_g - W_0)/W_0] \times 100 \quad (1)$$

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

FTIR studies

The Fourier Transform infrared spectra of original and VIm grafted PP sutures were recorded on a Perkin–Elmer Spectrum-BX FTIR system. The spectra were taken in the range of 400–4000 cm^{-1}.

Density measurements

The density of drawn polypropylene monofilament was measured at (65 ± 2)% RH and (27 ± 2)°C using density gradient column (Davenport, London). The column was prepared using a mixture of diethylene glycol and isopropanol.[26] Standard floats of known density were added to the column before the measurement, which settle down according to their densities, and a calibration plot was constructed. The samples were placed in the column and left as such for 24 h to settle down in the column. The density of samples was calculated from their respective height in the column.

Birefringence measurement

The refractive indices in transverse and longitudinal direction as well as diameter were measured for unmodified and modified sutures with the help of Lieca DMLP Microscope.

X-ray diffraction

X-ray diffraction pattern (intensity vs. diffraction angle) was recorded in the 2θ range of 10–35, on a Philips X-ray diffractometer equipped with scintillation counter. Cu Kα radiation (wavelength = 1.54 Å; filament current = 30 mA; voltage = 40 kV) was used for the generation of X-rays. All the samples were prepared by cutting the samples into the fine powder form and the X-ray diffractograms were obtained. The degree of crystallinity of various samples was evaluated from the X-ray diffraction pattern by separating the crystalline and amorphous portions under the diffraction pattern using the following expression.

$$\text{Degree of crystallinity} = (A_{cr})/(A_{cr} + A_{am}) \times 100 \quad (2)$$

where, A_{cr} is the area under crystalline peak and A_{am} is the area under amorphous halo.

Differential scanning calorimetry

The differential scanning calorimetric studies of polypropylene sutures were carried out on a PERKIN–

ELMER DSC-7 in the temperature range of 50–180°C. The ΔH_f value (heat of fusion) obtained from the area under melting thermogram and was used for the calculation of crystallinity of the sample by the following expression:

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

where ΔH_f is the heat of fusion the sample undergoing test and ΔH_{crys} is the heat of fusion of 100% crystalline PP and as taken as 163 J/g.[27]

Swelling measurements

The swelling of the PP suture was determined by placing the suture into the aqueous VIm solutions of different concentrations for 24 h at ambient temperature. The suture was removed and the adhering liquid was subsequently removed by blotting with a paper. The weight of the suture was determined and the degree of swelling was obtained from the following expression.

$$\text{Degree of swelling} = [(W_s - W_g)/W_g] \times 100 \quad (4)$$

where, W_g and W_s are the weights of the grafted and swollen sutures, respectively.

Scanning electron microscopy

The surface characteristics of various modified and unmodified sutures were monitored by scanning electron microscope, STEREOSCAN 360 (Cambridge Scientific). The sutures were first coated with a silver layer to provide surface conduction before their scanning.

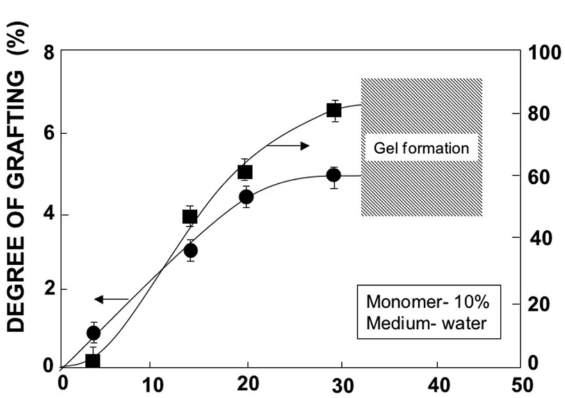

Figure 1 Variation of the degree of grafting and homopolymer with the radiation dose.

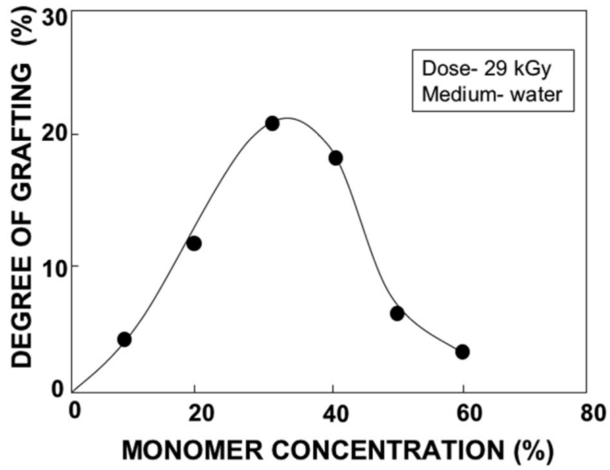

Figure 2 Variation of the degree of grafting with the monomer concentration.

RESULTS AND DISCUSSION

The grafting of VIm onto PP monofilament was carried out to produce suture material with active sites where an antimicrobial drug may be immobilized. A precise designing of the suture may be accomplished by proper control of the grafting conditions. In the following sections, a correlation between the degree of grafting and the reaction conditions has been investigated to establish optimum conditions for the suture development. The characterization of sutures as a function of the degree of grafting has also been discussed.

The influence of the radiation dose on the degree of grafting is presented in Figure 1. The degree of grafting increases with the increasing radiation dose. The increase in percent grafting with an increase in the radiation dose is essentially due to the higher number of free radicals at higher doses. However, the degree of grafting tends to level off beyond a dose of 20 kGy. Since, both the PP and the monomer are exposed to the radiation, significant homopolymerization of VIm proceeds during the grafting process. Almost 80% homopolymerization takes place at a radiation dose of 30 kGy. Virtually, complete conversion of monomer to homopolymer takes place at an irradiation dose of 40 kGy and the separation of the homopolymer from the suture becomes impossible due to gel formation. In the absence of sufficient monomer, the growing chains terminate fast by the recombination or by chain transfer to any component surrounding the radical site such as monomer, solvent or polymer chain and leads to the leveling off in the degree of grafting. Similar behavior in the grafting of VIm/acrylic acid mixture onto polyvinylalcohol has been reported by Ajji and Ali.[28]

The influence of the monomer concentration on the degree of grafting is shown in Figure 2. The degree of

Scheme 1

grafting increases with the increasing monomer concentration reaching maximum at 30% monomer concentration and then decreases fast. Similar maxima in the grafting of VIm-acrylic acid (60:40) mixture onto PP films has been observed by Nagib et al.[17] It was observed that the maxima originates at the monomer concentration of 2 mol/L in dioxane as the medium solvent. From the results in Figure 2, it may be stated that the grafting is influenced by the cumulative effect of the monomer availability and permeability to the grafting sites. As the monomer concentration increases, the monomer availability to the grafting sites also increases and this leads to higher degree of grafting. However, it may be mentioned that the swelling of the grafted matrix is significantly influenced by the composition of the reaction medium. Once the initial grafting has taken place, the grafted layer swells in the grafting medium and controls the monomer diffusion within the suture matrix. To establish the swelling factor, we monitored the degree of swelling of the PP suture in aqueous VIm solutions of different compositions. The swelling of the suture (with 9% graft level) was maximum at the 30–40% monomer concentration and this facilitates the accessibility of the monomer diffusion and its accessibility to the grafting sites within the PP matrix and leads to higher graft levels.

As a matter of fact, the viscosity of the grafting medium plays an important role. As the monomer concentration increases, the homopolymer content also increases which remains soluble in the reaction medium. As a result, the viscosity of the grafting medium increases significantly and hinders the monomer diffusion across the viscous medium to the suture and leads to the depletion of monomer at the propagating chains.[17] The ultimate fate of these growing chains is therefore to deactivate by mutual combination or by chain transfer to some impurity in the system where, XH is the any species present in the grafting medium (Sch. 1).

The presence of organic additives to the grafting medium leads to significant alteration in the grafting pattern as compared to the aqueous monomer system. The behavior for methanol addition was different than acetone on the graft variations. As observed in the preceding section, the grafting in pure water as the reaction medium increases with the monomer concentration, reaches a maximum and subsequently decreases because of enhanced homopolymerization. Therefore, addition of organics was followed to suppress homopolymerzation, so that monomer depletion in the grafting medium may be overcome. At 10% monomer concentration in water, water was replaced gradually by methanol in the range of 5–80%. The maxima was achieved at 40% methanol concentration and the maximum grafting of 9.4% was achieved (Fig. 3). It was observed that at a methanol concentration of above 20%, the homopolymer is completely suppressed so that the monomer depletion from the grafting medium is overcome and the grafting yield is also increased. Beyond 40% methanol content, the grafting tends to decrease and has also been observed in our earlier systems.[29] While, in case of acetone, the trend was entirely different where the degree of grafting initially increased linearly with the acetone fraction in the acetone–water mixture followed by an acceleration at 40% acetone content. The homopolymer formation is completely suppressed at 30% acetone content so that the viscosity of the grafting medium remains almost unchanged. This regulates the uninterrupted supply of the monomer to the propagating chains and is reflected in the autoacceleration similar to our earlier studies on the grafting of acrylamide into polyethylene films.[29] Both the acetone and methanol acted as homopolymer inhibitors for the grafting process and an acceleration in the grafting at 50% acetone content was observed. Studies of Ajji and Ali.[28] have also shown that both the methanol and acetone act as homopolymer inhibitor during the grafting of VIm/acrylic acid mixture on polyvinylalcohol. However, acceleration was observed when both these solvents were partially replaced by water. A maximum in the degree of grafting was achieved at methanol content of 60%. On the other hand, Xhili et al.[16] have reported that the addition of organics (acids and Methylene Blue) and inorganics (Fe^{2+}) leads to significant reduction in the limiting graft levels in PE–VIm system. However, an exact mechanism operating during the grafting in the presence of organics as inhibitor is not yet known.

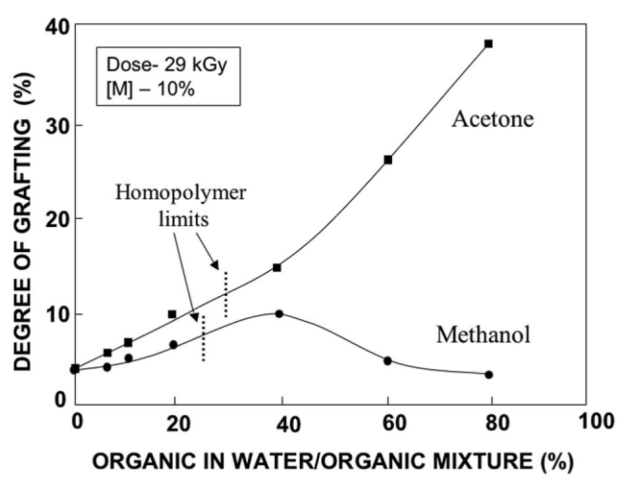

Figure 3 Variation of the degree of grafting with the organic in the grafting medium.

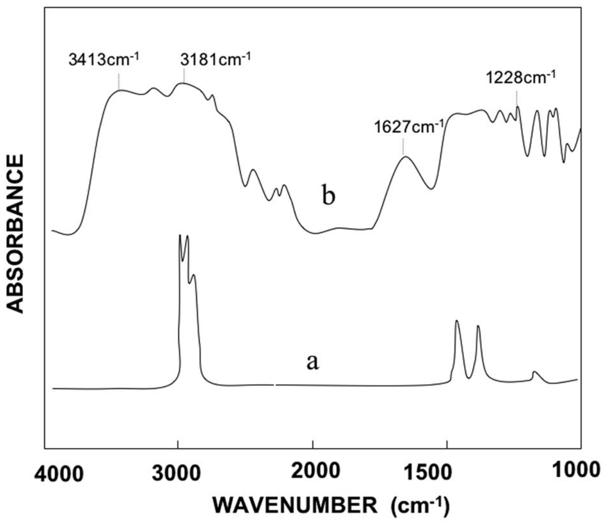

Figure 4 FTIR of (a) virgin PP and (b) PP-*g*-PVIm suture (degree of grafting 4.7%).

FTIR offers evidence of the PVIm grafts within the modified sutures (Fig. 4). The spectra shows prominent peaks at wave numbers 3400–3500, 3180, and 1640–1690 cm^{-1} which are the characteristic peaks of free N—H stretching, bonded N—H stretching and >C═N— stretching vibrations, respectively, in the grafted samples, which are absent in virgin PP suture. Besides these peaks, there is an additional peak found in grafted samples in the range of 1225–1256 cm^{-1} which is characteristic peak for >C—N—C< bond vibrations of vinylimidazole ring. The presence of such peaks in FTIR confirms the presence of VIm moiety in the grafted PP suture.

The density and birefringence of unmodified and grafted PP sutures is presented in Figure 5. The result shows that the density increases with the increase in the degree of grafting. This may be due to higher density of grafted moiety (VIm) and is reflected in an

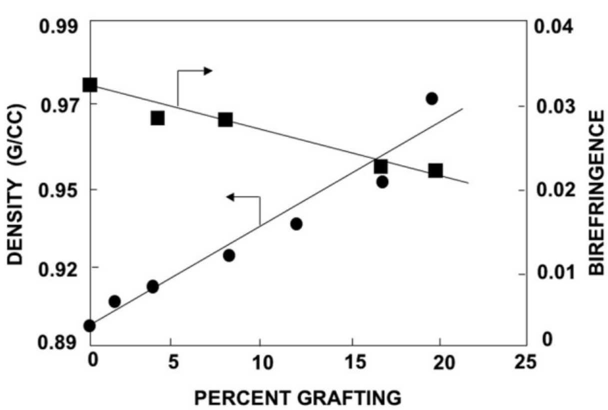

Figure 5 Variation of the density and birefringence with the degree of grafting.

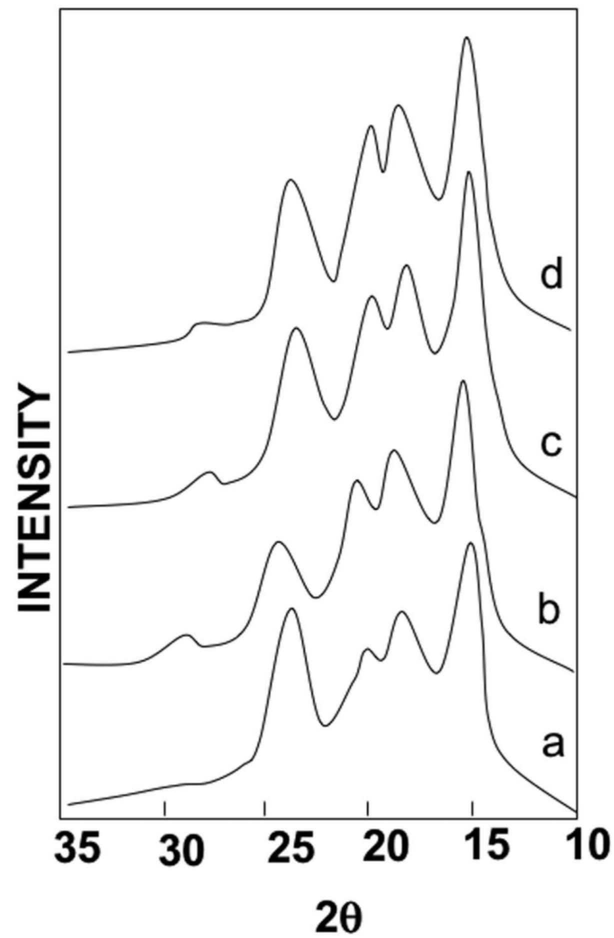

Figure 6 X-ray diffraction of (a) virgin PP; (b) 20 kGy exposed PP and PP-*g*-PVIm sutures with degree of grafting of (c) 4.7%; (d) 9.4%.

increase in the density of the suture. The birefringence of suture reveals that as the grafting increases, birefringence tends to decrease. This is the indication of the molecular chains orientation being impeded by the grafted PVIm chains.[30] Disorientation tends to be higher as the graft level in the suture increases.

The X-ray diffraction pattern of virgin and grafted sutures are presented in Figure 6. All the samples show identical diffraction patterns but the intensity of peaks diminished. These results indicate reduction in the crystallinity of the sutures in grafted samples. There is a close relationship of the crystallinity data with those obtained from differential scanning calorimetry (DSC). The DSC thermograms for sutures are presented in Figure 7. From the area under thermograms, heat of fusion was calculated. The crystallinity as obtained from eq. (2) for various samples showed gradual decrease with increase in the graft percentage (Fig. 8). We have observed that the PVIm is amorphous polymer. Therefore, the observed decrease in the crystallinity may be ascribed to the incorporation of the grafts into noncrystalline regions of the poly-

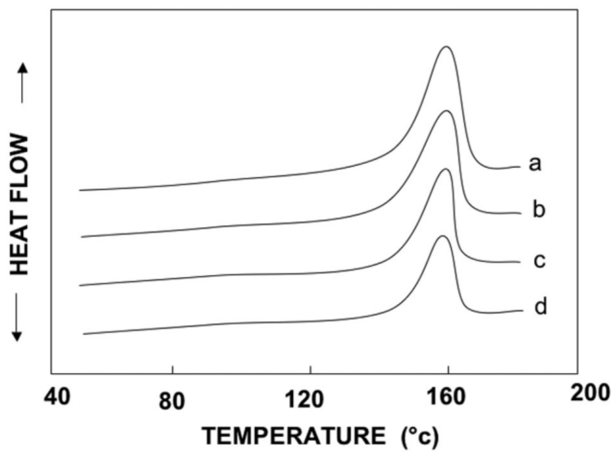

Figure 7 DSC thermograms of (a) virgin PP; (b) 20 kGy exposed PP and PP-*g*-PVIm sutures with degree of grafting of (c) 4.7%; (d) 9.4%.

mer, by pushing apart the molecular chains and thus disturbing the array of crystallites in the system.[31] The net result comes out as the reduced crystallinity. The crystallinity obtained from the X-ray diffractograms follows similar trend although the absolute values of crystallinity are slightly lower than that observed in DSC.

The scanning electron microscopy photographs of samples are shown in Figure 9. The results show slight nonhomogeneity in the grafted samples. The surface roughness in fact increases as the degree of grafting increases. This is the outcome of the incompatibility of the hydrophilic PVIm grafts with the hydrophobic PP matrix. Such behavior is prevalent in the grafting process and has been observed to be more intense in the grafting of acrylamide into polyethylene films.[32]

CONCLUSION

The present work is aimed at the development and modification of polypropylene monofilament so as to

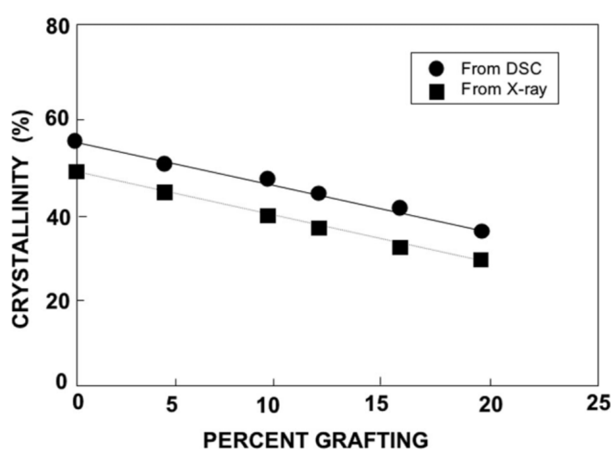

Figure 8 Variation of the crystallinity with the degree of grafting.

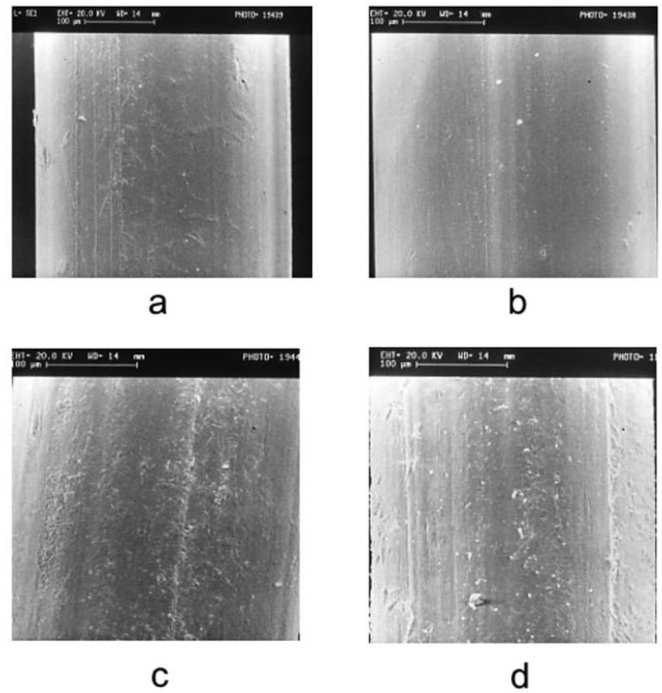

Figure 9 SEM of (a) virgin PP and PP-*g*-PVIm sutures with degree of grafting of (c) 4.7%; (d) 12%; (c) 17%.

make it a strong candidate to be used as a suture. Polypropylene monofilament was melt spun without any additive and then drawn to achieve required strength, followed by its grafting with VIm monomer. The grafting is significantly affected by the reaction conditions. The increase in radiation dose leads to the increase in the degree of grafting. The degree of grafting also increases with the monomer concentration, reaches a maximum at 30% monomer and then falls, abruptly. These observations may be attributed to the fallout of a cumulative effect of the monomer depletion and the monomer accessibility to the grafting sites. The monomer depletion due to homopolymerization of VIm is a crucial factor limiting the degree of grafting. However, the instantaneous swelling of the grafted PP in the reaction medium plays significant role in regulating the monomer diffusion to the grafting sites. This is where the addition of methanol and the acetone helps in preventing the homopolymerization.

X-ray diffraction studies showed that the crystallinity of grafted filament decreases with increased percentage of grafting. These observations were revealed by the DSC investigations. However, this decrease in crystallinity is due to the dilution of inherent crystallinity by the incorporation of the amorphous PVIm grafts. The surface morphology changes significantly on graft modification. The nonhomogeneity arises due to the incompatibility of the hydrophilic PVIm domains with the hydrophobic PP matrix which leads to the formation of independent structures on the suture surface. Subsequent investigations on the drug immobilization and release behavior as well as the antimicrobial nature of these sutures are being presented in a subsequent communication.[33]

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