

Hydrophobic Recovery Behavior of PMMA and PEA Ionomers Treated with PSII

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Abstract: The surfaces of poly(methyl methacrylate) (PMMA)-based and poly(ethyl acrylate) (PEA)-based ionomers were treated either with plasma or with plasma source ion implantation (PSII), and their hydrophobic recovery behavior was studied by measuring water contact angles. It was found that the hydrophobic recovery of the plasma-treated and PSII-treated surfaces of PMMA ionomers was much slower than that of the acid-form copolymers. This was due to the presence of hydrophilic ionic groups on the ionomer surface. In addition, in the case of the PMMA ionomers, a slow hydrophobic recovery behavior for a long period of time was observed. In the case of the PEA ionomer,

the water contact angle values were found to be larger than those for the PMMA ionomers. When the contact angle values of the PMMA and PEA ionomers were compared to those of polystyrene (PS) ionomers, it was found that the order of ionomers showing higher angle value at comparable aging time was as follows: PS ionomer > PEA ionomer > PMMA ionomer. This was due to the difference in polarity and matrix glass transition temperature of the ionomers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3100–3106, 2003

Key words: hydrophobicity; ionomers; plasma source ion implantation; surfaces

INTRODUCTION

Ionomers contain a small amount of ionic groups that are attached directly onto the relatively non-polar polymer backbone or exist as pendent groups along the polymer chains. The physical properties of polymers are changed drastically by the presence of ionic groups in the polymer matrix.^{1–3} Strong attractive forces between ionic groups lead to the formation of ionic aggregates (that is, multiplets)⁴ in the relatively non-polar polymer matrix; the spherical multiplets resemble physical cross-links. Eisenberg, Hird, and Moore proposed that the mobility of the polymer chains in the immediate vicinity of the multiplets is restricted, with the restriction decreasing as the distance between the polymer chain segments and the multiplet increases.⁵ They suggested that the reduction of the chain mobility is due to (i) chain anchoring to the multiplets, (ii) tension of polymer chains bridging between neighboring multiplets, and (iii) crowding of polymer chains. With increasing ion content, the restricted mobility regions begin to overlap. As a result, the sizes of these regions become large enough to exceed a threshold value for independent phase be-

havior, and these large regions of reduced mobility are called clusters.⁵ With increasing ion content, the glass transition temperature shifts higher and thus the ionomer becomes, naturally, more polar and thermally stable.

The hydrophilicity of polymers is one of the key factors that determine the surface properties of polymeric materials. It controls various properties of polymers, including wettability, adhesion, colorability, and anti-electrostaticity. Depending on the situation, sometimes more hydrophilicity or hydrophobicity of a polymer surface is desired. For modification of the surface properties of a polymer, a number of methods have been developed. Physical and chemical modifications are two main methods. The physical modifications include plasma,^{6,7} corona,^{8,9} flame,¹⁰ and ion beam treatments,¹¹ while the chemical modifications comprise chemical reaction and wet treatment.^{12,13}

Very recently, Kim et al. studied wetting properties of polystyrene-based ionomers treated with plasma source ion implantation (PSII).¹⁴ They observed that, upon aging of sulfonated polystyrene ionomers for a few days, the ionomers showed slower hydrophobic recovery, compared to the non-ionic polymers. Thus, it was concluded that the ionic interaction and the presence of ionic groups caused the slow hydrophobic recovery. It has been known that poly(methyl methacrylate) (PMMA) and poly(ethyl acrylate) (PEA) polymers are more polar than polystyrene (PS); the polarity values of these three homopolymers are 0.281,

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This paper is dedicated to Prof. Jung-Il Jin (Korea University, Korea) on the occasion of his 60th birthday.

0.205, and 0.168, respectively.¹⁵ Thus, it would be interesting to investigate the surface properties of ionomers based on the PMMA and PEA polymers, and compare the results with the experimental results of PS ionomers obtained by Kim et al.¹⁴ Therefore, in this study, we examined the surface properties of PMMA-based and PEA-based ionomers by using a water contact angle measurement technique. For the surface modifications, either the plasma treatment or plasma source ion implantation (PSII) treatment was utilized. The latter method is known to be more efficient for retarding the hydrophobic recovery as a function of aging time than the former. Both plasma-treated and PSII-treated ionomers were aged in air for various periods of time and characterized by water contact angle measurement, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

EXPERIMENTAL

Sample preparation

Poly(ethyl acrylate-co-acrylic acid) [P(EA-co-AA)] and poly(methyl methacrylate-co-methacrylic acid) [P(MMA-co-MAA)] samples were prepared by solution polymerization of purified monomers using benzoyl peroxide as the initiator. Dried and distilled benzene and tetrahydrofuran were used as the solvents for the PEA and PMMA copolymers, respectively, with the reaction temperature of 60°C. Conversion was less than 30% and 20% for the PEA and PMMA copolymers, respectively, yielding a compositional heterogeneity of less than 0.1. The polymer samples were recovered by precipitation into a rapidly stirred excess of hexane and methanol for the PEA and PMMA copolymers, respectively. The precipitated polymers were filtered, and then dried under vacuum at room temperature for the PEA copolymer and at 70°C for the PMMA copolymers, respectively, for at least one day. To determine the acid content, the acid samples were dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution and titrated with standard methanolic NaOH solution to the phenolphthalein end point. The acid content was 5.5 mol% for the PEA copolymer, and 4.7 mol% and 8.5 mol% for the PMMA copolymers. For the neutralization of the acid groups, a predetermined quantity of methanolic NaOH was added. The solutions were freeze-dried and then dried further under vacuum at room temperature for the PEA copolymer and at 70°C for the PMMA copolymers, for at least one day. For the preparation of thin polymer films, the ionomer samples (ca. 0.07 g) were dissolved in THF to make 7% (w/v) solution, and 1 mL of the ionomer solutions was deposited onto a disposable aluminum dish (inner diameter = 44 mm). Then, the solvent was allowed to evaporate slowly for more than 5 days. Subsequently, the thin film samples

were dried further under vacuum at room temperature for 12 h.

PSII apparatus

For PSI treatment of ionomer samples, we used an in-house-built PSII chamber at the Korea Institute of Science and Technology. A detailed description of the apparatus has been presented elsewhere.¹⁶ The pulse modulator system can deliver up to 10 A and 100 kV pulses. For the generation of the plasma, we used a power supply with 13.56-MHz radio frequency and an antenna placed inside the chamber. The pressure of the vacuum chamber was 1×10^{-5} Torr. A flow rate was altered to control the oxygen gas pressure. The plasma treatment was usually performed at the pressure of 1 mTorr and the radio frequency power of 200 W. Ionomer samples were placed on the oil-cooled stage surrounded by the plasma and pulse-biased to high negative potential up to -5 kV, with a pulse of 10 μ s, and 500 or 1000 Hz. The treatment time was 1 min.

Instrumental evaluation

Water contact angles were measured by the static sessile drop method, on a Ramé-Hart (Mount Lakes, NJ) model 100 contact-angle goniometer. To study the hydrophobic recovery behavior of ionomers, plasma-treated and PSII-treated samples were aged for different periods of time. To evaluate the changes in compositions and functional groups, the polymer surfaces were analyzed by using a PHI 5800 X-ray photoelectron spectrometer with monochromatic Al K- α radiation at the power of 350 W. Curve fitting and quantification of the peaks were accomplished by using the software supplied by the manufacturer. The alterations of surface morphology were detected by using a PSI UHV STM SU-2 atomic force microscope.

RESULTS AND DISCUSSION

From the previous study, it was found that O₂ plasma or O₂-PSII treatment introduced polar groups on the polymer surface; thus, the polymer surface became more hydrophilic. Figure 1 shows the results of water contact angle measurement as a function of aging time for the plasma-treated and PSII-treated poly(methyl methacrylate-co-methacrylic acid) containing 4.7 mol% of acid groups [P(MMA-4.7-MAA)] and its sodium-neutralized ionomer [P(MMA-4.7-MANa)]. Most of the water contact angle values in this work are averages of at least two independent experimental runs, and the deviation from the average is within $\pm 3^\circ$. It is shown that one-day aging increased the contact angles of the PSII-treated P(MMA-4.7-MAA) copolymers to ca. 19°, and that the contact angles increased with increasing aging time. Thus, when the

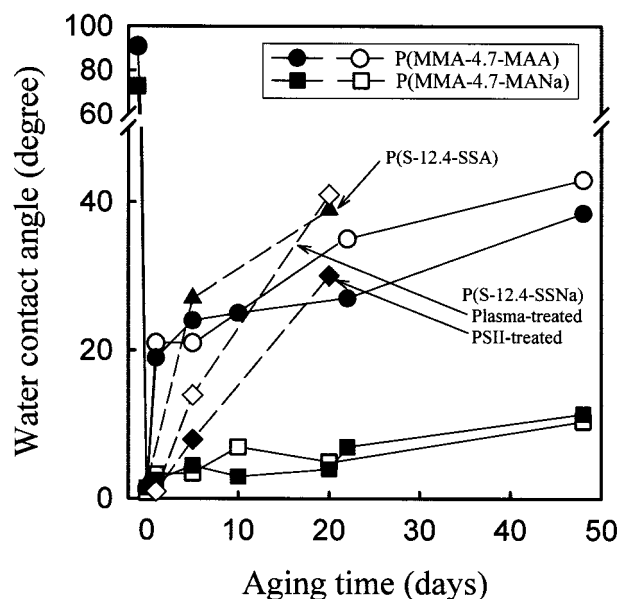


Figure 1 Water contact angle of plasma-treated (unfilled symbol) and PSII-treated (filled symbol) P(MMA-4.7-MAA) copolymers and P(MMA-4.7-MANa) ionomers as a function of aging time. The figure also includes water contact angle values obtained from P(S-12.4-SSA) copolymers as well as P(S-12.4-SSNa) ionomer (source: reference 14).

aging time of the samples lengthened from 5 through 22 days, and to 48 days, the angle values increased from ca. 24° through ca. 27°, and to ca. 39°, respectively. In Figure 1, it is also shown that, as expected, the contact angles of the PSII-treated samples are slightly lower than those of the samples treated only with plasma. At this point, it is worth mentioning that the contact angle of the PSII-treated poly(styrene-co-styrenesulfonic acid) containing 12.4 mol% of acid units, that is, P(S-12.4-SSA), aged for 5 days was ca. 27°, and that the contact angle increased to 39° with extending aging time from 5 to 20 days.¹⁴ In the present work, the contact angles of the treated P(MMA-4.7-MAA) copolymer were lower than those of the treated polystyrene-based copolymers at comparable aging time. This decreasing contact angle for the PMMA copolymers is probably due to the fact that the poly(methyl methacrylate) has a higher polarity value than the polystyrene does.

Figure 1 also shows that in the case of the samples without any treatment, the ionomer shows a lower water contact angle (that is, ca. 73°) than the acid-form copolymer (that is, ca. 91°). In addition, it is seen that the water contact angles of the PSII-treated and plasma-treated sodium neutralized ionomers, that is, P(MMA-4.7-MANa), are much lower than those of the acid form. This result implies that the presence of the ionic groups in the ionomer makes the polymer more hydrophilic. In addition, if the interaction between ionic groups is strong enough to form aggregates, the

mobility of polymer chain is reduced.⁵ As a result, the entering of polar groups under the surface of polymer matrix is retarded. It should also be noted that the type of surface treatment methods affected the surface properties of P(MMA-4.7-MAA); that is, the hydrophobic recovery was somewhat faster for a plasma-treated sample than for a PSII-treated sample (see Fig. 1). However, in the case of ionomer samples, the hydrophobic recovery was altogether too slow to determine the effects of the type of modification methods on the surface properties of ionomers.

Figure 1 also shows that the contact angle value of the ionomer increases only slightly with increasing aging time. For example, in the case of the plasma-treated and PSII-treated ionomers with extending aging time from 5 to 20 days, and to 48 days, the contact angle increased from ca. 3°, to 5°, and to ca. 11°, respectively. It should be stressed that the contact angle for the 48-day aged ionomer, that is, 11°, is just around one-fourth of the values obtained for the acid form polymers. This result is quite different from what we observed in the previous work on the wettability of the surface of PS ionomers.¹⁴ The contact angles of the PSII-treated sodium sulfonated polystyrene [P(S-12.4-SSNa)] ionomers aged for 5 and 20 days were ca. 8° and 30°, respectively, while those of the PSII-treated acid form copolymer at the comparable aging time were ca. 27° and ca. 39°, respectively.¹⁴ Thus, it should be stressed that the hydrophobic recovery is much slower (that is, much lower water contact angle) for the PMMA ionomers than for the PS ionomers at comparable aging time. This means that, compared to the PS-based ionomer system, the PMMA counterpart needed more time for the polar groups and ionic groups on the polymer surface to enter beneath the surface of polymer matrix. In other words, the presence of ionic groups in the PMMA ionomers played a much more important role in determining the surface properties of polymers than that in the PS-based ionomers.

Let us consider the multiplets and the degree of clustering in the two ionomer systems. It is known that, since the PMMA matrix is more polar than the PS matrix,¹⁵ the ionic groups of the PMMA ionomers are more soluble in the PMMA matrix.¹⁹ Thus the number of ionic groups forming ionic aggregates is relatively smaller for the PMMA ionomer than for the PS ionomer, making the PMMA ionomers less clustered as compared to the PS ionomers.^{18–21} Therefore, the number of ionic groups, not forming multiplets but residing on the polymer surface, should be larger for the PMMA ionomer than for the PS ionomer. As a result, hydrophobic recovery of the PMMA ionomers becomes slower due to the presence of the larger number of ionic groups on the surface, compared with that of the PS ionomers. Needless to say, the high polarity value of the PMMA makes the surface of the

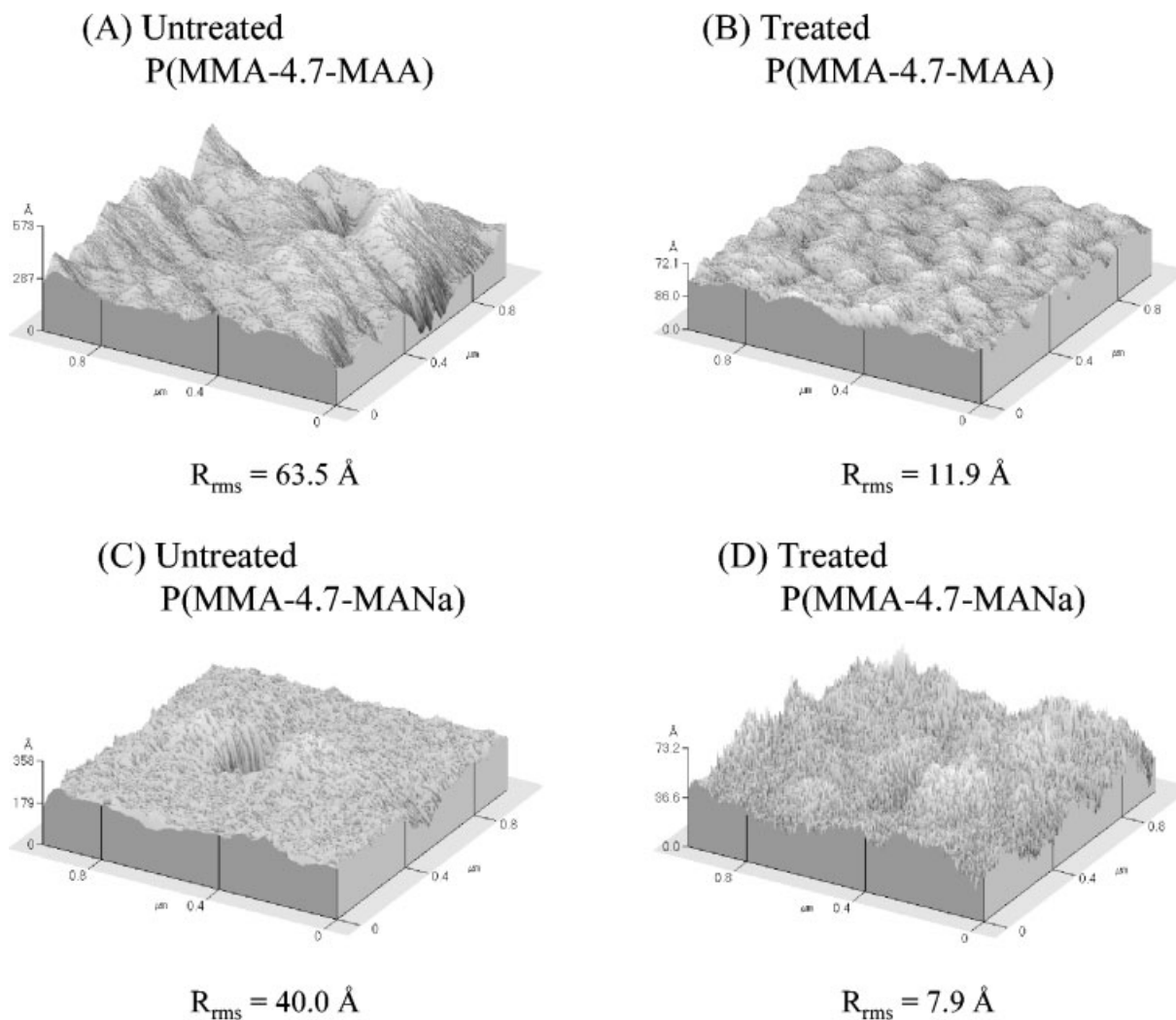


Figure 2 AFM images of (A) untreated and (B) PSII treated P(MMA-4.7-MAA) (C) untreated P(MMA-4.7-MANa) and (D) PSII treated P(MMA-4.7-MANa).

ionomer more hydrophilic, compared to the PS ionomer. It should also be noted that the hydrophobic recovery for the P(MMA-4.7-MANa) is very slow with time, compared with the P(MMA-4.7-MAA) acid form copolymer and the PS ionomers. This result implies that, in the case of polar PMMA ionomers, the presence of ionic groups significantly slows down the entering of the ionic groups and the polar groups, introduced by either plasma treatment or PSII treatment, beneath the surface of the polymer matrix. At this point, we do not have any clear explanation for this behavior. However, it can be suggested that the polar nature of the polymer, that is, the polymer matrix containing ester functional groups as well as the ionic groups existing either in the multiplet (leading to higher T_g) or singly on the polymer surface, altogether might cause the very slow hydrophobic recovery in the PMMA ionomers.

Figure 2 shows AFM images of the P(MMA-4.7-MAA) copolymer and its ionomer P(MMA-4.7-

MANa) before and after PSII treatment. The O_2 PSII treated PMMA copolymer and its ionomer was less rough than those of the original copolymer and ionomer. AFM studies gave the root mean square roughness R_{rms} value of 63.5 Å for untreated P(MMA-4.7-MAA), 40.0 Å for untreated P(MMA-4.7-MANa), 11.9 Å for PSII treated P(MMA-4.7-MAA), and 7.9 Å for PSII treated P(MMA-4.7-MANa). The AFM images of PSII-treated copolymer and ionomer are fairly uniform, which means that the contact angle measurement in this experiment was essentially not affected by the surface roughness.

In Figure 3, we illustrate the survey spectra and the C_{1s} core-level spectra of P(MMA-4.7-MANa) surfaces undergoing PSII treatment. The survey spectra reveal that the PSII treatment increases the oxygen and sodium concentration on the ionomer surface. The deconvoluted C_{1s} spectra indicate that the PSII-treated P(MMA-4.7-MANa) has slightly more oxygen functionalities on the surface, compared to peaks obtained

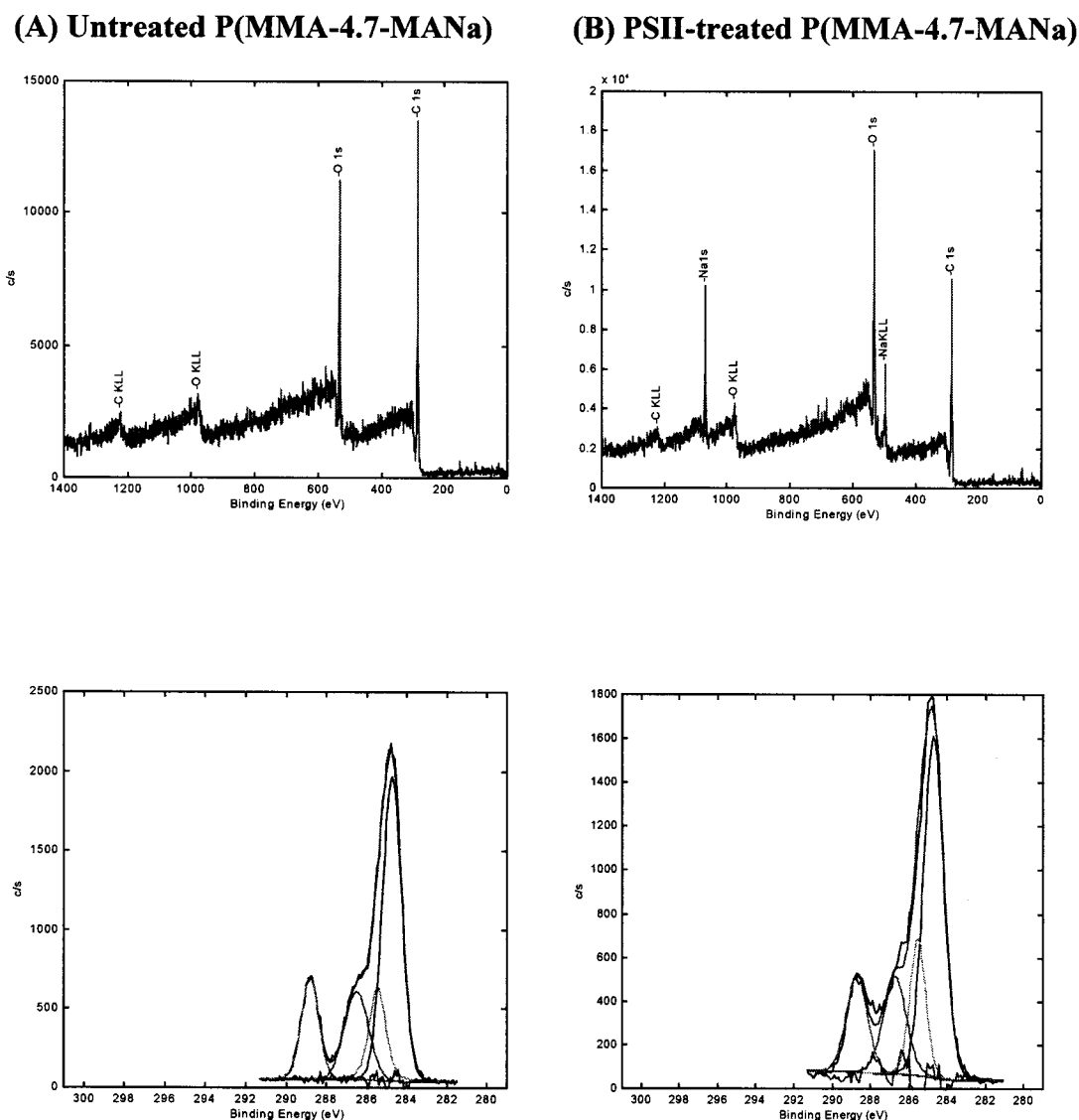


Figure 3 XPS survey and C_{1s} spectra of (A) untreated and (B) PSII treated P(MMA-4.7-MANa) samples.

from the untreated ionomer. The result from the survey and the C_{1s} spectra is consistent with the contact angle data that the PSII-treated surface of the P(MMA-4.7-MANa) ionomer is more hydrophilic than that of the unmodified P(MAA-4.7-MANa) ionomer.

Figure 4 shows the water contact angles as a function of aging time for the plasma-treated and PSII-treated PMMA copolymers [P(MMA-8.5-MAA)] and their sodium ionomers containing 8.5 mol% of functional groups, that is, P(MMA-8.5-MANa). It is shown that the contact angle values increase with increasing aging time, and level off above the aging time of 20 days. In the figure, again, it is observed that the contact angles of the ionomer samples are lower than those of the acid samples and that, as expected, the PSII treatment is more effective for the retardation of hydrophobic recovery than the plasma treatment. When the wetting properties (that is, water contact

angles) of the 8.5 mol% samples are compared to those of the 4.7 mol% sample, the contact angles of the untreated P(MMA-8.5-MAA) and (MMA-8.5-MANa) are lower than those of the untreated 4.7 mol% acid copolymer and its ionomer. This result is reasonable because more acid groups and ionic groups make the corresponding polymer more hydrophilic.

As previously mentioned in the introduction, PEA is less polar than PMMA. Thus, the hydrophobic recovery of the PEA ionomers is expected to be relatively faster than that of the PMMA ionomers. Figure 5 shows the water contact angles of P(EA-5.5-AA) and its ionomer form [P(EA-5.5-ANa)], containing 5.5 mol% of functional groups. The trend observed in PMMA copolymer system is also shown in this figure; that is, the treatment with either plasma or PSII decreased the water contact angle significantly, and the water contact angle increased with increasing aging

time. However, the water contact angles as a function of aging time were different between the PMMA and PEA ionomers. For example, when plasma or PSII-treated samples were aged for 48 days, the contact angles of the P(EA-5.5-AA) and its Na-ionomer are higher than those of the P(MMA-4.7-MAA) and its Na-ionomer. These differences in hydrophobic recovery behavior in the PEA and PMMA systems may be due to less polarity of the PEA and the lower T_g of the PEA (ca. $-24\text{ }^\circ\text{C}$),¹⁷ as compared with that of the PMMA. The lower T_g makes the ionic groups and the polar groups (introduced by either plasma treatment or PSII treatment) on the polymer surface enter beneath the surface of polymer matrix with more ease. Thus the two factors, that is, more hydrophobicity and lower T_g , are believed to be responsible for the higher water contact angles for the PEA ionomer, before and after either plasma treatment or PSII treatment, than for the PMMA ionomers.

Lastly, it should be mentioned that in the case of untreated samples the water contact angle for the P(EA-5.5-ANa) ionomer is higher than that for the acid sample. This is understandable. Since the PEA ionomer is known to be a well-clustered ionomer,²²⁻²⁴ most of the ionic groups would form multiplets. Thus, the ionic groups are not expected to exist singly on the surface of the ionomer, while the acid groups are able to reside on the surface. If this is the case, the PEA acid sample should be more hydrophilic than that of the PEA ionomer, which may be indicated by what we observed in this study.

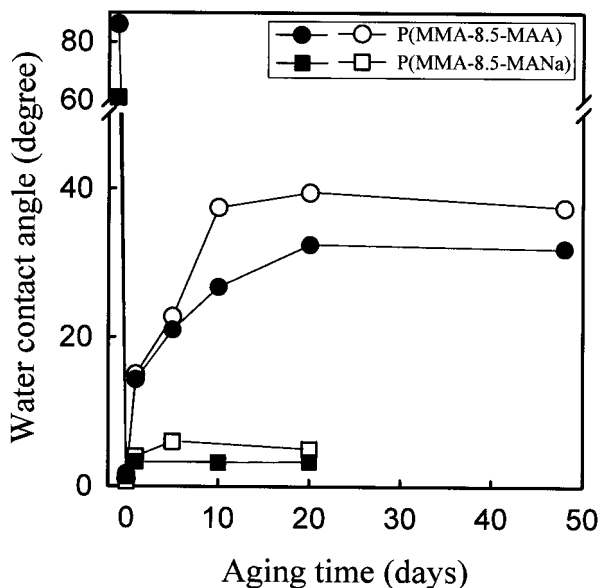


Figure 4 Water contact angle of plasma-treated (unfilled symbol) and PSII-treated (filled symbol) P(MMA-8.1-MAA) copolymer and P(EA-8.1-MANa) ionomer as a function of aging time.

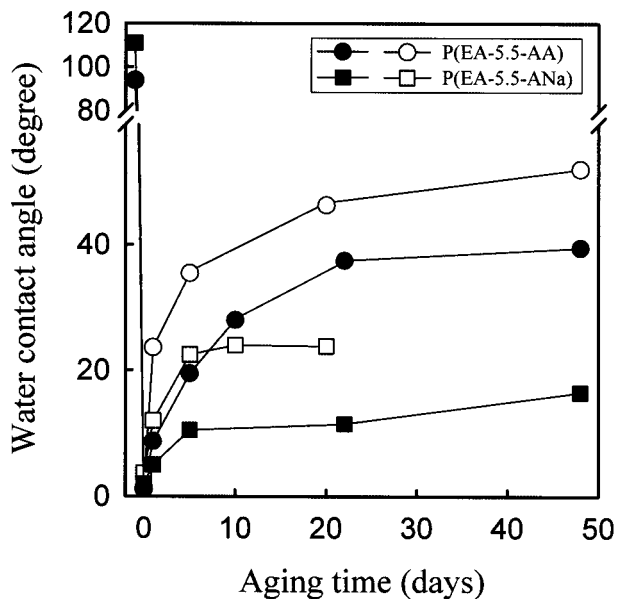


Figure 5 Water contact angle of plasma-treated (unfilled symbol) and PSII-treated (filled symbol) P(EA-5.5-AA) copolymer and P(EA-5.5-ANa) ionomer as a function of aging time.

CONCLUSION

The wettability of the PMMA and PEA ionomers was investigated by using a water contact angle measurement technique and their surfaces were characterized by XPS and AFM methods. It was found that the hydrophobic recovery of the plasma-treated and PSII-treated PMMA ionomers was much slower than that of the corresponding acid-form copolymers. This was probably due to the presence of hydrophilic ionic groups on the ionic polymer surface. It was also found that, with increasing ion content, the hydrophobic recovery of the PMMA ionomer became slightly slower. In the case of the PEA ionomer, the water contact angle values were found to be larger than those for the PMMA ionomers. When the contact angle values of the PMMA and PEA ionomers were compared with those of the PS ionomers, it was found that the water contact angle values of the ionomers were in the following order: PS ionomer > PEA ionomer > PMMA ionomer. In the case of the PMMA ionomer, the matrix T_g of which is similar to that of the PS ionomer, the ionic groups might be soluble in the relatively polar polymer matrix. Thus, more ionic groups, not participating in the multiplet formation, might reside on the ionomer surface. Therefore, the PMMA ionomer showed lower contact angles. It was also found that hydrophobic recovery was very slow for the PMMA ionomer with aging time. This implied that the presence of ionic groups in a relatively polar ionomer very strongly affected the retardation of hydrophobic recovery. In the cases of PMMA and PEA ionomers, since the matrix T_g of the PEA is much lower than that

of the PMMA, the polar groups and hydrophilic ionic groups of the PEA ionomer enter beneath the surface of polymer matrix more easily, as compared with those of the PMMA ionomer. In addition, the polarity value of the PEA is lower than that of the PMMA and thus the water contact angles of the PEA ionomers were higher than those of the PMMA ionomers.

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