# Structure and Properties of Ethylene Ionomers Neutralized with Binary Metal Cations

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ABSTRACT: The effects of mixing two metal cation ionomers on the structure and properties were investigated. Samples used in this study were binary mixtures selected from Li, Na, Mg, Cu(II), and Zn(II) salts of poly(ethylene-*co*-methacrylic acid) (EMAA). Stiffness, tensile, and melt index results in accordance with differential scanning calorimetry (DSC) and dynamic mechanical property measurements showed that binary cation mixtures gave rise to unexpectedly higher small-strain moduli if cations were selected from different metal groups such as alkali, alkaline earth, and transition metals. However, their large-strain moduli and properties measured in a molten state were essentially unchanged or as expected. For the binary mixtures exhibiting enhanced small-strain moduli, infrared results uncovered the appearance of a new peak in the carboxylate asymmetric stretching band at blend ratios where the binary mixtures exhibited the highest small-strain moduli. The results indicate that distinct changes take place in the local environment of neutralizing cations, which implies that ionic aggregates of these mixtures form a conjugated binary metal salt.

## Introduction

Ionomers are generally defined as polymers, in which small amounts of ionic groups are attached to the backbone chains. Ionic groups tend to form ionic aggregates in the hydrophobic polymer matrix.[1] The presence of ionic aggregates has been evidenced by X-ray diffraction,[2] small-angle X-ray scattering (SAXS),[3-5] dynamic mechanical[6-9] and dielectric[10,11] measurements, electron microscopy,[12] and electron spin resonance spectroscopy (ESR).[13-16] Ionic cross-links and the aggregation of ionic groups impart a dramatic increase in mechanical properties such as tensile strength, impact resistance, abrasion resistance, and stiffness.[17-19] These characteristic properties are essential for sodium, lithium, and zinc salts of poly(ethylene-*co*-methacrylic acid) (EMAA) to be used in a wide variety of industrial applications. The effects of neutralizing metal cation type on the morphology and properties of ethylene ionomers were examined in our previous study,[8] where K, Na, and Mg ionomers showed maximum stiffness near 33% neutralization and the Zn ionomer reached a stiffness plateau at ~70% neutralization. These neutralization degrees apparently agreed with those causing the microphase separation of ionic aggregates from the hydrocarbon matrix, found in our dielectric[11] and dynamic mechanical[9] relaxation studies. Different behavior of morphology and physical properties between the alkaline and alkaline-earth metal salts and the transition-metal salts was attributed to the difference in ionic interaction strength and the number of carboxyl groups that can associate with one metal cation. Cooper and his coworkers[20-24] have extensively studied the influence of neutralizing cation type on ionomer morphology and properties for model polyurethane ionomers using SAXS and extended X-ray absorption fine structure (EXAFS). Their works also remind us of the importance of ionic aggregation cohesiveness and cation chemistry in designing ionomer properties.

The technology of mixing two ethylene ionomers neutralized with different metal cations has been practiced for years in some industrial applications[25] because such mixed ionomers unexpectedly intensify their characteristic properties. However, there have been no systematic studies that focus on this interesting phenomenon. The concept of the mixture of two ionomers was recently presented by Visser and Cooper.[26] The study handled the effect of mixing sulfonated and carboxylated ionomers on the morphology and properties and uncovered the enhancement of the small-strain moduli for the mixed-anion system. This modulus enhancement was attributed to a combination of the effect of ion packing density, the ionic anchoring effect, and the degree of phase separation. Although their study is fairly suggestive, investigation is apparently required to determine if their concept can be translated to the case of cation mixtures of ethylene ionomers. Therefore, in this study, we attempt to elucidate the mechanism of the effect of mixing two metal cation ionomers on their structure and properties. Samples used in this study were binary mixtures selected from Li, Na, Mg, Cu(II), and Zn(II) salts of EMAA. For this purpose, mechanical properties using stiffness, tensile, and dynamic mechanical measurements, thermal properties using differential scanning calorimetry (DSC), and melt index measurements, moisture absorption, and spectroscopic measurements for binary mixtures were conducted, and the results were compared with those of their neat ionomers.

## Experimental Section

**Materials.** The precursor EMAA resins, EMAA(25) and EMAA(60), were from DuPont-Mitsui Polychemicals Co., Ltd., whose methacrylic acid unit is 5.4 mol % and melt indices are 25 and 60 g/10 min, respectively. The metal salts of EMAA were prepared by a melt reaction of EMAA with a stoichiometric quantity of cation sources such as metal hydroxides, metal carbonates, metal oxides, and metal acetates according to the method reported in our previous papers.[8,11] Characterization data for the metal salts of EMAA are listed in Table 1. We delineated our samples as EMAA(*N*)-*x*M, where *N*, *x*, and M are the melt index of the starting EMAA, the neutralization degree, and the metal cation, respectively. Mixed-cation ionomers were prepared by a melt blend of two of the Li, Na, Mg, Cu(II), and Zn(II) salts of EMAA at an indicated blend ratio using a Toyoseiki Laboplastomill at 453 K for 10 min. The samples were compression molded into 2- and 3-mm-thick sheets at 15 MPa and

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**Table 1. Metal Salts of Poly(ethylene-*co*-methacrylic acid)**

| ionomer descripn | cation | neutralizn (%) | base MI (g/10 min) | product MI (g/10 min) |
|---|---|---|---|---|
| EMAA(25)–0.3Na | $Na^+$ | 30 | 25 | 2.9 |
| EMAA(60)–0.6Na | $Na^+$ | 60 | 60 | 0.9 |
| EMAA(60)–0.4Li | $Li^+$ | 40 | 60 | 3.3 |
| EMAA(60)–0.6Li | $Li^+$ | 60 | 60 | 0.5 |
| EMAA(60)–0.6Mg | $Mg^{2+}$ | 60 | 60 | 0.8 |
| EMAA(60)–0.6Cu | $Cu^{2+}$ | 60 | 60 | 5.7 |
| EMAA(60)–0.6Zn | $Zn^{2+}$ | 60 | 60 | 0.9 |

453 K and then cooled to room temperature at a cooling rate of 30 K/min. Specimens for stiffness, tensile, differential scanning calorimetric (DSC), and dynamic mechanical measurements were aged at 296 K in a moisture barrier bag for 3–4 weeks before measurement because some of these properties are time-dependent and the changes are significant only for the first few weeks of aging.[27,28]

**Measurements.** Specimens for stiffness measurements were stamped out from 3-mm-thick sheets (100-mm length, 20-mm width, and 3-mm thickness) and were tested by using a Toyoseiki stiffness tester at 296 K according to ASTM D-747.

Dogbone specimens for tensile testing were stamped out from 2-mm-thick compression-molded sheets with a standard JIS K-6760 dumbbell and were tested using an Intesco Model 201 at 296 K, with a crosshead speed of 200 mm/min.

The melt index (MI) was measured as the weight of polymer flow (g/10 min) from a melt indexer at 463 K and under a 2160-g load.

A Rheospectoler Model DVE-V4 (Rheology Co., Ltd.) was used to measure dynamic mechanical properties. Specimens of approximately 20-mm length, 6-mm width, and 2-mm thickness were analyzed in the tensile mode at a constant tension, at a heating rate of 3 K/min from 223 to 393 K, and with a frequency of 10 Hz.

DSC measurements were conducted using a differential scanning calorimeter (DuPont DSC-990) at a heating and cooling rate of 10 K/min. A 10-mg specimen used for the measurement was taken from an aged compression-molded sheet. At the first heating, two endothermic peaks were observed near 325 and 365 K. The lower temperature peak was assigned to the order–disorder transition of ionic aggregates ($T_i$),[27,28] and the higher one corresponded to the melting of the polyethylene crystallites ($T_m$).[27,28] The crystallization temperature of the polyethylene region ($T_c$) was obtained from an exothermic peak in the cooling process near 335 K. These $T_i$, $T_m$, and $T_c$ were determined as a temperature exhibiting the maximum peak point on a DSC thermogram. The enthalpy changes of the $T_i$ peak ($\Delta H_i$) and the $T_m$ peak ($\Delta H_m$) were calculated from the peak area of each endothermic peak. Indium was used as a calibration standard. The degree of crystallinity in the polyethylene region ($X_c$) was calculated from the value of $\Delta H_m$ by assuming the heat of fusion of polyethylene crystallites is 290.4 J/g.

Specimens for moisture absorption measurements were 3-mm-thick sheets (100-mm length, 20-mm width, and 3-mm thickness), which were aged at 296 K and 50% relative humidity and were weighed every 15 days. The moisture content of the specimens was determined from the weight loss of the specimens after drying in a 450 K vacuum oven for 20 min. No conversion of acid to acid anhydride groups was confirmed by IR spectra during the drying process.

About 50-$\mu$m-thick films for Fourier transform infrared spectroscopic (FTIR) analysis were prepared by compression molding at 5 MPa and at 453 K. IR spectra were measured using a Digilab Model FTS-40 spectrometer at room temperature, where 64 scans at a resolution of 2 $cm^{-1}$ were signal averaged.

## Results and Discussion

**Stiffness.** Introducing ionic groups into the polyethylene backbone of EMAA provides superior stiffness over branched polyethylene or EMAA resins since ionic groups aggregate in the hydrophobic matrix and act as rigid cross-links. Stiffness increases with increasing neutralization, but the slope of the stiffness–neutralization plot depends on the type of neutralizing cations as explained in the Introduction.[8] In addition, ethylene ionomers exhibit a stiffness increase during aging at room temperature.[27,28] We attributed this increase to a gradual formation of some ordered structure in ionic aggregates during aging. The rearrangement of ionic groups probably furnishes stress in polyethylene amorphous regions attached to the ionic aggregates, which should result in facilitating the stiffness increase. Thus, stiffness changes due to the effect of neutralizing degrees, the type of neutralizing cations, and aging time are obviously characteristic for ethylene ionomers.

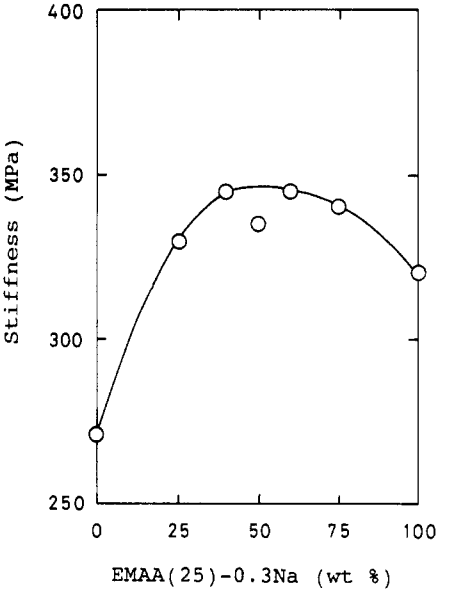


**Figure 1.** Plots of stiffness for binary mixtures of EMAA(60)–0.6Zn and EMAA(25)–0.3Na.

In order to examine the effect of mixing two metal cation ionomers, sodium (EMAA(25)–0.3Na) and zinc (EMAA(60)–0.6Zn) ionomers were mixed at different ratios and their stiffness was tested. Figure 1 shows the stiffness of mixed-cation ionomers of EMAA(60)–0.6Zn with EMAA(25)–0.3Na containing 0%, 25%, 40%, 50%, 60%, 75%, and 100% EMAA(25)–0.3Na. The sodium–zinc mixed ionomers exhibited higher stiffness than both of the neat ionomers at any blend ratios, and the highest stiffness was given around 40–75 wt % of EMAA(25)–0.3Na. Table 2 summarizes the stiffness of the sodium–zinc mixed ionomers and other mixed-cation ionomers. A similar stiffness increase was observed for a mixture of EMAA(60)–0.4Li and EMAA(60)–0.6Zn. However, mixtures of EMAA(60)–0.4Li and EMAA(25)–0.3Na and of EMAA(60)–0.6Cu and EMAA(60)–0.6Zn showed that stiffness was almost equal to that of the neat ionomers. These results revealed an interesting fact that ionomer stiffness can be strengthened by mixing two ionomers neutralized with different types of metal cations. Our limited results indicate that the combination of a cation from the alkali-metal group and the other metal cation groups may provide the possibility of enhancing ionomer stiffness.

**Tensile Properties.** Figure 2 shows tensile results for the same series of sodium–zinc mixed ionomers as in Figure 1. Plots of tensile strength and elongation increased almost monotonously with increasing EMAA(25)–0.3Na content. The results imply that the values of the mixtures simply represent the summation of a contribution of each component in accordance with their weight fraction. Our previous work[8] showed that the valence of cation and the degree of neutralization strongly influenced the tensile strength and elongation and that Na ionomers usually

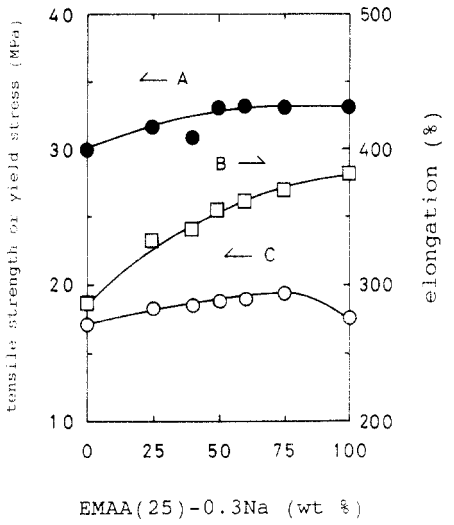


**Figure 2.** Plots of tensile properties for binary mixtures of EMAA(60)–0.6Zn and EMAA(25)–0.3Na: (A) tensile strength, (B) elongation, (C) yield stress.

**Table 2. Stiffness of Mixed-Cation and Their Neat Ionomers**

| ionomer blend (w/w) | stiffness (MPa) |
|---|---|
| EMAA(60)–0.6Zn | 270 |
| EMAA(25)–0.3Na/ EMAA(60)–0.6Zn = 25/75 | 330 |
| EMAA(25)–0.3Na/ EMAA(60)–0.6Zn = 40/60 | 345 |
| EMAA(25)–0.3Na/ EMAA(60)–0.6Zn = 50/50 | 335 |
| EMAA(25)–0.3Na/ EMAA(60)–0.6Zn = 60/40 | 345 |
| EMAA(25)–0.3Na/ EMAA(60)–0.6Zn = 75/25 | 340 |
| EMAA(25)–0.3Na | 320 |
| EMAA(60)–0.6Zn | 270 |
| EMAA(60)–0.6Zn/ EMAA(60)–0.4Li = 50/50 | 345 |
| EMAA(60)–0.4Li | 310 |
| EMAA(25)–0.3Na | 320 |
| EMAA(60)–0.4Li/ EMAA(25)–0.3Na = 50/50 | 315 |
| EMAA(60)–0.4Li | 310 |
| EMAA(60)–0.6Cu | 265 |
| EMAA(60)–0.6Zn/ EMAA(60)–0.6Cu = 60/40 | 280 |
| EMAA(60)–0.6Zn | 270 |

provided larger values than Zn ionomers. Therefore, our results basically agree with those previously obtained.

A different feature was seen for the yield stress results. A curve for the yield stress exhibited a vague peak centered around 75 wt % of EMAA(60)–0.3Na, but trends of the yield stress were identical with those seen for the stiffness results of the same series of sodium–zinc mixed ionomers. Stiffness and yield stress are measured under small strain, while tensile strength and elongation are measured under large strain. This experiment revealed that the enhancement appears only on the small-strain moduli and not on the large-strain moduli. In our previous work,[8,28] it is found that the structure and cohesiveness of ionic aggregates strongly influence stiffness and yield stress and that these properties are fairly correlated with the enthalpy change at $T_i$ determined by DSC. DSC measurements of a 4-fold-stretched ionomer film[8] revealed that an endothermic peak corresponding to the melting of ionic aggregates almost disappeared by the stretching. However, the other peak corresponding to the melting of polyethylene crystallites remained unchanged. The results clearly imply some

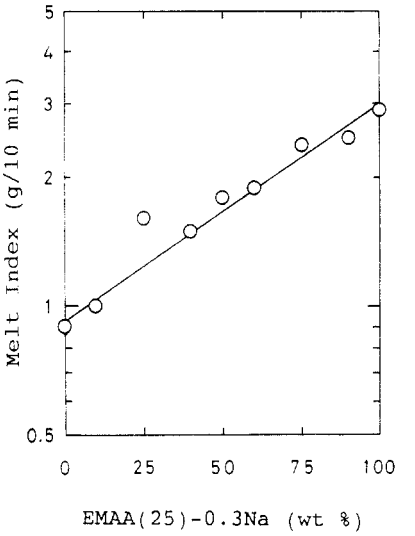


**Figure 3.** Plots of MI for binary mixtures of EMAA(60)–0.6Zn and EMAA(25)–0.3Na.

ordered structures in the ionic aggregates or more likely a part of the aggregates are unable to endure such large strain because, with increasing the elongation, sufficient energy is available to begin pulling ionic groups out of the ionic aggregates, resulting in a great number of ionic groups dispersed in the polymer matrix. Mixing two metal cation ionomers primarily influences the local structure of ionic aggregates. Therefore, the enhancement seen for binary metal cation mixtures becomes obvious only for small-strain moduli. Changes in DSC thermograms of the mixed-cation ionomers will be presented later.

**MI Data.** Figure 3 shows MI results for the sodium–zinc mixed ionomer series. MI of EMAA(60)–0.6Zn (0.9) was smaller than that of EMAA(25)–0.3Na (2.9), and the logarithm of MI linearly increased with increasing EMAA-(25)–0.3Na content. MI is usually used as an index of molecular weight of polymers, and if polymers are miscible, MI of multicomponent polymers can be calculated by a simple equation as:

$$\log \mathrm{MI_b} = \sum r_i \log \mathrm{MI}_i$$

where $\mathrm{MI_b}$ is MI of a mixed polymer, $r_i$ is the weight fraction of each component, and $\mathrm{MI}_i$ is the MI of each component. MI of the sodium–zinc mixed ionomers apparently follows this equation, and nothing unordinary is observed in this experiment. Because MI was measured at 463 K, both ionic and polyethylene crystallites were completely melted at this temperature. Therefore, it is quite natural that the mixtures did not show any enhancement in the MI behavior unlike stiffness and yield stress measurements. This finding convinces us that the enhancement of the small-strain moduli due to mixing two cation ionomers can be expected only at a temperature range where ionic aggregates remain in some ordered state.

**Dynamic Mechanical Properties.** Figure 4 illustrates the temperature dependence of dynamic mechanical properties for EMAA(25)–0.3Na, EMAA(60)–0.6Zn, and their 50/50 (w/w) mixture at 10 Hz. The storage modulus ($E'$) curves show that all the ionomers had almost the same $E'$ values below 300 K. However, a downturn in the $E'$ curve of the mixture at 325 K was about 10 K higher than that of EMAA(25)–0.3Na and EMAA(60)–0.6Zn. This downturn is regarded to be caused by the softening of ionic aggregates, resulting in the start of a micro-Brownian molecular motion of long hydrocarbon chains attached to ionic aggregates.[9] The results provided evidence that mixing EMAA(25)–0.3Na and EMAA(60)–0.6Zn obviously

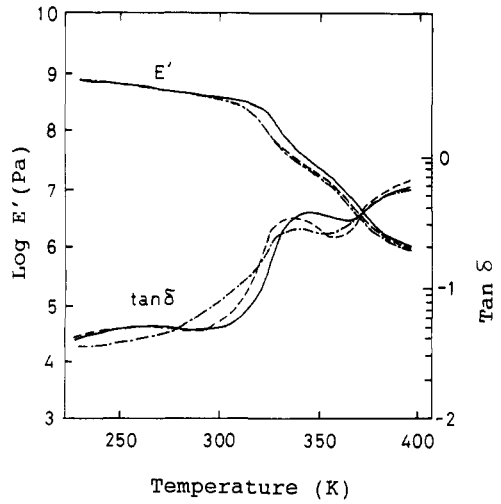


**Figure 4.** Temperature dependence of dynamic storage modulus ($E'$) and tan $\delta$ at 10 Hz for EMAA(25)–0.3Na/EMAA(60)–0.6Zn (50/50, w/w) (—), EMAA(25)–0.3Na (- - -), and EMAA(60)–0.6Zn (- • -).

increased $T_i$. The effect of increasing $T_i$ was confirmed by the DSC measurements, and details will be discussed later.

The difference in the $E'$ gradually became smaller along with a temperature increase, and the $E'$ curve of all the ionomers finally became almost identical above 380 K. A melting point of polyethylene crystallites of ethylene ionomers is around 365 K so that they are in a molten state above 380 K. As discussed in the melt index experiment, the property enhancement of the mixed-cation ionomers have been observed as long as ionic aggregates keep some ordered structures. The $E'$ behavior at elevated temperatures provided additional evidence that the effect of mixing the Na and Zn ionomers diminished above $T_i$ but that some degrees of the difference seemed to remain until polyethylene crystallites melted completely.

EMAA(60)–0.6Zn exhibited a peak on the tan $\delta$ curve at 340 K. This peak is related to $\beta'$ relaxation that originates from a micro-Brownian molecular motion of long segments in the amorphous region, where carboxylic acid dimers act as cross-links and restrict that motion. EMAA(25)–0.3Na and the mixture clearly exhibited two peaks on the tan $\delta$ curves near 260 and 340 K. These peaks are considered to represent $\beta$ and $\alpha$ relaxations, respectively. As discussed in our previous report,[9] the $\beta$ relaxation reflects a micro-Brownian segmental motion in the amorphous region, from which most ionic groups are excluded, and the $\alpha$ relaxation reflects the motion of the polymer chains attached to the ionic aggregate region. Therefore, the appearance of the two relaxations is regarded as an indication of phase separation of the ionic aggregate region from the amorphous region. This experiment revealed that the sodium–zinc mixed ionomer formed a phase-separated structure. EMAA(60)–0.6Mg is known to have a phase-separated structure,[9] and we found that a 50/50 (w/w) mixture of EMAA(60)–0.6Zn and EMAA(60)–0.6Mg also showed two peaks on the tan $\delta$ curve at 278 and 330 K (chart not included). These facts allow speculation that a phase-separated ionomer predominates the phase behavior of the binary mixtures.

**DSC Data.** DSC thermograms of the sodium–zinc mixed ionomer series are shown in Figure 5, and the data are summarized in Table 3. It is evident that all the DSC thermograms exhibited two endothermic peaks near 325 and 365 K. They are assigned to $T_i$ and $T_m$, respectively.[27,28] $T_i$ of the mixtures moved to a little bit higher temperature than that of the neat ionomers, and, to the

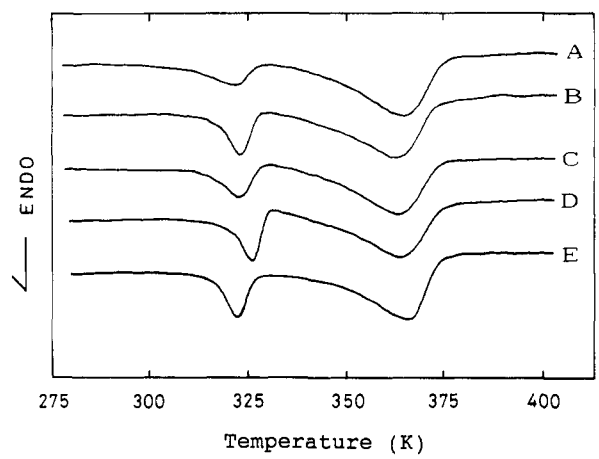


**Figure 5.** DSC thermograms in the first heating for EMAA(60)–0.6Zn/EMAA(25)–0.3Na for the following wt % EMAA(25)–0.3Na: (A) 0%, (B) 25%, (C) 50%, (D) 75%, (E) 100%.

**Table 3. DSC Data for Sodium–Zinc Mixed Ionomers[a]**

| EMAA(25)–0.3Na in blend (wt %) | $T_i$ (K) | $T_m$ (K) | $T_c$ (K) | $\Delta H_i$ (J/g) | $\Delta H_m$ (J/g) | $X_c$ (%) |
|---|---|---|---|---|---|---|
| 0 | 321 | 365 | 329 | 11.3 | 57.4 | 20 |
| 25 | 323 | 363 | 328 | 14.9 | 57.1 | 20 |
| 50 | 323 | 363 | 326 | 15.2 | 49.9 | 17 |
| 75 | 326 | 364 | 327 | 18.0 | 46.3 | 16 |
| 100 | 322 | 365 | 333 | 12.2 | 73.3 | 25 |

[a] Blends of EMAA(25)–0.3Na with EMAA(60)–0.6Zn.

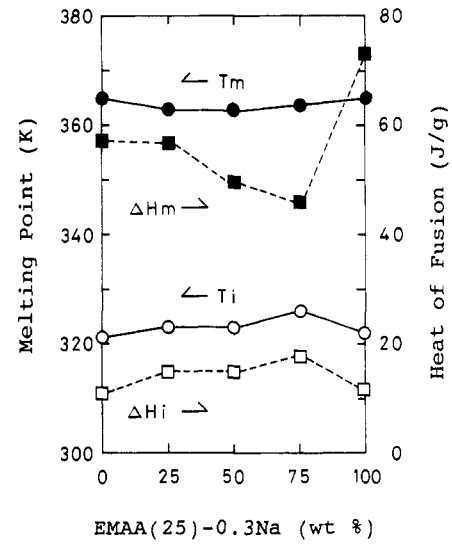


**Figure 6.** Melting point and the heat of fusion for binary mixtures of EMAA(60)–0.6Zn and EMAA(25)–0.3Na; $T_i$ = order–disorder transition temperature of ionic aggregates, $T_m$ = melting point of polyethylene crystallites, $\Delta H_i$ = heat of fusion of ionic crystallites, $\Delta H_m$ = heat of fusion of poly ethylene crystallites.

contrary, $T_m$ of the mixtures slightly decreased. The trend of the increasing $T_i$ qualitatively agrees with that observed in the dynamic mechanical measurements even though the different analysis technique may cause a shift of transition temperatures. Rather dramatic changes of $\Delta H_i$ and $\Delta H_m$ are seen in Figure 6. It is obvious that all the mixtures exhibited larger $\Delta H_i$ than that of the neat ionomers, and the maximum $\Delta H_i$ was given around 75 wt % of the EMAA(25)–0.3Na content. The $\Delta H_i$ curve also implies that the development of $\Delta H_i$ strengthens the ability of ionic cross-links to restrict the development of polyethylene crystallites. Stiffness and yield stress of ethylene ionomers are known to be closely related to values of $\Delta H_i$.[8] Therefore, it is understandable that the enhanced stiffness and yield stress should result from changes in the ionic

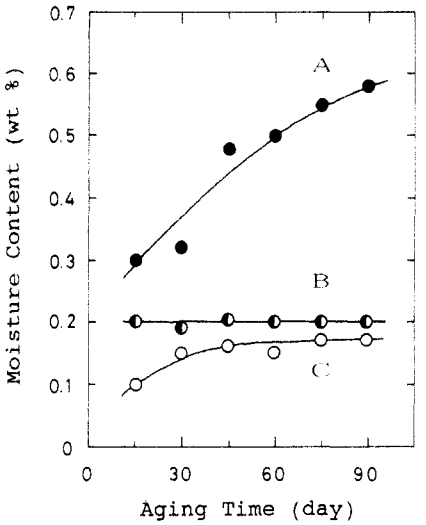


**Figure 7.** Moisture absorption of (A) EMAA(60)–0.6Na, (B) EMAA(60)–0.6Na/EMAA(60)–0.6Zn (50/50, w/w), and (C) EMAA(60)–0.6Zn during aging at 296 K and at 50% relative humidity.

aggregates such as an increase of the number of the ionic aggregates.

**Water Absorption.** Figure 7 shows moisture absorption results of EMAA(60)–0.6Na, EMAA(60)–0.6Zn, and their 50/50 (w/w) mixture during aging at 296 K and at 50% relative humidity. The moisture content of EMAA(60)–0.6Na continuously increased over the examined period of time and reached about 0.6 wt % after 90 days of aging. The effects of water sorption on the structure and properties of EMAA-based sodium ionomers were reported in our preceding paper.[29] In that paper, the equilibrium moisture content for EMAA(60)–0.6Na was determined to be approximately 1.2 wt % at 50% relative humidity so that the result obtained in this study is consistent with the previous one. In contrast to the Na ionomer, the mixture and EMAA(60)–0.6Zn apparently reached the equilibrium of moisture content within 45 days, and the equilibrium content was 0.2 wt % or less. Calculation shows that 0.2 wt % moisture implies 1 water molecule exists among 10 carboxylate–cation ion pairs.

An extremely small amount of moisture uptake by EMAA(60)–0.6Zn was observed in our previous study.[28] Surprisingly, the equilibrium moisture uptake for the mixture resembles that of the Zn ionomer. It is easily understood that water molecules are preferentially absorbed in the ionic aggregate regions. Therefore, this very small level of moisture uptake of the mixture allows speculation that the nature of the ionic aggregates should change on mixing two metal cation ionomers. To confirm this hypothesis, changes of the local environment of neutralizing cations were investigated using FTIR. A thorough discussion of the FTIR results will be given below.

**FTIR Spectroscopy.** FTIR measurements have been utilized as a powerful means to detect changes in the local environment of anions that are strongly affected by neutralizing cations. Many works[29-32] revealed that the carboxylate asymmetric stretching band of ethylene ionomers was significantly sensitive to the type of metal cation, degree of neutralization, temperature, aging time, and moisture absorption. Figure 8 shows spectral changes for a series of EMAA(25)–0.3Na and EMAA(60)–0.6Zn mixtures in the range 1300–1800 $cm^{-1}$. EMAA(60)–0.6Zn exhibited characteristic bands corresponding to the carboxylate asymmetric ($\nu_a(COO^-)$) and symmetric ($\nu_s(COO^-)$) stretching mode at 1585 and 1420 $cm^{-1}$, respectively. EMAA(25)–0.3Na exhibited a slightly different spectrum

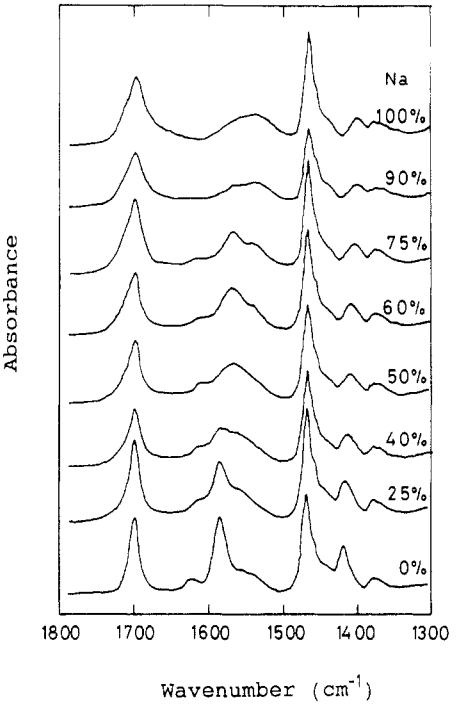


**Figure 8.** FTIR spectra for binary mixtures of EMAA(60)–0.6Zn and EMAA(25)–0.3Na in the range 1300–1800 $cm^{-1}$. The weight percent of EMAA(25)–0.3Na is indicated at the right of each infrared spectrum.

than EMAA(60)–0.6Zn: broader peaks centered around 1540 and 1400 $cm^{-1}$ are assigned to $\nu_a(COO^-)$ and $\nu_s(COO^-)$, respectively. Comparing the spectra of the mixtures with the neat ionomers shows that the peak assigned to the $\nu_s(COO^-)$ of EMAA(60)–0.6Zn gradually moved to the peak position of the $\nu_s(COO^-)$ of EMAA(25)–0.3Na with increasing the EMAA(25)–0.3Na content. Rather drastic spectral changes were found in the $\nu_a(COO^-)$ of the mixtures. To make it easier to understand the changes taking place in that region, the spectra around 1600 $cm^{-1}$ are magnified in Figure 9. The spectra clearly show that the mixtures produce a new peak at 1565 $cm^{-1}$ and that the peak becomes dominant when the EMAA(25)–0.3Na content is in the range of 50–75 wt %. The new peak is, of course, assigned to the $\nu_a(COO^-)$ of the mixtures, and the development of this peak strongly suggests that there is an interaction between sodium and zinc cations. We can refer to an interesting fact that a solid phase of the mixture of the sodium acetate, zinc acetate, and acetic acid was determined to be solvated sodium zinc acetate, whose composition was given as $Zn(C_2H_3O_2)_2 \cdot 2NaC_2H_3O_2 \cdot 4HC_2H_3O_2$.[33] Our results have shown the new peak at 1565 $cm^{-1}$ becomes dominant when the mole fraction of Na reaches 0.50–0.75 in the overall cation content. This value apparently coincides with the mole fraction of Na for the solvated sodium zinc acetate, namely, 0.67. Therefore, the FTIR results allow the prediction that the development of the new peak should represent the formation of a new structure in the ionic aggregates, which consists of a conjugated binary metal salt containing sodium and zinc carboxylate and unneutralized carboxylic acid. The IR[31,32] and EXAFS[34,35] studies furnished information that Zn and Na salts of EMAA have tetracoordinated and hexacoordinated structure, respectively. Considering the coordination structure and the Na/Zn blend ratio for the solvated sodium zinc acetate, a model of a conjugated binary metal salt of the sodium–zinc mixed ionomer is schematically depicted in Figure 10. It is evident from the model that an interaction force of the binary metal cation salt will result from an unlocalized

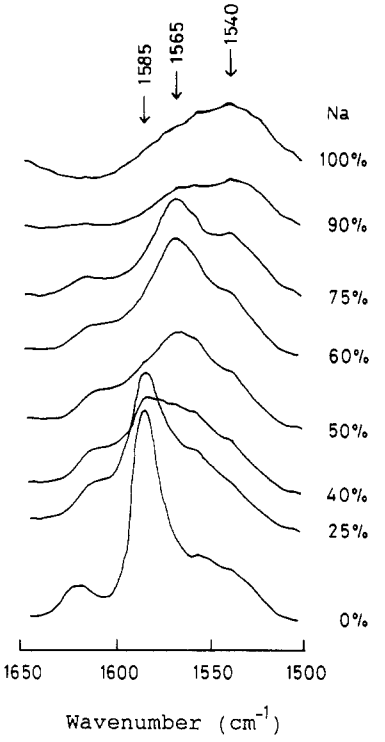


**Figure 9.** FTIR spectra of the carboxylate asymmetric stretching band for the same series as in Figure 8. The weight percent of EMAA(25)–0.3Na is indicated at the right of each infrared spectrum.

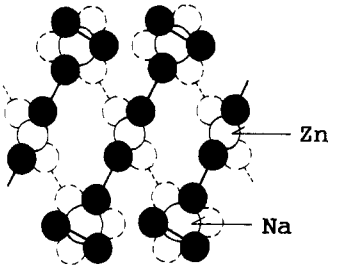


**Figure 10.** Schematic model for a conjugated binary metal salt of the sodium–zinc mixed ionomer. Small dot-lined circles are oxygen atoms below the plane of the paper and small dark circles are oxygen atoms above the plane of the paper. Lines connecting oxygen atoms mean that the connected oxygen atoms come from the same carboxylate or carboxylic acid groups.

electron of the carboxylate anion, which encompasses sodium and zinc cations.

We attempted a similar spectroscopic approach to mixed-cation ionomers, whose cation combination was found to have no effect in enhancing ionomer stiffness. The FTIR results are shown in Figure 11 for mixtures of EMAA(60)–0.6Cu and EMAA(60)–0.6Zn and in Figure 12 for a mixture of EMAA(60)–0.6Li and EMAA(60)–0.6Na. As is usually expected, $\nu_a(COO^-)$ of the mixtures exhibited a doublet peak that was simply the overlap of an individual peak of the neat ionomers, and there were no signs of the formation of a conjugated binary metal cation salt. We tried spectral fits for the Zn/Cu mixed system, and confirmed that the mixed-cation spectra are formed by the linear combination of the two pure components.

We also attempted a similar spectroscopic approach to other binary mixtures that should show the effect of enhancing the small-strain moduli. The results are summarized in Table 4. The binary mixture of EMAA(60)–0.6Zn and EMAA(60)–0.6Li, which exhibited the enhancement in the stiffness results, clearly showed a new doublet peak of $\nu_a(COO^-)$ at 1545 and 1620 cm$^{-1}$. A single peak of the $\nu_a(COO^-)$ of EMAA(60)–0.6Zn, located at 1585

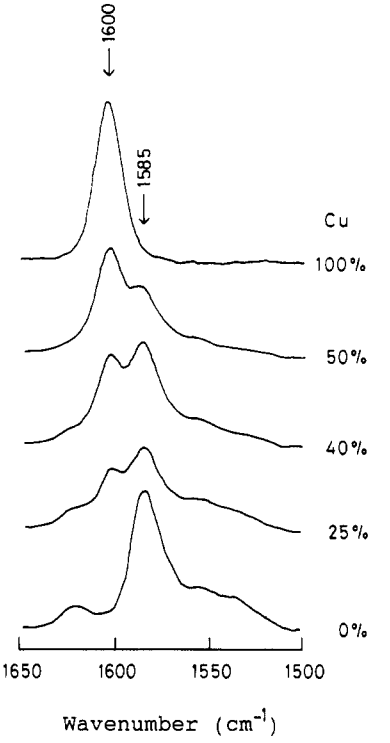


**Figure 11.** FTIR spectra of the carboxylate asymmetric stretching band for binary mixtures of EMAA(60)–0.6Zn and EMAA(60)–0.6Cu. The weight percent of EMAA(60)–0.6Cu is indicated at the right of each infrared spectrum.

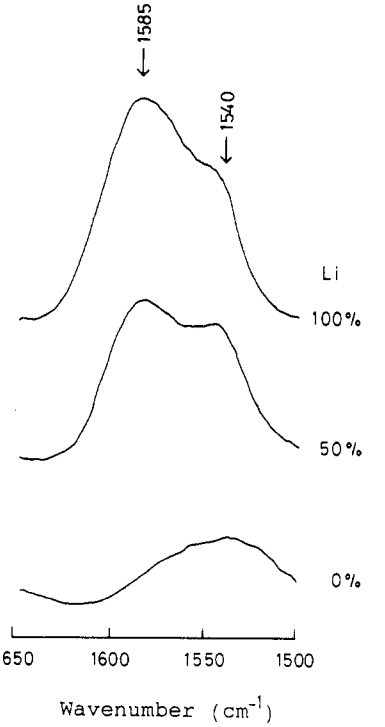


**Figure 12.** FTIR spectra of the carboxylate asymmetric stretching band for binary mixtures of EMAA(60)–0.6Na and EMAA(60)–0.6Li. The weight percent of EMAA(60)–0.6Li is indicated at the right of each infrared spectrum.

cm$^{-1}$, was found to split into a triplet peak at 1536, 1565, and 1620 cm$^{-1}$ when the FTIR spectra were taken above 373 K[32] or the sample was dried in a 333 K vacuum oven for 24 h prior to the FTIR measurements.[36] To eliminate the possibility of the drying effect, we dipped a 50-$\mu$m film of the mixture in water at room temperature for 10 days and confirmed that the FTIR spectrum, showing the new doublet peak, was unchanged by the water dipping. Therefore, we concluded that the Li and Zn mixture formed

**Table 4. Carboxylate Asymmetric Stretching Band for Mixed-Cation and Their Neat Ionomers**

| ionomer blend (w/w) | $\nu_a(COO^-)$ ($cm^{-1}$) |
|---|---|
| EMAA(60)–0.6Zn | 1585 |
| EMAA(60)–0.6Li | 1585 |
| EMAA(60)–0.6Mg | 1610 |
| EMAA(60)–0.6Na | 1540 |
| EMAA(60)–0.6Zn/ EMAA(60)–0.6Li = 50/50 | 1545, 1620 |
| EMAA(60)–0.6Zn/ EMAA(60)–0.6Mg = 50/50 | 1600 |
| EMAA(60)–0.6Li/ EMAA(60)–0.6Mg = 50/50 | 1565, 1615 |
| EMAA(60)–0.6Na/ EMAA(60)–0.6Mg = 50/50 | 1545, 1600 |

a new structure in the ionic aggregates. The mixture of EMAA(60)–0.6Zn and EMAA(60)–0.6Mg also showed a new peak of $\nu_a(COO^-)$ at 1600 $cm^{-1}$, indicating the formation of a new structure. The FTIR spectra of the other two mixtures, Li/Mg and Na/Mg, were rather complicated because both showed a doublet peak near the peak position of their neat ionomers. The peak position of the doublet peak of the Li/Mg mixture looked different from that of their neat ionomers, but the doublet peak of the Na/Mg mixture appeared to result from the overlap of their neat ionomer peaks. At this point, no definitive conclusion can be drawn about whether binary mixtures from Mg and alkali-metal ionomers form a conjugated metal cation salt or not. Further investigation has to be addressed on this matter.

Regarding the Na and Zn ionomer mixtures, the blend ratio, dominantly exhibiting the new $\nu_a(COO^-)$ peak, is in the range of 50–75 wt % of the EMAA(25)–0.3Na content, which exactly agrees with those providing the highest values of stiffness, yield stress, and $T_i$. Combining the FTIR findings with those obtained by the other experiments, it is concluded that the enhancement of the small-strain moduli originates from the formation of a new well-ordered structure or a conjugated binary metal salt in ionic aggregates.

## Conclusions

The experimental results reveal interesting facts that mixed-cation ionomers, if metal cations are selected from different metal cation groups, provide unexpectedly higher values for small-strain moduli such as stiffness and yield stress. However, no signs of the enhancement are observed for properties measured under large strain or in a molten state. The values of $\Delta H_i$ are known to govern stiffness and yield stress of ethylene ionomers, but the DSC thermogram shows that the $\Delta H_i$ peak diminishes when a large deformation is applied. Therefore, the effect of mixing two cation ionomers is assumed to be fundamentally related to the ionic aggregates. Actually, the DSC and dynamic mechanical measurements reveal that $T_i$ of the mixed-cation ionomers shifts to higher temperatures and $\Delta H_i$ apparently becomes larger.

The very small level of moisture absorption of the sodium–zinc mixed ionomer indicates that it is not only the number but also the nature of the ionic aggregates that primarily changes on mixing two metal cation ionomers. In order to prove this hypothesis, spectroscopic analysis is carried out and changes in the local environment of the neutralizing cation are detected: a new peak of $\nu_a(COO^-)$ develops for the mixed-cation ionomers that exhibit enhanced small-strain moduli. A blend ratio, dominantly exhibiting the new peak, agrees with those providing the highest values of stiffness, yield stress, and $T_i$. The development of this new peak is considered to represent the formation of a conjugated binary metal salt. Therefore, it is concluded that the enhancement of the small-strain moduli originates from the formation of a conjugated binary metal salt in ionic aggregates.

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