

Linear and Nonlinear Viscoelastic Properties of Ethylene Ionomer Melts

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ABSTRACT

The effects of ionic interaction on linear and nonlinear viscoelastic properties of poly-(ethylene-co-methacrylic acid) (EMAA) ionomers were investigated. We have measured zero shear viscosity and steady shear viscosity of EMAA ionomers. The samples used in this study were partially neutralized by Na and Zn ions, and the neutralization of each samples were changed various. Ionomer neutralized with binary metal ion (Na and Zn ions) were also measured. The zero shear viscosity is affected hardly neutralization. In the steady shear, ionomer which neutralized a little cation is fitted by K-BKZ model. For high neutralization ionomer, K-BKZ model is smaller than in step shear stress relation.

INTRODUCTION

Ionomers are polymers including a small amount of metal ionic salt groups. Above all, poly(ethylene-co-methacrylic acid)(EMAA) neutralized with metal cations are the most widely used as ionomers for various industrial applications. The structure and mechanical properties of ethylene ionomers were extensively investigated in both the solid and melt state. Ionic groups tend to form ionic aggregates in the hydrophobic polymer matrix. It has been investigated that the microphase separation of ionic aggregates and the hydrocarbon matrix take place according to the neutralization degree by the dielectric and dynamic mechanical relaxation studies. It is known that ionic aggregates were formed more than the neutralization degree of 35% in EMAA-Na ionomer and that of 80% in EMAA-Zn. It has been reported that physical properties of ionomers depend on the kind of added metal (*e.g.*, alkaline and transition metal) due to the difference in their ionic strength and the number of carboxyl groups

associated with one metal cation. Since the metal cation dependent characteristics of ionomers are essential in mechanical and rheological properties, under solid and melt state of ethylene ionomers have been studied. To clarify the roles of ionic bondings and its aggregates in ionomers under melts are very important research subject. In this study, linear and nonlinear viscoelastic properties of ethylene ionomer.

Experimental

We have measured melt viscosity of ethylene-methacrylic acid (EMAA) ionomers by means of steady flow and step shear. The base polymer is EMAA which methacrylic contents 5.4 mol%, the samples used in this study were neutralized by Na salts and metal cation contents were changed various.

Results and Discussion

We performed dynamic shear experiments under the linear region. The dynamic shear properties revealed that the time-material superposition was applicable to blend ionomers from 140°C to 200°C. The value of η_0 for Na increased with increasing neutralization degree, which was found for time-material superposition. The other hand, for Zn ionomers, until neutralization of 40% similar tendency were occurred phenomena, however the viscosities unexpectedly increased above 40%.

Figure 2 (a) and (b) show the start up of steady shear viscosities for EMAA-28%Na and EMAA-54%Na, respectively. And these results fitted by K-BKZ Model^{[1][2]} with damping parameter obtained from step shear were shown. For EMAA-28%Na, the experimental values agreed well with the prediction from the parameter. It is, however, quite unexpected that the K-BKZ calculation under predicted the experimental data in EMAA-54%Na. The best-fitted parameter for EMAA-54%Na from the transient shear viscosity was more large value. It should be noted that larger damping parameter required in the start-up of shear rather than in step-shear stress relation in EMAA-54%Na. This means that the characteristics of zinc-ionic aggregate in two types of measurements are completely different.

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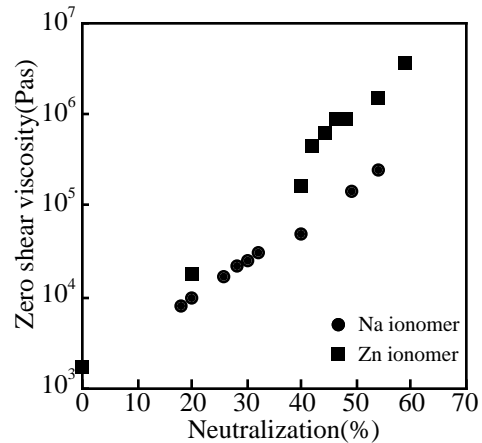


Fig.1 The dependence of η_0 on the neutralization level on η_0 for Zn and Na type ionomer.

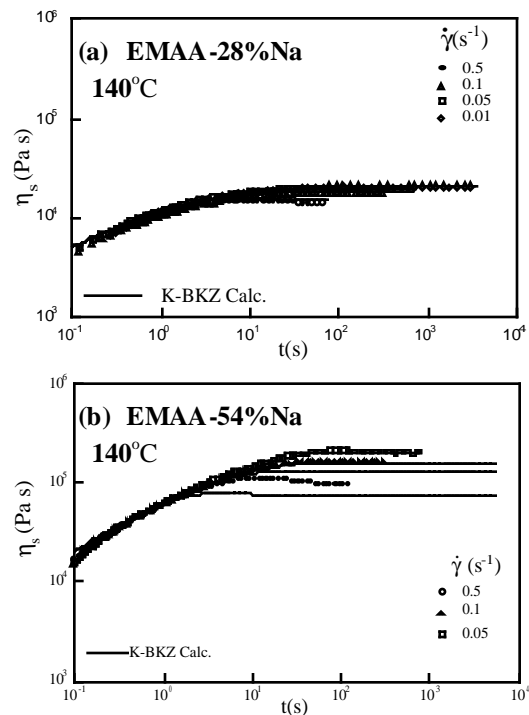


Fig.2 Transient shear viscosity under constant shear rate conditions for EMAA-28%Na(a) and EMAA-54%Na at 140°C. The solid line means calculation results of BKZ model (PSM type) with the damping parameter listed in each figures.