Bioinspired Catecholic Primers for Rigid and Ductile Dental Resin Composites

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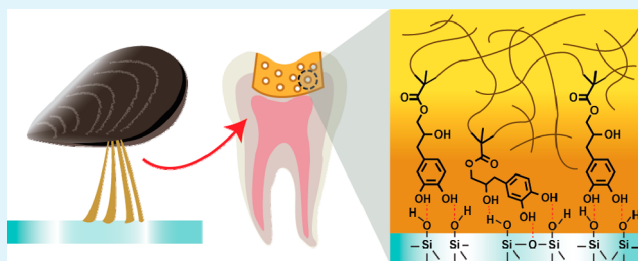[‡]Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, South Korea
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S *Supporting Information*

ABSTRACT: In the construction of dental restorative polymer composite materials, surface priming on mineral fillers is essential to improve the mechanical performance of the composites. Here we present bioinspired catechol-functionalized primers for a tougher dental resin composite containing glass fillers. The catecholic primers with different polymerizable end groups were designed and then coated on glass surfaces using a simple drop-casting or dip-coating process. The surface binding ability and possible cross-linking (coupling or chemical bridging between the glass substrate and the dental resin) of the catecholic bifunctional primers were evaluated using atomic force microscopy, contact angle measurements, and the knife shear bonding test and compared to a state-of-the-art silane-based coupling agent. Various mechanical tests including shrinkage and compression tests of the dental resin composites were also conducted. Compression tests of the composites containing the catecholic primed fillers exhibited enhanced mechanical properties, owing to the bidentate hydrogen bonding of catechol moieties to the oxide mineral surface. Furthermore, the superior biocompatibility of the primed surface was confirmed via cell attachment assay, thus providing applicability of catecholic primers for practical dental and biomedical applications.

KEYWORDS: catechol, primer, dental resin composites, surface priming, mussel-inspired

INTRODUCTION

Dental restoration is a treatment of dental caries to restore the function, integrity, and morphology of teeth.[1,2] Filling the missing parts of a tooth such as caries is the most common method of dental restoration. A variety of materials such as amalgam, glass ionomers, and resins have been used for dental restorations.[3,4] Polymethacrylate (PMA) resin composites (these are mixtures of dimethacrylate monomers resulting in cross-linked network materials) have been the most popular with several clinical advantages such as aesthetics, repairability, and versatility.[5,6]

PMA resins, however, have some issues in that they shrink during photoinitiated free radical polymerization and are much softer than human teeth. Therefore, dental PMA composites contain up to 80 wt % glass fillers to reduce the volume shrinkage during the curing of the resin composites and thereby avoid marginal leakage and secondary caries associated with interfacial adhesion failure between the tooth and resin composite,[7,8] as well as to increase the elastic modulus (rigidity) of the restoration.[9] Despite their popularity and clinical advances, several challenges remain for restorative resin composite materials, and the short lifetime of dental restorations (less than several years or months) causes the

need for repeated-restoration treatments followed by a dental crown and eventual tooth loss.[10,11] Therefore, demand for more durable and tougher restoration is high.

Currently, the most common approach to increase the rigidity of polymer composites is to incorporate hard-domains in the soft matrix; in dental composites, glass fillers are added to the PMA resin matrix due to their economical and esthetic advantages. However, in this state-of-the-art approach, an increase in hardness or rigidity often sacrifices flexibility (strain at fracture), which leads to a decrease in toughness. For more durable dental restorations, tougher resin composites are required to reduce the risk of issues with restorations such as marginal adhesion failure, staining, sensitivity, recurrent caries, and catastrophic fracture.[12,13] In our previous paper, we presented strong adhesion of a bioinspired catecholic primer to various minerals and PMA composites.[14] In this work, we have conducted further systematic studies in continuation of our endeavor in the development of practical dental applications.

a Biological primers
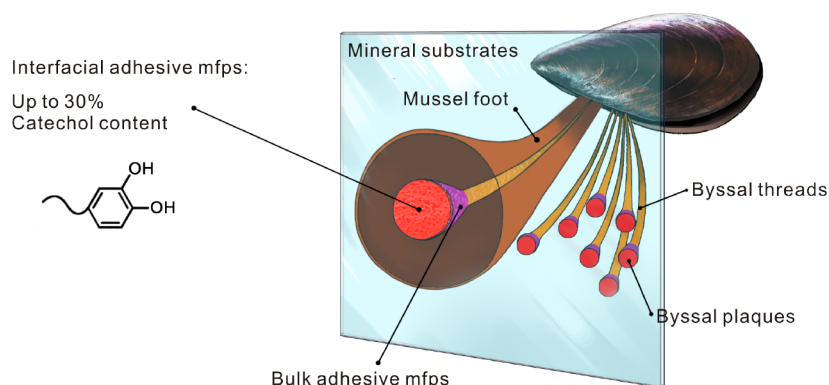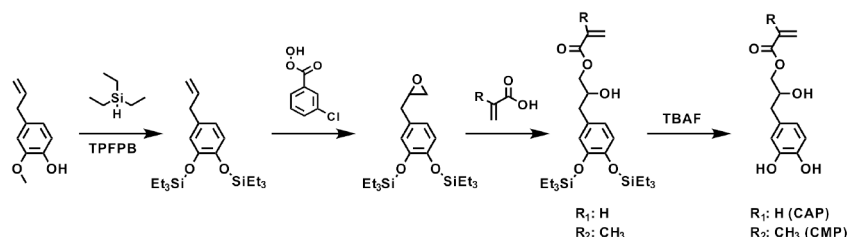

b Synthetic primer from eugenol

Figure 1. (a) Schematic cartoon of mussel byssal threads, which are produced in the mussel foot to adhere to mineral substrates. (b) Synthetic pathways of catecholic primers (catechol acrylate primer (CAP) and catechol methacrylate primer (CMP)) derived from eugenol.

In state-of-the-art dental resin composite technologies, surface modification of clean glass filler using a silane coupling agent is essential to increasing the wetting of inorganic fillers and providing a chemical bond between the dissimilar materials (e.g., glass and PMA resin).[15−17] Without the surface treatment, the filler content cannot be higher than 30 wt % due to poor mixing. The higher contents of filler can reduce resin amount per volume overall shrinkage; thus, hydrophobic surface treatment of glass fillers is essential for the dental composites. To date, silane-based primers (or silane coupling agents) have been the most popular and primarily used for inorganic fillers because they can bind covalently to various inorganic surfaces such as metal oxides and oxide minerals. However, only 10−20% of the chains of silanes chemically bind to the surfaces,[18] and their hydrolytic stability still remains an issue for dental applications.[19−21]

Our approach to providing more durable bonding between glass and resin surfaces is inspired by the adhesion mechanism of marine mussels and mussel foot proteins (mfp's).[22] One of the unique features of interfacial mfp's (that mussels use as surface primer prior to applying their bulk mfp's, Figure 1a)[23] is their high content of phenolic residues, especially 3,4-dihydroxyphenyl-L-alanine (DOPA) or catechol moieties. A majority of catechol functional residues exist in the interfacial mfp's up to 30 mol %; mussels use the catechol moieties as one of the key functional groups for surface adhesion.[24−26] Despite extensive research on the use of catechol moieties for synthetic adhesives in the past decade, only a few studies have applied this catechol chemistry for surface priming.[25] For example, a recent report by Seo et al. demonstrated that mussel-inspired dynamic bonds can overcome the challenges associated with the current silane-based priming in a load-bearing polymer composite.[14] It proposed that catecholic primer can be an alternative to the conventional silane coupling agent which cannot bind to mineral surfaces without using toxic chemicals.[18,27] The previous study showed that the synthetic catecholic primers from eugenol (used in a traditional temporary dental restoration) can enhance the adhesion performance and mechanical properties.[14] In contrast to the previous study using acrylic primers as a potential alternative of silane primers, here we employ methacrylate primers, which are clinically and economically more viable than acrylic primers, and optimize the priming process for practical dental applications. The coupling effect of the catechol-functionalized methacrylate primers via a simple dip-coating process was investigated for dental resin composite applications, and the results were compared to a conventional silane primer. In addition, the treatment conditions such as processing time, concentration, and shrinkage rate were carefully optimized. The standard knife shear and compression tests were also performed to evaluate the mechanical properties of the dental resin composites. Finally, the biocompatibility of the primed surfaces was studied via cell attachment assay.

■ MATERIALS AND METHODS

Reagents. The 1.0 M tetrabutylammonium fluoride (TBAF) solution in tetrahydrofuran (THF), 3-(trimethoxysilyl) propyl acrylate, bisphenol A glycerolate dimethacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), and camphorquinone (CQ) were obtained from Sigma-Aldrich. Triethylsilane-protected eugenol acrylate and triethylsilane-protected eugenol methacrylate were provided by Osaka Organic Chemical Industry Ltd (Japan, verified by ^{1}H and ^{13}C NMR in Supporting Information). Polysiloxane-coated barium glass powder (0.7 μm diameter) and bare barium glass powder were provided by Sukgyung AT (South Korea). Methanol, hexane, diethyl ether, and THF were purchased from Sigma-Aldrich. Glass slides (25 mm × 75 mm) were obtained from Fisher Scientific. All

chemicals were analytical reagent grade and used without purification unless otherwise indicated.

Instruments. ^{1}H NMR spectra were recorded at 298 K with a VNMRS 400 spectrometer operating at 400 MHz using $CDCl_3$ and CD_3OD. The surface morphologies of the primed surfaces were examined using an atomic force microscope (AFM, Dimension D3100, Veeco). Contact angles were obtained using a contact angle analyzer (DSA 100, KRUSS). The characterization of functionalized glass powder was studied using a Fourier-transform infrared (FT-IR) spectrophotometer (660-IR, Varian) and thermogravimetric analysis (TGA) analyzer (TGA Q50, TA Instruments). Cell attachment was observed using an inverted microscope (IX73, OLYMPUS). A Servo-hydraulic Universal Testing Machine (MTS 810, MTS System Corp.) was used for compressive fracture tests.

Synthesis of Catechol-Functionalized Primers. All reactions were carried out under argon unless otherwise noted. Triethylsilane-protected eugenol (meth)acrylate, synthesized as previously described,[15,28] was provided by Osaka Organic Chemical Industry. 3-(3,4-Dihydroxyphenyl)-2-hydroxypropyl acrylate (catechol acrylate primer, CAP) and 3-(3,4-dihydroxyphenyl)-2-hydroxypropyl methacrylate (catechol methacrylate primer, CMP) were prepared by deprotection of triethylsilane-protected eugenol (meth)acrylate as previously described.[14] The procedure for the deprotection is as follows (CAP): triethylsilane-protected eugenol acrylate (0.30 g, 0.643 mmol, 1.0 equiv) was dissolved in 40 mL of dry THF. Subsequently, TBAF solution (0.516 mL, 0.8 equiv) was slowly added and stirred for 1 h at room temperature. The solvent was removed using a rotary evaporator, and the crude material was purified using silica gel flash column chromatography with methanol to remove triethylfluorosilane. The product was further purified by silica gel flash column chromatography with hexane/ethyl acetate (1:1 v/v) to provide 121 mg (79.3% yield) of slightly brownish liquid. The product purity was verified by ^{1}H NMR.

Catechol acrylate primer (CAP) ^{1}H NMR (400 MHz, methanol-d_4): δ ppm 6.65 (d, 2H, Ar-*H*), 6.52 (q, 1H, Ar-*H*), 6.38 (d, 1H, —CH=C*H*$_2$), 6.15 (q, 1H, —C*H*=CH$_2$), 5.85 (d, 1H, —CH=C*H*$_2$), 4.09 (m, 3H, —C*H*(OH)CH$_2$OOC—), 2.75 (m, 2H, —C*H*$_2$CH-(OH)—). GC/MS, m/z = 238.1.

Catechol methacrylate primer (CMP) ^{1}H NMR (400 MHz, methanol-d_4): δ ppm 6.65 (d, 2H, Ar-*H*), 6.52 (q, 1H, Ar-*H*), 6.15 (s, 1H, —CH=C*H*$_2$), 5.63 (s, 1H, —CH=C*H*$_2$), 4.09 (m, 3H, —C*H*(OH)CH$_2$OOC—), 2.75 (m, 2H, —C*H*$_2$CH(OH)—), 1.95 (s, 3H, C*H*$_3$—C=CH$_2$). GC/MS, m/z = 252.1.

Static Contact Angle Measurement. The static contact angles of water on the priming substrates were measured to analyze surface hydrophilicity. The glass substrates were cleaned prior to use, and primer solutions (0.15 mg/mL) were spread over a glass surface and incubated for 5 min at room temperature. A 10 μL portion of deionized water was dropped onto the substrate, and all samples were analyzed in triplicate.

Knife Shear Test. The adhesive ability of each primer was determined on the basis of ISO 10477 and ISO 11405 using a material testing system (MTS). Glass slides were cleaned using sonication in acetone prior to testing. To prepare the silane-treated surface, 3-(trimethoxysilyl)propyl acrylate in methanol was dropped onto a glass slide. After 10 min incubation, the glass slides were transferred to a 100 °C oven and cured overnight. The excess amount of silane was rinsed with methanol. In case of catecholic primers, the primer solutions at various concentrations were spread over glass surfaces and incubated for 5 min at room temperature. After that, the surfaces were naturally dried. A PMA monomer blend is composed of camphorquinone (CQ, 0.33 wt %) and 2-dimethylaminoethyl methacrylate (DMAEMA, 0.66 wt %), as a photoinitiator and a co-initiator, respectively, and triethylene glycol dimethacrylate (TEGD-MA, 49.5 wt %) and bisphenol A glycerolate dimethacrylate (bis-GMA, 49.5 wt %) as methacrylate resin monomers. The PMA monomer blend was filled into a gelatin capsule (size 4, Torpac Inc.) and placed upon the primer-treated glass slide. The PMA monomer blend was cured for 3 min using a portable dental curing lamp (3M, Elipar DeepCure-S LED Curing Light LY-A180, 430−480 nm, 1470

mW cm^{-2}). The adhesive stress was measured by the materials testing system and converted to knife shear adhesion in Pascals. Each experimental set was repeated at least 10 times (n = 10), and the average and standard deviation were calculated.

Compression Test. To prepare the surface-treated glass fillers, 0.21 mg of CAP or CMP was dissolved in 10 mL of methanol, and 5 g of bare glass powders (0.7 μm diameter) provided by Sukgyung AT Co., Ltd. was added and stirred for 1 h at room temperature. The solvent was evaporated using a rotary evaporator and dried under vacuum. The characterization of functionalized glass powder was studied using an FT-IR spectrophotometer and TGA analyzer. Due to the low content of priming layer (several nanometers thin, 0.0042 wt %), FT-IR spectroscopy did not show any difference between bare glass powder and catechol-functionalized glass powder. In the case of TGA analysis, although there is no difference in TGA spectra of all samples, in contrast to bare glass showing no color changes after the TGA test, silane-coated glass (containing 5 wt % of polysiloxane) turned from white to black after the thermal decomposition, and the catecholic-functionalized glass powder turned gray. The color changes demonstrate the existence of organic content (Figure S5). During mixing of the fillers with the PMA resin blend (same as described in the previous section), the PMA monomer blend was placed on a 75 °C hot plate to reduce its viscosity, and dried glass fillers were added gradually at 70 wt %. The filler−PMA mixtures were filled into 8 mm cylindrical plastic molds and light-cured for 5 min. For uniform curing and size of each sample, we filled a transparent acrylate mold with the MA monomer blend and cured it using LED ultracapacitor curing light system (Demi Ultra, Kavo Kerr): 20 s quadrilateral exposures on side, followed by top and bottom exposures. After the curing, the top and bottom of resin composites were ground/polished to get the flat and similar lengths of samples using a custom built polishing machine. Slightly different height and diameter of each sample were measured, and the values were reflected in the measurements/analyses of the mechanical properties. Composites with commercial silane grafted fillers were also made using the same method. The knife shear stress was measured on the basis of ISO 6873 using the materials testing system. Each experimental set was repeated at least 10 times (n = 10), and the average and standard deviation were calculated.

Polymerization Shrinkage Test. Linear mold shrinkage was determined by comparing the length of resin composites after polymerization. The PMA monomer blend and filler−PMA blend mixture were filled into 15.85 mm cylindrical plastic molds and light-cured for 5 min. The heights of the specimens were measured after polymerization, and the shrinkage rate was calculated.

Cell Attachment Test. The cell adhesion test was performed using L929 mammalian fibroblast cells on the primer-treated glass substrates (1 × 1 cm^2). Each glass substrate was placed on a 24-well cell culture plate, sterilized by 70% ethanol solution, and UV irradiated for 30 min. After being equilibrated in phosphate-buffered saline (PBS) and media for 30 min, L929 cells were seeded onto the glass substrates at a density of 1 × 10^5 cells per substrate. The substrates were incubated for 24 h in 5% CO$_2$ at 37 °C. After 24 h, the substrates were transferred to new culture plates and washed three times with PBS to remove any nonadherent cells. Three glass slides were prepared for each primer (silane, CAP, and CMP), and the number of live cells was counted from three random locations on each slide. The bare glass slide without any modification served as a control.

Statistical Analysis. Knife shear test and compression test data were analyzed by a one-way ANOVA analysis with a level of statistical significance (α = 0.05) using the software of Microsoft Excel 2016. In the case that statistical differences were found, all pairwise comparisons were performed using Tukey's honest significant difference (HSD) test. The statistical evaluations were performed to determine significant differences in the 5% (α < 0.05).

■ RESULTS AND DISCUSSION

Synthesis of Catechol-Functionalized Primer. Catechol can form a bidentate hydrogen bond to oxide mineral and
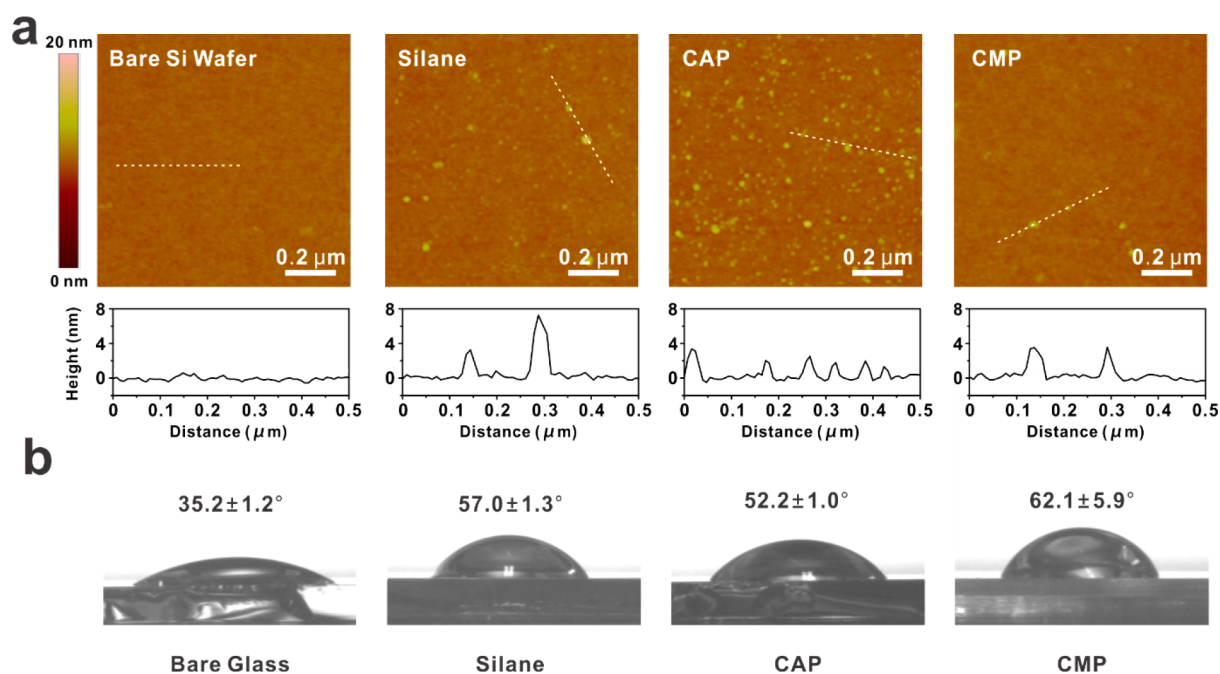
Figure 2. (a) Representative AFM images of bare silicon wafer and silane-, catechol-acrylate (CAP)-, and catechol-methacrylate (CMP)-primed surfaces with corresponding line scan profiles. (b) Static contact angles of the bare and the primed glass substrates.
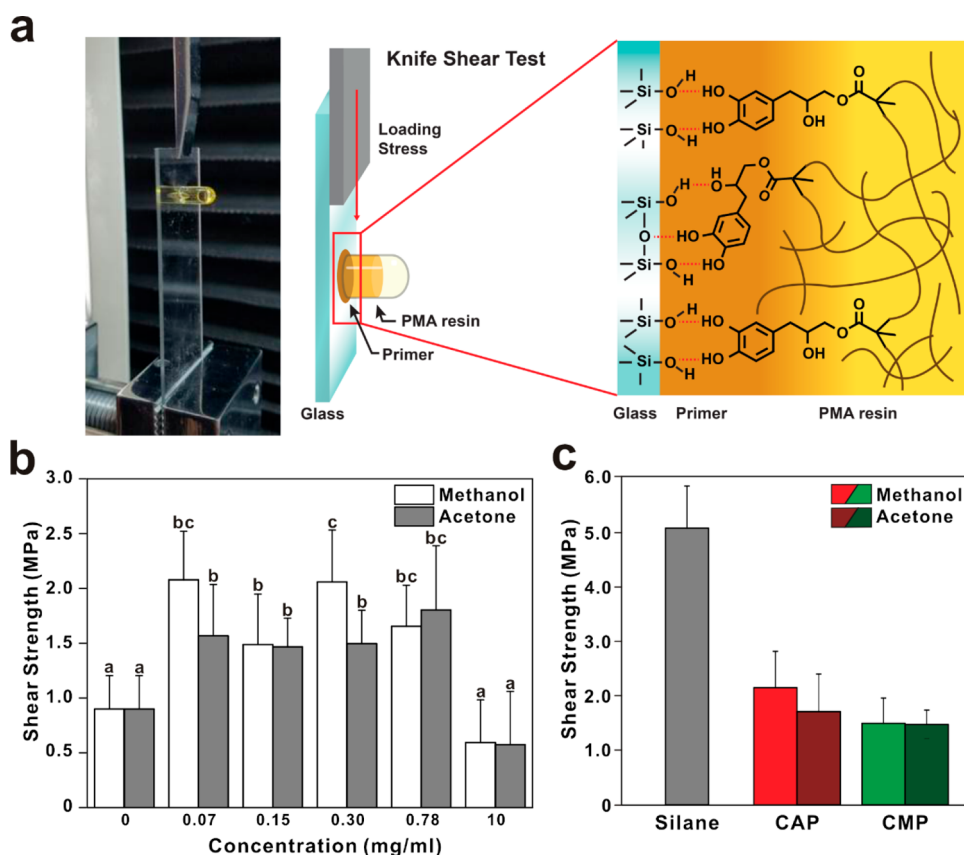

Figure 3. (a) Photograph of the knife shear test and schematic representation of catecholic primer bridging (coupling) between the glass and PMA resin. (b) Knife shear strength of methacrylate primer in various concentrations (0.07−10 mg/mL) and solvents (methanol and acetone). (c) Comparison of the knife shear strength of silane and catecholic primers (concentration: 0.15 mg/mL). Bars with the different letters are significantly different according to Tukey's HSD.

metal surfaces.[22] The binding lifetime of catechol's bidentate hydrogen bonding is 10^6 times longer than monodentate hydrogen bonding, and thus provides stronger and more durable adhesion.[29] The catecholic bifunctional monomers have been shown to form a uniform self-assembled monolayer whereas silane forms ill-defined multilayer films.[18]

Catecholic primers were synthesized from naturally abundant and commercially available eugenol straightforwardly. Dihydroxyl groups were protected by tris-(pentafluorophenyl)borane (TPFPB)-catalyzed silation during the synthesis due to the oxidation instability of catecholic moieties (see the synthetic scheme shown in Figure 1b).[14,28] The vinyl group of eugenol was epoxidized to provide a reaction site for acrylate or methacrylate via a nucleophilic S_N2 reaction of methacrylic acid; subsequently, the silyl protection group was removed by TBAF prior to surface priming.[30] The successful synthesis of two different catecholic primers functionalized with acrylate (CAP) and methacrylate (CMP) was confirmed by ^{1}H NMR spectra (Figure S1 in the Supporting Information). We hypothesized in this study that the difference between the methacrylate and acrylate end groups affects the bonding and mechanical performance of the primers due to their reactivity difference during free radical polymerization.[31]

Surface Morphology of Primed Surfaces. To compare the adsorption of the primer molecules to a silica surface, the morphology of each surface before and after the primer treatments was investigated using AFM on a silicon wafer. Figure 2a demonstrates that the height of molecular adsorption patches on the silica surfaces is less than 4 nm, which does not exceed the contour length of single primer molecules. Once the successful adsorption of the primers on the surface was confirmed, the static water contact angle was also measured to characterize the wettability of each surface. As shown in Figure 2b, the contact angle of bare glass was $35.2 \pm 1.2°$, whereas the contact angle of the silane- and catechol-treated surfaces increased up to $62.1 \pm 5.9°$ after the surface treatment. This significant increase in contact angle demonstrates the successful coating of primers and the increased hydrophobicity of the primed layer compared to the bare glass slide.

Knife Shear Test. The knife shear bonding test is a common method for evaluating the bonding performance of dental resins.[32] We carried out the knife shear stress test to evaluate the bonding performance related to possible cross-linking of the bifunctional primer at the interface between the glass and PMA resin, and also to optimize the treatment conditions. We primed the glass surface by drop-casting the primer solutions onto the glass substrate, and left the primers to self-assemble and the solvent to evaporate completely for 5 min at ambient condition (Figure S2 in the Supporting Information). While the catechol moieties bind to the glass surface with bidentate hydrogen bonding, the methacrylic end groups can face outward during the self-assembly as similarly demonstrated in the molecular dynamic simulation in our previous study (see also the schematic representation in Figure 3a). Subsequently, the dental PMA resin was applied and cured over the surface. During the visible light curing, the methacrylic end groups are cross-linked with other methacrylic groups in the PMA resin blend.

In our previous study, the self-assembly priming process involved multiple rinses to remove the excess primer molecules and drying steps prior to applying resins.[14] For practical dental applications, an improved processing method is required because treatment time is critical to clinicians and patients in clinical situations. In addition, the effect of different reactivities between the acrylate groups of the primer and the methacrylate groups of the dental PMA resin during the surface-initiated polymerization was not studied in the previous work.[23] We aimed in this work to minimize the processing steps and to

investigate the effect of methacrylic end groups in the catecholic primer as well. To enable the one-step priming process for practical dental applications, we reduced the concentration of the primer solutions to eliminate the rinsing and drying steps. For this, we assumed that each catecholic primer occupies 1.0 nm^2 on the substrate surface based on the molecular dynamic simulation in the previous report.[18] On the basis of this assumption, we estimated the concentration and amount of each solution to be applied per area, with the surface area calculated via the root-mean-squared (RMS) roughness (see Figure S3 in the Supporting Information). According to this calculation, we prepared the primer solutions as follows: RMS 10 nm (0.07 mg/mL), RMS 20 nm (0.15 mg/mL), RMS 40 nm (0.30 mg/mL), RMS 100 nm (0.78 mg/mL), and RMS 1200 nm (10 mg/mL). In addition, we prepared the primer solutions in two different solvents, i.e., acetone and methanol, to compare the effects of self-assemblies related to solubility and rapid drying via azeotropic removal of water molecules from the surface. Further, we prepared more practical dental PMA composites containing 70 wt % of glass fillers as in conventional dental PMA composites in comparison to the PMA composite containing 30 wt % of the fillers in the previous study.[14]

The average shear strengths of the different concentrations are shown in Figure 3b. The concentration range 0.07−0.78 mg/mL exhibited similar knife shear strengths. However, the knife shear strength was doubled when compared to the pristine glass control, which indicates that the CMP enhances the shear bonding performance by chemical bridging or coupling between the glass substrate and the PMA resin. In the case of a high concentration of primer solution (10 mg/mL), the maximum shear stress dropped to ~0.5 MPa, which is half that of the control experiment. This result suggests that the unbound inordinate catecholic molecules on the substrate interfere with the polymerization of the PMA blend at the surface by acting as a radical inhibitor, which causes lower shear stress than the bare glass substrate.[33]

We also compared the shear strengths of silane, CAP, and CMP. Interestingly, the silane-treated sample shows a higher knife shear bonding strength compared to samples with catechol treatments, whereas catechol-treated samples show better mechanical properties, presented later in this article. In other words, the effect of the catecholic dynamic bonds is much more pronounced in the actual composite test. This difference between the bonding test on the glass plates and mechanical property test of the composite containing the glass fillers is likely to be because the microfillers have several orders of magnitude higher surface area compared to the glass plate; thus, the catechol sacrificial bond is much more effective for enhancing the coupling on glass fillers but less effective on bonding properties. Due to the reactivity difference between acrylate and methacrylate during the polymerization,[31] we expected that it would affect the cross-linking of primers with PMA resin which, in turn, contributes to the difference in adhesion and shear bonding strength. However, as shown in Figure 3c, the knife shear bonding test results did not show a statistically significant difference. We speculate that surface adhesion of the catechol groups plays a more important role in the bonding performance than that arising from cross-linking between acrylate and methacrylate groups.

Compressive Test. We extended our study to produce the actual dental restorative composite using the catecholic methacrylate primers compared to previously reported acrylate
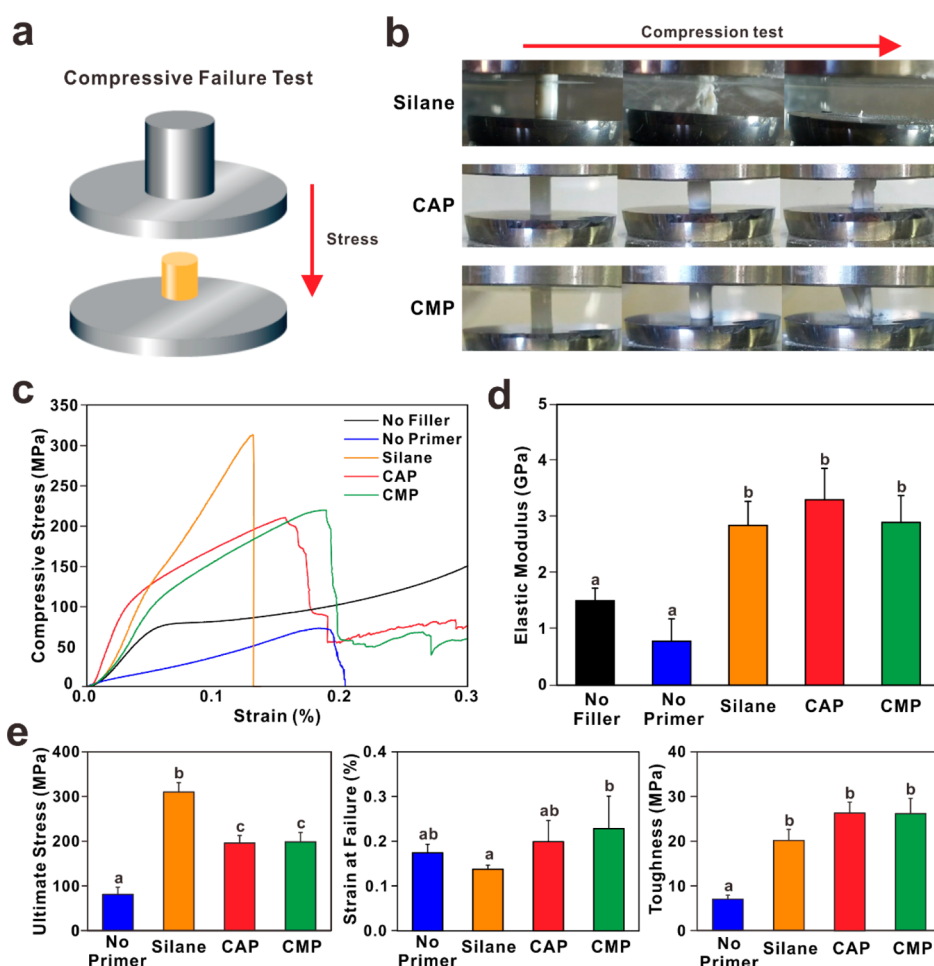
Figure 4. Compression tests of dental composites. (a) A schematic representation of the compression test. (b) Images of the silane, CAP, and CMP composite samples during the compression test. (c) Representative stress–strain curves for the dental composites. (d) Elastic modulus and (e) ultimate stress (left), strain at failure (middle), and toughness (right) of all dental composites prepared. Bars with the different letters are significantly different according to Tukey's HSD.

primers and silane coupling agents.[14] The mechanical properties of dental composites were determined by a compressive test using a material testing system (Figure 4a,b). In this study, we evaluated five different dental resin composites as follows: one without filler (no filler), one with bare glass filler (no primer), one with commercial silane-treated filler (silane), and two catecholic primer-treated glass fillers (CAP and CMP). Figure 4 shows a representative stress–strain curve for each composite sample. The mechanical properties of each resin composite were also determined from the stress–strain curve (Figure S4).

The key advantage of glass fillers is reducing polymerization-induced shrinkage of dental PMA resin composites, which is critical in practical situations because shrinkage and shrinkage stress are directly related to marginal leakage and secondary caries.[7,8] The high filler contents occupy the free volume of the composite resin to help reduce this shrinkage.[34] There are many factors that can affect the shrinkage rate such as temperature, filler contents, filler shapes, light penetration through the mold, etc. In this study, we set all the conditions to be the same to measure the relative values between the composite without fillers and the composite containing fillers, and between catecholic fillers and silane fillers (Table S1). As anticipated, we confirmed the clear differences between the filler- and no-filler-containing composites; and similarity

between the catechol filler- and the silane filler-containing composites. The resin composite containing both catechol (CAP and CMP) and silane priming fillers shows a 7-fold lower shrinkage rate (0.43%) compared to the no filler composite (3.12%). This significantly lower shrinkage of resin composite suggests a very close packing between catecholic priming filler and PMA resin, which is associated with better wetting and coupling effects between the dissimilar surfaces (filler and resin).

Because the composite without the filler showed a too high shrinkage rate as well as a too low elastic modulus (less than 1.5 GPa) to be used for dental restorations, we further limit our discussion only to the composite containing fillers. In the case of the no primer composite, as expected, the mechanical properties of the composite became worse due to the incongruities between glass filler and polymer resin. In a clear contrast, primer-treated glass fillers demonstrated much higher elastic modulus and toughness compared to that of bare glass filler due to the efficient mixing of fillers with PMA resin. When the PMA resin composite containing primed fillers is compared to the resin composite without the primer, the mechanical properties of primed resin composite show up to 4.2 times the elastic modulus, 3.7 times the toughness, and 3.8 times the ultimate stress. Especially, silane composite exhibits outstanding ultimate stress as with higher knife shear stress.

However, the silane composite exhibited a decrease in strain-at-failure because high rigidity usually compromises extensibility or flexibility. As a result, an increase in the rigidity of the resin composites often compromises a reduction in the toughness. With the introduction of dynamic bonding at the interface between the filler and resin surfaces, we have successfully diminished the trade-off, and the catecholic surface primed glass filler-containing composites exhibited high toughness while maintaining a high rigidity (~3 GPa). Interestingly, the stress–strain curve of catecholic primer-treated composite (CAP and CMP) showed a ductility in contrast to the silane-treated filler-containing composite. As also shown in Figure 4b, the silane-treated filler-containing resin composite was completely destroyed, whereas the catechol-treated filler-containing composite withstood and maintained its structure for a much longer time and at higher load. We believe the origin of these tough mechanical properties of the catecholic primer is the presence of abundant sacrificial hydrogen bonds. In other words, the energy dissipation associated with the gradual bond breakage is the key difference from the reliance on covalent coupling present in the silane composite. As seen in the shear bonding test, both CAP and CMP composites exhibited statistically similar properties in the compression test.

Cell Attachment Test. To further assess the possibility of using catecholic priming surfaces for practical dental applications, we studied the cell attachment and viability of L929 fibroblasts on the priming surfaces. After 24 h of incubation, the morphology of the cells on the bare glass slide and priming surfaces was investigated as shown in Figure 5. All surfaces showed that a significant number of cells were attached to the surface and grew without noticeable changes in the cell morphology. These results indicate that the priming surfaces did not have any toxic effects on the fibroblast cells. Considering the high biocompatibilities of the primers developed in this study, we suggest that these catecholic primers can potentially be used in a real clinical setting.

CONCLUSIONS

In summary, catechol-functionalized methacrylate primer (catechol–spacer–methacrylate) was developed for dental resin composites. In addition, we reduced the processing time and steps for the sake of clinical, industrial, and environmental viabilities. The synthesis of the primers was characterized by ^{1}H NMR and GC/MS, and the adsorption of the primers onto SiO_2 surfaces such as silicon wafer and glass substrates was confirmed by AFM and contact angle measurements. Catechol moieties can bind to the surface during their self-assembly, while methacrylate groups cross-link with dental polymethacrylate resin. These bifunctional molecules provide the binding of glass filler and polymeric resin matrix as a coupling agent as the common silane coupling agent. In turn, it provides similar rigidity with improved elongation, resulting in the 30% improvement in toughness of the PMA resin composites. Despite the difference between the chain end groups of CAP and CMP regarding their different reactivities, their mechanical performance was similar in dental resin. Both catecholic primers CAP and CMP show higher toughness compared to the conventional silane-based primers with similarly high rigidity and low shrinkage rate. In addition, the excellent biocompatibility of the primed surfaces clearly demonstrated their significant potential for dental and biomedical applications.
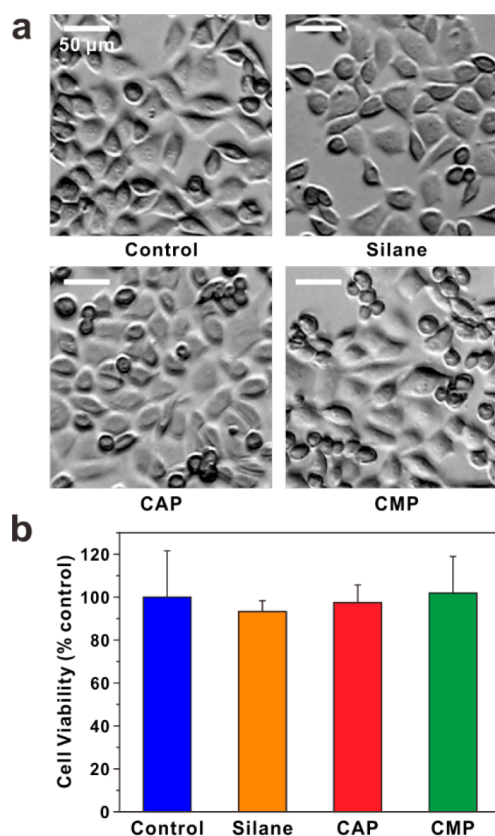

Figure 5. (a) Optical microscopy images of L929 cells seeded on the priming surfaces using various primer solutions for 24 h (conc 0.15 mg/mL). (b) Relative cell viability on the priming surfaces. The cell viability of the control group was normalized to 100%.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b14679.

^{1}H NMR data of primers, FT-IR and TGA spectra of functionalized glass filler, linear shrinkage test data, and detailed experimental methods (PDF)

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Author Contributions

∥E.S. and S.W.J. contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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