Wetting Properties of Polystyrene Ionomers Treated with Plasma Source Ion Implantation

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ABSTRACT: The wetting properties of polystyrene-based ionomers treated with plasma source ion implantation (PSII) were investigated by the measurement of water contact angles. When sulfonated ionomers were aged for a few days, the hydrophobic recovery for the ionomers became much slower than that for the nonionic polymers. However, when the samples were aged over 20 days, the water contact angle of the ionomers converged with that of the nonionic polymer. Thus, it was concluded that the ionic interaction between the ionic groups and the presence of ionic groups together resulted in the slow hydrophobic recovery and that the aging effect was significant for the ionomers. For the methacrylate ionomer of low ion content, on the other hand, it was found that the PSII treatment produced only a small change in hydrophobic recovery behavior. Thus, it was suggested that the low ionic content coupled with the small size of the ionic unit might cause changes only of a very insignificant degree in hydrophobic recovery behavior. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2500–2504, 2002

Key words: ionomers; contact angle; plasma; glass-transition; ion implantation; polystyrene

INTRODUCTION

The hydrophilicity/hydrophobicity of polymers is of importance in the determination of various polymeric properties, for example, wettability, adhesion, colorability, and anti-electrostaticity. Thus, in some cases, more hydrophilicity or hydrophobicity of polymers is desirable. To make more hydrophilic polymers, a number of methods have been developed.[1–9] They can be divided into two techniques, namely, chemical and physical modification methods. The physical methods involve plasma,[2,3] corona,[4,5] flame,[6] and ion-beam treatments,[7] whereas the chemical methods include wet treatments and a chemical reaction.[8,9]

A small amount of ionic groups, which attach either directly to the relatively nonpolar polymer backbone or exist as pendent groups along the polymer chains, change the physical properties of polymers significantly,[10–13] and these polymers are called *ionomers.* The dual nature of ionomers, that is, they are hydrophobic (due to the presence of a nonpolar polymer matrix) and hydrophilic (due to the presence of ionic groups), makes them interesting from both academic and industrial

points of view. In ionomers, strong attractive Coulombic forces between ionic groups lead to ion aggregation, termed *multiplets*,[14] within the relatively nonpolar polymer matrix, and the mobility of polymer chains surrounding the multiplet is restricted.[15] As an ion content increases, the restricted mobility regions of the polymer chains start to overlap, and the glass-transition temperature (T_g) shifts higher.[15]

The incorporation of ionic groups leads to a more hydrophilic and more thermally stable polymer due to a higher T_g. Thus, in this study, we attempted to explore the surface properties of polystyrene (PS)-based ionomers by using water contact angle measurement. Two different methods for the surface treatments were used: plasma treatment and plasma source ion implantation (PSII) treatment.[16] Treated PS ionomers were aged in air for various periods of time and characterized by the water contact angle measurement. At this point, it should be mentioned that PSII treatment is known to be more efficient for retarding the aging effect than the plasma treatment.[17]

EXPERIMENTAL

Sample Preparation

Poly(styrene-*co*-styrenesulfonic acid) (PSSA) polymer was prepared by the method developed by Makowski et al.[18] for homogeneous sulfonation of [molecular weight (MW) = ~300,000]. The poly(styrene-*co*-methacrylic acid) (PSMAA; MW = ~300,000) sample was prepared by the bulk polymerization of purified styrene and methacrylic acid monomers with benzoyl peroxide as the initiator. The detailed procedure was described elsewhere.[19] In the case of the PSMAA polymer, to yield a compositional heterogeneity of less than 0.1, we kept conversion to less than 10%. The polymer was recovered by precipitation into a rapidly stirred excess of methanol. The precipitated polymer was filtered and dried under vacuum at 80°C for at least 1 day. To determine the acid content, we dissolved the acid samples in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution and titrated it with a standard methanolic NaOH solution to the phenolphthalein end point. The acid contents for the sulfonic acid and methacrylic acid samples were found to be 12.4 and 2.1 mol %, respectively. To neutralize

the acid groups, we added a predetermined quantity of methanolic NaOH to the PSSA and PSMAA samples dissolved in a benzene/methanol (9/1 v/v) mixture, which gave poly(styrene-*co*-sodium styrenesulfonate) (PSSNa) and poly-(styrene-*co*-sodium methacrylate) (PSMANa) ionomers. The PSSA sample was also neutralized with NH_4OH to give a poly(styrene-*co*-ammonium styrenesulfonate) ($PSSNH_4$) ionomer. The solutions were freeze-dried and then dried further under vacuum at about 120°C for at least 1 day.

To make thin polymer films, we dissolved the ionomer samples (~0.07 g) in tetrahydrofuran to make a 7% (w/v) solution, and the ionomer solutions were 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

An in-house built PSII chamber at the Korea Institute of Science and Technology was used for PSII treatments. A detailed description of the apparatus was presented elsewhere.[20] The pulse modulator system was able to deliver 10 A, 100 kV pulses. To generate the plasma, we used a 13.56 MHz rf power supply and an antenna located inside the chamber. The base pressure of the vacuum chamber was 1×10^{-5} Torr. Variation of flow rate controlled the pressure of oxygen gas. The plasma treatment was usually performed at a pressure of 1 mTorr and an rf power of 200 W. Ionomer samples were placed on the oil-cooled stage surrounded by the plasma source and pulse-biased to high negative potential, that is, up to −5 kV, 10 μs, and 500 or 1000 Hz, and the treatment time was 1 min.

Instrumental Evaluation

Water contact angle was measured by the static sessile drop method, on a Rame–Hart (model 100) contact angle goniometer (Mount Lakes, NJ). To investigate the hydrophobic recovery behavior of ionomers, we aged plasma-treated and PSII-treated samples for different periods of time.

RESULTS AND DISCUSSION

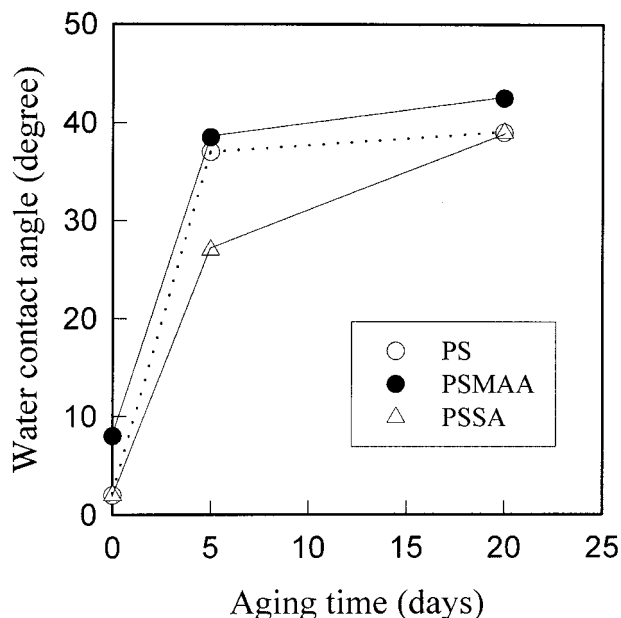The PSII treatment introduces polar groups on the polymer surface, and thus, the polymer sur-

Figure 1 Water contact angle for PSII-treated (○) PS, (●) PSMAA, and (△) PSSA polymers versus aging time.

face becomes more hydrophilic.[17] Figure 1 shows the results of the water contact angle measurements for the PSII-treated PS, PSSA, and PS-MAA polymers as a function of aging time. Most of the contact angle values presented in this article are averages obtained through at least two independent experimental runs, and the deviation from the average was less than ±3°. In Figure 1, it is shown that 5-day aging made the contact angles for the PS and PSMAA (containing 2.1 mol % acid groups) higher than that for the PSSA (containing 12.4 mol % acid groups). This might be due to the fact that the acid content of the PSSA polymer was relatively high. Therefore, in the PSSA polymer system, the interaction between acid groups was strong enough to form acid group aggregates, and thus, the mobility of polymer chain was reduced.[21,22] As a result, the entrance of polar groups under the surface of polymer matrix was retarded. However, for the PS-MAA polymer, the aging effect should be very weak; this can be understood because the acid content was relatively low. If the polymer samples were kept in air over a certain period of time (e.g., over 20 days), the water contact angles for the three polymers would naturally be expected to become similar to each other; this is indeed what we observed.

The water contact angles measured for the plasma and PSII-treated PSSA, PSSNa, and

PSSNH$_4$ ionomers as a function of time are shown in Figure 2. It is shown that the contact angle values of the PSSNa and PSSNH$_4$ ionomers were lower than those of the PSSA acid polymer. For example, in the case of the 5-day-aging samples, the water contact angle for the PSSA polymer was about 27°, whereas that for the PSSNa ionomer was about 8°. In addition, in the case of the PSII-treated samples kept for 20 days in air, the water contact angle for the PSSA polymer was about 39°, whereas those for sodium and ammonium ionomers were 30 and 27°, respectively. These results imply that the ionic interactions between ionic groups of the ionomers played an important role in the determination of the surface properties of polymer and that aging time affected the hydrophobic recovery behavior of the polymers. When the PSSA sample was neutralized with NaOH, the acid groups became more hydrophilic ionic groups. These ionic groups, in turn, aggregated to form multiplets, and thus, the polymer chains surrounding the multiplets experienced a reduction in their mobility.[15,23–30] As a result, the T_g of the polymer increased. Therefore, the polar groups and more hydrophilic ionic groups on the ionomer surface needed more time to enter beneath the surface of polymer matrix. However, in this system, the type of cation affected the contact
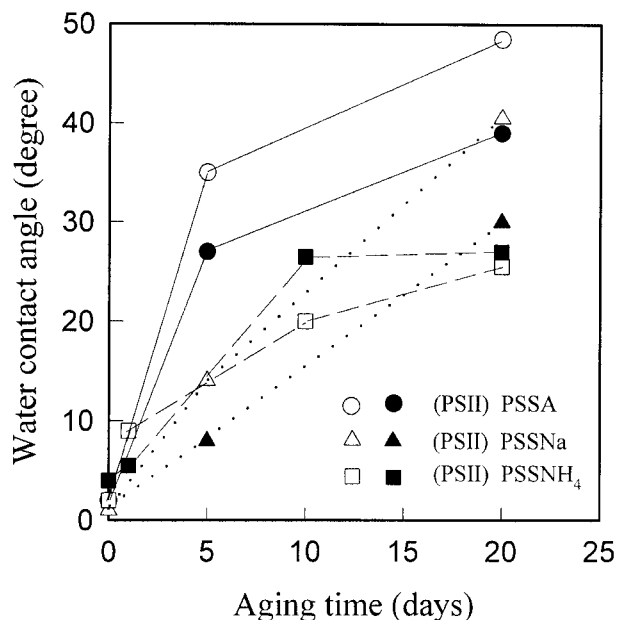

Figure 2 Water contact angles for (○, ●) PSSA, (△, ▲) PSSNa, and (□, ■) PSSNH$_4$ ionomers treated with plasma (unfilled symbols) and PSII (filled symbols) as a function of aging time.

angle only slightly. On the one hand, in the case of PSSNH$_4$ ionomer, the size of the cation was bigger than that of the PSSNa ionomer, and thus, the electrostatic force between ionic groups was stronger for the PSSNa than for the PSSNH$_4$ ionomer.[31] As a result, the T_g of the PSSNH$_4$ ionomer was lower than that of the PSSNa ionomer.[32,33] Thus, the entrance of the polar groups and hydrophilic ionic groups beneath the polymer surface was more difficult for the sodium ionomer than for the ammonium ionomer. On the other hand, however, because the size of the ammonium ion was larger than that of the sodium ion, the entrance of the ionic groups beneath the polymer surface was more difficult for the ammonium ionomer than for the sodium ionomer. Thus, these two oppositely driving factors controlled the surface properties of the ionomers simultaneously, and the resulting aspects are presented as what we observed here.

In Figure 2, the water contact angles of ionomers treated only with plasma are also shown. The water contact angles for the PSSA and PSSNa samples treated only with plasma were higher than those for the samples treated with PSII. These results can be understood. As mentioned before, the PSII treatment generated more polar groups on the polymer surface and more cross-links between the polymer chains than plasma treatment alone;[17,20] the PSII treatment also caused the thick PSII-treated surface layer, which was more stable than that obtained by the plasma treatment only. In the figure, it is shown that the change in treatment methods affected the water contact angle of the PSSNH$_4$ ionomer only slightly. This result implies that if the size of a cation is too large to reorient the ionic groups beneath the polymer surface, plasma treatment is enough to show the aging effect, which modifies only the uppermost layer of the ionomer.

The contact angles of the PSMAA acid polymer and PSMANa ionomer are shown in Figure 3 with the data of the PS homopolymer and PSSNa ionomer. It is shown that the contact angles of the PSMAA and PSMANa samples were not much different from that of the PS homopolymer. As mentioned before, this might be due to the fact that the ion content of PSMANa was only 2.1 mol %. Thus, the properties of ionomers might not have differed from those of the nonionic homopolymer. This study also found that the contact angles of the PSMAA and PSMANa polymers were higher than those of the PSSNa ionomer. This contact angle difference can also be under-
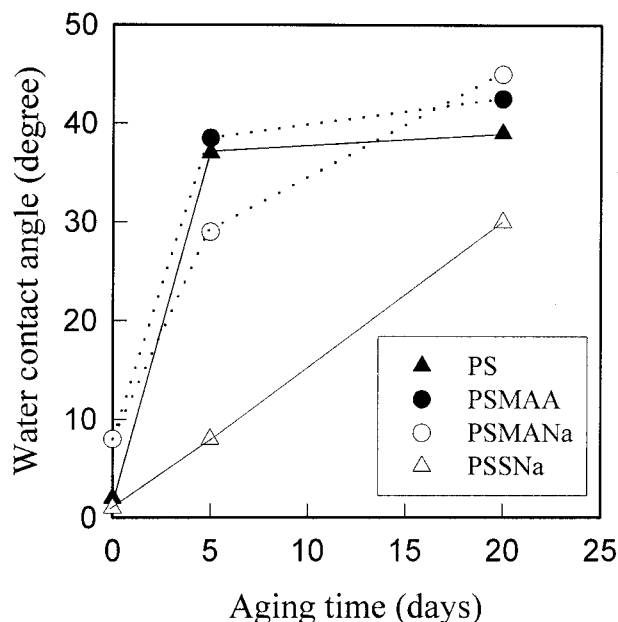

Figure 3 Water contact angles for PSII-treated (▲) PS, (●) PSMAA, (○) PSMANa, and (△) PSSNa ionomers as a function of aging time.

stood, if one considers the difference in ion contents between the PSMAA (2.1 mol %) and the PSSA (12.4 mol %) polymers. For the samples aged for 5 days, the angle difference was more than 20°, and the difference became smaller with aging time. Thus, for the samples aged for 20 days, the water contact angle of the PSSNa ionomer was lower than those of the PSMAA and the PSMANa ionomers by more than 10°. In addition, the size of the ionic unit in the copolymer may also have influenced the hydrophobic recovery rate, if the ion contents of the ionomers were the same. In the case of the PSSNa ionomer, the ionic unit was sodium benzenesulfonate, which is larger than sodium carboxylate in the PSMANa ionomer. Thus, it was more difficult for the sodium benzensulfonate ion pair to reorient than sodium carboxylate ion pair. Therefore, it could naturally be expected that the effect of the aging time on the water contact angle would be more significant in the PSSNa sample than in the PSMANa ionomer.

CONCLUSIONS

In this study, the wettability of PS based ionomers treated with plasma and PSII was investigated by the measurement of water contact an-

gles. When samples were aged for a few days in air, the hydrophobic recovery behavior became much slower for sulfonated PS ionomers than for a nonionic polymer. However, when the ionomers were aged over 20 days, the difference between water contact angles of the ionomers and the nonionic polymer became smaller. From the results, it was concluded that the ionic interaction between ionic groups coupled with the presence of the ionic groups made the hydrophobic recovery slow and that the effect of aging time on the surface properties was pronounced. In the case of the methacrylate ionomer, however, the effect of PSII treatment on the hydrophobic recovery was weak. Thus, it was postulated that due to the low ion concentration and the small size of the ionic unit, this ionomer showed a very small change in hydrophobic recovery behavior.

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