Dissimilar Materials Bonding Using Epoxy Monolith

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Supporting Information

ABSTRACT: The epoxy monolith with a highly porous structure is fabricated by the thermal curing of 2,2-bis(4-glycidyloxyphenyl)propane and 4,4′-methylenebis-(cyclohexylamine) in the presence of poly(ethylene glycol) as the porogen via polymerization-induced phase separation. In this study, we demonstrated a new type of dissimilar material bonding method for various polymers and metals coated with the epoxy monolith. On the basis of scanning electron microscopy (SEM) observations, the pore size and number of epoxy monoliths were evaluated to be 1.1−114 μm and 8.7−48 200 mm⁻², respectively, depending on the ratio of the epoxy resin and cross-linking agent used for the monolith fabrication. Various kinds of thermoplastics, such as polyethylene, polypropylene, polystyrene (PS), and polycarbonate (PC) bisphenol-A, and poly(ethylene terephthalate), were bonded to the monolith-modified metal plates by thermal welding. The bond strength for the single lap-shear tensile test of stainless steel and copper plates with the thermoplastics was in the range of 1.2−7.5 MPa, which was greater than the bond strength value for each bonding system without monolith modification. The SEM observation of fractured test pieces directly confirmed an anchor effect on this bonding system. The elongated deformation of the plastics that filled in the pores of the epoxy monolith, was observed. It was concluded that the bond strength significantly depended on the intrinsic strength of the used thermoplastics. The epoxy monolith bonding of hard plastics, such as polystyrene and poly(methyl methacrylate), was performed by the additional use of adhesives, solvents, and a reactive monomer. The epoxy monolith sheets were also successfully fabricated and applied to dissimilar material bonding.

INTRODUCTION

Monoliths are highly porous materials with a three-dimensionally continuous through-hole and mesh skeleton, i.e., a bicontinuous structure. 1−4 The high porosity and the strength of monoliths have been applied to the separation and support materials, such as column fillers for high-performance liquid chromatography, catalytic supports, and columnar reactors. 5−9 In general, monoliths are formed through any microphase separation processes, which can be categorized into polymerization-induced phase separation (PIPS), 10,11 non-solvent-induced phase separation, 12,13 and thermally induced phase separation. 14,15 Polymer monoliths are advantageous, unlike inorganic monoliths, because of their pH stability, easy functionalization, and modification. Epoxy monolith is one of the bicontinuous and porous materials formed by PIPS. The phase separation is induced by spinodal decomposition when an epoxy resin and a cross-linking agent are cured upon heating in the presence of a porogen. 16−23 The phase-separated structure of the epoxy resin is fixed by cross-linking reactions. Therefore, the rate of the cross-linking reactions significantly influences the pore size of the resulting monoliths. 16,17 Recently, metal components used in the automotive, aerospace, and microelectronics industries are increasingly replaced by polymer and composite materials. 24−28 At the same time, the importance of adhesives and adhesion technology has increased due to the diversity of used materials. 29−35 This accelerating trend requires a new reliable technology, including surface modification methods for dissimilar materials bonding. 36−50 In contrast to the intensive studies of epoxy monoliths as column fillers and separators for high-performance separation systems, 51−65 we can find no report regarding the application of epoxy monolith for adhesion in the literature. Our preliminary results revealed that epoxy monolith was available for bonding of a stainless steel (SUS430) plate and thermoplastics. 66,67 In this study, we demonstrate the validity of the epoxy monolith bonding for dissimilar material bonding between various metals and polymers. The bonding strength values were evaluated for polyethylene (PE), polypropylene (PP), polystyrene (PS), polyoxymethylene (POM), and acrylic−butadiene−styrene copolymer (ABS), polycarbonate (PC) bisphenol-A and poly(ethylene terephthalate) (PET) as the thermoplastics with steel, copper (Cu), and aluminum (Al) as the metals by a single lap-shear tensile test. In addition, epoxy monolith bonding with hard plastics, such as polystyrene (PS) and poly(methyl methacrylate) (PMMA), using commercial adhesives, solvents, and...
a polyfunctional monomer was examined. Epoxy monolith sheets were also successfully fabricated and used as the mediator for the dissimilar material bonding.

## RESULTS AND DISCUSSION

**Preparation of Epoxy Monolith.** The epoxy monolith was prepared on the surface of metal plates using 2,2-bis(4-glycidyloxyphenyl)propane (BADGE) and 4,4′-methylenebis(cyclohexylamine) (BACM) as the epoxy resin and the crosslinking agent, respectively, in the presence of poly(ethylene glycol) (PEG200, $M_n = 200$) as the porogen (Figure 1).

Thermal curing was carried out at $120\, ^\circ\mathrm{C}$ for 20 min, followed by removal of the porogen with ultrasonic water and subsequent drying. The porous structure of the epoxy monoliths was characterized by scanning electron microscopy (SEM) observations. The formation of continuous and highly porous structures of the monolith was confirmed by evaluation of the specific surface area (approximately $0.6\, \text{m}^2/\text{g}$) using the Brunauer–Emmett–Teller method.\(^{67}\)

Figure 2 shows the SEM images observed for the surfaces of the epoxy monoliths, which were prepared under the conditions of different $\gamma$ values, i.e., the ratio of the number of reacting amino hydrogens to an epoxy group. Table 1 summarizes the results of the evaluation of the porous structures of the epoxy monoliths prepared under the various conditions. The diameter and number of pores varied in the range of $1.1−114\, \mu\text{m}$ and $8.7−48\, 200\, \text{mm}^{-2}$, respectively, depending on the $\gamma$ values ($\gamma = 0.6−1.8$). For the epoxy cured under the conditions with a $\gamma$ value less than 0.4, accurate pore size and number were not determined because of the formation of too small pores. The SEM images of the cross section of the monolith layer (Figure 3) confirmed a continuous pore structure inside the entire epoxy monolith except for a skin layer attached to the metal plate. The thickness of the skin layer was less than several micrometers.

As shown in Table 1 and Figure 4, the number of pores per unit area decreased and the pore diameter increased with an increase in the $\gamma$ value. In contrast to the meaningful variation of the $\gamma$ values for control of the pore size and number, the $\omega$ value (the total weight fraction of BADGE and BACM) was limited around 0.3. Although tough and porous monoliths were successfully produced during the reactions under the conditions of $\omega = 0.30$ and 0.325, the monoliths obtained with an $\omega$ value less than 0.3 (for example, $\omega = 0.25$ and 0.275) were separated from a steel plate during ultrasonic irradiation for removal of the PEG after the curing reaction, as shown in Table 1. The existence of large pores in the monolith probably led to decreases in the toughness of the monolith itself and the bond strength between the steel plate and the monolith layer. The larger $\omega$ conditions resulted in the formation of monoliths containing smaller and fewer pores, which cannot be used as the bonding mediator in this study. These results agreed well with the experimental results for the preparation of epoxy monoliths used as the column fillers previously reported by Tsujioka et al.\(^{17}\) They reported that the size and number of pores depended on the reaction conditions for the epoxy monolith fabrication, such as the ratio of the number of amino hydrogens and epoxy groups, the amount of the porogen, and the curing temperature. The control of the pore size depending on the $\gamma$ value can be accounted for by the competitive reactions occurring during the epoxy curing process using amines as the cross-linker. The epoxy monolith skeleton with a bicontinuous structure is constructed by spinodal decomposition, whereas microparticles are produced via a nuclear growth mechanism under the metastable conditions.\(^{17}\) Because of sequential changes in the curing reaction conditions, some particles also formed in the cavity of the epoxy monolith, as seen in the SEM images. It is assumed that such particle formation may not give adverse effects for monolith bonding.

Figure 1. Chemical structures of compounds used for fabrication of epoxy monolith.

Figure 2. SEM images of the surfaces of epoxy monoliths prepared under the conditions of various $\gamma$ values and $\omega = 0.3$.  

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We evaluated the rates of two reactions for the epoxy curing, i.e., the polymer-chain extension and the cross-linking by the reaction of an epoxy group with primary and secondary amines. Typical reactions included in the curing process of an epoxy resin using an amine cross-linker are shown in Scheme 1.

It has been reported that the reactions of an epoxy moiety with amino groups proceed prior to the reaction with a hydroxy group and that the reaction rate of a primary amine is much higher than that of the secondary one.\textsuperscript{68−70} Figure 5 shows the differential scanning calorimetry (DSC) curves for the epoxy monolith fabrication systems with different $\gamma$ values. Dual exothermic peaks were observed for the curing systems in this study, except for the system with $\gamma = 1.4$, in which only a single exothermic peak was detected. The first peak was assigned as the exothermic event due to the opening of an epoxy group by the primary amine ($-R-NH_2$), as shown in eq 1 in Scheme 1, and the second one was due to the formation of a cross-linking point by the reaction between a residual epoxy group and the secondary amine ($-R-NH-R$) produced by the ring opening during the first step (eq 2 in Scheme 1). An excess amount of amine accelerates the chain growth of the primary epoxy resins rather than the formation of cross-linking points. It results in the promotion of the phase separation because of an increase in the molecular weight of the epoxy resins. However, the use of a smaller amount of amine led to the preferential formation of the cross-linking. 

![Table 1. Pore Size and Number Observed at the Surface of Epoxy Monolith Fabricated under Various Compositions with Different $\omega$- and $\gamma$-Values](image)

| $\omega$-value | $\gamma$-value | pore size at monolith surface (\(\mu\)m) | number of pores at monolith surface (mm\(^{-2}\)) | pore area at monolith surface (%) |
|----------------|----------------|------------------------------------------|-----------------------------------------------|---------------------------------|
| 0.30           | 0.4            | not determined                           |                                               |                                 |
| 0.30           | 0.6            | 1.15 ± 0.06                              | 48200 ± 9800                                  | 5.0 ± 1.3                       |
| 0.30           | 0.8            | 6.33 ± 0.75                              | 3626 ± 776                                    | 11.2 ± 2.1                      |
| 0.30           | 1.0            | 12.0 ± 1.9                               | 941 ± 283                                     | 10.0 ± 1.5                      |
| 0.30           | 1.2            | 17.6 ± 2.4                               | 335 ± 49                                      | 8.2 ± 2.2                       |
| 0.30           | 1.4            | 34.9 ± 5.2                               | 69 ± 20                                       | 6.4 ± 1.7                       |
| 0.30           | 1.6            | 55.0 ± 21.0                              | 38 ± 13                                       | 7.8 ± 2.7                       |
| 0.30           | 1.8            | 114.2 ± 23.7                             | 8.7 ± 2.1                                     | 8.8 ± 2.9                       |
| 0.25           | 1.0            | exfoliated                               |                                               |                                 |
| 0.275          | 1.0            | exfoliated                               |                                               |                                 |
| 0.325          | 1.0            | 10.1 ± 1.6                               | 1078 ± 172                                    | 8.6 ± 3.7                       |
| 0.35           | 1.0            | not determined                           |                                               |                                 |
| 0.40           | 1.0            | not determined                           |                                               |                                 |

Figure 4. Effects of $\gamma$ value on (a) pore size and (b) number of epoxy monoliths. $\gamma = 2[NH_2]/[epoxy]$. 

![Figure 3. SEM images of the cross section of epoxy monoliths prepared on an Al plate.](image)
of a network structure because of the fast consumption of the primary amines. The observed DSC exothermic curves in Figure 5 were quantitatively analyzed. As summarized in Table 2, the ratio of the enthalpies for the first- and second-step reactions, i.e., the $\Delta H_1/\Delta H_2$ values increased with an increase in the $\gamma$ value. The $\Delta H_1/\Delta H_2$ values were 82/18, 85/15, and 90/10 for the systems of $\gamma = 0.6, 0.8, \text{ and } 1.0$, respectively. Thus, it was revealed that the pore size was determined by the competitive reactions of the epoxy group with the primary and secondary amines.

**Metal/Plastic Bond Strength.** We determined bond strength for the bonding systems composed of steel, Cu, and Al plates modified with the epoxy monolith and various plastic plates. The bond strength values evaluated by a single lap-shear tensile test are summarized in Figure 6. The maximum bond strength approximately decreased in the order of PC, PET, ABS, and the other plastics. In the bonding systems using steel and Cu, failure events occurred at an interface between the monolith surface and the plastics and the bond strength significantly depended on the properties of the used plastics. This was because the mechanical stress was concentrated at the interface between the monolith and plastics when a shear force was applied. Consequently, the mechanical strength of the plastics determined the total performance of each monolith bonding system. The plastic deformation due to the stress concentration was directly confirmed by the SEM images of the fracture surfaces for both the epoxy monolith and the plastics, as discussed in the following section.

In contrast to the high bond strength observed for the systems using steel and Cu plates, all the plastics exhibited a poor bonding ability with an Al plate, as shown in the bond strength for the results using an untreated Al plate (U) in Figure 7. This case, failure invariably occurred between the Al plate and the epoxy monolith layer but not between the epoxy monolith surface and the plastics. This was due to the presence of an aluminum oxide layer on the surface of the Al plate. In fact, the bonding property was dramatically improved by chemical etch with an alkaline (A) or mechanical polish using a metal file (M) or sandpaper (S). Changes in the bond strength after the surface treatments are shown in Figure 7. The failure mode mostly changed to that between the epoxy monolith surface and the plastics. The pretreatment was also valid for the steel and Cu plates, but the magnitude of the strength improvement was less than that for Al (Table S2). This result indicated that the formation of the aluminum oxide layer significantly influenced the bond strength. The bond strength values for the Al/plastic bonding under the optimized conditions was similar to the results using steel and Cu plates, as shown in Figure 6.

Because a molten polymer is required to penetrate into the pores of the monolith during a thermal welding process for joint fabrication, the thermal-welding conditions (i.e., temperature and time) were optimized for each specimen. Figure 8a shows the bond strength values for the test pieces composed of the steel plate and several thermoplastics under different thermal-welding conditions.

![Figure 5](image_url)  
**Figure 5.** DSC trace for thermal curing of the epoxy system with (a) $\gamma = 0.6$ and (b) $\gamma = 1.0$. The heating rate was 10 °C/min in a nitrogen stream.

![Figure 6](image_url)  
**Figure 6.** Bond strength for epoxy monolith bonding between dissimilar materials including Al, steel, and Cu as the metals and PE, PP, POM, ABS, PET, and PC as the thermoplastics. For detailed bonding conditions such as thermal welding and pretreatment conditions, see Table S1 in the Supporting Information.

![Figure 7](image_url)  
**Figure 7.** Effect of chemical and mechanical treatments of Al plate surface using (A) NaOH aq, (M) a metal file, and (S) sandpaper on the bond strength for Al/plastic bonding systems. U indicates the results using an untreated Al plate. For detailed conditions and results, see Table S2 in the Supporting Information.

| $\gamma$ value | peak temperature ($^\circ$C) | enthalpy (kJ/mol) | $\Delta H_1/\Delta H_2$ |
|----------------|-------------------------------|-------------------|-------------------------|
| 0.6            | 111 | 144 | 298 | 66 | 82/18 |
| 0.8            | 109 | 140 | 350 | 62 | 85/15 |
| 1.0            | 110 | 139 | 442 | 49 | 90/10 |
| 1.4            | 111 | 144 | 298 | 66 | 82/18 |

*Total enthalpy for $\Delta H_1$ and $\Delta H_2$ due to the difficulty of peak separation.*

Table 2. DSC Analysis of Curing Processes of Epoxy Systems

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longer welding time increased the bond strength for each system. However, too high and too long welding processes resulted in some damage of the plastics, leading to a decrease in their bond strength, as shown in Figure 8b. We concluded that thermal welding should be performed at a temperature close to the melting point for the crystalline polymers or ca. $10^{-20}^\circ$C higher than the glass transition temperature for amorphous polymers.

**Mechanism of Epoxy Monolith Bonding.** Interfacial failures between the monolith and the thermoplastics were observed for all cases after the appropriate pretreatment of the metal surfaces. Simultaneously, they indicated the robust interaction between the metal and the epoxy layer. The toughness of the epoxy resin was also confirmed on the basis of no occurrence of the cohesive failure of the epoxy monolith. Figure 9 shows SEM images of the fracture surfaces after the single lap-shear tensile test as well as a schematic model for the stretched deformation and fracture of the polymers for the epoxy monolith bonding. A significant number of elongated needle-like structures was observed on both surfaces of the resins and the epoxy monoliths. The type of elongation of the plastics at the ductile failure positions was dependent on the mechanical property of the polymers. Highly stretched deformation of the debris was observed on the fracture surfaces of the PE, PP, and POM plates, whereas stumplike debris were detected on the surface of the ABS, PC, and PET plates. It is noted that the direct observation of the stretched debris out of the holes located at the monolith surfaces undoubtedly indicates a significant anchor effect for the present dissimilar material bonding system.

The penetration of the molten plastics into the pores of the epoxy monolith during the thermal-welding process was also
confirmed by SEM observations of the cross section of the specimens. Figure 9d shows the SEM image of the cross section for a test specimen for the Al/PE bonding system. The PE/monolith composite was separated from an Al plate after thermal welding of PE with a monolith-modified Al plate at 150 °C for 60 s; then, it was given for SEM observation. A layer of the epoxy monolith filled with PE was observed between the bulk PE layer and an unfilled epoxy monolith layer. The characteristics of both the epoxy materials with a high free energy and the thermoplastic resins with a low free energy and high fluidity are important to easy penetration of polymers into the monolith pores.

The penetration of thermoplastics into the pores is a key factor for determining the bond strength for the epoxy monolith bonding. Therefore, the size and number of the monolith pores were expected to have an effect on the bond strength. We checked the bond strength values for a series of Cu/PE and Cu/POM systems prepared under the conditions of various γ values in the range of 0.4–1.8, which were expected to provide the epoxy monoliths with a pore size in the range of approximately 1–10^3 μm and a pore number in the range of approximately 10–10^6 mm⁻² (see also Figure 4). The bond strength moderately depended on the γ values, i.e., the pore size. The maximum strength was observed for the monoliths prepared with γ = 1.4–1.6, as shown in Figure 10. This tendency was probably caused by the release of the stress concentration by an increase in the pore size, but a small number of large pores may have a weaker anchor effect. The fabrication of an epoxy monolith with the same pore size and different pore number was difficult because a change in the ω value resulted in the formation of fragile monolith materials, as described above (see also Table 1).

The bond strength was actually independent of the thickness of the whole epoxy monolith layer. It was because the plastics were introduced into the pores of the monolith by the thermal welding process and the structure around the interface of the monolith and the plastics mainly contributed to the bond strength. We also found no effect of the surface roughness on the bond strength. The epoxy monolith surface was gently ground with sandpaper (320), and it was used for the single lap-shear tensile test using Cu and PE or POM plates. As a result, the bond strength values were observed with or without the grinding treatment of the monolith surfaces (see Table S2 in the Supporting Information for the detailed results). This indicated less contribution of surface roughness to an increase in the bond strength. This result also suggests that the continuous pore structure of the epoxy monolith is important for the favorable performance of the monolith bonding system in this study.

Fabrication of Monolith Sheet. As described in the previous sections, the epoxy monolith was useful for dissimilar material bonding when it was coated on a metal surface. We also found the epoxy monolith was also available as the sheet. We fabricated a self-standing monolith sheet by the preparation of an epoxy monolith on an Al plate without any pretreatment. After the thermal curing and the subsequent treatments for the porogen removal, a cured thin epoxy layer was readily exfoliated from the Al plate because of the weak interaction between the monolith and the oxidized Al plate surface. The thickness of the monolith sheets was varied by the amount of the reaction mixture coated on the plate. The isolated monolith sheets were flexible and could be folded, as shown in Figure 11. DSC measurements of the epoxy materials fabricated in this study before and after curing indicated that the curing reaction started from 50 °C and was approximately completed at 150 °C. No exothermic peak was observed for the epoxy samples after curing at 120 °C for 20 min. The glass transition temperature was determined to be 139 °C for the cured material. When we carried out a tensile test of the monolith sheets prepared with different curing times, the maximum strength (strength at break) and modulus increased with an increase in the curing time and became an almost constant value after a 90 min curing (Table 3). Finally, a 6.6 MPa fracture strength was obtained for the sheet after a 120 min curing. The elongation value decreased from 25 to 15% along with the curing time, due to a further increase in the cross-linking density. The modulus values was 251–394 MPa.

Figure 10. γ value dependence of bond strength for (a) Cu/PE and (b) Cu/POM bonding systems using epoxy monoliths prepared under the conditions of various γ values.

Figure 11. Photographs of the epoxy monolith sheet.
Monolith Bonding for Various Materials. The monolith bonding technique is available for the bonding of various combinations of materials other than the thermal-weld bonding of metals and thermoplastics. The use of the monolith sheet and any adhesive or solvent was valid for the bonding of materials that cannot be thermally welded. Examples of the various types of dissimilar material bonding systems are summarized in Table 4.

The modification of the steel plate with the epoxy monolith increased strength for bonding between steel and PS, in which a commercial adhesive for plastic models or toluene was used for the welding of the epoxy monolith and PS. The monolith sheet was similarly available for the steel/PS bonding using two kinds of commercial adhesives appropriate for PS and steel. The bond strength increased from 0.1 to 0.4 MPa without monolith to 0.8–1.4 MPa with the monolith modifications. The failure occurred at an interface of the monolith surface and PS when the monolith was present between the steel and PS plates. For the bonding system of steel/PMMA, the use of a monolith coating on a steel plate combined with organic solvents as the plasticizers permitted the bonding with a strength of 0.7–1.1 MPa. Methyl ethyl ketone as the good solvent was more effective compared with acetone as the theta solvent for PMMA. It was expected that the plasticized PMMA by a good solvent more rapidly intruded into the pores of the epoxy monolith, resulting in the higher bond strength value. It is not easy to bond different kinds of plastic plates because the thermal-weld conditions should be carefully selected according to the properties of the thermoplastics. In such a case, nevertheless, it was effective to use the stepwise combination of thermal and solvent welding processes. We first performed the thermal welding of a PP plate with a monolith sheet; then, the other side of the sheet was bonded to a PC plate with toluene. The bond strength drastically increased from 0.02 to 1.5 MPa. The thermal curing of polyfunctional monomers can also be used for the monolith bonding systems. EDMA containing a small amount of BPO penetrated into the monolith fabricated on the steel plate and it was bonded with a PMMA plate, followed by heating at 90 °C. The greater bond strength (1.0–1.6 MPa) was confirmed, and the failure occurred at the interface of the steel and the monolith.

Table 4. Strength of Monolith Bonding Using Various Kinds of Bonding or Curing Systems

| adherends | monolith modification | adhesive or solvent | bond strength (MPa) | failure mode |
|-----------|----------------------|--------------------|---------------------|--------------|
| steel/PS  | monolith on a steel plate | commercial adhesive | 0.82 ± 0.15 | interface of monolith surface and PS |
| steel/PS  | none | commercial adhesive | 0.10 ± 0.04 | interface of steel plate and PS |
| steel/PS  | monolith on a steel plate | toluene | 1.40 ± 0.26 | interface of monolith sheet and PS |
| steel/PS  | none | toluene | 0.41 ± 0.10 | interface of steel plate and PS |
| steel/PS  | monolith sheet | commercial adhesives | 0.88 ± 0.01 | interface of monolith surface and PS |
| steel/PMMA | monolith on a steel plate | methyl ethyl ketone | 1.13 ± 0.22 | interface of monolith surface and PMMA |
| steel/PMMA | none | methyl ethyl ketone | ~0 | interface of steel plate and PMMA |
| steel/PMMA | monolith on a steel plate | acetone | 0.71 | interface of monolith surface and PMMA |
| steel/PMMA | none | acetone | ~0 | interface of steel plate and PMMA |
| PP/PC     | monolith sheet | thermal welding/toluene | 1.45 ± 0.62 | interface of monolith sheet and PC |
| PP/PC     | none | toluene | 0.022 ± 0.006 | interface of PP and PC |
| steel/PMMA | monolith on a steel plate | EDMA | 1.58 ± 0.38 | interface of steel plate and epoxy monolith |
| steel/PMMA | epoxy coating on a steel plate | EDMA | 1.04 ± 0.21 | interface of epoxy layer and adhesive layer (cured EDMA) |
| steel/PMMA | none | EDMA | ~0 | interface of steel plate and adhesive layer (cured EDMA) |

“Adhesive for plastic models. "Use of both adhesives for plastic models and metals. "EDMA: ethylene dimethacrylate. Curing at 90 °C for 1 h in the presence of benzoyl peroxide (BPO) (5 wt %).
In this study, we proposed a new method for dissimilar material bonding using the anchor effect of the epoxy monolith with a porous structure. This method was demonstrated to be valid for the bonding of metals, such as steel, Cu, and Al, with various thermoplastics. By using the monolith sheet and an adhesive (or solvent), this bonding procedure was applied to many kinds of adherends other than thermoplastics, such as acrylic thermosets. We revealed the pore size and number of epoxy monoliths controlled by the ratio of the epoxy resin and cross-linking agent during the monolith fabrication and the role of an anchor effect on this monolith bonding system by the SEM observations. Various kinds of thermoplastics were bonded to the monolith-modified metal plates by thermal welding with the bond strength in the range of 1.2–7.5 MPa for the single lap-shear tensile test. The epoxy monolith bonding of hard plastics and thermosets was also performed by the additional use of adhesives, solvents, reactive monomers, and the epoxy monolith sheets. The features of the epoxy monolith bonding are summarized as follows: (i) suitable for bonding between various dissimilar materials; (ii) easy fabrication of a monolith layer on a metal by coating and curing processes, (iii) no requirement of special chemicals for etching and apparatus for metal surface modifications, and (iv) applicable using adherends with various shapes. The epoxy monolith technique would be one of the invaluable bonding methods for various adherends, especially metal/polymer bonding. We are now continuing our investigation using high-performance engineering plastics and their composites to demonstrate the higher bond strength for this system.

**EXPERIMENTAL SECTION**

**General Procedures.** SEM observations were carried out using a Keyence VE-9800 at the acceleration voltage of 2.0–3.0 kV after Au vapor deposition of the polymer fracture surfaces and 0.8–1.0 kV without vapor deposition for the epoxy monolith surfaces on a metal plate. DSC measurement was carried out using Shimadzu DSC-60 at the heating rate of 10 °C/min in a nitrogen stream. The thickness of the epoxy monolith was determined using Peacock dial thickness Gauge (Ozaki mfg. Co., Ltd., Japan). The hot press was carried out using an AH-2003 from AsOne Co., Japan.

**Materials.** BADGE, BACM, and PEG200 were purchased from Tokyo Chemical Industry, Co., Ltd., Japan, and used without further purification. The purities of these chemicals were confirmed by 1H NMR spectroscopy. The plastic plates (thickness = 2–5 mm), SUS430, Cu, and Al plates (thickness = 0.5 mm for the metals), were purchased from AsOne Co., Japan and cut to a size of 10 mm × 50 mm. The commercial metal plates were cleansed with acetone and subsequently dried. EDMAs and BPO were purchased from Tokyo Chemical Industry, Co., Ltd., Japan, and Nacalai Tesque, Japan, respectively, and used as received. Commercial plastic model adhesive (CA-216, Cemedge Co., Ltd., Japan) and an epoxy adhesive (Araldite AR-30, Nichiban Co., Ltd., Japan) were used as the additional adhesives.

**Preparation of Epoxy Monolith.** BADGE, BACM, and PEG200 (typically 70 wt % for PEG200) at a ratio of 2[NH2]/[epoxy] (γ value = 0.40–1.8) were well mixed by a planetary centrifugal mixer (Thinky AR-100). The mixed paste was spread on a metal plate with a determined thickness, followed by thermal curing at 120 °C for 20–80 min. After curing, the samples were washed with ion-exchanged water with ultrasonics to remove the PEG200, stored in ion-exchanged water overnight, then dried in vacuo for 2 h at room temperature. The thickness of the epoxy monolith layer was 100–400 μm (typically ca. 200 μm). A monolith sheet was prepared according to a similar procedure using an Al plate without any surface treatment. The curing time was 20–120 min. The thickness of the monolith sheet was 300–400 μm. Two monolith sheets were bonded on each back side using a commercial epoxy adhesive and cured at room temperature overnight, followed by further curing at 70 °C for 1 h.

**Metal Surface Pretreatments.** Chemical and mechanical pretreatments of the metal plate surfaces were carried out using an alkaline solution (A), a metal file (M), sandpaper (S), or without any treatment (U) (see also Figure 7 and Table S2). As the chemical etching process, a metal plate was immersed in 10% NaOH aq at room temperature for 2.5–10 min, followed by washing with ion-exchanged water and drying. For the mechanical pretreatment, a metal plate was ground with a metal file or sandpaper (grain size #80) until the metal surface showed a metallic luster, typically for 10–20 min. The monolith surface was optionally ground with sandpaper of a smaller grain size (#320).

**Tensile Test.** Test pieces for the single lap-shear tensile measurement were prepared under various thermal-welding conditions of temperature and time depending on the properties of each plastic, then softly pressed at less than 0.1 MPa. The bonding area (overlapped area of two adherends, i.e., metals and plastic plates) was 10 mm × 10 mm. The tensile test was carried out using a Shimadzu Autograph AGS-X 1 kN or 5 kN at the tensile rate of 0.1 or 1.0 mm/min, according to JIS-K6850, which corresponds to ISO4587, as the standard. The number of test samples (N) was 3–6 for all measurements. The bond strength values were calculated on the basis of the applied force at break and the bonding area (100 mm²).

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