

Surface Modification of Polymethyl Methacrylate Intraocular Lenses with the Mixture of Acrylic Acid and Acrylamide via Plasma-Induced Graft Copolymerization

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ABSTRACT: An approach is presented for the graft copolymerization of acrylic acid (AAc) and acrylamide (AAm) mixture onto the surfaces of polymethyl methacrylate intraocular lenses (PMMA IOLs) treated with an Argon gas plasma, followed by the exposure to the oxygen atmosphere. In this case, peroxides formed by the plasma treatment are likely to be responsible for initiating the graft copolymerization. The amount of peroxides on the surface of PMMA IOLs was determined using 1,1-diphenyl-2-picrylhydrazyl, and the maximum amount was found with the plasma treatment at 30 W for 20 s under 5 mTorr pressure. The surfaces of the grafted PMMA IOLs were characterized using Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR), electron spectroscopy for chemical analysis, and contact angle meter. The FTIR-ATR spectrum of PMMA-g-AAc-AAm showed the characteristic band of PAAc at 1580 cm^{-1} together with those of PAAm at 1670 and 1630 cm^{-1} , confirming that the copolymer of AAc and AAm was successfully grafted onto the surfaces of PMMA IOLs. The experimental data of O1s/C1s and N1s/C1s reasonably concurred with the calculated data, a strong indication that the pH value of the reaction medium at 3.77 could produce a graft with an equal molar ratio. Surface tension of the samples increased to 52 dyn/cm due to the graft of the hydrophilic monomers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2361–2366, 2002

Key words: surface modification; polymethyl methacrylate; intraocular lenses; acrylic acid; acrylamide; graft copolymers; plasma polymerization; ESCA/XPS; FT-IR

INTRODUCTION

Surface modification of polymethyl methacrylate intraocular lenses (PMMA IOLs) offers an effec-

tive means of altering the biological interactions through the use of a particular material, thus producing a device that approaches biological inertness and compatibility.¹ Studies have demonstrated that interactions of corneal tissue and PMMA relative to surface adhesiveness and endothelial damage are considerably lessened by surface modification.² Furthermore, other studies

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have also shown that not only do less iris tissue damage and pigment dispersion occur in the surface-modified PMMA IOLs,^{3, 4} but modification of the surface using hydrophilic monomers may also lead to an appreciable improvement in its properties. The surface becomes hydrophilic, resulting in an increase in the smoothness, which not only reduces the endothelial cell damage but also results in a decrease in foreign body adhesion, thus improving the compatibility to cell contact and proliferation.³⁻⁵

In this study, acrylic acid (AAc) and acrylamide (AAm) were selected as the hydrophilic monomers to provide increased biocompatibility profiles to the surface of PMMA IOLs. Here, we report on the plasma-graft reaction procedures of the AAc and AAm mixture to the surface of PMMA IOLs with the aid of barium hydroxide as a pH controller. The methods for evaluating the structural changes on the surface of the samples are also presented.

EXPERIMENTAL

The PMMA IOLs (LK55), obtained from Lucid Korea Company, Ltd. (Seoul, Korea), were washed and Soxhlet-extracted consecutively for 48 h, each using methanol and ethanol to remove the additives, and were then vacuum-dried. AAc (Junsei Chemical Company) was purified using the inhibitor remover-replacement packing system (Aldrich Chemical Company). AAm (Junsei Chemical Company) was purified by recrystallization using chloroform, washed with cold methanol, and vacuum-dried. Barium hydroxide of an extra pure grade was used as a pH controller after recrystallization with 80 °C distilled water.

For the surface modification, an inductance-coupled plasma (ICP) apparatus was used to accommodate the hydrophilic monomers. The IOLs were placed on the bottom of the reaction chamber, which was evacuated to 5 mTorr, treated with 30 W of argon plasma for up to 30 s, and were then immediately exposed to the oxygen atmosphere by supplying oxygen gas to the reaction chamber. The plasma-treated IOLs were dipped into the aqueous monomer solutions under nitrogen atmosphere at 70 °C for 3 h. The residual monomers and homopolymers were removed by washing with 60 °C water.

Analysis

The amount of peroxide formed on the surface of the IOLs was quantified using 1,1-diphenyl-2-pic-

rylhydrazyl (DPPH). The plasma-treated IOLs were exposed to oxygen atmosphere and dipped into 60 °C DPPH/toluene solution (1×10^4 mol/L) for 2 h to decompose the peroxides on the surface of IOLs. The extent of DPPH molecule consumption was based on the difference in transmittance between the virgin and the treated IOLs at 520 nm as measured with a spectrophotometer.

Changes in chemical structure of the PMMA surface due to the graft of AAc and AAm were investigated by Fourier transform infrared spectroscopy in the attenuated total reflectance mode (FTIR-ATR). The FTIR-ATR spectra were obtained with a Nicolet Magma-IR spectrometer 550 equipped with a KRS-5 internal reflection element (incidence angle, 45°). The surface elemental compositions of a series of PP-g-AAc-AAm samples surfaces were determined with a Physical Electronic PHI 558 electron spectroscopy for chemical analysis (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 C1s, O1s, and N1s were taken, and the areas of the individual peaks were compared to examine the molar ratio of AAc and AAm of the graft.

The contact angle of liquid–solid interfaces (water, methylene iodide, and the graft) was measured with an Erma contact angle meter G-1. Surface tensions of all samples were calculated using Owens equation.⁶

RESULTS AND DISCUSSION

Peroxide Group Formation

In contrast to other studies on graft polymerization using a direct plasma technique, our work showed peroxide groups could be efficient initiators of graft polymerization on the plasma-treated surfaces.⁷ Several investigations have revealed that application of DPPH is highly effective for determining the amount of peroxide groups on the activated polymer surface.⁷⁻⁹ The number of peroxide groups increases with the increase in plasma treatment time, reaching a plateau at treatment times of 20, 40, and 50 s under 30, 20, and 10 W of power, respectively, and decreases thereafter (Figure 1). Clearly, longer Ar plasma exposure does not guarantee high peroxide formation. It should be noted that low peroxide concentrations at long plasma exposures were not due to

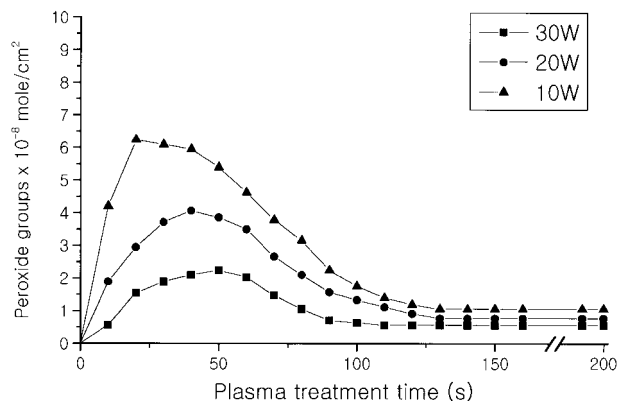


Figure 1 Formation of peroxide groups on the PMMA IOLs treated by Ar-plasma.

direct decomposition of the formed peroxide by the plasma because the plasma exposure was carried out in an atmosphere containing only the Ar gas, which should result in no peroxide formation.⁷⁻⁹ Thus, the peroxides must have been produced during the exposure of the samples to oxygen atmosphere after the plasma treatment, as proposed by Suzuki and colleagues.⁷

IR Spectra

The presence of the graft was confirmed by FTIR-ATR. The FTIR-ATR spectra of PMMA, PMMA-g-AAc, and PMMA-g-AAm IOLs are shown in Figure 2. The spectrum of PMMA IOL containing carboxyl groups (PMMA-g-AAc, Figure 2b) showed no significant differences from that of PMMA IOL, which has no carboxyl groups (Figure 2a), probably because the absorbance of carboxyl groups overlaps with that of the methyl ester of PMMA. However, as previously revealed by Kang and colleagues, alkaline treatment of AAc groups shifts the IR absorbance of the carboxyl groups to 1580 cm^{-1} , a confirmation that AAc groups are grafted onto the surface of PMMA IOLs (Figure 2c).¹⁰ The spectrum of PMMA-g-AAm IOLs (Figure 2d) revealed that the double peaks at 1630 and 1670 cm^{-1} appeared due to the carbonyl absorption of free and hydrogen-bonded amide groups of PAAm, respectively.¹¹ The IR spectrum of the graft copolymers of PMMA-g-AAc1-AAm1, prepared through an equal molar feed ratio of AAc and AAm, shows the characteristic bands of PAAm at 1630 and 1670 cm^{-1} , together with that of PAAc at 1580 cm^{-1} , confirming that the copolymer of AAc and AAm was successfully grafted onto the surface of PMMA IOLs¹² (Figure 2e).

ESCA Studies

Even though FTIR-ATR is recognized as a potent method for identifying the changes in chemical compositions of the polymer surface, the quantitative and qualitative analyses of the grafts cannot depend solely on FTIR. Therefore, ESCA was employed to achieve a precise analysis on the compositional changes of the samples. The C1s

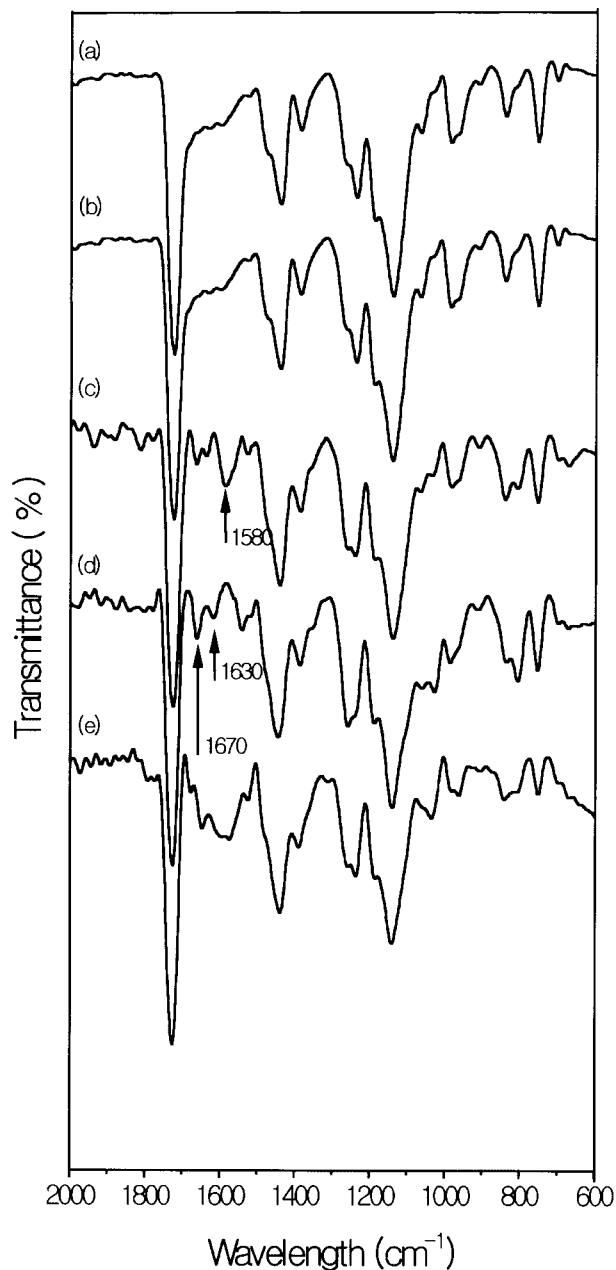


Figure 2 FTIR-ATR spectra of (a) PMMA, (b) PMMA-g-AAc, (c) PMMA-g-AAc treated with NaOH, (d) PMMA-g-AAm, and (e) PMMA-g-AAc-AAm.

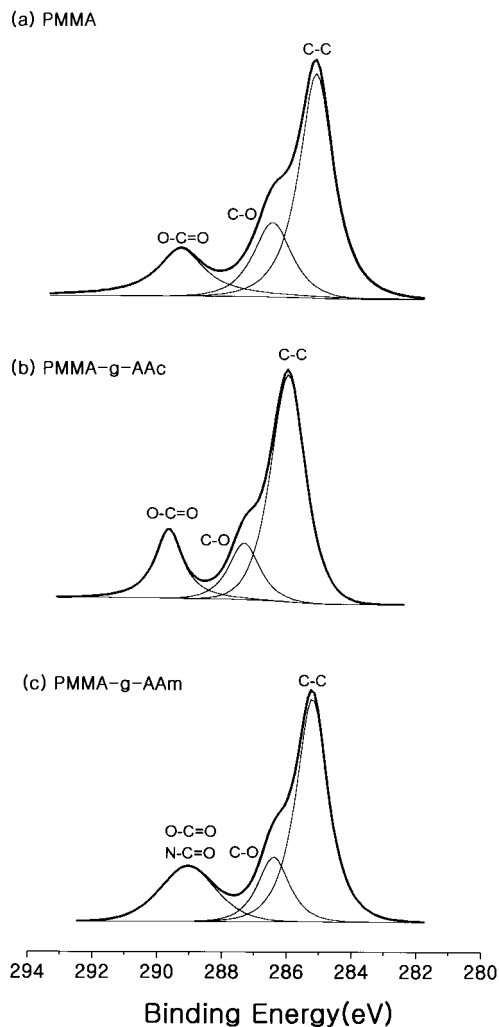


Figure 3 C_{1s} core spectra of the samples.

core spectrum of PMMA (Figure 3a) reveals the peaks at 289, 286.8, and 285 eV corresponding to $O-C=O$, $C-O$, and $C-C$ groups, respectively.¹³ The C_{1s} core spectrum of PMMA-g-AAc is shown in Figure 3b. Compared with Figure 3a, because PAAc does not possess a $C-O$ group in its structure, the peak at 286.8 eV assigned to the $C-O$ group is significantly decreased, whereas that at 289 eV is increased. In contrast, PAAm does not have a $C-O$ group, but instead has an $N-C=O$ group. Therefore, as in the case of PAAc, the peak at 286.8 eV is decreased, whereas that at 289 eV is increased and shifted to 288.7 due to the incorporation of the peak at 289.5, which was assigned to $N-C=O$ group (Figure 3c). O_{1s} and N_{1s} core spectra of PMMA-g-AAc-AAm surface were obtained by the incorporation of $-OH$, $O-C-O$, and $N-C=O$ groups of AAc and AAm. PMMA

has the O_{1s} core spectra at 533.77 and 532.21 eV due to the presence of $C-O$ and $O-C=O$ groups (Figure 4a). O_{1s} core spectra of PAAc revealed the presence of $-OH$ and $O-C=O$ groups at 532.19 and 533.53 eV, respectively, which are very close to those of PMMA (Figure 4a).¹³ However, the incorporation of PAAm results in the peak at 531.24 eV due to the $N-C=O$ group (Figure 4b). In the N_{1s} core spectra (Figure 5), the area of nitrogen peak at 399.8 eV increases with an increase in the feed content of AAm.

Effect of pH on Graft Reaction

Cabaness et al. determined that the content of AAc and AAm in their copolymers could be controlled by adjusting the pH.¹⁴ The reactivity ratio of AAc decreases, whereas that of AAm increases, with increasing pH value. At low pH values, AAm is present in its protonated form, resulting in a low reactivity. On the contrary, at high pH values, the reactivity of AAc decreases because of its dissociation. Indeed, in the graft-copolymerization, the pH of the reaction medium of the AAc and AAm mixture is critical for providing an equal molar ratio to their graft-copolymers, as revealed through our previous study in which an

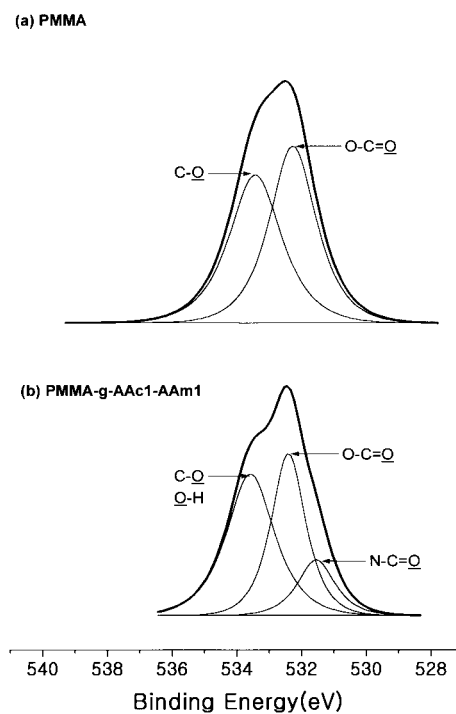


Figure 4 O_{1s} ESCA spectra of PMMA and PMMA-g-AAc1-AAm1.

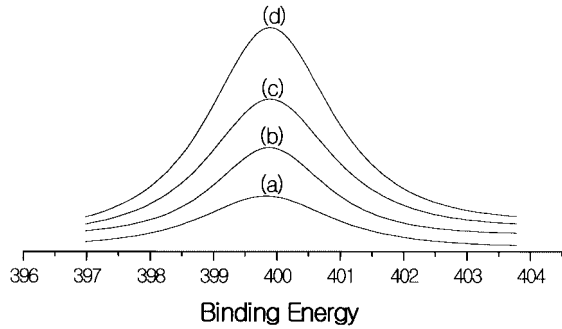


Figure 5 N_{1s} spectra of (a) PMMA-g-AAc4-AAm1, (b) PMMA-g-AAc3-AAm2, (c) PMMA-g-AAc2-AAm3, and (d) PMMA-g-AAc1-AAm4.

attempt was made to graft the mixtures of AAc and AAam to polypropylene surface using the liquid phase photo-graft technique.¹² The results revealed that a pH of ~ 3.77 provided an equal molar ratio of AAc and AAam to their graft-copolymers. Thus, this value was adopted in the present study to produce a graft with an equal molarity to that of the monomer feed. The areas of O1s and N1s core spectra were determined and plotted against the feed ratios of the two monomers (Figures 6 and 7, respectively). A plot of the experimental data concurs reasonably with the calculated data, which is a strong indication that the pH value of the reaction medium of ~ 3.77 could produce a graft with an equal molar ratio.

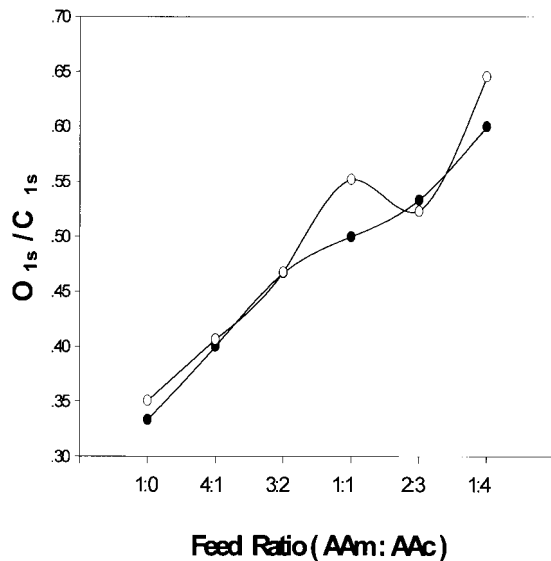


Figure 6 Changes in O_{1s}/C_{1s} of PMMA-g-AAc-AAm samples at pH 3.77. Key: (●) calculated O_{1s}/C_{1s} ; (○) experimental O_{1s}/C_{1s} .

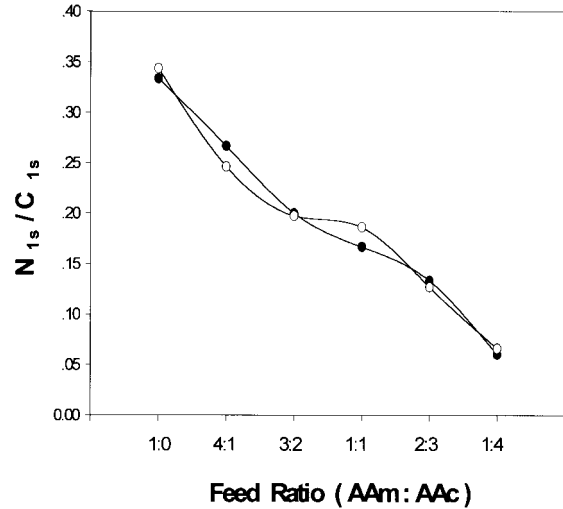


Figure 7 Changes in N_{1s}/C_{1s} of PMMA-g-AAc-AAm samples at pH 3.77. Key: (●) calculated N_{1s}/C_{1s} ; (○) experimental N_{1s}/C_{1s} .

The changes in surface tension and the wettability of PMMA-g-AAc-AAm IOLs are shown in Figures 8 and 9, respectively. Grafting of the two hydrophilic monomers onto the surface of PMMA IOLs not only increases the surface tension up to 52 dyn/cm, and but also significantly increases the wettability of the samples.

CONCLUSIONS

1. Surface modification of PMMA IOLs using the mixture of AAc and AAam was per-

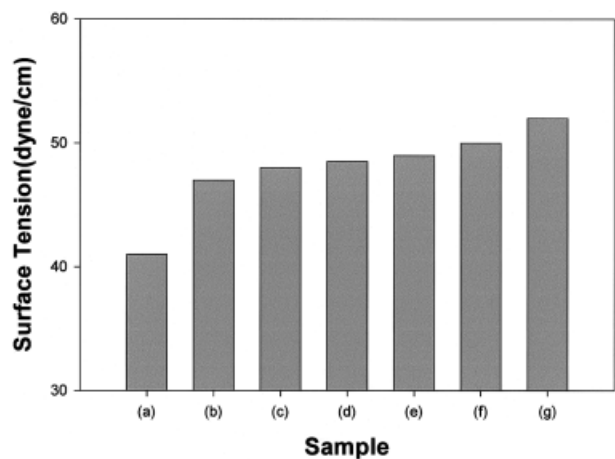


Figure 8 Changes in surface tension due to grafts: (a) PMMA; (b) PMMA-g-AAc; (c) PMMA-g-AAm1; (d) PMMA-g-AAc3-AAm2; (e) PMMA-g-AAc2-AAm3; (f) PMMA-g-AAc1-AAm4; and (g) PMMA-g-AAm.

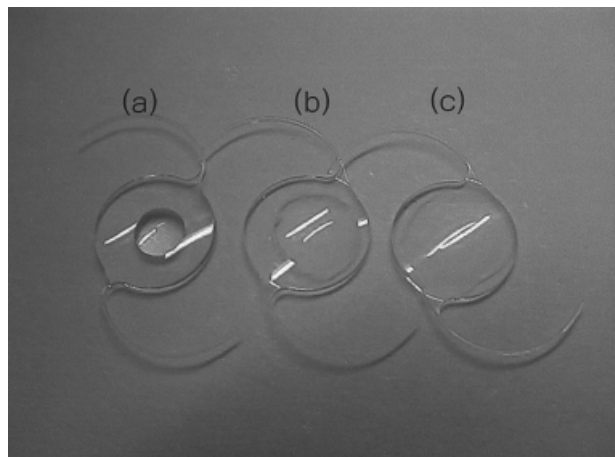


Figure 9 Changes in the wettability of the IOLs: (a) PMMA IOL; (b) PMMA-g-AAc IOL; (c) PMMA-g-AAm IOL.

formed to increase the biocompatibility profiles of IOLs surface through ICP CVD.

2. The amount of peroxides required for initiating the graft reaction was determined using DPPH, and the maximum amount, under plasma treatment with 30 W of power and 5 mTorr of pressure for 30 s, was $\sim 8 \times 10^{-8} \text{ cm}^{-2}$.
3. For the graft copolymerization, the pH of the reaction medium was adjusted to 3.77 to achieve an equal molar reactivity between AAc and AAm.
4. The presence of the graft was confirmed through the appearance of the characteristic bands of AAc and AAm in the FTIR-ATR spectra.
5. The compositions of the monomers on the surface of the graft were confirmed by comparing the areas of C1s, O1s, and N1s core spectra, and the plots of O1s/C1s and N1s/

C1s reasonably concurred with the calculated data.

6. The surface tension of the graft increased to a value of 52 dyn/cm, resulting in a significant increase in the wettability of the PMMA IOLs.

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