Radiation Grafting of Acrylic Acid onto Poly(ethylene terephthalate) Fabric

Bhuvanesh Gupta,[1] Navdeep Grover,[1,2] 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*

Received 11 January 2008; accepted 19 October 2008
DOI 10.1002/app.29546
Published online 28 January 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Radiation grafting of acrylic acid onto poly (ethylene terephthalate) (PET) knittings was investigated by preirradiation technique. The influence of the grafting conditions, such as reaction time, ferrous sulfate concentration, preirradiation dose, organic additives, monomer concentration, and reaction temperature on the degree of grafting was investigated. Precise control over the degree of grafting was achieved by proper selection of the reaction conditions. The organic solvents such as methanol, acetone, isopropanol, THF, and MEK when used as sole medium do not allow the grafting to proceed, probably due to the inhibitory action. However, reasonable grafting proceeded when a mixture of water and organic solvent was used. Attenuated total reflectance-FTIR spectroscopy analysis of the grafted knittings confirmed the existence of carboxylic acid groups in the knittings. The surface morphology, as studied by scanning electron microscopy (SEM), was significantly influenced by the addition of organic solvents in the reaction medium.
 J Appl Polym Sci 112: 1199–1208, 2009

Key words: PET knitting; acrylic acid; radiation; graft polymerization

INTRODUCTION

Textile materials offer interesting features, such as porosity and compliance, which are often not exerted by other polymeric materials. Surgical implantation of these materials is encounted with both thrombosis and inflammation at the site of injury.[1,2] These processes are interrelated, and both contribute to the healing of tissue into and around the material. Poly(ethylene terephthalate) (PET) in different shapes and forms is used worldwide clinically in cardiovascular devices.[3] However, PET is reputed to be both thrombogenic and moderately inflammatory in nature. Therefore, it is necessary to modify PET to make it bioreceptive for its application as biomaterial.

PET has excellent mechanical strength, good stability in the presence of body fluids, and high radiation resistance, which makes it suitable for sterilization but its surface needs precise modification for the immobilization of biomolecules.[4] The key requirement toward modification is that it should acquire specific functional groups where biomolecules can be immobilized. The modification of PET has been carried out by different methods involving chemical hydrolysis, UV, plasma, ozone, and graft polymerization to introduce various functional groups such as carboxylic acid, sulfonic acid, amide, amine, acrylate, pyrrolidone, and glycol.[4–14] Radiation induced grafting of vinyl monomers onto PET has been frequently used for various biomedical applications, such as artificial vascular prosthetic parts, laryngeal, esophageal, and sutures.[11,15–20] To improve the biomedical applicability, polymeric materials are often immobilized with biologically active components onto the surface. For example, research group of Biltresse and Attolini[21] have prepared cell adhesive PET membranes by surface grafting of RGD peptidomimetics. This microporous support was subsequently used for the *in vitro* cultivation of mammalian cells for investigating the transport of pharmacological agents through the cultured cells. RGD peptides (linear or cyclic) were used to promote cellular adhesion, a phenomenon of crucial importance in the case of substrates for tissue engineering. Recently, Bech et al.[22] used PET immobilized with carbohydrates after aminolysis for the application in protein recognition and cell culture. Zhang et al.[23] investigated the bioactivity of fibronectin (FN) immobilized on PET. In the first step, FN was covalently conjugated to an aminated PET surface via glutaraldehyde cross-linking. The surface was blocked by ethanolamine. In the second case, FN was physically adsorbed to the ethanolamine-blocked aminated-PET surface without FN conjugation.

Graft polymerization induced by γ-rays has been shown to be a promising way of combining two or more highly incompatible polymers; so that materials

Correspondence to: B. Gupta (bgupta@textile.iitd.ernet.in).
Contract grant sponsor: Council of Scientific and Industrial Research (CSIR), India.

with desirable properties are achieved.[24] Hu et al.[25] measured the peroxide density of 0.85 nmol/cm^2 on PET at 10 kGy with dose rate 7.8 kGy/h. On contact with the monomer, the irradiated polymer initiates grafting by thermal decomposition of peroxides and hydroperoxides. The sensitivity of polymer toward radiolytic degradation is an important factor before selecting the irradiation dose.[24,26] Recently, Jou et al.[16] modified the PET fibers by γ-ray induced graft polymerization of acrylic acid. The modified fibers were further grafted with chitosan (CS) via esterification and subsequently hyaluronic acid (HA) was immobilized. The results indicate that PET fibers not only exhibit antimicrobial activity but also improve the cell proliferation for fibroblast. In our earlier studies, PET knitting was modified by radiation induced graft polymerization of methacrylic acid and *N*-vinyl-2-pyrrolidone mixture.[11] The grafted surfaces were evaluated for collagen immobilization to make them bioreceptive for tissue engineering. In our previous work, we carried out the plasma induced graft polymerization of acrylic acid on PET films and subsequently collagen (type I and type III) immobilization and human smooth muscle cell expansion.[27,28] In this study, functional designing of the PET knitting under various conditions using preirradiation method was investigated. The effect of grafting conditions, such as the reaction time, ferrous sulfate concentration, preirradiation dose, organic additives, monomer concentration, and reaction temperature of preirradiated PET knittings on the degree of grafting, was investigated.

EXPERIMENTAL

Materials

Weft knitted textured PET fabric used in this study was of textured yarn of denier 80/34 supplied by Reliance Industries (Mumbai, India). Acrylic acid was supplied by Merck India and was distilled under vacuum. Ferrous sulfate, isopropanol, and tetrahydrofuran (THF) from Merck India were used as received. Acetone, methanol, and methyl ethyl ketone (MEK) from Qualigens Fine Chemicals, India, were also used as received. Distilled water was used for all experiments.

Knitting

Single end weft knitting was carried out on Krenzl, Switzerland, weft knitting machine of diameter, 3.5 in. Gauge was 14 needles/in.

Heat setting

For dimensional stability, heat setting was done at 200°C in free shrink condition on EARNST BENZAG, Switzerland heat setting machine.

Extraction of spin finish

Heat set knitted fabric was soxhlet extracted in methanol for 10 h for removal of the spin finish. Then it was removed and boiled in distilled water for 1 h and then dried overnight at 60°C.

Irradiation

Knitted PET fabrics were exposed to γ-rays from a ^{60}Co source (900 Curies) in the presence of air. The dose rate of radiation was 0.18 kGy/h.

Graft polymerization

Grafting was carried out in glass ampoules of 2 × 10 cm^2 size with B-24 joints. A weighed amount of irradiated fabric (~ 500 mg) was placed into ampoules containing aqueous monomer solution with specific additive (ferrous sulfate or organic solvents). Nitrogen was purged into the ampoule to remove air trapped inside the reaction mixture. The ampoule was subsequently placed in a water bath maintained at required temperature. After a desired period, the ampoule was removed and the sample was washed with boiling water to remove any homopoylmer adhering to the sample surface. The samples were dried in an oven at 60°C under vacuum and the degree of grafting was determined using the following expression.[29]

$$\text{Degree of Grafting } (\%) = \frac{W_g - W_i}{W_i} \times 100 \qquad (1)$$

Where, W_i and W_g are the weight of the ungrafted and grafted fabrics, respectively.

Functional group analysis by titration method

Functional group analysis was carried out by two procedures of titration. The results were compared with the values obtained by gravimetric method. In method I, PET sample was taken in a 250-mL round bottomed flask. Subsequently, 2 : 3 phenol : chloroform mixture was added and the contents were refluxed for dissolving the polymer. This was followed by cooling and titrating against 0.01*N* NaOH solution in benzyl alcohol, using tetrabromophenol as an indicator to blue end point. A blank experiment was also carried out.[30]

$$\text{COOH content (meq/g)} = \frac{(A - B) \times \text{Normality of NaOH} \times 1000}{\text{Weight of sample}} \qquad (2)$$

Where, A is the volume in mL of 0.01*N* NaOH for the sample, and B is the volume in mL of 0.01*N* NaOH for the blank.

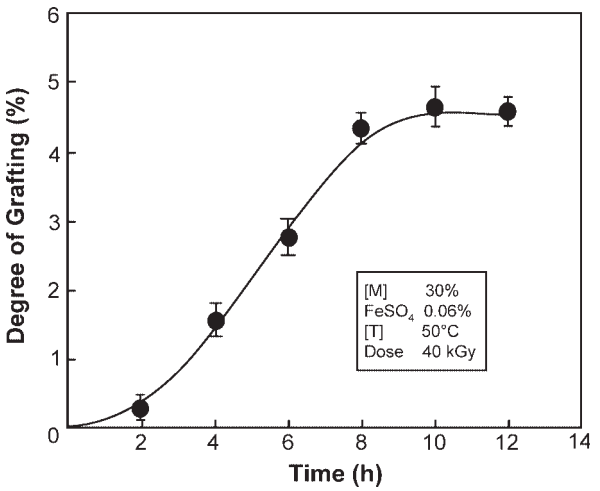

Figure 1 Influence of the reaction time on the degree of grafting. Reaction medium: water.

In method II, PET sample was taken in a 25 mL of 0.01*M* NaOH in measuring flask and were kept at 40°C for 24 h. The carboxylic acid groups of grafted acrylic acid were neutralized by 0.01*M* NaOH and concentration of remaining NaOH was determined by titration against 0.01*M* HCl using phenolphthalein as an indicator. A blank experiment was also carried out.

Attenuated total reflectance

Attenuated total reflectance-FTIR (ATR-FTIR) spectra were recorded on Perkin–Elmer spectrum one spectrometer.

Scanning electron microscopy

The surface characteristics of unmodified and modified PET knittings were studied using STEREO-SCAN 360 (Cambridge Scientific Industries), scanning electron microscope (SEM), after coating them with silver.

RESULTS AND DISCUSSION

The radiation-induced graft polymerization of acrylic acid onto PET fabric was carried out to optimize the influence of synthesis conditions on the degree of grafting. The influence of additives (ferrous sulfate and organic solvents), monomer concentration, preir-radiation dose, and reaction temperature on the degree of grafting was studied.

The influence of the reaction time on the degree of grafting is presented in Figure 1. With an increase in the reaction time, the percent grafting continue to increase unless all active sites are exhausted.[31] The optimum time for the grafting to reach equilibrium was found to be 10 h. In our previous studies, no saturation was observed during the grafting of methacrylic acid on to PET fabric up to 12 h.[11] Since each monomer has its own influence on grafting kinetics, the grafting of acrylic acid, as in our system, has tendency for faster homopolymerization than methacrylic acid leading to the quick gel formation. Under these conditions, the monomer availability to the growing sites is significantly hindered which is not the case of methacrylic acid where homopolymerization is slow and monomer availability stays efficiently. It is important to mention that the grafting does not proceed in the absence of any additive due to the extensive homopolymer formation. The addition of ferrous sulfate to the aqueous monomer solution suppresses homopolymer formation. As the ferrous sulfate concentration increases, the degree of grafting also increases initially, reaches the maximum, and then tend to decrease fast (Fig. 2). The homopolymer formation is also inhibited as the ferrous sulfate concentration increases. Virtually no homopolymer formation takes place at 0.1% of the ferrous sulfate concentration. The initial increase in the grafting is because of the diminishing homopolymerization with the increasing ferrous sulfate concentration so that sufficient monomer remains available for the grafting reaction. The maximum grafting is achieved at 0.04% ferrous sulfate concentration beyond which a drastic reduction of the degree of grafting occurs. It may be stated that in spite of the free monomer availability for grafting, the ferrous sulfate not only hinders the homopolymerization by deactivating the hydroxyl radical into hydroxyl anion [eq. (3)] but also deactivates the primary $PO^{\cdot}$ radicals as well as propagating poly(acrylic acid) chains [eqs. (4) and (5)] leading to the decrease in the degree of grafting.[24,32]

$$Fe^{2+} + POOH \longrightarrow Fe^{3+} + PO^{\bullet} + OH^{-} \qquad (3)$$

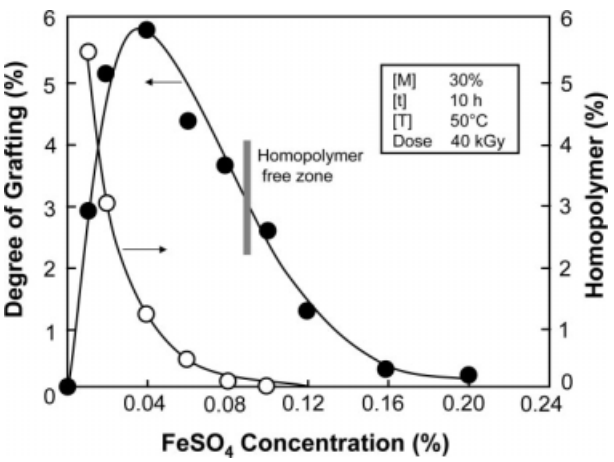

Figure 2 Influence of the ferrous sulfate concentration on the degree of grafting and homopolymerization. Reaction medium: water.

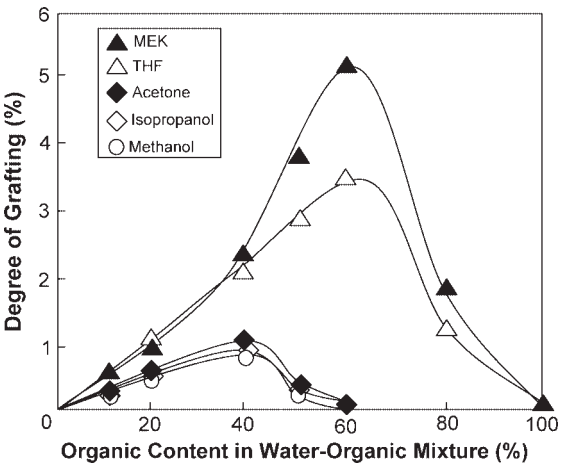

Figure 3 Influence of the various organic additives on the degree of grafting. Reaction conditions: monomer concentration, 30%; reaction time, 10 h; reaction temperature, 50°C; preirradiation dose, 40 kGy.

$$PO^{\bullet} + Fe^{2+} + H_2O \longrightarrow Fe^{3+} + POH + OH^{-} \quad (4)$$

$$PCHX^{\bullet} + Fe^{2+} + H_2O \longrightarrow Fe^{3+} + PCH_2X + OH^{-} \quad (5)$$

The variation of the degree of grafting on addition of organic additives in water is shown in Figure 3. The grafting in this system may be preferred to proceed by the Front Mechanism.[33,34] This mechanism has been observed to operate for graft polymerization of acrylic acid and styrene in Teflon-FEP films.[26] In traditional solution grafting process, the solvent is a carrier by which monomers are transported to the vicinity of the backbone. Therefore, the selection of an optimal solvent is very important for smooth graft polymerization. In general, the choice of solvent depends on several parameters, including the solubility of the monomer in the solvent, the swelling properties of the backbone, the miscibility of the solvents if more than one solvent is used, and the generation of free radicals in the presence of the solvent.[32]

The results in Figure 3 show that very little grafting takes place in methanol, isopropanol, and acetone, whereas relatively much higher grafting yields are obtained at 60% concentration of THF and MEK in water. These observations may be the outcome of the combination of several independent factors, such as extent of homopolymerization and the viscosity of the grafting medium. The alcohols are known to exert inhibitory influence on the degree of grafting.[35] The usual grafting reaction as per the eq. (6) may not be proceeding well and the growing chain transfer to the alcohols is fast and preventing the propagation steps [eqs. (7) and (8)]:

$$PO^{\bullet} + X \longrightarrow POX^{\bullet} \quad (6)$$

$$PO^{\bullet} + RH \longrightarrow POH + R^{\bullet} \quad (7)$$

$$PCHX^{\bullet} + RH \longrightarrow PCHXH + R^{\bullet} \quad (8)$$

where, R = CH_2OH, $(CH_3)_2COH$.

Acetone too falls in line with alcohols and inhibits the grafting as well as homopolymerization at 60% concentration (Table I). It may be stated that in spite of the inhibitory action, the significant gel formation takes place up to 50% methanol, isopropanol, and acetone addition. As a result, the graft levels in these additions are also very low. The gel formation in THF medium does not proceed. Instead, some homopolymer is formed in the reaction medium (i.e., 6.7% at 60% THF content). This is where a significantly large amount of monomer is left behind so that the grafting still proceeds well to produce higher graft levels.

Unlike other additives, MEK acts as the nonsolvent for the growing poly(acrylic acid) chains. This makes a complete change in the grafting process. MEK precipitates out poly(acrylic acid) homopolymer as soon as it is formed in the reaction medium.[32] As a result, the viscosity of the grafting medium is considerably maintained and chain termination is considerably suppressed ($k_{tr} \ll k_p$). The grafting maximum is observed at 60% of MEK in water and beyond 60% MEK, the degree of grafting shows decreasing trend. This may be due to the nonsolvent nature of MEK toward poly(acrylic acid), the grafted chains do not

TABLE I
Homopolymer Formation in Different Organic Additives

% Additives in water	Homopolymer formation in organic additives				
	Methanol	Isopropanol	Acetone	THF	MEK
10	Gel formation	Gel formation	Gel formation	Gel formation	Gel formation
20	Gel formation	Gel formation	Gel formation	Gel formation	Gel formation
40	Gel formation	Gel formation	Gel formation	18.5%	Gel formation
50	Gel formation	Gel formation	Gel formation	14.7%	Gel + Precipitation
60	No homopolymer	No homopolymer	No homopolymer	6.7%	Gel + Precipitation
80	No homopolymer	No homopolymer	No homopolymer	No homopolymer	Gel + Precipitation
100	No homopolymer	No homopolymer	No homopolymer	No homopolymer	Precipitation

Reaction conditions: monomer concentration, 30%; time, 10 h; temperature, 50°C; dose, 40 kGy.

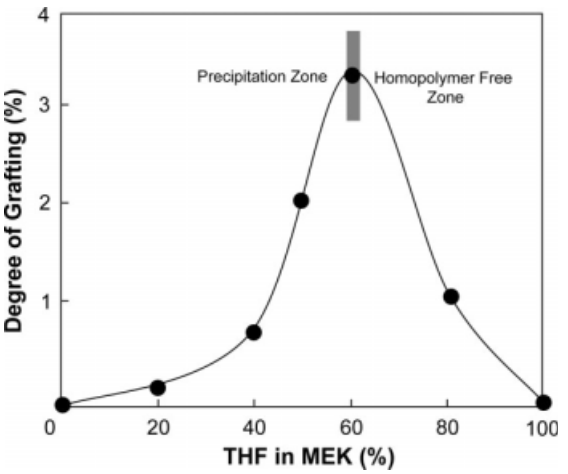

Figure 4 Influence of the THF concentration on the degree of grafting in MEK. Reaction conditions: monomer concentration in THF/MEK mixture, 30%; reaction time, 10 h; reaction temperature, 50°C; preirradiation dose, 40 kGy.

swell and enrichment of the grafted layer with monomer does not proceed well. As a result, the growing chain termination follows, providing a decreasing trend in the graft levels.

In an attempt to look into the role of swelling in grafting process, we tried to carry out the grafting under nonaqueous condition. Figure 4 shows the variation of the degree of the grafting with THF in MEK. The grafting maximum is observed at 60% of THF and slight turbidity was observed but no homopolymer was formed. As the fraction of THF increases, the chain transfer predominates which leads to lower graft level beyond 60% concentration. The inhibitory influence of THF (in water as well as in MEK) is interesting in achieving homopolymer free grafting reaction but it is difficult to predict any precise mechanism for this observation.

Looking at this observation, we confined our subsequent studies under MEK medium. The variation of the degree of grafting with the monomer concentration is presented in Figure 5. Initially, the degree of grafting increases and reaches maximum at 40% monomer concentration, and then decreases with further increase in monomer concentration. The initial increase in the degree of grafting with the increase in the monomer concentration is probably due to the unhindered accessibility of the monomer to the primary radicals, $P^{\cdot}$, resulting in a smooth initiation step and propagation step [eqs. (9) and (10)]:

$$P^{\bullet} + M \xrightarrow{k_i} \text{initiation} \tag{9}$$

$$PCHX^{\bullet} + M \xrightarrow{k_p} \text{propagation} \tag{10}$$

MEK, being a nonsolvent for poly(acrylic acid), maintains the viscosity of the grafting medium by separating the homopolymer but complete phase separation does not occur. As a result, the monomer accessibility to the grafting sites is maintained. The effective concentration of monomer is reduced by extensive homopolymerization at higher monomer concentration (beyond 40%). As a result, the rate of propagation (k_p) decreases considerably, and chain transfer (k_{tr}) to another species (Q), such as homopolymer in solution dominates over the chain propagation. The degree of grafting, as a result, showed a decreasing trend. The similar trend was also observed in our previous study on the acrylic acid grafting on PET films treated with argon plasma.[4] The prominent factors of the grafting system are homopolymerization and propagation chains. Since, we are using identical monomer in both cases, we are getting similar trend irrespective of activation method of PET backbone.

The overall scenario of the grafting process in this system leads to interesting observations. The sole use of organic solvents such as methanol, isopropanol, acetone, THF, and MEK do not allow the grafting reaction to proceed at all. The grafting proceeds only when they are used in combination with water as the grafting medium. Since, homopolymerization is not evident in pure organic solvents; the viscosity change factor is not there. The swelling of the grafted matrix, diffusion of the monomer into the swollen surface matter are secondary factors and are infact operating when organic-water mixture is used as the grafting medium.

The variation of the degree of grafting of acrylic acid with reaction time at different preirradiation doses is shown in Figure 6. It is evident that for all the doses, the degree of grafting increases with the increase in reaction time up to 8 h and then levels off. The equilibrium degree of grafting (at 10 h) increases with the increase in the radiation dose up to 40 kGy

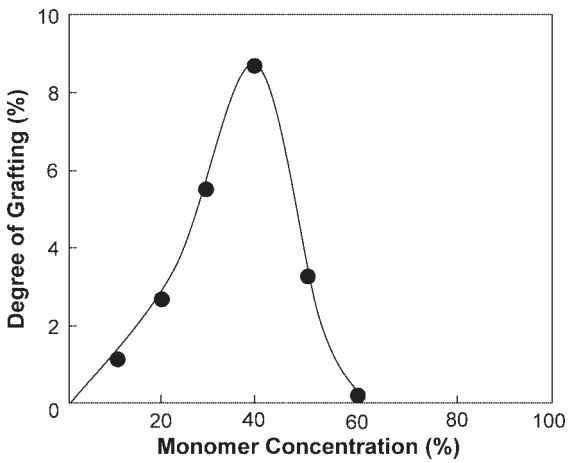

Figure 5 Influence of the monomer concentration on the degree of grafting. Reaction conditions: MEK in water, 60%; reaction time, 10 h; reaction temperature, 50°C; preirradiation dose, 40 kGy.

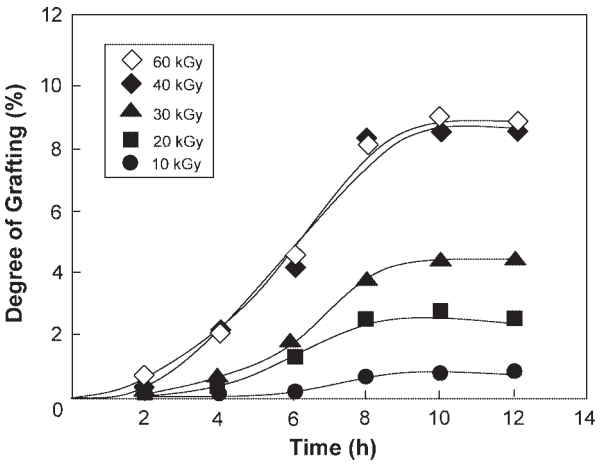

Figure 6 Influence of the reaction time on the degree of grafting at various preirradiation doses. Reaction conditions: MEK in water, 60%; monomer concentration in water/MEK mixture, 40%; temperature, 50°C.

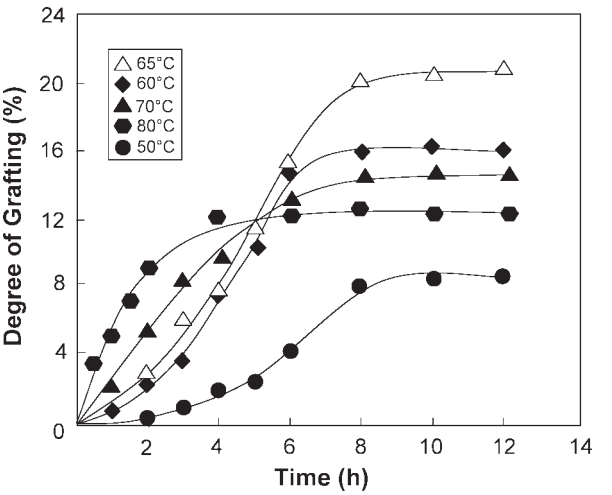

Figure 8 Influence of the reaction time on the degree of grafting at various temperatures. Reaction conditions: MEK in water, 60%; monomer concentration in water/MEK mixture, 40%; preirradiation dose, 40 kGy.

beyond which it levels off (Fig. 7). The initial increase in the graft levels is attributed to an increase in the number of active sites resulting from higher radiation dose.[7] As the irradiation is carried out in air; the active sites are partially consisting of peroxides.[25] For low doses, the number of active sites increases with increase in the radiation dose. However, the trend is not linear as in our previous studies on grafting of methacrylic acid on to PET fabric.[11] Since, we are using MEK/water mixture for the grafting of acrylic acid, this diminishes the swelling of the initially grafted layer when compared with the grafted layer in aqueous medium, which leads to the lower permeation of the monomer within the matrix. Once sufficient grafting has taken place, the monomer diffusion through the grafted layers is enhanced which reflects the acceleration in the grafting. At higher doses, however, it seems that the radiolysis of PET is in equilibrium with the deactivation of active sites. As new peroxides are generated, a significant fraction of the peroxides itself undergo radiolysis and are lost during the process. As a result, the grafting does not increase in spite of the increase in the irradiation doses beyond 40 kGy.[11]

The influence of the degree of grafting on reaction temperature with time is shown in Figure 8. The grafting was carried out from 50 to 80°C at a 40% monomer concentration. All curves are showing an increase in the degree of grafting with the reaction time. The initial rate of grafting increases linearly with the increase in the reaction temperature (Fig. 9). However, the equilibrium degree of grafting increases up to 65°C and thereafter tends to decrease

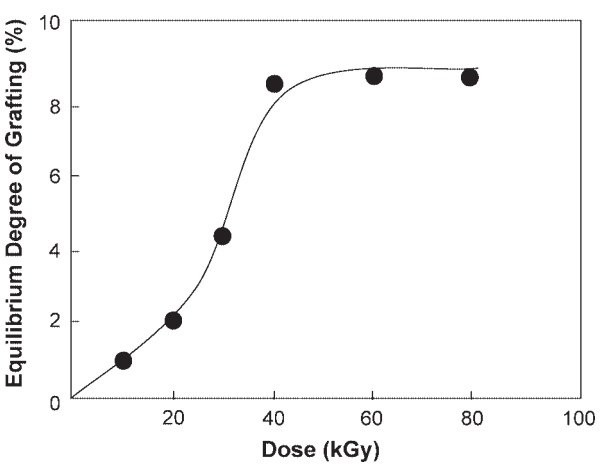

Figure 7 Variation of the equilibrium degree of grafting with the preirradiation dose. Reaction conditions: MEK in water, 60%; reaction time, 10 h; temperature, 50°C; monomer concentration in water/MEK mixture, 40%.

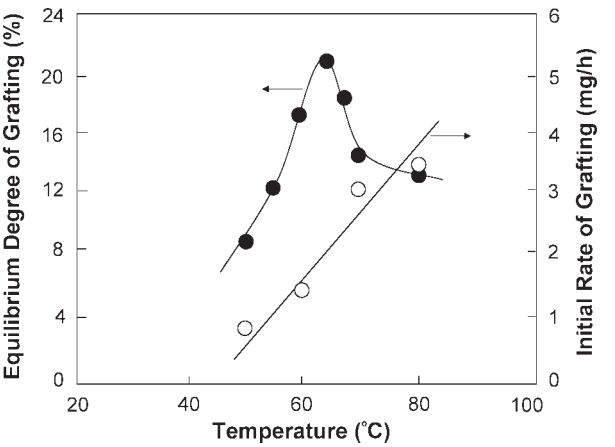

Figure 9 Variation of the equilibrium degree of grafting and the initial degree of grafting with the reaction temperature. Reaction conditions: MEK in water, 60%; monomer concentration in water/MEK mixture, 40%; reaction time, 10 h; preirradiation dose, 40 kGy.

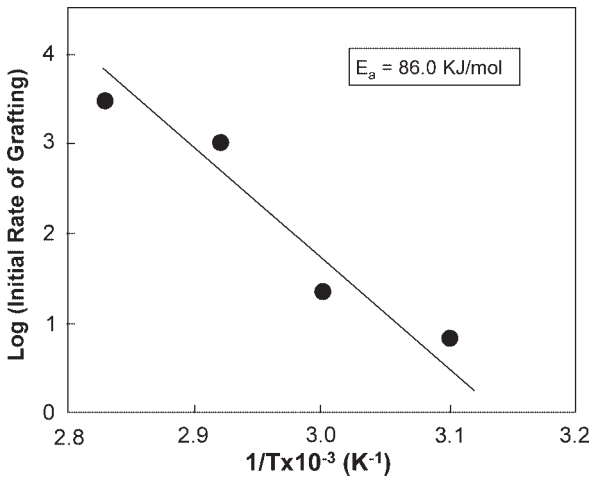

Figure 10 Arrhenius plot of the rate of grafting versus $1/T$. See Figure 9 for the conditions.

whereas in our previous studies, the sharp maximum was observed at 50°C.[4] It may be the because of the physicochemical nature (such as T_g) of the PET fabric when compared with the PET film which might contribute to the observed behavior.

It is proposed that in the early stages of the reaction, homopolymer formation was very limited which was separated by nonsolvent MEK and the local stationary concentration of monomer around the growing chain was maintained. This ensures fast initiation and propagation, leading to a high initial rate of grafting in the system. However, with the increasing temperature, the concentration of propagating chains is increased because of a higher peroxide decomposition rate, and the termination of the two growing chains by mutual recombination becomes a major factor. Once the homopolymer formation is extensive, the monomer depletion favors more chain transfer in the system. It is possible that the chain transfer steps given by eqs. (11) and (12) (at temperature higher than 65°C) dominated to such an extent that the limiting degree of grafting was reduced. It may also be possible that some of the primary radicals ($P^{\cdot}$) became deactivated in the reaction medium [eq. (13)], contributing to the reduced degree of grafting at higher temperatures.[4] Glass transition temperature seems to be an important factor in the observed behavior of reaction temperature. Schamberg and Hoigne[36] explained that at T_g, the polymer chains become more mobile. PET has T_g of $\sim$ 70°C, it can be assumed that with increasing temperature beyond 65°C, more and more primary radicals combine, and therefore, they cannot react with the monomer. Additionally, chain termination may be favored due to the increase in the diffusion rate of monomer. This would lead to a lower kinetic chain length. An increase in the rate of chain termination could explain the decrease in the grafting yield above T_g.

$$\mathrm{PCHX}^{\bullet} + \mathrm{PCHX}^{\bullet} \xrightarrow{k_c} \text{dead polymer} \qquad (11)$$

$$\mathrm{PCHX}^{\bullet} + \mathrm{Q} \xrightarrow{k_{tr}} \text{chain transfer} \qquad (12)$$

$$\mathrm{P}^{\bullet} + \mathrm{PCHX}^{\bullet} \longrightarrow \text{deactivation} \qquad (13)$$

The Arrhenius plot of the initial rate of grafting versus $1/T$ from 50 to 80°C, as presented in Figure 10, is linear. The activation energy obtained from the slope of the plot is 86.0 kJ/mol, whereas in our earlier work, reported activation energy for plasma induced graft polymerization of acrylic acid on PET films was 29.1 kJ/mol.[4] The higher value of activation energy for radiation induced graft polymerization is because of the contribution of diffusion of monomer into the bulk of PET matrix which also requires some energy, whereas in case of plasma activation, diffusion of monomer is limited on surface grafting only.

We tried to look into the possibility of determining the degree of grafting by two titration procedures and correlated it with gravimetric method [eq. (1)]. Proper correlation exists between the degree of grafting determined by these procedures (Fig. 11). Gravimetric and titration points fall on single straight line suggests that the grafts determined may be accompanied by any of these methods. Moreover, on comparing the two procedures of titration, it is found that the back titration (method II) is better because of the less uncertainty, whereas in method I, there is also the problem of dissolution as the degree of grafting is increased and the PET-*g*-AAc higher than 8% is not dissolved in that system.

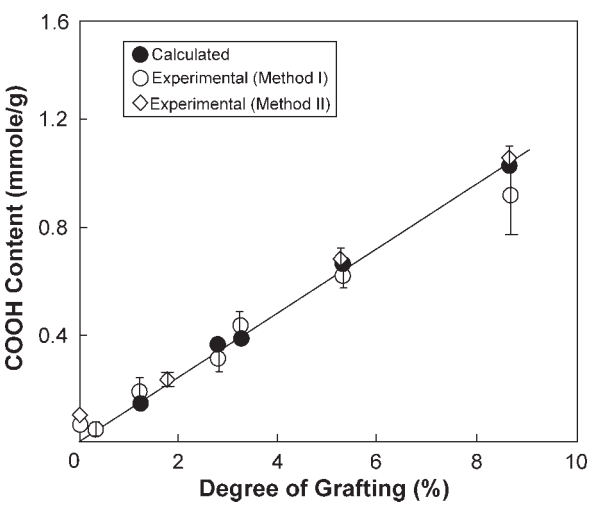

Figure 11 Variation of the carboxylic acid content with the degree of grafting.

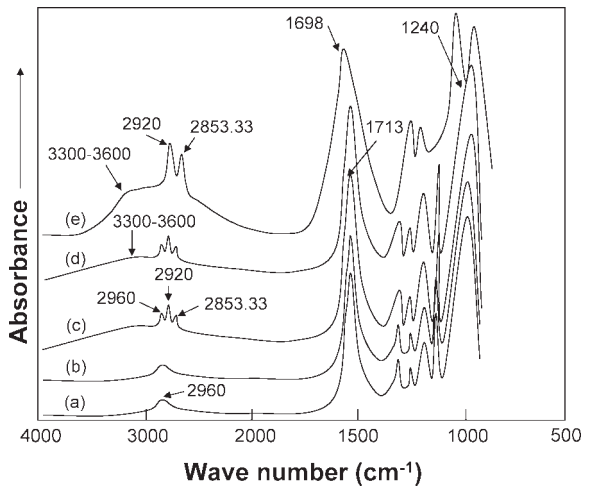

Figure 12 ATR-FTIR spectra of PET (a) virgin; (b) irradiated; (c) 4.4% grafted; (d) 8.4% grafted; and (e) poly(acrylic acid).

The FTIR of ungrafted and grafted PET samples are presented in Figure 12. PET showed characteristic peaks at 2960 cm^{-1} of CH_2 stretching, 1713 cm^{-1} of —C=O stretching of aromatic ester, and a strong band at 1240 cm^{-1} of aromatic ester [Fig. 12(a)]. There was no difference between virgin and irradiated PET fabric spectra [Fig. 12(b)]. Poly(acrylic acid) showed characteristic peaks at 3300–3600 cm^{-1} of hydrogen bonding of COOH, 1698 cm^{-1} of —C=O of COOH [Fig. 12(e)]. The characteristic peaks at 3300–3600, 2920, and 2853 cm^{-1} showed that acrylic acid had been grafted on the PET fabric. The grafted fabric also showed the characteristic peaks of PET at 2960, 1713, and 1240 cm^{-1} [Fig. 12(c) and 12 days].[18]

The surface morphology of the grafted fabric is strongly affected by the nature of the additives in reaction medium (Fig. 13). It is found that the surface roughness is increased by the grafting of acrylic acid which is due to the agglomeration of the grafted domains on the fiber surface.[11,17] However, the addition of ferrous sulfate and THF in the reaction medium shows less surface nonhomogenity when compared with MEK. Since, MEK is nonsolvent for poly(acrylic acid) due to which the grafted chains are precipitated which results in the formation of isolated domains of poly(acrylic acid), as agglomeration of the grafted chains, on the fiber surface.

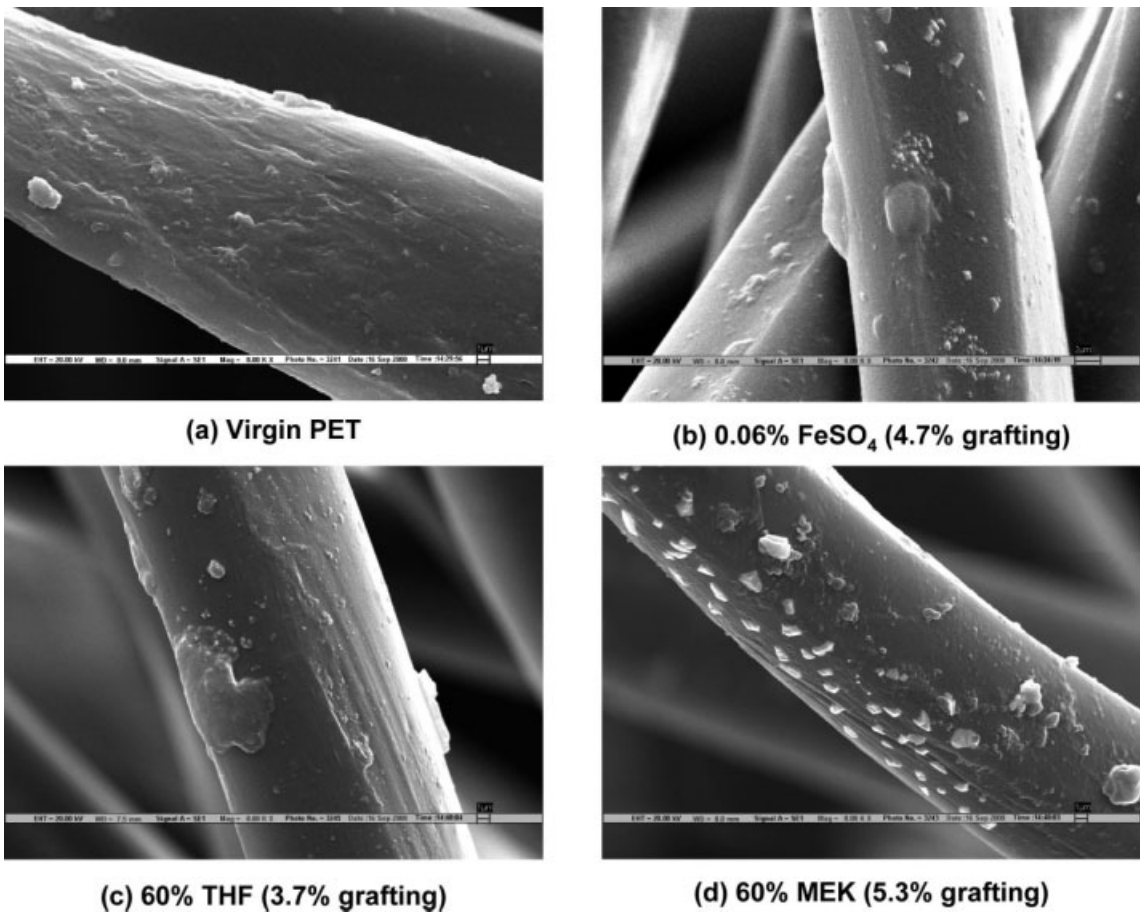

Figure 13 SEM of PET fabric (a) virgin and PET-*g*-PAA in (b) $FeSO_4$; (c) THF; (d) MEK in water as reaction medium. Reaction conditions: monomer concentration, 30%; reaction time, 10 h; reaction temperature, 50°C; dose, 40 kGy.

CONCLUSIONS

The preirradiation graft polymerization of acrylic acid onto PET fabric was strongly influenced by the nature of additives in the grafting medium, temperature of the graft polymerization, irradiation dose, and monomer concentration. It was observed that the graft polymerization is completely interrupted in absence of additives because of extensive homopolymerization. On addition of ferrous sulfate, the degree of grafting was increased initially because of the diminishing homopolymerization. Beyond 0.04% ferrous sulfate concentration, a drastic reduction in degree of grafting was observed due to the deactivation of the primary $PO^{\cdot}$ radicals as well as propagating poly(acrylic acid) chains. Addition of methanol, isoprpanol, and acetone in aqueous phase led to low graft levels because of gel formation and inhibitory action of these additives in the reaction medium, whereas the addition of THF and MEK in water showed a grafting maximum at 60%. In THF, instead of gel formation, only a little homopolymer is formed which ensures the availability of monomer for graft polymerization, whereas MEK acts as the nonsolvent for the growing poly(acrylic acid) chains. This precipitates out the poly(acrylic acid) as soon as it is formed in the reaction medium. As a result, the viscosity of the grafting medium was considerably maintained and grafting was proceeded nicely due to proper monomer accessibility. Beyond 60%, the inhibitory action was predominated in THF as well as in MEK. Since, the reasonable amount of grafting was obtained in THF/water and MEK/water system without gel formation, the gel free system can be designed without using the inorganic additives and the key factors for the grafting mechanism are the viscosity of reaction medium, swelling of grafted matrix, and the diffusion of the monomer into the swollen matrix. The degree of grafting was increased with the increase in the preirradiation dose up to 40 kGy and then leveled off. This is because the radiolysis of PET is in equilibrium with the deactivation of active sites beyond 40 kGy and grafting is not facilitated at higher doses. The increase in monomer concentration up to 40% led to an increase in the degree of grafting beyond which the graft level decreased. This is because beyond 40%, the effective monomer concentration decreases due to extensive homopolymerization. The reaction temperature influenced the grafting significantly. Abrupt fall in the equilibrium degree of grafting was taken place beyond the reaction temperature, 65°C. This is due to the extensive homopolymerization where effective monomer concentration is decreased. Moreover, due to the higher mobility of polymeric chains above 65°C (at T_g of PET) which facilitates the bimolecular termination of the grafting chains. It may also be possible that some of the primary radicals ($P^{\cdot}$) become deactivated in the reaction medium. The optimum preirradiation dose, monomer concentration, and temperature of the grafting were found to be 40 kGy, 40%, and 65°C, respectively. The overall activation energy for this graft polymerization was found to be 86.0 kJ/mol. The functional group analysis and ATR-FTIR spectroscopy analysis of the grafted knittings confirmed the existence of carboxylic acid groups in the knittings. The surface morphology on the grafted surface was strongly influenced by the nature of additives. Since, MEK is nonsolvent for poly(acrylic acid) which results in the precipitation of grafted chains and form isolated domains on fiber surface.

References

1. Anderson, J. M. Trans Am Soc Artif Intern Organs 1988, 34, 101.
2. Anderson, J. M. Cardiovasc Pathol 1993, 2, 33S.
3. Chinn, J. A.; Sauter, J. A.; Phillips, R. E., Jr.; Kao, W. J.; Anderson, J. M.; Hanson, H. R.; Aston, T. R. J Biomed Mater Res 1998, 39, 130.
4. Gupta, B.; Hilborn, J. G.; Bisson, I.; Frey, P. J Appl Polym Sci 2001, 81, 2993.
5. Zhu, Y. B.; Gao, C. Y.; He, T.; Liu, X. Y.; Shen, J. C. Biomacromolecules 2003, 4, 446.
6. Liu, Y.; He, T.; Gao, C. Colloids Surf B 2005, 46, 117.
7. Opwis, K.; Knittel, D.; Schöllmeyer, E. Biotechnol J 2007, 2, 347.
8. Piglowski, J.; Gancarz, I.; Staniszewska-Kus, J.; Paluch, D.; Szymonowicz, M.; Konieczny, A. Biomaterials 1994, 11, 909.
9. Kato, K.; Ikada, Y. Biotechnol Bioeng 1995, 47, 557.
10. Shin, Y.; Son, K.; Yoo, D. I. J Appl Polym Sci 2007, 103, 3655.
11. Gupta, B.; Revagade, N.; Atthoff, B.; Hilborn, J. Polym Adv Technol 2007, 18, 1.
12. Gupta, B.; Hilborn, J.; Hollenstein, C. H.; Plummer, C. J. G.; Houriet, R.; Xanthopoulos, N. J. J Appl Polym Sci 2000, 78, 1083.
13. Rebenfeld, Y. L.; Weigmann, H. D. Text Res J 1978, 22, 125.
14. Park, J. S.; Kim, J. H.; Nho, Y. C.; Kwon, O. H. J Appl Polym Sci 1998, 69, 2213.
15. Jou, C. H.; Lin, S. M.; Yun, L.; Hwang, M. C.; Yu, D. G.; Chou, W. L.; Lee, J. S.; Yang, M. C. Polym Adv Technol 2007, 18, 235.
16. Jou, C. H.; Yuan, L.; Lin, S. M.; Hwang, M. C.; Chou, W. L.; Yu, D. G.; Yang, M. C. J Appl Polym Sci 2007, 104, 220.
17. Gupta, B.; Mishra, S.; Saxena, S. Radiat Phys Chem 2008, 77, 553.
18. El-Arnaouty, M. B.; Abdel Ghaffar, A. M.; El Shafey, H. M. J Appl Polym Sci 2008, 107, 744.
19. An, A. H.; Friedman, R. J. J Microbiol Methods 1997, 30, 141.
20. Gupta, B.; Anjum, N. Adv Polym Sci 2003, 162, 35.
21. Biltresse, S.; Attolini, M.; Marchand-Brynaert, J. Biomaterials 2005, 26, 4576.
22. Bech, L.; Meylheuc, T.; Lepoittevin, B.; Roger, P. J Polym Sci Part A: Polym Chem 2007, 45, 2172.
23. Zhang, Y.; Chai, C.; Jiang, X. S.; Teoh, S. H.; Leong, K. W. Mater Sci Eng 2007, C27, 213.
24. Chapiro, A. Radiation Chemistry of Polymeric Systems; Wiley-Interscience: New York, 1962.
25. Hu, S. G.; Jou, C. H.; Yang, M. C. J Appl Polym Sci 2002, 86, 2977.
26. Gupta, B.; Chapiro, A.; Scherer, G. G. J Mol Sci 1996, 118, 231.

27. Bission, I.; Kosinski, M.; Ruault, S.; Gupta, B.; Hilborn, J.; Wurm, F.; Frey, P. Biomaterials 2002, 23, 3149.
28. Gupta, B.; Plummer, C.; Bission, I.; Frey, P.; Hilborn, J. Biomaterials 2002, 23, 863.
29. Anjum, N.; Gupta, B.; Gulrej, S. K. H.; Singh, H. J Appl Polym Sci 2006, 101, 3895.
30. Gupta, V. B.; Kothari, V. K. Manufactured Fibre Technology, 1st ed.; Chapman and Hall: London, 1997.
31. Gupta, B.; Anjum, N.; Gulrej, S. K. H.; Singh, H. J Appl Polym Sci 2007, 103, 3534.
32. Gupta, B.; Saxena, S.; Ray, A. R. J Appl Polym Sci 2008, 107, 324.
33. Gupta, B.; Büchi, F. N.; Scherer, G. G. J Polym Sci Polym Chem Ed 1994, 32, 1931.
34. Gupta, B.; Büchi, F. N.; Scherer, G. G.; Chapiro, A. Polym Adv Technol 1994, 5, 493.
35. Qi, R.; Yu, Q.; Shen, Y.; Liu, Q.; Zhou, C. J Appl Polym Sci 2006, 102, 5274.
36. Schamberg, E.; Hoigne, J. J Polym Sci Part A: Polym Chem 1970, 8, 693.