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Plasticization effects on the mechanical properties and morphology of cobalt and sodium neutralized poly(ethyl acrylate-*co*-acrylate) ionomers

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Abstract

The present study aimed to investigate the effects of plasticization on the mechanical properties and morphology of poly(ethyl acrylate) ionomers neutralized with either Co^{2+} or Na^{+}. In experiments, the dynamic mechanical properties of divalent Co^{2+}-neutralized poly(ethyl acrylate) ionomers containing polar and non-polar plasticizers were compared with those of the monovalent Na^{+}-neutralized ionomers. In the case of the ionomers plasticized with non-polar 4-decylaniline (4-DA), residing in non-ionic regions, the matrix and cluster T_gs of the ionomer decreased with increasing 4-DA contents. The decreasing rates of the matrix and cluster T_gs were found to be similar at 0.8 and 1.0 °C/(wt% of 4-DA) for the Co^{2+} and Na^{+} ionomers, respectively. The ionic modulus of the Co^{2+} ionomer changed only slightly with increasing 4-DA contents, but that of the Na^{+} ionomer decreased noticeably. In the SAXS study, it was observed that the un-plasticized Co^{2+} ionomer showed a strong small angle upturn and a very broad SAXS peak, indicating that the ionomer phase was compositionally heterogeneous. The plasticization of the Co^{2+} ionomer with 4-DA, however, induced a well-developed SAXS peak that was comparable to that of the un-plasticized Na^{+} ionomer. These results suggested that the addition of 4-DA to the Co^{2+} ionomer made the ionomer have more multiplets at a prevalent distance, leading to more clustering. In the case of the Co^{2+} ionomers plasticized with polar glycerol (Gly) that acted mainly as multiplet plasticizer, a very weak cluster glass transition, decreasing ionic modulus and only a well-developed small angle upturn were observed. These indicated that the addition of Gly to the Co^{2+} ionomer disrupted the multiplet formation, resulting in lower clustering.

Keywords: Ionomers; Plasticization; Divalent cation

1. Introduction

Ionomers are polymers that have a relatively small amount of ionic groups along polymer backbone chains. Since their first appearance ca. 40 years ago, the ionomers have been studied extensively because they exhibit unique physical properties that are due to the interactions between ionic groups [1–6]. It is well known that the ionic groups in a relatively non-polar polymer matrix form ionic aggregates (i.e. multiplets) [7]. According to the multiplet/cluster model for random amorphous ionomers (so-called EHM model), the multiplets reduce the mobility of polymer chain segments surrounding them [8]. With increasing ion concentration, the number of the multiplets increases. Eventually, the reduced mobility regions surrounding multiplets start overlapping. As the ion content increases further, the regions of the reduced mobility become large enough to show their own glass transition temperature (cluster T_g), which is higher than the T_g of ion-poor matrix regions (i.e. matrix T_g); these large regions of the reduced mobility are called clusters.

Tong and Bazuin reported that the addition of 4-decylaniline (4-DA) to poly(ethyl acrylate-*co*-sodium acrylate) P(EA-*co*-ANa^{+}) ionomers caused the decrease in the matrix and cluster T_gs of the ionomers at a similar decreasing rate of ca. 1 °C/(wt% of 4-DA) [9]. In addition, no crystalline melting peak was observed in a differential scanning calorimetry thermogram, meaning that the 4-DA molecules did not form phase-separated crystalline regions. Thus, it was suggested that the 4-DA acted not as filler but as plasticizer that resided in both the matrix and cluster regions. From this study, one question arises: What is the effectiveness of plasticization on the mechanical properties and

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morphology of poly(ethyl acrylate) PEA ionomers containing a divalent cation, instead of a mono-valent cation? To answer to this question, in the present study, we investigated the mechanical properties of P(EA-*co*-ACo^{2+}) ionomers containing various amounts of polar and non-polar plasticizers. It should be mentioned that the present work was devoted to the PEA ionomer, since the PEA ionomer, non-crystalline, did not have the complication in data analysis caused by the presence of crystalline regions. In addition, the PEA ionomers containing ca. 7 mol% of ions were used on the ground that, at ca. 7 mol% of ions, the PEA ionomer showed well-developed matrix and cluster loss tangent peaks, and 'ionic' modulus. Thus, it was rather easy to detect any changes occurred in the two loss tangent peaks and moduli upon plasticization.

2. Experimental

2.1. Sample preparation

A poly(ethyl acrylate-*co*-acrylic acid) P(EA-*co*-AA) sample was prepared by solution polymerization of purified ethyl acrylate and acrylic acid monomers using benzoyl peroxide as the initiator [10]; the acid content was 7.0 mol%. To neutralize the acid groups, a predetermined quantity of cobalt acetate tetrahydrate (Aldrich) in methanol was added to give a Co^{2+}-neutralized poly(ethyl acrylate-*co*-acrylate) P(EA-7.0-ACo^{2+}) ionomer. The solution was freeze–dried and then dried further under vacuum at 100 °C for 1 day. To prepare ionomer samples containing plasticizers, an acid form P(EA-*co*-AA) copolymer was dissolved in a mixture of benzene and methanol, and either a non-polar plasticizer 4-decylaniline (4-DA) or a polar plasticizer glycerol (Gly) was added to the solution. The amounts of plasticizer in the ionomer sample were ca. 10, 20, and 30 wt%. Subsequently, cobalt acetate in methanol was added to neutralize the acid groups of the P(EA-*co*-AA) copolymer in the solution. The ionomer solutions were freeze-dried, and then the powder form samples were dried further under vacuum at 50 °C for 1 day. For the dynamic mechanical thermal analysis (DMTA) and X-ray scattering studies, the un-plasticized and plasticized PEA ionomer samples were compression-molded at 60–80 °C, depending on the amount of plasticizer, under a pressure of 25 MPa. Then, the samples were annealed under vacuum at 100 °C for 1 day.

2.2. Dynamic mechanical thermal analysis

Dynamic mechanical property measurements were performed on a Polymer Laboratories DMTA (Mark II). The experiments were carried out in a dual cantilever-bending mode at five different frequencies. Experimental temperature ranges for the ionomers containing 4-DA and Gly were from −40 to 160 °C and from −20 to 160 °C, respectively, and a heating rate was 1 °C/min. Storage moduli (E') and loss tangents (tan δ) were obtained as a function of temperature.

2.3. Small-angle X-ray scattering experiments

The small-angle X-ray scattering (SAXS) experiments for the un-plasticized and plasticized ionomers were conducted at Station 4C1 of the PLS synchrotron radiation source (Pohang, Korea). The detailed condition for the experiments has been given elsewhere [11,12]. The wavelength of light was 0.1608 nm, and the generated beam energy was 3.1 keV (at 2.7 GeV operation mode). The two-dimensional gas-filled detector was used. The sample-to-detector distance was 30 cm, which allowed SAXS data to be obtained in a q range from ca. 0.2 to 5.0 nm^{-1}, where $q = 4\pi \sin \theta/\lambda$ (θ is half the scattering angle, and λ is the X-ray wavelength). The SAXS data were plotted as relative intensity vs. q after correction for sample absorption and background (the SAXS profile of air was subtracted from that of ionomer samples).

3. Results and discussion

Fig. 1 shows the storage moduli of P(EA-7.0-ACo^{2+}) ionomers containing various amounts of 4-decylaniline (4-DA) as a function of temperature. It is seen that, with increasing temperature, the modulus changes from a glassy modulus, through a relatively sharp glass transition (i.e. matrix T_g), through a slope-sided 'ionic' plateau, through a relatively smooth glass transition (i.e. so-called cluster T_g), to a rubbery plateau. As the amount of 4-DA increases, the modulus curve related to the matrix glass transition and the ionic plateau (i.e. modulus values between the two T_gs) shifts to lower temperatures. The storage moduli of ionomers containing glycerol (Gly) are also shown in the same figure. It is observed that the position of a sharp drop in a modulus curve due to the matrix glass transition at ca. 10 °C does not change much with the variation of the amount of Gly. Above the matrix glass transition, however, the modulus curve moves to lower values noticeably upon the addition of Gly, and the shape of the

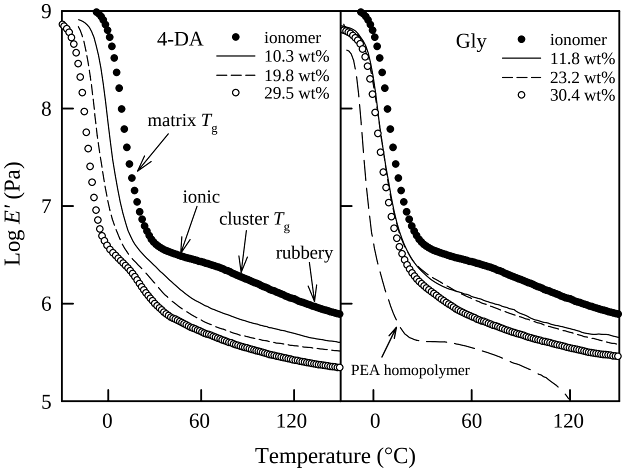

Fig. 1. Storage moduli as a function of temperature for the P(EA-7.0-ACo^{2+}) ionomers containing various amounts of 4-decylaniline (4-DA) (left) and for the ionomers containing various amounts of glycerol (Gly) (right), measured at 1 Hz. The storage modulus curve of the poly(ethyl acrylate) homopolymer is also seen in the same figure.

modulus curve of the Gly-plasticized ionomers becomes similar to that of a non-ionic polymer, i.e. no ionic plateau. For comparison, the modulus curve of PEA homopolymer is also shown in the same figure. The modulus changes from a glassy modulus, through a relatively sharp matrix T_g, through a rubbery plateau, to flow.

A characteristic feature found in the modulus plots is an ionic plateau that is related with the presence of ionic groups in the ionomer. The degree of clustering is responsible for the height of ionic plateau. For example, the increasing ion content results in the increasing amount of clustered materials in ionomers. This, in turn, leads to the shift of the ionic plateau to higher values. The ionic modulus (E'_{ionic}) is the storage modulus E' at the point of minimum slope of the ionic plateau. In Fig. 2, the ionic moduli of ionomers containing 4-DA and Gly plasticizers are shown as a function of the amount of plasticizer. It is clear that the ionic modulus of the Co^{2+} ionomers containing 4-DA decreases only slightly as the amount of the 4-DA increases [log E'_{ionic} (Pa) = 6.5 − 0.003 × (wt% of 4-DA), r^2 (linear least-squares correlation coefficient) = 0.9820]. Fig. 2 also shows the ionic moduli of PEA ionomer containing 5.0 mol% of Na-acrylate units, P(EA-5.0-ANa$^+$), and various amounts of 4-DA, which were obtained from Ref. [9]. It is seen that the ionic modulus of the un-plasticized P(EA-5.0-ANa$^+$) ionomer is lower than that of the un-plasticized P(EA-7.0-ACo^{2+}) ionomer. This is mainly due to the fact that the ion content of the Na^+-ionomer (i.e. 5.0 mol%) is lower than that of the Co^{2+}-ionomer (i.e. 7.0 mol%) [3–6,8,10]. Again, the ionic modulus of the P(EA-5.0-ANa$^+$) ionomer decreases with increasing amount of plasticizer [log E'_{ionic} (Pa) = 6.0 − 0.015 × (wt% of 4-DA), r^2 = 0.9977]. The decreasing rate for the Na^+ ionomer system is, however, higher than that of the Co^{2+} ionomer system. This indicates that the plasticization effect on the decreasing ionic modulus is stronger for the mono-valent Na^+ ionomer system, compared to the divalent Co^{2+} ionomer system. In the case of the Gly-containing ionomers, the ionic modulus decreases drastically and then gently, with increasing amount of Gly.

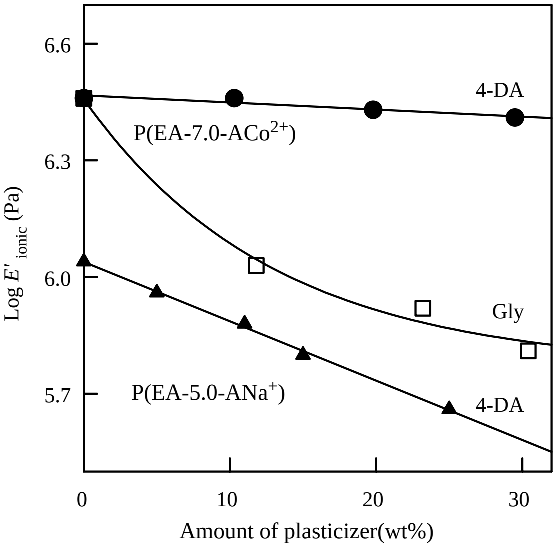

Fig. 2. Ionic moduli of the P(EA-7.0-ACo^{2+}) ionomers containing various amounts of 4-DA and Gly vs. the amount of plasticizer (at 1 Hz). Data for the P(EA-5.0-ANa$^+$) ionomers containing various amounts of 4-DA were obtained from Ref. [9].

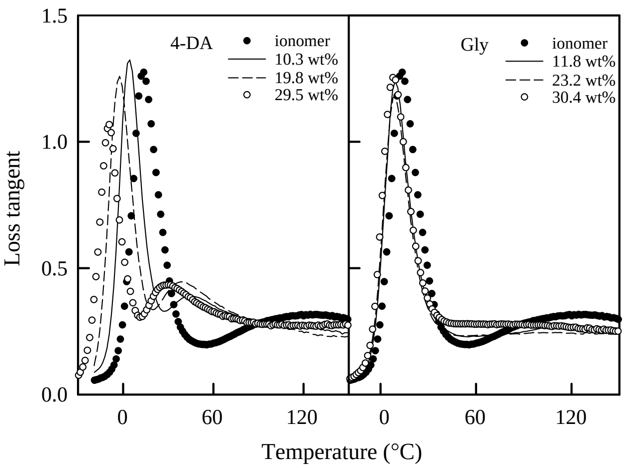

Fig. 3. Loss tangents vs. temperature for the P(EA-7.0-ACo^{2+}) ionomers containing various amounts of 4-decylaniline (4-DA) (left) and for the ionomers containing various amounts of glycerol (Gly) (right), measured at 1 Hz.

The loss tangent curves for the P(EA-7.0-ACo^{2+}) ionomers containing various amounts of plasticizers are shown in Fig. 3. In the case of 4-DA-containing ionomers, as the amount of the 4-DA increases, the loss tangent peak for the matrix T_g shifts to lower temperatures, with decreasing its height. The loss tangent peak for the cluster T_g also shifts to lower temperatures strongly and then gently, but its height increases. Since the height (or size) of the loss tangent peak represents indirectly the relative amount of material showing the corresponding glass transition [13–16], the above finding implies that the amount of matrix regions decreases but the amount of cluster regions increases, as the 4-DA content increases. For the P(EA-7.0-ACo^{2+}) ionomers containing Gly, the position and size of the matrix loss tangent peak do not change significantly, with increasing Gly content. The position of the broad peak for the cluster glass transition, however, moves to lower temperatures gradually. It is also seen that the width of the cluster peak becomes wider with increasing Gly content, and that at 30.4 wt% of Gly content, the cluster peak becomes almost flat. The glass transition temperatures obtained from the positions of the loss tangent peak maximum as a function of weight percentage of plasticizer for the two ionomer systems are shown in Fig. 4. For comparison, the data of the P(EA-5.0-ANa$^+$) ionomers containing 4-DA, obtained from Ref. [9], are also included in the same figure. In the case of the Gly-containing P(EA-7.0-ACo^{2+}) ionomers, the matrix T_g remains more or less constant, but the cluster T_g decreases gradually with increasing Gly content. In the case of the P(EA-5.0-ANa$^+$) ionomers plasticized with 4-DA, as was mentioned before, the matrix and cluster T_gs decrease more or less linearly, and the decreasing rates of T_gs are as follows:

$$\text{Cluster } T_g(^\circ\text{C}) = 53 - 1.0 \times (\text{wt\% of } 4-\text{DA})(r^2 = 0.9789)$$

$$\text{Matrix } T_g(^\circ\text{C}) = 10 - 1.1 \times (\text{wt\% of } 4-\text{DA})(r^2 = 0.9885)$$

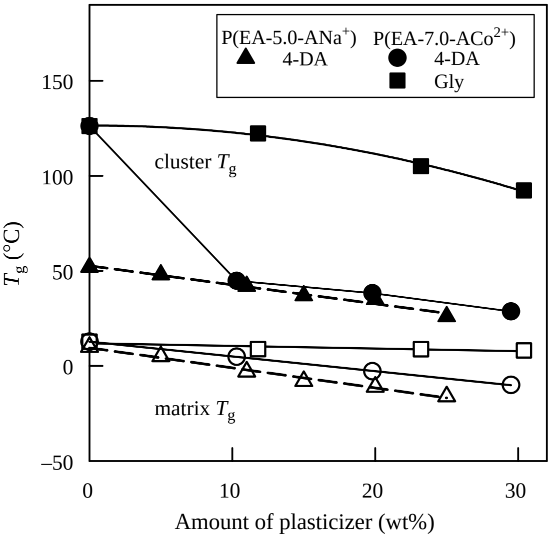

Fig. 4. Glass transition temperatures of the P(EA-7.0-ACo^{2+}) ionomer and ionomers containing 4-DA and Gly vs. the amount of plasticizer (at 1 Hz). Data for the P(EA-5.0-ANa^{+}) ionomers containing various amounts of 4-DA were obtained from Ref. [9].

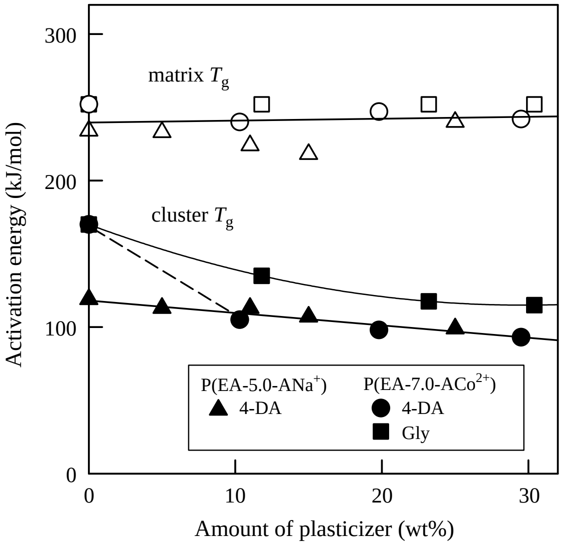

Fig. 5. Activation energy for the matrix and cluster glass transitions of the P(EA-7.0-ACo^{2+}) ionomer and ionomers plasticized with 4-DA and Gly vs. the amount of plasticizer. Data for the P(EA-5.0-ANa^{+}) ionomers containing various amounts of 4-DA were obtained from Ref. [9].

In the case of 4-DA-containing P(EA-7.0-ACo^{2+}) ionomers, it is clear that the matrix T_g decreases slowly, while the cluster T_g decreases fast and then slowly. It is interesting to note that, above 10 wt% of 4-DA, the rate of the decreasing cluster T_gs is more or less similar to that of the decreasing matrix T_g, and that the cluster T_g becomes close to but slightly higher than that of P(EA-5.0-ANa^{+}) ionomer. The relationships between T_gs of P(EA-7.0-ACo^{2+}) ionomer and the amount of 4-DA plasticizer are as follows:

$$\text{Cluster } T_g(°\text{C}) = 54 - 0.8 \times (\text{wt\% of } 4-\text{DA})(r^2 = 0.9891)$$

$$\text{Matrix } T_g(°\text{C}) = 13 - 0.8 \times (\text{wt\% of } 4-\text{DA})(r^2 = 0.9998)$$

As mentioned before, the rates of decreasing matrix and cluster T_gs are found to be similar for the Na^{+} ionomer (1.0 °C/wt% of 4-DA) and for the Co^{2+} ionomer (0.8 °C/wt% of 4-DA) systems. In addition, the matrix T_g as well as cluster T_g of the 4-DA-containing P(EA-5.0-ANa^{+}) are lower than those of the 4-DA-containing P(EA-5.0-ACo^{2+}) ionomers at a comparable 4-DA content, which is due to the lower ion content for the Na^{+} ionomer, compared to the Co^{2+} ionomer.

Activation energy values (E_as) for the matrix and cluster glass transitions can be calculated using an Arrhenius plot of log(frequency) vs. inverse temperature of a loss tangent peak maximum [10,13,14]. The E_as for the matrix and cluster glass transitions vs. the amount of plasticizer are shown in Fig. 5. In the case of the matrix glass transition, the addition of 4-DA and Gly to the PEA ionomers does not change the E_as strongly. In the case of the cluster glass transition, with increasing amount of plasticizer, the addition of Gly decreases the E_a fast and then slowly, and that of 4-DA decreases it drastically and subsequently very slightly. In the case of the Na^{+} ionomer, the addition of the 4-DA does not change the E_as for the matrix and cluster glass transitions strongly (again, the E_a data were obtained from Ref. [9]). In addition, it is interesting to note that the E_as of the un-plasticized Na^{+} ionomer, and the Na^{+} and Co^{2+} ionomers plasticized with 4-DA remain more or less constant.

The small-angle X-ray scattering (SAXS) profiles of the un-plasticized P(EA-7.0-ACo^{2+}) ionomer and the ionomers plasticized with 4-DA and Gly are shown in Fig. 6. For comparison, the SAXS profile of the sodium neutralized ionomer containing 7.0 mol% of ions is also shown in the same figure. In the case of the P(EA-7.0-ANa^{+}) ionomer, the small-angle upturn (SAUT) and small-angle ionomer peak at $q_{\max}$ = ca. 2.6 nm^{-1} are seen. This $q_{\max}$ value corresponds to the Bragg spacing between scattering centers of ca. 2.4 nm, which

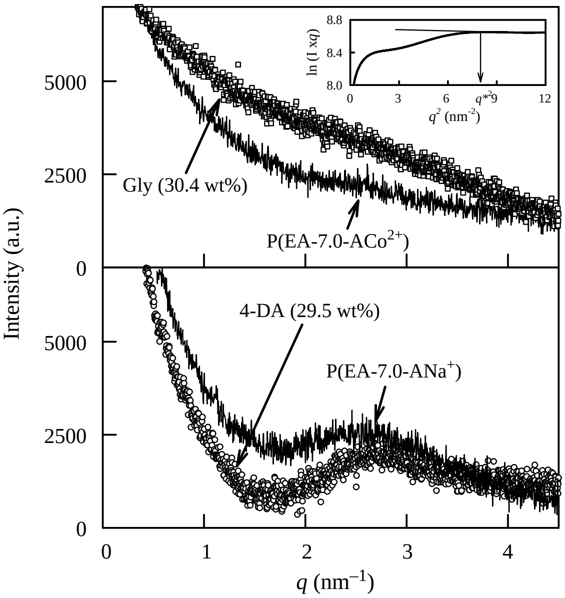

Fig. 6. SAXS profiles of P(EA-7.0-ANa^{+}) and P(EA-7.0-ACo^{2+}) ionomers, and Co^{2+} ionomers plasticized with 4-DA and Gly. The inset shows a plot of ln($I \times q$) vs. q^2 for the Na^{+}-neutralized ionomer. The meaning of the arrow is described in the text.

is in good accordance with the inter-multiplet distances for the P(EA-5.0-ANa$^+$) ionomers reported previously by Tong and Bazuin, who performed a thorough SAXS study on the 4-DA containing ionomers [9]. At this point, it is worth recalling that the majority of the SAUT would be caused by the compositional heterogeneity of the ionomers [17–20]. For the Co^{2+} ionomer, a very weak shoulder-like peak at q = ca. 2.6 nm^{-1} and a more developed SAUT are observed. This indicates that when the ionomer is neutralized with Co^{2+}, the ionomer phase becomes more heterogeneous compositionally. In the case of the Co^{2+} ionomer plasticized with Gly, only a very profound SAUT is observed; the upturn shifts to higher angles. However, the addition of 4-DA to the Co^{2+} ionomer results in the appearance of well-developed SAXS peak at q = ca. 2.6 nm^{-1}; the position and shape of the peak are similar to those of the un-plasticized Na$^+$ ionomer. This implies that the plasticization of the Co^{2+} ionomer with 4-DA induces more ionic aggregates, multiplets, at a prevalent distance, which is exactly what we could expect from the dynamic mechanical results. Now, it would be interesting to compare the persistence lengths of the polymer chains of the plasticized ionomers. The persistence length of ionenes is known to be calculated from the value of $2.87/q^*$, where q^* is the angle at which the X-ray scattering data begin to deviate from the linear extrapolation line in the plot of log[scattering intensity $(I)\times q$] vs. q^2 [21]. Using this relationship, we can calculate the persistence lengths of the ionomers from the SAXS data. The inset in Fig. 6 shows the plot for the Na$^+$ ionomer. The extrapolated line starts to deviate from the SAXS data at q^* = ca. 2.93 nm^{-1}, which corresponds to a persistence length of ca. 0.98 nm. The persistence lengths calculated from the q^* values for the Co^{2+} ionomer and ionomers plasticized with 4-DA and Gly are listed in Table 1. When the cation is changed from Na$^+$ to Co^{2+}, the persistence length seems to increase a little. As expected, the addition of 4-DA plasticizer to the ionomer leads to a decrease in persistence length slightly. In the case of the Gly-containing ionomer, the addition of plasticizer makes the persistence length not detectable. This is in good agreement with the interpretation of mechanical data, i.e. the ionomer plasticized with Gly seems to behave like a non-ionic copolymer.

At this point, it might be useful to compare the Co^{2+} and Na$^+$ ionomer systems to understand the plasticization effect on the mechanical properties and morphology of the Co^{2+} ionomer. In the case of divalent cation-containing ionomers, three ionic moieties (i.e. one cation + two anions) have to move to form multiplets, compared to only two ionic moieties (i.e. one cation + one anion) for ionomers containing a mono-valent cation. Thus, when the ionic groups tend to form multiplets, the polymer chains of the Co^{2+} ionomer experience more steric hindrance than those of the Na$^+$ ionomer, which results in the decrease in the number of multiplets and the low degree of clustering. For a cluster glass transition, two main mechanisms are involved; the relaxation of polymer chains in clustered regions [3,8] and the hopping of ionic groups from one multiplet to another [22–30]. Thus, the cluster T_g of the divalent Co^{2+} containing ionomers would be higher than that of the mono-valent Na$^+$ containing ionomers since three ionic moieties have to move at the same time, compared to two ionic moieties for the Na$^+$ ionomer. It should also be mentioned that, in the present work, the ion content of Co^{2+} ionomer is higher than that of the Na$^+$ ionomer, which naturally leads to a higher cluster T_g for the Co^{2+} ionomer system [3–6,8,10].

Table 1
SAXS data for the P(EA-7.0-ANa$^+$) ionomer, P(EA-7.0-ACo^{2+}) ionomer and its ionomers plasticized with 4-DA and Gly

Ionomers	$q_{\max}$ (nm^{-1})	D_{Bragg} (nm)	Persistence length (nm)
P(EA-7.0-ANa$^+$)	2.6	2.4	0.98
P(EA-7.0-ACo^{2+})	2.6	2.4	1.03
P(EA-7.0-ACo^{2+}) + 4-DA	2.6	2.4	0.96
P(EA-7.0-ACo^{2+}) + Gly	–	–	–

Now, let us discuss the role of plasticizers [3–6,30–37]. The 4-DA is a plasticizer of low polarity, and its amine groups can interact with the carboxylate ester groups of the PEA ionomer via H-bonding [9]. Therefore, the 4-DA molecules reside in non-ionic regions, i.e. matrix and clustered regions, but not in multiplets. This leads to the decrease in both the matrix and cluster T_gs in parallel [9]. In the present work, the cluster T_g of Co^{2+} ionomer, being much higher than that of Na$^+$ ionomer, decreases drastically upon adding 4-DA to the ionomer. Above 10 wt%, the matrix and cluster T_gs decrease more or less in parallel, with increasing 4-DA content. Once a certain amount of 4-DA is added to the ionomer, and, thus, the matrix and cluster phases, not multiplets, are plasticized enough to make the cluster T_g drop down sufficiently, the Co^{2+} ionomer forms more multiplets at a prevalent distance and begins to behave like the Na$^+$ ionomer. At this stage, the effect of the type of cations on the cluster T_g seems to be no more operative. If this were the case here, for example, the unexpectedly small decrease in ionic modulus of the Co^{2+} ionomers plasticized with 4-DA could be explained. According to Fig. 3, with increasing 4-DA content, the height of the matrix loss tangent peak decreases, but that of the cluster peak increases. In addition, the SAXS results indicate that the plasticization of the Co^{2+} ionomer with 4-DA induces more multiplets (Fig. 6). These suggest that, upon plasticization, the degree of clustering increases, leading to an increasing ionic modulus. Naturally, however, the plasticization of the ionomers, having relatively non-polar backbones, with non-polar molecules decreases the degree of clustering, which, in turn, decreases the ionic modulus, seen in the 4-DA-containing Na$^+$ ionomer system (Fig. 2). This means that the two factors mentioned above take the opposite direction, i.e. counterbalancing each other's effects. Therefore, the ionic modulus does not change significantly. In the case of Gly, polar plasticizer, it would dissolve the ionic groups of ionomers, resulting in the interruption of interactions between ionic groups in multiplets [31–38]. The weakening of ionic interaction, in turn, causes the disruption of multiplets, which leads to the decrease in the cluster T_g as well as its activation energy, with only a minor effect on the matrix T_g of ion poor regions and its activation energy. At this point, it should be mentioned that if the multiplets were fully plasticized with polar additives, the type of cations might be no more important factor for controlling the mechanical properties of the ionomers. It should also be mentioned that the weakening of ionic interaction naturally gives rise to a lower degree of clustering. Therefore, the ionic modulus of the ionomers decreases upon adding Gly to the PEA ionomer; this is what we observed here.

This section is devoted to the discussion on the effectiveness of 4-DA and Gly on the decreasing T_g of ionomers. On the basis of both classical and statistical thermodynamics, Chow proposed a model for the calculation of the T_g of a polymeric system containing diluents and vacant lattice sites [39]. In this model that takes into account of free volume (holes), polymer chains are thought to be immovable below their T_g, but small plasticizer molecules (i.e. diluents) can move and fill the holes of the polymer matrix. The relationship between T_gs and the classical and statistical thermodynamics parameters is as follows:

$$\ln\left(\frac{T_g}{T_{g0}}\right) = \beta[(1-\theta)\times\ln(1-\theta)+\theta\times\ln\theta]$$

where T_g and T_{g0} are the glass transition temperatures of the plasticized and un-plasticized polymers, respectively. The β and θ equal $k(N+L)/\Delta C_p$ and $N/(N+L)$, respectively, where $(N+L)$ represents the number of lattice sites, ΔC_p is the difference in heat capacity between the liquid and the solid, and N is the number of the plasticizer molecules. The two terms mentioned above are defined as follows:

$$(N+L) = \frac{zm_pN_A}{M_p} \text{ and } N = \frac{m_dN_A}{M_d}$$

where z is the coordination number, m_p and m_d are the mass of polymer and plasticizer, respectively, N_A is Avogadro's number, and M_p and M_d are the molecular weight of the polymer and plasticizer, respectively. At relatively low concentration of the plasticizer in the polymer sample, the experimental T_gs are found to be in good agreement with the calculated T_gs with $z=2$. At this point, it should be mentioned that even though the coordination number z is found to depend on a fitting parameter [40], in the present work, the calculation of T_gs with $z=2$ will give us useful information on the effectiveness of plasticization of PEA ionomer with 4-DA or Gly on the decreasing matrix and cluster T_gs. Fig. 7 shows the matrix and cluster T_gs of plasticized ionomers as well as the T_gs calculated using the above model as a function of the amount of plasticizer. It is seen that the calculated matrix and cluster T_gs decrease with increasing amounts of plasticizer. In addition, the decreasing rates are higher for the cluster T_g than for the matrix T_g. Furthermore, the decreasing rates of the matrix and cluster T_gs of the Gly system are higher than those of the 4-DA system. First of all, let us look at the cluster T_g. On one hand, the experimental cluster T_g of the Gly-containing ionomer is much higher than the calculated cluster T_g. This finding is supportive to the interpretation that the role of the Gly molecules is not to fill the holes in clustered regions but to dissolve the ionic aggregate, i.e. the Gly is plasticizer not for the matrix phase but for the ionic domains. On the other hand, the experimental cluster T_gs of 4-DA containing ionomer system are lower than the calculated values. This can be understood. The 4-DA molecules reside in the cluster regions to fill the free volume, which, in turn, makes the behavior of the 4-DA plasticized divalent Co^{2+} ionomers similar to that of the plasticized mono-valent Na^+ ionomers. Thus, when the 4-DA was added to the un-plasticized Co^{2+} ionomer, the cluster T_g of the ionomer decreased drastically. Since the plasticized Co^{2+} ionomer is assumed to behave like the plasticized Na^+ ionomers, we tried to calculate the cluster T_g of the Na^+ ionomer system plasticized with 4-DA, assuming that the cluster T_g of the un-plasticized Na^+ ionomer (7.0 mol% of ions) would be 68 °C [41]. In Fig. 7, it is seen that the calculated values are more or less similar to the experimental data. This implies that when the addition of 4-DA to the ionomer makes the Co^{2+} ionomer behave like the Na^+ ionomer, and that the 4-DA acts as 'normal' plasticizer for the clustered regions of the ionomer, at least to some extent. In the case of matrix glass transition, the calculated T_gs are lower than the experimental data. This is understandable; since there are ion pairs that exist singly in the matrix regions or in multiplets that do not form clustered regions, the plasticization decreases the matrix T_gs not so significantly, but to some extent. Overall, the findings mentioned above illustrate that the addition of 4-DA to the ionomer is more effective to decrease the cluster T_g of the Co^{2+} ionomer than the addition of Gly, but the types of the plasticizer are not much important for the decreasing matrix T_g.

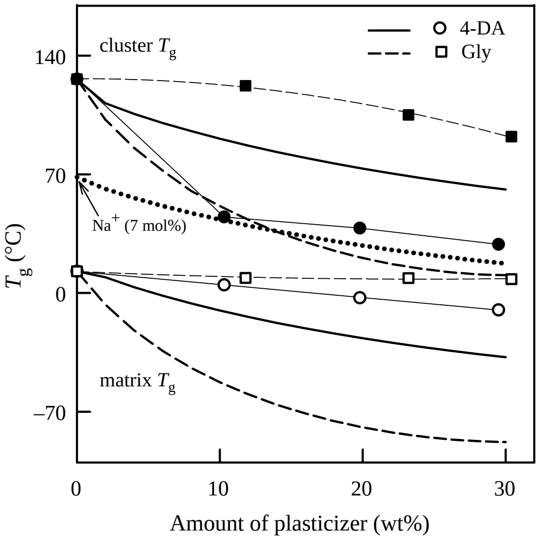

Fig. 7. T_gs of the P(EA-7.0-ACo^{2+}) ionomer and ionomers containing 4-DA and Gly vs. the amount of plasticizer. Long dashed lines represent the calculated T_gs of the ionomer containing Gly, and short dashed lines represent those of the ionomer containing 4-DA. A dotted line represents the calculated cluster T_gs of the Na+ ionomer plasticized with 4-DA.

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