Impact Fracture Behavior of Ethylene Ionomer and Structural Change After Stretching

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ABSTRACT: We carried out tensile impact test and very low speed tensile test on ethylene-based Ionomers (E/15wt %MAA) to clarify the relation between impact toughness and high-ordered structure. We also studied the changes in high-ordered structure under deformation by observing Differential Scanning Calorimetory (DSC) and Small-Angle X-ray Scattering (SAXS) of fractured surface. Na Ionomers showed ductile fracture in both high speed tensile impact (3 m/s) and very low speed tensile (2 mm/min). The disappearance of secondary melting point (Ti) in Na Ionomers was due to the destruction of ordered structure surrounding the ionic aggregate. Similar behavior was observed in 60% (or less) neutralized Zn Ionomers. However, 80% neutralized Zn Ionomer showed brittle failure in high-speed tensile impact, and Ti did not disappear. SAXS studies of Na and Zn Ionomers after fracture, show no change both after molding (no aging) and after aging. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1712–1720, 2001

INTRODUCTION

Ethylene Ionomers, composed of ethylene, acid monomer, and neutralized acid monomer, have ionic branches on its chain. Ion is phase separated from the hydrophobic matrix and form ionic aggregates.[1] Ionic aggregate acts as physical crosslinkage.[2–5]

First, Longworth et al.[6] discovered new peaks at a low degree of X-ray scattering, which was identified as the ionomer peak. The discovery was followed by a lot of morphological studies using X-ray scattering and various kinds of structural models.[7–11] Representatives are core-shell model by MacKnight[2,8] and liquid-like model by Yarusso and Cooper.[11]

According to the previous thermal analytical studies of Ionomer,[12–14] it is known that the endothermic peak lower than the melting point of polyethylene crystalline appears after a few weeks of aging. Yano and Hirasawa[12,13] identified this peak as order–disorder transition of ionic aggregate. Historically, this peak is called the T_i peak because of its strong relation to the presence of ionic aggregate. Tsujita[14] identifies this peak as the melting point of semicrystalline polyethylene. Nevertheless, these discussions have not come to a conclusion, we use the word "Ti" in this article for convenience.

High-impact toughness is one of the most important physical properties of Ionomer. It depends on the presence of ionic aggregate, and the structure of ionic aggregate has not been clarified perfectly because of its colloid-order dimensions.

Focusing on the impact toughness of ethylene Ionomer, the relationship between high-order structure and impact characteristics was not sufficiently interpreted.

In this article, to clarify the role of the high-order structure, especially ionic aggregate, in de-

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Table I Identification of Ionomer Based Ethylene–Methacrylic Acid Copolymer in This Study

Sample Abbreviation	Metal Ion	Degree of Neutralization	Melt Flow Rate of Ionomer
20Na	Na	20	13
40Na	Na	40	2.6
60Na	Na	60	0.6
80Na	Na	80	0.06
20Zn	Zn	20	14
40Zn	Zn	40	3.1
60Zn	Zn	60	1.1
80Zn	Zn	80	0.4
EMAA	—	0	60

An ethylene–methacrylic acid copolymer containing 15 wt % methacrylic acid was used as a base polymer of the Ionomers.

formation of Ionomer, the deformation in a high and very low-speed tensile test, thermal analysis, and small-angle X-ray scattering of tensile-fractured Ionomer was carried out.

EXPERIMENTAL PROCEDURE

Materials

Ethylene–methacrylic acid copolymers (Methacrylic acid content was 15 wt %) ionized with Zn ions, and Na ions were used in the experiment as an ethylene-base Ionomers. Neutralization degree was 20, 40, 60, and 80 mol %. Specimens for the fracture tests were obtained by compression molding at 180°C, followed by quick cooling and aging at room temperature. Sample identifications are listed in Table I.

Aging Conditions

Aging conditions were: dry, 51%RH and 98%RH. The dry condition was achieved by placing samples in a vacuum desiccator. The 51%RH condition was obtained by using $CaSO_4 \cdot 5H_2O$ supersaturated aqueous solution in a desiccator. The 98%RH condition was obtained by using $Ca(NO_3) \cdot 4H_2O$ supersaturated aqueous solution in a desiccator. Aging periods were 2 weeks and 2 months.

Fracture Test

Tensile Impact Test

The uniaxial tensile impact test was carried out under the test speed of 3 m/s at a room temperature of 23°C using a Dynatup-8250 (General Research Co.). The test specimen used was ASTM D1822 type L for the tensile impact test whose parallel part was 3.18 mm width, 2 mm thickness, and 10 mm length. The 5.77 kg-weight was dropped from the 0.45 m high (impact speed was 3 m/s).

Very Low Speed Tensile Test

The very low speed tensile test was carried out under the test speed of 2 mm/min at a room temperature of 23°C using a tensile tester (Intesco model 210B). The same dumbbell specimens as an impact test were used for testing.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measurements of the samples were carried out by using Seiko Instrument Industries Model DSC22. Each sample was heated from −20 to 130°C at a heating rate of 5.0°C/min. The sample weight was ca. 10 mg, and the reference was Al_2O_3. Thermal properties of ionomers such as melting temperature (T_m), heat fusion (ΔH_m), secondary melting temperature (T_i) and secondary heat fusion (ΔH_i) were all determined from the DSC thermograms. Figure 1 shows the typical thermogram of ethylene Ionomer.

Small-Angle X-ray Scattering

Small-angle X-ray scattering (SAXS) measurements were made on a Rigaku Denki RINT1500 using pinhole collimation and a two-dimensional position-sensitive detector (PSPC). Lamp voltage

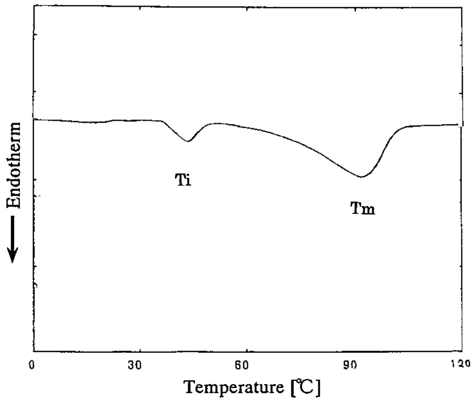

Figure 1 Typical DSC thermogram of ethylene Ionomer.

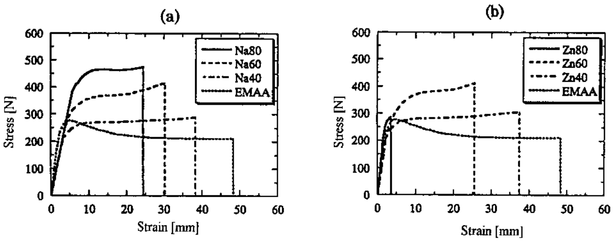

Figure 2 Stress–strain curve on tensile impact (3 m/s) tests. Tensile tests were carried out immediately after molding: (a) Na type, (b) Zn type.

and current were 40 kV and 200 mA, respectively, and radiation was CuKα (λ = 1.542 Å).

RESULTS

Tensile Impact Test

Figure 2(a) shows stress–strain curve of the tensile impact fracture test after compression molding (no aging). As can be seen in the figure, the stress at failure reduced as the neutralization of Na reduced, while the strain at failure reduces with increasing neutralization. Thus, EMAA on its own has the lowest stress at failure, and the strain at failure is the highest. Similarly, Zn ion shows the same behavior, as can be seen in Figure 2(b).

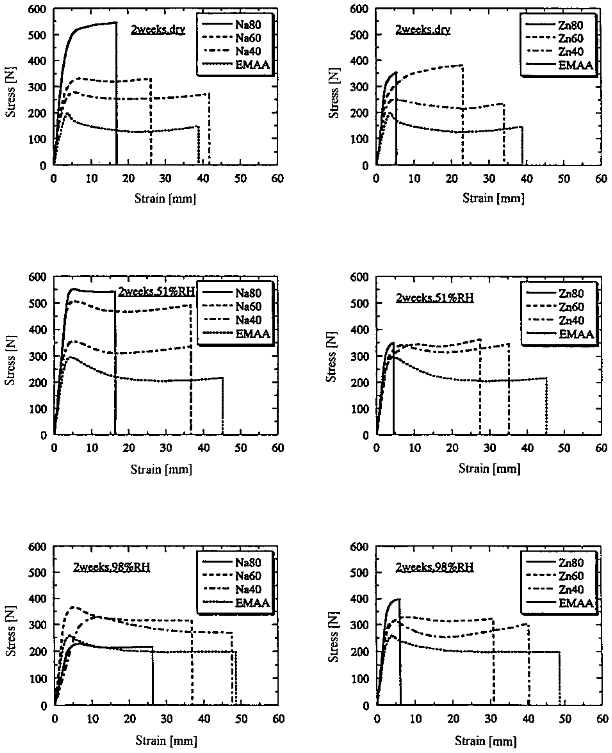

Figure 3 Stress–strain curve on tensile impact (3 m/s) tensile tests. Tensile tests were carried out after 2 weeks aging.

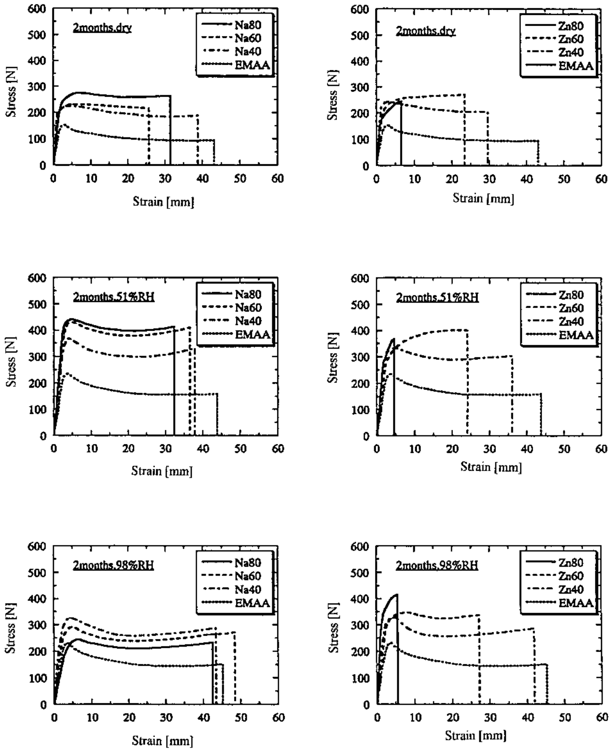

Figure 4 Stress–strain curve on tensile impact (3 m/s) tests. Tensile tests were carried out after 2 months aging.

Figures 3 and 4 show stress–strain curves of the tensile impact fracture test after 2 weeks and 2 months aging, respectively. Stress–strain curves in all aging conditions except Zn80 showed ductile failure. Zn80 showed brittle failure with less than 10 mm strain at failure. In both the Na Ionomer and Zn Ionomer except for Zn80, strain at failure decreased and the maximum stress increased as the degree of neutralization increased. The humidity of the aging condition is affected more in Na Ionomers than Zn Ionomers, i.e., strain at failure and maximum stress of Na Ionomer increased after aging under 51%RH, strain at failure also increased and the maximum stress decreased after aging under 98%RH. Because of high absorbency of the Ionic aggregate, Na Ionomer was plasticized with water. That is why high aging humidity and long aging period eliminate the dependence of Na ion content.

Figure 5 shows the effect of neutralization on strain at failure. Samples were aged for 2 weeks

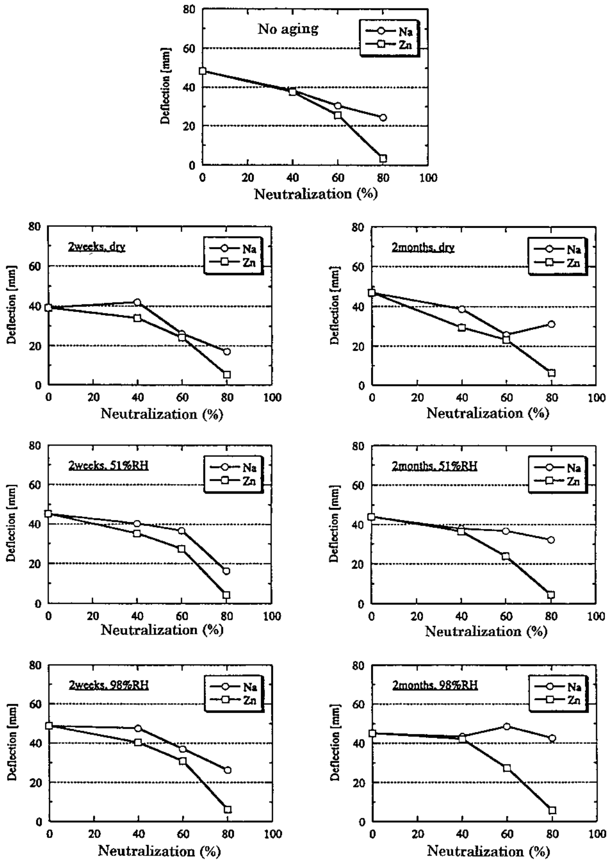

Figure 5 Relation between deflection and neutralization degree on tensile impact (3 m/s) tests.

also 2 months. It is observed that all samples showed similar behavior. The only point here is that strain at failure remains unaffected until above 40% neutralization where it reduces with increasing neutralization.

Very Low Speed Tensile Test

As well as tensile impact test, stress–strain curves are obtained under three different aging conditions after compression molding, no aging (Fig. 6), 2 weeks (Fig. 7), and 2 months (Fig. 8). Different from the case of tensile impact test, even 80Zn showed ductility.

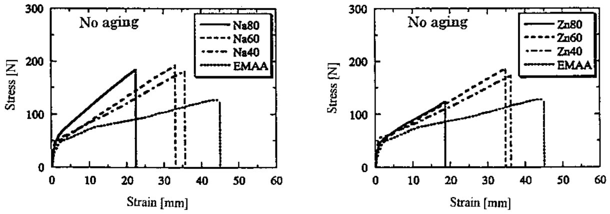

Figure 6 Stress–strain curve on very low speed tensile (2 mm/min) tests without aging.

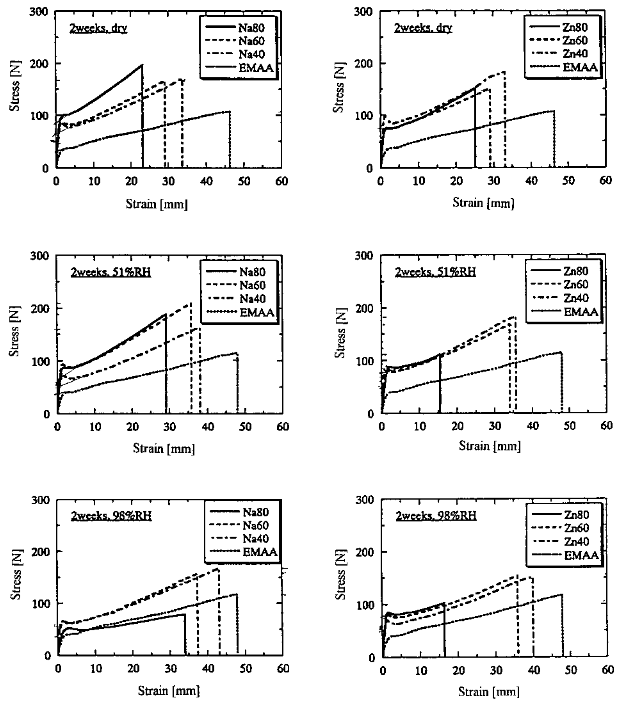

Figure 7 Stress–strain curve on very low speed tensile (2 mm/min) tests after 2 weeks aging.

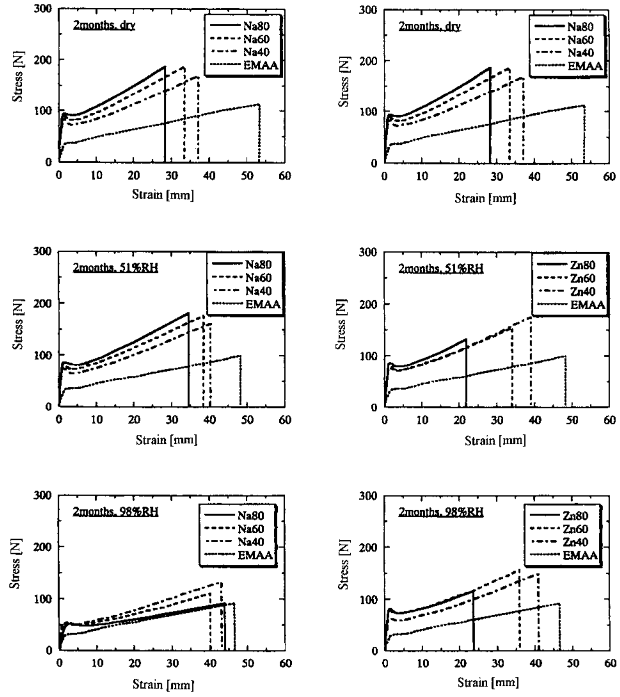

Figure 8 Stress–strain curve on very low speed tensile (2 mm/min) tests after 2 months aging.

Table II Aging Effects of Ionomers on T_i, ΔH_i, T_m, and ΔH_m Measured with DSC

Sample	Aging Humidity %RH	Aging Period	T_i °C	ΔH_i kJ/kg	T_m °C	ΔH_m kJ/kg
EMAA	—	No aging	—	—	92.6	63.2
40Na	—	No aging	—	—	92.1	51.6
60Na	—	No aging	—	—	90.5	39.4
80Na	—	No aging	—	—	86.8	17.5
40Zn	—	No aging	—	—	92.1	42.1
60Zn	—	No aging	—	—	91.6	54.9
80Zn	—	No aging	—	—	88.3	44.5
EMAA	Dry	2 weeks	33.6	4.0	92.9	63.3
40Na	Dry	2 weeks	43.0	7.5	92.3	47.7
60Na	Dry	2 weeks	46.7	8.7	90.5	42.1
80Na	Dry	2 weeks	54.4	11.8	88.1	39.7
40Zn	Dry	2 weeks	34.7	8.0	92.1	53.4
60Zn	Dry	2 weeks	45.7	4.5	92.4	55.7
80Zn	Dry	2 weeks	50.0	9.9	90.8	49.1
EMAA	51%RH	2 weeks	25.5	2.2	92.6	75.3
40Na	51%RH	2 weeks	44.6	10.1	92.4	53.2
60Na	51%RH	2 weeks	44.3	8.7	90.8	41.4
80Na	51%RH	2 weeks	45.4	10.1	89.1	36.5
40Zn	51%RH	2 weeks	43.8	5.9	92.4	47.7
60Zn	51%RH	2 weeks	44.6	6.8	92.6	57.9
80Zn	51%RH	2 weeks	49.1	9.7	91.3	46.6
EMAA	98%RH	2 weeks	41.6	4.6	92.6	83.0
40Na	98%RH	2 weeks	44.9	7.2	93.2	41.1
60Na	98%RH	2 weeks	45.4	10.7	92.1	47.3
80Na	98%RH	2 weeks	48.4	10.0	92.9	61.5
40Zn	98%RH	2 weeks	45.6	12.6	92.7	60.7
60Zn	98%RH	2 weeks	49.4	12.5	92.9	59.7
80Zn	98%RH	2 weeks	52.1	15.5	91.3	47.3
EMAA	Dry	2 months	26.3	4.0	93.2	71.4
40Na	Dry	2 months	51.8	3.7	92.9	42.0
60Na	Dry	2 months	52.9	15.9	91.3	43.7
80Na	Dry	2 months	57.5	12.5	88.4	26.9
40Zn	Dry	2 months	49.7	13.1	92.1	51.4
60Zn	Dry	2 months	48.1	7.1	92.9	52.8
80Zn	Dry	2 months	56.4	16.9	91.0	50.5
EMAA	51%RH	2 months	39.7	4.1	91.6	80.8
40Na	51%RH	2 months	44.6	9.2	91.3	60.3
60Na	51%RH	2 months	44.9	7.3	90.2	52.3
80Na	51%RH	2 months	43.8	11.8	90.	46.8
40Zn	51%RH	2 months	44.3	9.9	91.3	59.4
60Zn	51%RH	2 months	47.0	10.4	91.3	62.1
80Zn	51%RH	2 months	49.4	11.6	88.6	53.6
EMAA	98%RH	2 months	41.6	5.5	92.9	64.7
40Na	98%RH	2 months	46.2	12.5	94.5	65.7
60Na	98%RH	2 months	45.9	12.7	93.2	58.8
80Na	98%RH	2 months	51.3	15.6	92.1	52.4
40Zn	98%RH	2 months	45.9	10.1	93.7	62.8
60Zn	98%RH	2 months	50.8	12.6	93.2	77.2
80Zn	98%RH	2 months	52.6	14.9	91.3	45.8

As well as tensile test, the aging effect was observed strongly in Na Ionomers. After 2 months aging under 98%RH, impact behavior was not different among all neutralization ranges because of plastization of the ionic aggregate with water.

DSC

Before Stretching

Aging effects of Ionomers on DSC pattern were studied before the impact test (Table II).

In the case of Na Ionomers, T_m (melting point of polyethylene crystalline) and ΔH_m (heat of fusion of polyethylene crystalline) decreased as neutralization increased. Especially in 80Na, crystallization of crystalline polyethylene was restricted by ionic aggregates so that ΔH_m immediately after molding was very small. Because T_m after 2 weeks' aging and that after 2 months' aging under vacuum are about the same, crystallization is considered to finish within 2 weeks. On the other hand, crystalline polyethylene continued to increase to be the same T_m as that of EMAA under humid condition of 51%RH and 98%RH.

Because the cohesiveness of Na ionic aggregates is strong enough to restrict the molecular movement during the cooling process, crystallization of polyethylene crystalline is restricted; however, plasticizing of ionic aggregates by moisture absorption helped to accelerate the crystallization process.

Although the T_i peak was not found in the Na Ionomer immediately after molding, the peak appeared after aging under vacuum conditions. Those T_i peaks were higher when neutralization were higher and the aging periods were longer. T_i peaks aged under humid condition (51%RH and 98%RH) showed the same tendency but lower than those aged under vacuum condition.

As the neutralization degree of the Na Ionomer increased, the shape of the T_i peak became broader (Fig. 9).

In the case of the Zn Ionomer, T_m and ΔH_m were independent of neutralization. T_m did not change after aging. As the ionic aggregate of the Zn Ionomer restricts the polymer main chain much weaker than that of the Na Ionomer, crystallization of polyethylene was slightly obstructed.

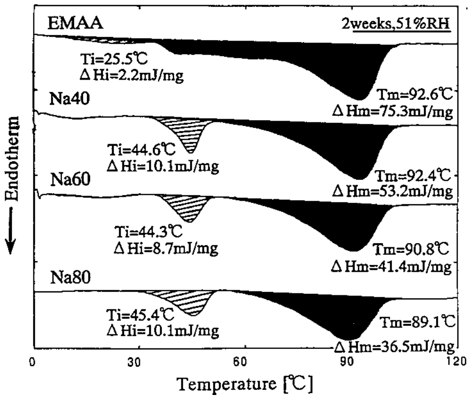

Figure 9 DSC thermograms of Na Ionomers after 2 weeks, 51%RH aging.

Similar to Na Ionomer, the T_i peak of the Zn Ionomer, which is observed after aging, was higher when neutralization was higher. In this case, the aging period was longer and the aging humidity was low. However, humidity dependency was much smaller than the Na Ionomer and the shape of the T_i peak was independent of neutralization.

After Stretching

Table III shows the change of the DSC pattern of 60Na, 80Na, 60Zn, and 80Zn after tensile impact fracture and static tensile fracture.

Na Ionomer; T_i peak of aged Na Ionomer disappeared after tensile impact fracture. However, there was essentially no change in the T_m peak.

Zn Ionomer; T_i peak of aged 60Zn disappeared after both tensile impact and very low speed tensile fracture, regardless of aging condition. The T_i peak of aged 80Zn did not disappear after tensile impact fracture regardless of aging condition, while it did disappear after very low speed tensile fracture.

Change in ionic aggregate after tensile fracture is considered to be strongly related to the degree of stretching. Degree of stretching of 80Zn after tensile impact was low enough to the extent that the ordered structure of ionic aggregates was preserved.

Small-Angle X-ray Scattering

Figure 10 shows the SAXS pattern of 80Na and 80Zn broken by a tensile impact test and very low speed tensile test just after molding. 80Na and 80Zn have an Ionomer peak at $2\theta = 3$ degrees and 5 degrees, respectively. The position of the Ionomer peak did not shift after tensile fracture.

DISCUSSION

The ionic aggregate of the ionomer behaves as physical and reversible crosslinkage. When an ethylene–methacrylic acid copolymer is neutralized, the density of the crosslinkage becomes high, then deformation becomes more elastic. Therefore, maximum stress becomes big and

Table III Changes of T_i, ΔH_i, T_m, and ΔH_m After Tensile Stretching Measured with DSC

Sample	Aging Humidity %RH	Aging Period	Status	T_i °C	ΔH_i kJ/kg	T_m °C	ΔH_m kJ/kg
60Na	Dry	2 weeks	B	46.7	8.7	90.5	42.1
			I	46.2	3.8	90.2	37.8
			S	39.8	2.7	90.7	46.0
60Na	Dry	2 months	B	52.9	15.9	91.3	43.7
			I	41.6	2.8	90.0	42.2
			S	35.5	3.4	91.8	50.6
60Na	51%RH	2 weeks	B	44.3	8.7	90.8	41.4
			I	37.9	0.5	90.8	41.3
			S	30.9	1.9	90.5	45.8
60Na	51%RH	2 months	B	44.9	7.3	90.2	52.3
			I	37.6	1.5	91.0	53.3
			S	29.3	7.6	90.7	54.7
60Na	98%RH	2 weeks	B	45.4	10.7	92.1	47.3
			I	—	—	92.9	50.8
			S	—	—	94.0	57.5
60Na	98%RH	2 months	B	45.9	12.7	93.2	58.8
			I	44.9	1.5	94.0	37.2
			S	29.3	1.2	93.5	42.0
60Zn	Dry	2 weeks	B	45.7	4.5	92.4	55.7
			I	42.5	1.7	92.1	48.0
			S	33.9	1.3	91.8	62.6
60Zn	Dry	2 months	B	48.1	7.1	92.9	52.8
			I	39.0	1.0	92.1	58.2
			S	33.6	0.8	92.9	60.9
60Zn	51%RH	2 weeks	B	44.6	6.8	92.6	57.9
			I	41.6	2.1	92.4	49.6
			S	31.9	1.9	92.1	60.9
60Zn	51%RH	2 months	B	47.0	10.4	91.3	62.1
			I	34.4	1.8	91.6	59.6
			S	28.8	7.5	91.0	58.6
60Zn	98%RH	2 weeks	B	49.4	12.5	92.9	59.7
			I	49.9	2.4	93.2	57.1
			S	30.2	0.9	92.9	65.0
60Zn	98%RH	2 months	B	50.8	12.6	93.2	77.2
			I	50.8	2.0	93.5	57.0
			S	29.8	7.5	91.6	65.5
80Na	Dry	2 weeks	B	54.4	11.8	88.1	39.7
			I	41.6	2.2	88.0	18.4
			S	43.5	0.6	87.8	20.2
80Na	Dry	2 months	B	57.5	12.5	88.4	26.9
			I	37.9	2.1	88.3	28.6
			S	34.7	1.0	90.2	36.2
80Na	51%RH	2 weeks	B	45.4	10.1	89.1	36.5
			I	37.1	1.2	89.1	30.9
			S	40.3	1.7	90.0	40.8
80Na	51%RH	2 months	B	43.8	11.8	90.0	46.8
			I	41.1	3.5	91.0	39.6
			S	34.9	2.7	89.9	46.7
80Na	98%RH	2 weeks	B	48.4	10.0	92.9	61.5
			I	41.6	3.1	93.7	55.6
			S	—	—	94.2	39.4
80Na	98%RH	2 months	B	51.3	15.6	92.1	52.4
			I	37.9	1.8	93.5	31.8
			S	29.0	1.5	93.7	47.5

Table III *Continued*

Sample	Aging Humidity %RH	Aging Period	Status	T_i °C	ΔH_i kJ/kg	T_m °C	ΔH_m kJ/kg
80Zn	Dry	2 weeks	B	50.0	9.9	90.8	49.1
			I	50.2	11.2	90.0	40.6
			S	36.5	1.0	91.0	48.3
80Zn	Dry	2months	B	56.4	16.9	91.0	50.5
			I	46.7	5.2	91.0	50.6
			S	45.1	1.6	91.3	53.8
80Zn	51%RH	2 weeks	B	49.1	9.7	91.3	46.6
			I	45.7	5.1	91.3	46.6
			S	40.8	0.9	91.6	51.7
80Zn	51%RH	2months	B	49.4	11.6	88.6	53.6
			I	49.4	12.0	89.9	50.8
			S	33.1	1.8	91.0	44.9
80Zn	98%RH	2 weeks	B	52.1	15.5	91.3	47.3
			I	47.3	8.1	91.3	51.8
				31.5	4.9	92.3	58.9
80Zn	98%RH	2months	B	52.6	14.9	91.3	45.8
			I	51.5	14.7	92.1	51.1
			S	30.9	2.6	91.8	58.0

Status: B; before deformation, I; after tensile impact, S; after very low speed tensile.

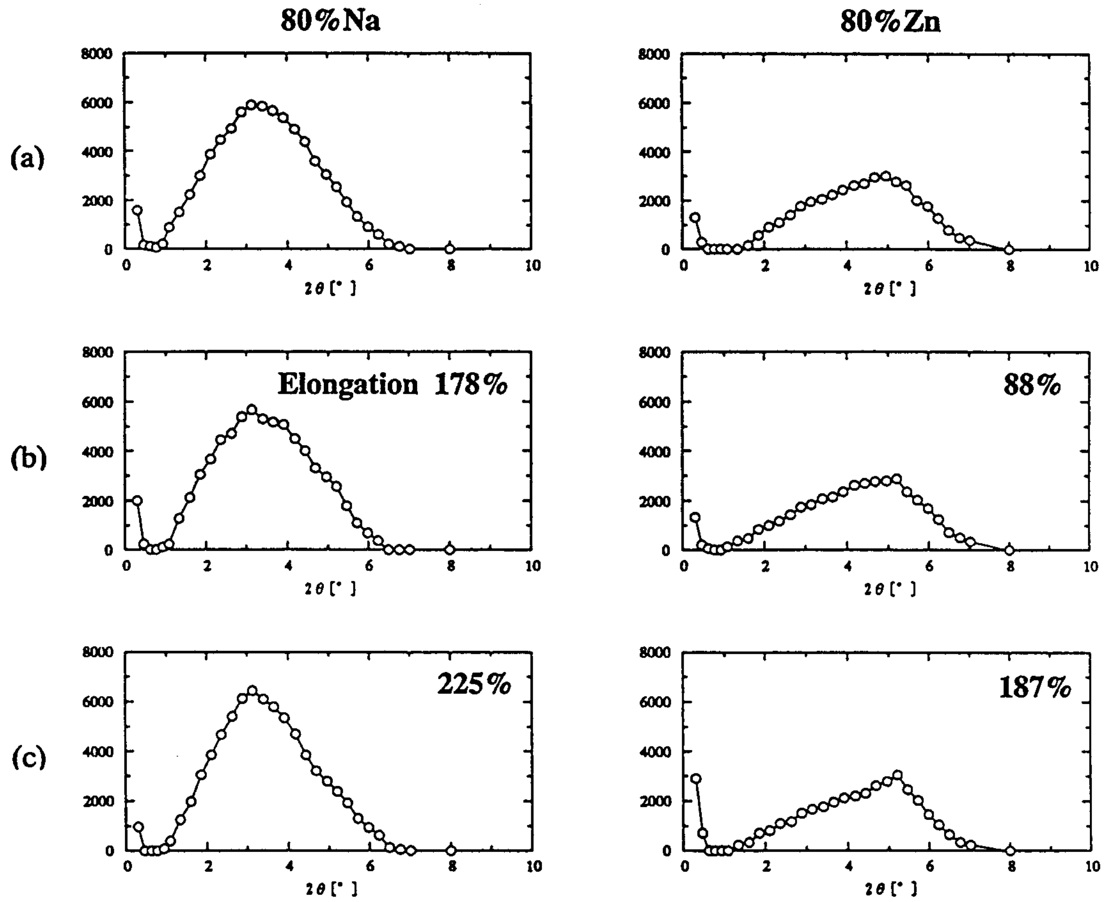

Figure 10 Changes in SAXS pattern of 80Na and 80Zn by tensile deformation without aging: (a) before deformation; (b) after tensile impact (3 m/s) deformation; (c) after very low speed tensile (2 mm/min) deformation.

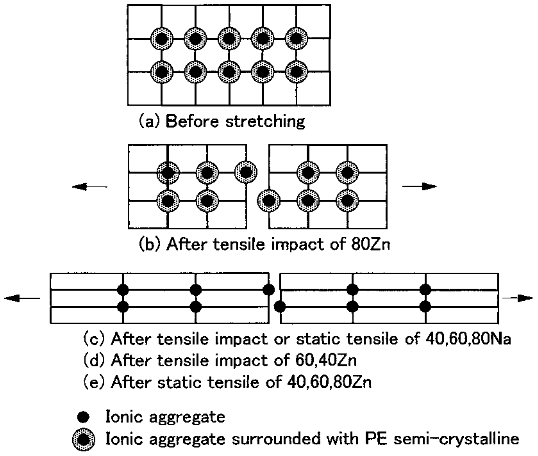

Figure 11 Schematic models of Ionomers before and after tensile deformation. Solid circle indicates ionic aggregate. Double circle indicates ionic aggregate surrounded with PE semicrystalline, where the melting point is T_i. Solid lines indicate amorphous polymer chains. In these models, PE crystalline was ignored: (a) before stretching of Ionomer, (b) after tensile impact fracture of 80Zn; (c) after tensile impact or very low speed tensile fracture of 40, 60, and 80Na; (d) after tensile impact fracture of 40 and 60Zn; (e) after very low speed tensile fracture of 40, 60, and 80Zn.

strain at failure becomes smaller. When the neutralization degree becomes higher, deformation becomes more elastic, and the destruction mode changes from ductile to brittle.

As for "the hardness," the crosslinkage of the Zn aggregate is stronger than the Na aggregate. Furthermore, the strength of the crosslinkage is made weak by moisture and the influence of moisture for the Na aggregate is stronger than the Zn aggregate. This behavior is explained by the theory of ion hopping or acid-cation exchange[15,16] reported for melt rheology of Ionomers. In Na ionomers, carboxylic acid hops between ionic aggregates during the stretching process. Moisture helps ion hopping. On the other hand, in the Zn ionomers, ion hopping does not occur, because unneutralized carboxylic acid is located out of the ionic aggregates. (Relaxation time of Zn aggregates is much longer than Na aggregates).

Figure 11 shows schematic models of Ionomers both before and after stretching. In the case of 80Zn, PE semicrystalline is not destroyed after tensile impact. In the other cases, PE semicrystalline were destroyed by stretching.

CONCLUSION

We have come to the conclusion that major factors that determine impact behaviors of ionomers are degree of crosslinkage with ionic aggregates and "the hardness" of ionic aggregates. We found that a highly neutralized Zn Ionomer was very brittle because of the high degree of crosslinkage and long relaxation time of ionic aggregates.

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