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Dynamic mechanical properties of three different combinations taken from styrene-*co*-itaconate, styrene-*co*-methacrylate, and styrene-*co*-sulfonate ionomers

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Abstract

Dynamic mechanical properties of three different styrene-based ionomer blends containing ca. 5 mol% of ionic repeat units were investigated; the three ionic units were itaconate (ITANa), methacrylate (MANa), and styrenesulfonate (SNa). For SNa-MANa ionomers, it was observed that this ionomer system showed only two loss tangent peaks, implying that this ionomer system resembles a typical miscible system. When the ion content increased, however, the ionomer blend showed two cluster loss tangent peaks, indicating the presence of phase-separated cluster regions. This suggests that, with increasing ion content, the role of ionic units becomes more important than that of host non-ionic units to determine ionomer properties. In the case of ITANa-MANa and ITANa-SNa ionomers, however, it was suggested that the multiplets of the MANa and SNa ionomers might be disrupted upon the addition of the ITANa ionomers. In addition, the SEM images showed that the fracture surfaces of ionomers changed upon blending.

Keywords: Ionomer; Blend; Polystyrene

1. Introduction

During last three decades, the properties and morphology of styrene-based ionomers have been studied extensively [1–4]. It is well known that, owing to the formation of ionic aggregates, called multiplets [5], the styrene ionomers show significant changes in their physical properties, compared to the non-ionic polystyrene. For example, some styrene ionomers show two glass transitions (T_gs) [3]. In addition, the styrene ionomers show an X-ray scattering peak at a very small angle, i.e. an small-angle X-ray scatter (SAXS) peak. To interpret two T_gs behavior of amorphous random ionomers as well as the ionomer SAXS peak, Eisenberg, Hird, and Moore proposed the multiplet/cluster model, so-called EHM model [6]. According to the EHM model, the polymer chains surrounding multiplets experience reduction in their mobility. When an ion content is very low, only a few multiplets are present. With increasing ion content, the regions of reduced mobility start to overlap, and eventually the restricted mobility regions become a large continuous phase, called clustered regions [6]. When the dimension of clustered regions exceeds ca. 10 nm, the ionomer exhibits two T_gs, i.e. the matrix T_g at relatively low temperatures and the cluster T_g at relatively high temperatures. In this model, the SAXS peak position is related with inter-multiplet spacing [7,8].

Over the years, a large amount of information on various ionomer blends has been accumulated [1–4,9,10], and styrene ionomer blends have also been studied [11–15]. Here, the styrene ionomer blend means a mixture of two styrene-based polymers, in which the main polymer chains consist of styrene units as well as a small amount of various ionic units. Therefore, one of the advantages of the study on these ionomer blends is that the complication caused by the repulsion of the two polymer backbone chains that have different chemical structures can be avoided. In the cases of the polystyrene-based ionomer blend systems studied by the groups of Eisenberg, MacKnight, and Weiss [11–14], the primary interactions between two different ionomers (i.e. sulfonated polystyrene and styrene-*co*-4-vinylpyridine

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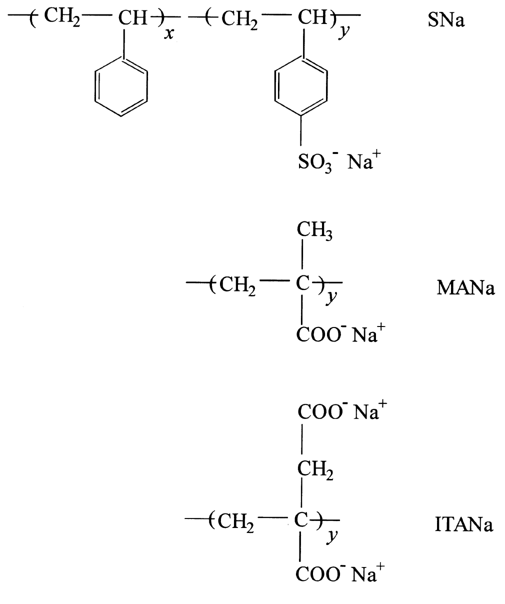
copolymers) are connected with ion/coordination, hydrogen bond-assisted ion/ion, and ion/dipole interactions. Recently, Kim et al. studied very briefly the mechanical properties and morphology of a 5/5 (w/w) blend of styrene-*co*-styrenesulfonate ionomer and styrene-*co*-methacrylate ionomer containing ca. 9 mol% of ionic groups [15]. In this system, the interactions between the two ionomers are ion pair/ion pair interactions. It was found that three loss tangent peaks were observed. Thus, the authors suggested that there were styrene matrix region, methacrylate-rich region, and sulfonate-rich region. Unfortunately, however, the effect of the ratio of the amounts of the two styrene-based ionomers on the mechanical properties had not been investigated in that study.

Thus, in the present work, we explore the effects of the weight ratio of styrene-based ionomers on the mechanical properties of ionomer blends having ion pair/ion pair interactions. In addition, we also attempt to investigate the effect of the type of ionomers on the dynamic mechanical properties of the ionomer blends. To do so, we prepare three different styrene-based ionomer blends; a poly(styrene-*co*-sodium styrenesulfonate, SNa) ionomer blended with a poly(styrene-*co*-sodium methacrylate, MANa) ionomer (for simplicity, we refer to this as SNa-MANa), a poly(styrene-*co*-sodium itaconate, ITANa) ionomer mixed with the MANa ionomer (ITANa-MANa), and the ITANa ionomer added to the SNa ionomer (ITANa-SNa). At this point, it should be noted that the strength of the interactions between Na-sulfonate ion pairs is stronger than that between Na-carboxylate ion pairs [1–4,16–19]. In the case of the ITANa ionomer, it has two ionic groups per ionic repeat unit (the chemical structures of the three pure ionomers are shown in Scheme 1). Thus, the results obtained in the present work will give us the information on the relationships between the numbers of ionic groups—strength of ionic interactions—properties of ion pair/ion pair blends. In addition, local environmental changes of ionic groups and morphologies of ionomer blends are also discussed briefly.



Scheme 1.

2. Experimental

2.1. Polymer preparation

Poly(styrene-*co*-methacrylic acid) (M_W = ca. 300,000) random copolymer was prepared by bulk polymerization of purified styrene and methacrylic acid monomers; poly (styrene-*co*-itaconic acid) (M_W = ca. 300,000) random copolymer was prepared by solution polymerization of purified styrene and itaconic acid monomers, dissolved in a small amount of dioxane. Detailed procedures have been described elsewhere [20,21]. To prepare poly(styrene-*co*-styrenesulfonic acid), polystyrene ($M_n = 127,000$ and $M_w = 269,000$) was synthesized by bulk polymerization. For the homogeneous sulfonation of the polystyrene, the method developed by Makowski et al. was used [22]. The contents of methacrylic acid, itaconic acid, and sulfonic acid units were found to be 5.1, 5.6, and 5.2 mol%, respectively. To prepare ITANa-MANa ionomer blends, predetermined amounts of the styrene-based itaconic acid and methacrylic acid copolymers were dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution, and the acid groups were neutralized with methanolic NaOH. The solution was freeze-dried and then dried further under vacuum at 120 °C for 24 h. For the preparation of SNa-MANa and ITANa-SNa ionomer blends, a similar procedure was applied.

2.2. Mechanical property measurements

For the dynamic mechanical thermal analysis (DMTA) experiments, ionomer blend samples were compression-molded at 250 °C and a pressure of 25 MPa. The transparent samples were removed from the mold and annealed under vacuum at 130 °C for at least 12 h. The dimensions of the molded samples were ca. $2.7 \times 7.0 \times 30\ \text{mm}^3$. For the mechanical property measurements, we used a Polymer Laboratories DMTA (Mark II). The experiments were carried out in a dual cantilever bending mode at frequencies of 0.3, 1, 3, 10, and 30 Hz; a heating rate was 1 °C/min. From the experiments, we obtained storage moduli (E') and loss tangents as a function of temperature.

2.3. Spectroscopy and microscopy

To make sample specimens for an infrared spectroscopy study, we pelletized ionomer samples with KBr powder. A fourier transform infrared spectrophotometer (Bruker, IFS-85) was used with a scanning number of 64 and resolution of 8 cm^{-1}. Samples for a scanning electron microscopy (SEM) study were prepared by fracturing compression-molded samples in liquid nitrogen. A field-emission scanning electron microscope (Hitachi, S-4700) was utilized with platinum sputter coating on the fracture surface of the specimen.

3. Results and discussion

It should be noted that all the ionomer blend samples are transparent because all the samples consist mainly of styrene units. Let us begin this part of the paper with an ionomer blend system containing two ionomers having only one ionic group per ionic repeat unit, i.e. SNa-MANa system. Fig. 1 shows the storage moduli and loss tangents of SNa-MANa ionomers as a function of temperature (the ratio of the SNa and MANa ionomers is on the basis of their weights). In the case of the pure MANa ionomer, with increasing temperature, the storage modulus changes from a glassy modulus, through a glass transition, through a relatively long ‘ionic plateau’, through a relatively weak glass transition, to a rubbery plateau and a sample flow region. At this point, it should be mentioned that the ionic plateau is the segment of the modulus curve in the temperature range between the two glass transitions, where the modulus decreases slightly with temperature. It is known that the ionic plateau is associated with the degree of clustering; that is, the higher degree of clustering leads to the higher ionic plateau [3,4,6,18,21]. It is also recognized that the width of the ionic plateau is mainly related to the strength of ionic interactions; i.e. the stronger ionic interaction results in the wider ionic plateau [3,4,18,23]. At this point, the differences in the mechanical properties of SNa and MANa ionomers are worth mentioning. Firstly, the ionic interaction between Na-sulfonate ionic groups is stronger than that between Na-methacrylate ionic groups [3,4,16–19,23]. As a result, the second T_g, i.e. cluster T_g, for the SNa ionomer is higher than that for the MANa ionomer, and, thus, the ionic plateau of the sulfonate ionomer is extended to higher temperatures. Secondly, the height of the ionic plateau is lower for the SNa ionomer than for the MANa ionomer; this can be understood. The ionic groups of the SNa ionomer are attached to the *para* position of a benzene ring, while those of the MANa ionomer are directly appended to the polymer main chain. Thus, multiplets formed in the SNa ionomer are larger than those in the MANa ionomer because the distance between the ionic group and the main chain is longer for the SNa ionomer, leading to less steric hindrance for the ionic groups to form multiplets. Since the size of the multiplet is larger, there are fewer multiplets in number. If the thickness of the restricted mobility layer were similar in these two ionomers, the total volume of materials of restricted mobility would be smaller for the SNa ionomer [3,4,6,18]. In addition, the strength of the ionic interactions also changes the size of multiplets. That is, the stronger ionic interactions, the more ion pairs per multiplet. This also increases the size of the multiplet for the SNa ionomer, compared to that for the MANa ionomer [3,4,6,18]. Regarding the arguments mentioned above, the change in the mechanical properties of SNa-MANa ionomers with changing relative amounts of the two ionomers can be understood. In other words, with increasing SNa ionomer content, the ionic plateau shifts to lower values, while the width of the plateau becomes wider. To interpret the ionic plateau more quantitatively, we plotted the ionic modulus (i.e. modulus at the minimum slope of the plateau) of SNa-MANa ionomers as well as those of ITANa-SNa and ITANa-MANa systems as a function of the weight percentage of the two ionomers (Fig. 2). Fig. 2 shows that, as expected, the ionic modulus for the SNa-MANa system decreases monotonously with increasing SNa ionomer content. This aspect will be discussed again below.

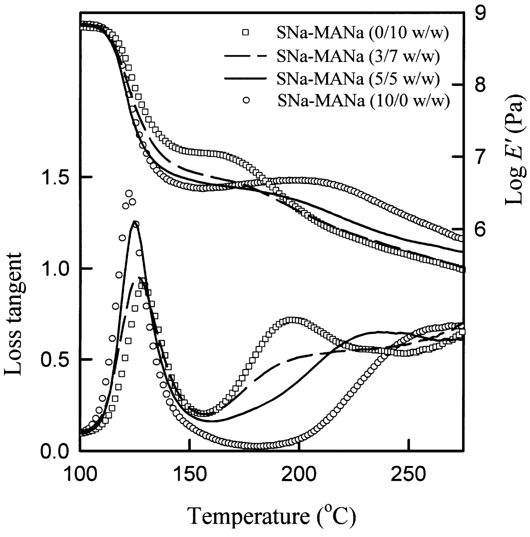


Fig. 1. Storage moduli (E') and loss tangents of SNa-MANa ionomer blends as a function of temperature (measured at 1 Hz). The weight ratios of the two ionomers are also indicated.

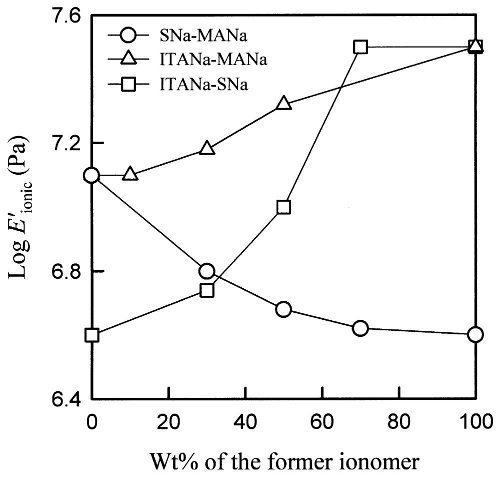


Fig. 2. Ionic moduli of SNa-MANa, ITANa-MANa, and ITANa-SNa blends with the increasing weight percentage of former ionomers (1 Hz data).

Shown in Fig. 1 are a matrix loss tangent peak at low temperatures and a cluster peak at high temperatures. It is observed that the height of the matrix peak decreases with increasing SNa ionomer content, but that the peak position remains relatively constant. In the case of the cluster peak, however, it shifts to higher temperatures with increasing SNa ionomer content. At this point, it should be stressed that the presence of only two loss tangent peaks implies that this ionomer blend system resembles a 'typical' miscible blend and behaves like a unblended pure styrene ionomer system that usually has two loss tangent peaks. Fig. 3 shows the matrix and cluster T_gs obtained from the position of the maximum of loss tangent peaks of SNa-MANa ionomer blends as a function of the weight percentage of the two ionomers. This figure also includes the data for another two ionomer blend systems. Again, it is clear that, with increasing SNa ionomer content in the SNa-MANa ionomers, the cluster T_g increases significantly, but the matrix T_g increases only slightly. Furthermore, in Fig. 3, it is seen that the cluster T_gs of SNa-MANa system are very close to cluster T_gs calculated using the Fox equation for homogeneous blend systems. Again, this indicates that 5 mol% SNa-MANa ionomer is a typical miscible blend. Therefore, it can be suggested that the ionic groups of the MANa ionomer form new multiplets with those of the SNa ionomer, and, thus, that the dynamic mechanical properties of the ionomers lie in between those of the pure SNa and MANa ionomers. As a result, the clustered regions of the SNa and MANa ionomers are miscible to make one relatively homogeneous clustered regions. This might be what we observed here.

To investigate the ion content effects, we measured the mechanical properties of two SNa-MANa (5/5 w/w) ionomers; one contains 6.9 and 6.8 mol% of ions, and the other has 8.9 and 8.7 mol% of ions, respectively. Fig. 4 shows the loss tangents of these two ionomer blends containing ca. 7 and 9 mol% of ions vs. temperature. Again, three loss tangent peaks are seen for each blend, and the peaks shift to higher temperatures with increasing ion contents. These results illustrate that at high ion contents the polystyrene-based ionomer blends, indeed, exhibit phase-separation, at least to some extent. Especially, the presence of two cluster peaks indicates that two types of multiplets might exist in this ionomer blend; carboxylate-rich multiplet and sulfonate-rich multiplet. These two types of multiplets are naturally responsible for two different types of clustered regions. As was mentioned before, the low cluster T_g is due to the glass transition of clustered regions containing carboxylate-rich multiplets, while the high cluster T_g is associated with the glass transition of clustered regions containing sulfonate-rich multiplets [15]. At low ion contents, the ionic characters of two ionomers are relatively weak, compared to the characteristic nature of polymer matrix (i.e. polystyrene). Thus, the two ionomers are miscible. With increasing ion content (i.e. the polymer becomes more ionized), however, each ionomer shows its own ionic character more strongly, leading to phase-separation. In addition, the increase of ion content also changes the chemical structures of ionomers significantly; i.e. copolymerization effects. This also makes two ionomers less miscible. At this point, it should be noted that the 5 mol% SNa-MANa ionomer blend showed only two loss tangent peaks, while 7 and 9 mol% ionomer blends exhibited three peaks. This suggests that there is a critical ion content, at which each polystyrene-based ionomer starts to form its own phase-separated regions. This can be explained. According to the work from the group of Eisenberg, at ca. 6 mol% of ion contents the MANa ionomers show the conversion of matrix regions-dominant materials to clustered regions-dominant materials [3,4,6,21,24,25]. Thus, ca. 7 and 9 mol% MANa ionomers are clustered regions-dominant materials, while the 5 mol% MANa ionomer is a matrix regions-dominant material.

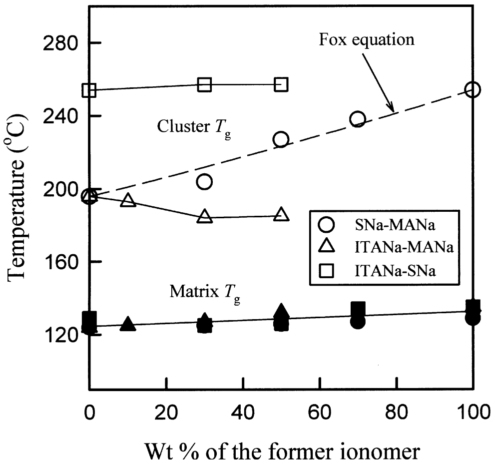


Fig. 3. Glass transition temperatures of SNa-MANa, ITANa-MANa, and ITANa-SNa blends with increasing the weight percentage of former ionomers (1 Hz data).

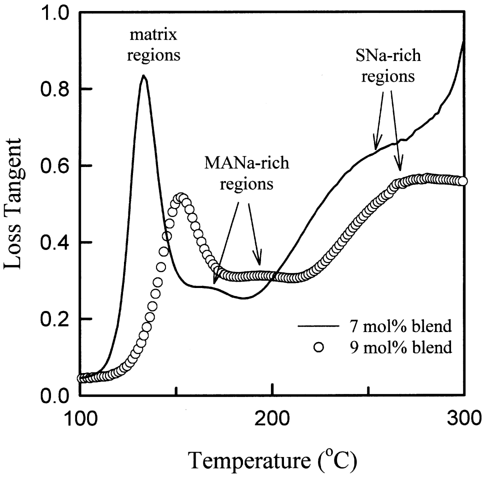


Fig. 4. Loss tangents of 5/5 (w/w) blends of SNa-MANa ionomers as a function of temperature (measured at 1 Hz). One ionomer contains 6.9 and 6.8 mol% of ion, and the other contains 8.9 and 8.7 mol% of SNa and MANa ionic groups, respectively.

Therefore, the difference in miscibility of ca. 5 and 7 mol% SNa-MANa samples is not surprising.

Now, let us discuss two ionomer blends containing an ITANa ionomer that has two ionic groups per ionic repeat unit. The dynamic mechanical properties of ITANa-MANa and ITANa-SNa ionomer blends are shown in Figs. 5 and 6, respectively. In the case of ITANa-MANa ionomers, it is seen that the ionic modulus increases and the ionic plateau becomes wider with increasing ITANa contents. It is also found that the cluster loss tangent peak of the MANa ionomer shifts to lower temperatures, and that the size of the peak decreases noticeably with increasing ITANa content, and even decreases more rapidly than the decreasing weight ratio of MANa ionomer in the ionomer blends. These findings are different from those for the SNa-MANa ionomer blend system. At this point, the high cluster T_g of the ITANa ionomer is worth recalling. The ionic groups of the ITANa ionomer experience difficulty when they form ionic aggregates owing to steric hindrance [20]. Therefore, two ionic groups at closest approach probably form 'ionic bonds' rather than multiplets. These ionic bonds, acting as three-dimensional physical crosslinks, are surely different from the multiplets found in pure SNa and MANa ionomers. It should also be noted that the ionic modulus of the ITANa ionomer is maintained at much higher temperatures, compared to that of the MANa ionomer. This is due to the fact that, for the relaxation of the chains in ion-rich regions, three ionic moieties of the ITANa ionomer (i.e. two sodium cations and one itaconate anionic unit) have to hop simultaneously at and above the cluster T_g, while only two ionic moieties need to hop for the MANa ionomer [20]. Therefore, the ITANa ionomer has relatively high second T_g and, thus, exhibits a relatively long ionic plateau. In addition, due to weak clustering of the ITANa ionomer, the cluster loss tangent peak, expected to be at ca. 250 °C [20], is not observed in the present study. Now, let us go back to the ionomer blends. If the MANa and ITANa ionomers were mixed and, thus, formed new multiplets containing ionic groups of both the MANa and ITANa ionomers, two cluster loss tangent peaks of the MANa and ITANa ionomers should merge into one peak, placed in between the cluster T_gs of the two ionomers. However, this is not the case here. Thus, it can be suggested that the mixing process of these two ionomers may not form new multiplets that would, in turn, lead to the formation of new clustered regions. Thus, it is speculated that the introduction of the ITANa ionomer to the MANa ionomer might induce the formation of ionic bonds between some of carboxylate ionic groups of both the MANa ionomer and the ITANa ionomer; leading to the disruption of the formation of multiplets of MANa ionomers. This naturally reduces the degree of clustering of the MANa ionomer, resulting in the shift of the cluster T_g peak of the MANa ionomer to lower temperatures. In the case of ITANa-SNa blends, it is seen that with increasing ITANa contents the ionic modulus increases rapidly and levels off (Figs. 2 and 6). This suggests that the presence of the ITANa ionomer would affect the modulus values more strongly than that of the SNa ionomer. It is also observed that the cluster T_gs of the ITANa-SNa ionomers are relatively constant at ca. 255 °C. In this system, the role of the ITANa ionomer in the blends is thought to be the same as that in the ITANa-MANa ionomer system. However, morphological changes affect only the modulus of the blends because the cluster T_gs of both the SNa and the ITANa ionomers are in the range of 250–260 °C.

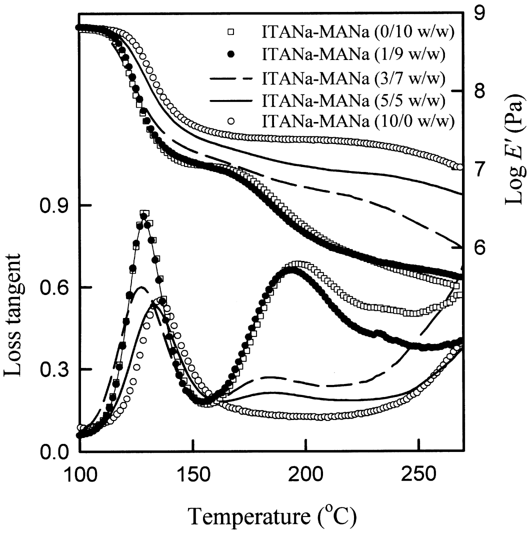


Fig. 5. Storage moduli (E') and loss tangents of ITANa-MANa ionomer blends as a function of temperature (measured at 1 Hz). The weight ratios of the two ionomers are also indicated.

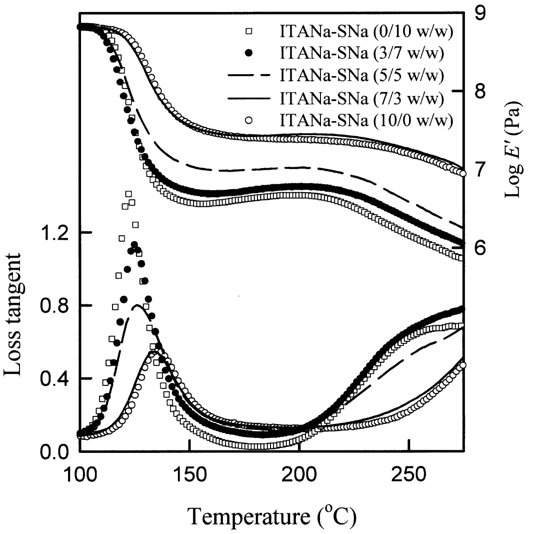


Fig. 6. Storage moduli (E') and loss tangents of ITANa-SNa ionomer blends as a function of temperature (measured at 1 Hz). The weight ratios of the two ionomers are also indicated.

Now, it should be stressed that the storage modulus curves in Figs. 1, 5, and 6 suggest three possible areas of practical applications of these ionomer blends. First, when one wants to have an ionomer, whose ionic modulus is lower but remains relatively constant to much higher temperatures than that of an MANa ionomer, we should blend the MANa ionomer with an SNa ionomer of a comparable ion content. Second, if an ionomer, whose ionic modulus is higher and remains relatively constant to much higher temperatures than that of an MANa ionomers, were desirable, the MANa ionomer should be mixed with an ITANa ionomer of a

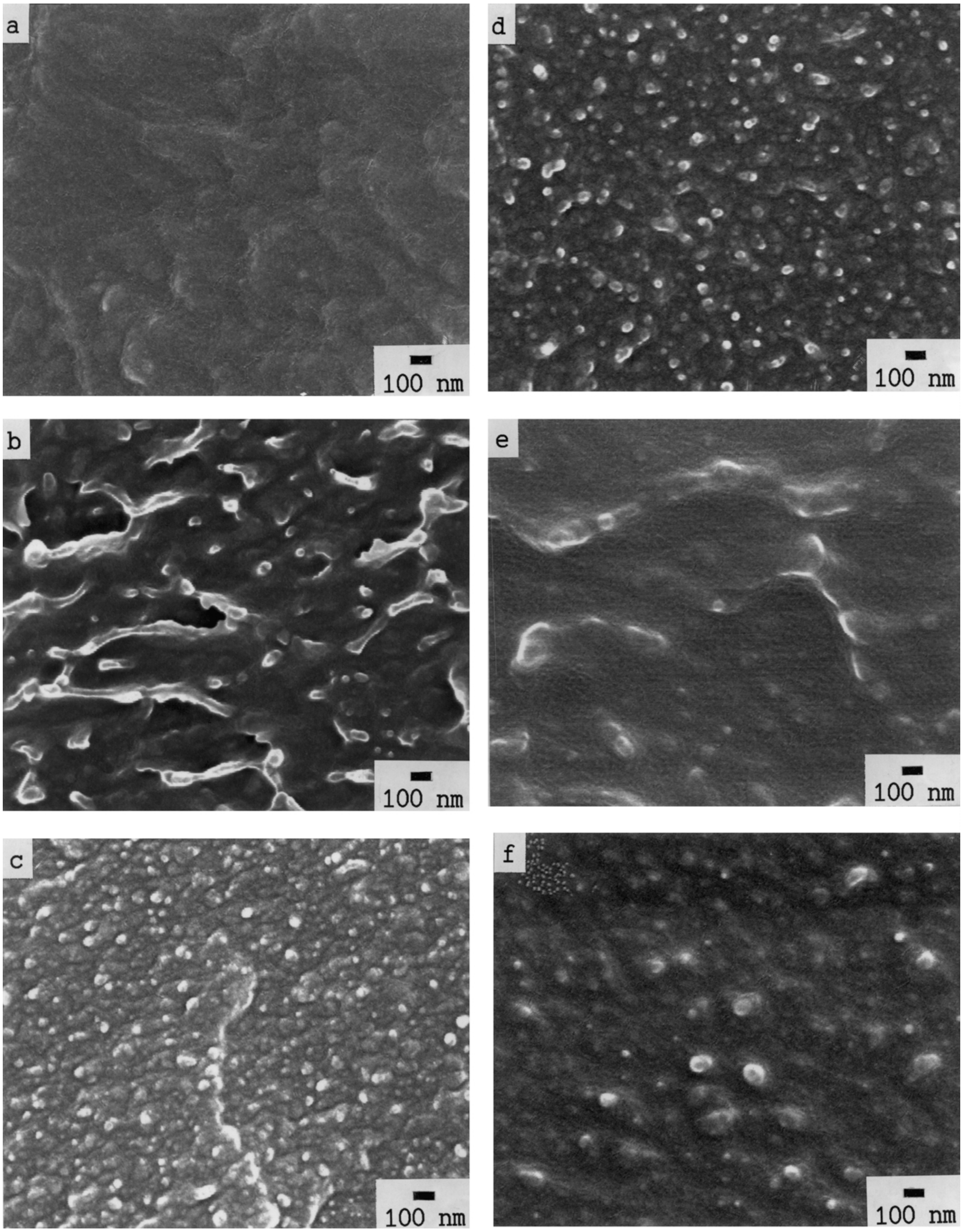


Fig. 7. Scanning electron microscopy images of (a) MANa ionomer, (b) SNa ionomer, (c) ITANa ionomer, (d) SNa-MANa blend, (e) ITANa-SNa blend, and (f) ITANa-MANa blend. The weight ratio of the two ionomers in the blend is 5/5.

comparable ion content. Third, if one would like to reduce the ionic modulus values of an ITANa ionomer, without changing a second glass transition, one should make the ITANa ionomer blend with an SNa ionomers of a comparable ion content. That is, through these three methods one could obtain styrene ionomers having desirable mechanical properties.

It is known that an infrared (IR) spectroscopy can be used to investigate the possible local environmental changes in ionomer blends [26–30]. Thus, in the present work, we performed IR spectroscopic measurements of pure ionomers and their blends. It is found that, upon mixing, new IR bands are not observed (not shown here); only the intensities of bands change in accordance with the ratio of the amounts of two styrene ionomers. These results indicate that the blending does not change the local interactions between ionic groups significantly. According to a recent report by Weiss et al., the miscibility between liquid crystalline polymers and zinc sulfonated styrene ionomers did not depend on specific interactions between polymer chains [30]. Thus, the above findings are understood.

Fig. 7 shows the SEM images of the three styrene-based ionomers and their mixtures (5/5 w/w). For the MANa ionomer (7-a), much smoother surface is seen. In the case of the SNa ionomer (7-b), the surface looks like that of a sticky paper. For the ITANa ionomer (7-c), a number of white features distributed on the surface are observed. Upon the addition of MANa ionomer to SNa ionomer (7-d), the size of the white features of the SNa ionomer becomes smaller, but the number increases drastically. In the case of the ITANa-SNa ionomer (7-e), it is seen that the sizes of the white features increase, but the number decreases significantly. A similar result is also observed for ITANa-MANa ionomer (7-f). These observations indirectly imply that a blending process changes the morphology of ionomers, which, in turn, alters the mechanical properties, as well. At this point, our previous finding in a SAXS study on the blend of SNa (10.6 mol% of ions) and MANa (10.8 mol% of ions) is worth recalling [15]. A well-developed SAXS peak and a weak SAXS peak were observed for the SNA and MANa ionomers, respectively. However, the SNA-MANa ionomer showed only a very broad shoulder-like feature. Thus, it was suggested that the mixing process interrupted the relatively ordered arrangement of scattering centers (i.e. multiplets), resulting in scattering centers of various scattering intensities at varying distances. This information is supportive for the morphological changes upon blending in the present work.

Acknowledgements

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References

[1] Schlick S, editor. Ionomers: characterization, theory, and applications. Boca Raton: CRC Press; 1996.

[2] Tant MR, Mauritz KA, Wilkes GL, editors. Ionomers: synthesis, structure, properties and applications. New York: Blackie; 1997.

[3] Eisenberg A, Kim J-S. Introduction to ionomers. New York: Wiley; 1998.

[4] Kim J-S. Ionomers. In: Kroschwitz JI, editor. Encyclopedia of polymer science and technology. New York: Wiley-Interscience; 2002.

[5] Eisenberg A. Macromolecules 1970;3:147.

[6] Eisenberg A, Hird B, Moore RB. Macromolecules 1990;23:4098.

[7] Yarusso DJ, Cooper SL. Macromolecules 1983;16:1871.

[8] Moore RB, Bittencourt M, Gauthier M, Williams CE, Eisenberg A. Macromolecules 1991;24:1376.

[9] Smith P, Hara M, Eisenberg A. In: Ottenbrite RM, Utracki LA, Inoue S, editors. A review of miscibility enhancement via ion–ion and ion–dipole interactions. Current topics in polymer science, vol. 2. New York: Hanser Publishers; 1987. p. 256–83.

[10] Bazuin CG. In: Salamone JC, editor. Ionomers (compatibilization of blends). Polymeric materials encyclopedia, vol. 5. Boca Raton: CRC Press; 1996. p. 3454–60.

[11] Smith P, Eisenberg A. Polym Prep (Am Chem Soc; Polym Chem Div) 1982;23:17.

[12] Lu X, Weiss RA. Macromolecules 1991;24:5763.

[13] Smith P, Eisenberg A. Macromolecules 1994;27:545.

[14] Douglas EP, Waddon AJ, MacKnight WJ. Macromolecules 1994;27:4344.

[15] Kim J-S, Kim H-S, Nah YH, Eisenberg A. Polym Bull 1998;41:609.

[16] Lundberg RD, Makowski HS. A comparison of sulfonate and carboxylate ionomers. In: Eisenberg A, editor. Ions in polymers. Advances in chemistry series 187, Washington DC: American Chemical Society; 1980. Chapter 2.

[17] Lefelar JA, Weiss RA. Macromolecules 1984;17:1145.

[18] Hird B, Eisenberg A. Macromolecules 1992;25:6466.

[19] Song J-M, Hong M-C, Kim J-S, Yoo J, Yu J-A, Kim W. Macromol Res 2002;10:304.

[20] Kim J-S, Hong M-C, Nah YH. Macromolecules 2002;35:155.

[21] Kim J-S, Jackman RJ, Eisenberg A. Macromolecules 1994;27:2789.

[22] Makowski HS, Lundberg RD, Singhal GL. US Patent 870,841; 1975.

[23] Kim J-S, Yoshikawa K, Eisenberg A. Macromolecules 1994;27:6347.

[24] Eisenberg A, Navratil M. Macromolecules 1973;6:604.

[25] Hird B, Eisenberg A. J Polym Sci Part B: Polym Phys 1990;28:1665.

[26] Rouse GB, Risen Jr WM, Tsatsas AT, Eisenberg A. J Polym Sci Polym Phys Ed 1979;17:81.

[27] Lu X, Weiss RA. Macromolecules 1991;24:4381.

[28] Rajagopalan P, Kim J-S, Brack HP, Lu X, Eisenberg A, Weiss RA, Risen Jr WM. J Polym Sci Part B: Polym Phys 1995;33:495.

[29] Nishioka A, Takahashi T, Masubuchi Y, Takimoto J-I, Koyama K. Polymer 2001;42:7907.

[30] Weiss RA, Ghebremeskel Y, Charbinneau L. Polymer 2000;41:3471.