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Solid state reaction of bifunctional bicyclo orthoesters and carboxylic acids and their metal adhesive properties

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Abstract

Five kinds of novel bifunctional bicyclo orthoesters (BOEs) were synthesized and copolymerized with multi-functional carboxylic acids, having plural carboxyl and hydroxyl groups, to develop functional materials usable as non-volatile adhesives. In a solid-state reaction of BOEs with the carboxylic acids, mechanical mixing converted the BOE moiety to a corresponding hydrolyzed form via ring-opening and isomerization reactions. The solid-state reaction, requiring moisture and mechanical stress, was accelerated by the higher reactivity given by the α-hydroxyl group in the acids. Superior adhesive bonding to the Ni–Cr alloyed metal substrate was achieved via a heating process at 150 °C, and high average tensile strengths of ∼80 MPa were obtained by using mixtures of BOEs and DL-tartaric acid. This highly adhesive property was achieved not only by polycondensation of BOE-hydrolyzates and the carboxylic acids, but also by polyaddition of BOEs and the carboxylic acids.

Keywords: Bicyclo orthoester; Polycondensation; Metal adhesive

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1. Introduction

Bicyclo ortho esters (BOEs) polymerize with Lewis acid catalysts such as $BF_3 \cdot OEt_2$ to give polyethers containing pendant ester groups via a double ring-opening isomerization process. BOEs are expected to be suitable monomers for precision molding materials and adhesives, because they show no shrinkage and only a slight expansion in volume during their polymerization [1].

In general, high molecular weight and highly elastic polymers have favorable physical properties that give them many practical applications. However, both high molecular weight and high elastic polymers are difficult to obtain from BOEs. This is because the polymerization process necessarily involves a main chain fission reaction [2–4] as well as the structural change involved in changing a rigid monomer to a flexible polymer, such change being inherent to the creation of an expandable polymer [5]. These problems may be overcome in the structural design of BOE and its copolymerization with other monomers. In our previous report, we succeeded in a selective polyaddition copolymerization of bifunctional BOEs with bi- and tri-functional acid chlorides to obtain crosslinked copolymers quantitatively, in which the double ring-opening reaction of BOEs occurred to produce the corresponding alternative copolymers with very little volume change (± 0.0 to -0.6%) [6,7]. However, in the previous study the obtained network copolymers were rubber-like materials, because the bifunctional BOEs had aliphatic groups linking BOE moieties.

To minimize any volume change during the polymerization, bulk polymerization is essential, because with bulk polymerization there is no volatile component to cause any shrinkage in volume. One of the serious issues associated with the use of adhesives is the escape of volatilized formaldehyde and other volatile solvents from adhesives used in interior decorating causing the so-called ‘sick building syndrome’. Thus, non-volatilized adhesives are required for interior finishing and in fact many kinds of non-volatilized adhesives have already been developed [8].

In this study, novel types of bifunctional BOEs were designed and synthesized with the aim of producing rigid aromatic backbone structures as well as ones with a flexible aliphatic ether structure for comparison with aromatic types (Scheme 1). To clarify whether BOE could be used as a

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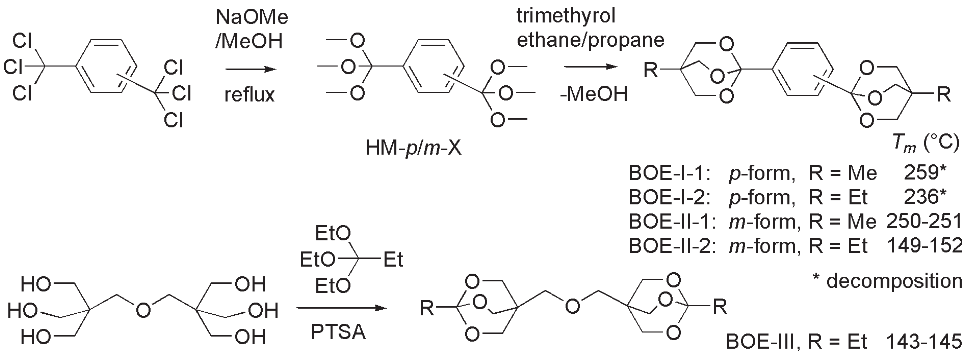


Scheme 1. Syntheses of bifunctional BOEs.

non-volatilized functional adhesive, the synthesized BOEs were copolymerized with multi-functional comonomers having plural carboxyl and hydroxyl groups. Polycondensation via esterification of hydroxyl and carboxyl groups is a widely used methodology in polymer synthesis [9] and is associated with a large volume shrinkage of 18–66% [10,11]. However, Kume et al. [12] have studied the polymerization behavior of BOE having a hydroxyl group, in which the hydroxyl group of poly(BOE) was dehydrated to give a crosslinking polymer with a small volume shrinkage (2.46%). Hence, this result encouraged us to study the reaction of BOEs with multi-functional comonomers. This article deals with the synthesis of novel BOEs, the reaction of BOEs with multi-functional carboxylic acids having plural carboxyl and hydroxyl groups in a solid state, and polyaddition and/or polycondensation of BOEs with the comonomers.

2. Experimental section

2.1. Materials

Raw materials, α,α,α,α′,α′,α′-hexachloro-*p*-xylene, α,α,α,α′,α′,α′-hexachloro-*m*-xylene, dipentaerythritol, trimethylolpropane, trimethylolethane, triethyl orthopropionate, and *p*-toluenesulfonic acid monohydrate (PTSA) were purchased from Tokyo Kasei Kogyo Co., Ltd and used as received. Sodium stick was obtained from Wako Pure Chemical Industries, Ltd, and used as received. Carboxylic acids: DL-tartaric, DL-malic, citric, adipic, terephthalic, glycollic, 2-hydroxyisobutyric, 2,2-bis(hydroxymethyl)propionic, and 3,4-dihydroxybenzoic acids were purchased from Wako Pure Chemical Industries, Ltd, and dried in vacuo overnight. Other chemicals and solvents, such as triethylamine, methylene dichloride (CH_2Cl_2), chloroform ($CHCl_3$), dimethylsulfoxide (DMSO), boron trifluoride ethylether complex ($BF_3 \cdot OEt_2$), methanol, benzene, toluene, xylene, ethyl benzoate, hexane, and tetrahydrofuran (THF) were obtained from Wako Pure Chemical Industries, Ltd, dried by ordinary methods, and then purified by distillation. Metal substrate, Ni–Cr alloy (5 mm in diameter and ≈15 mm in height, with a hole at one side for the tensile strength test) was obtained from Towa Giken Co. Ltd, and prepared by its circular section surface being polished with emery paper (No. 320) and then defatted with CH_2Cl_2.

2.2. Measurements

^{1}H and ^{13}C NMR spectra were recorded on Hitachi R-24B and JEOL FX-60Q spectrometers using tetramethylsilane as an internal standard in chloroform-*d* ($CDCl_3$), dimethylsulfoxide-d_6 (DMSO-d_6), and methanol-d_4 (MeOH-d_4). FT-IR spectra were recorded from KBr disks on a Hitachi 260-30 spectrometer. Elemental analysis was carried out with a Yanaco CHN analyzer. Mass (MS) spectra were recorded on a Hitachi M-80 system.

Thermal properties were analyzed with a Perkin–Elmer differential scanning calorimeter DSC-1B and a Shimadzu DT-30 thermal analyzer at a heating rate of 5 °C min^{-1} in nitrogen flow.

Adhesive properties were evaluated with a Toyo Boldwin Tensilon UTM-II testing machine in a tensile mode at 23 °C with a crosshead speed of 2 mm min^{-1}. The tensile strength was estimated as equivalent to the value at the breaking point in a stress–strain diagram.

2.3. Synthesis of hexamethoxy xylenes

Precursors, α,α,α,α,′,α′,α′-hexamethoxy-*p*-xylene (HM-*p*-X) and α,α,α,α′,α′,α′-hexamethoxy-*m*-xylene (HM-*m*-X) were prepared in a similar manner as that used by Saigo et al. [13] (Scheme 1). The α,α,α,α′,α′,α′-hexachloro-*p*-xylene (21.91 g, 0.07 mol) was added into a solution of sodium methoxide (0.455 mol) in methanol (250 mL), and the solution was refluxed under stirring for 27.5 h. After the solution had been cooled to ambient temperature, the solvent was evaporated to obtain a white precipitate. A mixture of benzene and water (300 and 200 mL, respectively) was then added to dissolve the precipitate. The organic layer was separated and dried over sodium sulfate (20 g). The solvent was evaporated to obtain a white solid. This white solid material was then dissolved in methanol 500 mL and the reaction process was repeated twice in the same manner except that the reflux time was increased to 64 h, resulting in the production of 13.79 g of the white solid. The white material was crystallized from a methanol solution to obtain HM-*p*-X as a white crystalline 7.42 g in a 37.1% yield. Mp: 118–122 °C. ^{1}H NMR ($CDCl_3$, δ): 3.20 (s, 18H, –OC*H*$_3$), 7.70 ppm (s, 4 H, aromatic ring-*H*). FT-IR: 850($\delta_{\text{Ar-H}}$), 1025, 1070, 1085 cm^{-1} ($\nu_{\text{C–O–C}}$). Mass spectrum

(EI): m/z 286 (M^+). Elem. Anal.: Calcd for $C_{14}H_{22}O_6$: C, 58.72; H, 7.76. Found: C, 58.36; H, 7.70%.

HM-*m*-X was synthesized from α,α,α,α′,α′,α′-hexachloro-*m*-xylene and sodium methoxide in a similar manner to the process used in the synthesis of HM-*p*-X. Yield: 30.9%. Mp: 95–97 °C. ^{1}H NMR ($CDCl_3$, δ): 3.14 (s, 18H, –OC*H*$_3$), 7.29–7.80 ppm (m, 4H, Ar-*H*). FT-IR: 810, 815, 865, 905 ($\delta_{\text{Ar-H}}$), 1030, 1070, 1090 cm^{-1} ($\nu_{\text{C–O–C}}$).

HM-*p*-X and HM-*m*-X were also prepared in a similar manner to a method reported by Lapporte [14] from the exactly the same hexachloride compounds and sodium methoxide in methanol for 5 h at 200 °C and 4.4 MPa in an autoclave giving yields of 67.0 and 56.0%, respectively.

2.4. Syntheses of bifunctional bicyclo orthoesters (BOEs)

According to the method as described in the literature [4], five kinds of bifunctional BOEs were synthesized (Scheme 1).

2.4.1. 1,4-Bis-(4-ethyl-2,6,7-trioxabicyclo[2,2,2]oct-1-yl)benzene: BOE-I-2

To a mixture of HM-*p*-X (2.86 g, 10.0 mmol) and trimethylolpropane (0.268 g, 2.00 mmol) in 20 mL of xylene, a catalyst, PTSA (0.02 g, 0.12 mmol), was added. The reaction mixture was heated in a temperature range of 100–110 °C. After a theoretical amount of methanol was collected in a Dean–Stark trap, 0.05 g of triethylamine was added to neutralize the reaction mixture. The mixture was cooled to ambient temperature and filtered to obtain a white precipitate. The precipitate was crystallized from CH_2Cl_2 to obtain BOE-I-2 (2.63 g) as a white solid in a 72.7% yield. Mp: 236 °C (decomposition). ^{1}H NMR ($CDCl_3$, δ): 0.82 (t, 6H, –C*H*$_3$), 1.29 (q, 4H, –C*H*$_2$–CH$_3$), 4.03 (s, 12H, –C*H*$_2$–O–), 7.46 ppm (s, 4H, Ar-*H*). FT-IR: 840 ($\nu_{\text{Ar-H}}$), 990, 1010, and 1100 cm^{-1} ($\nu_{\text{C–O–C}}$). Mass spectrum (EI): m/z 362 (M^+). Elem. Anal.: Calcd for $C_{20}H_{26}O_6$: C, 66.27; H, 7.24. Found: C, 65.80; H, 7.28%.

2.4.2. 1,4-Bis-(4-methyl-2,6,7-trioxabicyclo[2,2,2]oct-1-yl)benzene: BOE-I-1

BOE-I-1 was synthesized from HM-*p*-X and trimethylolethane in a similar manner to that for BOE-I-2. Yield: 64.1%. Mp: 259 °C (decomposition). ^{1}H NMR ($CDCl_3$, δ): 0.87 (s, 6H, –C*H*$_3$), 4.06 (s, 12H, –C*H*$_2$–O–), and 7.58 ppm (s, 4H, Ar-*H*). FT-IR: 840 ($\nu_{\text{Ar-H}}$), 990, and 1100 cm^{-1} ($\nu_{\text{C–O–C}}$). Mass spectrum (EI): m/z 333 ($M^+ - 1$). Elem. Anal.: Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.64. Found: C, 64.06; H, 6.48%.

2.4.3. 1,3-Bis-(4-methyl-2,6,7-trioxabicyclo[2,2,2]oct-1-yl)benzene: BOE-II-1

BOE-II-1 was synthesized from HM-*m*-X and trimethylolethane in a similar manner to that for BOE-I-2. Yield: 72.0%. Mp: 250–251 °C. ^{1}H NMR ($CDCl_3$, δ): 0.86 (s, 6H, –C*H*$_3$), 4.04 (s, 12H, –C*H*$_2$–O–), and 7.15–7.93 ppm (m, 4H, Ar-*H*). FT-IR: 700, 730, 805 ($\nu_{\text{Ar-H}}$), 885, 895, 980, 1000, 1100, and 1120 cm^{-1} ($\nu_{\text{C–O–C}}$). Elem. Anal.: Calcd for $C_{18}H_{22}O_6$: C, 64.65; H, 6.64. Found: C, 64.46; H, 6.75%.

2.4.4. 1,3-Bis-(4-ethyl-2,6,7-trioxabicyclo[2,2,2]oct-1-yl)benzene: BOE-II-2

BOE-II-2 was synthesized from HM-*m*-X and trimethylolpropane in a similar manner to that for BOE-I-2. Yield: 72.0%. Mp: 149–152 °C. ^{1}H NMR ($CDCl_3$, δ): 0.82 (t, 6H, –C*H*$_3$), 1.34(q, 4H, –C*H*$_2$–CH$_3$), 4.07 (s, 12H, –C*H*$_2$–O–), and 7.17–7.97 ppm (m, 4H, Ar-*H*). FT-IR: 700, 720, 805 ($\nu_{\text{Ar-H}}$), 910, 980, 1000, 1095, and 1120 cm^{-1} ($\nu_{\text{C–O–C}}$). Elem. Anal.: Calcd for $C_{20}H_{26}O_6$: C, 66.27; H, 7.24. Found: C, 66.19; H, 7.36%.

2.4.5. Bis-(1-ethyl-2,6,7-trioxabicyclo[2,2,2]oct-4-yl-methyl)ether: BOE-III

A mixture of triethyl orthopropionate (17.6 g, 100 mmol), dipentaerythritol (12.7 g, 50 mmol), ethyl benzoate (100 mL), and PTSA (0.20 g, 1.16 mmol) was heated at 140 °C for 1 h in a temperature range of 180–200 °C for 6 h under stirring. After ethanol 17 mL (13.4 g, 290 mmol) was collected in a Dean–Stark trap, 1 g of triethylamine was added to neutralize the reaction mixture. The solvent was evaporated at reduced pressure to obtain a viscous transparent liquid. Hexane (100 mL) was added to the viscous liquid to extract a soluble component. The hexane layer was separated and concentrated to obtain a white crystalline product. After cooling, the reaction mixture was filtered to obtain BOE-III in the form of white prisms (0.46 g) in a 1.4% yield. Mp: 143–145 °C. ^{1}H NMR ($CDCl_3$, δ): 0.94 (t, 6H, –C*H*$_3$), 1.70 (q, 4H, –C*H*$_2$–CH$_3$), 3.11 (s, 4H, –C*H*$_2$–O–C*H*$_2$–), and 3.93 (s, 12H, –C*H*$_2$–O–). FT-IR: 915, 925, 940, 985, 1000, 1055, and 1102 cm^{-1} ($\nu_{\text{C–O–C}}$). Mass spectrum (FD): m/z 330 (M^+). Elem. Anal.: Calcd for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.08; H, 7.95%.

2.5. Cationic polymerization of bifunctional BOEs

In a typical procedure, $BF_3 \cdot OEt_2$ (3.79 μL, 15 μmol) was introduced to a solution of BOE-I-1 (0.05 g, 150 μmol) in CH_2Cl_2 (2 mL) in a glass ampoule. The ampoule was sealed and heated at 130 °C to start the polymerization. After the reaction had proceeded for 20 h, the ampoule was cooled to ambient temperature and broken to obtain a transparent gel-like product and a liquid layer. The liquid layer was analyzed by ^{1}H NMR and FT-IR and the gel-like product was dried, weighed at 0.46 g (92% yield), then analyzed by FT-IR.

2.6. Solid-state reaction of BOEs and carboxylic acids at room temperature

In a typical procedure, BOE-I-2 (0.665 g, 1.84 mmol) and DL-tartaric acid (0.331 g, 2.20 mmol) were mixed in an agate mortar and ground for 10 min at 23 °C and 50%RH. After the solid-state reaction, the mixture was analyzed by FT-IR to evaluate the conversion of BOE moiety by comparing the absorbance of characteristic bands of the raw material and product.

To isolate the reaction product, the ground mixture was dissolved into THF and concentrated to remove the crystallized raw materials. The residual viscous solution was dissolved in methanol 20 mL. Then, the methanol-soluble part was concentrated and poured into 100 mL of water to obtain a white precipitate. After filtration and drying, hydrolyzed product: BOE-I-2-H was isolated as a white crystal in a 34% yield based on BOE-I-2. Mp: 125.5–126.5 °C. ^{1}H NMR (DMSO-d_6, δ): 0.86 (t, 6H, –CH_3), 1.40 (q, 4H, –CH_2–CH$_3$), 3.37 (d, 8H, –CH_2–OH), 4.15 (s, 4H, –COO–CH$_2$–), and 8.05 ppm (s, 4H, Ar-H). ^{13}C NMR (MeOH-d_4, δ): 7.0 (–CH$_3$), 22.4 (–CH$_2$–CH$_3$), 43.6 (*tert*-C), 62.6 (–CH$_2$–OH), 65.7 (–COO–CH$_2$–), 129.7 (non-substituted Ar-C), 134.6 (substituted Ar-C), and 166.1 ppm (–COO–). FT-IR: 730 ($\nu_{\text{Ar-H}}$), 1720 ($\nu_{\text{C=O}}$), and 3350 cm^{-1} ($\nu_{\text{O–H}}$). Elem. Anal.: Calcd for $C_{20}H_{30}O_8$: C, 60.29; H, 7.59. Found: C, 60.15; H, 7.62%.

BOE-I-1 was reacted with DL-tartaric acid in a similar manner to that for BOE-I-2, resulting in the production of BOE-I-1-H in a 44% yield. Mp: 170–173 °C. ^{1}H NMR (DMSO-d_6, δ): 0.91 (s, 6H, –CH_3), 3.20–3.55 (d, 8H, –CH_2–OH), 4.16 (s, 4H, –COO–CH$_2$–), and 8.08 ppm (s, 4H, Ar-H). FT-IR: 730 ($\nu_{\text{Ar-H}}$), 1715 ($\nu_{\text{C=O}}$), and 3300 cm^{-1} ($\nu_{\text{O–H}}$).

BOE-II-1 was reacted with DL-tartaric acid in a similar manner to that for BOE-I-2, resulting in the production of BOE-II-1-H in a 60% yield. Mp: 121–125 °C. ^{1}H NMR (DMSO-d_6, δ): 0.94 (s, 6H, –CH_3), 3.40 (d, 8H, –CH_2–OH), 4.20 (s, 4H, –COO–CH$_2$–), and 7.6–8.6 ppm (m, 4H, Ar-H). FT-IR: 725 ($\nu_{\text{Ar-H}}$), 1720 ($\nu_{\text{C=O}}$), and 3500 cm^{-1} ($\nu_{\text{O–H}}$).

BOE-II-2 was reacted with DL-tartaric acid in a similar manner to that for BOE-I-2, resulting in the production of BOE-II-2-H in an 86% yield. Mp: 74–77 °C. ^{1}H NMR (DMSO-d_6, δ): 0.88 (t, 6H, –CH_3), 1.44 (q, 4H, –CH_2–CH$_3$), 3.37–3.46 (d, 8H, –CH_2–OH), 4.20 (s, 4H, –COO–CH$_2$–), and 7.6–8.6 ppm (m, 4H, Ar-H). FT-IR: 730 ($\nu_{\text{Ar-H}}$), 1720 ($\nu_{\text{C=O}}$), and 3400 cm^{-1} ($\nu_{\text{O–H}}$).

BOE-III was reacted with DL-tartaric acid in a similar manner to that for BOE-I-2, resulting in the production of BOE-III-H in a 50% yield. Mp: 83–86 °C. ^{1}H NMR (DMSO-d_6, δ): 1.04 (t, 6H, –CH_3), 2.32 (q, 4H, –CH$_2$–CH$_3$), 3.30 (s, 4H, –CH_2–O–CH_2–), 3.37 (d, 8H, –CH_2–OH), and 3.95 ppm (s, 4H, –COO–CH_2–). FT-IR: 1735 ($\nu_{\text{C=O}}$), and 3100–3600 cm^{-1} ($\nu_{\text{O–H}}$). Elem. Anal.: Calcd for $C_{16}H_{30}O_9$: C, 52.45; H, 8.25. Found: C, 52.01; H, 8.39%.

2.7. Copolymerization of BOE and adipic acid at high temperatures

BOE-I-2 and adipic acid were mixed in various feed ratios: [BOE]/[COOH] = 1:1–1:4 and the mixtures were transferred into glass ampoules. The ampoules were sealed under vacuum and heated at 160 °C for 15 h in an oil bath. After the reaction, the ampoules were broken and the obtained products were analyzed by FT-IR.

2.8. Condensation behavior of BOE and DL-tartaric acid at high temperatures

In an agate mortar, prescribed amounts of BOE-I-2 and DL-tartaric acids were mixed at 23 °C and 50%RH. After grinding for 2 min, the mixture was transferred into aluminum pans for TG/DTA measurements. The aluminum pans were heated at a heating rate of 5 °C min^{-1} from room temperature to 190 °C, and then cooled down. This heating–cooling cycle was repeated 4 times.

2.9. Adhesion test of metal substrates

In an agate mortar, prescribed amounts of BOE and a carboxylic acid were mixed at 23 °C and 50%RH. To measure the adhesive properties of the cured products, cylindrical test pieces made of Ni–Cr alloy (Towa Giken Co. Ltd, 5 mm in diameter and $\approx$15 mm in height, with a hole at one side for conducting a tensile strength test) were used as a substrate. The circular section on the side opposite the hole was polished with emery paper (No. 320) and defatted with CH_2Cl_2. The ground powder mixture of BOE and carboxylic acid was applied as a coating over the sectional surface of one test piece and then the coated surface of this test piece was brought face to face with that of another. One set of such pieces was placed in a high-pressure polymerization chamber under a nitrogen atmosphere and heated at 150 °C for 15 h under 0.4 MPa for curing. After the reaction, the tensile strength of the adhered metal pieces was measured with a Toyo Boldwin Tensilon UTM-II testing machine. Tensile strength was calculated by taking the average value of three samples prepared in the same manner.

3. Results and discussion

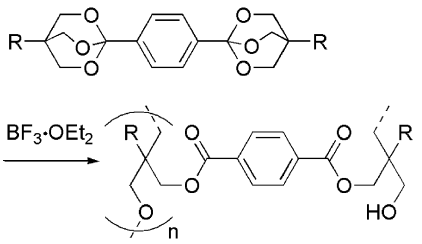
3.1. Synthesis of bifunctional BOEs

Five kinds of bifunctional bicyclo orthoesters (BOEs) were newly synthesized (Scheme 1). The BOE-I and -II series having aromatic linkage groups showed considerable thermal resistance, especially, *para*-substituted BOEs: BOE-I-1 and -2 showed no melting point, decomposing at temperatures higher than 230 °C. Aliphatic bifunctional BOE: BOE-III also showed a relatively high melting point at 143–145 °C. These BOEs exhibited poor solubility in organic solvents. In particular, BOE-I-1 and -2 dissolved only slightly in CH_2Cl_2 and DMSO, whereas BOE-II-1 and BOE-III were soluble in CH_2Cl_2 and $CHCl_3$, and BOE-II-2 in addition to being soluble in CH_2Cl_2 and $CHCl_3$was also soluble in acetone, toluene and xylene.

Thus, the high crystallinity and poor solubility of BOEs must be as a result of their symmetrical structures. These properties suggest that a solid-state reaction is favorable for the BOEs.

3.2. Ring-opening polymerization of bifunctional BOEs

Cationic polymerization of BOE-I-1 and -2 was carried out in CH_2Cl_2 with $BF_3\cdot Et_2$ (10 mol%) as a cationic initiator for 20 h at 130 °C, resulting in the quantitative production of an insoluble viscous gel and white solid products, respectively. From FT-IR analysis of the insoluble products, new absorption bands at 3500–3450, 1725 and 730–735 cm^{-1}, assigned to $\nu_{\text{O–H}}$, $\nu_{\text{C=O}}$, and $\delta_{\text{Ar-H}}$, respectively, were evident instead of at



Scheme 2. Cationic polymerization of BOE.

1100, 990, and 840 cm^{-1}, assigned to $\nu_{\text{C–O–C}}$, and $\delta_{\text{Ar-H}}$, respectively, for the original BOE-I-1. ^{1}H-NMR spectrum of a small amount of the soluble part showed new signals at 8.09 (Ar-*H*), 4.60–4.25 (–COO–CH$_2$–), 3.67 (–O–CH$_2$–), and 3.45–3.30 (HO–CH$_2$–) ppm, instead of at 7.46 (Ar-*H*) and 4.03 (–O–CH$_2$– in BOE) ppm. These results indicate that the ring-opening polymerization of BOEs produced crosslinked homopolymers via the ring-opening isomerization of the BOE ring (Scheme 2). However, the formation of hydroxyl groups suggests that chain transfer reactions occurred, resulting in the formation of short length chains and mechanically weak materials [13].

3.3. Solid-state reaction of BOEs and carboxylic acids

In our previous report [7,15,16], we conducted a selective polyaddition copolymerization of aliphatic ester-type bifunctional BOEs and spiro orthoesters (SOEs) with multi-functional acid chlorides to achieve the double ring-opening isomerization of BOE and SOE moieties. This resulted in the formation of crosslinked rubber-like materials with very little volume change (+0.5 to −0.6%). In this study, to produce rigid materials from the synthesized BOEs, polyaddition copolymerization with multi-functional carboxylic acids in bulk was examined. All the reactions were carried out in a solid-state by mechanical grinding in an agate mortar.

BOEs were mixed with bifunctional carboxylic acids, DL-tartaric, DL-malic, and adipic acids, then ground at 30 °C for 2 min under 70%RH. Conversion of BOE moiety was evaluated by FT-IR, which made use of characteristic IR absorption bands at 805 (BOE-I-1 and -2) and 840 cm^{-1} (BOE-II−1 and −2), that were assigned to the out-of-plane bending vibration of aromatic protons ($\nu_{\text{Ar-H}}$) in BOEs. After the reaction in the solid state, the absorption band disappeared and a new absorption band at 730 cm^{-1} appeared indicating the production of corresponding BOE hydrolyzates. In the case of the reaction of BOE-III with carboxylic acids, two absorption bands at ≈1700 ($\nu_{\text{C=O,carboxylicacid}}$) and 1735 cm^{-1} ($\nu_{\text{C=O,hydrolyzed BOE-III}}$) were used for the evaluation. The conversion (%) of BOE was calculated from the absorbance of each band (Fig. 1) according to Eq. (1), in which it was tentatively assumed that the corresponding two bands had the same molar extinction coefficient as each other.

$$\text{Conversion}(\%) \cong \frac{\log \frac{I_{0\text{B}}}{I_{\text{B}}}}{\log \frac{I_{0\text{A}}}{I_{\text{A}}}\frac{I_{0\text{B}}}{I_{\text{B}}}} \times 100 \qquad (1)$$

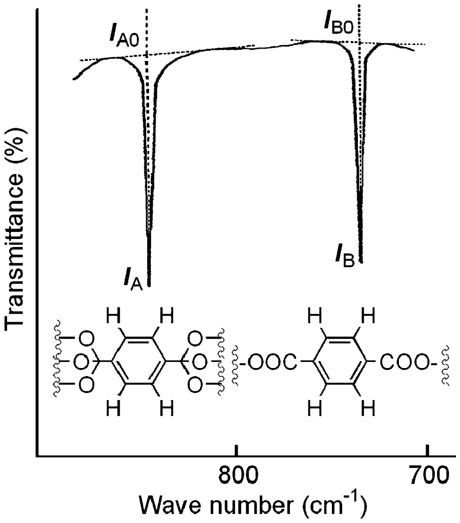


Fig. 1. Characteristic IR absorption bands of the BOE-I series with products derived from the solid-state reaction.

Results of the equimolar reactions of BOEs and the carboxylic acids are listed in Table 1. Addition of the acids caused a remarkably high conversion of BOE moieties even in such a solid state. No consumption of BOE occurred under an absolutely dry condition or without the carboxylic acids (data not shown), meaning that the ring-opening reaction of BOE was caused by the combined effect of carboxylic acid and water molecules absorbed from the atmosphere. DL-Tartaric and DL-malic acids were particularly effective compared to adipic acid. These three acids have different chemical structures with different numbers of hydroxyl groups. In Table 2, results of the solid-state reaction of BOE-I-2 with many kinds of acids at 23 °C under 50%RH are listed. Under these conditions, the conversion decreased in comparison with the results in Table 1. Interestingly, no effect was observed upon the addition of an outer hydroxyl group (adipic acid+trimethylolpropane). Glycollic acid, which has a hydroxyl group at the α-position of the carboxyl group, showed a similar high conversion; however, 2-hydroxyisobutyric acid, which has a steric hindrance, showed a lower activity. Moreover, 2,2-bis(hydroxymethyl)propionic and 3,4-dihydroxybenzoic acids, which have plural hydroxyl groups at the β-position and the *m*- and *p*-positions on the aromatic ring, showed no conversion of BOE moiety.

Table 1
Reaction of BOEs and carboxylic acids in a solid state

BOE	Conversion of BOE (%)			
	–	DL-Tartaric acid	DL-Malic acid	Adipic acid
I-1	0	94	100	24
I-2	0	95	100	13
II-1	0	100	100	17
II-2	0	100	100	44
III	0	60	59	31

Conditions: [BOE]/[COOH]=1:1, grinding for 2 min at 30 °C and 70%RH.

Table 2
Reaction of BOE-I-2 and carboxylic acids in a solid state

Carboxylic acid	Unit ratio in feed [BOE]/[COOH]/[OH]	Conversion of BOE (%)
DL-Tartaric acid	1:2:2	97
DL-Malic acid	1:2:1	66
Adipic acid	1:2:0	0
Adipic acid + trimethylolpropane	1:2:0.67	0
Glycollic acid	1:2:2	72
Glycollic acid	1:4:4	89
2-Hydroxyisobutyric acid	1:4:4	19
2,2-Bis(hydroxymethyl)propionic acid	1:4:8	0
3,4-Dihydroxybenzoic acid	1:4:8	0

Conditions: [BOE]/[COOH] = 1:1, grinding for 2 min at 23 °C and 50%RH.

These results suggest that the hydroxyl group at the α-position of the carboxyl group enhanced the acidity of the acids, so working as an auto-accelerator during the reaction.

3.4. Analysis of solid-state reaction products of BOEs and DL-tartaric acid

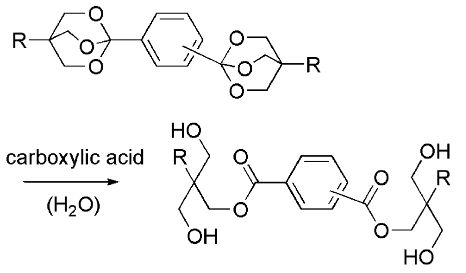
After the solid-state reaction of BOEs and DL-tartaric acid, the products were successfully isolated and characterized. The ^{1}H NMR analysis of the products from the BOE-I and -II series showed that a typical singlet of methylene protons on the BOE ring in a narrow range of 3.9–4.1 ppm had disappeared. On the other hand, a new singlet and doublet appeared in a range of 4.15–4.20 and 3.2–3.6 ppm, which were assigned to methylene protons situated between ester group and tertiary carbon ($-COO-CH_2-C$), and methylene protons adjacent to hydroxyl group ($HO-CH_2-C$), respectively. These changes in chemical shift indicate the hydrolytic ring-opening isomerization of the BOE moiety and the corresponding formation of ester and hydroxyl groups.

The reaction of BOE-III with DL-tartaric acid also gave a corresponding ring-opening hydrolysis product. Thus, the main reaction in the solid-state is a hydrolytic ring-opening addition reaction of the BOE moiety catalyzed by carboxylic acid (Scheme 3).

3.5. Polyaddition and polycondensation reactions of BOEs and carboxylic acids at high temperatures

To determine the addition reaction of BOE moiety and the carboxyl group, BOE-I-2 and adipic acid (T_m = 153 °C) were heated at 160 °C for 15 h in bulk in a sealed glass ampoule. The reaction was carried out under various feed ratios: [BOE]/[COOH] = 1:1–1:4, resulting in the formation of a transparent insoluble rigid polymer in the case of [BOE]/[COOH] = 1:2. Other products were opaque due to the presence of residual raw materials. An FT-IR spectrum of the transparent rigid polymer showed typical absorption bands at 3450 (ν_{O-H}), 1735 ($\nu_{C=O}$), 1270 (ν_{C-O-C}), and 730 cm^{-1} (ν_{Ar-H}). On the other hand, typical bands of BOE-I-2 and adipic acid at 1700 cm^{-1} ($\nu_{C=O}$) disappeared. These results indicate that, even in the absence of water vapor, the BOEs and bifunctional carboxylic acids can copolymerize at high temperature via the ring-opening isomerization of BOE moiety and the addition of the carboxyl group. However, various sub-reactions, such as condensation and transesterification, also must occur to give a networked rigid polymer.

For the formation of a networked polymer, a condensation reaction is required in addition to a polyaddition reaction, in which the hydroxyl group must function not only as an accelerator during the solid-state reaction, but also as a crosslinking site during the condensation reaction. To clarify the condensation behavior of BOEs and carboxylic acids, DSC and TG measurements were carried out with BOE-I-2 and DL-tartaric acid. Fig. 2 shows profile changes during repeated DSC measurements of the mixture with a feed ratio of [BOE]/[COOH] = 1:2. In the first scan, an endothermic peak was seen at 162 °C due to the melting of the acid (T_m = 168 °C) and a following exothermic peak occurred at 170 °C due to an exothermic reaction. In the second scan, the profile was drastically changed, with the endo/exothermic peaks disappearing and only a glass transition point (T_g) being observed at 66 °C. When the cycle was repeated, the T_g value clearly increased up to 105 °C in the fourth scan. In Fig. 3, changes in the TG profile of the same sample are shown. In the first scan, approximately 2 wt% of the total weight was lost at temperatures over 170 °C, and in the second scan the weight loss started from a lower temperature, about 130 °C, this



Scheme 3. Hydrolytic ring-opening addition reaction of the BOE moiety catalyzed by carboxylic acid in the solid-state.

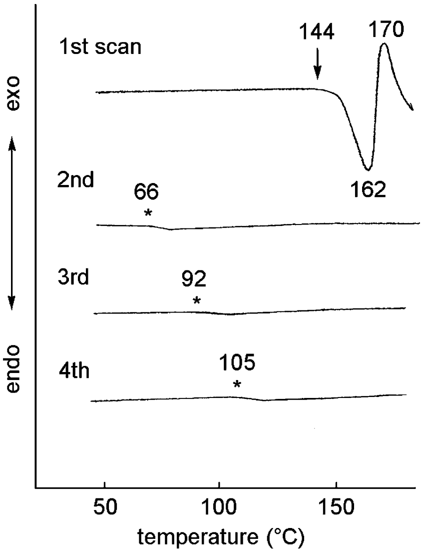


Fig. 2. Changes in DSC profile of a reaction mixture of BOE-I-2 and DL-tartaric acid ([BOE]/[COOH] = 1:2). Heating rate: 5 °C min^{-1}.

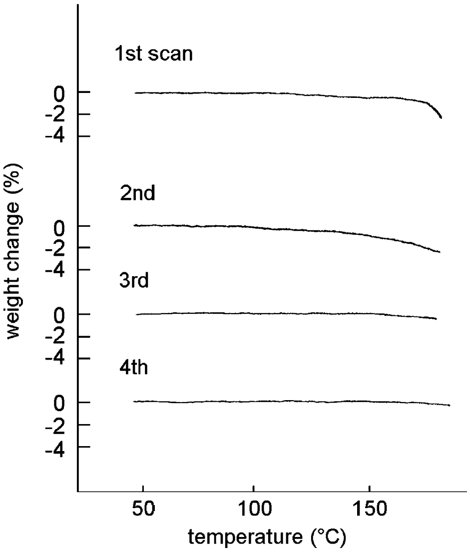


Fig. 3. Changes in TG profile of a reaction mixture of BOE-I-2 and DL-tartaric acid ([BOE]/[COOH] = 1:2). Heating rate: 5 °C min^{-1}.

temperature being near the melting point of BOE-I-2-H, 125.5–126.5 °C. In the third and fourth scans, the degree of weight loss decreased with the cycle. Observed weight loss must reflect a hydration reaction, because the intensity of the characteristic absorption band $\nu_{\text{O–H}}$ at 3350 cm^{-1} in the FT-IR spectrum decreased after the heating process.

Taking the results of DSC and TG measurements into consideration, the reaction of BOE-I-2 and DL-tartaric acid could be clearly explained as follows: (1) the ring-opening isomerization of BOE-I-2 occurred to form the hydrolyzate during grinding at room temperature; (2) in the heating process, the polyaddition and polycondensation reactions among the BOE, hydroxyl, and carboxyl groups began to construct a networked polymer; and then (3), a further dehydration reaction continued to make a more rigid polymer with a corresponding increase in T_g.

3.6. Metal adhesive properties of powder mixtures of BOEs and carboxylic acids

Since the synthesized BOEs consist of two BOE groups and a linkage group, the polyaddition and polycondensation of BOEs with bifunctional carboxylic acids led to crosslinked rigid polymers, which were expected to show adhesive properties. This was because they included many polar groups, such as the hydroxyl, carboxyl, ester, and ether groups. To evaluate the adhesive properties of the crosslinked polymers, their ground powder mixtures were applied to the adhesion of a metal substrate, for which a Ni–Cr alloy used in dental restoration was used. The mixed powder was distributed on a surface of the metal substrate and then the surface was brought face to face with the surface of another metal substrate. One set of the test pieces was heated at 150 °C for 15 h in a high-pressure polymerization chamber under a nitrogen atmosphere. The adhesion property was evaluated by measuring its tensile strength.

The curing reaction of BOE-I-2 with various carboxylic acids such as DL-tartaric (TA), citric (CA), DL-malic (MA), adipic (AA), and terephthalic acids (TPA) was carried out. These acids have carboxyl + hydroxyl groups present in the molecules, which are, 2 + 2, 3 + 1, 2 + 1, 2 + 0, and 2 + 0 for TA, CA, MA, AA, and TPA, respectively. The samples were prepared with a unit ratio of [BOE]/[COOH] = 1:2 in feed. The results are shown in Fig. 4. The sample prepared with DL-tartaric acid showed the highest value of 68.8 MPa. This obtained adhesion value was larger than the values obtained when using three kinds of commercially available non-solvent-type adhesives, which showed values in a tensile strength range of 25–60 MPa under the same conditions. On the other hand, with TPA, no adhesive strength was obtained. Indeed, in a TG measurement of the mixed sample with TPA, no weight loss due to the polycondensation was observed. It is obvious that the tensile strength is related to the number of carboxyl and hydroxyl groups in a molecule. As references, the adhesion test with only carboxylic acid was examined without BOE, resulting in poor tensile strength values such as 4.7, 3.0, 0, and 0 MPa for TA, MA, AA, and TPA, respectively. These results show clearly that the number of carboxyl and hydroxyl groups affected the adhesion property.

The synthesized BOEs were mixed with DL-tartaric acid at a unit ratio of [BOE]/[COOH] = 1:2 and the adhesive strength evaluated. As shown in Fig. 5, the adhesive strength of all the cured products was adequately high in a tensile strength range of 75–80 MPa. These high adhesive strengths must be attributable to the BOE-hydrolyzates as the main component after the solid-state reaction with carboxylic acids as shown in Scheme 3. Fig. 5 shows also the tensile strength values using the corresponding BOE-hydrolyzates with DL-tartaric acid at a unit ratio of [BOE-hydrolyzate]/[COOH] = 1:2. Though the

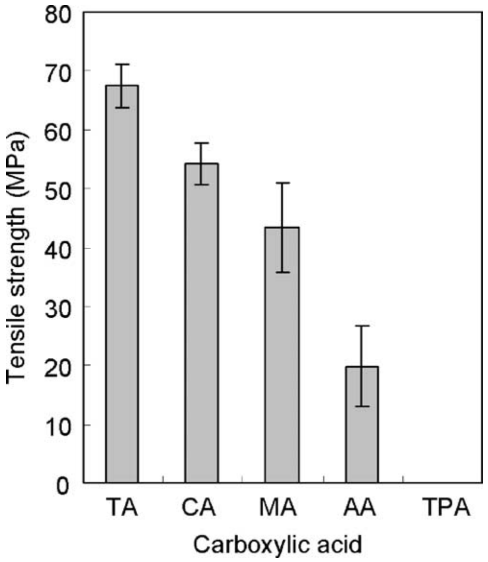


Fig. 4. Metal adhesion property of cured products of the BOE-I-2/carboxylic acid composites. Curing was carried out at 150 °C for 15 h, and [BOE]/[COOH] = 1:2 in feed. Abbreviation; adipic acid (AA), DL-malic acid (MA), DL-tartaric acid (TA), citric acid (CA), and terephthalic acid (TPA). Bars indicate standard deviation values.

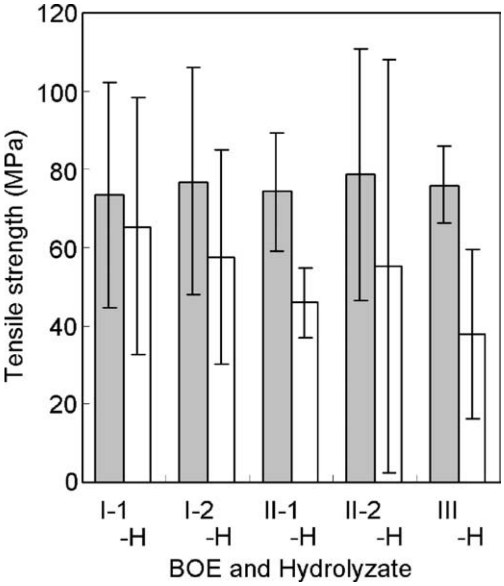


Fig. 5. Metal adhesion property of cured products of the BOE and BOE-hydrolyzate (BOE-H)/DL-tartaric acid composites. Curing was carried out at 150 °C for 15 h in feed ratios of [BOE]/[COOH] = 1:2 and [BOE-hydrolyzate]/[COOH] = 1:2. Bars indicate standard deviation values.

hydrolyzate mixtures also exhibited relatively high adhesive strength values in a range of 40–70 MPa, obviously, their values were less than those for the BOE mixtures. These results suggest that the ring-opening isomerization polyaddition of BOE units also contributed to the adhesive property of the BOE mixtures. Moreover, the adhesive strength of BOE-hydrolyzate mixtures was in the order of BOE-I-H series > BOE-II-H series > BOE-III-H. It is considered that this order reflected the rigidity of BOE structures and the T_m values.

To clarify the effect of the feed ratio on the adhesive property, BOE-I-2 and DL-tartaric acid were mixed with various feed ratios in a range of [BOE]/[COOH] = 1:0.5–1:3.0 and evaluated for adhesive strength. As shown in Fig. 6, the tensile strength changed depending on the feed ratio and the highest value of 76.4 ± 24.8 MPa was found at [BOE]/[COOH] = 1:1.5. This result must reflect a unit ratio that is effective in forming a proper crosslinking structure of the cured product.

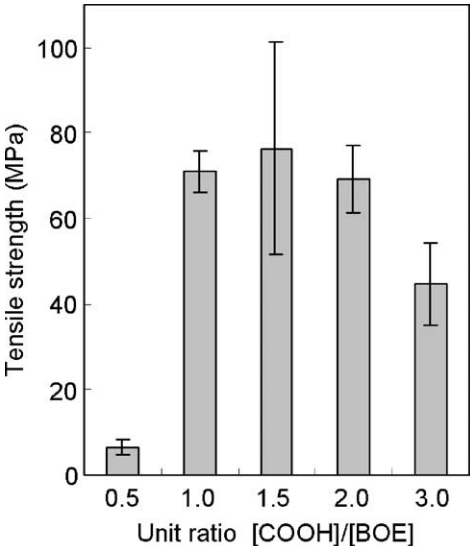


Fig. 6. Metal adhesion property of cured products of BOE-I-2/DL-tartalic acid composites in various unit ratios [COOH]/[BOE] in feed. Curing was carried out at 150 °C for 15 h. Bars indicate standard deviation values.

The effect of curing time on the adhesive property was also evaluated using BOE-I-2 and carboxylic acids, TA and AA. Results are shown in Fig. 7. When composition ratio of [COOH] in feed was high, the adhesive strength property appeared rapidly. The sample *c*: [BOE]/[COOH in TA] = 1:2 exhibited relatively high adhesion strength even after 2 h, then, however, the adhesive strength increased only slightly to reach a nearly constant value after 5 h. The sample *a*: [BOE]/[COOH in TA] = 1:1 increased in strength gradually and reached the same strength level as sample *c* after 15 h as shown in Fig. 6. On the other hand, in the reaction with AA: sample *d*: [BOE]/[COOH in AA] = 1:2 showed a low strength value of 5 MPa even after 5 h, which increased slowly up to 20 MPa at 15 h as shown in Fig. 4. These time courses for adhesion strength suggest that the hydroxyl group plays an important role in the rapid formation of the crosslinking structure.

3.7. Plausible reaction mechanism

In Scheme 4, a plausible reaction pathway is depicted. The solid-state reaction of BOEs and carboxylic acids proceeded at room temperature under a mechanical process by grinding. The reaction was accelerated by the higher reactivity given by the α-hydroxyl group in the acids, but such acceleration did not occur under absolutely dry conditions. The reaction resulted in the hydrolysis of BOE moiety accompanying the ring-opening isomerization. In the following heating process, dehydration and crosslinking reactions occurred to produce cured materials.

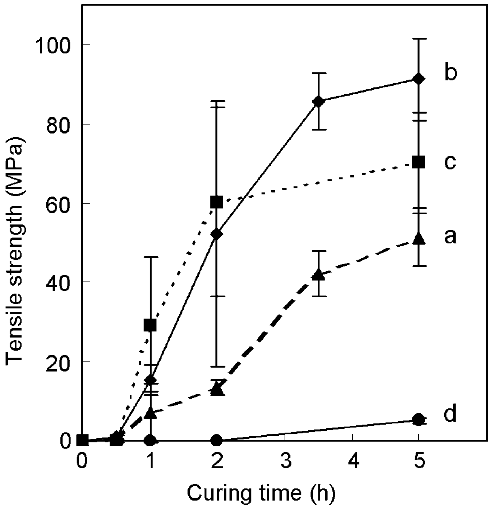
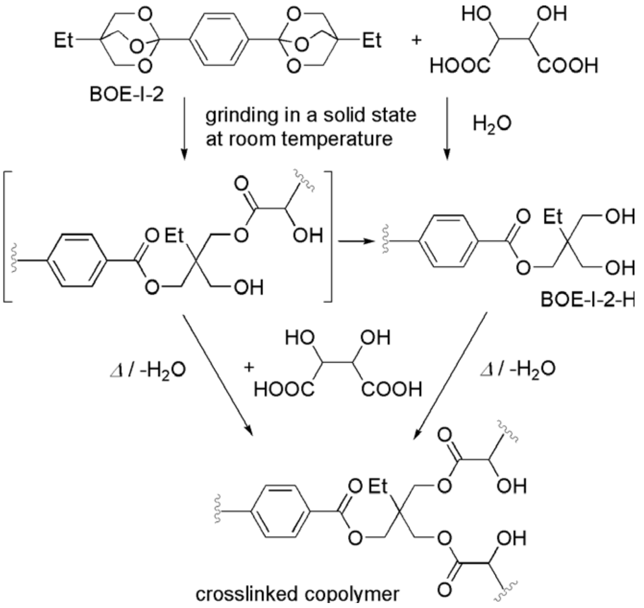


Fig. 7. Relationship between curing time and tensile strength. Curing of BOE-I-2 and carboxylic acids was carried out at 150 °C in feed ratio of [BOE]/[COOH] = (a) 1:1, (b) 1:1.5, (c) 1:2, (d) 1:2. Carboxylic acid: (a), (b), (c) DL-tartaric acid; (d) adipic acid. Bars indicate standard deviation values.



Scheme 4. Plausible pathway for the reaction of BOE-I-2 and DL-tartaric acid.

In the mechanical process, the effect of the hydroxyl group in the acids markedly corresponded to the decrease in pKa_1 value at 25 °C, such as TA ($pKa_1 = 2.82$ for D-form and 2.99 for L-form), MA (3.24), AA (4.26) [17]. The hydroxyl groups must absorb water molecules from the atmosphere and form hydrogen bonding with oxygen on a BOE ring to accelerate the hydrolysis of the BOE moiety. Moreover, in the heating process, the hydroxyl group must cause the dehydration reaction with a carboxyl group to function as a crosslinking site, resulting in a crosslinked product showing a high adhesive property.

In this mechanism, BOE groups may be regarded as precursors of corresponding hydrolyzates, which are substantial functional groups causing the dehydration and crosslinking reactions. However, we can be sure that some BOE groups, remaining even after the solid-state reaction, react with carboxylic acids to form corresponding polyaddition products as shown in Scheme 4. This reaction gives the products an excellent adhesive strength, which was higher than that of the products that had only undergone curing with BOE-hydrolyzates and carboxylic acids as shown in Fig. 5.

4. Conclusions

Five kinds of novel bifunctional BOEs were synthesized and copolymerized with multi-functional carboxylic acids having plural carboxyl and hydroxyl groups. In a solid-state reaction of BOEs with the carboxylic acids, mechanical mixing led the BOE moiety to a corresponding hydrolyzed form via the ring-opening and isomerization reactions. The solid-state reaction required moisture and mechanical stress, and was accelerated by the higher reactivity given by the α-hydroxyl group in the acid.

By heating at 150 °C, the mixtures of BOEs and the carboxylic acids were dehydrated and cured to produce crosslinking rigid polymers, resulting in high adhesive bonding to a Ni–Cr alloyed metal substrate. Average tensile strengths of cured products were in a range of 20–80 MPa dependent on the number of hydroxyl groups in the acid molecules. This high adhesive property was achieved not only by polycondensation of BOE-hydrolyzates and the carboxylic acids, but also by polyaddition of BOEs and the carboxylic acids.

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