Water Absorption Effects on the Thermal Transition and Stiffness of Ethylene Ionomers

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SYNOPSIS

Changes in the thermal transition and stiffness of ionomers occurring during aging or water absorption were investigated. Ionomers used in this study are Na, K, Mg, and Zn salts of poly(ethylene-co-methacrylic acid) (EMAA), whose methacrylic acid unit is 5.4 mol %. It was found that ionomer stiffness is subject to water absorption and the effect differs with the neutralizing cations. Water absorption effects on the thermal transition, measured by differential scanning calorimetry (DSC), indicate that there are no significant changes in the higher-temperature endotherm assigned to a melting of polyethylene (PE) crystallites. However, the lower-temperature endotherm, which we attribute to an order–disorder transition of ionic aggregates (T_i), exhibits significant changes upon water absorption. The mechanism of the water absorption effects on the thermal transition and stiffness is described. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Unique properties of ionomers originate from a small amount of ionic groups, which aggregate in media of low dielectric constant and act as rigid crosslinks.[1-3] Several proposed models[4-8] depict the ionomer structure and focus on the size and distribution of ionic aggregates. A closer comparison between the proposed models and experimental data, primarily obtained from small-angle X-ray and small-angle neutron scattering, has been of keen interest to many workers.

The ionic crosslinks impart dramatic increases in mechanical (e.g., stiffness, tensile strength, impact resistance, abrasion residence), melt (e.g., melt viscosity, melt tension), and chemical properties (e.g., oil resistance) of ethylene ionomers.[9-12] These characteristic properties are essential for ethylene ionomers to be used in a wide variety of industrial applications. We currently studied the structure of hydrated Na salts of poly(ethylene-co-methacrylic acid) (EMAA) using infrared spectroscopic, differ-

ential scanning calorimetric (DSC), thermogravimetric, X-ray diffractometric, and dielectric measurements, and found that water absorption gives rise to significant changes in the ionic aggregate regions but minimal changes in the polyethylene (PE) crystalline regions.[13,14] These results indicate that hydrophilic ionic groups in ethylene ionomers are strong absorption sites of water molecules and therefore the water absorption preferentially affects the structure of the ionic aggregates. Other studies[4,15,16] using small-angle or wide-angle X-ray scattering experiments confirmed that water plasticizing effects occur in the ionic aggregates. All the experimental data obtained in the previous reports[4,13-16] allow speculation that ionomer properties are extremely subject to water absorption. From a viewpoint of industrial applications, clarifying such water absorption effects is very important in designing properties of finished products. However, little attention has been paid to systematically studying these effects. In this paper, we report the results of water absorption effects on the thermal transition and stiffness of Na, K, Mg, and Zn salts of EMAA, and present an interpretation for the relationship between the changes in the thermal transition and stiffness.

EXPERIMENTAL

Materials

The starting EMAA was from Du Pont-Mitsui Polychemicals Co., Ltd., whose methacrylic acid content is 5.4 mol %. The metal salts of EMAA were prepared by a melt reaction of EMAA with a stoichiometric quantity of cation sources according to the method described in our previous paper.[12] Characterization data for the metal salts of EMAA are listed in Table I. We delineate our samples as EMAA-xM, where x and M mean neutralization degree and metal cation, respectively. The samples were compression-molded into 3-mm thick sheets at 15 MPa and 453 K, and then cooled to room temperature at a cooling rate of about 30 K/min. All the sheets were clear and transparent, showing no signs of unreacted metal salts. The formation of metal carboxylate was confirmed by the infrared spectra.

Measurements

A 10-mg specimen for DSC measurements was taken from the compression-molded sheets and was tested, using a Du Pont DSC-990, at a heating rate of 10 K/min under N_2 over a temperature range 273–423 K. All results were obtained in the first heating. DSC thermograms of aged EMAA-based ionomers exhibit an endothermic peak about 30 K below a melting of polyethylene crystallites (T_m). From the DSC results with dilatometric, dielectric, and dynamic mechanical results, we attribute this endotherm to an order–disorder transition of the ionic aggregates (T_i).[17-20] The T_i and T_m were determined as a temperature exhibiting the maximum peak point. The enthalpy changes at T_i (ΔH_i) and T_m (ΔH_m) were calculated from the peak area of each endothermic peak. The instrument was calibrated using Indium (mp = 156.6°C, ΔH = 28.45 cal/g).

Table I Metal Salts of EMAA

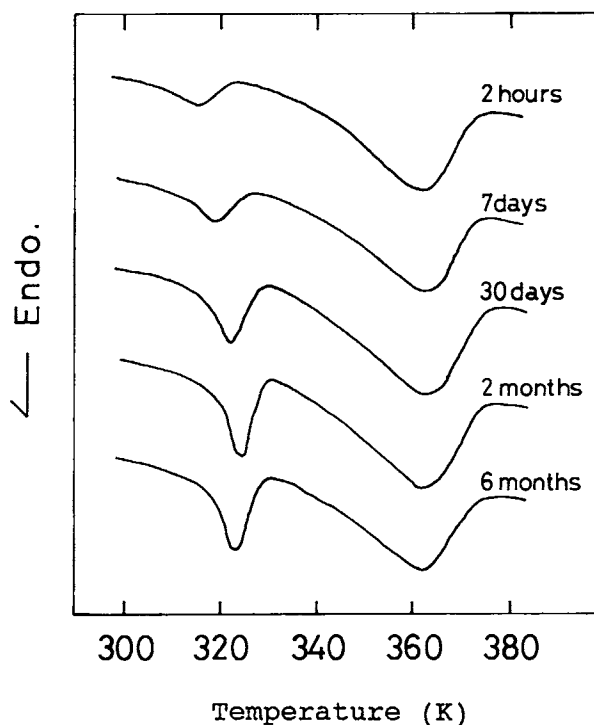| Ionomer	Cation	Neutralization (%)	MFR[a] (g/10 min)
EMAA	—	0	60
EMAA–0.6Na	Na^+	60	1.0
EMAA–0.6K	K^+	60	1.3
EMAA–0.6Mg	Mg^{2+}	60	0.8
EMAA–0.6Zn	Zn^{2+}	60	3.6

[a] Melt flow rate under 2160-g load at 463 K.

Figure 1 Changes of DSC thermograms of the first heating for EMAA-0.6Na during aging at 296 K and at 50% relative humidity. The aging time is indicated at the right of each DSC thermogram.

Specimens for stiffness measurements were stamped out from 3-mm-thick sheets (100 mm long × 20 mm wide × 3 mm thick) and were tested using a Toyoseiki Stiffness Tester at room temperature according to ASTM D-747.

Moisture content of 3-mm-thick specimens (100 mm long × 20 mm wide × 3 mm thick) was determined from weight loss of the specimens after drying in a 473 K oven for 10 min. No conversion of acid-to-acid anhydride groups during the drying process was confirmed by the infrared spectra.

RESULTS AND DISCUSSION

Changes of DSC Thermograms during Aging

Figure 1 shows changes of DSC thermograms of EMAA-0.6Na during aging at 296 K and at 50% relative humidity. The first heating presents two endothermic peaks near 325 K and 365 K in the case of the 6-month-aged sample. The peak position and area of the higher temperature peak, assigned to T_m, are almost unchanged during the aging. However, the lower temperature peak, assigned to T_i, apparently shifts to higher temperatures and increases in
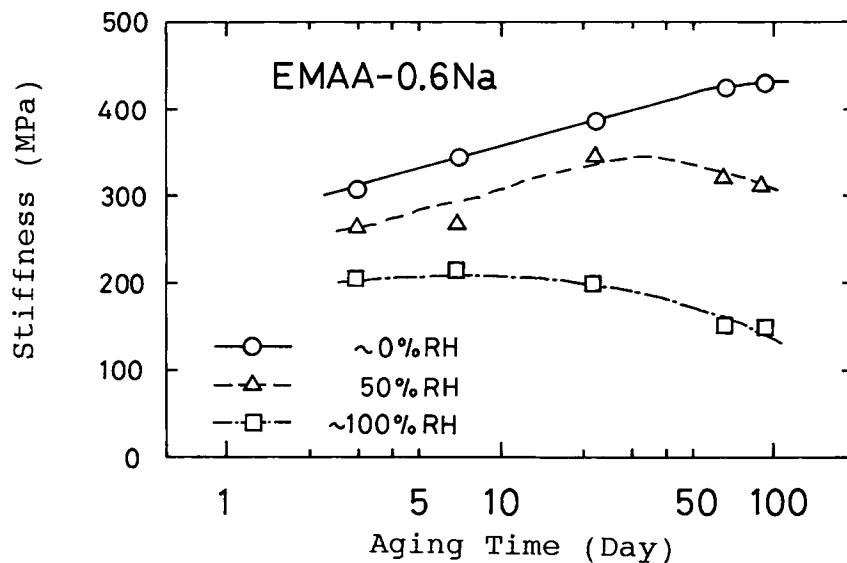
Figure 2   Changes of stiffness for EMAA-0.6Na during aging at 296 K and at different humidities of ∼ 0%, 50% and ∼ 100%.

magnitude during the first 2 months of aging, and then shows a sign of decreasing the peak position and area. A similar effect of the annealing time on the DSC curves is observed on the Na salt of EMAA,[21] the Zn salts of EMAA (EMAA-xZn)[18,22] and the complex Zn salts of EMAA with 1,3-bis(aminomethyl)cyclohexane (EMAA-xZn-yBAC; y is the equivalent ratio of BAC to carboxylic acid).[17,18]

In our model,[12,17-20] the development of the enthalpy change at T_i is explained as a gradual for-

mation of some ordered structure in ionic aggregates during the aging. The rearrangement of the ionic groups occurring during the aging causes significant tension in polyethylene (PE) amorphous regions, resulting in an increase in stiffness.

Stiffness Changes during Aging

Stiffness data of EMAA-0.6 Na were obtained during aging at 296 K and at different humidities of ∼ 0%, 50% and ∼ 100%. Humidity was controlled
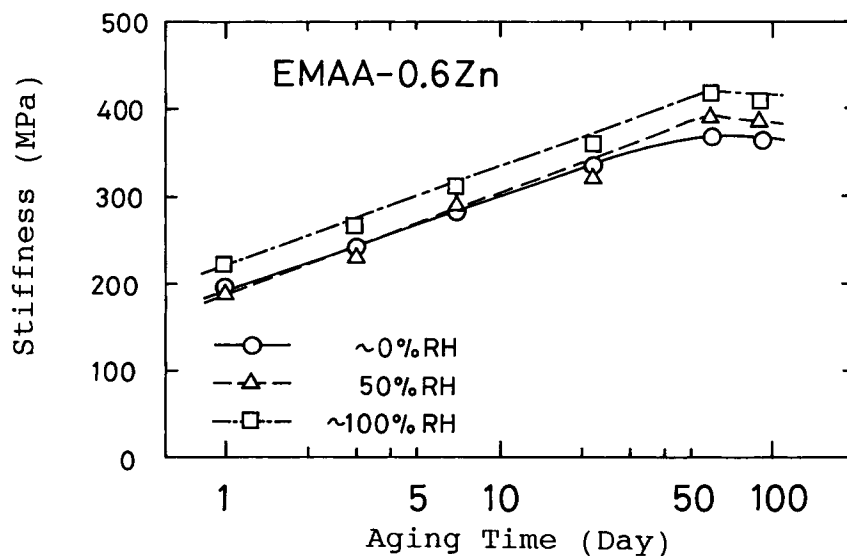

Figure 3   Changes of stiffness for EMAA-0.6Zn during aging at 296 K and at different humidities of ∼ 0%, 50% and ∼ 100%.
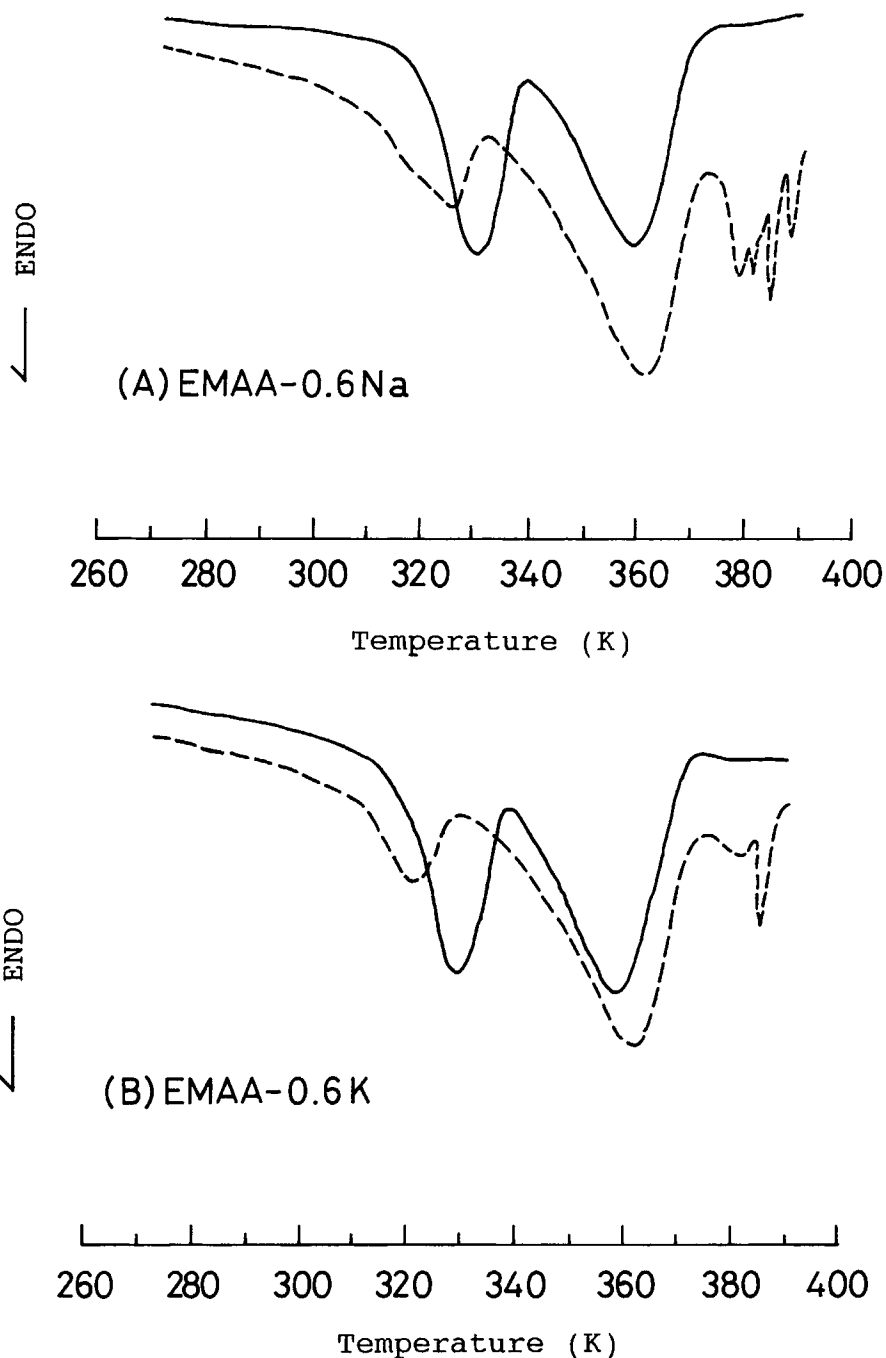
Figure 4 DSC thermograms of the first heating for (A) EMAA-0.6Na, (B) EMAA-0.6K, (C) EMAA-0.6Mg, and (D) EMAA-0.6Zn before (—) and after (– – –) water immersion at 293 K for a week.

using a desiccator with anhydrous $CaSO_4$ for ~ 0% relative humidity (RH) condition, and with water for ~ 100% RH condition. Samples of 50% RH and these two desiccators containing the other samples were stored in a temperature-and-humidity-controlled room. The results are shown in Figure 2.

At ~ 0% RH, the stiffness of EMAA-0.6 Na continuously increases with the aging. At 50% RH, EMAA-0.6 Na shows a continuous increase of stiffness during the first 3-4 weeks of the aging; during this aging period, the stiffness is always smaller than that of the ~ 0% RH condition by approximately
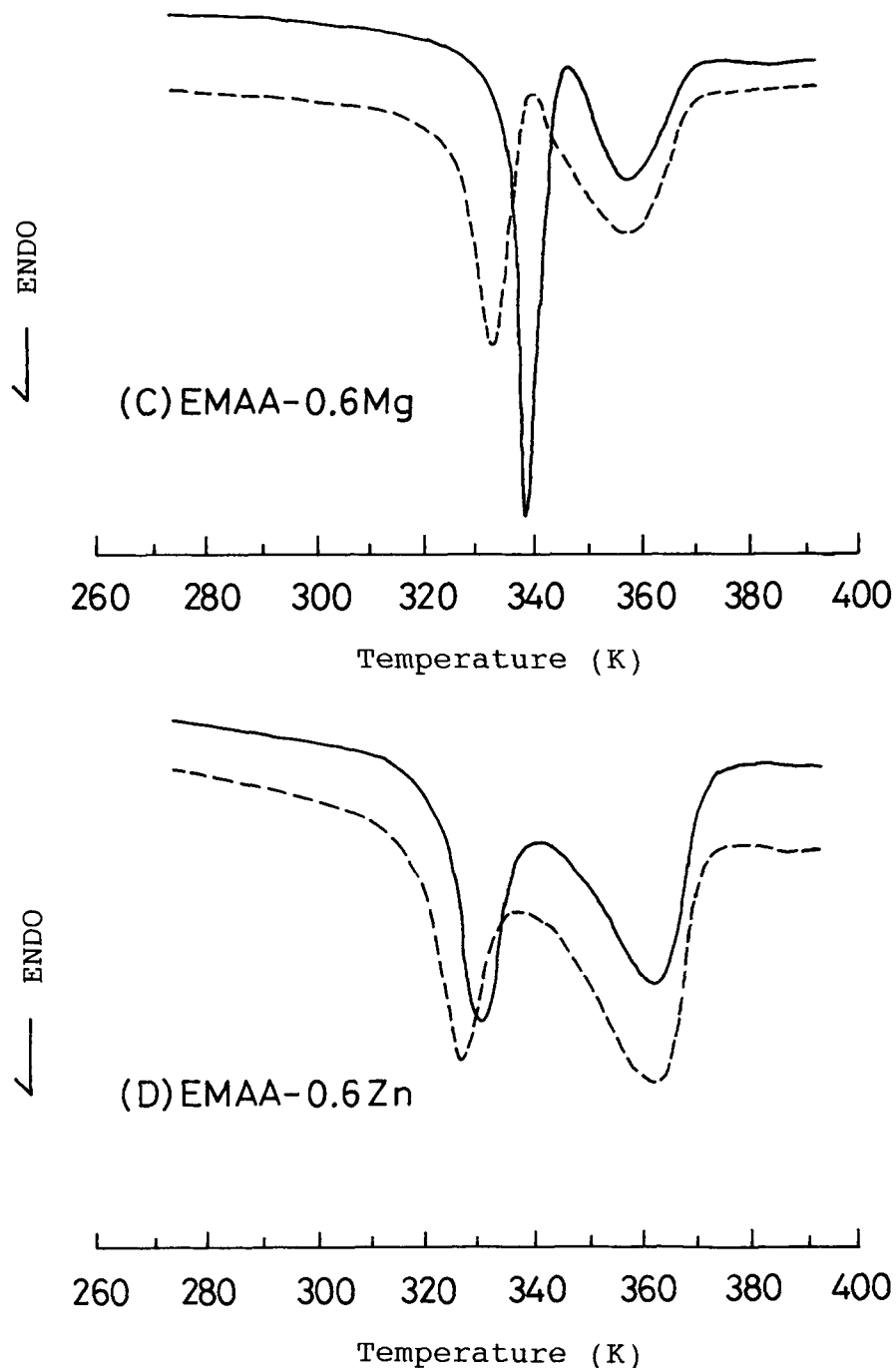
Figure 4 (Continued from the previous page)

50 MPa. The stiffness of EMAA-0.6 Na then starts decreasing around 30 days of the aging. Different results are obtained at ∼ 100% RH, where the stiffness curve shows little increase and keeps decreasing during the aging.

Using the method described above, stiffness data of EMAA-0.6 Zn were obtained during aging at 296 K and at different humidities of ∼ 0%, 50% and

∼ 100%. The results are shown in Figure 3. In contrast to EMAA-0.6 Na, the stiffness curves of EMAA-0.6 Zn continuously increase with the aging at all humidity conditions, and show signs of reaching equilibrium only after a 60-day aging. The stiffness under ∼ 100% RH is a bit higher than that of the other humidity conditions, but the difference is probably within experimental error. These results

Table II   Water Content of Ethylene Ionomers Aged at Different Humidity Conditions for 90 Days

Ionomer	Water Content (Wt %)		
	$\sim$ 0% RH	50% RH	$\sim$ 100% RH
EMAA–0.6Na	0.06	0.56	3.80
EMAA–0.6Zn	0.04	0.16	0.22

indicate that the stiffness of EMAA–0.6 Zn is insensitive to humidity conditions.

We reported that stiffness of EMAA-xZn and EMAA-xZn-yBAC gradually increases with aging at room temperature when the samples are aged at room temperature under dry nitrogen.[17,18] We explain that this increase is caused by the development of ordered structure in the ionic aggregates as described in the discussion of the thermal transition changes. Our stiffness results obtained at $\sim$ 0% RH well agree with the previous observation.[17,18] In addition, the results uncovered the interesting fact that the humidity condition, under which the samples are aged, influences stiffness changes and that the effect differs with the type of neutralizing cations; the stiffness of EMAA–0.6 Na is extremely sensitive to the humidity, while that of EMAA–0.6 Zn is insensitive. Water content of the samples aged at each relative humidity condition for 90 days is listed in Table II. Water content of EMAA-0.6 Na abruptly increases with increasing humidity. On the other hand, the water content of EMAA–0.6Zn is relatively small, and is only 0.22 wt % even in the sample aged at $\sim$ 100% RH, which is less than half of that of EMAA–0.6 Na aged at 50% RH. Itoh et al.[23] studied water vapor sorption to the Na and Zn salts of ionomer membranes, and discovered that ionomers with an increasing neutralization absorb considerable water and that Na salts hydrate about 30 times more water than the Zn salts. Our results are clearly

consistent with their findings. The smaller amount of water absorption with EMAA–0.6 Zn is probably attributed to less dissociation of a Zn–carboxylate bonding as pointed out by Itoh et al.[23] Consequently, our results revealed that water uptake during the aging also influences the changes of ionomer stiffness, which is primarily caused by the rearrangement of the ionic groups that occurs during the aging.

Changes of DSC Thermograms and Stiffness upon Water Immersion

To investigate the effects of water absorption on the structure and properties of ethylene ionomers, changes in DSC thermograms and stiffness were examined as a function of water content. Samples used were EMAA–0.6 Na, EMAA–0.6 K, EMAA–0.6 Mg, and EMAA–0.6 Zn, which were aged at room temperature and at 40–50% RH for two years and then dipped in water at 293 K for a week. DSC results are shown in Figure 4 and the data are summarized in Table III with the water content and stiffness results. It is evident from Table III that EMAA–0.6 Na and EMAA–0.6 K easily absorb a large quantity of water, while an increase in water content for EMAA–0.6 Mg and EMAA–0.6 Zn is minimal. The DSC thermograms show that the T_m and ΔH_m of all the ionomers are almost unchanged by the water immersion. A slight reduction of ΔH_m of EMAA–0.6 Na and EMAA–0.6 K probably results from an erratic reading caused by the peaks around 380 K, which are due to the release of absorbed water. The water immersion causes a great reduction of ΔH_i of EMAA–0.6 Na and EMAA–0.6 K, but basically no changes on ΔH_i of EMAA–0.6 Mg and EMAA–0.6 Zn even though their T_i shifts to slightly lower temperatures. A similar trend is seen for stiffness results; EMAA–0.6 Na and EMAA–0.6 K become less stiff upon the water immersion, but EMAA–0.6 Mg and EMAA–0.6 Zn are as stiff as before the water immersion. These results again demonstrate that the

Table III   Changes of DSC Thermogram and Stiffness upon Water Immersion

Ionomer	Water Content (Wt %)	Stiffness (MPa)	ΔH_i (J/g)	ΔH_m (J/g)
EMAA–0.6Na	0.69[a]/2.24[b]	477[a]/246[b]	16[a]/9[b]	44[a]/38[b]
EMAA–0.6K	1.27/3.47	331/152	17/8	54/43
EMAA–0.6Mg	0.23/0.45	399/391	20/20	19/20
EMAA–0.6Zn	0.09/0.16	404/399	15/14	54/59

[a] Before and [b]after water immersion at 293 K for a week.

water absorption causes a considerable effect on the T_i endotherm and ionomer stiffness, and that the effect differs with the type of neutralizing cations. This difference may be attributed to the affinity of the metal salts for water molecules.

Mechanism of Water Absorption Effects

This study uncovered the interesting fact that ionomer stiffness closely correlates with changes of the T_i endotherm no matter what treatment is given (e.g., aging at room temperature or water absorption). The mechanism of the water absorption effects on the stiffness and the T_i endotherm is explained as follows: A small amount of water molecules is absorbed around metal cations and acts as coordinated water. Additional water absorption plasticizes the ionic aggregates and loosens their ordered structure or ionic crosslinks, resulting in the reduction of stiffness and the enthalpy change at T_i. Such water molecules probably exist in the vicinity of the ionic aggregates as liquid water and form an inverted micellar structure. This model proposes an explanation compatible with the experimental data obtained in this study and all previous reports[4,13–16] on the water plasticizing effects.

Another important aspect this study has revealed is the water absorption effects on DSC thermograms. As explained in the Experimental section, we attribute the T_i endotherm to an order-disorder transition of the ionic aggregates. However, some researchers[21,22] still suspect that this transition is due to the melting of very small polyethylene crystallites similar to the second crystallization that develops when polyethylene is annealed at elevated temperatures.[24,25] We have shown that the T_m endotherm of all the ionomers, clearly assigned to the polyethylene crystallites, is almost unchanged by the water immersion, but that the water absorption exhibits a considerable effect on the T_i endotherm and this effect differs with the type of neutralizing cations. Consequently, these results provide supporting evidence that the T_i endotherm represents structural changes in the ionic aggregates and apparently has no relationship with polyethylene crystallites.

CONCLUSION

The results reported in this paper provide the following new findings:

1. Ionomer stiffness is subject to water absorption and the effect differs with the neutral-

izing cations. The difference is attributed to the affinity of the metal salts for water molecules.

2. The changes in ionomer stiffness well correlate with the enthalpy changes at T_i no matter what treatment is given, while the T_m endotherm of all the ionomers is almost unchanged by aging or by water immersion. These results strongly suggest that the T_i endotherm represents some structural change in the ionic aggregates and apparently has no relationship with polyethylene crystallites.

The mechanism of the water absorption effects is explained as follows: Water absorption primarily occurs at the ionic aggregates and loosens their ordered structure or ionic crosslinks, resulting in the reduction of both the stiffness and the enthalpy change at T_i.

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