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Melt rheology of ethylene ionomers blended with a small-molecule acid

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Abstract

A novel EMAA ionomers with the incorporation of low molecular weight carboxylic acid have been developed to reduce melt rheology without changing the complete transparency of ionomers. Here, a blend of EMAA-59Zn (93 wt%) and montanic acid (MA, $C_{27}H_{55}COOH$, 7 wt%) was investigated in terms of TGA, DSC, FT-IR, and dynamic shear viscosity. A good heat stability of MA during melt blending preparation and melt viscosity measurement was confirmed by TGA. DSC showed only one peak (86.9°C) for the blend sample, and FT-IR exhibited additional peaks (1545, 1625 cm^{-1}) by the blending. These facts suggested that the blend is a homogeneous mixture and the blend induced an additional new coordination structure between Zn and carboxylic acid. Dynamic melt rheological measurement exhibited a significant decrease of storage modulus and loss modulus by the blending. The reduction of melt rheology was more than the addition of plasticizing effect and the decrease of neutralization. The newly induced coordination structure implies a relationship with the unexpected additional reductions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Melt rheology; EMAA ionomer; Low molecular weight acid

Ethylene ionomers are polymers containing hydrophilic ionic salt groups attached pendently to hydrophobic polyethylene backbone [1]. A most typical example is poly(ethylene-*co*-methacrylic acid) (EMAA) which is partially neutralized by metal ions, introduced by DuPont under the Surlyn tradename since the late 1960s. Ionic aggregates, which are induced above a certain neutralization degree by the difference between hydrophobic and hydrophilic environments, have been a primary focus to understand remarkable mechanical properties in ionomers [2–4]. It has been widely recognized that the increase of neutralization in EMAA ionomers results in substantial enhancement of mechanical properties such as modulus and hardness in particular [5,6]. To improve a local environment in ionic aggregates, a group of EMAA ionomers, which are the complex zinc salts of EMAA with 1,3-bis(aminomethyl)cyclohexane (BAC), have been developed, showing outstandingly increased modulus [7]. While the modulus increased with the increased neutralization or with the addition of BAC, the melt processability has always been sacrificed because of the high melt viscosity which is caused by stronger ionic interaction [7].

Some melt rheological studies on EMAA ionomers have been published to examine the role of ionic aggregates at molten stage, by varying neutralization degrees [2–4,8–11]. Very few studies have been carried out about reducing melt viscosity of EMAA ionomers with keeping the constant neutralization degree by blending low molecular acid. Iwami et al. demonstrated that viscosity of EMAA ionomers can be reduced by blending stearic acid [12]. However, the detail mechanism of the reduction in melt viscosity has not been examined in their results. There has been, moreover, a concern on the thermal stability of stearic acid, which needs to be improved in future when considering a processing temperature around 220°C and a long measurement time (e.g. 1 h at 140°C) for dynamic shear viscoelasticity. Recently, a systematic investigation of EMAA ionomers with the incorporation of thermally stable low molecular weight carboxylic acid have been initiated in our laboratory [13]. Here, we describe an outstanding reduction of melt viscosity, that results from the combination of an unexpected striking interaction between low molecular weight carboxylic acid and zinc ion, and a plasticizing effect.

EMAA ($M_n = 19\,200$, $M_w = 94\,500$) whose methacrylic acid content was 15.0 wt% (5.4 mol%) was used as the matrix of ionomers. Ethylene ionomers investigated here were EMAA neutralized partially by zinc ion, 59% of neutralization degree, in which, it was reported, ionic aggregates were formed due to its high neutralization [5,6]. These

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are designated as EMAA and EMAA-59Zn, respectively. All these samples were provided by Mitsui–DuPont Polychemicals. Low molecular weight carboxylic acid is a group of carboxylic acid compounds, including saturated alkyl mono- or di-carboxylic acid, unsaturated alkyl mono- or di-carboxylic acid, and aromatic carboxylic acid, etc. As one of typical model examples having an excellent thermal stability and miscibility for accurate melt rheological studies, here montanic acid (MA, $C_{27}H_{55}COOH$, BASF) was picked up because of its substantial high thermal stability. The thermal gravimetric analysis (TGA, TA instrument 2960) of MA under nitrogen showed 247°C as the initial decomposition temperature, in which 5 wt% of the initial weight was lost at a heating rate of 5 K/min. the decomposition temperature of stearic acid which was used by Iwami et al. was 203°C and it is not enough thermally stable. It was obvious that thermal stability of MA was much higher, compared to that of stearic acid. A blend sample of EMAA-59Zn (93 wt%) and MA (7 wt%) was prepared by means of melt compounding in a counter-rotated twin screw extruder (PCM30, 30 mm, $L/D = 31.5$; Ikegai) at 190–200°C. The obtained sample was designated as EMAA-54Zn–MA, because the neutralization degree of zinc based on the total carboxylic acid from both EMAA and MA became 54%. This composition provides that the molar ratio of methacrylic acid from EMAA to carboxylic acid from MA is 10–1. As a reference sample for the comparison with EMAA-54Zn–MA, EMAA-54Zn was prepared through a melt compounding of EMAA-59Zn (90 wt%) and EMAA (10 wt%) by the same procedure written above. Differential scanning calorimetric (DSC) measurements were conducted on 8 mg specimen at a heating rate of 5 K/min using a Parkin Elmer Model DSC-7. About 10 mm-thick films for Fourier transform infrared spectroscopic (FT-IR) analysis were prepared by compression molding at 453 K. IR spectra were measured using a Nicolet Model Magna-IR Spectrometer 750 at room temperature, where 32 scans at a resolution of 4 cm^{-1} were signal averaged. Melt rheological experiments for dynamic shear were conducted using a rotational rheometer (Rheometrics, ARES) in the range from 0.01 to 100 rad/s at 140°C, where all samples showed the excellent thermal stability and reproducibility. The input strain in oscillatory shear was sufficiently small to provide reliable linear viscoelastic data.

A great attention was paid, before experiments, for the moisture content due to its high sensitivity to properties such as DSC, FT-IR, and dynamic shear rheology [7,13,14]. All pellet samples were dried in a vacuum oven at 80°C for 2 weeks to eliminate moisture as completely as possible. The moisture content was measured by Karl–Fischer method (METTLER KF-Coulometer DL37, Dryingoven DO337). The water percentages of EMAA, EMAA-54Zn, EMAA-54Zn–MA, and EMAA-59Zn after drying were measured by Karl–Fischer method at 180°C for 30 min under nitrogen (99.999%) flow (200 ml/min), and value 80, 140, 140, and 140 ppm, respectively.

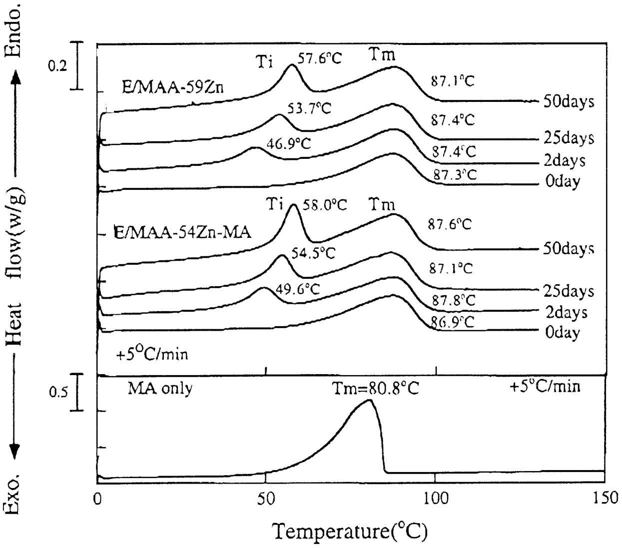

Fig. 1. DSC curves in the first heating for EMAA-59Zn, EMAA-54Zn–MA, and MA under various annealing periods at room temperature in a dried desiccator. The annealing time indicated in the figure means the period just after rapid cooling down to room temperature with liquid nitrogen from the molten stage of the samples at 180°C for 10 min.

Firstly, we have examined the miscibility of MA in EMAA-54Zn–MA by using DSC. Samples of EMAA-54Zn–MA which are 3 mm thick and disk shape gave complete transparency, which was quite similar to those of EMAA-59Zn. The first heating just after rapid cooling down with liquid nitrogen from a molten stage of EMAA-59Zn showed only one endothermic peak at 87.3°C as shown in Fig. 1. Along with longer annealing period at room temperature, two endothermic peaks were observed at 46.9 and 87.4°C. These trends were well described in former literature [7,15].

Fig. 1 also reveals that the presence of MA, whose melting peak is located at 80.8°C, does hardly appear. The T_m peak and its enthalpy change of EMAA-54Zn–MA was not affected by the annealing time and was similar to that of EMAA-59Zn. While the Ti peak and its enthalpy change of EMAA-54Zn–MA was also shifted to higher temperature and became larger, respectively. It should be remarkable that the enthalpy changes of T_i in EMAA-54Zn–MA after 2, 25, 50 days (9.6, 10.8, 14.4 J/g, respectively) was about 20% larger than those in EMAA-59Zn (7.3, 9.0, 12.1 J/g, respectively). Anyway, the evidence of no peak from MA in DSC of EMAA-54Zn–MA supports the excellent miscibility during long annealing periods, which would be related to larger enthalpy change of T_i peaks, indicating some interaction between MA and ionic aggregates.

Secondly, to get more insight into the local interaction between MA and ionic aggregates, the measurement of FT-IR was performed. Fig. 2 shows, for easy understanding, the FT-IR only in the range between 1500 and 1650 cm^{-1}, where a clear drastic change takes place. EMAA-59Zn gave a characteristic peak, corresponding to the carboxylate

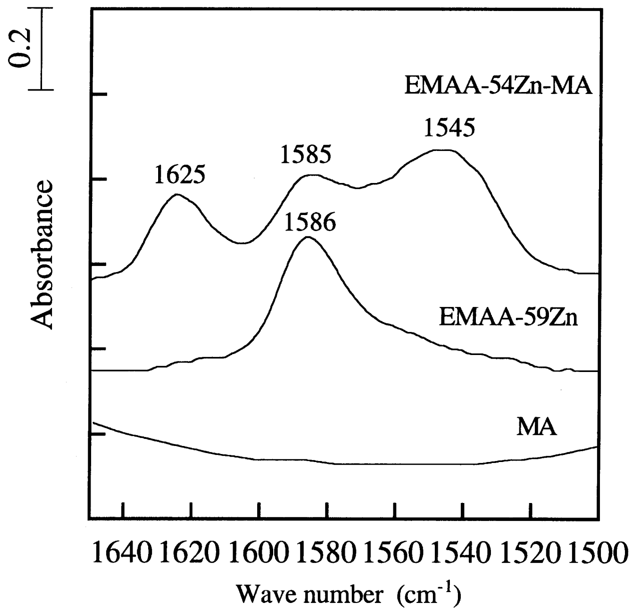

Fig. 2. Infrared spectra in the range of 1500–1650 cm^{-1} for EMAA-59Zn, EMAA-54Zn–MA, and MA at room temperature.

asymmetric (ν_a(COO−)) stretching mode at 1586, which means tetracoordinated zinc carboxylate structure. This is quite similar to what was frequently reported before [16,17]. While, MA does not have any characteristic bands in the region. An unexpected striking feature was observed in EMAA-54Zn–MA, which had three characteristic bands, as shown in Fig. 2. Those are 1545, 1585, and 1625 cm^{-1}, all of which stand for carboxylate asymmetric (ν_a(COO−)) stretching. The band 1545 cm^{-1} can be from the sum of two bands of 1536 and 1565 cm^{-1}. Thus, 1545, 1585, and 1625 cm^{-1} could be explained as hexacoordinated zinc carboxylate, tetracoordinated zinc carboxylate, and zinc acid salt structures, respectively [16,17]. It is easily imagined that carboxylic acid from MA can become partially carboxylate by exchanging between proton and zinc during melt compounding. Considering a small amount of carboxylic acid or carboxylate from MA, mentioned earlier, the local environmental change in ionic aggregates detected in FT-IR was enormously large. FT-IR clarified that the coordination structural change was taken place by the addition of MA. However, it is, at present, difficult to precisely mention whether carboxylates, which gave hexacoordinated and zinc acid salt structures, are from MA or EMAA. This must wait future structural studies.

Vanhoorne and Register [11] reported an interesting melt rheological feature, in which melt rheology of zinc EMAA ionomer was hardly affected by the presence of free carboxylic acid, since zinc seemed to have tetracoordinated carboxylate structure and has no possibility to receive the effect of proton from free carboxylic acid. The influence of proton can be a key to understand the melt rheology of EMAA ionomer, since proton gives influence on the equilibrium of bond and dissociation between zinc and carboxylate at molten stage. If the neutralization degree was constant, the controlling of the equilibrium seems to be the most important fundamental factor which determines the melt rheology of EMAA ionomers. Our recent data supports that a trace amount of water decreases zero-shear viscosity of zinc EMAA ionomers, which seems to be explained by coordinate structural change detected by FT-IR [13]. Returning to the main subject, the drastic change of coordinated structures in EMAA-54Zn–MA detected by FT-IR might affect melt rheology, which brought us the motivation about the melt rheological studies below.

Thirdly, the dynamic shear viscoelasticity was investigated for EMAA-54Zn and EMAA-54Zn–MA, both of which have the same neutralization degree. Our intention is to clarify the effect of MA on melt rheology by excluding the influence of neutralization degree. Storage modulus G' and loss modulus G'' as a function of angular frequency for EMAA-54Zn and EMAA-54Zn–MA were obtained. Fig. 3 displays that the superposition of curves from the two samples at the reference of EMAA-54Zn was successful, and the shift factor a_T of EMAA-54Zn–MA was 0.43 which can be expressed as follows:

$$G', G''(\omega, \text{EMAA-54Zn}) = G', G''(\omega/0.43, \text{EMAA-54Zn–MA}) \qquad (1)$$

This suggests that the relaxation spectrum of EMAA-54Zn–MA can be obtained by shifting those of EMAA-54Zn by 0.43 times. It also means a significant reduction of zero-shear viscosity in EMAA-54Zn–MA with the incorporation of MA by a factor of 0.43. It is known that low molecular weight compounds behave as plasticizers to decrease frictions among polymeric chains, resulting in a reduction of

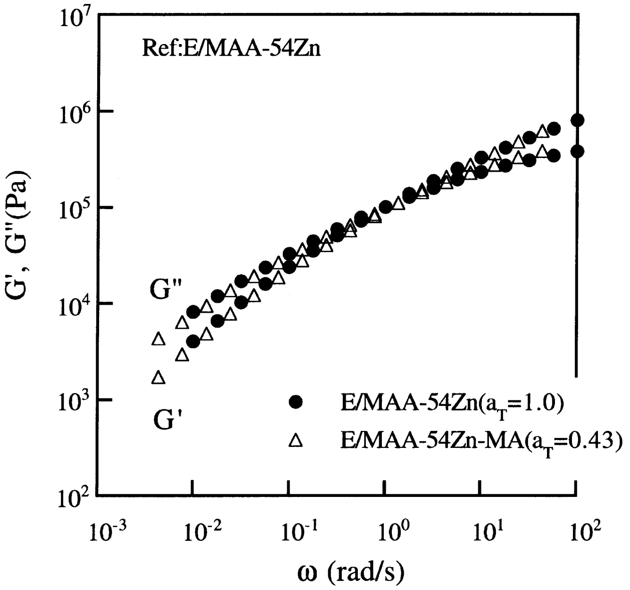

Fig. 3. Super-master curves of G', G'', and η^* from EMAA-54Zn (●) at 140°C and EMAA-54Zn–MA (△) at 140°C. The reference material is EMAA-54Zn at 140°C.

melt rheology. The plasticizing effect could be analyzed and estimated from the difference between EMAA with and without MA by using dynamic shear measurement, suggesting a factor of 0.55. This allows us to determine the effect of reduction in zero-shear viscosity, excluding the plasticizing effect, which was calculated to be 0.78 (= 0.43/0.55). This can be related to the local environmental change which was derived by the incorporation of MA. The coordinated structure induced by the addition of MA includes hexa and salt structures, which can provide proton. By a catalytic effect of proton, this could make the equilibrium toward dissociation, which should be similar to the mechanism of influence of water on the equilibrium, observed recently [13]. To confirm this interpretation, a montanic ester (ME), whose acid was terminated, was used for the similar melt rheological study, suggesting the influence of reduction of ME in zero-shear viscosity, excluding the plasticizing effect, was almost none. It would be, therefore, safe to state that the local environmental change, especially, coordinated structure change, in ionic aggregate resulted in a remarkable reduction of zero-shear viscosity.

A significant reduction of melt viscosity through the incorporation of low molecular acid has been demonstrated, which was induced by a local environmental change in ionic aggregates and a plasticizing effect. A class of EMAA ionomers with the incorporation of low molecular weight acid gives a potential interest to modify and understand an internal local structures in ionic aggregates, which opens a new aspects in the research of EMAA ionomers. More detailed analyses are under way and will be published elsewhere.

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