Viscoelastic Behaviors of Ethylene Ionomer Treated by Nitric Acid

INTRODUCTION

It is well known that salt groups in ethylene ionomers are possible to form ionic aggregates separated from hydrocarbon phases.[1-4] The ionic aggregates are composed of multiplets of few ion pairs in the case of less than a few mole percents of salt groups and of clusters of more ion pairs in the case of more than a few mole percents.[3] Although many models[5-8] about a cluster structure are proposed, the model of MacKnight, Taggart, and Stein is reasonable to accept; it consists a core structure of densely packed ions and a surrounding matrix ion separated by a shell of polyethylene chain units. Mechanical characteristic properties of ethylene ionomers were interpreted in terms of apparent physical crosslinkings of the ionic aggregate in the cluster. The presence of such crosslinkings gives rise to a rubbery plateau even in a molten state above the melting point of ethylene ionomers, indicative of elastomeric properties. It is important to know the influence of acid to ethylene ionomer elastomeric materials for a practical use. In the present article, we examine the effect of the concentration of nitric acid to viscoelastic behaviors, especially elastomeric properties of a rubbery plateau at a high temperature range. range.

EXPERIMENTAL

The copolymer of ethylene (E) and methacrylic acid (MAA) or its salt, whose acid content is 5.4 mol % and whose degrees of neutralization are 60% Na and 90% Zn, was designated as E-0.054MAA, E-0.054MAA−0.60Na, and E-0.054MAA−0.90Zn, respectively. These samples were treated by $7N$, $3.5N$, $1.8N$, and $0.4N$ nitric acid aqueous solution for 25 h and washed by a large amount of water and dried under vacuum. Dynamic viscoelastic measurement of the sample thus treated was carried out under ambient humidity at the frequency of 110 Hz at the temperature range from −150 to 90°C by Rheovibron DDV-II-C manufactured by Toyo-Baldwin Co. Ltd. There might be little effect of sorbed water to the dynamic viscoelasticity,
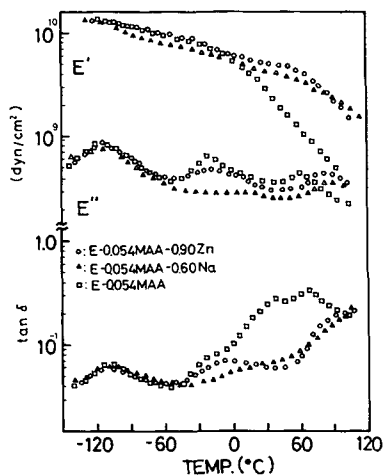

Fig. 1. The temperature dependence of dynamic modulus (E'), loss modulus (E''), and tan δ of E-0.054MAA (□), E-0.054MAA−0.60Na (△), and E-0.054MAA−0.90Zn (○) untreated by a nitric acid.

because the degree of hydration of the ethylene ionomer is thought to be very small under ambient humidity, less than 1%, according to our results.[9]

RESULTS AND DISCUSSION

Figure 1 shows the dynamic viscoelastic properties of dynamic modulus (E'), loss modulus (E''), and tan δ of E-0.054MAA, E-0.054MAA–0.60Na, and E-0.054MAA–0.90Zn which are not treated by nitric acid. The E' of E-0.054MAA–0.60Na and E-0.054MAA–0.90Zn was approximately the same below 0°C, but it decreased very slowly at a high temperature range compared to the E' of E-0.054MAA, reflecting characteristic physical crosslinking due to the presence of ionic aggregates. Attention is focussed on the behavior of the dynamic modulus at a high temperature range in the following section. The dynamic viscoelastic properties of E-0.054MAA, E-0.054MAA–0.60Na, and E-0.054MAA–0.90Zn treated by the nitric acid with the concentrations of 0.4N, 1.8N, and 3.5N for 25 h, are shown in Figures 2, 3, and 4, respec-
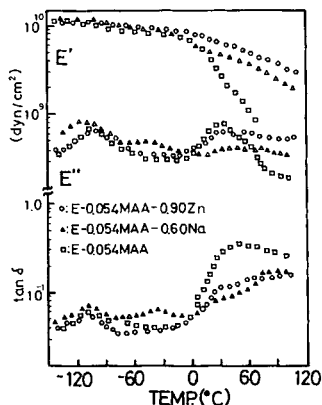

Fig. 2. The temperature dependence of dynamic modulus (E'), loss modulus (E''), and tan δ of E-0.054MAA (□), E-0.054MAA–0.60Na (△), and E-0.054MAA–0.90Zn (○) treated by 0.4N nitric acid for 25 h.
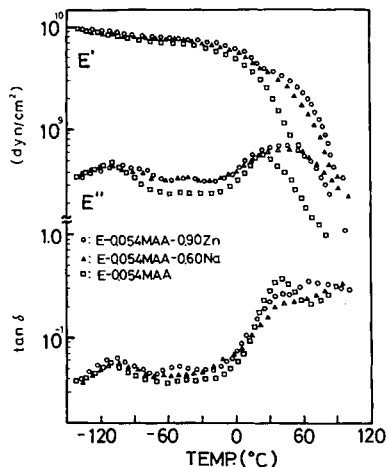

Fig. 3. The temperature dependence of dynamic modulus (E'), loss modulus (E''), and tan δ of E-0.054MAA (□), E-0.054MAA–0.60Na (△), and E-0.054MAA–0.90Zn (○) treated by 1.8N nitric acid for 25 h.
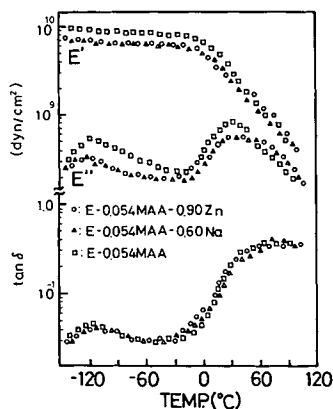
Fig. 4. The temperature dependence of dynamic modulus (E'), loss modulus (E''), and tan δ of E-0.054MAA (□), E-0.054MAA−0.60Na (△), and E-0.054MAA−0.90Zn (○) treated by 3.5N nitric acid for 25 h.

tively. The γ dispersion around −120°C which was attributed to the local molecular motion was not affected by nitric acid treatment and was substantially the same as the γ dispersion of ethylene ionomer untreated. This suggests the impossible degradation of a backbone at the concentration range of nitric acid studied here.

The dynamic modulus did not substantially change by 0.4N nitric acid treatment. Thus it can be said that the ionic aggregates were not affected by 0.4N nitric acid and played the role of physical crosslinking at a high temperature range above the melting temperature of a crystal of ethylene ionomer. However, the E' of E-0.054MAA−0.60Na and E-0.054MAA−0.90Zn treated by 1.8N nitric acid began to decrease abruptly at about 60°C as shown in Figure 3, contrary to the E' of E-0.054MAA−0.60Na and E-0.054MAA−0.90Zn untreated. With a further increase of the nitric acid concentration, the trend decreasing the E' at a high temperature range was remarkable. Figure 4 illustrated approximately the same dynamic viscoelastic behavior of E-0.054MAA−0.60Na and E-0.054MAA−0.90Zn treated as that of E-0.054MAA. The characteristic rubbery plateau at a high temperature range disappeared with the nitric acid treatment of a higher concentration than 3.5N. This is indicative of the transformation from a salt form of ethylene ionomer to an acid form and also the disappearance of the ionic aggregates.

In conclusion, the acid form of ethylene ionomer, E-0.054MAA, could not be affected by the nitric acid treatment studied here. On the other hand, the salt form, E-0.054MAA−0.60Na and E-0.054MAA−0.90Zn, was influenced remarkably with the increase of the nitric acid concentration and followed the disappearance of the physical crosslinking characteristic to the ionic aggregates.

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