The Crystallization and Formation of Cluster of Ethylene Ionomer during Physical Aging

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Synopsis

The effect of the physical aging of ethylene ionomers was studied for the samples with the acid content of 5.4 mol%, and the degree of neutralization, 0%, 60% Na, 60% Zn, and 90% Zn. The information about the crystal and the cluster part of the physically aged ionomers was obtained by differential scanning calorimetry and by dynamic viscoelastic measurements, respectively. The degree of crystallinity and the dynamic modulus for the ionomers of the degree of neutralization 0%, 60% Na and 60% Zn increased gradually with the aging time; on the other hand, the crystallinity of 90% Zn remained constant and the modulus at 100°C increased to a certain value up to a period of 100 h, but thereafter the crystallinity increased remarkably and the modulus remained. These facts indicate that the crystallization of neutralized ethylene ionomer starts after clustering and the clustering would finish at early stage of the physical aging for intermediately neutralized ethylene ionomer. The physical aging effect of the ethylene ionomers was, thus, found to be important to material design.

INTRODUCTION

The copolymer which in part contains ionic salt groups of carboxyl, sulfonic acids, and pyridinum groups in a side chain region is, in general, called ionomer. Ionic groups are, therefore, charged and result in ion–ion interaction between them. It is well known that ionic groups in the ionomers form ionic aggregates, playing a role of physical crosslinking.[1-4] Otocka et al.[5] have found the ionic aggregates which are composed of approximately at most eight ion pairs of a telechilic polybutadiene with a terminal carboxyl group, and Rigdahl and Eisenberg[6] have investigated the aggregates called the cluster with more ion pairs of styrene ionomer with about 6 mol% styrene sulfonic acid group. Succeedingly, the cluster has been found commonly for various types of ionomers with ion content more than several mol%. Many attempts to understand the cluster structure were tried for ethylene ionomer with a crystallizable base ethylene unit. Thus the ethylene ionomer is composed of three phases of crystalline and amorphous phases and cluster. Although the cluster structure of the ethylene ionomer has not been fully established, its structural model by Longworth and Vaughan[7] represents a fundamental feature of a crystalline ionomer and is shown in Figure 1. The crystalline phase with a certain lamellar thickness and the cluster exist separately, but it

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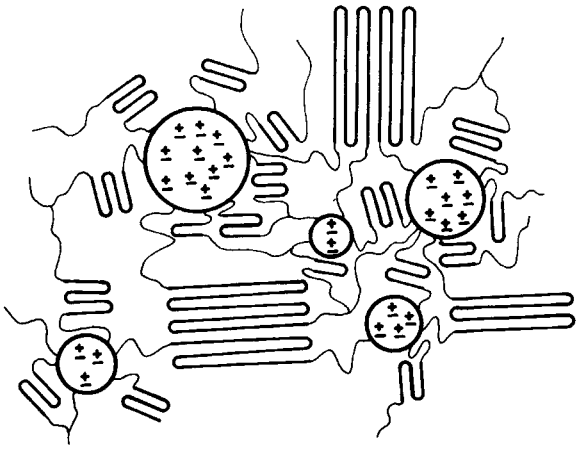

Fig. 1. Structure model of a crystalline ionomer proposed by Longworth and Vaughan.[7]

is noted that the polymer chain of ethylene ionomer must interpenetrate into both phases. One of authors[8] has reported that lamellar thickening of ethylene ionomer occurred during annealing below its melting temperature, similar to polyethylene, although there exists cluster. This indicates an incorporation of mobile ethylene unit into lamellar crystal and existence of mobile chain in cluster. Thus the mobile polymer chain appears to affect the crystallization of the ethylene unit and the formation of cluster from the molten state above the melting temperature. In fact, it was found in our laboratory[9] that some physical properties of ethylene ionomer prepared by a compression molding were different during long physical aging at ambient temperature, suggestive of the crystallization and clustering. It is interesting to know the correlations of the competitive crystallization and clustering during long physical aging as well as in the process of early stage.

In the present paper, the aging time variation in the crystallization and the formation of cluster was searched by differential scanning calorimeter (DSC) and dynamic mechanical measurement for the ionomer with various degrees of neutralization during physical aging for a period of 10^5 h. The crystallization of about half of the degree of attainable crystallinity has already finished at a very early stage despite the degree of neutralization. The remaining crystallization occurred gradually during physical aging for a long period for the ionomer with lower degree of neutralization, while it did start to occur after a period of 100 h, at which the formation of cluster is likely to finish for the ionomer with higher neutralization, i.e., 90% Zn.

EXPERIMENTAL

Ethylene ionomers, copoly(ethylene–methacrylic acid), and its salt, with acid content of 5.4 mol% and the degree of neutralization of 0%, 60% Na, 60% Zn, and 90% Zn, which are kindly supplied from Mitsui-Dupont Polychemical Co. Ltd., were used here. These are designated as E–0.054MAA,

E–0.054MAA–0.60Na, E–0.054MAA–0.60Zn, and E–0.054MAA–0.90Zn, respectively.

The specimen studied here was compression-molded at 150°C of molten state for 1 h and thereafter quenched very rapidly using liquid nitrogen and kept at 25°C for a long period. Two kinds of measurements for the small part of the specimen thus prepared were carried out at a certain aging period.

To get the information of crystalline part of the ionomer, DSC measurement of the specimen of about 20 mg weight was accomplished at the heating rate of 5°C/min at the temperature range from 0 to 125°C by DSC (SSC/560 manufactured by Seiko Electronics Co. Ltd.). The melting temperature and heat of fusion of the ethylene ionomer at a certain period were obtained from the DSC thermograms.

The dynamic mechanical properties (dynamic and loss modulus and tan δ) were measured by the Rheovibron (DDV-II-C, Toyo Baldwin Co. Ltd.) at the heating rate of 2°C/min at the temperature range from 20°C to around 140°C at the frequency of 110 Hz in order to provide the information about the formation of cluster during physical aging.

RESULTS AND DISCUSSION

Time Variation of Melting Behavior

DSC thermograms of physically aged ethylene ionomer of E–0.054MAA and E–0.054MAA–0.90Zn are typically shown in Figure 2. Both thermograms fundamentally demonstrate two endothermic peaks ascribed to melting of crystalline parts of ethylene ionomer, despite the aging time. Lower melting peak shifts to higher temperature with the increase of the aging time and becomes sharp, while higher melting peak does not do very remarkably. Furthermore, the lower melting peak of the ethylene ionomer with the higher degree of neutralization becomes sharper than that with the lower degree. These might indicate small but more homogeneous lamellar thickness as the degree of neutralization or the aging time increases. Exothermic small peak appears around 62°C for only the neutralized ethylene ionomer, demonstrating a recrystallization around 62°C during heating. The recrystallization might relate to the formation and stability of cluster, but one cannot further discuss it in detail at the present.

The time variation of the lower melting temperature (T_l) of all the ethylene ionomers is shown in Figure 3. The T_l rises with the increase of the degree of neutralization in the whole aging time range and is nearly independent of the species of salts such as Na and Zn. The T_l rises gradually with the increasing aging time, irrespective of the degree of neutralization. These facts support the fact that the presence of cluster in the ethylene ionomers results in the crystallization into the small but much thicker and more homogeneous lamellar crystal whose melting temperature corresponds to the T_l.

Figure 4 shows the time variation of the higher melting temperature (T_h) of all the ethylene ionomers. The T_h of E–0.054MAA is about 4°C higher than that of the neutralized ethylene ionomer (E–0.054MAA–0.60Na, E–0.054MAA–0.60Zn, and E–0.054MAA–0.90Zn). Different from the lower

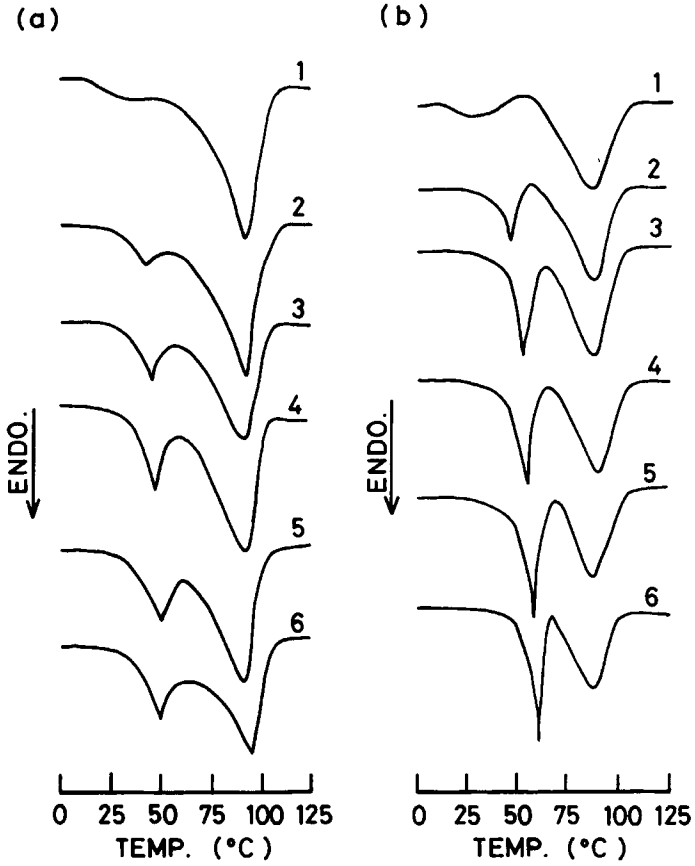

Fig. 2. DSC thermograms of E–0.054MAA (a) and E–0.054MAA–0.90Zn (b) at various physical aging times: (1) 5 min; (2) 1 day; (3) 30 days; (4) 200 days; (5) 500 days; (6) untreated.

melting temperature behavior, T_h is lowered by the metal salts such as Na and Zn. There, however, appears to be no difference in the species of the metal salts. Furthermore, there is almost no effect of physical aging on T_h, which represents the melting temperature of a larger lamellar crystal, indicating that its thickening finishes at a comparatively early stage of aging. Physical aging can have an effect on the lower melting temperature of the small lamella, but cannot on the higher melting temperature of the large lamella in the ethylene ionomers.

The degree of crystallinity of the physically aged ethylene ionomer is plotted against the aging time in Figure 5. The degree of crystallinity of E–0.054MAA is higher than that of the other neutralized ionomer at the whole aging time and, interestingly increases gradually with the aging time. This might be due to the disturbance of the crystallization by hydrogen bond between methacrylic acid groups. The 60% neutralized ethylene ionomer shows almost the same trend as E–0.054MAA. Because the neutralized ionomer has less hydrogen bond, a different explanation is necessary: the disturbance of crystallization by the presence of cluster. Again there is no difference of crystallinity between the species of the metal salts. The trend of

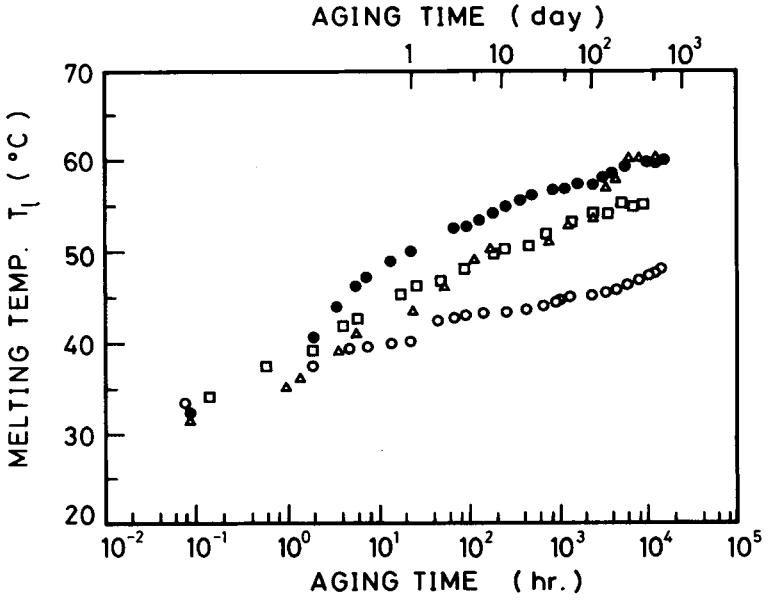

Fig. 3. Lower melting temperature (T_l) of E–0.054MAA (○), E–0.054MAA–0.60Na (△), E–0.054MAA–0.60Zn (□), and E–0.05MAA–0.90Zn (●) against physical aging time.

the relation of the degree of crystallinity and aging time is varied for highly neutralized ethylene ionomer of E–0.054MAA–0.90Zn, which can contain more clusters: The degree of crystallinity does not change remarkably but rather remains constant up to the aging time of a period of 100 h; thereafter it increases considerably. The crystallization is considered to be disturbed by the formation of cluster up to this aging time. On the other hand, its formation will finish at that time as described later so that the crystallization is

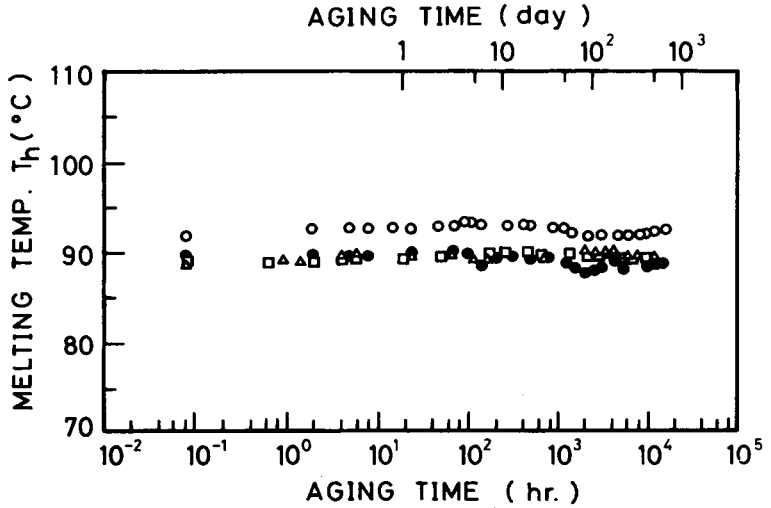

Fig. 4. Higher melting temperature (T_h) of E–0.054MAA (○), E–0.054MAA–0.60Na (△), E–0.054MAA–0.60Zn (□), and E–0.054MAA–0.90Zn (●) against physical aging time.

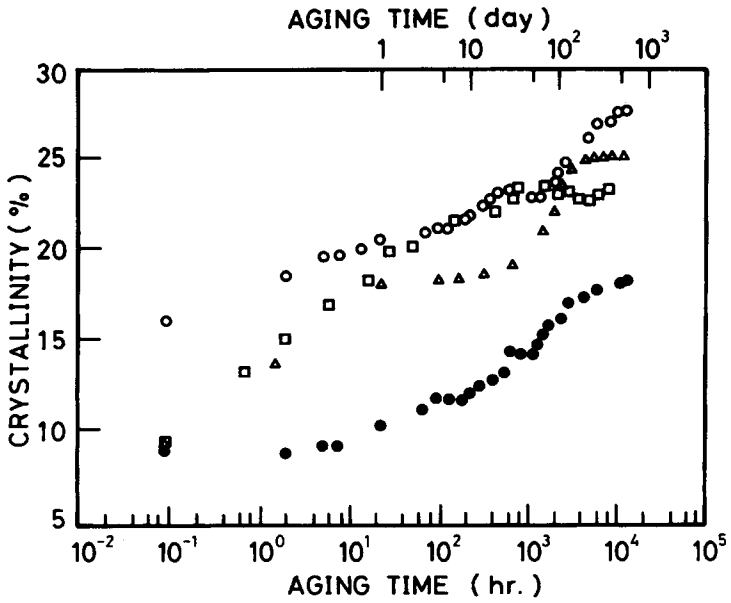

Fig. 5. The plot of the degree of crystallinity of E–0.054MAA (○), E–0.054MAA–0.60Na (△), E–0.054MAA–0.60Zn (□), and E–0.054MAA–0.90Zn (●) against the physical aging time.

considered to start because of no disturbance by clustering. Such explanation is fundamentally applied also to intermediately neutralized ethylene ionomer of 60% degree of neutralization. Namely, because the formation of cluster might finish at very initial stage of the aging time, the crystallization starts initially without disturbance by clustering.

Time Variation of Dynamic Modulus

The dynamic modulus (E') of all the ethylene ionomers untreated is shown in Figure 6. A considerable decrease of the E' of E–0.054MAA is observed around 40°C, which is ascribed to α dispersion of the crystalline part of the ethylene ionomer. A similar decrease of the E' of the neutralized ethylene ionomer is also observed at the temperature range from 50 to 80°C and assigned to a molecular motion of cluster by Otocka and Kwei[10] and to α dispersion of the crystalline part. The characteristics of the behavior is that the higher modulus of the neutralized ethylene ionomer remains nearly constant above its melting temperature, similar to the rubbery plataeu observed for a crosslinked rubber at a higher temperature range. This modulus is dependent on the degree of neutralization: higher degree, higher modulus. Such modulus behaviors of the neutralized ethylene ionomer are believed to be caused by physical crosslinking formed by cluster. Therefore this result might be interpreted by the content of cluster. If the dynamic modulus E' in the rubbery plateau is assumed to be a measure of the cluster content, one can estimate the cluster content during physical aging by measuring E'.

As described in the previous section, the crystallization proceeded gradually during physical aging. This also affects E' and one can expect an increase in E'. The time variation of E' of E–0.054MAA, E–0.054MAA–0.60Na,

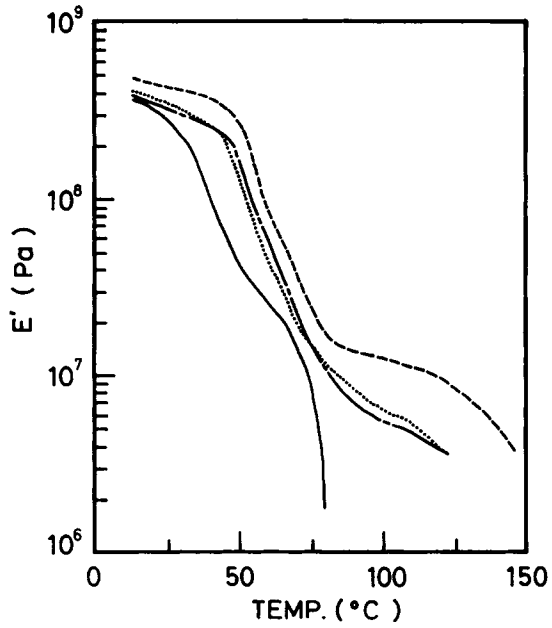

Fig. 6. The dynamic modulus E'–temperature relations of E–0.054MAA (—), E–0.054MAA–0.60Na (- - -), E–0.054MAA–0.60Zn (– – –), and E–0.054MAA–0.90Zn (– – –).

E–0.054MAA–0.60Zn, and E–0.054MAA–0.90Zn is shown in Figures 7–10, respectively. The typical measured temperature of E' was selected as 25, 50, 70, and 100°C at which there exist both or either small and/or large lamellar crystals, and only cluster after melting of all the crystals, respectively. The E' at 25°C gradually increases with the increase of physical aging time, indicative of the clustering and the crystallization during the aging. The difference

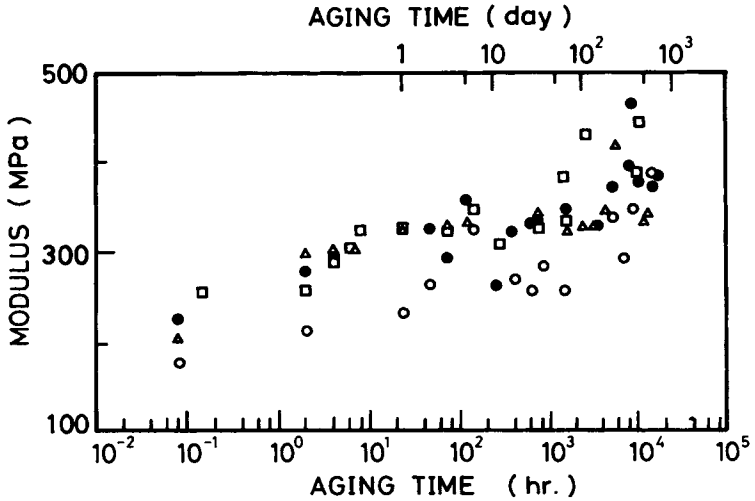

Fig. 7. The aging time dependence of dynamic modulus E' at 25°C of E–0.054MAA (○), E–0.054MAA–0.60Na(△), E–0.054MAA–0.60Zn (□), and E–0.054MAA–0.90Zn (●).

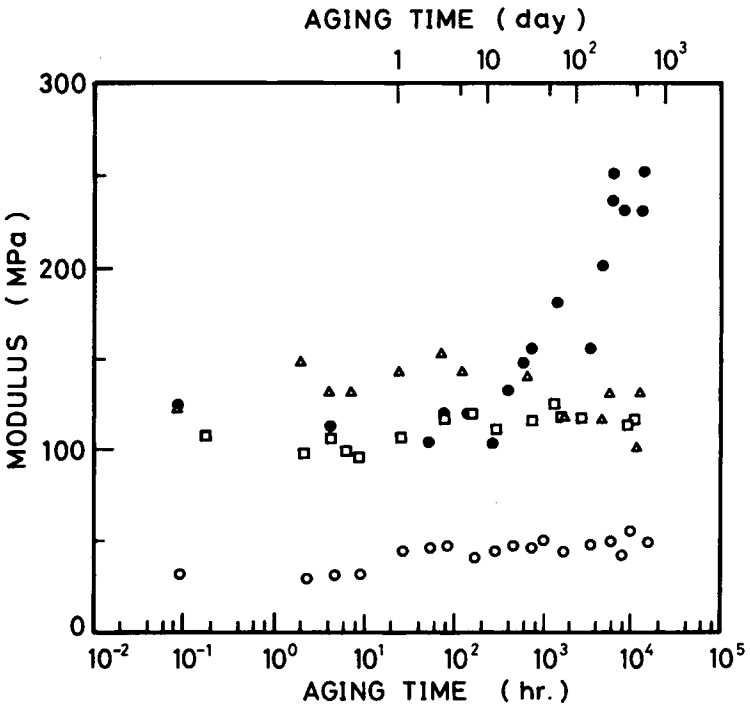

Fig. 8. The aging time dependence of dynamic modulus E' at 50°C of E–0.054MAA (○), E–0.054MAA–0.60Na (△), E–0.054MAA–0.60Zn (□), and E–0.054MAA–0.90Zn (●).

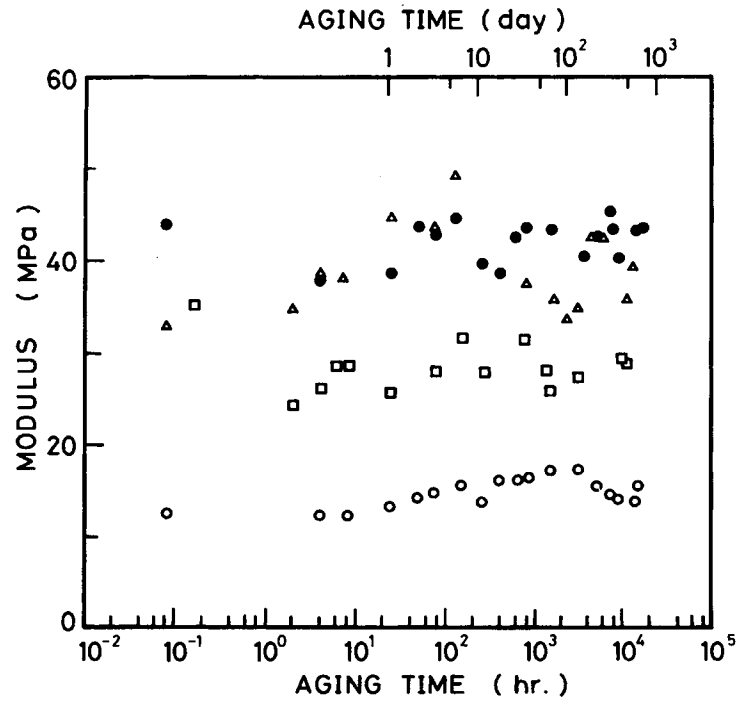

Fig. 9. The aging time dependence of dynamic modulus E' at 70°C of E–0.054MAA (○), E–0.054MAA–0.60Na (△), E–0.054MAA–0.60Zn (□), and E–0.054MAA–0.90Zn (●).

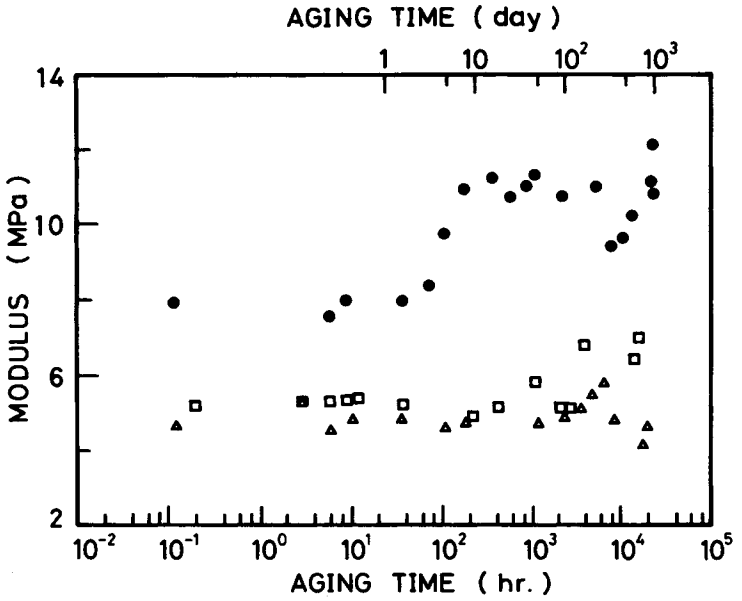

Fig. 10. The aging time dependence of dynamic modulus E' at 100°C of E–0.054MAA (○), E–0.054MAA–0.60Na (△), E–0.054MAA–0.60Zn (□), and E–0.054MAA–0.90Zn (●).

of the E' at 25°C between E–0.054MAA and neutralized ethylene ionomers might be due to the presence of cluster, while that at 50°C exhibits no remarkable increase except for E–0.054MAA–0.90Zn. This might mean the presence of the smaller lamellar crystal at 50°C as seen from Figure 2, which enhances the modulus. The E' at 70°C does not vary very much. It is interesting to examine the E' of the neutralized ethylene ionomers at 100°C because it gives the information about the cluster content, not the crystal one. The E' at 100°C of E–0.054MAA–0.60Na and E–0.054MAA–0.60Zn does not change considerably with the increasing aging time, meaning that the cluster has already been constructed at the very initial stage and cannot be formed during the aging time measured. The formation of cluster is considered to have been performed on cooling from the molten state. On the other hand, the E' at 100°C of E–0.054MAA–0.90Zn remains approximately constant up to the aging time of about 40 h and increases considerably up to about 100 h; then it approximately levels off. This indicates the clustering up to the aging time of 100 h, suggestive of the cluster formation for the highly neutralized ethylene ionomer.

At the conclusion of the crystallization and formation of cluster, during physical aging, these behaviors correlate each other with the presence of cluster characteristic to the ionomer, different from a general cyrstalline polymer. The crystallization of the highly neutralized ethylene ionomer is disturbed and cannot proceed while the cluster continues to develop up to a period of 100 h of the physical aging. After this period at which clustering finished, the crystallization could start, as seen from Figure 5 (E–0.054MAA–0.90Zn).

As for the intermediately neutralized ethylene ionomer, the ion clustering must already terminate at the very initial stage of physical aging so that the

crystallization begins to start initially. These explanations also support the increase of the dynamic modulus at 25°C. Thus one could obtain the high modulus, controlling physical aging through the crystallization and clustering. The high modulus at lower temperature is, in particular, enhanced by the crystallization, whereas that above the melting temperature, by the cluster formation. It was also found that the crystallization and clustering of the ethylene ionomer were affected for a very long period and that the effect of physical aging to the material design should be noted.

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