Graft Copolymerization of Mixtures of Acrylic Acid and Acrylamide onto Polypropylene Film

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ABSTRACT: Liquid phase ultraviolet irradiation in the presence of benzophenone as a photosensitizer and barium hydroxide as a pH controller were used to graft the mixtures of acrylic acid and acrylamide to a polypropylene surface. The surface of the grafted polypropylene samples were characterized by Fourier transform infrared spectroscopy-attenuated total reflectance, electron spectroscopy for chemical analysis, scanning electron microscopy, and a contact angle meter. The pH value of the reaction medium that produced the graft with equal molar ratio was found to be ~ 3.77. The optimal reaction condition was found at a monomer feed of 25%, a reaction time of 30 min, and a benzophenone concentration of 1%. Surface tension of the samples increased to a value of 40 dyn cm⁻¹ due to the graft of the hydrophilic monomers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 251–256, 1999

Key words: acrylic acid; acrylamide; polypropylene; UV irradiation; graft polymerization; surface modification

INTRODUCTION

Graft copolymerization of polypropylene (PP) with water-soluble vinyl monomers leads to an appreciable improvement in its properties.¹ A major advantage of this modification is that whereas the bulk properties of PP are retained, the surface becomes hydrophilic.² The changed properties of the surface enable PP to have easier printability, better adhesion to other materials, greater comfort in fabrics, and easier dispersion in nonsolvents.³ In addition, the surface modification with hydrophilic monomers can provide the specific functionalities to allow further modification and functionalization of the PP surface for possible

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biomedical applications, such as immobilization of the antigens, enzymes, and proteins via covalent binding. 4,5

In this study, acrylic acid (AAc) and acrylamide (AAm) were selected as the hydrophilic monomers to provide two different types of functional groups, as well as specific charge levels to the surface of PP. This article reports the photograft reaction procedures of PP-g-AAc-AAm with the aid of benzophenone (BP) as a photosensitizer and barium hydroxide [Ba(OH₂)] as a pH controller. It also reports the evaluation methods of structural surface changes of the samples.

EXPERIMENTAL

Materials

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The PP film in the thickness range of 25–50 μ m was obtained from Suh Tong Co., Korea. This film

was immersed in acetone, and Soxhlet extracted with methanol and acetone, consecutively for 48 h, each to remove additives. The films were then vacuum-dried. AAc (Junsei Chemical Co.) was purified using the inhibitor remover-replacement packing system (Aldrich Chemical Co.). AAm (Junsei Chemical Co.) was purified by recrystallization from chloroform, washed with cold methanol, and dried in a vacuum. BP (Janssen Chemica, Belgium), recrystallized from methanol and vacuum-dried, was used as the photosensitizer. Ba(OH)₂ of an extra pure grade was used as the pH controller after recrystallization with 80°C distilled water.

Preparation

The aqueous reaction medium for the photoinduced graft reaction with a given concentration of AAc, AAm, BP, and $Ba(OH)_2$ was prepared. PP film, cut into strips of $5 \times 5 \text{ cm}^2$, was immersed in the reaction medium. The reaction chamber, which contains the reaction medium, was deoxygenated by purging with nitrogen gas, and irradiated by a medium pressure mercury lamp in a temperature-controlled bath.

After irradiation, grafted films were removed from the reaction solution and washed with hot water to remove the absorbed unreacted chemicals, followed by a Soxhlet extraction with acetone for 48 h. The films were then dried in a vacuum until the constant weight was attained. To get the optimal reaction conditions, a series of exploratory graft reactions was performed by changing pH of the reaction medium, the monomer concentrations, BP concentration, and the irradiation time.

Analysis

The modified PP surfaces were characterized by Fourier transform infrared (FTIR) spectroscopyattenuated total reflectance (ATR) mode, electron spectroscopy for chemical analysis (ESCA), contact angle goniometry, and scanning electron microscopy. The changes in chemical structure of the PP surface due to the graft of AAc and AAm were investigated by FTIR-ATR. The FTIR-ATR spectra were obtained using a Nicolet Magma-IR spectrometer 550 equipped with a KRS-5 internal reflection element (incidence angle: 45°). The absorption ~ 1710 cm⁻¹ (the stretching vibration of the carbonyl groups from polyacrylic acid) were compared with the absorption ~ 1615 and 1660 cm⁻¹ (the carbonyl absorption of free and hydro-

gen-bonded amide groups from polyacrylamide). The surface elemental composition of a series of PP-g-AAc-AAm samples surface was determined using a Physical Electronic PHI 558 ESCA spectrometer. The source was a 10 kV-30 mA monochromatized X-ray beam from a magnesium anode. Wide scan (0-1000 eV) and high-resolution scans (20 eV wide) for $C_{\rm 1s},~O_{\rm 1s},$ and $N_{\rm 1s}$ were taken, and the areas of the individual peaks were compared to examine the molar ratio of AAc and AAm of the graft. Scanning electron micrographs of PP-g-AAc-AAm samples were obtained using a JEOL microscope JSM LV 5410 with the energy of incident electron of 15 KeV. The contact angle of liquid-solid interfaces (water, methylene iodide, and the graft) was measured with the use of an Erma contact angle meter G-1. Surface tensions of all samples were calculated by Owens Equation.¹² The graft yields of the samples were determined by weight measurement methods, using an Electronic Analytical Balance (Mettler AT 281 Delta Trac). The grafting amount of the treated samples was calculated as follows:

Graft Yield (%) =
$$\frac{W_a - W_b}{W_b} \times 100$$
,

where W_b and W_a represent the weight of the PP film before and after the graft reaction, respectively.

RESULTS AND DISCUSSION

Infrared (IR) Spectra of the Samples

The presence of the graft was confirmed by using IR spectroscopy. The FTIR-ATR spectra of PP, PP-g-AAc, PP-g-AAm, and PP-g-AAc-AAm are shown in Figure 1. In the IR spectrum of PP [Fig. 1(a)], the absorption in the region $\sim 2900 \text{ cm}^{-1}$ is due to $-CH_2$ stretching, and the absorption bands in 1465 and 1373 cm^{-1} might be related to =CH₂ and -CH₃ bending, respectively, of PP.^{6,7} The IR spectrum of the PP-g-AAc [Fig. 1(b)] shows the characteristic band of PAAc $\sim 1710 \text{ cm}^{-1}$ which is ascribed to the C=O stretching of AAc.⁸ In the spectra of PP-g-AAm shown in Figure 1(c), a double peak at 1615 and 1660 cm⁻¹ appear due to the carbonyl absorption of free and hydrogenbonded amide groups of PAAm, respectively.9 Figure 1(d) represents the IR spectrum of the graft copolymers of PP-g-AAc1-AAm1, prepared with the equal molar feed ratio of AAc and AAm. This



Figure 1 ATR spectra of (a) PP, (b) PP-g-AAc, (c) PP-g-AAm, and (d) PP-g-AAc-AAm.

IR spectrum shows the characteristic bands of acrylamide at 1615 and 1660 cm⁻¹, together with that of AAc at 1710 cm⁻¹, confirming that the copolymer of AAc and AAm was successfully grafted onto the surface of PP film.

Effects of pH on Graft Reaction

The changes in the ratios of $C_{1s}/N_{1s}/O_{1s}$ of PP-g-AAc-AAm due to the pH value of the reaction medium determined by ESCA are summarized in Table I. These results demonstrate that the contents of two monomers in their copolymer can be controlled by changing the pH of the reaction medium. As studied by Cabaness and colleagues,¹⁰ the reactivity ratio of AAc decreases with increasing pH, whereas the reactivity ratio



Figure 2 O_{1s} ESCA spectra of PP-g-AAc-AAm.

of AAm increases with increasing pH. At low pH values, AAm is present in its protonated form causing its reactivity to be low. At high pH values, the reactivity of AAc decreases because of its dissociation. The result shows that a pH value ~ 3.77 produces a graft with the same molar ratio as that of monomer feed. PP-g-AAc-AAm surface shows O_{1s} and N_{1s} core spectra resulting from the incorporation of -OH, O-C=O, and N-C=O groups of AAc and AAm. In the O_{1s} core spectra shown in Figure 2, the oxygen peak in C=O groups at 532 eV remains constant, but the peak in —OH groups at 533 eV (indicating the presence of -COOH groups of AAc) increases with an increase in the feed content of AAc. In the N_{1s} core spectra shown in Figure 3, the area of nitrogen peak at 399 eV increases with an increase in the feed content of AAm. The areas of the O_{1s} and N_{1s} core spectra are taken and plotted against the feed ratios of the two monomers. A plot of the experimental data concurs with the calculated data reasonably, as shown in Figures 4 and 5.

Table I Effect of pH on the Molar Ratios of PP-g-AAc1-AAm1

	ESCA (cts.)					Molar Ratio
pH	C_{1s}	O_{1s}	$\rm N_{1s}$	O_{1s}/C_{1s}	N_{1s}/C_{1s}	of Grafts (AAc : AAm)
2.26	93542	54535	7764	0.583	0.083	1: 0.42
2.75	70575	40724	6211	0.577	0.088	1:0.43
3.77	51155	24554	8696	0.480	0.167	1:1.00
4.00	55047	26857	10404	0.477	0.189	1: 1.45
6.25	77945	31407	20497	0.403	0.263	1:4.00



Figure 3 N_{1s} ESCA spectra of PP-g-AAc-AAm.

Effects of Monomer Concentration on Graft Reaction

The graft reaction was performed for 30 min, with 1 wt % of BP at a reaction temperature of 60°C, and with a pH of 3.77 to examine the graft yield with respect to the changes in the concentration of the monomer mixtures. In Figure 6, the graft yield rises sharply to 25 wt % of the mixture of AAc and AAm concentration, and then levels off. The final stage is explained as a result of the consumption of active sites on the polymer surface. Because photoactivation of BP occurs exclusively in the solution layer, graft copolymerization of AAc and AAm would no longer proceed when the active sites on the PP surface are consumed.¹¹



Figure 4 Changes in O_{1s}/C_{1s} of PP-g-AAc-AAm samples at pH 3.77. (\Box) Calculated O_{1s}/C_{1s} . (\bigcirc) Experimental O_{1s}/C_{1s} .



Figure 5 Changes in N_{1s}/C_{1s} of PP-g-AAc-AAm samples at pH 3.77. (\Box) Calculated N_{1s}/C_{1s} . (\bigcirc) Experimental N_{1s}/C_{1s} .

Effects of BP Concentration on Graft Reaction

Figure 7 shows the effects of BP concentration on the graft yield with a reaction temperature of 60° C and 25 wt % of monomer concentration at pH 3.77. The graft yield increases with a BP concentration increase of 1 wt %; however, >1 wt % of BP, the graft yield decreases slowly. This phenomenon occurs because the activated sites of PP surface increase with increasing value of BP concentration, as long as the concentration of BP in the reaction medium is < 1 wt %. However, any addition of BP above the 1 wt % level, the number of activated BP increases in the reaction medium,



Figure 6 Effect of monomer concentration on the graft yield of PP-g-AAc1-AAm1. Grafting conditions are as follows: BP concentration = 1 wt %; irradiation time = 30 min; temperature = 60°C ; pH = 3.77.



Conc. of benzophenone (wt. %)

Figure 7 Effect of BP concentration on the graft yield of PP-g-AAc1-AAm1. Grafting conditions are as follows: monomer concentration = 25 wt %; irradiation time = 30 min; temperature = 60°C ; pH = 3.77.

which is in turn, directly initiate monomers and enhance homopolymerization. Therefore, concentration of monomers and BP should be balanced to achieve efficient surface graft polymerization.¹¹

Effects of Reaction Time

Figure 8 shows the effect of irradiation time on the graft yield of PP-g-AAc-AAm at various mono-



Figure 8 Effect of reaction time on the graft yield of PP-g-AAc1-AAm1. Grafting conditions are as follows: monomer concentration = 25 wt %; BP concentration 1 wt %; temperature = 60°C ; pH = 3.77.



Figure 9 Scanning electron micrograph of a PP-g-AAc-AAm surface [enlargement: (a) $200 \times$ and (b) $500 \times$. Grafting conditions are as follows: monomer concentration = 25 wt %; BP concentration = 1 wt %; temperature = 60°C; irradiation time = 30 min; pH = 3.77.

mer concentrations. The concentration of BP is fixed at 1 wt %, and the amount of monomers are fixed at 25 wt %. Graft yield of the PP-g-AAc-AAm increases with an increase in reaction time up to 30 min. After 30 min, the graft yield reaches an equilibrium.

Scanning Electron Microscopy and Surface Tension of the Graft

Figure 9 is a scanning electron microgram of the surface of a PP-g-AAc-AAm sample. It shows sorts of entangled filaments $\sim 25 \ \mu m$ in diameter, covering the whole area of a PP surface. This grafted surface provides hydrophilic properties to polypropylene PP. Figure 10 represents the



Figure 10 Changes in surface tension due to grafts: (a) PP; (b) PP-g-AAc; (c) PP-g-AAc; (d) PP-g-AAc4-AAm1; (e) PP-g-AAc3-AAm2; (f) PP-g-AAc2-AAm3; and (g) PP-g-AAc1-AAm4.

changes in surface tension of PP-g-AAc-AAm samples prepared in this study. This graft of two hydrophilic monomers onto a hydrophobic surface of PP successfully produces a significant increase in the wettability of the sample.

CONCLUSIONS

- 1. Mixtures of AAc- and AAm-grafted copolymer onto isotactic PP films were fabricated under a liquid-phase ultraviolet irradiation technique.
- 2. The appearance of IR peaks of C=O stretching of AAc, and the appearance of the carbonyl absorption of free and hydrogen-bonded amide groups, confirmed the presence of the graft.

- 3. Compositions of the monomers on the surface of PP-g-AAc-AAm were confirmed by comparing intensities of $C_{1s}/O_{1s}/N_{1s}$ core spectra. Because the reactivity of AAc and AAm varied in pH, the pH of the reaction medium was set to 3.77 to give the equal molar ratio between AAc and AAm.
- 4. At a monomer feed of 25% and a reaction time of 30 min, the optimal reaction condition of PP-g-AAc-AAm took place in a reaction medium of 1% BP.
- 5. The surface tension of the graft increased with an increase of the graft yield up to 40 dyn cm⁻¹.

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