

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) by means of a radical-initiated melt grafting reaction. FTIR and ESCA were used to characterize the formation of PPgAA. The content of AA grafted onto PP was determined by using hydrochloric acid/xylene titration. Blends of PP with 0 to 100% wt of Polypropylene grafted with Acrylic Acid (PP-g-AA) were prepared by melt mixing. The effect of the modified polymer content on the surface of cast films was characterized through FTIR-ATR and ESCA analysis as well as contact angle and ink adhesion measurements. Roughness of the cast films was analyzed by atomic force microscopy (AFM). The influence of the content of PPgAA on the crystallization structure of PP was investigated by DSC. The contact angles of water on cast film surfaces of PP/PPgAA blends decreases with increasing modified polymer content and decreasing PPgAA molecular weight.

INTRODUCTION

Polypropylene has become one of the largest and faster growing polyolefin 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, poor 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 has been proven to be a viable method to give additional properties by means of grafting unsaturated polar groups onto the backbone of non polar resins (1-4). Several grafting monomers such as maleic anhydride (MAH), maleic acid (MA), dibutyl maleate (DBM), acrylic acid (AA) and its esters, have been reported in the literature (5-9). Graft copolymers are widely recognized as novel, potential additives to impart improved compatibilizing influence as an interaction promoter, in binary or multi-component polymer blends (10-12) and they are finding

growing use in reactive blending (13-15). Functionalized polyolefins are often used as in situ compatibilizers of polymer alloys such as polyolefin / polyamides, polyester (16-20) because in many cases the grafted monomer functionality are able to react with -OH, -COOH, and NH₂. Several reports of using AA grafted polyolefins as in situ compatibilizer can be found in the literature (21-23). It is well known that the polar groups grafted onto the polyolefin also changes the surface energy and difficulty to dye. AA and its esters were also grafted on the surface of polyolefins to improved the wettability and adhesion (24). Similar to polymers alloys coextrusion process often involves the use of different incompatible polymers such as PA or EVOH, used as the oxygen resistant layers and polyolefins as the moisture barrier layers. Due to their incompatibility, these multilayer structures often require an intermediate tie layer such as a functionalized polyolefins as tie layers can be found in the literature (25-27).

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 PP7PPgAA 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 preparation and characterization of these blends prior to the coextrusion process are reported.

EXPERIMENTAL

Materials

The materials used in this work were a polypropylene, PP supplied by PEMEX with melt index of 3 g/10 min (230 °C). Reagent grade AA was purchased from Aldrich with 99% of purity and used without purification. The PPgAA synthesized in laboratory was designed as PPgAA (Lab). A low molecular grade of PPgAA (designed as PPgAA (Deg)) was obtained degrading the PPgAA in a Brabender mixing chamber operating at 175 °C and 50 rpm. under N₂ atmosphere until 50 % torque decrease was observed. A commercial PPgAA grade Polybond 1001 (designed as PPgAA (Com)) was supplied by Uniroyal Chem. with melt index of 40 g/10 min (230 °C). The molecular weight for the materials used are reported in Table 1.

TABLE 1. Basic Characteristics of the Raw Materials.

| Polymer | AA Cont. (mol %) | M _w (g/mol x 10 ⁻³) | M _n (g/mol x 10 ⁻³) | M _w / M _n |
|-------------|---------------------|---|---|---------------------------------|
| PP | 0 | 416 | 77 | 5.41 |
| PPgAA (Lab) | 1.2 | | | |
| PPgAA (Deg) | 1.2 | 226 | 93 | 2.43 |
| PPgAA (Com) | 6.0 | 134 | 50 | 2.86 |

Grafting procedure

Two different procedures for PPgAA preparation were used. In one procedure PP was introduced into a mixing chamber of a

Brabender-like apparatus at 175 °C. After PP was melted, predetermined amounts of monomer (AA) and initiator (DCP) were added directly into the mixing chamber and mixing was continued for 6 min at 50 rpm. In other procedure, PP, monomer and initiator were combined in a vessel at room temperature for about 30 min prior to being charged into the Brabender mixer in order that this mixture would be absorbed by the PP. The mixture was then blended for 10 min at 175 °C and 50 rpm. Mixing torque and melt temperature were recorded as function of time for each run. Concentrations of AA and DCP are shown in

Table 2.

| PP (wt %) | DCP (wt %) | AA (wt %) | Cont. of AA in PPgAA (mol %) | | MFI ^(a) (g / 10 min) | |
|----------------|-----------------|----------------|--------------------------------------|------------|--------------------------------------|------------|
| | | | Proc. 1 | Proc. 2 | Proc. 1 | Proc. 2 |
| 100 | 0 | 0 | 0 | | 3.5 | |
| 90 | 0.01 | 10 | 0.07 | 1.10 | 3.5 | 4.0 |
| 90 | 0.03 | 10 | 0.78 | 1.16 | 3.8 | 5.2 |
| 90 | 0.07 | 10 | 0.9 | 1.2 | 4.3 | 7.2 |
| 90 | 0.09 | 10 | 0.8 | 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 |

^(a) ASTM D1238, 230 °C / 2.16 Kg.

Proc. 1 : Procedure with direct PP-DCP-AA incorporation

Proc. 2 : Procedure with Previous PP-DCP-AA impregnation

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 poly (acrylic acid) homopolymer which might be formed during the free-radical grafting process. Then purified graft copolymer was dried under a vacuum at 60 °C.

Grafting characterization

A Nicolet-710 fourier transform infrared spectro photometer and VG CLAM 200 photoelectron spectrometer from VG (Microtech Ltd) were used to qualitatively characterize the formation of PPgAA. 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 0.03 N ethanolic potassium hydroxide solution to the first red color of the end point.

Phenolphthalein/ethanol was used as the red indicator. The grafting level (GL) was determined by using the following relations:

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

$$\text{Acid number} \quad (\text{ml of KOH} / \text{g of PP}) = \frac{\text{ml of KOH} \times \text{N KOH} \times 56.11}{\text{g of PP}} \quad (2)$$

Blends preparation and characterization

PP/PPgAA blends were prepared by melt mixing using a Brabender mixing chamber operating at 175 °C and 50 rpm. Cast films of the PP/PPgAA blends were obtained using Xylene at 120 °C and casting them on a glass plate and evaporating the solvent in a vacuum oven at 120 °C for 8 hours. Chemical composition of the blend films surface was investigated by attenuated total reflection infrared spectroscopy (FTIR-ATR) using a Nicolet 710 spectrometer and an ATR accessory element with 45 degree entrance face and by XPS analysis using an VG CLAM 200.

Contact angles of distilled water on the unmixed homopolymers and blend cast films were measured. Liquid droplets were placed on samples of each film and a photograph of the droplet was obtained through a low

magnification (ca. 100x) by using a home made apparatus. Each contact angle was the average of at least 8 measurements. The height (h) and the base (W) of the droplet were measured from the photograph and from geometric consideration, the contact angle was obtained using a microscope with image analysis.

Ink adhesion measurements were made 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 dupont 910 differential scanning calorimeter was used to investigate thermal behavior of PP/PPgAA blends. Heating and cooling rates were 10°C per min. Specimens weight was about 10 mg.

Cristallinity was calculated by the heat of fusion of the PP peak on the polymer blend, on the assumption that H of PP was 209 J / g (21) when it was all in the crystalline state.

RESULTS AND DISCUSSION

FTIR spectra of the plain PP and PPgAA are shown in **Figure 1**. It is clearly seen that a new absorption band at 1720 cm⁻¹, which is attributed to carbonyl groups of AA appear for the PPgAA sample. This result verifies that AA has been grafted onto PP molecular chains. **Figure 2** shows XPS spectra of the plain PP and PPgAA. As can be seen, the intensity of the oxygen peak of PPgAA 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. Mean while the larger oxygen peak observed in the PPgAA 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.

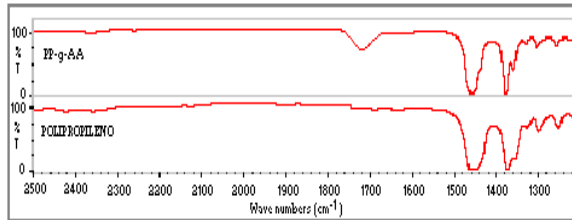


Figure 1. FTIR spectra of (a) PP and (b) PPgAA

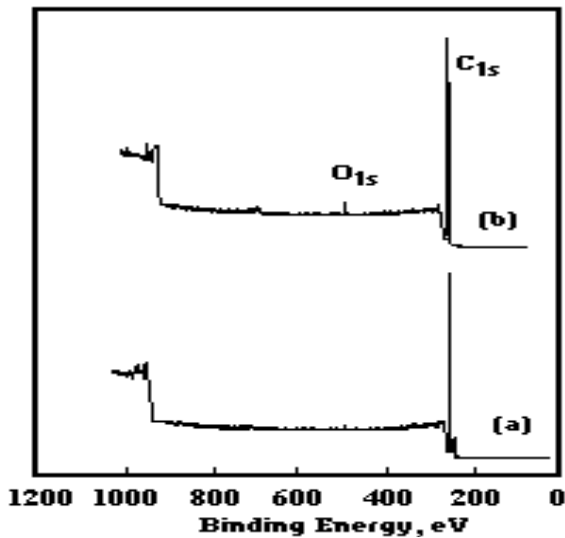
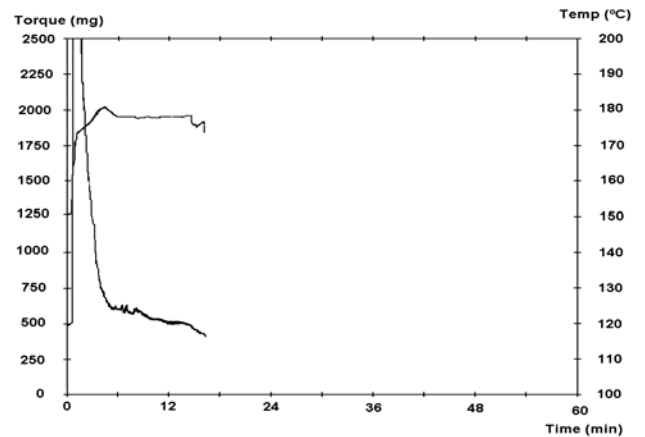


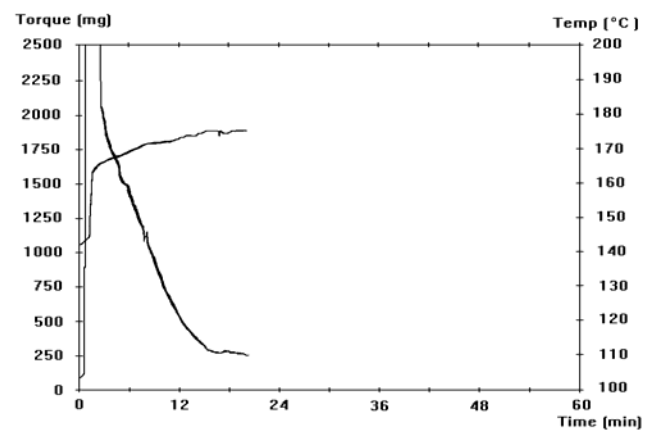
figure 2. XPS spectra of (a) Plain PP and (b) PPgAA

On PPgAA preparation two different methods were used, in both methods a noticeable reduction on torque was observed during melt mixing (Figure 3). This is attributed to the DCP initiator which creates free radicals that reduce the PP chain length forming active sites for grafting AA onto PP. However, the reduction on torque was more drastic for the procedure in which the DCP and AA were combined with PP prior to being mixed, compared with the direct DCP and AA incorporation into PP. This is attributed to the reduction in monomer evaporation during mixing and 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 2).



(a)



(b)

Figure 3. Torque-time curves for (a) mixture with direct DCP and AA incorporation and (b) mixture with previous DCP and AA impregnation into PP.

The content of AA in PPgAA is dependent upon concentration of initiator and monomer as well as of the preparation procedure used. As shown in Table 2, When the monomer concentration was kept at 10 %, a maximum AA content occurred at the DCP concentrations, the melt index of PPgAA increased significantly. This feature can be related to the competition between the grafting reaction of PPgAA with 1.2 mol% of AA was

selected for further studies and was designed as PPgAA(Lab).