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ORIGINAL PAPER

Effects of the cation valence on the mechanical properties of sulfonated polystyrene ionomers containing dicarboxylate salts

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Abstract The dynamic mechanical properties of Ba(II)-neutralized poly(styrene-*co*-styrene sulfonate) ionomers-containing Ba salt of aliphatic diacid were investigated and compared with those of Na(I)-neutralized ionomers-containing Na diacid salt. It was found that the addition of diacid salts led to a negligible change in the matrix and cluster T_gs of the Ba and Na ionomers regardless of the chain length of the aliphatic diacid salts. The log E' of Ba ionomers, however, increased linearly with increasing chain length of Ba diacid salt, which was different from that of Na ionomers. On increasing wt% of the salts in the ionomers, the matrix T_gs of Ba and Na ionomers did not change, but the cluster T_gs increased slightly for Ba and Na ionomers, except for the Na ionomer-containing C_{16} diacid salt. In addition, the log E' increased linearly with the wt% of diacid salts, but the increasing rate was higher for the Ba ionomers, compared to Na ionomers. Thus, it was suggested that the Ba diacid salts would face more difficulty in the formation of multiplet with the ionic groups of the ionomers, compared to Na ionomer system; thus, more Ba diacid salts were phase-separated, which showed a stronger filler effect. In addition, since the Ba ionomers did not flow easily above the cluster T_g of the ionomers, it was proposed that the multiplets of Ba ionomers acted still as effective physical cross-links above cluster T_g, to some extent. Finally, it was concluded that the difference in anionic groups, the increasing amount of Ba salts, and the divalent cation enhanced the filler effects strongly.

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Introduction

Polymers having a small amount of ionic groups, called ionomers, show enhanced mechanical properties, compared to their non-ionic counterparts. Thus, during the last four decades, extensive studies have been performed on the mechanical properties and morphologies of the ionomers [1]. The unique properties of the ionomers are owing to a strong interaction between the ionic groups of the ionomers. As per the Eisenberg–Hird–Moore (EHM) model for amorphous random ionomers, the ionic groups in a polymer matrix aggregate to form so-called multiplets and the multiplets reduce the mobility of the polymer chains surrounding them [2]. With increasing ion contents of the ionomer, the number of the multiplets increases, and the size of the reduced mobility regions naturally increases as well. Once the size of the reduced mobility regions along with the multiplets exceeds a certain size, e.g., ca. 100 Å, the ionomer starts to behave as materials that have two different regions, i.e., ion-poor and ion-rich regions, and the latter is so-called cluster [2]. Now, the materials show two glass transitions (T_gs): one is a matrix T_g and the other is attributed to the T_g of the cluster regions.

The mechanical properties and morphology of ionomers can be tailored by varying a number of factors including the type, size, position of ionic groups, the degree of neutralization, and the type of additives, plasticizers and neutralizing agents [1]. For example, in the cases of ionomers-containing additives, Agarwal et al. [3] studied the mechanical properties of Zn-sulfonated ethylene–propylene–ethylidene norbornene (Zn-sEPDM) terpolymer-containing Zn stearate salt. They found that the Zn stearate salt was phase-separated and acted as filler, resulting in the increase in the matrix T_g of the ionomer, and that the Zn stearate salt acted also as a “multiplet” plasticizer at higher temperatures. Plante et al. [4] investigated the dynamic mechanical properties of matrix-dominant (i.e., low ion content) and cluster-dominant (i.e., high ion content) carboxylated polystyrene (PSC) ionomers blended with chemically identical mono- and bifunctional styrene oligomers. They found that both the matrix and cluster regions of the ionomers were plasticized by the monofunctional oligomers. On the other hand, the bifunctional oligomers in the ionomers of low ion contents showed anti-plasticization behavior at low oligomer contents. However, in the ionomers of high ion contents, the oligomers became phase-separated due to the relatively small amounts of non-ionic polymer matrix. In a subsequent study, the authors studied the effects of the addition of monodispersed, tertiary amine-terminated styrene oligomers on the dynamic mechanical properties of lightly sulfonated PS ionomers [5]. The ionomer was also plasticized by the monofunctional styrene oligomers, but much less than that by the monofunctional alkyl oligomers, due to the bulkiness and stiffness of the styrene segments of the oligomer. In the case of the bifunctional oligomers, they showed a very weak plasticization effect and, at their higher concentrations, they became phase-separated despite extensive inter-component interactions. In the case of ethylene-based ionomers, Wakabayashi and Register [6] studied the morphology and mechanical properties of fatty acid salt-containing ethylene–methacrylate ionomers neutralized with mono- and divalent cations.The authors found that the changes in the properties of the ionomers depended both on the type of cations and on the crystallizability of the fatty acid and ionomers. However, the information obtained from the above studies was not enough to understand the mechanical properties and morphology of ionomers-containing oligomeric materials. Thus, recently, our group attempted to investigate the dynamic mechanical properties of PS-based ionomers-containing sodium salts of aliphatic monocarboxylic acid (MCA) or dicarboxylic acid (DCA) [7–10]. We found that the DCAs were phase-separated and increased the modulus of the ionomer. However, the effects of divalent cations on the properties of PS ionomers-containing DCAs have not been explored, yet. Therefore, in this study, we studied the dynamic mechanical properties of PS ionomers-containing barium salts of succinic acid [$Ba^{2+}/^{-}OOC–(CH_2)_2–COO^{-}$], adipic acid [$Ba^{2+}/^{-}OOC–(CH_2)_4–COO^{-}$], dodecanedioic acid [$Ba^{2+}/^{-}OOC–(CH_2)_{10}–COO^{-}$], and hexadecanedioic acid [$Ba^{2+}/^{-}OOC–(CH_2)_{14}–COO^{-}$], and compared the results with those obtained from PS ionomers-containing DCAs, but neutralized with monovalent cation, sodium. By selecting short to long alkyl chain additives, we could also see the effects of alkyl chain lengths on the dynamic mechanical properties of the ionomers.

Experimental

Sample preparations

Polystyrene (PS) homopolymer (MW = ca. 500,000) was synthesized by the method described elsewhere [11]. Poly(styrene-*co*-styrenesulfonic acid) copolymer was prepared by the sulfonation of PS using the method reported by Makowski et al. [12]. In order to determine the content of styrenesulfonic acid units, the copolymer sample was dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5 % (w/v) solution. The resulting solution was titrated with methanolic NaOH solution to the phenolphthalein end point. The acid content was 4.0 mol%. To prepare the ionomer-containing DCAs, the DCA and copolymer in an acid form were dissolved in a benzene/methanol (9/1, v/v) mixture, and the acid groups of the DCA and copolymer were fully neutralized with methanolic $Ba(OH)_2$ solution. As the first set of samples, the mole ratio of the acid groups of the DCA to those of the copolymer was kept at 1/1. As the second set of samples, the amount of barium succinate and barium hexadecanedioate in the ionomer increased systematically to ca. 30 wt%. The samples were freeze-dried and dried further under a vacuum at ca. 150 °C for 24 h. For the dynamic mechanical studies, the samples were compression molded at ca. 260 °C with a pressure of ca. 25 MPa. The molded samples were annealed under a vacuum at 150 °C for 24 h. The notations used for the samples are 4.0-$BaC_x(-y)$, where 4.0-Ba is the sulfonated PS ionomer neutralized with Ba^{2+}, C_x indicates barium neutralized DCAs having "x" number of the carbon atoms in the chain, i.e., C_4 (barium succinate), C_6 (barium adipate), C_{12} (barium dodecanedioate), and C_{16} (barium hexadecanedioate), and y is wt% of DCAs. For comparison, the data obtained from the sodium neutralized sulfonated PS ionomer sample containing 4.5 mol% of ions (sample notation = 4.5-NaC_x) were used [10].

Dynamic mechanical property measurements

The storage modulus (E') and loss tangent (tan δ) of each sample were measured as a function of temperature using a TA Instruments' Q 800 dynamic mechanical analyzer (New Castle, DE) in a dual cantilever-bending mode. The samples were heated at a heating rate of 1 °C/min. The detailed data analysis was performed using the data obtained at 1 Hz. Deconvolutions on the loss tangent data were performed using PeakFit program (Systat Software Inc.) to obtain the sizes and positions of the loss tangent peaks. The best fits were achieved by assuming an exponential background and fitting the matrix and cluster peaks with Gaussian area peaks.

X-ray experiments

To record X-ray diffraction (XRD) patterns, we used a PANalytical X' pert PRO MPD X-ray diffractometer (Almelo, the Netherlands). The scanning speed and sampling width were 0.3°/min and 0.018°, respectively.

Results and discussion

In Fig. 1, it is seen that with increasing temperature the modulus curves pass through a glassy modulus, a matrix T_g, an ionic plateau (the plateau between the matrix T_g and cluster T_g), a cluster T_g, a rubbery plateau, to sample flow. It is clear that above the matrix T_g, the moduli increase slowly and systematically for the ionomers-containing BaC_x. In this study, the width of the ionic plateau between the matrix and cluster T_gs does not change significantly with changing the type of BaC_x. At this point, it should be mentioned that at cluster T_g the relaxation of polymer chains in restricted mobility regions [1, 2] and the hopping of ionic groups from one multiplet to another occur simultaneously [13–15]. Thus, the cluster T_g depends on the strength of interactions between the ionic groups in multiplets. The interaction between cation–sulfonate ion pairs is stronger than that between cation–carboxylate ion pairs [13, 16], leading to higher temperature for the hopping of sulfonate/cation ion pairs. Thus, the similar widths of ionic plateau imply that the multiplets might consist of similar ionic groups, i.e., Ba-sulfonate ionic groups, which are not strongly altered by the addition of BaC_x that have Ba-carboxylate ionic groups. In the loss tangent plots, two peaks are seen; a large peak at low temperatures is due to the matrix T_g and a very small peak at high temperatures is due to the cluster T_g. At this point, it should be mentioned that the sizes of the matrix peaks of the Ba- and Na-sulfonated ionomers are similar to each other. Since the relative sizes of the loss tangent peak of PS ionomers are known to be related with the relative amounts of the matrix and cluster regions [14, 17, 18], and the degree of clustering is related with ion contents [1, 2], and the ion contents of Ba and Na ionomers are similar to each other, the similarity in the matrix peak sizes is not surprising. In the case of the cluster peak, however, the Na ionomer has a much larger peak than the Ba ionomer does, which can be understood. In this study, one Ba^{2+} cation needs two sulfonate anions for the electrical neutrality (i.e., $–SO_3^{-}Ba^{2+}\ {}^{-}O_3S–$), which causes more difficulty in the hopping of ionic groups in multiplets, compared to Na^{+} that needs only one anion for the electrical neutrality (i.e., $–SO_3^{-}\ Na^{+}$). Thus, the ion-hopping for the Ba ionomer in a time scale of the DMA experiments is not as active and operative as that for the Na ionomer at cluster T_g. Therefore, the Ba ionomer still shows a hint of strong "physical" cross-linking effect even above cluster T_g, resulting in a very gentle decreasing modulus curve in the temperature range of cluster T_g. In addition, the modulus curve for sample flow of Ba ionomers descends very slowly, compared to that of Na ionomer. This leads to a smaller sized cluster loss tangent peak for the Ba ionomer in comparison with the Na ionomer. It is also observed that the position of the matrix and cluster loss tangent peaks change negligibly as the alkyl chain length of the DCAs changes. This is different from the matrix T_gs found in PSC ionomers containing 7 mol% of Ba(II)-carboxylated styrene units and Ba(II)-bifunctional styrene oligomers [4]; the PSC ionomer system showed an anti-plasticization effect on the matrix T_g (i.e., increasing and subsequently decreasing matrix T_g with increasing oligomer wt%). This might be due to the fact that the identical the chemical structure of PS matrix and styrene oligomers and the ionic groups, i.e., Ba-carboxylate; in this case, one might expect plasticization effect. On the other hand, in this study, the chemical structures of the

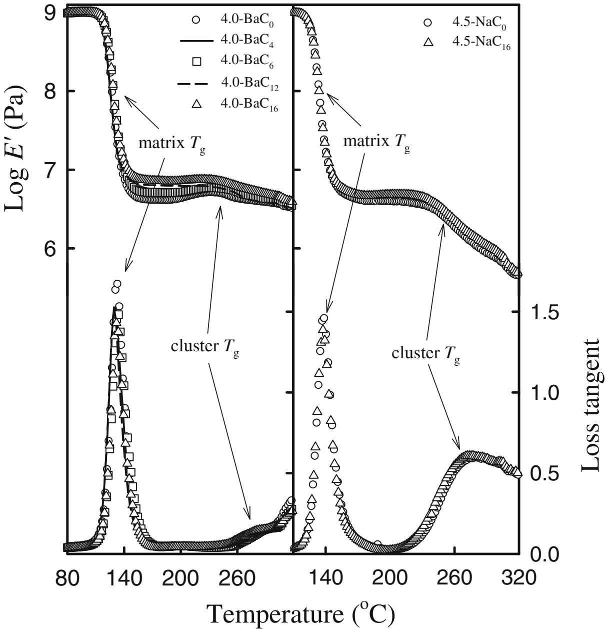


Fig. 1 Storage moduli (E') and loss tangents of 4.0-BaC$_x$ ionomers as a function of temperature, measured at 1 Hz. Data for 4.5-NaC$_x$ ionomers were obtained from Ref. [10]

BaC_x and PS matrix and the types of anionic groups are different; thus, one can expect more possible phase-separation, rather than possible plasticization.

In Fig. 2, the ionic moduli (E'_{ionic}, the values of modulus in the ionic plateau regions at a point of minimum slope) of the samples as a function of the number of the carbon atoms of BaC_x are shown. The results obtained from 4.5-NaC_x are also shown in the same figure. It is seen that the addition of the DCAs increases the E'_{ionic} significantly. In the case of the 4.0-Ba ionomer system, the log E'_{ionic} increases linearly with increasing number of the carbon atoms of the BaC_x as follows: log E'_{ionic} (Pa) $= 6.6 + 0.016 \times$ (the number of the carbon atoms of BaC_x) ($r^2 = 0.9990$), where r^2 is a linear least-squares correlation coefficient. Since the modulus of the filled polymeric material increases as the filler content in the material increases, one can consider that the increasing E'_{ionic} of the present system is due to the role of BaC_x in 4.0-Ba system as filler particles. In the case of 4.5-Na ionomer system, the E'_{ionic} of pure ionomer is similar to that of 4.0-Ba ionomer; the log E'_{ionic} of 4.5-Na ionomers increases initially at a similar rate to that of 4.0-Ba ionomers. However, for the 4.5-NaC_{12} and 4.5-NaC_{16} ionomers, the ionic moduli deviate from those of 4.0-Ba ionomers significantly, and they are not much different from that of 4.5-NaC_6 ionomer. In the previous study, we proposed that the NaC_4 and NaC_6 in the 4.5-Na ionomer might act mainly as filler and NaC_{12} and NaC_{16} as plasticizer and filler, and, thus, the ionic modulus did not increase with increasing chain length of NaC_x [10]. Therefore, in this study, we can suggest that the BaC_x in the 4.0-Ba ionomer system act mainly as filler; this will be discussed in more detail later.

It is also seen that the matrix and cluster T_gs obtained from the deconvoluted loss tangent peak positions of 4.0-BaC_x ionomers remain more or less constant at ca. 130

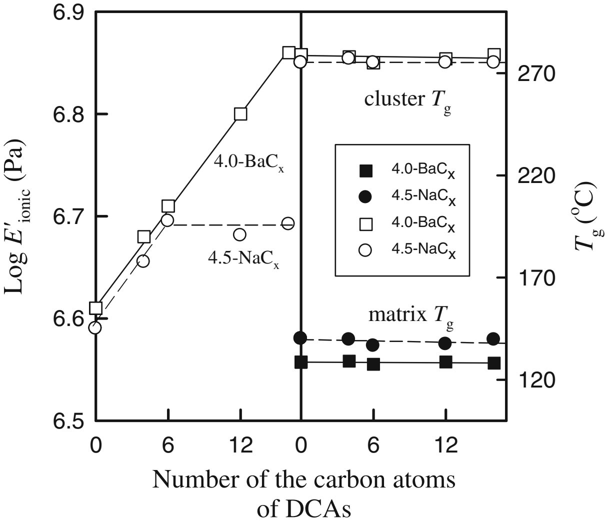


Fig. 2 Ionic moduli (E'_{ionic}) and matrix and cluster T_gs of 4.0-BaC_x and 4.5-NaC_x ionomers as a function of number of the carbon atoms of DCAs, measured at 1 Hz. Data for 4.5-NaC_x ionomers were obtained from reference 10

and 280 °C, respectively, regardless of the addition of the BaC_x to the ionomers. In the case of 4.5-NaC_x ionomer system, the matrix and cluster T_gs also remain more or less constant at ca. 140 and 275 °C, respectively, upon the addition of the NaC_x to the 4.5-Na ionomer. At this point, it should be noted that the average matrix T_g of the 4.5-Na ionomers is higher than that of 4.0-Ba ionomers. This is due to the higher ion content of 4.5-Na ionomer, compared to 4.0-Ba ionomer. This aspect that the matrix T_g of amorphous ionomers depends not on the type of cations but on the ion content has been discussed in more detail elsewhere, and, thus, the interested readers are referred to the original paper [19]. In the case of cluster T_g, the T_gs of 4.5-Na and 4.0-Ba are not much different, even though the ion content of 4.5-Na is slightly higher than that of 4.0-Ba. This can be understood. Since the ion-hopping of 4.0-Ba ionomer at a cluster T_g requires the movement of two anionic groups and one cation (Ba^{2+}) from one multiplet to another simultaneously to keep electrical neutrality, the hopping of Ba-sulfonate is more difficult than that of Na-sulfonate, leading to a higher cluster T_g, compared to that of Na-sulfonate. The above results, i.e., similar matrix and cluster T_gs, indicate that the BaC_x and NaC_x are phase-separated and thus acted as filler particles, to some extent.

In this work, we also studied the effects of the amounts of the BaC_x on the mechanical property of the 4.0-Ba ionomer. To do so, we prepared the 4.0-Ba ionomers having up to ca. 30 wt% of either BaC_4 or BaC_{16}. Figure 3 shows the modulus and loss tangent plots of the 4.0-Ba ionomer systems having varying amounts of BaC_4 as a function of temperature. As expected, on the addition of BaC_4, there is a strong increase in the height of the ionic plateau. In the case of loss tangent plots, the height of the matrix loss tangent peaks decreases with increasing BaC_4 amount, but the height of the shoulder-like cluster loss tangent peak changes only slightly. In the case of ionomers-containing BaC_{16}, similar results were observed (not shown here).

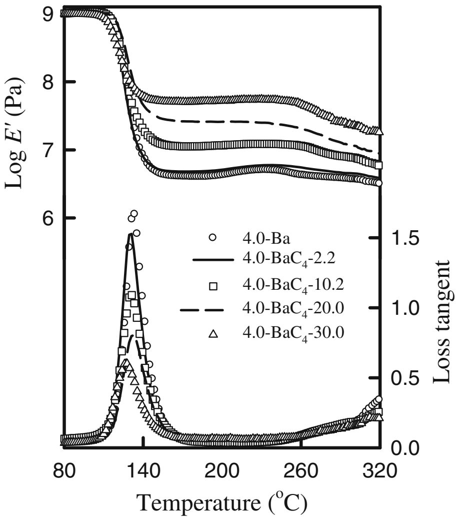


Fig. 3 Storage moduli (E') and loss tangents of 4.0-BaC_4 ionomers containing various amounts of BaC_4 as a function of temperature, measured at 1 Hz

Figure 4 shows the E'_{ionic}s and T_gs of the 4.0-Ba ionomers as a function of the wt% of the BaC_4 and BaC_{16}. The data obtained from the 4.5-Na ionomer-containing NaC_4 and NaC_{16} are also included in Fig. 4. It is seen that, as expected, the E'_{ionic}s of the 4.0-Ba and 4.5-Na ionomer systems increase significantly with increasing wt% of the DCAs. Moreover, it is interesting to note that the E'_{ionic} data of the 4.0-Ba ionomers-containing BaC_4 and BaC_{16} and the 4.5-Na ionomers-containing NaC_4 and NaC_{16} can be superimposed. This suggests that the increasing E'_{ionic} depends strongly on the amounts of DCAs, not the type of DCAs. However, it should be noted that the increasing rate of E'_{ionic}s of 4.0-Ba ionomers is slightly higher than that of 4.5-Na ionomers. The increasing rates are as follows:

For 4.0-Ba ionomer,

$$\log E'_{\mathrm{ionic}}(\mathrm{Pa}) = 6.6 + 0.036 \times (\mathrm{wt\%\ of\ BaC}_x)\ \left(r^2 = 0.9867\right)$$

and for 4.5-Na ionomer

$$\log E'_{\mathrm{ionic}}(\mathrm{Pa}) = 6.6 + 0.030 \times (\mathrm{wt\%\ of\ NaC}_x)\ \left(r^2 = 0.9891\right).$$

This difference in the increasing rates indicates that the role of BaC_x as filler particles might be more effective than that of NaC_x. In Fig. 4, it is also seen that the matrix T_gs of the 4.0-Ba and 4.5-Na ionomers remain more or less constant at ca. 130 and 140 °C, respectively, regardless of the amount and type of the DCAs. The cluster T_gs of the 4.0-BaC_4, 4.0-BaC_{16}, and 4.5-NaC_4 ionomers are similar to each other and increase slightly with increasing wt% of DCAs. In the case of 4.5-NaC_{16} ionomer, however, the cluster T_g changes only marginally up to ca. 10 wt% of NaC_{16} and then decreases significantly upon the further addition of NaC_{16}. From the above findings, it can be suggested that in the cases of NaC_4 and BaC_4 salts, the chain length is probably too short to show a strong plasticization effect, if there is any; they might be just phase-separated and act as filler. On the other hand, the

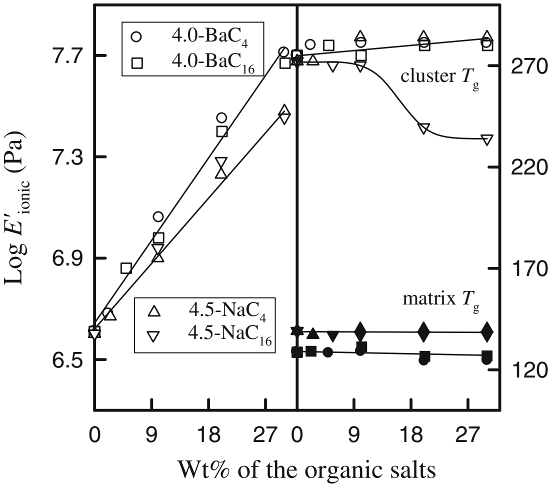
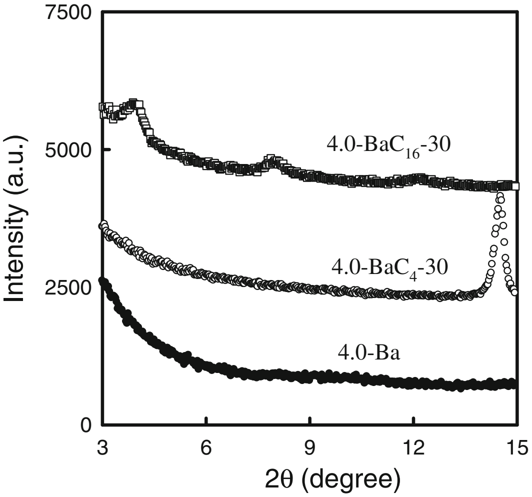


Fig. 4 Ionic moduli (E'_{ionic}) and matrix and cluster T_gs of 4.0-BaC_x and 4.5-NaC_x ionomers as a function of wt% of DCAs, measured at 1 Hz. Data for 4.5-NaC_x ionomers were obtained from reference 10

Fig. 5 XRD patterns of the Ba ionomer and those containing 30 wt% of Ba_4 and Ba_{16}. The XRD patterns were shifted vertically for clarity



NaC_{16} needs one anion/one cation pair to form electrically neutral ion pairs. Thus, energetically it is possible that some of NaC_{16} salts participate in the formation of multiplets with ionic groups of the ionomer. If this is the case, NaC_{16} will act as plasticizers for the cluster regions, to some extent, by making the mobile alkyl chains reside in the restricted mobility regions. Needless to say, the rest of the NaC_{16} salts can act as filler, by forming crystalline domains, which increases the ionic modulus. It is also possible that some of NaC_{16} salts make partially or fully formed inverse micelle-like structures in the matrix. In the case of the Ba ionomer system, it has divalent cations that cause the difficulty in the formation of multiplets with ionic groups of ionomers, by reducing the statistical possibilities of the number of arrangements of BaC_{16} salts significantly. Therefore, more BaC_x salts act as filler, compared to NaC_x salts.

The XRD patterns of the 4.0-Ba ionomers are shown in Fig. 5. The pure 4.0-Ba ionomer does not show a XRD peak in the 2θ range studied here. In the case of the 4.0-BaC_4-30 ionomer, a sharp XRD peak is observed at $2\theta =$ ca. 14.5° ($D_{\mathrm{Bragg}} =$ ca. 0.61 nm), indicating the presence of the crystalline domains of the BaC_4 in the ionomer. For the 4.0-BaC_{16}-30 ionomer, a XRD peak is also seen at $2\theta =$ ca. 3.9° ($D_{\mathrm{Bragg}} =$ ca. 2.2 nm). The position of the peak is similar to that of the peak found for the 4.5-Na ionomers-containing NaC_4 and NaC_{16} salts (not shown here) [10]. It should be noted that the Bragg distances of ca. 0.6 and 2.2 nm are similar to the distances between the ionic groups of the fully extended BaC_4 and BaC_{16} organic salts, respectively. This implies that the BaC_x is phase-separated and forms crystalline domains in the 4.0-Ba ionomers, and thus acts as filler.

Conclusions

(1) When the mole ratio of the ionic groups of the Ba ionomer to those of the BaC_x was kept at 1:1, the log E'_{ionic} of the ionomer increased linearly with

increasing the number of the carbon atoms of the BaC_x. It was also observed that the matrix and cluster T_gs of the Ba ionomers-containing BaC_x did not change with increasing chain length of BaC_x.

(2) The above two aspects indicated that the BaC_x in the Ba ionomer acted mainly as phase-separated filler particles, which was different from the Na ionomers-containing NaC_{12} and NaC_{16} in that the NaC_x acted both as filler and plasticizer.

(3) In addition, since the Ba ionomers did not flow easily above the cluster T_g of the ionomers, it was proposed that the multiplets of Ba ionomers acted still as effective physical cross-links above cluster T_g, to some extent.

(4) The increasing rate of log E'_{ionic} of Ba ionomers as a function of the wt% of BaC_x was higher than that of Na ionomers. In addition, the XRD profiles showed that BaC_x formed phase-separated crystalline domains in the 4.0-Ba ionomer matrix, which acted as filler particles.

(5) The above findings indicated that the filler effect of BaC_xs in the Ba ionomers was more profound than that of NaC_xs in the Na ionomers.

(6) Thus, finally, we can conclude that if the type of anionic group of DCAs is different from that of the ionomer, the divalent cation, rather than monovalent cation, is used to neutralize the acid groups, and the amount of DCAs in the ionomer increases, we will find a more profound filler effect.

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