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Effects of various carboxylated benzene salts on the mechanical properties and morphology of poly(styrene-*co*-methacrylate) ionomers

Ho Seung Jeon[a], Sung-Hwa Oh[a], Joon-Seop Kim[a*], Yeonhee Lee[b,*]

[a]*Department of Polymer Science and Engineering, Chosun University, Gwangju 501-759, South Korea*
[b]*Advanced Analysis Center, Korea Institute of Science and Technology, Seoul 130-650, South Korea*

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Abstract

Dynamic mechanical properties and morphology of poly(styrene-*co*-sodium methacrylate) ionomers containing aromatic organic salts possessing one, two, and four sodium carboxylate ion pairs per salt molecule, i.e. Na-benzoate, Na-isophthalate, and Na-benzenetetracarboxylate, respectively, were investigated. The addition of the organic salts increased the ionic modulus noticeably and lowered the cluster T_g slightly. Thus, it was suggested that some of the organic salts might reside in/near multiplets, acting as plasticizer, while the rest of the salts formed aggregates, acting as filler. It was also found that the amount of the organic salts, not the number of ion pairs per one organic salt molecule, played a key role in the determination of the mechanical properties of the ionomers. It was also observed that the experimental ionic modulus data were much higher than the calculated values using filler concepts, which implied that the addition of salts also changed the nature of the polymer matrix significantly.

Keywords: Ionomer; Filler; Salts

1. Introduction

During the past over 35 years, the effects of ionic interactions on the properties and morphology of polymers containing ionic groups have been investigated extensively [1–3]. Polymers containing a small amount of ionic groups, called ionomers, exhibit very unique properties and various morphology, compared to non-ionic polymers. For example, the unique properties and morphology include the presence of two glass transitions, high melt viscosity, and the appearance of a small-angle X-ray scattering peak [1–5].

According to the Eisenberg–Hird–Moore model for amorphous random ionomers, the interactions between ionic groups and the difference in the polarity values of ionic groups and non-polar polymer matrix lead to ionic groups forming aggregates [6]. These ionic aggregates, called multiplets [7], reduce the mobility of polymer chains surrounding them [6]. When the ion content is low, the size of the reduced mobility regions of polymer chains is too small to show their own glass transition (T_g). However, as the ion content increases, the reduced mobility regions start to overlap. When the size of the overlapping regions, so-called clusters, becomes larger than a certain dimension, e.g. 10 nm, the regions exhibit their own glass transition, i.e. cluster T_g, which is higher than a matrix T_g [6].

From 1970s the mechanical properties, morphology, and spectroscopy of styrene ionomers have been studied widely in a number of research groups, including the groups of Eisenberg [8–14], Lundberg [15–18], Cooper [19–21], Risen [22–24], Weiss [25–30], Bazuin [31,32], Hara [33–35], Register [36], Moore [36–39], Suchocka-Gałas [40,41], Winey [42,43], and our group [44–47]. However, the effects of the addition of various organic aromatic salts on the properties of polystyrene ionomers have not been investigated thoroughly. Recently, Nah et al. studied the effects of the sodium *p*-toluate and sodium *p*-toluenesulfonate on the mechanical properties of the poly(styrene-*co*-sodium methacrylate) and sodium-sulfonated polystyrene ionomers [45]. It was found that the organic salts acted both as plasticizer as well as filler. However, in that system, the salts had only one ion pair per one salt molecule, and, thus, two questions arose; (1) what would be the effects of the

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* Corresponding authors. Address: Department of Polymer Science and Engineering, Chosun University, Gwangju 501-759, South Korea. Tel.: +82-62-230-7211; fax: +82-62-232-2474.
E-mail address: joon@mail.chosun.ac.kr (J.S. Kim).

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number of ion pairs per one organic salt molecule on the ionomer properties, and furthermore (2) would the organic salts disrupt the formation of multiplets as plasticizer or form phase-separated entities, which act as filler? To answer the questions, in the present study, we investigated the dynamic mechanical properties and morphology of poly(styrene-*co*-sodium methacrylate) ionomers containing low molecular weight (MW) sodium salts of various carboxylated benzene. Especially, we chose three different aromatic organic salts, which possess one, two, and four sodium carboxylate ion pairs, i.e. Na-benzenecarboxylate, Na-isophthalate, and Na-benzenetetracarboxylate, respectively. From the results obtained in this study, we could clarify the roles of three organic salts in the ionomer, and understand the effects of the number of ion pairs per salt molecules and the significance of the effects.

2. Experimental section

2.1. Sample preparation

Poly(styrene-*co*-methacrylic acid) [P(S-*co*-MAA)] was prepared by bulk polymerization of purified styrene and methacrylic acid monomers using benzoyl peroxide as the initiator (MW = ca. 300,000) [8,14]. The reaction temperature was 60 °C, and conversion was less than 7%, yielding compositional heterogeneity of less than 0.1. The polymer sample was recovered by precipitation into a rapidly stirred excess of methanol. The precipitated polymer was filtered, and dried under vacuum at 120 °C for 24 h. To determine the acid content, the P(S-*co*-MAA) copolymer was dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution and titrated with standard methanolic NaOH to the phenolphthalein end point; the acid content was 7.6 mol%. To obtain ionomers containing the organic salts of low MW, three different aromatic carboxylic acids, i.e. benzenecarboxylic acid (i.e. benzoic acid, Bz), 1,3-benzenedicarboxylic acid (i.e. isophthalic acid, Iso), and 1,2,4,5-benzenetetracarboxylic acid (i.e. pyromellitic acid, Tetra), were added to a mixture of benzene/methanol (9/1, v/v) containing the P(S-*co*-MAA) copolymer. The amount of the aromatic carboxylic acid was varied to make the ratios of the number of the acid groups in (aromatic carboxylic acid/P(S-*co*-MAA) copolymer) of 1/1, 2/1, 4/1, and 8/1. Subsequently, a predetermined quantity of methanolic NaOH was added to the solution to neutralize the acid groups of aromatic carboxylic acids and P(S-*co*-MAA) copolymer. It should be mentioned that the maximum amount of the aromatic carboxylic acid in the samples depended on the solubility of the resulting ionomers. For example, in the case of the sample containing a large amount of benzenetetracarboxylic acid molecules, upon the addition of NaOH to the solution, the multifunctionality of sodium benzenetetracarboxylate (NaTetra) molecules induced physical cross-linking of NaTetra molecules with the ionic groups of the ionomer. Thus, the solubility of the resulting ionomer sample decreased drastically, and the ionomer containing NaTetra molecules was precipitated out. Therefore, in the present work, for the sake of a uniform condition of sample specimen, only samples obtained from a homogeneous solution were used. That is, the maximum ratios of acid groups in (organic acid/copolymer) were 8/1, 4/1, and 2/1 for NaBz-, NaIso-, and NaTetra-containing samples, respectively. The solutions were freeze-dried and then dried further under vacuum at 170 °C for 24 h. The sample notation used is x-y, where x is the type of organic salts, and y denotes the ratio of the number of the sodium carboxylate ion pairs of the aromatic organic salts to that of the ionomer.

2.2. Dynamic mechanical property measurements

For the mechanical property measurements, the sodium-neutralized ionomers, i.e. P(S-*co*-MANa) ionomers, containing different amounts of aromatic salts were compression-molded at 230–260 °C and a pressure of 25 MPa for 5 min. The mold was allowed to cool to below 100 °C. The sample was removed from the mold, and annealed under vacuum at 130 °C for 24 h. The dimensions of the molded sample were ca. $2.5 \times 7.0 \times 30\ \text{mm}^3$. To determine the mechanical properties of ionomers, a dynamic mechanical thermal analyzer (Polymer Laboratories, DMTA Mark II) was used. The experiments were carried out in a dual cantilever bending mode at frequencies of 0.3, 1, 3, 10, and 30 Hz. Storage moduli (E') and loss tangents ($\tan\delta$) were obtained as a function of temperature at a heating rate of 1 °C/min. Even though dynamic mechanical measurements for each sample were conducted at five different frequencies, detailed analysis was performed only on 1 Hz data. Curve de-convolutions were performed on the loss tangent data using the Peakfit (SPSS Inc.) software. The best fits were obtained taking an exponential equation as a background and fitting matrix and cluster loss tangent peaks with two Gaussian area functions.

2.3. X-ray and microscopy experiments

To prepare the samples for an X-ray study, the sample preparation method used for the DMTA experiments was also applied. The X-ray diffraction (XRD) patterns of compression-molded ionomers were recorded using an X-ray diffractometer (Rigaku Co., D/MAX-3C). The Cu radiation ($\lambda = 0.15418$ nm) was utilized, and the power of the X-ray generator was 35 kV and 15 mA. The scanning speed was 1°/min, and the sampling width was 0.01°. Samples for scanning electron microscopy (SEM) were prepared by fracturing compression-molded samples under liquid nitrogen. A field-emission scanning electron microscope (Hitachi, FE-SEM S-4700) was utilized with platinum sputter coating on the fracture surface of the specimen. The morphology of the surface of fractured sample was also investigated using atomic force microscope (PSI UHV STM SU-2).

3. Results

Fig. 1 shows the storage modulus and loss tangent values of the P(S-*co*-MANa) ionomer and ionomers containing different amounts of sodium benzoate (NaBz) as a function of temperature. With increasing temperature, the modulus changes from a glassy modulus, through a matrix glass transition, through an ionic plateau (i.e. the modulus between matrix and cluster T_gs), through a cluster glass transition, to a rubbery plateau. It is seen that above ca. 120 °C the modulus values of the organic salt-containing ionomers become higher with increasing NaBz salt content. In the same figure, two loss tangent peaks are also shown. The peak at low temperatures is due to the glass transition (T_g) of matrix regions, while the other peak at high temperatures is due to the T_g of cluster regions [3–6,9,12,14]. In the figure, it is also observed that the position of the peak for the matrix T_g remains relatively constant, while the peak for the cluster T_g shifts to lower temperatures slightly with increasing organic salt content. In addition, the two peak areas are shown to decrease with increasing organic salt content.

Figs. 2 and 3 show the storage modulus and loss tangent values of the P(S-*co*-MANa) ionomer and ionomers containing different amounts of sodium isophthalate (NaIso) and sodium benzenetetracarboxylate (NaTetra) salts, respectively, as a function of temperature. Again, above the matrix T_g the storage modulus values for the salt-containing ionomers are shown to be higher than that for the pure ionomer, and that the modulus values increase with increasing organic salt content. The trends in the loss tangent peaks as a function of salt content are also found to be similar to that for the ionomer system containing NaBz salts.

The glass transition temperatures (T_gs) obtained from the positions of the loss tangent peak maxima for the matrix and cluster glass transitions are shown in Fig. 4 as a function of the ratio of the number of ionic groups in (organic salts/ionomer). It is clear that the matrix T_gs remain relatively constant at ca. 136 ± 0.7 °C, which is independent of the

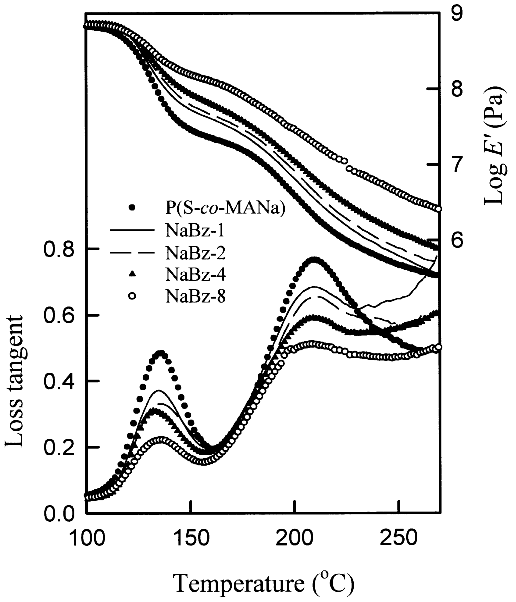


Fig. 1. Storage moduli and loss tangents as a function of temperature for the P(S-*co*-MANa) ionomer and ionomers containing various amounts of NaBz salts, measured at 1 Hz.

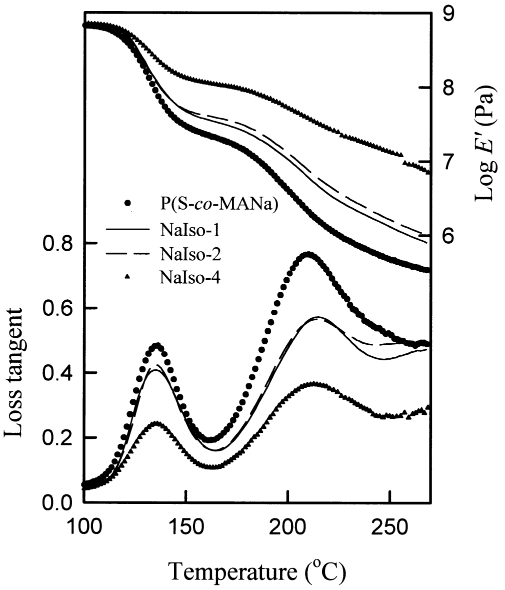


Fig. 2. Storage moduli and loss tangents as a function of temperature for the P(S-*co*-MANa) ionomer and ionomers containing various amounts of NaIso salts, measured at 1 Hz.

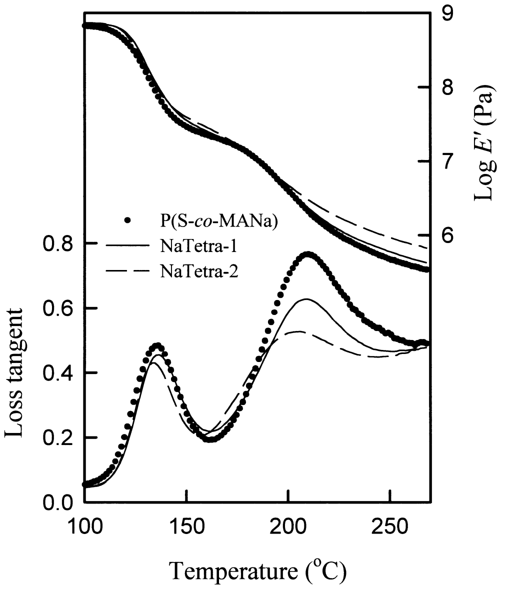


Fig. 3. Storage moduli and loss tangents as a function of temperature for the P(S-*co*-MANa) ionomer and ionomers containing various amounts of NaTetra salts, measured at 1 Hz.

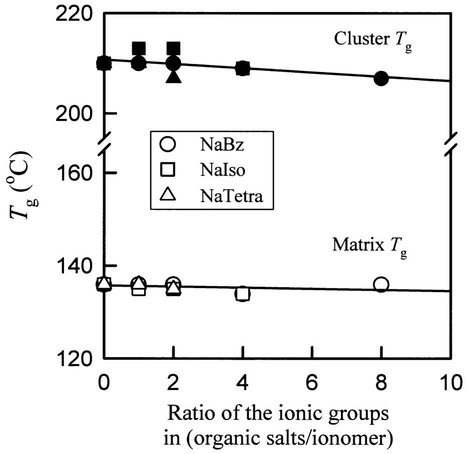


Fig. 4. Glass transition temperatures of the matrix and cluster regions of the ionomer and those containing various organic salts as a function of the ratio of the ionic groups in (organic salts/ionomer), measured at 1 Hz.

type and amount of organic salts added. In the case of cluster T_gs, however, they change slightly upon the addition of organic salts. For example, the cluster T_g of the ionomer containing NaBz-8 is only ca. 3 °C lower than that of the pure ionomer. This result is surprising because a very high weight percentage of the organic salts in this sample, i.e. ca. 46%, induced only a minor change in the cluster T_g.

Fig. 5 shows the peak areas as a function of (a) the ratio of the number of ionic groups in (organic salts/ionomer) and (b) the weight percentage of organic salts in ionomers. First of all, comparison of Fig. 5(a) with Fig. 5(b) reveals that the superimposition of the data is better, when the data are plotted against the weight percentage of organic salts. Secondly, it is also observed that the area under the matrix loss tangent peak decreases more rapidly with increasing organic salt content, compared to the cluster peak area. Thirdly, it is evident in Fig. 5 that the decrease in the areas is more likely independent of the type of organic salts, and is only affected by the weight fraction of the organic salts in the ionomer. At this point, it should be worth recalling that the ratio of the matrix and cluster peak areas is suggested to be related with the relative amounts of the matrix and cluster regions, respectively [3–5,9,12,14,45].

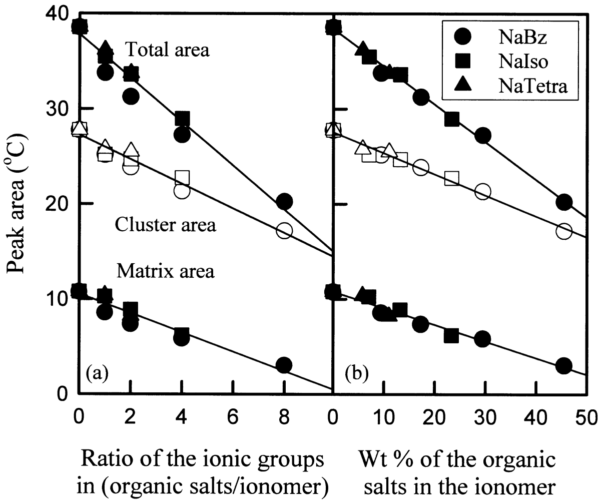


Fig. 5. Areas under the loss tangent peaks and the sum of the areas as a function of the amount of organic salts in the ionomer (1 Hz data).

Shown in Fig. 6(a) are the ionic modulus values (E'_{ionic}) as a function of the ratio of the number of ionic groups in (organic salts/ionomer). This figure shows that the ionic modulus increases with increasing organic salt content, and that the increasing rates of ionic modulus for the three ionomer systems are different. However, it is worth noting that when the ionic modulus data are plotted as a function of the weight percentage of the organic salts in the ionomer sample, all the data are superimposed on one curve (Fig. 6(b)). This figure implies, again, that the mechanical properties of ionomers are more or less independent of the type of the organic salts, but strongly depend only on the amount of the organic salts.

In Fig. 7, XRD patterns for polystyrene, P(S-*co*-MANa) ionomer, and their salts-containing samples are shown. It is interesting to note that in the case of the polystyrene and ionomer samples containing NaBz organic salts, there is a peak at $2\theta =$ ca. 6° (this angle corresponds to the Bragg distance between scattering centers of ca. 1.5 nm), and the peak intensity increases with increasing organic salt content. After due consideration of the bond lengths in the sodium benzoate molecule (i.e. C–H bond length = ca. 0.11 nm, C–C bond length in benzene = ca. 0.14 nm, $C(sp^2)-C(sp^2)$ single bond length = 0.148 nm, and C–O bond length in carboxylate = ca. 0.126 nm [48,49]), we suggest that the XRD peak might be ascribed to the formation of regular micelle type aggregation of NaBz salts; the diameter of the micelle is more likely in the range of ca. 1.5 nm. In the case of the polystyrene and ionomer samples containing NaIso and NaTetra salts, an XRD peak is not observed. The

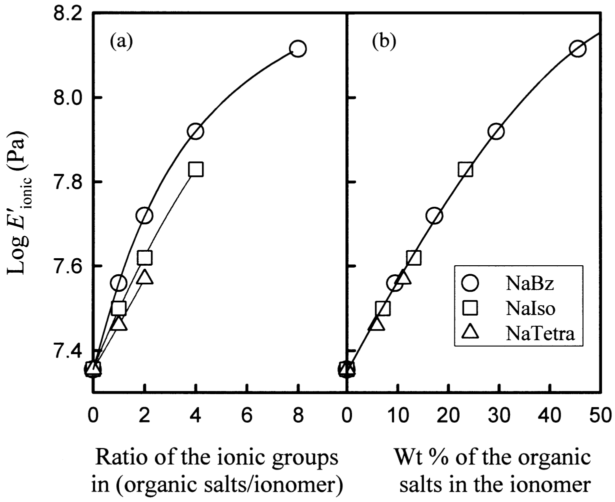


Fig. 6. Ionic modulus values for the ionomer and those containing organic salts as a function of (a) the ratio of ionic groups in (organic salts/ionomer) and (b) the weight percentage of organic salts in the ionomer, measured at 1 Hz.

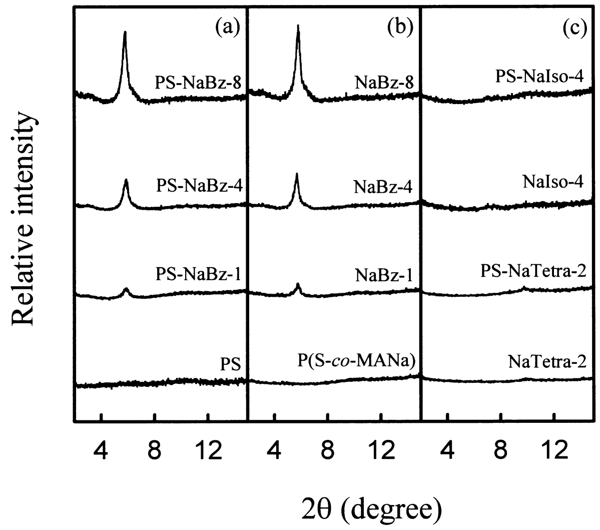


Fig. 7. XRD patterns of (a) styrene homopolymer containing NaBz organic salts, (b) ionomers containing NaBz salts, and (c) styrene homopolymer and ionomers containing NaIso and NaTetra salts. Each curve was shifted up by the same magnitude with respect to each other for clarity.

reason for the absence of the peak for these samples is not known at present. The result, however, indicates that the morphology of the organic salts in polystyrene homopolymer might be not much different from that in P(S-*co*-MANa) ionomers.

SEM and atomic force microscopy images of the fracture surfaces of some of ionomers containing organic salts are shown in Figs. 8 and 9. In Fig. 8, unlike the pure ionomer sample, the organic salt-containing ionomers show small white particles distributed on the fracture surface of the samples. These white particles are believed to be the aggregates of phase-separated organic salts. Fig. 9 shows the roughness of the surfaces of various ionomer samples. From this figure, the root mean square roughness values of the fracture surfaces of the pure ionomer, NaBz-4, NaIso-2, and NaTetra-1 are found to be 43, 88, 51, and 29 nm, respectively. This means that, first of all, the addition of the salts changes the roughness of the surfaces of the pure ionomer, and that the roughness increases with increasing salt content, as expected. The results shown in Figs. 8 and 9 indicate that the type and amount of salts affect the nanometer-scale topology of the ionomer surfaces. At this point, it should be mentioned that, judging from the difference in the melting temperatures of benzoic acid (mp = 122 °C) and its sodium salt (mp (= 300 °C) [50], the melting temperature of the sodium salts form of isophthalic acid (mp of isophthalic acid = 347 °C) and benzenetetracarboxylic acid (mp of benzenetetracarboxylic acid = 276 °C) are expected to be well above 300 °C. Thus, in the temperature range for the DMTA experiments, the melting peak of the phase-separated organic salts would not be expected; DSC thermograms indeed showed no melting peak up to ca. 260 °C for all the samples (not shown here).

4. Discussion

First of all, let us discuss the possibility of preferential plasticization by the addition of organic salts to ionomers [3–5,30,37,50–52]. At this point, it is worth recalling that when the sodium dodecylbenzenesulfonate (SDBS) molecules were added to the sodium-sulfonated polystyrene (NaSPS) ionomer, the cluster T_g of the ionomer decreased significantly, with only minor decrease in the matrix T_g [37]. Thus, it was suggested that the ionic groups of the SDBS surfactant incorporated into ionic aggregates, with the non-polar alkyl chain of the surfactant residing in restricted mobility regions. Therefore, only the cluster regions were plasticized by the SDBS molecules. In the same study, it was also found that the heights of the loss tangent peaks for the matrix and cluster T_gs did not change significantly upon the addition of the SDBS surfactants. In the present work, if the ionic groups of the organic salt, e.g. NaBz salt, form ionic aggregates with the ionic groups of the ionomer, the phenyl groups of the NaBz salt molecules, residing in the restricted mobility regions, should introduce more room into the clustered regions [3–5]. However, judging from the present results, the plasticization effect by the addition of the organic salts is relatively very weak, since the increasing amount of organic salts changes the cluster T_g only marginally. In addition, if all of the organic salt molecules act as plasticizer, especially as preferential plasticizer for the cluster phase, the ratio of the areas under the matrix and cluster loss tangent peaks should not change significantly with plasticizer content. This is not the case here, judging from Fig. 5. It should also be noted that, in the present work, if all of the organic salt molecules reside in and/or near the multiplet and act as preferential plasticizer, the functionality of the salt molecules should affect the degree of plasticization, at least to some extent. However, this is also not observed here. Thus, we postulate that even though some of the salt molecules may act as plasticizer, resulting in the small change in the cluster T_g, the main role of the organic salts in the present system might not be plasticizer.

At this point, it should be mentioned that Nah et al. observed that the cluster T_g of the P(S-*co*-MANa) ionomer decreased by ca. 10 °C, when the amount of sodium toluate molecules in the ionomer became ca. 30 wt% [45]. However, in the present study the cluster T_g changed only slightly. The reason for this discrepancy in the decreasing cluster T_gs is not clearly known at present, but it might be due to the following two factors. Nah et al. prepared samples by mixing the Na-neutralized organic salts and Na-neutralized ionomers, while in the present case the acid form organic compound and copolymer were mixed first, and then NaOH solution was used to neutralize acid groups. In addition, the methyl group of the toluate should also be considered. That is, the bulky methyl group of the toluate, compared to the hydrogen of the benzoate, might introduce more room into the restricted mobility regions, when both of them act as preferential plasticizer. Thus, the difference in

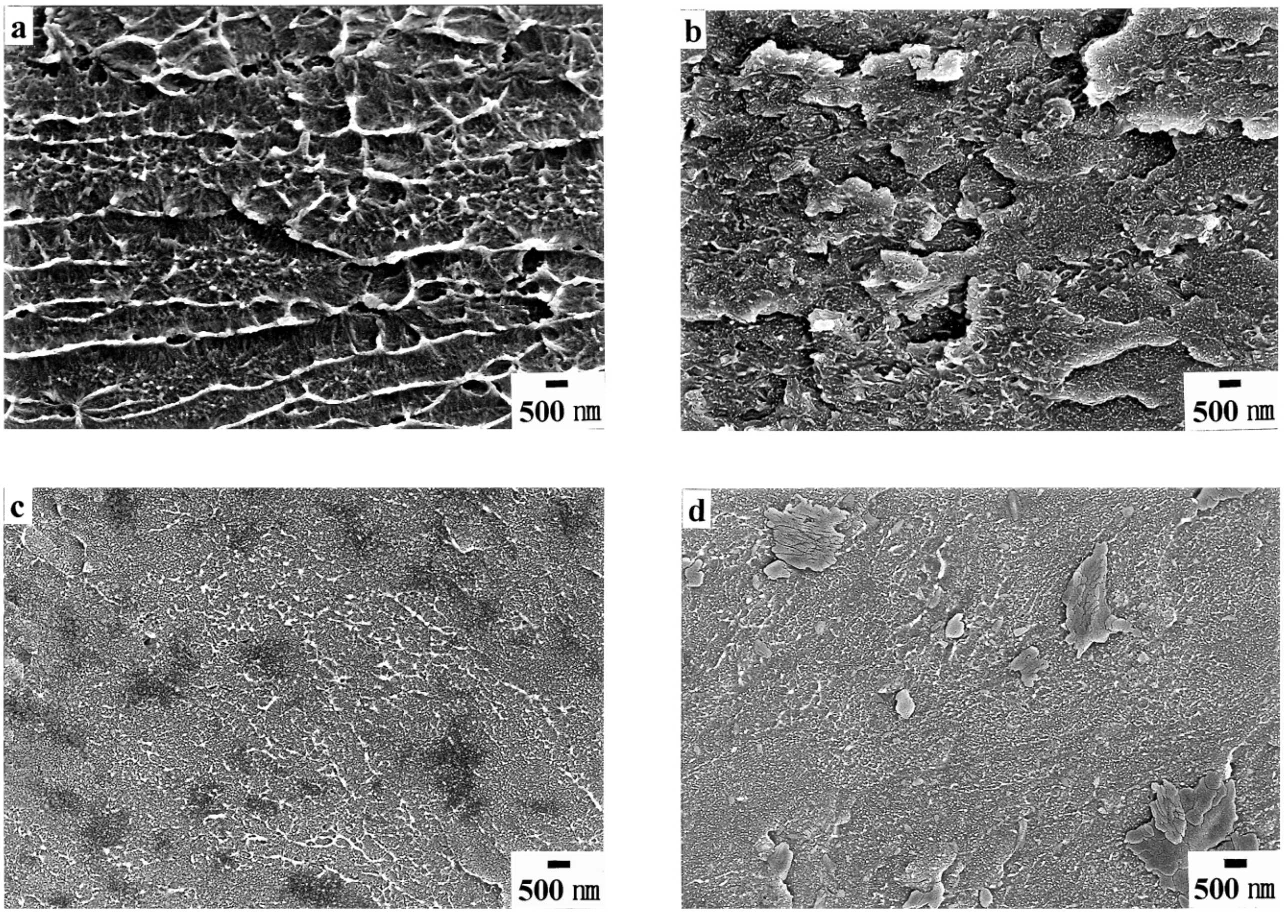


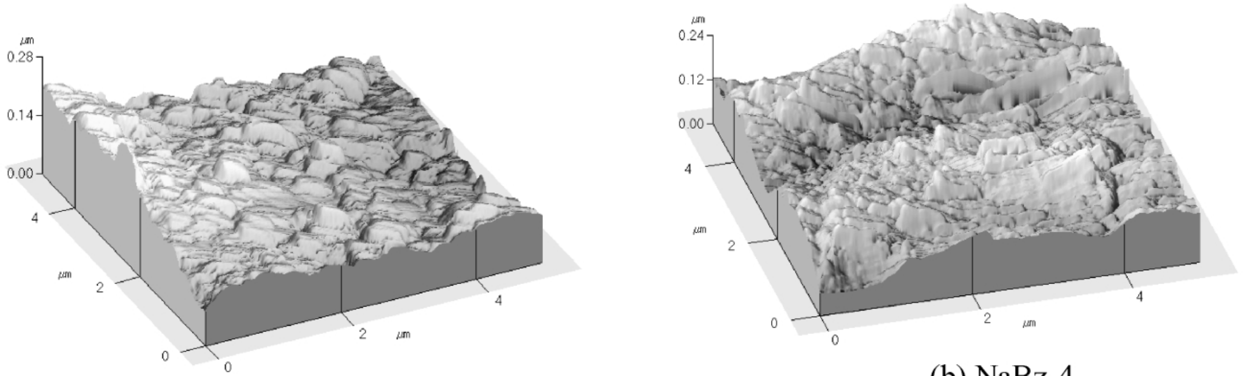
Fig. 8. Scanning electron micrographs of the fracture surfaces of (a) P(S-*co*-MANa) ionomer and ionomers containing (b) NaBz-4, (c) NaIso-2, and (d) NaTetra-1.

the sample preparation methods and the presence of the methyl group of toluate may cause the dissimilarity in the decreasing rates of cluster T_gs as a function of organic salt content.

Now, let us move on to the discussion of filler effects. Since the modulus value of the material increases upon the addition of filler [53], the increase of ionic modulus by the addition of organic salts to the ionomer might be due to filler effects. The SEM and AFM images have clearly shown that, in the present work, the organic salts in ionomers are phase-separated, which possibly act as filler. At this point, it is worth mentioning that the Guth equation represents the relationships between the Young's modulus and the volume fraction of filler

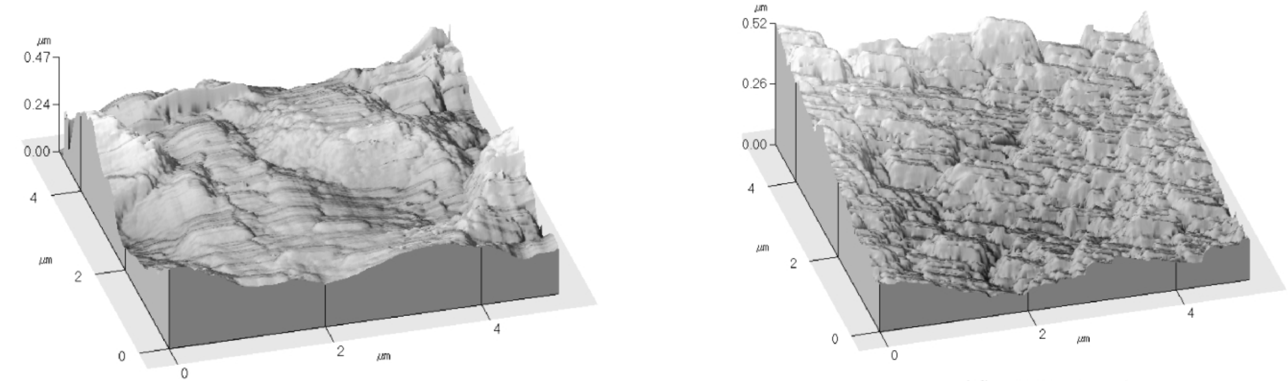
$$E^*/E = 1 + 2.5V_f + 14.1V_f^2,$$

where E^* and E are the Young's modulus of the filled and unfilled samples, respectively, and V_f is the volume fraction of filler in the sample [53,54]. This equation is known to be applicable to the system, which contains non-elastic and spherical filler particles up to ca. 30 vol.% of filler in a sample. In the present work, the ionic modulus of the ionomers containing the organic salts of low molecular weight is taken as E^*, and that of the pure P(S-*co*-MANa) ionomer is taken as E. In order to calculate the volume fraction of the salts, the density (d) values of the ionomer and the organic salts are needed. The density of the ionomer is ca. 1.137 g/cm^3, which was obtained using a pycnometer by our group. In the case of organic salts, even though the direct measurement of the density is not possible, an indirect method of the density evaluation is available with an examination of the density values of some common compounds, the chemical structure of which resembles that of the organic salt. They are formic acid ($d = 1.22$ g/cm^3)/sodium formate ($d = 1.92$ g/cm^3), acetic acid ($d = 1.049$ g/cm^3)/sodium acetate ($d = 1.53$ g/cm^3), and oxalic acid ($d = 1.65$ g/cm^3)/sodium oxalate ($d = 2.34 \times$ g/cm^3) [55]. Thus, after consideration of the density of the benzoic acid ($d = 1.32$ g/cm^3) [55], we roughly assume that the density of sodium benzoate would be ca. 2.0 g/cm^3. With these data and the weight fractions of the organic salts, it is possible to calculate the volume fractions of the salt molecules in ionomers. At this point, it should be mentioned that in this investigation we only calculate the density of sodium benzoate, since the relevant data for the other two organic salts, i.e. NaIso and NaTetra salts, are not available. Fig. 10 shows the ratios of E^*/E obtained from the experimental modulus data and those from the calculated



(a) P(S-*co*-MANa)

(b) NaBz-4



(c) NaIso-2

(d) NaTetra-1

Fig. 9. AFM images for the fracture surfaces of (a) P(S-*co*-MANa) ionomer and ionomers containing (b) NaBz-4, (c) NaIso-2, and (d) NaTetra-1.

values using the Guth equation as a function of the volume fraction of the organic salts in ionomers. It is seen that there are major deviations between the experimental data and the calculated values, which will be discussed in detail below.

Very recently, Huber and Vilgis attempted to predict the hydrodynamic reinforcement contribution in elastic matrix containing spherical soft core–hard shell particles [56], and, thus, we also tried to apply their approach to our system in order to quantify the filler effect on the ionic modulus. In the present system, the phase-separated organic salt particles are thought to have hard shell consisting of ionic groups and soft core containing benzene rings. The Huber and Vilgis equation for the effective elastic modulus is as follows

$$E^*/E = 1 + [\mu]\phi/(1 - 0.4[\mu]\phi),$$

where $[\mu]$ is an intrinsic modulus and depends on E_m/E_{shell} and r_{shell}/r_{core} values, which are moduli of matrix and shell, and radii of the shell and core, respectively (the detailed discussion on this prediction is beyond the scope of this publication, and, thus, interested readers are referred to the original paper [56] and references therein). After the simple application of the equation to the present system, it was found that the range of predicted values was still lower than the experimental data. For example, the predicted value of E^*/E for the sample containing totally rigid shell (i.e. $E_{shell}/E_m \to \infty$) was less than 2 at the volume fraction of filler of ca. 0.3. In the case of the system for $E_{shell}/E_m = 10$, the increase in the ratio of r_{shell}/r_{core} from 6/5 to ∞ changes the E^*/E value only from ca. 1 to 2, respectively. This result and Fig. 10 imply that the increase in the ionic modulus by the addition of the NaBz salts is due to (1) the presence of the rigid, spherical filler particles in the ionomers, (2) the changes in the sizes and shapes of filler

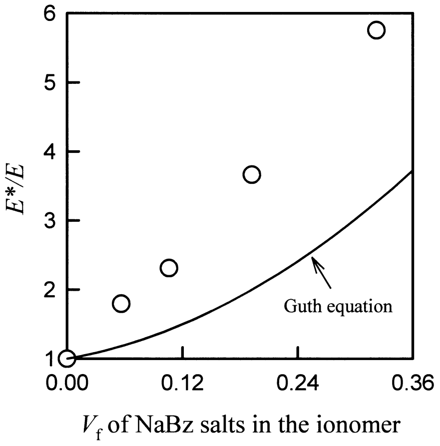


Fig. 10. The ratio of the ionic modulus of pure ionomer to that of the ionomer containing NaBz salt as a function of volume fraction of the salts in the ionomer: points are experimental data, and the curve indicates the calculated values using the Guth equation.

particles (e.g. aggregation of the filler particles), and (3) the change in the nature (especially, the mechanical properties as well as the relative amounts) of polymer matrix and cluster regions (judging from the change in the ratios of the two loss tangent peak areas as a function of salt content). Finally, it should also be mentioned that if the three different organic salts acted not as plasticizer but as filler, the functionality of the salt would not be expected to change the filler effect significantly. Only the amount, not the type, of the organic salts would be the main factor controlling the mechanical properties of the materials; this is indeed what we observed in the present study.

5. Conclusions

In this study, the mechanical properties and morphology of poly(styrene-*co*-sodium methacrylate) ionomers containing three different organic salts of low molecular weight, i.e. Na-benzoate, Na-isophthalate, and Na-benzenetetracarboxylate, were investigated. It was observed that the addition of the organic salts to the ionomer increased the ionic modulus of the ionomer noticeably and decreased the cluster T_g slightly. Thus, it was suggested that some of organic salts might reside in and/or near the multiplet and act as preferential plasticizer for the restricted mobility regions, resulting in the slightly lower cluster T_g, while the majority of the organic salts were phase-separated and formed aggregates; these aggregates acted as filler. It was also found that with increasing weight percentage of organic salt, the ionic modulus increased, and that the number of ion pairs per one organic salt molecule did not affect the ionic modulus significantly. Thus, it was concluded that the amount of the salts, not the number of ion pairs per one organic salt molecule, controlled the modulus of the ionomers. In addition, it was observed that with increasing salt content, the area under the matrix loss tangent peak decreased more rapidly than that under the cluster loss tangent peak. Furthermore, the ionic modulus values calculated using the Guth approach and the Huber and Vilgis' equation were found to be lower than the experimental values. These results indicated that the addition of the organic salts altered the nature of polymer matrix and clustered regions simultaneously, as well.

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