

Characterization of Acrylic Acid Grafted Poly(ethylene terephthalate) Fabric

Navdeep Grover,^{1,2} Harpal Singh,² Bhuvanesh Gupta¹

¹Department of Textile Technology, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

²Centre for Biomedical Engineering, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

Received 9 July 2009; accepted 4 February 2010

DOI 10.1002/app.32220

Published online 12 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The preirradiation grafting of acrylic acid (AA) onto poly(ethylene terephthalate) (PET) had been found to affect the thermal and physical characteristics of fabric. The grafted fabrics with various graft levels were characterized by thermal gravimetric analysis (TGA), ATR-FTIR spectroscopy, contact angle, differential scanning calorimetry (DSC), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM). The initial decomposition temperature and T_{50} were increased with the increase in degree of grafting. The percentage crystallinity was decreased as the degree of graft-

ing increases. The detailed elemental analysis was done by X-ray photoelectron spectroscopy (XPS). The atomic ratio (O_{1s}/C_{1s}) was found to increase significantly with increasing the degree of grafting and reached 0.64 at 14.5% grafting from 0.38 for virgin PET. The surface topography and morphology was strongly influenced as the degree of grafting was increased. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3498–3505, 2010

Key words: PET; acrylic acid; radiation; graft polymerization; TGA; DSC; XRD; XPS

INTRODUCTION

The polymer matrix undergo considerable changes during the radiation induced graft polymerization depending on the nature and the amount of monomer being grafted.^{1–7} These changes may be in terms of mechanical strength, thermal stability, crystallinity and elemental composition. Zaharescu and Ciuprina⁸ showed PET belongs to the radiation-degradable polymers and the effect of bond scissions may be assessed by current measurements. The presence of oxygen in the irradiation area accelerates the degradation of polymer substrate because the mobility of oxygen increases the reaction probability of free radical and the amount of restoring oxygen that reacts with formed radicals is expected to depend on the thickness of the sample. Ionizing radiation can induce excitations or radical formations in polyesters that can evolve in charge transfer, chain break, disproportionation, β -scission and other ordinary ion and radical reactions. Increasing formation of radicals with the dose (time) can allow intermolecular radicalic reactions effective for an increase in the molecular weight. Oxygen stored in the polymer is a

well-known radical scavenger; it quickly reacts with formed radicals producing peroxides that can evolve into stable products like alcohols, aldehydes, ketones, carboxylic acids, and esters.⁹ Hu et al.¹⁰ measured the peroxide density of 0.85 nmol/cm² 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 towards radiolytic degradation is an important factor before selecting the irradiation dose.^{11,12}

El-Gendy and El-Shanshoury¹³ studied the effect of radiation dose on the thermal degradation of PET fabric. The degradation process follows second-order kinetics and is independent of radiation dose or heating rate. DSC and XRD studies revealed changes in the fabric crystallinity attributed to irradiation. DSC measurements show a linear increase in the heat of fusion with an increase in dose at a rate of 0.855 kJ kg⁻¹ kGy⁻¹. XRD analysis confirmed structural changes, arrangement, and/or formation of compact crystal lattice with patterns deviating from those of unirradiated fiber. The grafting of methacrylic acid (MAA) deteriorated severely the thermal stability by shifting the T_{50} to lower values and decreasing the kinetic parameters. DSC measurements supported the deteriorating effect of grafting on the first stage by decreasing the degree of crystallinity of untreated samples. This conclusion is reached through the decrease in T_g from 353 to 339 K and increasing the heat of glass transition ΔH_g

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

Contract grant sponsors: Council of Scientific and Industrial Research (CSIR).

from 9.76 to 48.4 kJ/kg, as the degree of grafting increased from 12.7 to 28%, respectively.¹⁴

Kattan and El-Nesr⁴ studied the thermal characteristics of γ -radiation induced grafting of AA onto PET films. The results of DSC showed decrease in the heat capacity step and the glass-transition temperature with increasing grafting yield. Moreover, the grafting forms structural irregularities that inhibit the crystallization and change the size of crystalline domains that appear during the DSC scan. The results of TGA showed the extent and rate of weight loss increases with an increasing grafting yield. Faterpeker and Potnis⁵ also showed that melting temperature, heat of fusion, and mass fractional crystallinity of PET was not affected by the grafting of poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (PVA). No individual glass transition and melting points corresponding to the graft PVAc and PVA were observed, indicating thereby that graft copolymer mainly exists in the form of free chains inside the PET matrix. PVA graft copolymer degraded at much lower temperatures than PVA in powder form. Thermal stability of PET fiber was not affected by graft PVAc, whereas PET-g-PVA showed an additional degradation point at 360°C. Huglin and Zlatev⁶ studied the thermal stability of AA grafted PET and their sodium, calcium and lead salts. Below 300°C the changes occurring in PET are physical (e.g., glass transition, crystallization, melting), whereas above this temperature, chemical processes occur (e.g., cross-linking, depolymerization, decomposition). The number of both types of change below 300°C is increased on grafting and even at higher temperatures the weight losses in PET-PAA are comparable with those in PET. Hence grafting to produce an acidic copolymer seems to offer no advantages from the standpoint of thermal stability. The reduced weight loss at temperatures above 300°C is quite marked for the ionomers PET-PACa and PET-PAPb and the stability of acidic copolymer was found to be lower than that of ungrafted PET: enhanced thermal stability was obtained only in the metallated copolymers. Recently, El-Arnaouty et al.⁷ observed that the thermal stability of the grafted films increases by two ways: as the degree of grafting increases and by increasing the content of acrylonitrile in the sample.

The present investigation is aimed at the evaluation of the thermal and physical properties in PET fabric after the radiation induced grafting of AA. The influence of reaction parameters of radiation induced grafting of AA onto PET fabric were reported earlier.¹⁵

EXPERIMENTAL

Materials

Weft knitted textured PET fabric used in this study was of textured yarn supplied by Reliance Indus-

tries, India, of denier 80/34. Acrylic acid (AA) was supplied by Merck India and was distilled under vacuum. Methyl ethyl ketone (MEK) from Qualigens Fine Chemicals, India, was 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 inches. Gauge was 14 needles/inch.

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 ⁶⁰Co 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 cm² size with B-24 joints. A weighed amount of irradiated fabric was placed into ampoules containing monomer and the solvent (MEK/water mixture). 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 homopolymer 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.¹⁵

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

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

Thermogravimetric analysis (TGA)

TGA studies were carried out using a Perkin-Elmer TGA-7 in the range of 50–600°C. The heating rate

was 10°C/min. The measurements were made under a constant flow rate (20 mL/min) of nitrogen. The initial decomposition temperature (IDT) was obtained as the tangent at a point where the weight loss starts. The T_{50} was taken as the temperature where 50% weight loss in the thermogram occurs.

Differential scanning calorimetry (DSC)

DSC analysis of samples was carried out on Perkin–Elmer–Pyris system in the temperature range of 50–300°C. The heating rate was 10°C/min and the thermograms were run under nitrogen atmosphere. The heat of fusion (ΔH_f) was obtained from the area under the melting thermogram. The crystallinity in sample was obtained by 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 PET and was taken as 28.1 cal/g.⁵

X-ray diffraction analysis (XRD)

X-ray diffraction studies on the samples were carried out on PHILIPS, Holland, CuK α X-ray generator to trace the morphological changes in the material. Scanning was carried out in 2θ range of 0–40° at wavelength of 1.54 Å.

Attenuated total reflectance (ATR-FTIR)

The spectra were recorded on Perkin–Elmer spectrum one spectrometer. The PET samples were placed on a zinc selenide crystal. All spectra were corrected for background. A total of 32 scans were signal averaged at a resolution of 2 cm⁻¹.

X-ray photoelectron spectroscopy (XPS)

X-Ray photoelectron spectroscopic studies were carried out (four scans) on Perkin–Elmer Model PHI 1257 spectrometer, with dual anode Mg/Al 25 kV X-ray source, of power 150W. The radiation used for the present study was AlK α radiation. The resolution of the instrument was 0.2 eV. Probing X-ray photons were incident at an angle of 45° to the substrate normal and the axis of rotational hemispherical analyzer was parallel to the substrate normal.

Contact angle measurement

Contact angle measurements on fabrics were made on DCAT 21 Tensiometer from Dataphysics using Wilhelmy method. The filament has taken from fab-

ric and was mounted on the holder and the force exerted on the contact of the filament with water surface was measured. The contact angle of the sample was obtained from the force by in-built software. These techniques have been included in experimental.

Atomic force microscopy (AFM)

Topographical studies of the fibre surface were carried out in air using atomic force microscope (AFM), molecular imaging (MI), USA make AFM equipment and was operated in the contact mode using an etched silicon tip attached to the end of a cantilever. Cantilevers used for this mode NSC 12 (c) were from MikroMasch having force constant 4.5 N/m and frequency 150 kHz.

Scanning electron microscopy (SEM)

The surface characteristics of unmodified and modified PET fabrics were studied using CARL ZEISS EVO 50, scanning electron microscope, after coating them with silver.

RESULTS AND DISCUSSION

The grafting of AA onto PET fabric has been found to affect the thermal and physical characteristics of fabric. A significant variation in the IDT, crystallinity, elemental composition and surface topography and morphology has been observed as a function of the degree of grafting.

The TGA results are shown in Figure 1, indicating that for virgin and irradiated PET degradation proceeds at 412.5°C. Looking at the degradation pattern of poly(acrylic acid) (PAA), it can be seen that it

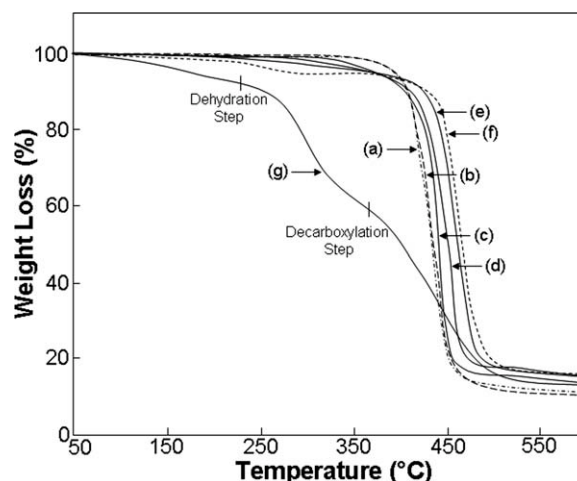


Figure 1 TGA thermograms of PET fabrics (a) virgin; (b) irradiated; (c) 5.3% grafted; (d) 9.5% grafted; (e) 14.5% grafted; (f) 21.5% grafted and (g) PAA film.

TABLE I
Initial Decomposition Temperature (IDT) and Temperature Corresponding to 50% Degradation (T_{50}) of Different Grafted Samples

Sample	IDT (°C)	T_{50} (°C)
Virgin PET	412.5	437.5
Irradiated PET	412.5	437.5
PET-g-AA (5.3%)	422.5	442.5
PET-g-AA (9.5%)	426	446
PET-g-AA (14.5%)	438	456
PET-g-AA (21.5%)	240, 444	280, 462.5

shows dehydration up to 225°C followed by decarboxylation in step II up to 370°C. The grafting of AA onto the PET fabric enhances the thermal stability of PET-g-AA. The IDT and T_{50} of PET-g-AA reveals the observed behavior (Table I). This behavior has also been observed in our previous study on the grafting of AA onto PP films.¹⁶ The increase in IDT and T_{50} is due to the formation of stable anhydride by the cyclization of PAA chains at elevated temperatures and eliminate water molecules, which is reflected in the loss beyond 225°C. This is clearly observed at 21.5% grafting by a supplementary stage decomposition at 240°C which can be attributed to the cyclization of AA grafted onto the PET fabric (Fig. 2).^{4,17} The formation of anhydride is also confirmed by ATR-FTIR spectra in Figures 3 and 4. The hydrogen bonding peak around 3300–3600 and 3385 cm^{-1} in PAA and 21% grafted fabric respectively, disappears after thermal treatment by TGA upto 350°C. The appearance of peak at 1808 and 1813 cm^{-1} in PAA and 21.5% grafted fabric respectively, after thermal treatment by TGA upto 350°C, show the symmetric $\text{C}=\text{O}$ stretching of anhydride ring.¹⁶

DSC thermograms of grafted and ungrafted PET fabric are presented in Figure 5. The virgin PET fabric showed a peak at 254.10°C, which was transformed to dual melting thermogram from 9.5% grafted sample. This is the indication of destruction and reorganization of crystallites within the fibers of PET fabric.¹⁸ ΔH_f (heat of fusion) is related not only to the content of crystals (the fraction in crystalline form) but also the perfectibility of the crystals. For irradiated sample ΔH_f is decreased in comparison to

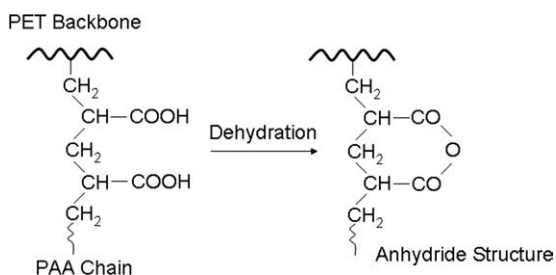


Figure 2 Anhydride formation by cyclization of grafted poly(acrylic acid) (PAA) on PET surface.

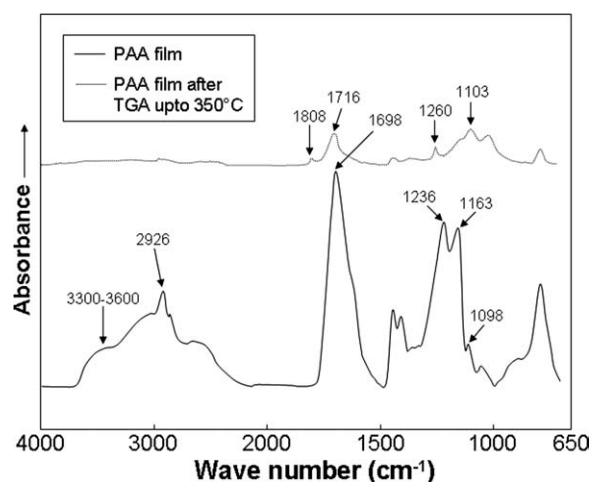


Figure 3 ATR-FTIR spectra of poly(acrylic acid) (PAA) films, before and after heat treatment.

virgin PET (Fig. 6), it can be explained that the cohesive energy is decreased in crystals and volume fraction of crystals remain unchanged.¹⁹ ΔH_f also decreases with an increasing grafting (Fig. 6). Since, the grafting process forms irregular structures in noncrystalline region and thus thereby interferes with the crystallinity. It has been observed that decrease in crystallinity occurs with increase in the degree of grafting (Fig. 7), both by XRD (shown in Fig. 8) and DSC method. It has been observed that the decrease in crystallinity measured by DSC is very close to theoretical calculated value of inherent crystallinity of PET in respective grafted samples. The theoretical inherent crystallinity has been calculated by

$$\text{Inherent crystallinity} = C (\%) \times [1/1 + G] \quad (3)$$

where, $C (\%)$ is the crystallinity of irradiated PET, G is the extent of grafting and $[1/1 + G]$ represents

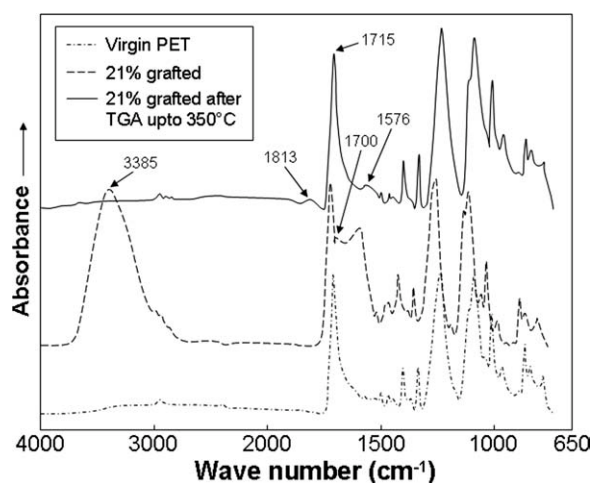


Figure 4 ATR-FTIR spectra of 21.5% grafted PET, before and after heat treatment.

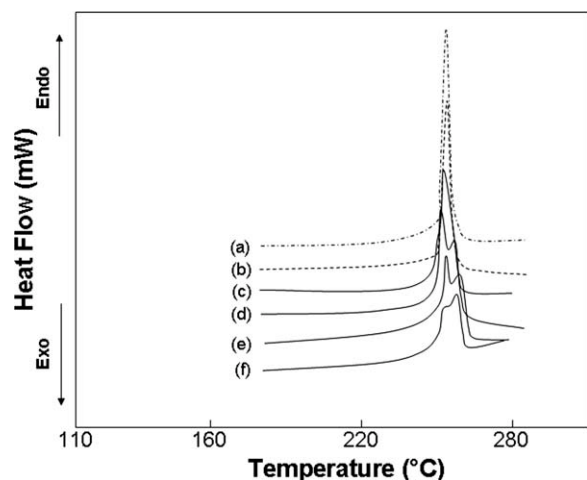


Figure 5 DSC thermograms of PET fabrics (a) virgin; (b) irradiated; (c) 5.3% grafted; (d) 9.5% grafted; (e) 14.5% grafted; and (f) 21.5% grafted.

the weight fraction of polymer in the grafted matrix.¹⁶

The incorporation of PAA grafts would never lead to the enhancement in crystallinity of the PET sample due to the amorphous nature of PAA.¹⁶ In fact, a decrease in the heat of fusion of grafted samples may be because of the addition of amorphous PAA chains within the PET matrix. It is a clear indication that this decrease in crystallinity is due to the dilution of inherent crystallinity by the incorporation of the amorphous PAA grafts. These results therefore suggest that the grafting proceeds solely within the noncrystalline region of PET matrix and the inherent crystallites remain unaffected. The similar results were obtained in our previous publication of grafting of AA onto PP films.¹⁶

The surface composition of virgin and grafted PET as investigated by XPS is presented in Table II and Figure 9. The virgin PET sample shows the lowest

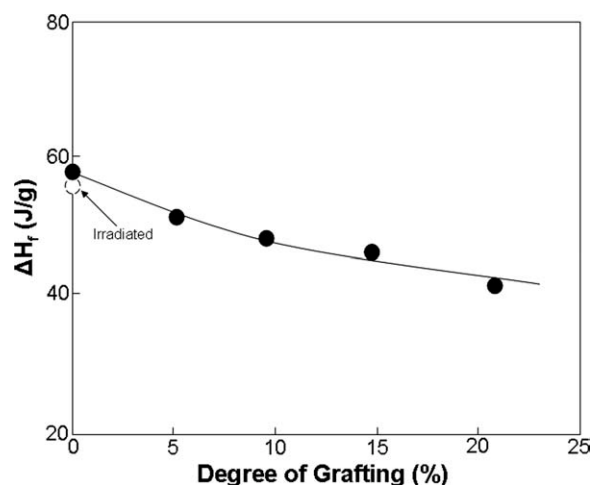


Figure 6 Influence of the degree of grafting on heat of fusion.

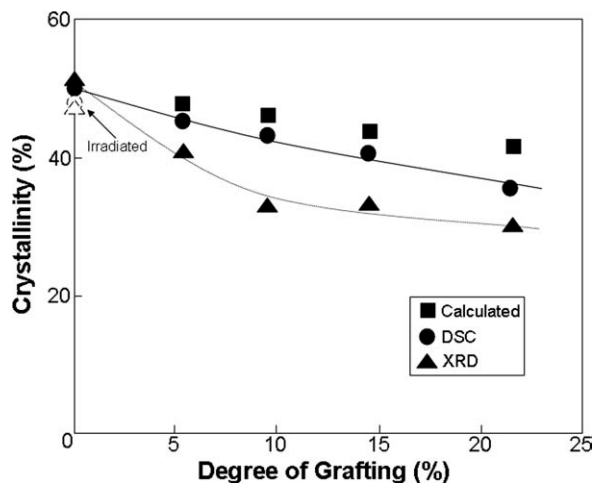


Figure 7 Influence of the degree of grafting on percentage crystallinity.

carbon and oxygen content at the surface. The irradiated PET shows an increased atomic ratio (O_{1s}/C_{1s}) from 0.38 for virgin PET fabric to 0.42. This is because irradiation is carried out in air, so the oxygen reacts with generated radicals during irradiation. The atomic ratio increases from 0.42 to 0.64 with increase in grafting upto 14.5% and then levels off (Fig. 9). Considering the penetration power of X-rays to be nearly 4–6 nm, it may be stated that the top layer of the PET fabric surface is similar with PAA surface (at higher grafting) which has atomic ratio of 0.66 theoretically. Whereas at lower graft level, the fabric surface layer is composed of both the PET and PAA chains. This is the visualization of the grafting mechanism. It is observed that the grafting is a diffusion controlled process and diffusion of monomer depends on the grafting medium which acts as a carrier for monomer diffusion.¹⁵ In our

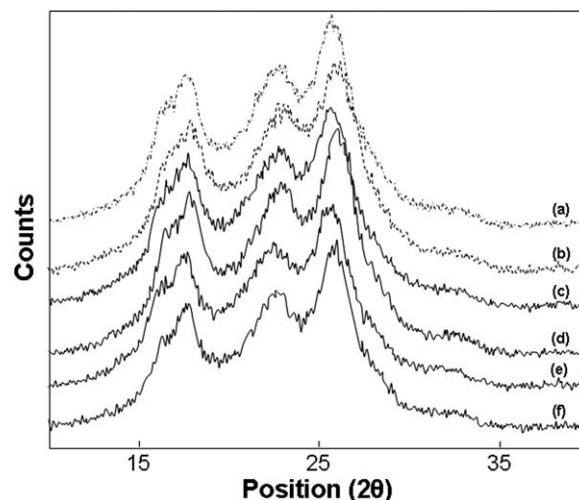


Figure 8 X-ray diffraction pattern of PET fabrics (a) virgin; (b) irradiated; (c) 5.3% grafted; (d) 9.5% grafted; (e) 14.5% grafted; and (f) 21.5% grafted.

TABLE II
The Quantification of Elements C and O From XPS

Sample	C/at%	O/at%
Virgin PET	72.6	27.4
Irradiated PET	70.6	29.4
PET-g-AA (2.4%)	68.4	31.6
PET-g-AA (5.3%)	64.8	35.2
PET-g-AA (9.5%)	62.2	37.8
PET-g-AA (14.5%)	60.9	39.1
PET-g-AA (21.5%)	60.6	39.4

system, we have used MEK (60% in water) which act as a nonsolvent for PAA chains. Therefore, during grafting process the growing PAA chains get precipitated out and prevent the grafted zone from swelling and retard the monomer migration within the surface layers. The initial grafting takes place on the PET surface and further grafting follows onto the subsequent grafted layers by progressive monomer addition onto the grafted layers whereas penetration through the grafted layers is less. Therefore, as the graft level increases, the oxygen content also increases because of the graft addition onto the surface layers and become 39% at higher grafting which is very close to pure PAA (40%).

The contact angle measurement with different degree of grafting is presented in Figure 10 which also support the results obtained by XPS. The contact angle is decreased from 76° (virgin PET) to 40° (at 14.5% grafting) and 38° (at 21.5% grafting). Since, PAA is hydrophilic in nature which reduces the contact angle with increase in the graft level and at higher grafting (at 14.5 and 21.5%), the surface of PET fibres are almost completely covered by grafted AA, the contact angle remains lowest and almost constant.

The topography of fibre surfaces, as observed by AFM, is shown in Figure 11. The roughness is

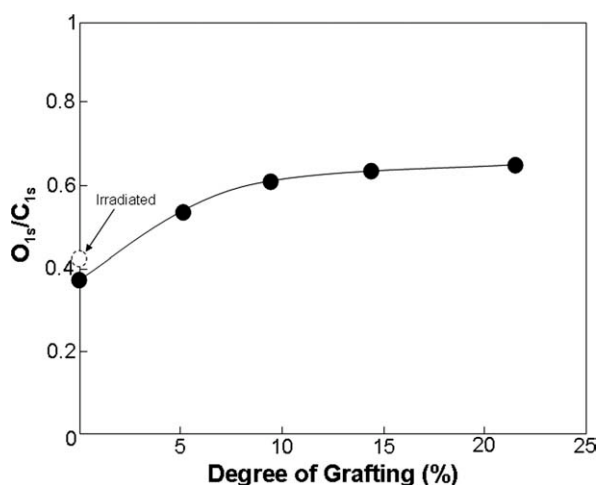


Figure 9 Variation of O_{1s}/C_{1s} with the degree of grafting on PET fabrics.

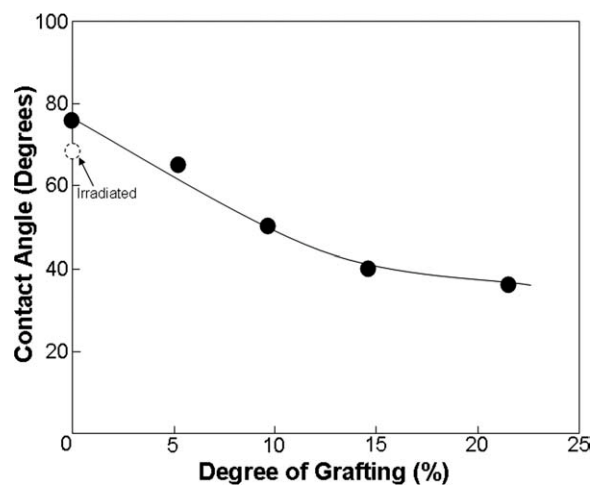


Figure 10 Variation of contact angle with the degree of grafting on PET fabrics.

increased on gamma treatment is due to the chain break, disproportionation and β -scission. Roughness is a measure of the texture of a surface. It is quantified by the vertical deviations of a real surface from its ideal form. If these deviations are large, the surface is rough; if they are small the surface is smooth. Therefore, when the grafting is increased, there are large vertical deviations in comparison to virgin surface. The increase in the number of vertical deviations may be due to the increase in the number of grafted chains at higher grafting. At 21.5% grafting, the surface become smoother as in virgin PET fibre surface which may be due to the almost complete covering of grafted AA onto the surface [see also Fig. 12(g)].

The surface morphology of grafted fabric is strongly affected as the grafted AA increases on the PET surface (Fig. 12). The gamma treated surface seems to be rough in comparison to virgin PET surface. The distinction is attributed to the fragmentation of polymer chains caused by the surface etching.²⁰ As the degree of grafting increases, it is found that the surface roughness is also increased upto 14.5% grafting. At 21.5% grafting, a layer of PAA is deposited which may be due to the longer chain length of grafted AA. The AFM and SEM observations clearly indicate that the grafted chains form their own domains and morphologies at the surface.

CONCLUSIONS

The graft polymerization of AA onto PET led to considerable changes in physical and thermal properties of the fabrics. The IDT and T_{50} of PET-g-AA were increased with increase in the degree of grafting due to the formation of stable anhydride by the cyclization of PAA chains at elevated temperatures. DSC

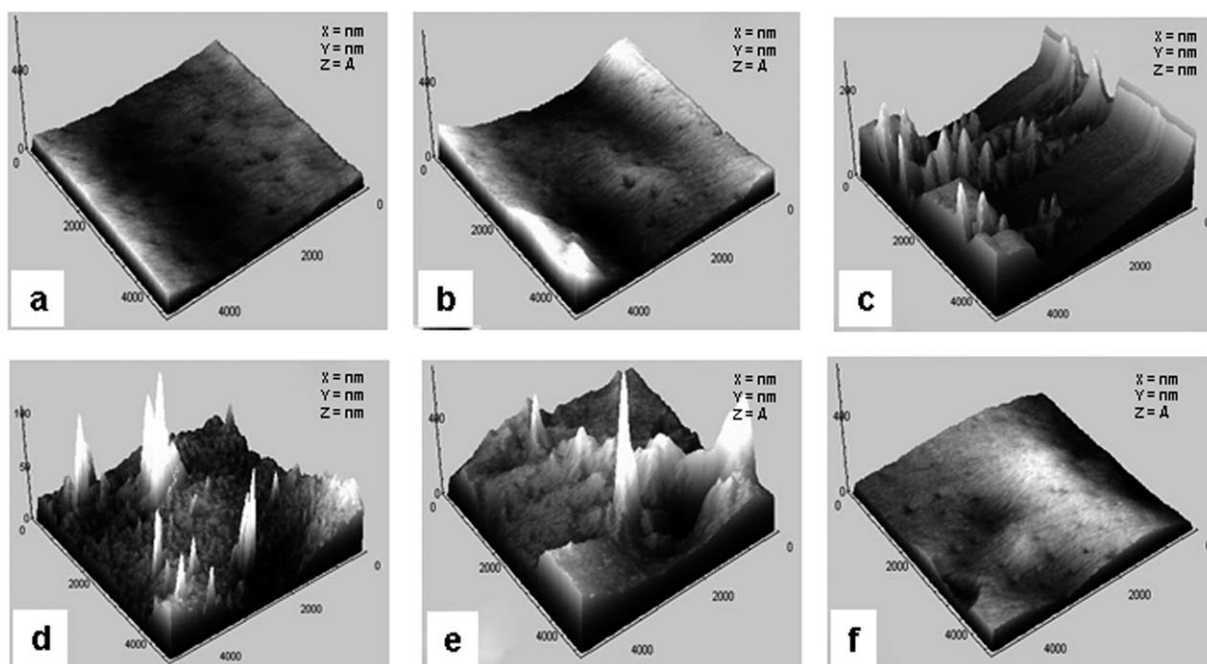


Figure 11 AFM of PET fabrics (a) virgin; (b) γ -irradiated; and PET-g-AA in (c) 5.3% grafting; (d) 9.5% grafting; (e) 14.5% grafting; (f) 21.5% grafting.

thermograms of grafted fabrics were shown the appearance of dual melting thermogram from 9.5% of grafting. This is the indication of destruction and reorganization of crystallites within the fibers of PET fabric. Both the heat of fusion and crystallinity were decreased with an increase in grafting because of the addition of a PAA chain within the noncrystalline region. The elemental compositions of various PET samples were shown that there was significant

increase in O_{1s}/C_{1s} ratio on irradiation as well as with increase in the degree of grafting. This is the evidence of the visualization of the grafting mechanism. The surface topography and morphology on the grafted surface was strongly influenced with the increase in grafting which was carried out in MEK/water (60:40) mixture and observations were clearly indicated that the grafted chains form their own domains and morphologies at the surface.

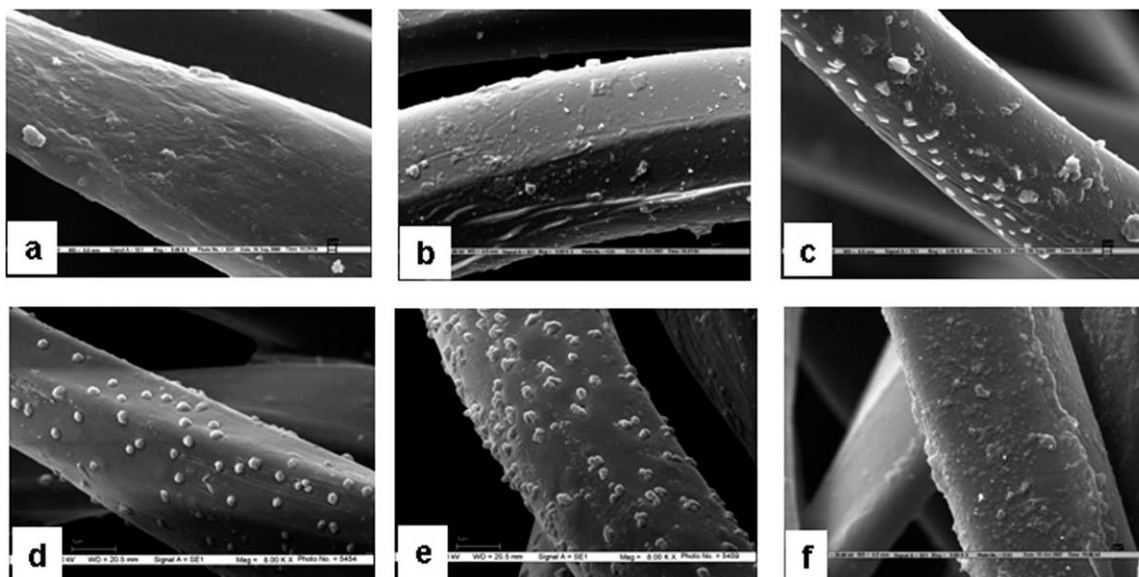


Figure 12 SEM of PET fabrics (a) virgin; (b) γ -irradiated; and PET-g-AA in (c) 5.3% grafting¹⁵; (d) 9.5% grafting; (e) 14.5% grafting; (f) 21.5% grafting.

References

1. Stannett, V.; Walsh, W. K.; Bittencourt, E.; Liepins, R.; Surles, J. R. *J Appl Polym Sci* 1977, 31, 201.
2. Liepins, R.; Surles, J. R.; Morosoff, N.; Stannett, V. T.; Barker, R. H. *Rad Phys Chem* 1977, 9, 464.
3. Zahran, A. H.; Stannett, V.; Liepins, R.; Morosoff, N. *Rad Phys Chem* 1980, 16, 265.
4. Kattan, M.; El-Nesr, E. *J Appl Polym Sci* 2006, 102, 198.
5. Faterpeker, S. A.; Potnis, S. P. *J Appl Polym Sci* 1982, 27, 3349.
6. Huglin, M. B.; Zlatev, V. B. *Eur Polym J* 1974, 10, 199.
7. El-Arnaouty, M. B.; Ghaffar, A. M. A.; El-Shafey, H. M. *J Appl Polym Sci* 2008, 107, 744.
8. Zaharescu, T.; Ciuprina, F. *Nucl Inst Methods Phys Res B* 2005, 236, 575.
9. Mariani, M.; Ravasio, U.; Consolati, G.; Buttafava, A.; Giola, M.; Faucitano, A. *Nucl Inst Methods Phys Res B* 2007, 265, 245.
10. Hu, S. G.; Jou, C. H.; Yang, M. C. *J Appl Polym Sci* 2002, 86, 2977.
11. Chapiro, A. *Radiation Chemistry of Polymeric Systems*; Wiley-Interscience: New York, 1962.
12. Gupta, B.; Chapiro, A.; Scherer, G. G. *J Mol Sci* 1996, 118, 231.
13. El-Gendy, E. H.; El-Shanshoury, I. A. *J Appl Polym Sci* 2004, 92, 3710.
14. El-Gendy, E. H.; El-Shanshoury, I. A. *J Appl Polym Sci* 2006, 101, 1007.
15. Gupta, B.; Grover, N.; Singh, H. *J Appl Polym Sci* 2009, 112, 1199.
16. Anjum, N.; Gupta, B.; Riquet, A. M. *J Appl Polym Sci* 2006, 101, 772.
17. Gupta, B.; Muzyyan, N.; Saxena, S.; Grover, N.; Alam, S. *Radiat Phys Chem* 2008, 77, 42.
18. Jain, R.; Gupta, B.; Anjum, N.; Revagade, N.; Singh, H. *J Appl Polym Sci* 2004, 93, 1224.
19. Yiqun, Z.; Danliang, J.; Xinfang, C.; Zhanchen, C.; Yuxia, L.; Hua, L. S. *Radiat Phys Chem* 1994, 43, 459.
20. Gupta, B.; Mishra, S.; Saxena, S. *Rad Phys Chem* 2008, 77, 553.