General paper

STRUCTURE AND PROPERTIES OF IONOMERS BASED ON ETHYLENE-CO-METHACRYLIC ACID COPOLYMER (EMAA)

Effects of Ion Aggregates

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Abstract: Fourier-transform infrared spectra (FTIR) measurement was made on zinc and sodium ionomers (EMAA-Zn and EMAA-Na) of ethylene-co-methacrylic acid copolymer. It was found that the asymmetry stretching vibration peak of C-O bond of COO⁻ group in ion aggregates of EMAA-Na appeared at lower wavenumber, compared with EMAA-Zn. This means that complete and stable ion aggregates exist in EMAA-Na. Differential scanning calorimetry (DSC) measurement showed that endotherm peak (T_i) in lower temperature range resulted from melting of subcrystallites of crystalline ethylene in EMAA and EMAA ionomers. Tensile properties and dynamic viscoelasticity of EMAA greatly changed with the introduction of ionic groups.

Key words: *Ionomers, Ethylene-co-methacrylic acid copolymer, Dynamic mechanical properties, Thermal properties, Tensile properties, Ion aggregates*

1. INTRODUCTION

Ionomers have very high modulus and stiffness because of the existence of multiplets and clusters originated from aggregation of ionic groups in matrix [1]. Some researchers put special emphasis on the study of ionomer structure and proposed some models.

From small angle X-ray scattering (SAXS) results, Marx et al. proposed that ion aggregates could form in EMAA ionomers [2]. Yarusso and Cooper suggested that the ion aggregate cores were enclosed by matrix layer [3]. Although these two models can successfully explain the results from SAXS experiments, these can not account for the changes of the mechanical properties due to the introduction of ionic groups into the matrix. MacKnight et al. [4] proposed the core-shell model: ion aggregates consist of ion rich core and low ion concentration shell. Eisenberg et al. [5] proposed the multiplet-cluster model which is based on an idea that ionic groups aggregate to form multiplets and ion clusters. This model can explain a wide range of experimental observations. However, none of the above models can completely explain all phenomena observed in the experiments on EMAA ionomers. For example, the appearance of endotherm peak (T_i) in lower temperature range of DSC thermogram after introduction of ionic groups can not be explained by these models. In this paper, we will give the explanations for the cause of appearance of endotherm peak (T_i) and changes of mechanical properties of EMAA with the introduction of ionic groups.

2. EXPERIMENTAL

2.1. Samples

EMAA and its ionomers (EMAA-Zn and EMAA-Na) were supplied by duPont-Mitsui Polychemicals Co., Ltd. The content of methacrylic acid (MAA) in EMAA is 5.4mol% and the neutralization degrees of EMAA-Zn and EMAA-Na are 60% and 55%, respectively. Melt index of EMAA is 60g/10min at 190°C, and those of EMAA-Zn and EMAA-Na are 1.0g/10min and 0.9g/10min, respectively.

2.2. Preparation of Sample Films

The sample films were compression molded at 195°C for about 5 minutes and quenched to room temperature. The cooling rate was about 80°C/min. The thickness of EMAA and EMAA ionomer samples for FTIR experiment was less than 40μm. The thickness of sample films for DSC and wide angle X-ray diffraction (WAXD) as well as mechanical property measurements was 1mm.

2.3. Measurements

Fourier-transform infrared spectra (FTIR) were obtained by Jasco FT/IR-410 spectrophotometer with a resolution of 2cm⁻¹ at room temperature. WAXD measurement was carried out by a vertical Goniometer (RINT 2000, Rigaku) using CuKα radiation ($\lambda = 0.154\text{nm}$) at 25°C. Thermal analysis was carried out with DSC 3100 (Mac Science) at a heating rate of 10°C/min in nitrogen atmosphere. The Weight of sample specimen was about

4.5mg.

Tensile properties were measured at 23°C and 50°C using a tensile tester RTM-50 (with heating chamber) made by Orientec Co. Tensile speed was 100mm/min. The initial length was 20mm. The humidity of atmosphere was about 50%. Dynamic viscoelastic properties were measured in dry air with Rheometrics Solids Analyzer (RSA-II) using temperature sweep mode from room temperature. Heating rate was 1°C/min. The angular frequency and dynamic strain were 10s⁻¹ and 0.001, respectively. Static strain of magnitude of 0.001 was applied to the sample during the measurement.

3. RESULTS AND DISCUSSION

3.1. Structure of Ion Aggregates

FTIR spectra of EMAA and its ionomers in the range of 1800~1500cm⁻¹ are shown in Fig.1. According to Coleman et al. [8] and Brozoski et al. [9], FTIR spectra in this range mainly reflect the internal structure of ion aggregates. Fitting each peak by the following function with Gaussian and Lorentzian terms, one can separate the overlapping peaks of IR spectra.

$$I(\nu) = h_G \exp \left[(-\ln 2) \times \frac{(\nu - \nu_0)^2}{(\sigma/2)^2} \right] + h_L \left[\frac{(\sigma/2)^2}{(\nu - \nu_0)^2 + (\sigma/2)^2} \right], \quad (1)$$

where ν_0 is the peak position in cm⁻¹, and h_G and h_L are the peak heights of Gaussian and Lorentzian functions, respectively. σ is the half-width of the bands.

According to MacKnight et al. [10], the peaks at 1750cm⁻¹ and 1700cm⁻¹ (Fig. 1) are ascribed to asymmetry stretching vibration peak of C-O bond in monomeric carboxylic acid and dimerized carboxylic acids, respectively. Peak at 1750cm⁻¹ is very small while the peak at 1700cm⁻¹ is very large. This indicates that the carboxylic acid groups exist mainly as dimers at room temperature.

After EMAA was neutralized with Zn²⁺, new peaks appear. The peak at 1620cm⁻¹ is ascribed to asymmetry stretching vibration of C-O bond in COO⁻ group forming hydrogen-bond within zinc acid salt. New broad peak from 1600cm⁻¹ to 1500cm⁻¹ is separated into three peaks at 1585cm⁻¹, 1568cm⁻¹ and 1538cm⁻¹. Coleman et al. [8] proposed a specific coordinated complex model for FTIR spectra of EMAA-Zn. The peaks at 1585cm⁻¹ and 1568cm⁻¹ (and 1538cm⁻¹) are the asymmetry stretching vibration of C-O bond in tetracoordinated and hexacoordinated zinc carboxylates, respectively. We can see that ion aggregates in EMAA-Zn ionomer consist of coordinated zinc carboxylates. Compared with the peaks at 1568cm⁻¹ and 1538cm⁻¹, the peak at 1585cm⁻¹ is much sharper. This means that the coordinated zinc carboxylates exist mainly

Fig.1. FTIR spectra of EMAA and its ionomers from 1800cm⁻¹ to 1500cm⁻¹.

as form of tetracoordination.

After EMAA is neutralized with Na⁺, new peaks appear around 1550cm⁻¹. The peak at 1700cm⁻¹ becomes broad. This peak is separated into two peaks at 1696cm⁻¹ and 1662cm⁻¹. According to Coleman et al. [8], dimerized carboxylic acids exist outside and within ion aggregate. We can think that the peaks at 1696cm⁻¹ and 1662cm⁻¹ are asymmetry stretching vibrations of C-O bond of dimerized carboxylic acids outside and within the ion aggregates, respectively.

Compared with the peak at 1696cm⁻¹ in EMA-Na, the peak at 1700cm⁻¹ in EMA-Zn is sharp. This indicates that dimerized carboxylic acids in EMA-Zn mainly exist outside the ion aggregate.

Peak around 1550cm⁻¹ for EMA-Na is also separated into three peaks. Brozoski et al. [9] and Han et al. [11] used the multiplet-cluster model to assign the peaks. The peak at 1582cm⁻¹ is associated with asymmetry stretching vibration of C-O bond in clusters, but the peak at 1553cm⁻¹ is the overlapping mode of asymmetry stretching vibration of C-O bond in multiplets and clusters, and the peak at 1535cm⁻¹ is ascribed to asymmetry stretching vibration of C-O bond in multiplets.

Han et al. [11] proposed that the multiplet-cluster model was suitable for the alkali metal and alkaline earth metal ionomers such as EMA-Na, but specific coordinated complex model was suitable for the transition metal ionomers such as EMA-Zn, because they found that for all alkali and earth metal ionomers, the absorption

Fig.2. FTIR spectra of EMAA and its ionomers from 735cm^{-1} to 705cm^{-1} .

intensity of peak at 1700cm^{-1} reduced and the peak shifted to a lower wavenumber as the neutralization degree increased. No such changes were observed for the transition metal ionomers, meaning that two mechanisms of ionomer formations existed.

Compared with EMAA-Na, the ion aggregate peak of EMAA-Zn is sharp and exists at higher wavenumber. We think that the phenomena are caused by the ion species. EMAA-Zn is a transition metal ionomer but EMAA-Na is an alkali metal ionomer. According to Eisenberg, with the same ionic neutralization degree, complete ion multiplets and clusters can form in EMAA-Na. Ion aggregates in EMAA-Na are stable because they mainly consist of ion multiplets and clusters. A broad ion aggregate peak of EMAA-Na appears at lower wavenumber. However, in EMAA-Zn, ion aggregates mainly consist of tetracoordinated zinc carboxylates and ion aggregate peak appears at higher wavenumber. This means that ion aggregates are unstable relative to those in EMAA-Na.

3.2. Structure of Ethylene Phase

Changes of rocking vibration of C-H bond in ethylene phase for EMAA and EMAA ionomers are shown in Fig. 2. A broad peak from 735cm^{-1} to 705cm^{-1} is separated into three peaks. MacKnight et al. [10] made assignment for these peaks. The peaks at 729cm^{-1} and 719cm^{-1} are associated with the rocking vibration of C-H bond in the plane of crystalline ethylene phase polarized along b and a crystal axes, respectively. These peaks remain almost unchanged. This means that rocking vibration of C-H bond

Fig.3. Wide-angle X-ray diffraction patterns of EMAA and its ionomers.

for crystalline ethylene phase is almost independent of the introduction of ionic groups. However, the peak at 723cm^{-1} , which is associated with the rocking vibrations of C-H bond in amorphous phase, becomes small. This means that the introduction of ionic groups affects the rocking vibration of C-H in amorphous phase.

Figure 3 shows WAXD patterns for EMAA and its ionomers. The X-ray peak ($2\theta \approx 20^\circ$) exists in EMAA ionomers and remains unchanged with ionic neutralization. This peak consists of reflections from [110] ($2\theta = 21^\circ$) and [200] ($2\theta = 23.5^\circ$) crystal planes in crystalline ethylene phase [7]. The positions of X-ray peaks of EMAA and its ionomers are almost the same. This means that d-spacing of crystal planes in crystalline ethylene phase does not change with the introduction of ionic groups.

3.3. Thermal Properties

Figure 4 shows the DSC thermograms of EMAA and its ionomers from 20°C to 120°C . We can see that one peak (T_g) exists around 40°C – 50°C and another peak (T_m) exists around 90°C . The peak at 90°C is melting peak of ethylene phase and its area remains almost unchanged. This means that the crystallinity of EMAA does not change with introduction of ionic groups.

MacKnight et al. [12] considered the transition (T_g) in lower temperature range as the glass transition of amorphous phase in EMAA. But it changes to endotherm peak with the introduction of ionic groups. It is difficult to explain these endotherm peaks (T_g) using a proposal by MacKnight. Other researchers thought that absorbed water in ionomers caused the endotherm peak (T_g) [9,13–16]. In

Fig. 4. DSC thermogram of EMAA and its ionomers from 20°C to 120°C.

order to avoid the effect of water absorption, all measurements in the present study were run immediately after sample films were prepared and the films had no chance to absorb water. This means that these endotherm peaks (T_i) can not be considered to be caused by absorbed water.

Tadano et al. [7] and Hirasawa et al. [17,18] ascribed the endotherm peak (T_i) in DSC thermogram to be the order-disorder transition in ion aggregates. However, in our unpublished data, not only EMAA ionomers but EMAA also show similar peaks (T_i) in DSC thermogram by aging process [19]. We think that the order-disorder transition model is not reasonable either.

Kohzaki et al. [20] explained that the endotherm peak (T_i) in DSC thermogram is caused by subcrystallites in ethylene. We think that this explanation is more reasonable than others from the following reasons: the ethylene phase peak in WAXD patterns of both EMAA and EMAA ionomers strongly depends on the thermal histories. On the other hand, an ion aggregate peak appearing at $2\theta = 4^\circ$ in WAXD pattern does not change with sample thermal history [19].

Endotherm ($\Delta H_i = 6.70 \text{ J/g}$) of small lower temperature peak (T_i) of EMAA-Zn is larger than that ($\Delta H_i = 5.44 \text{ J/g}$) of EMAA-Na. This means that much more subcrystallites of crystalline ethylene form in EMAA-Zn.

3.4. Mechanical Properties

Figure 5 shows stress-strain behavior of EMAA and its ionomers at 23°C (solid lines) and 50°C (broken lines). We can see that Young's modulus and yield stress as well as tensile strength of EMAA ionomers are much higher than those of EMAA. The result of DSC measurements

Fig. 5. Stress-strain behavior of EMAA and its ionomers measured at two temperatures.

shows that the endotherm peaks (T_i) appear around 43°C and 49°C for EMAA-Zn and EMAA-Na, respectively. Young's modulus and yield stress of EMAA ionomers at 50°C decrease quite a lot, but are still higher than those of EMAA. This means that ion aggregates still exist at 50°C, although subcrystallites have been melted. Tensile properties of EMAA ionomers have stronger dependence on measurement temperature than those of EMAA.

Figure 6 is the temperature dependence curves of E' and $\tan\delta$ for EMAA and its ionomers. The α' peak, which was ascribed by Tachino to the order-disorder transition of ion aggregates [21], is not observed in Fig. 6. After EMAA is neutralized with Zn^{2+} and Na^+ , the moduli increase quite a lot at temperature higher than 20°C because of cross-links of ion aggregates. In temperature dependence curves of $\tan\delta$, there is one broad peak at 25°C for EMAA, but for EMAA ionomers, there is one transition around 45°C. We think that the changes of peak temperature of $\tan\delta$ vs. T curves are also caused by the effect of cross-links of ion aggregates.

4. CONCLUSIONS

Endotherm peaks (T_i) in DSC thermograms appear around 43°C and 49°C for EMAA-Zn and EMAA-Na, res-

Fig. 6. Temperature dispersions of E' and $\tan\delta$ of EMAA and its ionomers.

pectively. These peaks (T_i) are caused by the melting of subcrystallites in ethylene phase. Mechanical properties of EMAA greatly change with the introduction of ionic groups. WAXD peaks and rocking vibrations of C-H bond as well as melting peaks of ethylene phase remain unchanged after EMAA is neutralized with ionic groups.

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