Polypropylene/Polypropylene-Grafted Acrylic Acid Blends for Multilayer Films: Preparation And Characterization

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ABSTRACT: Polypropylene (PP) was functionalized with acrylic acid (AA) and styrene (st) as a comonomer by means of a radical-initiated melt-grafting reaction. FTIR, ESCA, and ^{1}H-NMR spectroscopies were used to characterize the formation of polypropylene grafted with acrylic acid (PP-*g*-AA) and polypropylene grafted with acrylic acid and styrene (PP-*g*-AAst). The content of AA grafted onto PP was determined by using volumetric titration. Blends of PP with 0–100 wt % of PP-*g*-AA were prepared by melt mixing. The effect of the modified polymer content on the surfaces of cast films was characterized through FTIR–ATR and ESCA analysis as well as contact-angle, wetting-tension, and ink-adhesion measurements. The influence of the content of AA on the melting and crystallization temperature of PP was investigated by DSC. The contact angles of water on cast-film surfaces of PP/PP-*g*-AA blends decreases with increasing modified polymer content and decreasing PP-*g*-AA molecular weight. A notorious improvement on wetting tension was observed with increasing modified polymer content and decreasing PP-*g*-AA molecular weight. From FTIR–ATR and ESCA spectra of the blends, a calculation was made of the carbonyl index on the films' surfaces. It was found that the higher the carbonyl index, the lower the contact-angle value for the polypropylene blends. An increase in crystallization temperature of PP was observed when AA monomers were grafted into PP and with increasing PP-*g*-AA content in the blend, probably caused by a nucleation effect of AA monomers that would improve the crystallization capability of PP. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1497–1505, 2001

Key words: acrylic acid; polypropylene-grafted acrylic acid; styrene; contact angle; wettability

INTRODUCTION

Polypropylene (PP) has become one of the largest and faster growing polyolefins in use. PP is widely employed because of its low cost and versatile properties. However, PP is limited in several applications due to its low surface energy, lack of reactive sites, difficulty to dye, extremely poor hygroscopicity, weakness as a barrier to oxygen and many organic solvents, low melting and sticking temperatures, low impact strength, sensitivity to oxidation, and poor compatibility with polar polymers such as PA and EVOH. Chemical modification by means of grafting unsaturated polar groups onto the backbone of nonpolar resins has proven to be a viable method of providing PP with additional properties.[1–4] Several grafting monomers such as maleic anhydride (MAH), maleic acid (MA), dibutyl maleate (DBM), acrylic acid (AA), and glycidyl methacrylate (GMA) have been reported in the literature.[5–9] Styrene has been

Table I   Basic Characteristics of the Raw Materials

Polymer	AA Cont. (mol %)	M_w (g/mol $\times 10^{-3}$)	M_n (g/mol $\times 10^{-3}$)	M_n/M_w
PP	0	300	98	3.0
PP-*g*-AA	1.2	281	96	2.96
PP-*g*-AA (low)	1.2	200	90	2.22
PP-*g*-AAst	3.0	214	93	2.43
PP-*g*-AA(C)	6.0	134	50	2.86

used as a comonomer for the grafting of MA and GMA[10,11] onto PP. It was found that the grafting degree (GD) increased substantially with the addition of only small quantities of styrene and that the extent of chain scission was less severe. This increased GD was attributed to the formation of a charge transfer complex between styrene and the monomer, which is believed to be more reactive than the monomer alone toward the PP macroradical.

Graft copolymers are widely recognized as novel potential additives for imparting improved compatibilizing influence as an interaction promoter, in binary or multicomponent polymer blends,[12–14] and they are finding growing use in reactive blending.[15–17.] Functionalized polyolefins are often used as *in situ* compatibilizers of polymer alloys such as polyolefin polyamides and polyesters[18–22] because in many cases the grafted monomer functionality is able to react with —OH, —COOH, and NH$_2$. Several reports of using AA-grafted polyolefins as *in situ* compatibilizers can be found in the literature.[23–25] It is well known that the polar groups grafted onto the polyolefin also change the surface energy and difficulty to dye. AA and its esters were also grafted on the surface of polyolefins to improve the wettability and adhesion.[26] Similar to polymer alloys, the coextrusion process often involves the use of different incompatible polymers such as PA or EVOH, used as the oxygen-resistant layers, and polyolefins, used as the moisture barrier layers. Because of their incompatibility, these multilayer structures often require an intermediate tie layer such as a functionalized polyolefin to promote the adhesion needed. Several reports of using functionalized polyolefins as tie layers can be found in the literature.[27–29]

In the present study graft copolymerization of polypropylene with acrylic acid was attempted using dicumyl peroxide (DCP) as the initiator. The purpose was to use PP/PP-*g*-AA blends as an effective moisture barrier external layer and PA as an oxygen resistant central layer in a multilayer structure with adequate interfacial adhesion without using additional tie layers. The performance of these blends in three-layer coextruded films will be reported in a later article. The influence of concentrations of monomer, initiator, and preparation method on the grafting degree of PP-*g*-AA as well as the characterization of PP/PP-*g*-AA blends prior to the coextrusion process are reported.

EXPERIMENTAL

Materials

The materials used in this work were polypropylene (PP), supplied by PEMEX, with a melt index of 3 g/10min. Reagent-grade acrylic acid (AA) and styrene (St), with a purity of 99%, were purchased from Aldrich and used without further purification. The modified polypropylenes synthesized in the laboratory using AA and AA with St were designed as PP-*g*-AA and PP-*g*-AAst respectively. A low molecular grade of PP-*g*-AA [designated as PP-*g*-AA(low)] was obtained by degrading the PP-*g*-AA in a Brabender mixing chamber operating at 175°C and 50 rpm under an N$_2$ atmosphere until 50% torque decrease was observed. A commercial PP-*g*-AA–grade Polybond 1001 [designed as PP-*g*-AA(C)] was supplied by Uniroyal Chemical; it had a melt index of 40 g/10min (230°C). The molecular weight for the materials used are reported in Table I.

Grafting Procedure

Two procedures for were used in PP-*g*-AA preparation. In one procedure PP was introduced at 175°C into a mixing chamber of a Brabender-like apparatus. After the PP was melted, predetermined amounts of monomer (AA) and initiator (DCP) were added directly into the mixing cham-

Table II Effect of Concentration of DCP, AA, and Preparation Procedure on Content of AA in PP-*g*-AA and MFI

| PP (wt %) | DCP (wt %) | AA (wt %) | Cont. of AA in PP-*g*-AA (mol %) | | MFI[a] (g/10 min) | |
			Proc. 1	Proc. 2	Proc. 1	Proc. 2
100	0	0	0		3.0	
90	0.01	10	0.70	1.10	3.4	4.0
90	0.03	10	0.78	1.16	3.8	5.2
90	0.07	10	0.90	1.20	4.3	7.2
90	0.09	10	0.80	1.09	4.7	7.5
95	0.07	5	0.20	0.60	4.2	6.8
85	0.07	15	0.91	1.07	4.2	6.5
90	0.07	10/1*	—	3.0	—	7.8

[a] ASTM D1238, 230°C/2.16 Kg.
[b] 10/1 : 10 wt % of AA and 1 wt % of St.
Procedure 1: Procedure with direct PP–DCP–AA incorporation.
Procedure 2: Procedure with previous PP–DCP–AA impregnation.

ber, and mixing was continued for 6 min at 50 rpm. This procedure was designed as direct incorporation. In the other procedure, prior to being charged into the Brabender mixer for about 30 min, PP, monomer, and initiator were combined in a vessel at room temperature so that this mixture would be absorbed by the PP. This procedure was designed as previous impregnation. The mixture was then blended for 10 min at 175°C and 50 rpm. Mixing torque and melt temperature were recorded as a function of time for each run. The concentrations of AA and DCP are shown in Table II. PP-*g*-AAst was prepared mixing 1% of styrene, 10% of AA, and 0.07% of DCP into PP using the previous-impregnation procedure described above.

The grafted PP samples were milled to mesh 4, extracted using boiling xylene for 20 min, and then precipitated in acetone at room temperature. The dissolving-precipitating procedure was conducted three times to remove residual AA and traces of the poly(acrylic acid) homopolymer that might be formed during the free-radical grafting process. The purified graft copolymer was dried under a vacuum at 60°C.

Grafting Characterization

A Nicloet-710 Fourier transform infrared spectrophotometer and a VG CLAM 200 photoelectron spectrometer were used to qualitatively characterize the formation of PP-*g*-AA. The content of AA grafted into PP was determined using a hydrochloric acid–xylene titration method. A copolymer sample of about 1 g was dissolved in 100 mL of xylene at 130°C. After the sample was completely dissolved, the solution was titrated with 0.03N ethanolic potassium hydroxide solution to the first red color of the end point. Phenolphthalein–ethanol was used as the red indicator. The grafting degree (GD) was determined using the following relations[30]:

$$\text{GD \%} = \frac{\text{Acid Number} \times 72}{561} \quad (1)$$

Acid Number (mL of KOH/g of PP)

$$= \frac{\text{mL of KOH} \times \text{N KOH} \times 56.11}{\text{g of PP}} \quad (2)$$

The ^{1}H-NMR spectra of the copolymers were run on a Varian Gemini-200 BB. Solutions suitable for NMR measurements were prepared by dissolving 10–15 mg of purified grafted polymers in a mixture of 1,2,4-trichlorobenzene and deuterated chloroform heated at 115°C.

Blends Preparation and Characterization

PP/PP-*g*-AA blends were prepared by melt mixing, using a Brabender mixing chamber operating at 175°C and 50 rpm. Cast films of the PP/PP-*g*-AA blends were obtained by using xylene at 120°C and then casting them on a glass plate and evaporating the solvent in a vacuum oven at 120°C for 8 h. The chemical composition of the

surfaces of the blend films was investigated by attenuated total reflection infrared spectroscopy (FTIR–ATR) using a Nicolet 710 spectrometer and an ATR accessory element with a 45° entrance face and by XPS analysis using an VG CLAM 200 photoelectron spectrometer.

Contact angles of distilled water on the unmixed homopolymers and blend-cast films were measured. Liquid droplets were placed on samples of each film using a Pasteur micropipette, and a photograph of the droplet was obtained through a low magnification (ca. 100x) by using a homemade apparatus. Each contact angle was the average of at least eight measurements. The height (h) and the base (w) of the droplet were measured from the photograph and from geometric considerations; the contact angle was obtained using a microscope with image analysis.

Wetting tension measurements were made following the ASTM D 2578. This test method covers the measurement of wetting tension of polyethylene and polypropylene film surfaces in contact with drops of specific test solutions in the presence of air.

Ink adhesion measurements were made by sandwiching a thin layer of ink between two cast films and measuring the force required to peel the films apart with a crosshead speed of 17 cm/min using a Kayeness 1075 tensile tester.

A Du Pont 910 differential scanning calorimeter was used to investigate the thermal behavior of PP/PP-*g*-AA blends. Heating and cooling rates were 10°C/min. Specimen weight was about 10 mg.
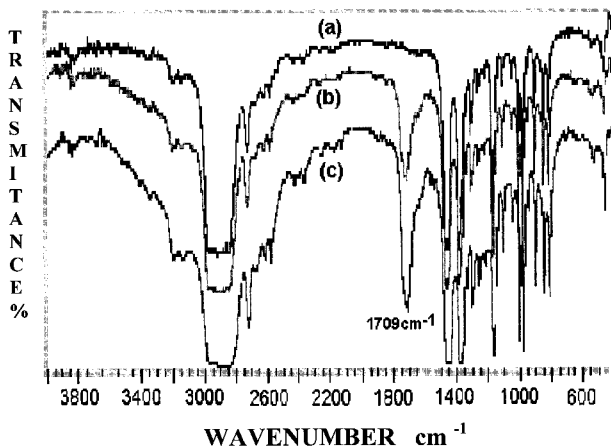

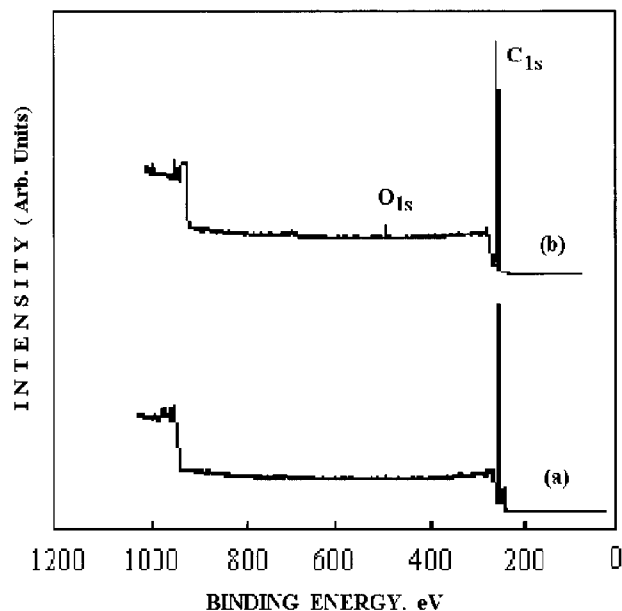**Figure 1**   FTIR spectra of (a) PP, (b) PP-*g*-AA, and (c) PP-*g*-AAst.

Figure 2   XPS spectra of (a) plain PP and (b) PP-*g*-AA.

RESULTS AND DISCUSSION

The FTIR spectra of the plain PP, PP-*g*-AA, and PP-*g*-AAst are shown in Figure 1. It can clearly be seen that a new absorption band at 1709 cm^{-1}, attributed to the carbonyl groups of AA, appears for both the PP-*g*-AA and PP-*g*-AAst samples. It also can be seen that the intensity of this band is much stronger for the PP-*g*-AAst sample. This result could be attributed to AA moieties grafted onto PP chains. Figure 2 shows the XPS spectra of the plain PP and the PP-*g*-AA. As can be seen, the intensity of the oxygen peak of the PP-*g*-AA is significantly larger than the value of the plain PP. The small oxygen peak of the plain PP comes from the absorbed oxygen of the air on the surface of the sample. Meanwhile, the larger oxygen peak observed in the PP-*g*-AA sample comes from the absorbed free oxygen in the air, as well as from the oxygen element of the carbonyl groups of the grafted PP.

The ^{1}H-NMR spectra are shown in Figure 3. It can be seen that PP shows the characteristic signals at 1.03 ppm for [dCH3], 1.42 ppm for [mCH2], and 1.74 ppm for [mCH]. On the other hand, PP-*g*-AAst and PP-*g*-AA(C) show, in addition to the PP characteristic signals, strong signals at 2.16 ppm, which is related to the CH proton from AA. This result verifies that AA has been grafted onto PP molecular chains.
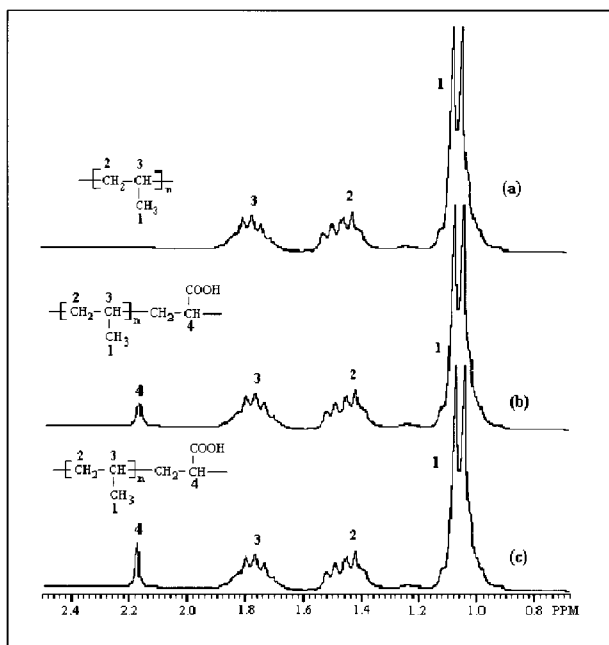
Figure 3 ^{1}H-NMR spectra for (a) PP, (b) PP-*g*-AAst, and (c) PP-*g*-AA (C).

Two methods were used with the PP-*g*-AA preparation, for both of which a noticeable reduction on torque was observed during melt mixing (Fig. 4). This is attributed to the DCP initiator, which creates free radicals that reduce the PP chain length, forming active sites for grafting AA and/or St onto PP. However, compared to the direct DCP and AA incorporation into PP, the reduction on torque was more drastic for the procedure in which the DCP and AA were combined with PP prior to being mixed. This can be attributed to the reduction in monomer evaporation during mixing and to better reactive absorption by PP when using the previous-incorporation procedure, which promotes more active sites and a more efficient grafting of AA onto PP (Table II).

The content of AA in PP-*g*-AA is dependent on the concentration of the initiator and monomer as well as on the preparation procedure used. As shown in Table II, when the monomer concentration was kept at 10%, a maximum AA content occurred at the DCP concentration of 0.07%. With increasing DCP concentrations, the melt index of PP-*g*-AA increased significantly. This feature can be related to the competition between the grafting reaction of PP-*g*-AA and the degradation of PP, which reduces the chain's length. Based on the data in Table II, PP-*g*-AA with 1.2 mol % of AA was selected for further studies. When using sty-

rene as a second monomer, a noticeable increase in grafting degree with no significant change in melt index were observed. This is in agreement with previous studies[10,11] that attributed the increase on grafting degree to the formation of a charge transfer complex between styrene and monomer, which is believed to be more reactive toward the PP macroradical than just the monomer alone.

The FTIR–ATR spectra of the surfaces of the films are summarized in Figure 5. The peak at 1709 cm^{-1} is related to the C=O stretching, which was used to differentiate one film from another. The spectra of the PP film show an almost insignificant peak at 1709 cm^{-1}, while the blends with PP-*g*-AA show a notorious peak at this wavenumber. Blends using PP-*g*-AA(low) and PP-*g*-AA(C) showed higher absorbance bands at this wavenumber. With a definition of the carbonyl index (CI) as the ratio between the peak at 1709 cm^{-1} and a constant reference peak height at 900 cm^{-1}, it was noted that this index (Table III) increased with the functionalized PP content. It can be inferred from this increase on C=O stretching absorbance that the films' surfaces contain increased amounts of C=O polar groups as the content of modified polymer in the blend is also increased. From Table III it can be observed
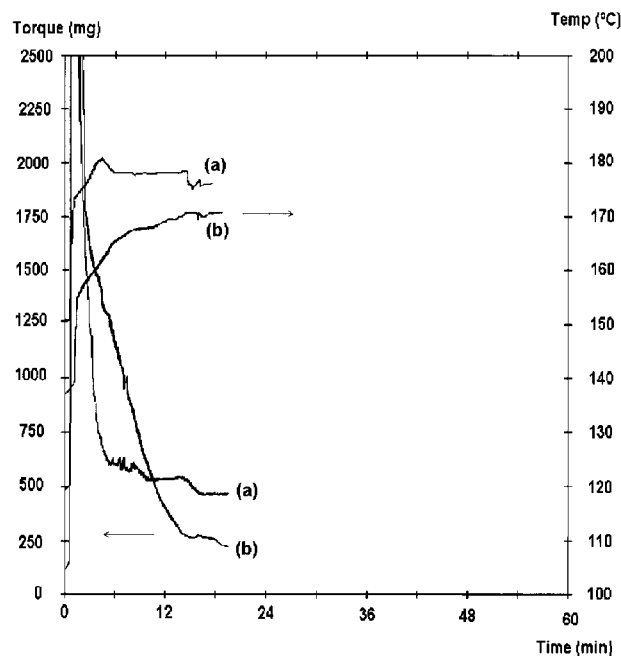

Figure 4 Torque-time curves for (a) mixture with direct DCP and AA incorporation and (b) mixture with previous DCP and AA impregnation into PP.
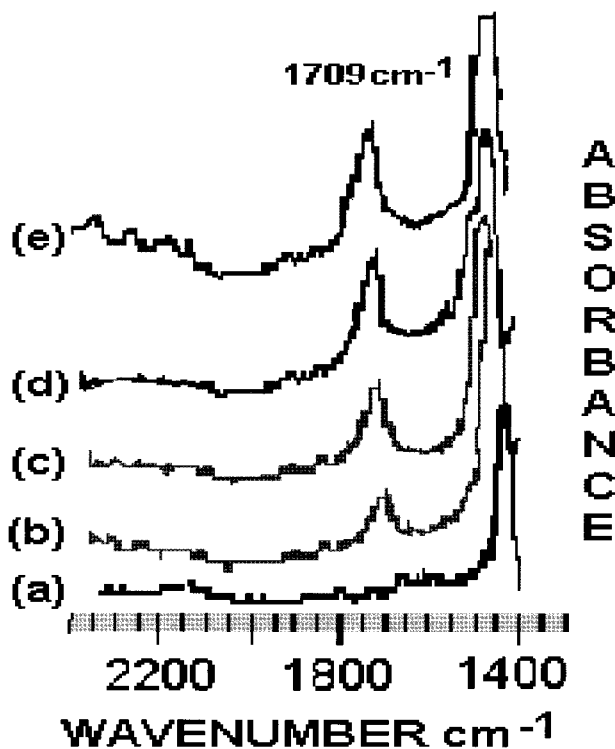
Figure 5 FTIR–ATR spectra of PP/PP-*g*-AA blends: (a) 100/0, (b) 50/50, and (c) 0/100; of PP/PP-*g*-AA(low) blend: (d) 50/50; and of PP/PP-*g*-AA(C) blend: (e) 50/50.

Figure 6 XPS spectra of PP/PP-*g*-AA blends: (a) 100/0 and (b) 50/50; of PP/PP-*g*-AA(low) blend: (c) 50/50, and PP/PP-*g*-AA(C) blend: (d) 50/50.

that for a similar PP-*g*-AA content on the blend, when using PP-*g*-AA of a lower molecular weight [PP-*g*-AA(low) and PP-*g*-AA (C)], higher carbonyl indexes were obtained.
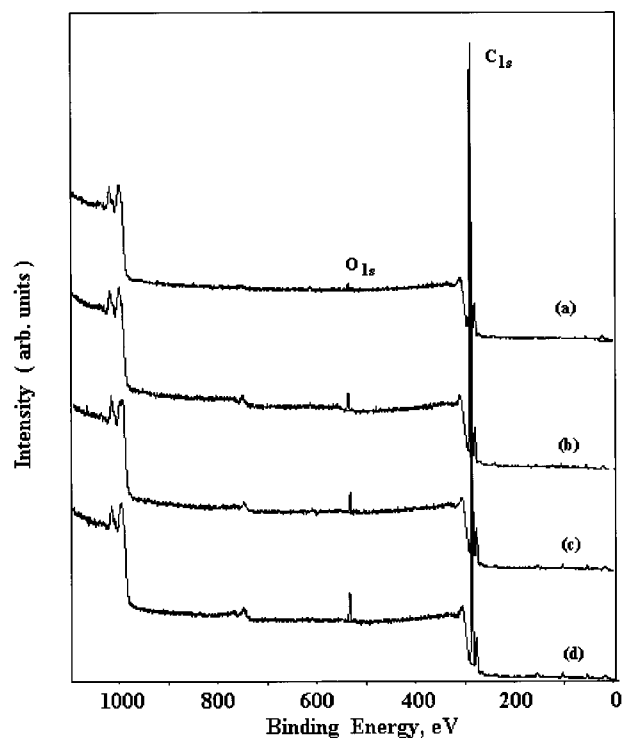
Figure 6 displays the XPS spectra of the PP/

PP-*g*-AA blends. As can be seen, with an increasing content of PP-*g*-AA in the blend, the intensity of the oxygen peak increases significantly. Table III shows the carbon (C) and oxygen (O) content obtained from XPS analysis for the different PP/

Table III   Carbonyl Index, C/O Ratio, Wetting Tension, and Contact Angle of Water on PP/PP-*g*-AA Blends

PP/PP-*g*-AA	Carbonyl Index (A 1709 cm^{-1}/A 900 cm^{-1})	C (%)	O (%)	θe (Degree $\pm$ 2)	Wetting T. (Dynes/cm)
100/0	0.045	99.85	0.14	121	30
75/25	0.33	—	—	118	30
50/50	0.551	99.04	0,916	111	31
25/75	—	—	—	106	31.5
0/100	1.36	97.28	2.65	101	33
PP/PP-*g*-AA (low)					
100/0	0.045	99.85	0.14	121	30
50/50	0.83	96.79	3.07	102	32
0/100	1.89	—	—	100	34
PP/PP-*g*-AA(C)					
100/0	0.045	99.85	0.14	121	30
50/50	3.43	96.60	3.31	99	35
0/100	6.17	—	—	97	36

PP-*g*-AA blends. The C:O ratio shows a behavior similar to that of the carbonyl index obtained by FTIR–ATR. This also suggests that the films' surfaces will contain increased amounts of C=O polar groups as the content of modified polymer in the blend is also increased. Similar to the results obtained with FTIR–ATR, a significant increase in oxygen content was found when PP-*g*-AA of lower molecular weights was used (Table III).

Displayed on Figure 7 are the photographs of four water drops on cast films of PP/PP-*g*-AA blends in the proportions 100/0, 75/25, 50/50, 25/75, and 0/100. It can be seen that with an increasing percentage of PP-*g*-AA, contact angles trends to decrease monotonically. This result suggests that the surface polarity of the films is augmented by an increase of the content of PP-*g*-AA on the blend.

The contact angle is very sensitive to the chemical and structural changes occurring on the polymer surface because the liquid makes contact with the outermost molecular layer of the surface.[31,32] The contact angles of water on the cast films of PP/PP-*g*-AA blends using PP-*g*-AA with different molecular weights are tabulated in Table III. All the equilibrium contact angles of the blends decrease when compared with the values of the control PP. For a similar PP-*g*-AA content in the blend, the contact angle of water shows a more notorious reduction when using PP-*g*-AA(low) of a lower molecular weight because such
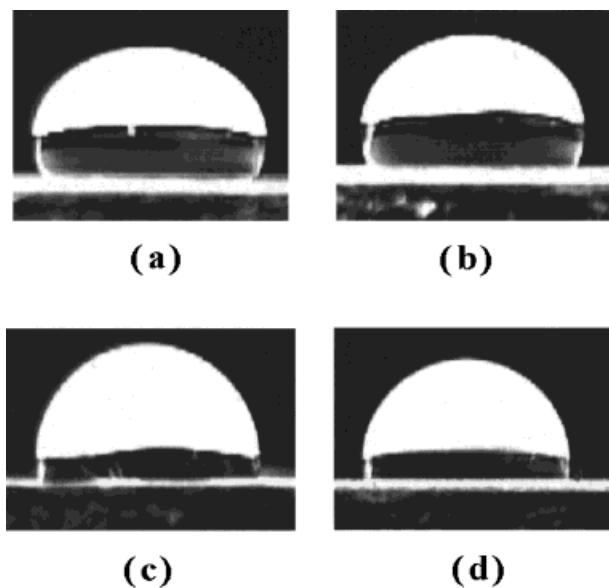

Figure 7   Water drops on cast films of PP/PP-*g*-AA blends: (a) 100/0, (b) 75/25 (c) 50/50, and (c) 0/100.
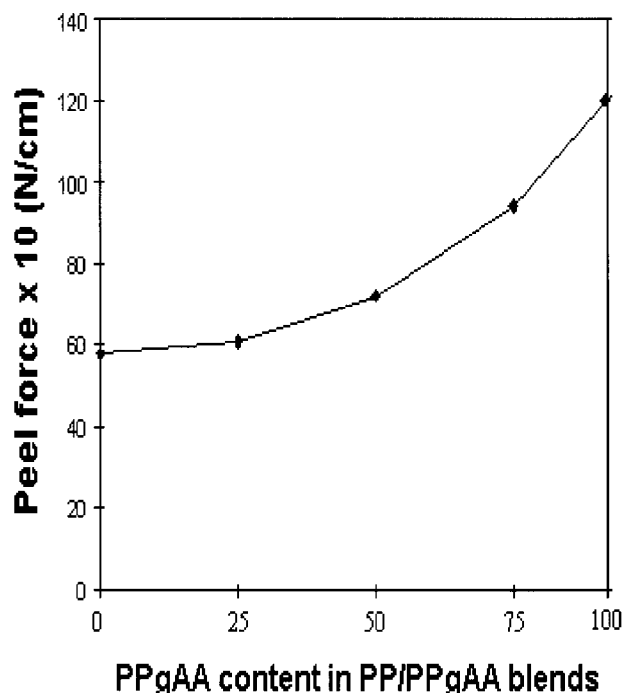

Figure 8   Ink adhesion as a function of PP-*g*-AA content in PP/PP-*g*-AA blends.

a lower molecular weight would improve migration of the PP-*g*-AA chains to the surface during preparation of the films and consequently would improve the surface polarity of the films, as was observed by FTIR–ATR and XPS analysis. Higher values of the carbonyl index and C:O ratio means more functional groups are present on the surface, and, as expected, the surface energy of the solid would be enhanced. This augmented surface polarity reduces the measured contact angle and increases the wetting of the liquid on the film surface. This was also observed from the wetting tension measurements (Table III), in which an increase on modified polymer content increases the wetting tension. This increase is more notorious when using modified polymers of a lower molecular weight.

Figure 8 shows the results of ink-adhesion measurements as a function of PP-*g*-AA content. It can be seen that below a PP-*g*-AA content of 50%, adhesion is almost negligible, and above this value, it rises rapidly to about 120 N/cm when using pure PP-*g*-AA. This result also suggests that the surface polarity of PP/PP-*g*-AA blends is augmented by an increase of the content of PP-*g*-AA, which promotes a better wetting of the ink on the surface.

DSC thermograms of the plain PP and of different AA contents in PP-*g*-AA are shown in Fig-

ure 9. Functionalization of AA onto PP did not result in any significant change in the melting temperature (T_m) of the polymer (167°C). The crystallization peak temperature (T_c) of PP (125°C) shifted to a higher temperature and was observed at 130°C and 132°C for PP-*g*-AA (AA = 1.2%) and PP-*g*-AA(C) (AA = 6%), respectively. Thermograms for the plain PP and PP/PP-*g*-AA blends are shown in Figure 10. T_m and T_c showed a behavior similar to that observed for the PP and PP-*g*-AA. The monomer-grafted position could account for these results. During the reaction initiated by DCP, the grafting reaction occurred on PP, and AA was bonded to PP. The grafted AA monomer acted as a nucleation agent. This might improve the crystallization capability of PP and crystallize it at higher temperatures. Similar results were found by other authors[20,33] who reported a nucleation effect of carbonyl groups on the crystallization of i-PP.

CONCLUSIONS

FTIR results confirmed that AA was grafted onto molecular chains of PP. The content of AA in
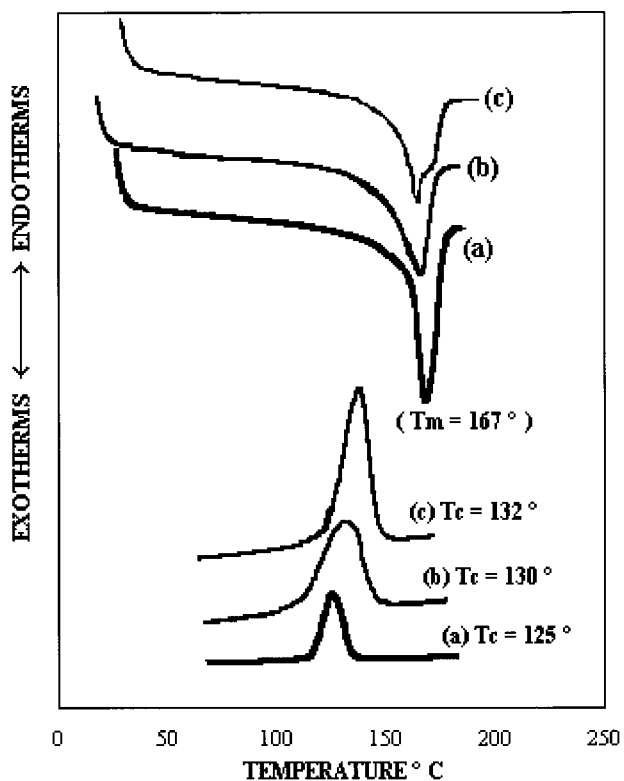
Figure 9 DSC melting and cooling thermograms of (a) plain PP, (b) PP-*g*-AA (AA = 1.2%), and (c) PP-*g*-AA (C) (AA = 6%).
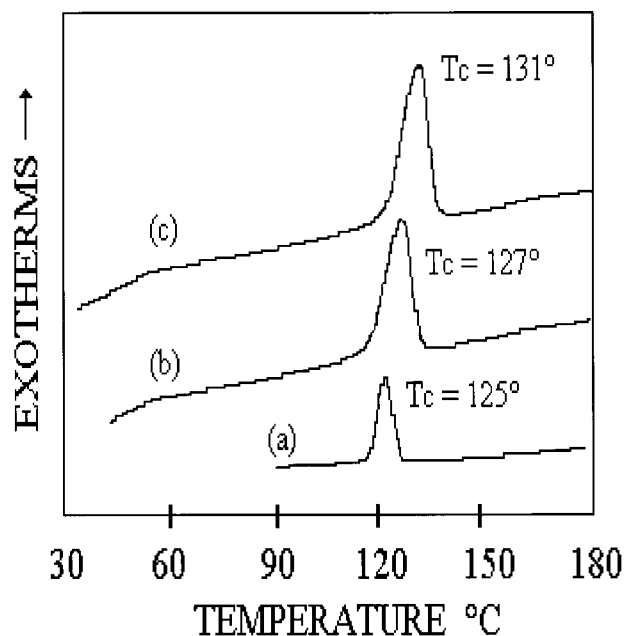
Figure 10 DSC cooling curves of (a) plain PP, (b) 50/50 PP/PP-*g*-AA, and (c) 50/50 PP/PP-*g*-AA(C).

PP-*g*-AA changed with the concentration of the initiator and monomer as well as with the incorporation procedure used. High functionalization levels with small amounts of chain degradation were obtained when using the previous PP-reactive impregnation method with an appropriate concentration of initiator. Using styrene as a second monomer produced a noticeable increase in grafting degree with no significant change in melt index. Thus, the carbonyl polar groups on the surface increase when the content of functionalized PP increases. Th contact angle of water on cast-prepared smooth surfaces of PP/PP-*g*-AA blends decreases when the modified polymer content increases. The surface polarity of PP/PP-*g*-AA blends is augmented by an increase of PP-*g*-AA content, increasing wetting tension and promoting a better wetting of a liquid on the surface. The functionalization of AA onto PP does not change melting temperature and increases the crystallization temperature of the polymer in both PP-*g*-AA and PP/PP-*g*-AA blends.

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