Structure of Multinetwork Elastomer: Comparison with Hydrogen Bond Cross-Linking Elastomer

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ABSTRACT: Earlier, we developed a multinetwork elastomer (MNE) by using a covalent bond, hydrogen bond, and clay plane bond. By taking advantage of the characteristics of each cross-linking, the thermoplastic elastomer shows excellent compression set resistance (indicators of how much it recovers when the rubber is compressed), good flowability, and high tensile properties. In the previous report, it was thought that the cross-linked part was hydrogen bonded to the end face of the clay. However, it was estimated that the cross-linked part also has ion–dipole interaction with ammonium cations and/or anionic parts on the clay surface by further structural analysis, and a new estimated structure was proposed. In addition, it was found that the addition effect of organic clay was a specific phenomenon in the MNE from the comparison with the hydrogen bond cross-linking elastomer (HBE). In a HBE that expresses physical properties only by the hydrogen bond, the interaction between the clay and the hydrogen bond cross-linkage weakened the hydrogen bond cross-linking between polymers to cause deterioration of the physical properties. However, in the MNE with stable covalent cross-linking, cross-linking does not change, and the hydrogen bond cross-linking site interacts with the clay surface to cause nonlocalization of the cross-linking part. Therefore, the physical properties have been improved.

1. INTRODUCTION

Cross-linking is one of the most important factors for rubber properties. Since Charles Goodyear discovered sulfur vulcanization in 1839, the rubber industry has developed. Since the interaction between rubber chains consisting of hydrocarbons is very weak, the rubber cannot show good mechanical properties without cross-linking. Therefore, the rubber goods are cross-linked by covalent bonds such as sulfur or peroxide cross-link. However, since the covalent bond, which has high bond energy, cannot be cleaved by heating, the rubber cannot be remolded. Hence, more than 50% of worn-out tires are burned as a thermal energy source without material recycling. Reusage of the waste vulcanized rubber as a raw material is an urgent issue for environmental conservation. On the other hand, the thermoplastic elastomer is cross-linked by physical interaction between the polymer chains instead of covalent bond. Since the physical cross-linking can be easily cleaved by heating, the thermoplastic elastomer can be remolded. However, since the bonding energy of the physical interaction is low, the mechanical properties, especially compression set, are poor.

Until now, attempts to use different types of cross-linking together have been carried out. For example, double networks consisting of sulfur and peroxide cross-links have been reported to increase strength of the rubber.\(^1\)\(^\text{−}\)\(^6\) Moreover, in the field of gel science, double networks using strong and weak cross-links have been reported to increase the strength, because the weak cross-link is destroyed sacrificially to dissipate energy, prior to breaking of the strong cross-link.\(^7\) Further, in the field of polymer clay nanocomposites, it is known that clay is added into polyamide and polyolefin to increase strength,\(^8\)\(^\text{−}\)\(^10\) and the addition of clay to a gel increases strength too,\(^11\) because the clay plane interacts with the polar groups of polymers and dissipates energy under external stresses. Consequently, since the stress concentration to the polymer chain is prevented, the strength increases.\(^12\) We have developed a thermoreversible cross-linking rubber, which is recyclable, reformable and has similar mechanical properties to those of vulcanized rubber at room temperature, by using supramolecular hydrogen bonds.\(^13\)\(^\text{−}\)\(^16\)

Although the mechanical properties for deformation in a short time such as tensile properties were good, creep resistance (compression set) of the elastomer was high (poor) due to the cleavage of the hydrogen bonds under heating (70 °C, 22 H, 25% compression ≥ 50%). The creep resistance (compression set) is one of the most important properties for rubber goods. If

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the compression set is high, the rubber goods cannot be used due to deformation. Therefore, with the aim of developing a higher performance elastomer, we examined a multinetwork system with three kinds of cross-linking of hydrogen bonds, covalent bonds, and clay plane bonds. As a result, we have developed an elastomer that is thermoplastic but very strong and creep resistant by taking advantage of the characteristics of hydrogen bonds, covalent bonds, and clay plane bonds. It shows a good compression set by covalent bonding, good fluidity by the dissociation of hydrogen bonds during heating, and good tensile properties due to the increased hysteresis energy of clay plane bonds. In this study, to improve the cross-linking structure proposed in the previous report to a more accurate structure, we propose a new estimation structure by further structural analysis by comparison with a hydrogen bond cross-linked elastomer (HBE).

2. EXPERIMENTAL SECTION

2.1. Materials. The compounds described below were used.

- 3-Amino-1,2,4-triazole (ATA): Kanto Chemical Co., Inc.
- Tris(2-hydroxyethylisocyanurate)(THI): Nissei Corporation, NISSEI THEIC
- Organic clay: [Si$_3$(Al$_{1.34}$Mg$_{0.66}$O)$_{42}$O$_{12}$O$_6$(OH)$_{42}$][NR$_3$)$_2$]
- Maleated ethylene-butene elastomer (maleated EBM): MITSUI CHEMICALS, INC, Tafmer MH5020, MFR; 1.2 g/10 min (230 °C), density: 866 kg/m$^3$, hardness (Shore A) 55, ethylene content: 56 weight%, maleic anhydride unit: 2.02 nm (powder X-ray diffraction peak value 2$\theta$ = 4.369°)
- Maleated ethylene-butene elastomer (maleated EBM): MITSUI CHEMICALS, INC, Tafmer MH5020, MFR; 1.2 g/10 min (230 °C), density: 866 kg/m$^3$, hardness (Shore A) 55, ethylene content: 56 weight%, maleic anhydride ratio: 1.48 wt %.

2.2. Synthesis. 2.2.1. Synthesis of Elastomers Having Only Surface Cross-Linking: Addition of Organic Clay to Maleated EBM (Table 8, Run 1). An amount of 60 g (9.06 mmol; maleic anhydride unit) of maleated EBM was masticated at 20 rpm at 180 °C for 2 min in an internal mixer (Toyo Seiki Co., Ltd., LaBoplast Mill 10C100, capacity 100 c). Subsequently, 0.6 g of organic clay was added and kneaded for 12 min to give the thermoplastic elastomer (Table 2).

2.2.2. Synthesis of Hydrogen-Bonded Cross-Linked Elastomer (HBE): Additional Reaction of ATA to Maleated EBM (Table 8, Run 2). An amount of 60 g (9.06 mol; maleic anhydride unit) of maleated EBM was masticated at 20 rpm at 180 °C for 2 min in the internal mixer. Subsequently, 0.762 g (9.06 mmol) of 3-amino-1,2,4-triazole (ATA) was added and kneaded for 12 min to give the thermoplastic elastomer. The introduction of ATA to the maleated EBM was identified by IR analysis, which showed the disappearance of peaks based on acidic anhydride at 1690 cm$^{-1}$ and the existence of peaks due to imide (Table 3).

| Table 1. Analysis Data of Maleated EBM |
|----------------------------------------|
| IR (ATR-FTIR)                          |
| 2959, 2918, 2850 (C=O of maleic anhydride), 1461 (–CH$_2$– bending), 1379 (–CH$_3$ bending), 1263, 1021, 771, 719 cm$^{-1}$ |
| solid state $^{13}$C NMR (499.7 MHz) $\delta$ in ppm |
| 10.87 (–CH$_3$), 25.96 (branch –CH$_2$–), 26.84, 29.92, 31.89, 33.29 (–CH$_2$–CH(–CH$_2$–)–CH$_3$–), 38.85 (–CH$_2$–CH(–CH$_2$–)–CH$_3$–) |
| TGA analysis (heating rate: 10 °C/min, under N$_2$) |
| $T_d$ = 40.4 °C |

| Table 2. Analysis Data of Run 1 in Table 8 |
|----------------------------------------|
| IR (ATR-FTIR)                          |
| 2959, 2918, 2850 (C=O of maleic anhydride), 1461 (–CH$_2$– bending), 1379 (–CH$_3$ bending), 1265, 1093, 1036, 917, 771, 719, 628, 516, 462 cm$^{-1}$ |
| solid state $^{13}$C NMR (499.7 MHz) $\delta$ in ppm |
| 10.87 (–CH$_3$), 25.96 (branch –CH$_2$–), 26.84, 29.92, 31.89, 33.29 (–CH$_2$–CH(–CH$_2$–)–CH$_3$–), 38.85 (–CH$_2$–CH(–CH$_2$–)–CH$_3$–) |
| TGA analysis (heating rate: 10 °C/min, under N$_2$) |
| $T_d$ = 420.5 °C |

| Table 3. Analysis Data of Run 2 in Table 8 |
|----------------------------------------|
| IR (ATR-FTIR)                          |
| 2959, 2918, 2850 (C=O of maleic anhydride), 1461 (–CH$_2$– bending), 1379 (–CH$_3$ bending), 1264, 771, 720 cm$^{-1}$ |
| solid state $^{13}$C NMR (499.7 MHz) $\delta$ in ppm |
| 10.87 (–CH$_3$), 25.96 (branch –CH$_2$–), 26.84, 29.92, 31.89, 32.55, 33.36 (–CH$_2$–CH(–CH$_2$–)–CH$_3$–), 38.85 (–CH$_2$–CH(–CH$_2$–)–CH$_3$–) |
| TGA analysis (heating rate: 10 °C/min, under N$_2$) |
| $T_d$ = 532.0 °C |

2.2.3. Synthesis of Elastomers Having Hydrogen Bond and Clay Plane Bond: Addition Reaction of Organic Clay and ATA to Maleated EBM (Table 8, Run 3). An amount of 60 g (9.06 mmol; maleic anhydride unit) of maleated EBM was masticated at 20 rpm at 180 °C for 2 min in an internal mixer. Subsequently, 0.6 g of organic clay was added and kneaded for 4 min. Moreover, 0.762 g (9.06 mmol) of 3-amino-1,2,4-triazole (ATA) was added and further kneaded for 8 min to give the thermoplastic elastomer. The introduction of ATA to the maleated EBM was identified as with Run 2 (Table 4).

2.2.4. Synthesis of Hydrogen-Bond and Covalent Bond Cross-Linking Elastomer: Additional Reaction of THI to Maleated EBM (Table 8, Run 4). An amount of 60 g (9.06 mmol; maleic anhydride unit) of maleated EBM was masticated at 20 rpm at 180 °C for 2 min in an internal mixer. Subsequently, 0.789 g (0.003 mol; OH: 9.06 mmol) of THI was added and kneaded for 12 min to give the thermoplastic elastomer. The introduction of THI to the maleated EBM was identified by IR analysis, which showed the disappearance of peaks based on acidic anhydride at 1690 cm$^{-1}$ and the existence of peaks due to ester (Table 5).

2.2.5. Synthesis of Covalent Bond, Hydrogen Bond, and Clay Plane Bond (Multinetwork Elastomer): Addition Reaction of Organic Clay and THI to Maleated EBM (Table 8, Run 5). An amount of 60 g (9.06 mmol; maleic anhydride unit) of maleated EBM was masticated at 20 rpm at 180 °C for 2 min in an internal mixer. Subsequently, 0.6 g of organic clay was...
added and kneaded for 4 min. Finally, 0.789 g (0.003 mol, OH: 9.06 mmol) of THI was added and further kneaded for 8 min. The introduction of THI to the maleated EBM was identified as with Run 4 (Table 6).

2.2.6. Synthesis of Covalent, Hydrogen Bond, And Surface Cross-Linking Elastomer: Addition Reaction of THI and Organic Clay to Maleated EBM (Table 8, Run 6). An amount of 60 g (9.06 mmol; maleic anhydride unit) of maleated EBM was masticated at 20 rpm at 180 °C for 2 min in an internal mixer. Subsequently, 0.789 g (0.003 mol, OH: 9.06 mmol) of THI was added and kneaded for 8 min. Finally, 0.6 g of organic clay was added and further kneaded for 4 min. The introduction of THI to the maleated EBM was identified as with Run 4 (Table 7).

2.3. Evaluation. 2.3.1. Procedure of Making Sheets. Sheets of the obtained elastomers were prepared by press molding at 200 °C for 10 min under 18 MPa of pressure and successive cold press molding for 2 min under the same pressure. Sheets having the size: 2 mm × 15 cm × 15 cm were obtained.

2.3.2. Hardness. Shore A hardness is measured by stacking five pieces of the obtained sheets according to ASTM D 2240.

2.3.3. Tensile Properties. No. 3 dumbbell-like test pieces were punched from the obtained sheet. Stress–strain properties were measured at a speed of 500 mm/min on a Toyo Seiki Seisaku-sho Strograph VE instrument according to JIS K6251 using type 3 dumbbells (N = 3). The 100% modulus [MPa], 300% modulus [MPa], tensile strength (Tg) [MPa], and elongation at break (Eg) [%] were measured at room temperature. 100% and 300% modulus are the stresses at 100% and 300% elongation, respectively. Here, 100% modulus correlates with cross-linking density.

2.3.4. Compression Set. Compression set was measured according to JIS K6262. A disk-shaped sample (12.5 ± 0.5 mm ø) was cut from the sheet, and the height was adjusted to 12.5 ± 0.5 mm by stacking seven pieces of the disk-shaped sample. The stacked columnar sample was compressed 25% from the original height and kept at 70 °C for 22 h. After releasing the pressure, the sample was kept at room temperature for 30 min and the height was measured. By comparing the before and after heights, the compression set ratio was calculated.

2.3.5. Glass Transition Temperature (Tg) and Hysteresis Energy. The glass transition temperature (Tg) and hysteresis energy were measured with a dynamic viscoelasticity analyzer using a Rheoel-E4000 apparatus (UBM Co., Ltd., tension mode) at a 3 °C/min heating rate, 0.1% strain, and 10 Hz frequency. Tg values for each elastomer were determined from the peak top of tan δ. Each hysteresis energy was estimated by tan δ.

2.3.6. 5% Weight Decrease Temperature. The 5% weight decrease temperature (T5%), which was determined as the temperature at which decreased by 5% from the initial weight, was measured with a thermogravimetric analyzer on a TA Instruments model DSC2920 instrument at 10 °C/min of heating rate.

### Table 4. Analysis Data of Run 3 in Table 8

| IR (ATR-FTIR) | 2960, 2925, 2854, 1787 (C=O), 1727 (C=O), 1639 (−NH−CO−), 1596, 1526 (−NH−CO−), 1449, 1376, 1176, 1044, 835, 728 cm⁻¹ |
| solid state ¹³C NMR (499.7 MHz) δ in ppm | 18.7 (s, CH₂=CH(C=H)−), 23.9 (s, CH₂=CH(C=H)−), 26.5 (s, –CH₂−CH=), 28.6 (s, –CH₂−CH=), 32.0 (s, –CH₃), 37.7−41.0 (m, –CH₃, –CH₂−), 109.0 (bs, −C(CH₃)=CH₂), 111.4 (s, −C(=CH₂)=CH₂), 125.3 (s, −CH₂−C(=CH₂)=CH₂), 135.1 (s, −CH₂−C(=CH₂)=CH₂), 149.0 (bs, −N=CH−CH−NH−), 175.8 (bs, −N=CH−CO−), 185.7 (bs, −COOH) |
| elemental analysis | found: C, 83.40; H, 10.97; N, 2.84; O, 2.79. |
| TGA analysis (heating rate: 10 °C/min, under N₂) | Td₅ (5% weight loss temperature): 429.1 °C |

### Table 5. Analysis Data of Run 4 in Table 8

| IR (ATR-FTIR) | 2959, 2919, 2851, 1791 (C=O of maleic anhydride), 1729 (C=O), 1697 (C=O), 1558 (−COO−), 1460, 1379, 1262, 1097, 802, 720 cm⁻¹ |
| solid state ¹³C NMR (499.7 MHz) δ in ppm | 18.7 (s, CH₂=CH(C=H)−), 23.9 (s, CH₂=CH(C=H)−), 26.5 (s, –CH₂−CH=), 28.6 (s, –CH₂−CH=), 32.0 (s, –CH₃), 37.7−41.0 (m, –CH₃, –CH₂−), 109.0 (bs, −C(CH₃)=CH₂), 111.4 (s, −C(=CH₂)=CH₂), 125.3 (s, −CH₂−C(=CH₂)=CH₂), 135.1 (s, −CH₂−C(=CH₂)=CH₂), 149.0 (bs, −N=CH−CH−NH−), 175.8 (bs, −NH−CO−), 185.7 (bs, −COOH) |
| elemental analysis | found: C, 83.40; H, 10.97; N, 2.84; O, 2.79. |
| TGA analysis (heating rate: 10 °C/min, under N₂) | Td₅ (5% weight loss temperature): 429.0 °C |

### Table 6. Analysis Data of Run 5 in Table 8

| IR (ATR-FTIR) | 2959, 2919, 2850 (C−H stretching), 1790 (C=O of maleic anhydride), 1734 (C=O), 1698 (C=O), 1677, 1461 (−CH₃−bending), 1379 (−CH, bending), 1264, 1094, 1037, 969, 767, 720 cm⁻¹ |
| elemental analysis | found: C, 84.1; H, 14.5; N, < 0.1; O, 1.3 |
| dynamic viscoelasticity analysis | Td₅ ~ 51.9 °C |
| TGA analysis (heating rate: 10 °C/min, under N₂) | Td₅ (5% weight loss temperature): 420.0 °C |

### Table 7. Analysis Data of Run 6 in Table 8

| IR (ATR-FTIR) | 2959, 2918, 2850 (C−H stretching), 1790 (C=O of maleic anhydride), 1735 (C=O), 1697 (C=O), 1677, 1462 (−CH₃−bending), 1379 (−CH, bending), 1265, 1094, 1038, 969, 768, 720 cm⁻¹ |
| dynamic viscoelasticity analysis | Td₅ ~ 52.0 °C |
| TGA analysis (heating rate: 10 °C/min, under N₂) | Td₅ (5% weight loss temperature): 420.3 °C |
2.3.7. Self-Healing Property. A sheet (1 mm × 5 cm × 5 cm) with a 5 mm notch was heated at each temperature for 10 min, increasing every 20 °C from 60 °C. The self-healing temperature was determined by adhering the notch part.

2.3.8. Infrared Analyses (IR). IR analyses were performed using a Thermo Fisher scientific model FT-IR Nicolet iS10 instrument by the ATR method.

2.3.9. Solid NMR Analyses. Solid NMR analyses were performed using a CSX-270W instrument (manufactured by JEOL).

2.3.10. Recyclability. Recyclability was evaluated via the capability of reforming more than 10 times.

2.3.11. Atomic Force Microscopy (AFM) Measurement. The AFM measurement in this study was performed using a commercial AFM system OXFORD INSTRUMENTS Asylum Research Jupiter XR with a Fast Force Map mode (Set point 100 nN, Points:256, Force Dist:1.50 μm, Z rate:200 Hz). A cantilever used in this mode was made by Asylum Research (AC240TS-R3) with a nominal spring constant of 2 N m\(^{-1}\) and a tip radius of 7 nm. Before the measurement, the actual spring constant of the cantilever was measured by following Sader’s method.

2.3.12. Small Angle Neutron Scattering (SANS) Measurement. Small angle neutron scattering measurements were performed at BL-20 at the Ibaraki Prefectural Material Structure Analyzer (iMATERIA) in the Materials and Life Science Experimental Facility (MLF), Japan Proton Accelerator Research Complex (J-PARC), Tokai Village, Ibaraki Prefecture, Japan under a user program (Proposal No. 2020BM0001).

The measurement samples (1 mm × 15 mm ø) were swollen with 150 wt % toluene-\(d_8\) to visualize the cross-linking structure. The two-dimensional scattering was obtained regarding detector sensitivity, and a one-dimensional scattering profile was obtained by taking the background in consideration of the transmittance and taking the circular average. It was converted to absolute strength using a glassy carbon standard sample.

3. RESULTS

3.1. Synthesis and Physical Properties. As a method for introducing a hydrogen bonding and covalent bonding moiety to the elastomer, an addition reaction of maleic anhydride moiety followed by a reaction of active hydrogen compounds, in the solid phase, has been used. The reasons are as follows: (1) Since the addition reaction of active hydrogen compounds to the cyclic acid anhydride moiety has been known to proceed very effectively, the reaction of maleated elastomer with active hydrogen compounds was expected to proceed efficiently even in the solid phase kneading process. (2) At the same time as the generation of covalent cross-linking, carboxylic acid, ester (reaction of acid anhydride structure and hydroxyl group), and amide (reaction of acid anhydride structure and amine) were generated, and they were expected to function as a strong hydrogen binding site. (3) Since the addition reaction of maleic anhydride to rubber has been industrially established as the simplest introducing method of polar groups,\(^{18,19}\) maleated rubber is industrially available. As the substrate polymer, commercially available maleic acid grafted ethylene butene rubber (maleated EBM) was selected, because the rubber has low \(T_g\), low hardness, and sufficient mechanical strength.

The addition reaction of the active hydrogen compounds to maleated EBM was carried out by kneading at 20 rpm, 180 °C for 14 min in an internal mixer. The reaction between various active hydrogen compounds (hydroxyl groups and amino groups) and acid anhydride groups were confirmed by ATR-IR and solid-state NMR analysis. The introduction of active hydrogen compounds was identified by the decrease in absorption near 1790 cm\(^{-1}\) based on the acid anhydride structure as well as the appearance of the peaks based on ester or imide (Scheme 1).

The physical properties of the obtained elastomer are shown in Table 8.

As a hydrogen bond cross-linking, the previously performed 3-amino-1,2,4-triazole was reacted to the maleated EBM\(^{15-16}\) (Table 8 Run 2). In this reaction with EBM as the main chain, it was confirmed that the reaction did not stop at amic acid but
Table 8. Formulations and Properties of Test Samples

| run | cross-linking type | 1 | 2 | 3 | 4 | 5 | 6 |
|-----|-------------------|---|---|---|---|---|---|
|     |                   | PB | HB | HB | HB | HB | HB |
|     | +PB +CB +CB +CB +PB +PB |
| maleated ethylene butene rubber (phr) | 100 | 100 | 100 | 100 | 100 | 100 |
| organic clay (phr) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| 3-amino-1,2,4-triazol (ATA, phr) | 1.27 | 1.27 | 1.27 | 1.27 | 1.27 | 1.27 |
| tris(2-hydroxyethyl) isocyanurate (THI, phr) | 1.31 | 1.31 | 1.31 | 1.31 | 1.31 | 1.31 |
| Shore A hardness | 56 | 57 | 57 | 49 | 49 | 50 |
| 100% modulus (MPa) | 1.39 | 1.63 | 1.67 | 2.15 | 1.56 | 1.54 |
| 300% modulus (MPa) | 1.98 | 2.41 | 2.41 | – | 3.41 | 3.00 |
| tensile strength (MPa) | 5.30 | 9.62 | 7.25 | 4.99 | 5.02 | 4.29 |
| elongation at break (%) | 1630 | 1191 | 1273 | 257 | 448 | 428 |
| tear strength (N/cm) | 308 | 314 | 318 | 207 | 223 | 200 |
| compression set (%) | 90 | 79 | 85 | 38 | 32 | 54 |

*aOrganic clay was added after addition of THI. bHB: hydrogen bond, CB: covalent bond, PB: clay plane bond. cParts per one hundred of rubber by weight.

progressed to imide from IR and NMR analysis as shown in Scheme 1. In this case, although the tensile strength and the elongation at break are sufficient, the compression set is high (poor). Cleavage of the hydrogen bonds under heating (70 °C) may result in the high compression set. Next, tris(2-hydroxyethyl)isocyanurate (THI) was selected as a cross-linking agent that simultaneously generates hydrogen bonds and covalent bonds. It is expected that THI can generate three covalent cross-linking points and the isocyanurate ring can form hydrogen bonds with carboxylic acid and ester, which is generated by the reaction of the maleic anhydride moiety and the hydroxyl group. In THI (hydrogen bond + covalent bond, Run 4), although the tensile strength and the elongation at break are low, the compression set is low (good). The low compression set might be caused by the stable covalent cross-linking under heating (Table 8 Run 4). Meanwhile, the low tensile strength and elongation at break should be caused by the lack of hysteresis energy. Since stress may concentrate on specific points by the lack of hysteresis energy, the elastomer structure may be broken quickly. Since the tensile properties may be improved by increasing the hysteresis energy and reducing the stress concentration by interaction between the polymer and filler, the addition effect of the filler was examined. The addition of carbon black and silica, which are common fillers for rubber, led to severe shrinkage of the sheet due to the low dispersion of the filler by the low interaction between the polymer and the filler. Since it has been reported that the mechanical strength of polymer nanocomposites is made to be higher by clay addition, we examined the addition of clay to the elastomer. First, untreated bentonite was used as the clay. However, untreated montmorillonite cannot be dispersed sufficiently in the elastomer. Therefore, organic clay was used to improve the dispersion according to the method of Usuki et al. As a result, significant improvements of elongation at break and compression set were observed (MNE, Run 5). This was presumed to be due to the higher dispersion of clay by the interaction of hydroxyl groups on the clay end face and/or ammonium salts between the layers with carboxy groups, ester bonds, and isocyanurate rings in the cross-linked part of the polymer. In general, compression set correlates with cross-linking density, but in this case the compression set decreases even though the 100% modulus, which correlates with the cross-linking density, is reduced. Clay interacts with the hydrogen bond sites of the cross-linking part and may suppress the hydrogen bonds from dissociation and recombination during compression set test.

In this synthesis, in the case of kneading organic clay before hydrogen bonding + covalent bond cross-linking (Run 5) and the case of kneading organic clay after the cross-linking (Run 6), Run 5 had higher physical properties (high tensile strength and low compression set) than Run 6. This is considered to be due to the fact that the cross-linking part and the clay surface interact more easily because the cross-linking progressed after the organic clay interacted with the acid anhydride group. On the other hand, when organic clay is added after hydrogen bond + covalent cross-linking, it is found that the cross-linking is tight and does not interact well with organic clay. When only organic clay is added (Run 1), the 100% modulus (cross-linking density) is low and the compression set is also very high, because cross-linking did not proceed. Furthermore, since organic clay is added to the hydrogen bond cross-linking elastomer (HBE, Run 3), the tensile strength decreases (Run 2 → 3) and the compression set increases. It is likely that the hydrogen bond cross-linking between polymers is weakened by interaction of the hydrogen bond cross-linking with clay. In summary, in the case of HBE, the tensile strength decreased and compression set increased due to the addition of clay (comparison between Run 2 and 3), while in MNE (Run 5) tensile strength increased, and compression set decreased with the addition of clay (comparison between Run 4 and 5). Therefore, the addition effect of organic clay is likely to be specific in this multinetwork system.

As for examination of other cross-linking agents and variation amounts of THI and clay, please refer to the previous report.

The physical properties of the obtained elastomer (Table 8 Run 5) are shown in Table 9.

Table 9. Properties of MNE*

| properties | value |
|------------|-------|
| glass transition temperature (°C) | −41.3 |
| 5% weight loss temperature (°C) | 403 |
| recyclability | >10 times |
| self healing temperature (°C) | 140 |

Table 8, Run 5. a Determined by DSC. b Determined by TGA under N2. c Time of reforming. d Self-adhesion ability

The glass transition temperature (T_g) of the obtained elastomer, which is observed via a dynamic mechanical analyzer (DMA), was almost same as that of the starting maleated EBM (T_g = −40.4 °C). It indicates that cross-linkages do not disturb the micro-Brownian motion of the main chain segment. The obtained elastomer has similar good properties at low temperature, such as low brittle temperature, to those of the starting elastomer. Moreover, the 5% weight loss temperature was very high (403 °C), which is about 100 °C higher than that for the general thermoplastic elastomer. The obtained elastomer has thermoplasticity and can be recycled at least 10 times without deterioration of the properties. It was confirmed that the...
tensile strength after 10 times reforming was maintained at 93% (4.67 MPa) of the initial strength. Moreover, the self-healing temperature, which can adhere itself by heating, was confirmed at 140 °C. The 1 mm thickness sheet having a 5 mm notch was heated at each temperature for 10 min, increasing every 20 °C from 60 °C. Adhesion of the notch was confirmed at 140 °C, which can be derived from the recombination of hydrogen bonds (adhesion strength 3.65 MPa, retention rate 73%). The introduction of covalent bonds can improve the compression set but deteriorate the self-healing property. This is thought to be due to the difficulty of recombination of cross-linking. Self-healing materials are important research subjects from the viewpoint of long-life and maintenance free, and it is shown that the MNE can be expected to be applied as a self-healing material.

3.2. Structural Analysis. 3.2.1. Transmission Electron Microscopy (TEM). TEM images of Run 3 and Run 5 samples are shown in Figure 1.

The added clay can be confirmed as a black streak. In HBE (Run 3), clay did not disperse and existed as linear aggregates as shown in Figure 1a and b. Since the interlayer of organic clay has been confirmed to be 2.02 nm from powder X-ray diffraction, the interlayer does not appear to spread from the image. It is presumed that the HBE is not intercalated between the layers of clay, but may be hydrogen bonded to the hydroxyl group at the clay end.

On the other hand, in the MNE (Run 5), clay was dispersed unevenly as shown in Figure 1c. The size of the clay is 100–300 nm (Figure 1c) and appears to be oriented in the direction of the arrow at intervals of about 10–15 nm (Figure 1D). Since the interlayers of organic clay before addition are 2.02 nm, it is presumed that the interlayers are spread by interacting with the cross-linking part. Clay exists orientationally in the clay presence part, but there is no effect by orientation because clay is not uniformly dispersed in the elastomer.

3.2.2. Infrared Spectroscopy (IR) Measurement. Figure 2 shows IR spectra of maleated EBM, Runs 1–3, and organic clay.

By adding only organic clay (Run 1), the absorption of acid anhydride was confirmed at 1790 cm⁻¹ and the absorption of carboxylic acid could not be confirmed, so it can be seen that the acid anhydride structure does not react with organic clay. In addition, the absorption of carbonyl groups of acid anhydrides of maleated EBM (1789 cm⁻¹) has shifted slightly the number of the high wave number (1 cm⁻¹), which may suggest a little interaction. In the HBE (Run 2), the peak of the carbonyl group of imides was confirmed at 1729 cm⁻¹. When organic clay was added to the HBE (Run 3), the peak of the carbonyl group of 1729 cm⁻¹ shifted slightly to 1727 cm⁻¹ by a few low wave numbers. This suggests that the ionicity of the carbonyl group is slightly increased by interacting with the clay surface.
Next, Figure 3 shows IR spectra of maleated EBM, Runs 1, 4, 5, and organic clay.

The addition of THI (Run 4) reduces the absorption of acid anhydrides as a raw material at 1790 cm$^{-1}$, but does not completely disappear. Since this absorption does not decrease even if THI is added excessively, the OH group is enough, but the reaction seems to stop. Furthermore, the absorption peak of acid anhydride (1790 cm$^{-1}$) almost disappeared with the addition of THI and organic clay (Run 5). The presence of ammonium salts in organic clay is considered to be a catalyst to promote the reaction between acid anhydride groups and OH groups. An absorption peak also appeared at 1734 cm$^{-1}$. This peak seems to have shifted from 1729 cm$^{-1}$ due to the interaction of the carboxylic acid with clay. This tendency is the opposite of the low wavenumber shift by the clay addition to HBE. Since the layers of clay are spreading in the TEM image, it is thought that the hydrogen bond between carboxylic acids is weakened by ion–dipole interaction with ammonium salts between the layers to result in a high wavenumber shift.

3.2.3. DMA Measurement. In the DMA measurement of HBE (Run 2) and addition of clay to HBE (Run 3), a decrease in tan $\delta$ representing hysteresis energy (Run 2 $\rightarrow$ Run 3) was observed with the addition of clay (Figure 4). However, in the case of MNE, an increase in tan $\delta$ (Run 4 $\rightarrow$ Run 5) was observed with the addition of clay. This supports the increase in tensile strength due to energy dissipation.

3.2.4. AFM Measurement. AFM measurement of the elastomer surface was performed in a viscoelastic mode that sensed the Young’s modulus of the sample (Figure 5). The light color part of the image corresponds to the high elasticity part, and the dark color part corresponds to the low elasticity part. In the organic clay addition system (Run 1, PB), the low elasticity part is widely observed to form a domain of about 10–20 nm, and a highly elastic part surrounds the domain. In Run 2, the color is slightly lighter than that of Run 1 and the elastic

Figure 3. IR spectra of the obtained elastomers synthesized by 1 phr of organic clay (Run 1), 1 equiv of THI (Run 4), and 1 equiv of THI with 1 phr of organic clay (Run 5). HB: hydrogen bond, CB: covalent bond, PB: clay plane bond.

Figure 4. DMA graph of the obtained elastomers. HB: hydrogen bond, CB: covalent bond, PB: clay plane bond. The lower panel of Figure 4 is reproduced from Figure 6 in ref 17 under a CC-BY license.
modulus is increased. Furthermore, when clay is added to the HBE, it can be seen that the elastic modulus increases and the domain becomes larger. This is thought to be a big reflection of the hardness of clay. On the other hand, in the Run 4 sample (HB+CB) in which covalent bonds and hydrogen bonds are introduced, a thin part of the high elastic color spreads throughout the sample, but the domain size (about 20−30 nm) of the low elastic modulus portion is a little larger than that for Run 1. On the other hand, in multinetwork systems (covalent bonds, hydrogen bonds, and organic clay) (Run 5, HB+CB +PB), the domain size of the low elastic modulus portion was slightly increased and more dispersed than that in Run 4, and the intermediate modulus of elasticity was widely observed. It also can be seen that the elastic modulus decreases. This is consistent with the phenomenon that modulus is decreasing in a tensile test. Organic clay itself could not be observed in Run 3 and Run 5. Therefore, by changing the push depth of the probe from about 20−100 nm to a few nm and changing the probe diameter from 7 nm to less than 5 nm, a white point with a high Young’s modulus was observed (Figure 5, right panel). It is considered to be clay probably because it looks streaky when increasing the addition amount (4 phr). From this, if the push depth is too deep, it seems that the difference in the Young’s modulus of the clay on the surface could not be sensed well due to the averaging of the Young’s modulus in the depth direction. That is, it is considered that clay exists in the images for Run 1, Run 3, and left of Run 5 in Figure 5, but it is not possible to sense it. Consequently, the modulus was increased by the addition of clay in HBE, whereas the modulus was reduced in MNE.

3.2.5. Small Angle Neutron Scattering Measurement. Next, small angle neutron scattering was measured to study the cross-linking state (Figure 6).

In Figure 6, the small angle neutron scattering of HBE (Run 2) was compared to HBE with added organic clay (Run 3). Run 3 has a slightly higher scattering intensity than Run 2 does. Since the clay was not dispersed in the TEM image, it is thought that the hydrogen bond cross-linkage is hydrogen bonded to the hydroxyl group on the clay end surface and the hydrogen bond cross-linkage becomes uneven (biased); it is in line with the result of the physical property decrease due to the addition of clay (Run 2 → Run 3). In Run 4 (hydrogen bond and covalent bond, HB+CB), the scattering intensity is high over the entire wavenumber, and the peak of scattering is observed around the wavenumber $q = 0.03$.
organic clay after the cross-linking reaction by THI and of Run 5 with kneaded clay before the cross-linking reaction were compared. It can be seen that Run 6 has a higher scattering intensity than Run 5 does, which indicates that the dispersion state of the hydroxyl group of THI and the maleic acid of maleated EBM, covalent cross-linking by esters is generated and carboxylic acid is generated at the same time. Isocyanurate rings are considered to be complexly hydrogen-bonded with carboxylic acids and esters. Clay also seems to interact with carboxylic acids and esters, and isocyanurate rings at cross-linking points.

In Figure 9 schematically shows the effect of clay. In hydrogen bonding + covalent bond cross-linking, the distance between the cross-linking points (low modulus of elasticity) is agglomerated at about 20 nm (Figure 9a) from AFM (Figure 5) and SANS (Figure 6) images. However, with the addition of clay, the domain size of the low elastic modulus part is slightly increased and dispersed, and the intermediate elastic modulus is wider (Figure 5, Figure 9 AFM image, arranged cross-linking point is an image). It is considered that the cross-linking point interacts with the clay surface as in Figure 9b, and the cross-linking point is delocalized. Therefore, it is considered that the hysteresis energy increased, the stress concentration was suppressed, and consequently the tensile property was improved.

Since the OH group of clay exists only on the end face, it was considered that the cross-linked part was hydrogen bonded to the hydroxyl group on the end face of clay in the previous report. However, the cross-linked part seems to also have ion–dipole interaction with ammonium cations and/or anionic parts on the clay surface by various measurement. The rationale is as follows.

- In the TEM measurement, it is found that the interlayer distance extends from 2 nm to 10–15 nm, and it is assumed that an elastomer is intercalated between layers (the spread between layers cannot be confirmed by the addition of clay to the HBE).
- In the IR measurement, the absorption of the carbonyl group of 1729 cm\(^{-1}\) was shifted to 1734 cm\(^{-1}\) by adding clay. This is explained as follows: carboxylic acid interacts with ammonium cations or anionic parts on the clay surfaces by ion–dipole interactions and weakens the hydrogen bonds between carboxylic acids (dimers) (double bonding character increase). It resulted in a shift to a high wavenumber (high wavenumber shift cannot be confirmed by the addition of clay to the HBE).

The physical properties and structural analysis results of Run 3 and Run 5 are summarized in Table 10. The results of HBE + OC (Run 3) is opposite to that of MNE (Run 5).

### 4. DISCUSSION

The structure of the cross-linking point of the MNE is expected as shown in Figure 8 (A: plane view, B: 3D view). By reaction between the hydroxyl group of THI and the maleic acid of maleated EBM, covalent cross-linking by esters is generated and carboxylic acid is generated at the same time. Isocyanurate rings are considered to be complexly hydrogen-bonded with carboxylic acids and esters. Clay also seems to interact with carboxylic acids and esters, and isocyanurate rings at cross-linking points.

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- In the TEM measurement, it is found that the interlayer distance extends from 2 nm to 10–15 nm, and it is assumed that an elastomer is intercalated between layers (the spread between layers cannot be confirmed by the addition of clay to the HBE).
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| Table 10. Summary of Physical Properties and Structural Analysis Results of Run 3 and Run 5 |
|---------------------------------|---------------------------------|
| HBE + OC (Run 3)                | MNE (Run 5)                     |
| tensile properties              |                                 |
| compression set                 |                                 |
| TEM                             | spread between the layers cannot |
|                                 | be confirmed                    |
| IR(C=O)                         | high wavenumber shift cannot be |
|                                 | confirmed                      |
| DMA                             | tan δ down: hysteresis E down   |
| AFM                             | modulus up                      |
| SANS                            | Scattering intensity up         |

The physical properties and structural analysis results of Run 3 and Run 5 are summarized in Table 10. The results of HBE + OC (Run 3) is opposite to that of MNE (Run 5).
The results of SANS, AFM, and DMA suggest that cross-linking points interact with the clay surface and are delocalized (delocalization is not observed by the addition of clay to the HBE).

As a conclusion of this paper, we propose a new structure in Figure 10.

From the TEM image (Figure 1), clay is not uniformly dispersed in rubber, but is localized near the cross-linking point, such as in Figure 10a (wide view) due to hydrogen bonding and ion–dipole interactions. Hydrogen bonding and ion–dipole interactions with the clay surface suppress cross-linking aggregation as shown in Figure 10b (view from above), and it is considered to be solidified and dispersed in the 100–300 nm square and intervals of 10–15 nm as shown in Figure 10c (only three layers are described for simplification in the figure). Organic clay is not exfoliated but intercalated by polymers.

The adding effect of clay was greatly different between HBE and MNE. In HBE, the addition of clay resulted in a decrease in tensile properties and an increase (deterioration) of compression set. Since the spread between layers in TEM images and the high wavenumber shift of carbonyl groups in IR results could not be confirmed, HBE was not intercalated between the layers of clay (does not interact with ammonium cations and/or anionic parts between layers). It is considered that the hydroxyl group on the clay end surface and the hydrogen bond cross-linking part of the polymer interact to weaken the hydrogen bond cross-linking between polymers to cause the deterioration of physical properties.

On the other hand, in the MNE, the addition of clay improved the tensile property and compression set, and an interlayer spread via TEM, high wavenumber shift via IR, and a decrease of scattering intensity in SANS measurement were observed. In the MNE, the cross-linking site does not recombine because of the
stable covalent cross-linking. Moreover, the hydrogen bond cross-linking site forms a hydrogen bond with the hydroxyl group on the end surface of the clay and also shows ion–dipole interactions with the ammonium cations and/or anionic parts on the layer surfaces and intercalated between the layers of clay, causing nonlocalization (homogenization and sparse) of the cross-linking part to improve the physical properties.

5. SUMMARY

In order to improve the structure proposed in the previous report, further structural analyses were carried out by comparison with the HBE. In the previous report, it was considered that the cross-linked part was hydrogen bonded to the hydroxyl group on the end surface of the clay, but further structural analysis estimated that the cross-linked part has also an ion–dipole interaction with ammonium cations and/or anionic parts on the clay surface and a new structure was proposed. Furthermore, the addition effect of clay was greatly different between HBE and MNE. In the HBE, which expresses physical properties only by hydrogen bond cross-linking, the hydrogen bond cross-linking between the polymers was weakened by the interaction between the hydrogen bond cross-linking and the hydroxyl group of the clay end surface. On the other hand, in the MNE, the recombinant of the cross-linking itself does not occur due to the stable covalent bond cross-linking. It is presumed that the hydrogen bond cross-linking site interacted with the clay surface and intercalated between the layers of clay, causing nonlocalization of the cross-linking part, and the physical properties were improved.

The ion–dipole interaction of carboxy groups and isocianurate rings seems to influence the reason why MNE is intercalated between layers. In the future, we would like to find better cross-linking groups and create high-performance thermoplastic elastomers by conducting a comparative examination (synthesis and structural analysis) with various cross-linking groups to elucidate the role of ion–dipole interactions and hydrogen bonds in detail.

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Notes
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