Surface Designing of Polypropylene by Critical Monitoring of the Grafting Conditions: Structural Investigations

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ABSTRACT: Polypropylene-*g*-polyacrylic acid copolymers were prepared by graft polymerization of acrylic acid onto polypropylene (PP) using electron beam preirradiation method. Samples with various graft levels were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). The physical structure of grafted PP was significantly affected by the graft content. While XPS revealed an increase in the oxygen content on the PP surface, the crystallinity of the graft copolymer decreased with an increase in the degree of grafting. The heat of fusion as obtained from DSC decreased with the increase in the degree of grafting and was ascribed to the dilution of inherent crystallinity by the incorporation of amorphous polyacrylic acid grafted chains. The thermal stability of graft copolymers was also enhanced as compared to the virgin PP. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 772–778, 2006

Key words: polypropylene; acrylic acid; radiation grafting; XPS; X-ray diffraction; DSC; TGA

INTRODUCTION

The development of polymers for food packaging has created enormous interest with respect to the inherent quality of food during long term storage.[1,2] One of the requirements of food packaging has been to utilize antimicrobial packaging so that microbial infection could be controlled in the food items during storage. This is where a substantial amount of work is being directed to the incorporation of antimicrobial agents into such polymers/polymeric devices, so that they acquire ability to kill as well as inhibit the growth and metabolism of microbes.

The incorporation of antimicrobial agents onto the packaging surfaces has been visualized as appropriate alternatives. This may be achieved by blending the antimicrobial agent into the polymer or by the immobilization of the agent onto the polymer surface. However, the modification of polymer needs to be carried out in such a way that it acquires polar or ionic functional groups, where a specific drug may be linked up. Polypropylene is paraffinic in nature and is devoid of any polar site wherein the antimicrobial agent may be immobilized. Therefore, the functionalization of the polymer needs to be carried out prior to any antimicrobial treatment.

Radiation-induced grafting has been an interesting approach towards the modification of polymers, because the resultant material not only retains most of its original characteristics but also acquires additional properties of the grafted moiety.[3–10] Another advantage of the process is that the grafting may be accomplished in any form irrespective of the polymer shape and size.[11] However, the structure of the polymer may undergo considerable changes during the graft modification process depending on the nature and the amount of monomer being grafted. These changes may be in terms of the crystallinity, mechanical strength, and thermal stability depending on the compatibility of the grafted component with the backbone matrix. The grafted material may behave as the bicomponent system as observed in FEP-*g*-polystyrene system,[12] or else, it may undergo multi-step degradation pattern as evident from the thermogravimetric analysis (TGA) pattern of polyethylene-*g*-polyacrylamide films.[13] In our previous investigation, we have reported the preirradiation grafting of acrylic acid onto polypropylene (PP) sheet in such a way that the grafts remain confined to the surface layers.[14] It was observed that by following grafting reaction in pure acrylic acid, the graft enrichment was achieved on the surface. Any addition of solvent for polyacrylic acid, such as water in the reaction medium, led to the graft migration deep into the bulk of the matrix. The surface confinement of the grafts leaves behind a large fraction of the polymer bulk intact, so that mechanical

properties of the modified PP are expected to be significantly retained. In spite of the low graft levels, it is bound to show significant impact on the structure and properties of the modified matrix. The present investigation is aimed at the evaluation of the structural changes in PP matrix occurring during the grafting of acrylic acid. These changes occurring in terms of crystalline structure and thermal behavior are presented in this paper.

EXPERIMENTAL

Materials

Polypropylene (PP) of 1-mm thickness was received from Goodfellow Cambridge Ltd. (UK). Acrylic acid and Mohr's salt was supplied by Aldrich (Germany). Acrylic acid was used without any purification. RBS-35 was supplied by Chemical Products (Belgium). Distilled water was used for all the experiments.

Irradiation

Electron beam (Linear electron accelerator CIRCE II) was used for the irradiation of polypropylene sheets. The energy of electron beam was 10 MeV and the power was 20 kW with the speed of 0.44 m/min (IONISOS laboratory, Orsay, France). The irradiation was carried out in air for the dose of 100 kGy. Samples were exposed twice for the irradiation (dose of 50 kGy each). After the irradiation, polypropylene sheets were kept at $-80°C$ prior to the grafting reaction.

Grafting reaction

Grafting reaction was carried out in a closed reactor.[14] The required amount of monomer solution in water was added to the glass reactor along with the Mohr's salt as homopolymer inhibitor. The reactor was placed in an oven at 70°C. Electron beam irradiated PP sheet (100 kGy) was placed in monomer solution in a closed reactor. Argon was continuously purged into the reaction mixture to create inert atmosphere. After a desired period, grafted PP sample was taken out and washed with distilled water in ultrasonic water bath at 40°C. Grafted PP samples were dried overnight in an air oven at 40°C. The degree of grafting 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 ungrafted and grafted PP sheets, respectively.

X-ray photoelectron spectroscopy

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

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. Cu Kα radiation (wavelength, 1.54 Å; filament current, 30 mA; voltage, 40 kV) was used for the generation of X-rays.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) studies on samples were carried out on Perkin–Elmer DSC-7 system. Vacuum dried samples were loaded into DSC, and the thermograms were run in the temperature range 50–180°C under nitrogen atmosphere at a heating rate of 10°C/min. The heat of fusion (ΔH_f) was obtained from the area under the melting thermograms. The crystallinity of PP was obtained from the following expression:

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

Where, ΔH_f is the heat of fusion of the sample and $\Delta H_{f(\text{crys})}$ is the heat of fusion of 100% crystalline PP and was taken as 163 J/g.[15]

Thermogravimetric analysis

TGA studies on samples were carried out on Perkin–Elmer TGA-7 system. The thermograms were run in the temperature range 50–550°C under nitrogen atmosphere at a heating rate of 10°C/min. 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.

RESULTS AND DISCUSSION

The grafting of acrylic acid onto polypropylene was carried out to functionalize the polymer in such a way that the surface layers acquire carboxyl groups. Distinct differences arise in terms of the surface chemistry when grafting on PP was carried out under pure monomer and aqueous monomer conditions and has

TABLE I
XPS Data on PP-g-PAAc Samples

Sample	Grafting conditions	C_{1s}			O_{1s}			O_{1s}/C_{1s}
		Side 1	Side 2	Average	Side 1	Side 2	Average	
Virgin PP	–	89.6	93	91.3	10.4	7.0	8.7	0.09
5.8% Graft	80% [M]	74.5	75.2	74.8	25.4	24.7	25.0	0.33
10.7% Graft	80% [M]	75.8	75.5	75.6	24.2	24.5	24.3	0.32
4% Graft	Pure [M]	70.7	69.5	70.1	29.3	30.5	29.9	0.43
10.8% Graft	Pure [M]	71.8	71.0	71.4	28.2	29.0	28.6	0.40

been evident from the contact angle and IR microscopy investigations.[14] However, specific changes in physical structure of polypropylene as a function of the degree of grafting have also been observed in this system. A precise monitoring of the structural features of samples containing different graft levels has revealed interesting informations.

The surface composition of virgin and grafted PP as investigated by XPS is presented in Table I. In spite of the paraffinic nature of PP, it has 8.7% oxygen content. This may be the outcome of the processing of the polymer at elevated temperature, which leads to the thermo-oxidative degradation of the matrix and partially due to the surface oxidation of the polymer during storage. The C_{1s} content in PP decreases and the O_{1s} increases significantly in the grafted samples. Both the sides of the PP sheet show identical C_{1s} and O_{1s} content. This reflects the efficiency of the grafting process in imparting the surface graft homogeneity under our experimental set up. Moreover, the C_{1s} and O_{1s} contents remain identical in samples containing different amount of polyacrylic acid (PAAc) but prepared at specific monomer concentration. This is the visualization of the grafting front mechanism, as reported in our earlier publication.[14] It is observed that the grafting is a diffusion controlled process, where the initial grafting takes place on the PP surface and further grafting follows into the subsequent layers by progressive monomer penetration through the grafted layers. Therefore, even if the graft level increases, the oxygen content does not increase because of the graft migration within the surface layers. The O_{1s}/C_{1s} ratio for the samples prepared under 80% monomer concentration and in pure monomer were found to be 0.33 and 0.43, respectively, (Table I). However, a pure PAAc layer on PP surface would have given O_{1s}/C_{1s} ratio of 0.66. Moreover, XPS can monitor 4–6 nm on the polymer surface. Therefore, it may be stated that at least this surface layer is composed of both the PP and PAAc chains.

The most significant finding of XPS investigation is that the graft distribution on PP surface is the function of the grafting medium. The grafting in pure monomer leads to higher O_{1s} content as compared with the grafting under aqueous monomer conditions. The comparison of 10.8% grafted sample prepared under these conditions shows that the O_{1s} content on the surface prepared under aqueous conditions is 24.3%, while it moves to 28.6% when the grafting is accomplished in pure monomer. This is the outcome of the PAAc enrichment on the PP surface when the reaction is carried out under pure monomer. This strengthens our earlier assumption that in the diluted monomer, water acts as the vehicle for the monomer permeation within the surface layers so that most of the grafts tend to move inside and relatively little grafts remain on the surface.[14] Under pure monomer conditions, the PAAc chains get precipitated out and instead prevent the grafted zone from swelling and retard the monomer migration within the surface layers.

The X-ray diffraction patterns of samples with different degrees of grafting are presented in Figure 1. The crystalline reflections for unmodified and grafted PP occur at identical angles. However, the intensity of the crystalline peak decreases with an increase in the degree of grafting. The X-ray diffraction for PAAc formed during the grafting process shows its amorphous nature, which has been observed by other workers as well.[16] The variation in the percent crystallinity with the degree of grafting is presented in Figure 2. Interestingly, the electron beam exposure of PP leads to slight enhancement in the crystallinity from 52.8 to 54.2%. This may be attributed to the fact that chain scission dominates during the e^- beam irradiation, and these short chains tend to reorganize themselves into crystalline structures subsequently.[17] Since the grafting is carried out on exposed samples, a comparison of the crystallinity in grafted samples needs to be carried out with that of the exposed PP sample. The results in Figure 2 show a decrease in the crystallinity with the increase in the degree of grafting. It may be stated that since PAAc chains are amorphous in nature and the apparent decrease in crystallinity may be assigned to the dilution of the inherent crystallinity of PP by the incorporation of amorphous PAAc grafted component.[18,19]

DSC thermograms of the ungrafted and grafted PP samples are presented in Figure 3. All the thermograms show identical shape but the area under the thermograms for grafted samples diminishes as com-
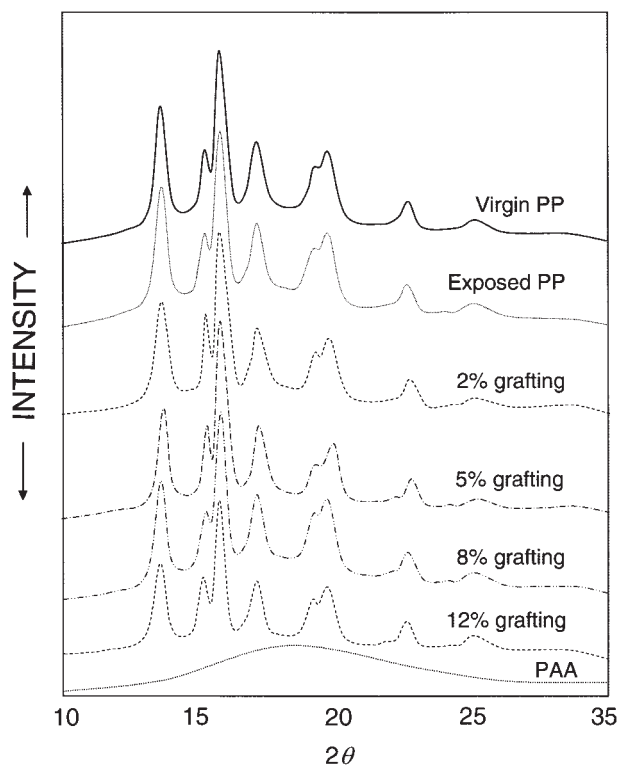
Figure 1 X-ray diffraction patterns of PP-*g*-PAAc copolymers with different degrees of grafting.
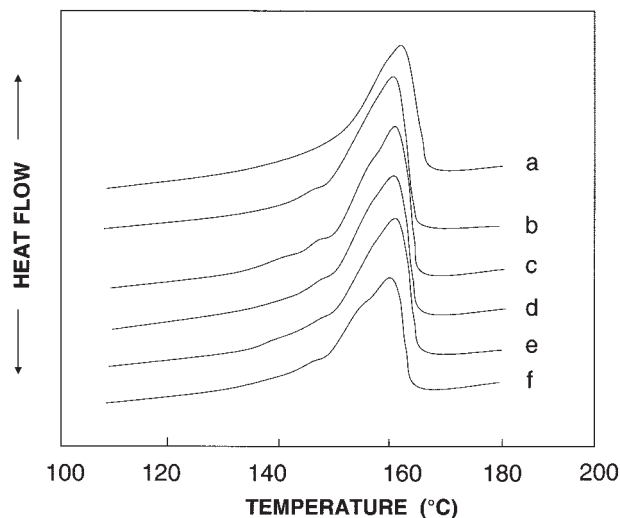

Figure 3 DSC thermograms of virgin PP (a) exposed PP (b) and PP-*g*-PAAc copolymers with different degrees of grafting: (c) 2%, (d) 5%, (e) 8%, and (f) 12%.

pared with PP. The variation in the heat of fusion and the melting temperature with the degree of grafting is presented in Figure 4. The melting peaks remain identical as a result of the grafting process. This suggests that the perfection of crystallites is not impeded by the grafting process. The exposure of the PP to a radiation dose of 100 kGy increases the heat of fusion from 74 to 77.5 J/g. These results strengthen the X-ray diffraction observations that the crystalline reorganization takes

place during the irradiation of PP, as discussed in the preceding sections.

A comparison of the heat of fusion values of the grafted samples with that of the exposed sample shows considerable loss in heat of fusion. The higher the degree of grafting, the lower is the heat of fusion. The X-ray diffraction studies have revealed that the PAAc is amorphous in nature (Fig. 1). Therefore, incorporation of PAAc grafts would never lead to the enhancement in crystallinity of the PP sample. In fact, a decrease in the heat of fusion of grafted samples may be because of the addition of amorphous PAAc chains within the PP matrix. The crystallinity of samples, as calculated from the heat of fusion values, i.e., eq. (2), is presented in Figure 5. Therefore, if we follow the amorphous nature of PAAc, the crystallinity should be
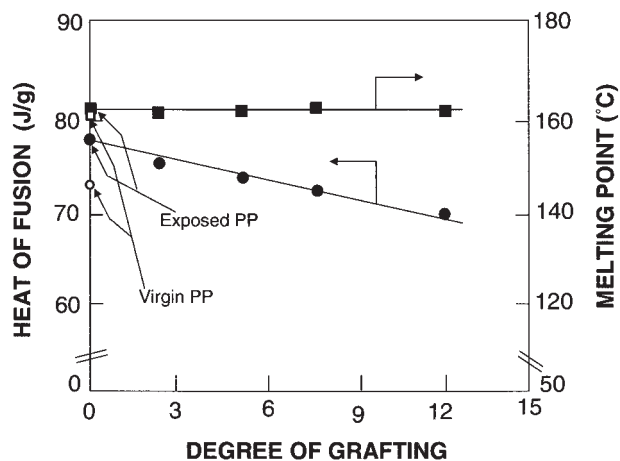

Figure 2 Variation of the percent crystallinity with the degree of grafting in PP-*g*-PAAc copolymers.

Figure 4 Variation of the heat of fusion and the melting temperature with the degree of grafting in PP-*g*-PAAc.
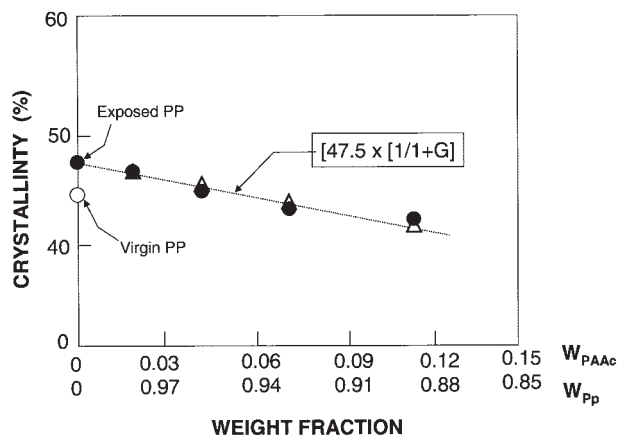
Figure 5 Variation of the crystallinity with the weight fraction of PP and PAAc in PP-*g*-PAAc copolymer matrix (●) calculated crystallinity; (Δ) experimental values.

Figure 6 Thermogravimetric analysis thermograms of virgin PP, exposed PP and PP-*g*-PAAc copolymers with different degrees of grafting.

a function of the PP fraction (Wpp) within the graft copolymer matrix. The crystallinity of a grafted polymer may therefore be corrected for the weight fraction of PP as per the following equation,

$$\text{Inherent crystallinity} = 47.5 \times [1/1+G] \quad (3)$$

where, 47.5 is the crystallinity of electron beam irradiated PP, G is the extent of grafting and $[1/1 + G]$ represents the weight fraction of PP in the grafted matrix.. Therefore, if the PAAc exerts dilution over the inherent crystallinity, the crystallinity in the graft copolymers must follow the trend according to the eq. (3), as depicted by the straight dotted line in Figure 5. The crystallinity of the grafted samples as obtained from the thermograms falls on this straight line. This suggests that the inherent crystallinity of PP is not impeded by the grafting process and the observed behavior of loss in crystallinity is essentially due to the addition of amorphous PAAc chains within the PP matrix. These results therefore suggest that the grafting proceeds solely within the noncrystalline region of PP matrix and the inherent crystallites remain unaffected. Our findings are well supported by the observations on FEP-*g*-polystyrene graft copolymer films and sulfonated membranes.[12,20] It was observed that the grafting of polystyrene does not influence the inherent crystallinity of the FEP films. However, the sulfonation of these grafted films leads to significant destruction of the crystalline regions in the FEP matrix. A cumulative effect of the dilution effect of the grafted polystyrene component and the crystal defect has been proposed for the crystallinity loss in these studies. Li et al.[21] have investigated the crystalline changes in styrene grafted PTFE films by X-ray diffraction. It has been proposed that the deviation in crystallinity from the expected line is due to dilution effect and the crystalline decomposition. However,
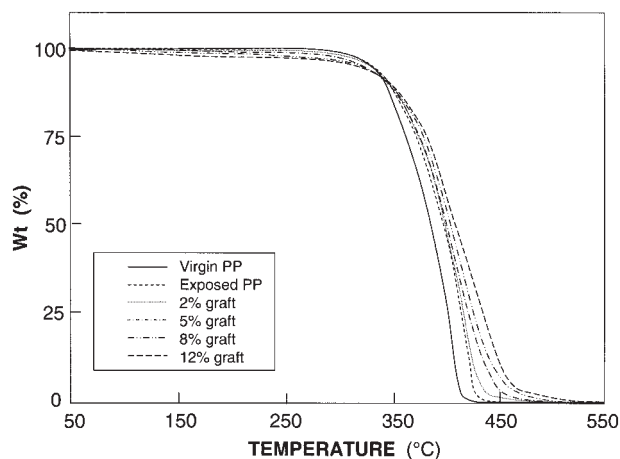
authors have compared the crystallinity of grafted samples with that of the nonexposed films. The preirradiation of PTFE is bound to change the crystallinity of the films even before any grafting is initiated and could have changed the pattern of the crystallinity variation.

TGA thermograms of virgin and grafted PP samples are presented in Figure 6. The virgin PP shows stable thermogram up to ~310°C beyond which smooth degradation takes place undergoing complete weight loss at 450°C. The electron irradiation of PP enhances the thermal stability of PP, which is reflected in an increase in initial decomposition temperature (IDT) from 310 to 330°C (Fig. 7). T50 temperature is also enhanced in the exposed sample. The grafting of PAAc onto PP further enhances thermal stability of the PP matrix. The degradation pattern moves to relatively higher temperature and a significant increase
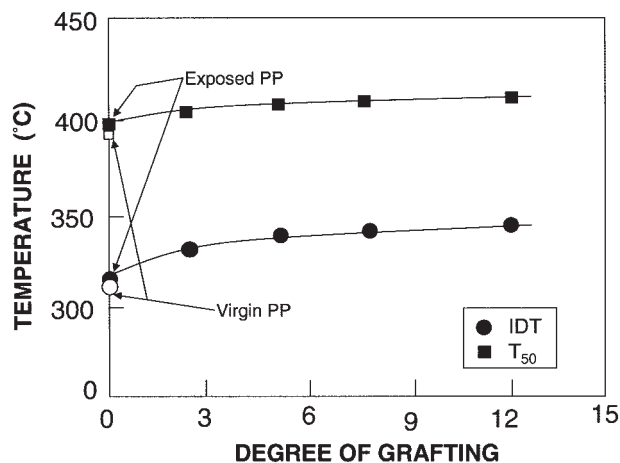

Figure 7 Variation of the IDT and T50 with the degree of grafting in PP-*g*-PAAc copolymers.
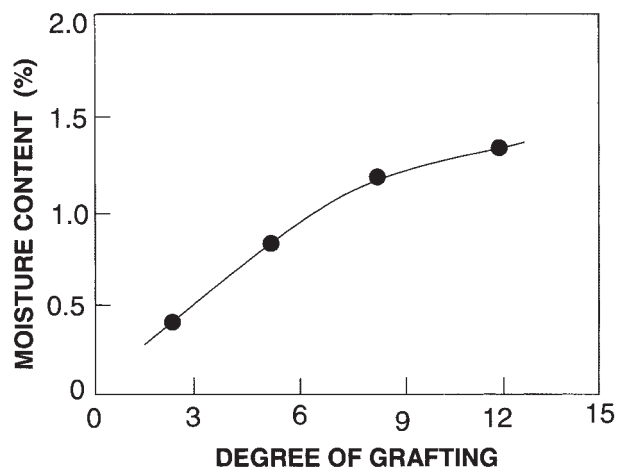
Figure 8 Variation of the moisture content with the degree of grafting in PP-*g*-PAAc copolymers.

Figure 9 Schematic representation of the cyclization reaction involving carboxyl groups in PP-*g*-PAAc copolymers.

in the IDT and T50 is observed. This is evident from the fact that IDT increases from 315 to 339°C and T50 is enhanced from 386 to 416°C for a sample with graft levels of 12%.

The grafted samples undergo weight loss right from the beginning of the thermogram and get stabilized around 180–200°C (Fig. 7). This may be ascribed to the dehydration process where moisture is eliminated from the hydrophilic matrix. Such a behavior has been the characteristics of several graft copolymer systems. Earlier study based on the TGA-FTIR-MS has shown that the loss of moisture from the grafted matrix proceeds up to 200°C.[22] This is the reason that we have monitored the weight loss in the range of 50–200°C as the dehydration step in our system. The weight loss in the dehydration step has been found to increase with the increase in the degree of grafting (Fig. 8). This is because of the fact that with the increase in the grafting, the hydrophilicity of the matrix also increases and the interaction of water with the grafted matrix is enhanced. One of the observations of the Figure 6 is the slow weight loss that prevails even after the dehydration process is over. It may be proposed that the carboxyl groups from the PAAc chains undergo cyclization at elevated temperatures and eliminate water molecules, which is reflected in the loss beyond 180°C. The decarboxylation of PAAc at elevated temperature may follow the interaction of two carboxyl groups for the same or adjacent chains to produce six-membered anhydride structures (Fig. 9). These anhydrides contribute to the higher thermal stability of the grafted matrix in our system. The formation of anhydrides by cyclization has also been reported in polymethacrylic acid as well and is projected to contribute to the thermal stability.[23]

The spectra for the sample with 12% grafting before and after the heat treatment at 220°C for 30 min is presented in Figure 10. The untreated sample shows
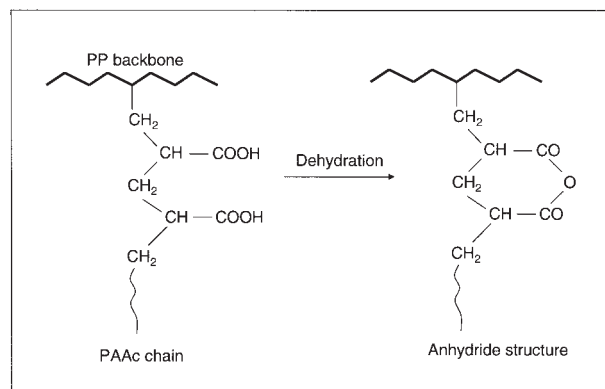
characteristic peak for carboxyl group at 1742 cm−1. However, the heat treatment of this sample leads to the origin of peaks characteristics of the anhydride structures. The appearance of dual peak at 1773 and 1808 cm−1 may be assigned to the symmetric —C=O stretching in anhydride ring.[24,25] However, the peak for carboxyl group at 1742 cm−1 diminishes slightly and shifts to 1738 cm−1 in the heat treated sample. The heat treatment leads to the appearance of another peak at 1061 cm−1, which is the characteristic of the O=C—O—C=O anhydride vibrations.[26] The peaks at 896 and 940 cm−1 may be the outcome of the out of plane —C—O— anhydride bending. These observations provide enough evidences for the cyclization reaction to anhydride structures that contribute to the better thermal stability of the grafted matrix as observed in the TGA thermograms.

CONCLUSIONS

Electron beam induced preirradiation grafting of acrylic acid onto polypropylene offers attractive way
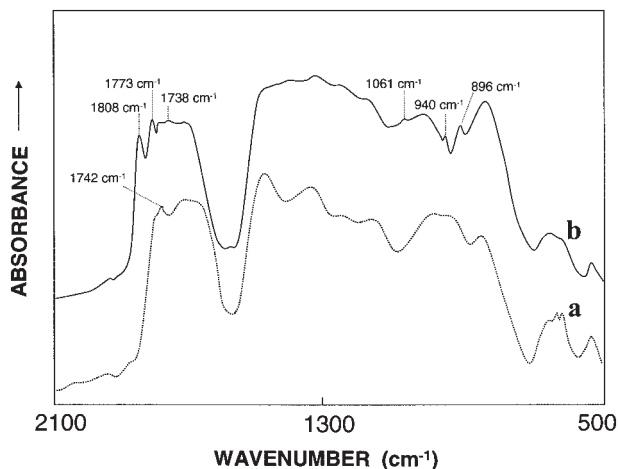

Figure 10 FTIR of the PP-*g*-PAAc copolymer with 12% degree of grafting. (a) before heat treatment; (b) after heat treatment at 220°C for 20 min.

to modify polymers for specific applications. The combination of the extremely hydrophilic PAAc with hydrophobic PP leads to significant changes in the physical structure of the copolymer structure. The crystallinity of the copolymers is significantly reduced with the increase in the degree of grafting. The X-ray diffraction and the DSC reveal that the PAAc grafts are incorporated within the PP matrix and exert dilution effect on the inherent crystallinity. The thermal stability of the grafted films is also significantly enhanced as compared with the virgin PP. This is due to the dehydration process involving two carboxyl groups from the same or adjacent chains which undergo cyclization and lead to the anhydride structures of higher thermal stability. The evidence towards the anhydride formation arises from FTIR investigations.

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