Functionalization of amine-cured epoxy resins by boronic acids based on dynamic dioxazaborocane formation

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ARTICLE

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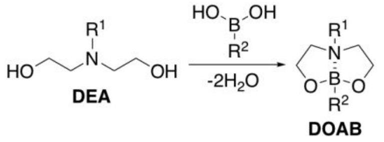
Functionalization of epoxy resins after curing is challenging because of their thermosetting properties. The intrinsic reactive chemical structures of epoxy resins can be used to overcome this challenge. Herein, we demonstrated functionalization of post-cure epoxy resins based on dynamic dioxazaborocane (DOAB) formation between diethanolamine (DEA) units in amine-cured epoxy resins and boronic acid modifiers. The cured epoxy resins were modified using a phenylboronic acid and a linear polymer with boronic acid pendants functionalized with spiropyran groups as a dye and a functional coating. Furthermore, cross-linked polymers containing boronic acid groups, *i.e.*, an acrylamide gel and a methacrylic elastomer, were synthesized, which behaved as adhesives for cured epoxy resins. These results provide novel possibilities for application of dynamic DOAB formation to functionalize amine-cured epoxy resins.

Introduction

Epoxy resins are widely used as thermoset materials in coatings, glues, electric encapsulants, and building materials due to their excellent chemical and physical properties. Epoxy resins exhibit excellent chemical resistance, thermal stability, mechanical strength, and insulation.[1] These properties are largely attributed to their three-dimensional (3D) cross-linked structures generated during curing, where epoxides on the prepolymers and curing agents such as amines and anhydrides react. These cross-links allow for thermosetting of the epoxy resins, making them excessively rigid or insoluble and preventing functionalization after curing.

Conventional approaches to obtain epoxy resins with specific functionalities after curing involve inclusion of additives in prepolymers or substitution of existing reactants with functionalized compounds. For example, nanoclay and carbon fiber additives are commonly used to impart thermal resistance and toughness to cured epoxy resins.[2] In contrast, prepolymers that can form reversible ester, disulfide, and Diels-Alder bonds enable recycling and self-healing of the resins.[3–6] However, these units must be included *before* curing to realize the desired properties *after* curing.

To modify existing cured epoxy resins, the reactivity of intrinsic chemical structures in the amine-cured epoxy resins, diethanolamine (DEA) units, can be utilized.[7–9] These units arise from the ring-opening reaction of epoxides by amine curing agents, and react with boronic acids to form 1,3,6,2-dioxazaborocanes, or DOABs (Scheme 1). Because of intramolecular B-N interactions, DOABs are more stable than trigonal boronate esters toward heat, air, and moisture,[10–12] allowing boronic acids as modifiers to stably bind to epoxy resins. Indeed, boronic acids react with DEA units on rigid bisphenol-A type epoxy resins pre-cured by aliphatic amines when the steric demand in the vicinity of boron atom is low. Moreover, the addition of fluorescent and bifunctional boronic acids to a cross-linked epoxy resin changed the fluorescence and mechanical properties of the original resin, respectively.[13] This suggested that this type of modification method is feasible for existing amine-cured epoxy resins. Despite these results, advanced applications of dynamic DOAB formation for post-cure functionalization of epoxy resins have not been reported. To provide a proof of concept and assess potential applicability,



Scheme 1. DOAB formation from a DEA and a boronic acid.

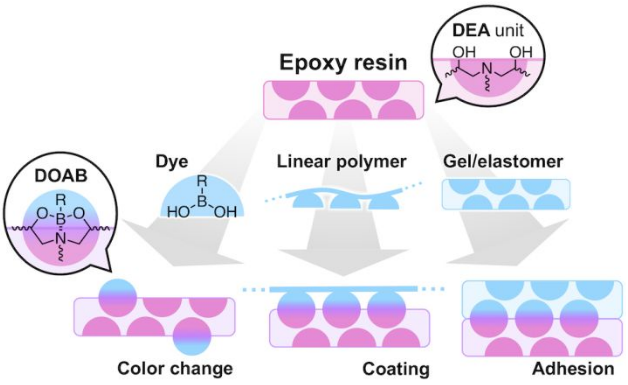


Fig. 1. Functionalization of epoxy resins based on DOAB formation.

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the modification of amine-cured epoxy resins was achieved by developing functionalized boronic acids for use as dyes, coatings, adhesive gels, and elastomers. Each of the modifiers were first confirmed to react with DEA units in model reactions and were subsequently successfully functionalized onto epoxy resins (Fig. 1).

Experimental

Materials

All reagents and solvents used in this study were purchased from, Tokyo Chemical Industry (Tokyo, Japan), Kanto Chemical (Tokyo, Japan), FUJIFILM Wako Pure Chemical Corporation (Tokyo, Japan), and Sigma-Aldrich (MO, USA), and used as supplied unless otherwise mentioned. *n*-Butyl acrylate, hexyl methacrylate, and styrene were filtered over activated basic alumina prior to use.

Measurements

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker topspin AVANCE III HD500 spectrometer at 25 °C in hexadeuterodimethyl sulfoxide (DMSO-d_6) or chloroform-*d* ($CDCl_3$). Spectra were referenced to an internal TMS standard (0.00 ppm) in $CDCl_3$ or DMSO-d_6 (2.50 ppm) for the ^{1}H NMR spectra and DMSO-d_6 (39.5 ppm) for the ^{13}C NMR spectra. Fourier transform infrared (FT-IR) spectra were recorded on a JEOL FT/IR-4100 spectrometer on a NaCl plate. Attenuated total reflection (ATR-FTIR) spectra were recorded on the same spectrometer equipped with an ATR apparatus. Gel permeation chromatography (GPC) measurements were carried out at 40 °C on TOSOH HLC-8320 GPC system equipped with a guard column (TOSOH TSK guard column Super H-L), three additional columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector, and a UV-vis detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene standards (number average molecular weight (M_n) = 4,430−3,242,000 g mol^{-1}; polydispersity index (PDI) = 1.03−1.08) were used to calibrate the GPC system. UV-vis absorption spectra were recorded on a JEOL V-550 spectrophotometer. Glass transition temperatures (T_g) of polymers were estimated by differential scanning calorimetry (DSC) measurements carried out on a SHIMADZU DSC-60A Plus with a heating rate of 10 °C/min under N_2 flow. Tensile tests and T-peel tests were performed at 25 °C on a SHIMADZU EZ-L instrument equipped with 50 N load cell at 50 mm/min.

Synthesis

Spiropyran-functionalized boronic acid (SpBA)[14] 3-Carboxyphenylboronic acid (1.20 g, 7.23 mmol) and 4-dimethylaminopyridine (0.442 g, 3.61 mmol) were pre-dried under vacuum overnight in a round bottom flask. The solid was then suspended in 5.00 mL of anhydrous *N*,*N*-dimethylformamide (DMF) together with 1-(2-hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran (SpOH) (1.27 g, 3.61 mmol) and *N*,*N*'-diisopropylcarbodiimide (0.913 g, 7.23 mmol). The solution was stirred at 25 °C for 24 h and left in the freezer overnight to precipitate the urea, which was filtered afterwards. The crude product was precipitated from the filtrate in water, dried in ethyl acetate (EtOAc) over anhydrous magnesium sulfate, and chromatographed on silica gel using EtOAc and hexane as the eluent. **SpBA** was obtained as brown powder. Yield 0.928 g, 51.4%. ^{1}H NMR (500 MHz, DMSO-d_6) : δ /ppm 0.74−0.78 (m, 3H, CH_2CH_3), 0.79−1.35 (m, 16H, CH_2, CCH_3), 1.50−1.54 (br, 2H, NCH_2CH_2), 2.17−3.58 (m, 8H, NCH_2), 4.11−4.22 (m, 4H, CH_2O), 4.26−4.61 (m, 4H, OC*H*, OCH_2), 5.87−5.92 (m, 1H, OC=C*H*), 6.76−6.86 (m, 2H, aromatic, 1H, OC=C*H*), 6.98−6.97 (m, 6H, aromatic), 6.98−7.00 (m, 2H, aromatic), 7.01−7.13 (m, 6H, aromatic), 7.77−8.05 (m, 3H, aromatic), 8.14−8.21 (m, 1H, aromatic), 8.27 (br, 1H, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6); δ/ppm 166.05, 159.10, 146.46, 140.55, 138.88, 135.49, 135.14, 130.72, 128.62, 128.32, 127.83, 127.77, 127.70, 125.77, 122.92, 121.84, 121.61, 119.46, 118.71, 115.47, 106.33, 59.81, 52.45, 42.03, 25.58, 19.49; FT-IR (NaCl): $\tilde{\nu}$/cm^{-1} 3405, 1713, 1610, 1518, 1482, 1336, 1273, 1169, 1090, 955, 807, 747, 515, 493, 476, 466. ESI: 535.1449 [M+Cl]$^-$, calculated for $C_{27}H_{25}BN_2O_7$ [M+Cl]$^-$: 535.7613.

Elastomeric epoxy resin (ER) 2,2-Bis(4-glycidyloxyphenyl) propane (DGEBA) (0.800 g, 2.35 mmol) and poly(propylene glycol) bis(2-aminopropyl ether) (D2000, average M_n ~ 2000 g mol^{-1}) (2.35 g, 1.18 mmol) were mixed thoroughly in a glass vial by using magnetic stirrer. After degassed under vacuum, the mixture was poured into a Teflon mold (ϕ = 5 cm) and heated at 120 °C for 3 h and 140 °C for 3 h. The cured sample was removed from the mold as a transparent pale-yellow elastomer, **ER**. Yield 2.76 g, 87.5 %.

Linear polymer with pendant boronic acids (PBA)[15] *n*-Butyl methacrylate (BMA) (2.34 g, 16.4 mmol), 4-vinylphenylboronic acid (VBA) (270 mg, 1.83 mmol), and 2,2'-azobis(isobutyronitrile) (AIBN) (30.0 mg, 0.183 mmol) were dissolved in anhydrous *N*,*N*-dimethylacetamide (DMAc) (1.50 mL). The solution was purged with nitrogen gas for 2 h and was stirred at 80 °C. The reaction mixture was exposed to air and diluted with an excess amount of DMAc immediately after it became highly viscous. The solution was then dropped to a mixture of water and methanol (v/v = 3/1). The obtained white precipitate was dried under vacuum to give **PBA** as white solid. Yield 1.68 g, 64.7 %. M_n 34,400 g mol^{-1}, PDI 3.19. Note that GPC measurement was carried out with the protection of boronic acid groups by adding 2,3-butanediol to the sample solution. ^{1}H NMR spectrum was taken with additional 30 μL of MeOD to hydrolyze intermolecular/intramolecular boroxines. ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 0.57−0.94 (br, 3H, CH_3), 1.18−1.38 (br, 2H, CH_3CH_2), 1.59 (br, 2H, $CH_3CH_2CH_2$), 1.71−1.93 (br, 2H, CCH_2), 3.92 (br, 2H, OCH_2), 6.99 (br, aromatic), 7.41−7.58 (br, aromatic); FT-IR (NaCl): $\tilde{\nu}$/cm^{-1} 3503, 2959, 2874, 1731, 1609, 1471, 1341, 1243, 1153, 1065, 1018, 965, 833, 752, 654, 472, 445.

The reference sample was synthesized with styrene instead of VBA in the same manner using BMA (2.34 g, 16.4 mmol), styrene (190 mg, 1.83 mmol), and AIBN (30.0 mg, 0.183 mmol) to give **PSt** as colorless transparent solid. Yield 2.08 g, 82.4 %. M_n 39,400 g mol^{-1}, PDI 1.79. ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm 0.58-0.96 (br, 3H, C*H*$_3$), 1.17-1.41 (br, 2H, CH$_3$C*H*$_2$), 1.61 (br, 2H, CH$_3$CH$_2$C*H*$_2$), 1.81-1.93 (br, 2H, CC*H*$_2$), 3.94 (br, 2H, OC*H*$_2$), 7.01-7.21 (br, aromatic); FT-IR (NaCl): $\tilde{\nu}$/cm^{-1} 2959, 2874, 1727, 1467, 1385, 1240, 1146, 1067, 967, 755, 701, 493, 482, 465.

Linear epoxy polymer (EP)[13] DGEBA (0.820 g, 2.42 mmol) and 1-propylamine (0.200 mL, 2.42 mmol) were dissolved in 0.900 mL of DMF in a glass vial. After being stirred at 100 °C for 3 h, the reaction mixture was precipitated into a mixture of acetone/hexane (v/v = 3/2). The obtained white solid was dried under vacuum to give **EP** as white solid. Yield 0.617 g, 64.0 %. M_n 33,800 g mol^{-1}, PDI 2.36. ^{1}H NMR (500 MHz, DMSO-d_6): δ/ppm, 0.73–0.77 (m, 3H, CH$_2$C*H*$_3$), 1.35–1.39 (m, 2H, C*H*$_2$CH$_3$), 1.53 (br, 6H, CC*H*$_3$), 2.40–2.62 (m, 6H, NC*H*$_2$), 3.78–3.93 (m, 6H, OC*H*$_2$C*H*OH), 4.81–4.84 (m, 2H, O*H*), 6.74–6.78 (m, 4H, aromatic), 7.03–7.05 (m, 4H, aromatic); ATR-FTIR: $\tilde{\nu}$/cm^{-1} 3377, 2959, 1606, 1506, 1457, 1362, 1294, 1233, 1180, 1032, 825, 553, 424, 406.

Linear polymer with spiropyran and boronic acid pendant groups (PSpBA)[16] Vinyl monomer with a spiropyran group (**SpMA**) was synthesized according to the literature.[17] BMA (303 mg, 2.13 mmol), VBA (45.0 mg, 0.304 mmol), **SpMA** (251 mg, 0.609 mmol), and AIBN (100 mg, 0.609 mmol) were dissolved in dry toluene (6 mL). The solution was purged with nitrogen gas for 1 h and was stirred at 65 °C for 24 h. After cooled down to the room temperature, the reaction mixture was dropped into a mixture of methanol and water (v/v = 4/1). The precipitate was dried under vacuum to give **PSpBA** as red brown solid. Yield 0.574 g, 96.3%. M_n 3,700 g mol^{-1}, PDI 2.56. Note that GPC measurement was carried out with the protection of boronic acid groups by adding 2,3-butanediol to the sample solution. ^{1}H NMR spectrum was taken with additional 30 μL of MeOD to hydrolyze intermolecular/intramolecular boroxines. ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm 0.87-0.93 (br, 3H, C*H*$_3$), 1.17 (br, 3H, C*H*$_3$), 1.19-1.28 (br, 2H, CH$_3$C*H*$_2$), 1.37 (br, 2H, CH$_3$CH$_2$C*H*$_2$), 1.59 (br, 3H, C*H*$_3$, 2H, CC*H*$_2$), 1.80 (br, 3H, C*H*$_3$), 3.37 (br, 2H, NC*H*$_2$), 3.93 (br, 2H, OC*H*$_2$), 5.86 (br, 1H, OCC*H*), 6.70-7.21 (br, aromatic), 7.94-8.03 (br, aromatic); FT-IR (NaCl): $\tilde{\nu}$/cm^{-1} 3494, 2959, 2872, 1725, 1610, 1578, 1522, 1482, 1339, 1271, 1168, 1090, 1019, 956, 810, 747, 682, 475.

The reference sample **PSpSt** was synthesized in the same manner using BMA (60.6 mg, 0.426 mmol), styrene (6.34 mg, 60.9 μmol), **SpMA** (51.2 mg, 0.122 mmol), and AIBN (20.0 mg, 0.183 mmol). Yield 82.2 mg, 68.8 %. M_n 6,960 mol^{-1}, PDI 2.36. ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm 0.86–0.93 (br, 3H, C*H*$_3$), 1.17 (br, 3H, C*H*$_3$), 1.28 (br, 2H, CH$_3$C*H*$_2$), 1.37 (br, 2H, CH$_3$CH$_2$C*H*$_2$), 1.59 (br, 3H, C*H*$_3$, 2H, CC*H*$_2$), 1.81–1.90 (br, 3H, C*H*$_3$), 3.38-3.47 (br, 2H, NC*H*$_2$), 3.93 (br, 2H, OC*H*$_2$), 5.88–5.89 (br, 1H, OCC*H*), 6.74–7.17 (br, aromatic), 8.02 (br, aromatic); FT-IR (NaCl): $\tilde{\nu}$/cm^{-1} 2960, 2873, 1728, 1611, 1578, 1523, 1483, 1459, 1339, 1271, 1170, 1090, 1026, 957, 810, 747, 702, 474.

Rigid epoxy resin (ER') DGEBA (0.500 g, 1.47 mmol) and 1,4-diaminobutane (64.8 mg, 0.734 mmol) were mixed thoroughly in a Teflon mold (ϕ = 2 cm) and heated at 120 °C for 3 h and 140 °C for another 3 h. The cured sample was removed from the mold as a transparent pale-yellow solid **ER'**. Yield 0.546 g, 96.6 %.

Boronic acid-containing gel (BAgel)[15] Acrylamide (AAm) (792 mg, 11.0 mmol), *N*,*N'*-methylenebisacrylamide (MBAAm) (100 mg, 0.648 mmol), and VBA (192 mg, 1.30 mmol) were sealed in a flat-bottom glass vial and dissolved in 1.4 mL of anhydrous DMAc. The solution was then purged with argon gas for 1 h. After 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) (40 mg, 0.130 mmol in 1 mL of DMAc) was injected into the vial, the solution was kept purged for 30 min and left at 25 °C for 20 h to form a gel. The colorless transparent gel was repeatedly washed with DMAc and water, and stored in water.

The reference gel **Stgel** was prepared in the same manner using AAm (792 mg, 11.0 mmol), MBAAm 100 mg, 0.648 mmol), styrene (135 mg, 1.30 mmol), and V-70 (40 mg, 0.130 mmol).

Boronic acid-containing elastomer (BAel)[18] Hexyl methacrylate (HMA) (745 mg, 4.38 mmol), 2-methyl-2-propenoic acid 1,1'-(4,13-dioxo-5,12-dioxa-3,14-diazahexadecane-1,16-diyl) ester (HDA, cross-linker, synthesized according to ref. [18]) (104 mg, 0.243 mmol), and VBA (36.0 mg, 0.243 mmol) were sealed in a flat-bottom glass vial and dissolved in 1.00 mL of anhydrous DMAc. The solution was then purged with argon gas for 1 h. After V-70 (15 mg, 49 μmol in 0.900 mL of DMAc) was injected into the vial, the solution was kept purged for 30 min and left at 25 °C for 20 h to form a gel. The resulting gel was repeatedly washed with chloroform and methanol and dried under vacuum at elevated temperatures from 25 to 100 °C. Yield 0.769 g, 86.9 %.

The reference elastomer **Stel** was prepared in the same manner using HMA (745 mg, 4.38 mmol), HDA (104 mg, 0.243 mmol), styrene (25.3 mg, 0.243 mmol), and V-70 (15 mg, 49 μmol). Yield 0.508 g, 58.1 %.

Elastomer containing protected boronic acids (BEel) First, the ester of VBA and 2,3-butanediol (4,5-dimethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane) (VBE) was prepared. VBA (269 mg, 1.82 mmol) and 2,3-butanediol (164 mg, 1.82 mmol) were mixed in 9 mL of THF with magnesium sulfate (43.8 mg, 0.364 mmol). The mixture was stirred at 25 °C overnight, filtered and concentrated. VBE was quantitatively obtained as a transparent liquid and used as it is in the following polymerization.

The elastomer containing VBE (**BEel**) was prepared in a similar manner as **BAel** using HMA (745 mg, 4.38 mmol), HDA (104 mg, 0.243 mmol), VBE (49.1 mg, 0.243 mmol), and V-70 (15 mg, 49 μmol). Yield 0.620 g, 69.0 %.

Model reactions

Reaction of PBA with EP Solutions of **PBA** (12.3 mg in 200 μL of DMF) and **EP** (5.20 mg in 300 μL of DMF) were prepared.

The **PBA** solution was added dropwise to the **EP** solution and constantly mixed with magnetic stirrer. The **PBA** solution was added dropwise until gelation was no longer observed (25 % of prepared **PBA** solution was used by the end of this procedure.) The gel was dried in air and used for characterization.

As a reference experiment, 50 µL of **PSt** solution (13.4 mg in 200 µL of DMF) was dropped in **EP** solution of the same amount as above.

Transesterification 4-Methylphenylboronic acid (BA) (3.00 mg, 22.1 µmol) and either diethanolamine (DEA) (2.32 mg, 22.1 µmol) or 2,3-butanediol (1.99 mg, 22.1 µmol) were mixed in 700 µL of DMSO-d_6 and transferred in NMR test tubes. ^{1}H NMR spectra were taken after the mixtures were prepared (0, 2, 4, 6, 8, 24, and 48 h). The solutions were mixed in the sonication bath before each measurement. ^{13}C NMR spectra were taken for characterization of DOAB and DOB after 48 h.

After the reactions reached the equilibrium, the same molar amount of either DEA or 2,3-butanediol were added to the NMR test tubes containing 2,3-butanediol or DEA respectively to observe the transesterification. The solutions were mixed in the sonication bath and subjected to the same ^{1}H NMR measurements as above.

The reaction ratio was calculated based on the integral values of signals corresponding to the aromatic rings of BA, DOAB (the ester of DEA and BA), and DOB (the ester of 2,3-butanediol and BA).

DOAB: ^{1}H NMR (500 MHz, DMSO-d_6): δ/ppm 2.24 (s, 3H, CH_3), 2.79–2.84, 3.02–3.09 (m, 4H, NCH_2), 3.75–3.78, 3.83–3.88 (m, 4H, OCH_2), 6.78 (br, 1H, NH), 7.00 (d, J = 7.43, 2H, aromatic), 7.32 (d, J = 7.76, 2H, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6); δ/ppm 135.47, 133.12, 127.83, 63.36, 51.10, 21.45. EI: 205.1270 [M]$^+$, calculated for $C_{11}H_{16}BNO_2$ [M]$^+$: 205.0640.

DOB: ^{1}H NMR (500 MHz, DMSO-d_6): δ/ppm 1.21 (d, J = 6.06, 3H, Ar-CH_3), 1.32 (d, J = 5.90, 6H, CHCH_3), 4.65–4.71 (m, 2H, OCH), 7.21 (d, J = 7.63, 2H, aromatic), 7.59 (d, J = 7.79, 2H, aromatic); ^{13}C NMR (125 MHz, DMSO-d_6); δ/ppm 141.63, 134.67, 128.51, 75.71, 21.06, 16.94. EI): 190.1168 [M]$^+$, calculated for $C_{11}H_{15}BO_2$ [M]$^+$: 190.0491.

Results and discussion

Boronic acid-containing dye

Spiropyran has long been exploited as a dye and studied to create novel materials with chromism.[19] For example, polymers functionalized with spiropyran moieties exhibit changes in color, contact angle, and electrostatic interactions with their surrounding molecules in response to stimuli such as light, solvent polarity, and mechanical stress via ring-opening isomerization of the spiropyrans to merocyanines.[20–23] While screening functional groups on boronic acids to develop a modifier for epoxy resins, spiropyran was found to be an ideal compound to endow the resins with several desirable features simultaneously.

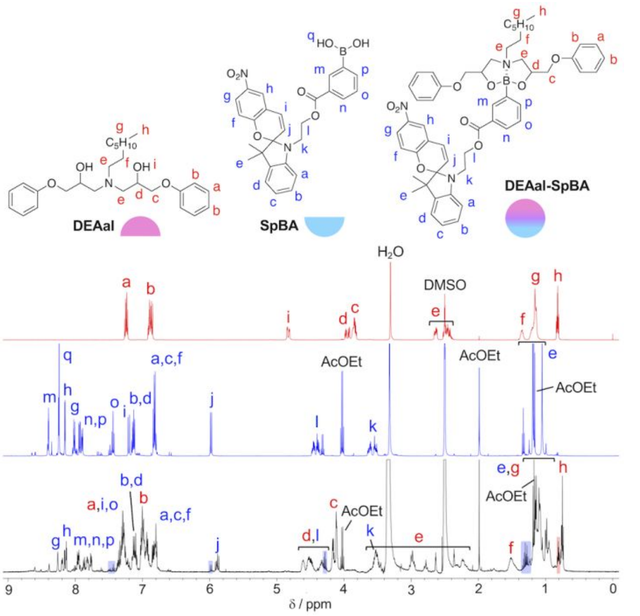


Fig. 2. ^{1}H NMR spectra of **DEAal** (red), **SpBA** (blue), and their adduct **DEAal-SpBA** (black) in $CHCl_3$. Signals from **SpBA** are seen in the spectra of **DEAal-SpBA** due to the hydrolysis in equilibrium with DOAB formation.

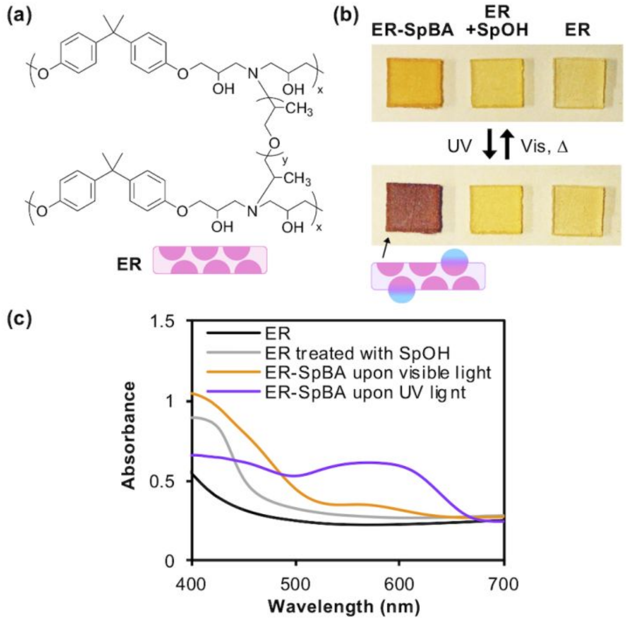
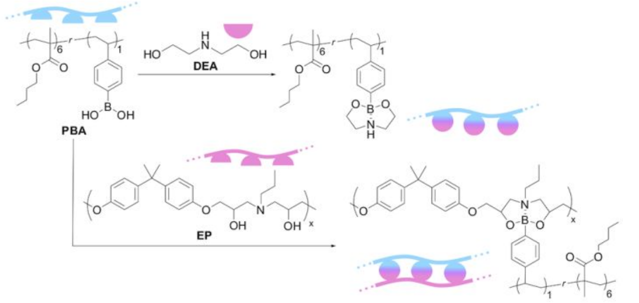


Fig. 3. (a) Chemical structure of **ER**. (b) Photochromism of **ER** immersed in **SpBA**, SpOH, and pristine **ER** (from left to right) and (c) their solid-state UV spectra.

Spiropyran was incorporated into a boronic acid via condensation of hydroxyl group on spiropyran and boronic acid carboxyl group. The obtained **SpBA** showed photochromism under UV irradiation (254 nm) from orange to purple (Fig. S1. ESI†) derived from the change in the chemical structure from spiropyran to merocyanine.[19] **SpBA** formed the DOAB structure, as confirmed by the ^{1}H NMR spectrum of the mixture containing equimolar amounts of **SpBA** and a DEA (**DEAal**)[13] that resembles a model bisphenol-A-type epoxy polymer (Fig. 2). FT-IR analysis also supported this conclusion, where the signal from hydroxyl groups decreased after mixing **SpBA** and **DEAal** (Fig. S2. ESI†).

This confirmed that boronic acid groups maintained their reactivity in the proximity of spiropyran.

SpBA was subsequently used to functionalize the elastomeric cross-linked epoxy resin, **ER** (T_g = –44.5 °C; Fig. 3a). **ER** was cut into squares (7 mm × 7 mm × 1 mm) and immersed for 5 min in a THF solution of **SpBA** (5.0×10^{-2} M). The samples were then washed with THF/methanol using a Soxhlet extractor and dried in air. As shown on the left side of Fig. 3b, **ER** treated with **SpBA** (**ER-SpBA**) became colored after the treatment, suggesting that **SpBA** reacted with the DEA units in **ER**. The coloring was more obvious after UV irradiation (254 nm) for 4 min, showing photochromism (Fig. 3b and 3c). Considering that the reference samples treated with spiropyran containing a hydroxyl group (SpOH) and **ER** did not change colors after the treatment (samples in the middle and right of Fig. 3b), it was clear that **SpBA** was incorporated into **ER** by DOAB formation and not by other possible interactions such as π- π stacking of aromatic rings. The T_g of **ER** treated with **SpBA** (**ER-SpBA**) (–41.4 °C) was almost identical to that of **ER**, indicating that the treatment did not affect the original thermal properties of **ER**. These results demonstrated that **SpBA** can act as a dye for epoxy resins with the color changing.



Scheme 2. Reactions of **PBA** with low-molecular-weight **DEA** (top) and linear epoxy polymer **EP** (bottom).

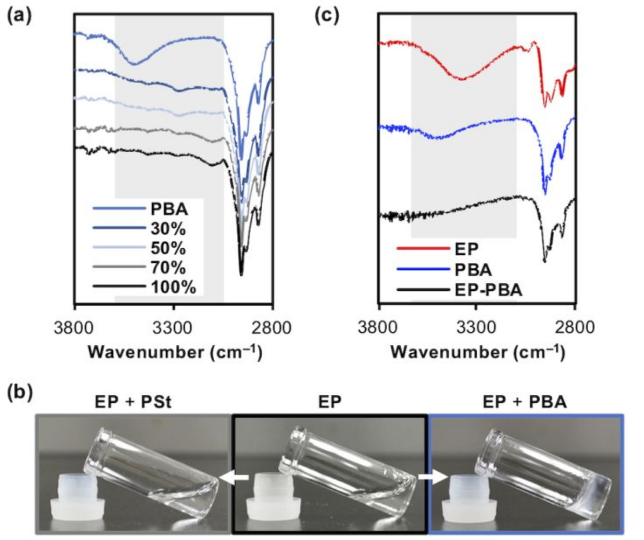
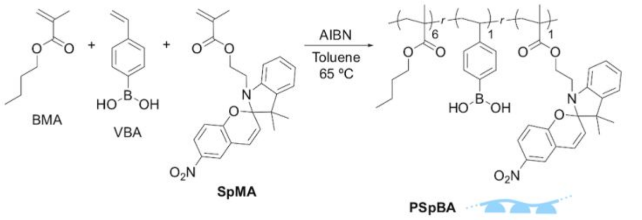


Fig. 4. (a) FT-IR spectra of **PBA** upon gradual addition of DEA from 30 to 100 % to boronic acid pendants. (b) Reaction of **EP** (middle) with **PBA** (right) and the reference polymer **PSt** (left). (c) ATR-FTIR spectra of **EP** (red), **PBA** (blue), and **EP-PBA** (black).

Boronic acid-containing a linear polymer for coating

Next, a polymer-based coating agent containing boronic acid was developed to functionalize the surface of epoxy resins, which often exist as insoluble rigid materials after curing. First, the reactivity of the pendant boronic acid groups on the polymer side chains was investigated. *n*-Butyl methacrylate (BMA) was used as the backbone of the polymer as it is widely used in commercial coatings.[24] 4-Vinylphenyl boronic acid (VBA) was free-radically copolymerized with BMA to afford **PBA** as the polymer-based coating agent. When low-molecular-weight DEA was added to the **PBA** solution (Scheme 2 top), the signal intensity of the hydroxyl groups decreased in the corresponding FT-IR spectra (Fig. 4a). This indicated that the reaction of the boronic acid groups and DEA occurred. In addition, gelation was observed when a liner epoxy polymer **EP** solution was added to a **PBA solution** (Scheme 2 bottom, Fig. 4b). In contrast, the mixture of **EP** and reference polymer (**PSt**) composed of styrene instead of VBA remained solution, indicating that gelation of **EP** and **PBA** was caused by DOAB formation as cross-linking points and not by polymer chain entanglement. The T_g of the dried gel (61.8 °C) was larger than that of **EP** (48.5 °C) and **PBA** (40.2 °C), indicating that the polymer chains lost mobility during the cross-linking reaction between **PBA** and **EP** accompanied by DOAB formation. In addition, the peak originating from the hydroxyl groups on **PBA** and **EP** disappeared in FT-IR spectrum of the dried gel (Fig. 4c). These results demonstrate that the pendant boronic acid groups on the polymer chains can react with low-molecular-weight DEAs and DEA units on epoxy polymers to form DOABs.

Spiropyran was incorporated to **PBA** to obtain a functional polymer coating that showed chromism on epoxy resin surfaces.



Scheme 3. Synthesis of **PSpBA** (BMA: VBA: **SpMA** = 7:1:2 in the feed).

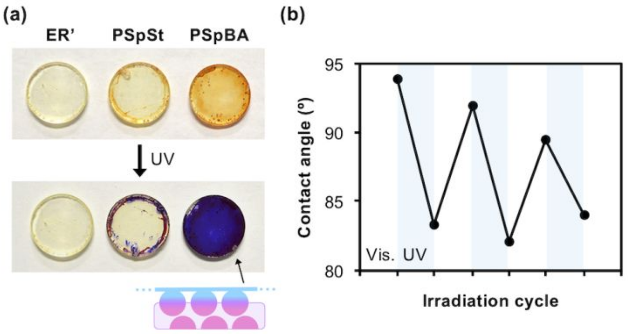


Fig. 5. (a) Appearance of **ER'** (left) after treatment with **PSpSt** (middle) and **PSpBA** (right). **PSpSt** peeled off from **ER'** except for the edge where coloring was observed. (b) Reversible wettability change of the **PSpBA** coating on **ER'** surface for water droplets in air.

Spiropyran was incorporated to **PBA** to obtain a functional polymer coating that showed chromism on epoxy resin surfaces. The spiropyran-functionalized monomer **SpMA** was synthesized according to methods described in the literature[17] and copolymerized with VBA and BMA (Scheme 3). The photochromism of the resulting polymer, **PSpBA**, was confirmed in the UV-vis spectra shown in Fig. S3, ESI†. The rigid **ER'** (T_g = 115 °C) was then used as an epoxy resin to be functionalized. **ER'** was cured with the short-distance cross-linker, 1,4-diaminobutane, so it would exhibit high solvent resistance and marginal swelling. A THF solution of **PSpBA** (6.30 mg in 0.100 mL) was drop-casted on **ER'** and dried overnight in air. As a result, **PSpBA** formed a coating on the **ER'** surface while the reference polymer with styrene instead of VBA (**PSpSt**) easily peeled off (Fig. 5a). ATR-FTIR analysis showed that the signal from the hydroxyl groups at the **ER'** surface decreased after **PSpBA** treatment (Fig. S4, ESI†), indicating that the boronic acids on **PSpBA** formed DOABs with the DEA units on **ER'**. The coating changed color from orange to purple after 10 min of UV irradiation, which was reversed by leaving the sample under visible light for a day or heating at 80 °C for 10 min to facilitate the reverse isomerization of merocyanine (Fig. S5, ESI†). In addition to the color change, the water contact angle on the sample surface changed reversibly, as shown in Fig. 5b. The decreased magnitude of wettability change was likely due to the interaction between the spiropyran nitrogen atoms and boronic acid boron atoms, which stabilized the merocyanine form and prevented reverse isomerization.[25] It should be noted that **PSpBA** stuck on the surface of **ER** through the DOAB formation and responded reversibly to stimuli over three cycles showing photochromism. This demonstrates the application of polymer-based coatings with boronic acid groups for functionalization of amine-cured epoxy resins.

Boronic acid-containing gel for adhesion

As another application of DOAB formation, the bonding of cross-linked polymers bearing boronic acid to epoxy resins via DOAB formation was attempted. Acrylamide-based gels whose pendant boronic acid groups react with diols were first examined.[26,27] **BAgel** (Fig. 6a) was prepared by copolymerizing VBA, acrylamide, and *N*,*N*'-methylenebisacrylamide in DMAc. The obtained gel stored in water was cut into cuboids (5 mm × 5 mm × 7 mm), immersed in THF for a few minutes for solvent displacement, and left on **ER** (5 mm × 5 mm × 7 mm) for 12 h at 25 °C. Tensile testes were then carried out for the facile estimation of the adhesion strength. Although the reference gel synthesized with styrene instead of VBA (**Stgel**) did not attach to **ER**, **BAgel** adhered well to **ER** (Fig. 6b) with a strength of 0.173 MPa, as calculated by the average rupture stress of six samples (Fig. S6, ESI†). Therefore, it is apparent that boronic acids can form DOABs to bond to DEAs between cross-linked material surfaces.

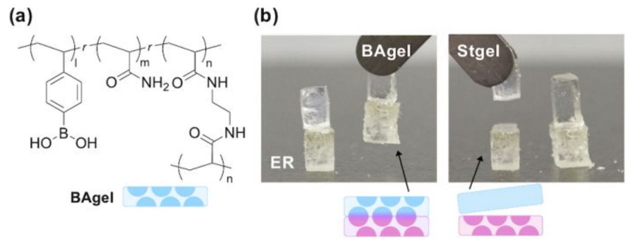
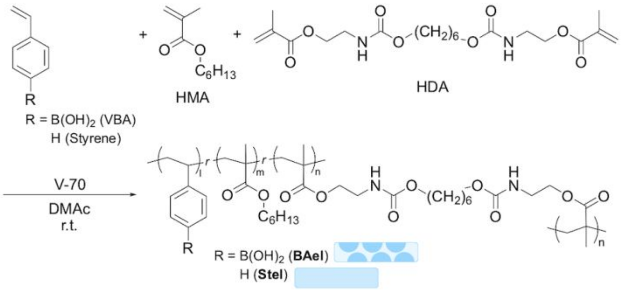


Fig. 6. (a) The chemical structure of **BAgel** (l:m:n = 5:85:10 in the feed). (b) **BAgel** adhered to **ER** (left), while **Stgel** did not (right).



Scheme 4. Synthesis of **BAel** and its reference **Stel** (l:m:n = 5:90:5 in the feed).

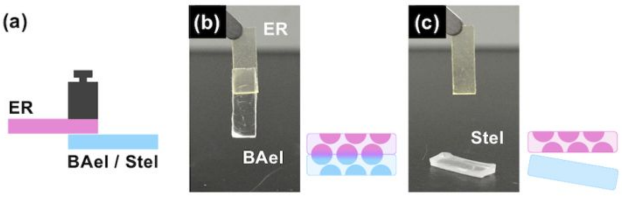
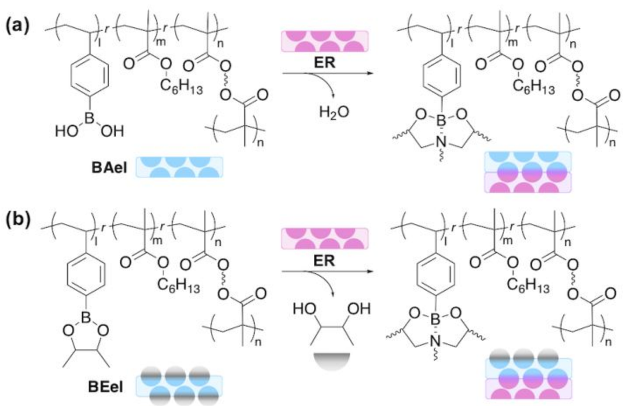


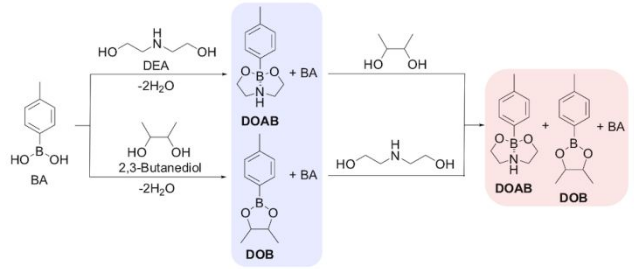
Fig. 7. (a) Adhesion of **ER** and elastomers. (b) **BAel** adhered to **ER**, while (c) **Stel** did not.

Boronic acid-containing elastomer for adhesion

Boronic acid-containing elastomers and epoxy resins were adhered without any solvent. To create the boronic-acid containing elastomer, hexyl methacrylate (HMA) was used instead of BMA as a skeleton for a flexible cross-linked polymer material. The elastomer **BAel** was obtained by copolymerizing VBA, HMA, and hexylene-containing diacrylate (HDA) in DMAc (Scheme 4). The resulting gel was washed repeatedly with chloroform and methanol and dried under vacuum. The dry **BAel** was cut into a rectangular film (5 mm × 15 mm × 1.5 mm) and one third of the surface (5 mm × 5 mm) was contacted with the surface of the rectangular film **ER** (5 mm × 15 mm × 1.2 mm). After being held together overnight by placing 80 g of weights on top of the samples (Fig 7a), **BAel** and **ER** adhered, although



Scheme 5. Adhesion of **ER** and (a) **BAel** via direct DOAB formation and (b) **BEel** via transesterification.



Scheme 6. Reaction of **BA** with DEA or 2,3-butanediol and transesterification of esters.

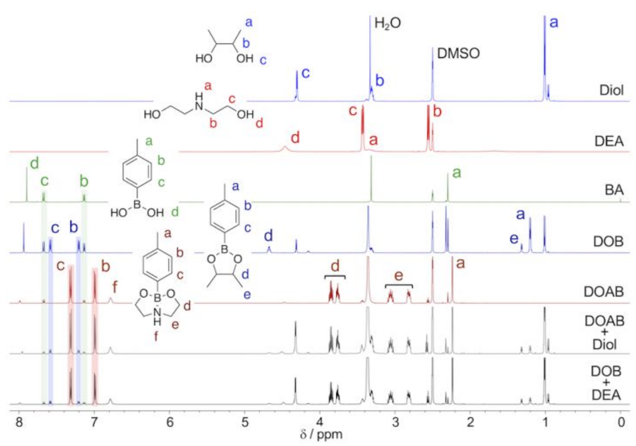


Fig. 8. ^1H NMR spectra of esters and esters mixed with a counterpart diol in DMSO-d_6 (Figs. S7–S10, ESI†).

the control sample with styrenes instead of VBAs (**Stel**) did not attach to **ER** (Fig. 7b and 7c). The subsequent T-peel test (Fig. S6, ESI†) showed that **BAel** was firmly attached to **ER** with a rupture stress of 0.149 MPa. This clearly demonstrates that DOABs can be formed in bulk to adhere elastomers.

Adhesion via transesterification

Polymerization of boronic acid monomers can be hindered by the formation of the six-membered cyclic boronic anhydrides, boroxines.[28] Boroxines are readily formed from three boronic acids acting as cross-linkers between polymer chains,[29–31] leading to low yields and reduced homogeneity of the resulting polymers.[32] This inspired the synthesis of an elastomer with boronic acid groups protected with 1,2-diols, as is often performed to address the adverse effects of boroxines on polymerization.[33] **BEel**, the elastomer containing boronic esters, or 1,3,2-dioxaborolanes (DOB) was prepared to check if the protection would affect the adhesion strength with **ER** (Scheme 5).

For DOBs to form DOABs, boronic acids must undergo transesterification (Scheme 6 bottom). To better understand transesterification, the reactivities of DEAs and diols were compared in model reactions. First, the low-molecular-weight DEA or 2,3-butanediol were added to an equimolar amount of 4-methylphenylboronic acid (BA) to form DOAB or DOB, respectively (Scheme 6, first step). The ^1H NMR spectra of two-component solutions (blue in Scheme 6, 4th and 5th spectra from the top in Fig. 8) showed that the equilibrium ratios of DOAB: BA and DOB: BA were 90:10 and 56:44, respectively. This indicated that the DEAs bind to boronic acids more favorably than diols. A third component, 2,3-butanediol or DEA, was then added to the DOAB solution or the DOB solution respectively (Scheme 6, second step). From the ^1H NMR spectra of the three-component solutions (red in Scheme 6, bottom two spectra in Fig. 8), both mixtures reached the same equilibrium ratio of DOAB: DOB: BA = 84:10:6. This suggested that DOAB formation preferred over DOB formation when DEAs and diols are competitively reacted with boronic acids. In addition, the DOAB ratios in the two- and three-component solutions were nearly as high. Therefore, the adhesion strengths of **BAel** and **BEel** should be comparable.

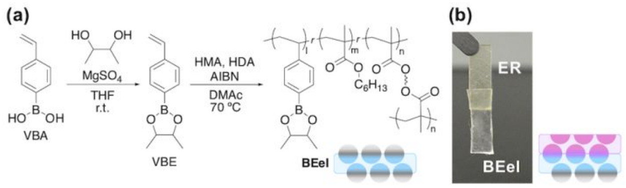


Fig. 9. (a) Synthesis of VBE and **BEel**. (b) Appearance of **BEel** adhered to **ER**.

To determine if these results apply to adhesion (Scheme 5b), an elastomer with VBA protected with 2,3-butanediol (VBE) was prepared (Fig. 9a). VBE was readily synthesized by overnight mixing of VBA, 2,3-butanediol, and magnesium sulfate as a dehydrating agent. VBE was subsequently copolymerized with HMA and HDA to afford the elastomer **BEel**. After being left on the **ER** overnight, **BEel** adhered, as shown in Fig. 9b. The T-peel test of the bonded sample showed an adhesion strength, or rupture stress, of 0.238 MPa. **BEel** bound to **ER** 1.6 times stronger than **BAel** (Scheme 5a), in contrast to the expectations derived from the model reaction. Thus, it was assumed that the number of boronic acids on **BAel** surface was reduced compared to that of DOBs on **BEel** because of the boroxine. The hydrophilic hydroxyl groups of boronic acids likely exist as boroxines on the hydrophobic elastomer surface, making less boronic acid groups available for adhesion. In addition, 2,3-butanediol that was replaced by DEA units may have acted as a plasticizer, [34,35] untangling the polymer chains, which allowed DEA units to encounter DOBs on the **BEel** more often. Therefore, **BEel** contained more boronic acids available via transesterification to form DOABs, resulting in larger adhesion strength.

It should be noted that the adhesion between **ER** and **BAel**/**BEel** was achieved between materials with completely different chemical structures. The adhesion of such dissimilar materials is often challenging because the differences in chemical properties such as hardness, hydrophilicity, and linear expansion coefficients prevent polymer chains at the interface from entangling and forming bonds.[36,37] Adhesion between dissimilar materials is often facilitated by the formation of non-covalent bonds, such as metal-ligand coordination bonds and host-guest interactions,[38–40] whereas **ER** and **BAel**/**BEel** were adhered via DOABs as robust covalent bonds. Therefore, we believe that the results presented herein provide a novel example of adhesion between dissimilar bulk materials, which is simple for application in many other systems using DEA units and boronic acids.

Conclusions

Four applications of DOAB formation to functionalize amine-cured epoxy resins were demonstrated using newly developed boronic acid-containing modifiers. First, the low-molecular-weight boronic acid with a spiropyran group (**SpBA**) was synthesized and acted as a dye for the bisphenol-A type epoxy resin, **ER** and showed photochromism. Second, the linear poly(butyl methacrylate) with pendant boronic acid groups (**PBA**) was prepared and confirmed to form DOAB with low-molecular-weight DEA and DEA units on the linear epoxy polymer. Furthermore, **PBA** with spiropyran groups (**PSpBA**) was applied to the surface of a rigid epoxy resin **ER'** and changed the wettability of the surface upon UV irradiation. Third, the polyacrylamide gel with boronic acid moieties (**BAgel**) attached to **ER**, suggesting that DOABs were formed between the surfaces of the cross-linked materials. Finally, dynamic DOAB formation on the material surface was applied for the adhesion of bulk materials. The boronic-acid containing elastomer (**BAel**) adhered to the **ER** without solvents and the adhesive strength was further improved by protecting boronic acids with diols in advance.

These applications are just some of a large number of possible applications of dynamic DOAB formation in the modification of epoxy resins. Different polymer backbones and functional groups can be introduced to both the epoxy resins and boronic acids. Dynamic DOAB formation between DEA units and boronic acids provides a promising method to functionalize many existing and newly developed amine-cured epoxy resins.

Conflicts of interest

There are no potential conflicts of interest to declare.

Acknowledgements

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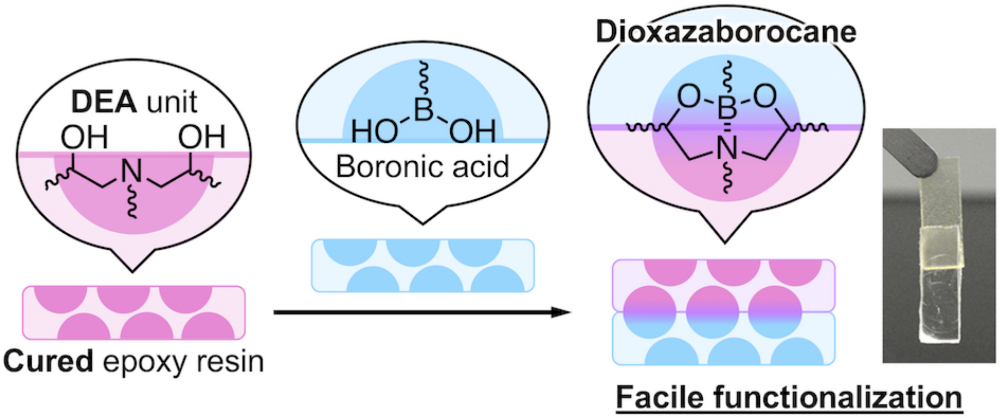

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