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SUBMICRO-PATTERNING OF CURABLE DENTAL MATERIALS BY MOLDING METHODS: A SCREENING TRIAL

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We investigated patterning with curable dental materials via micro/nano-molding as a screening trial. We used typical curable dental materials such as a composite resin (CR), acrylic resin, varnish, adhesive resin, restoration, sealer, cement, tooth desensitizer, and gypsum with either a cyclo-olefin polymer (COP) mold or polydimethylsiloxane (PDMS) mold that had holes, pillars, and grooves with 0.5 μm diameters and 1 μm heights. The COP mold was suitable for patterning of holes and grooves with Bondfill SB after 2 h curing, while PDMS mold was suitable for patterning of pillars with Bondfill SB at the 0.5 μm scale after 2 h curing. Most of the curable dental materials could be patterned using the COP or the PDMS mold. However, dental impression materials could not be patterned as required. In addition, the COP mold was suitable for many organic pillars, while the PDMS mold was suitable for inorganic pillars. Further, we achieved patterning on the curved surface of an artificial tooth with flowable CR using the COP thin film mold. We conclude that for the formation of uniform shaped patterns, it is important to cure within a suitable time and to select mold types depending on the type of curable dental material.

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Keywords: Curable dental materials; COP film; PDMS; Molding method; Submicrometer-patterning

1. Introduction

The design of surface topography is important for medical and dental biomaterial surfaces. Recent studies have shown that cell adhesion, spreading, and morphology are significantly affected by surface topographical patterns [1-6]. Recently, various functions have been realized by specific surface pattern designs. Specific pillar patterns with high aspect ratios in the submicrometer range reduce fibrinogen and platelet responses [7]. Stem cell differentiation is regulated by the size and type of micro- and nano-patterned surfaces [8]. The polydimethylsiloxane (PDMS) elastomer micro-patterns based on the skin of sharks prevent the formation of bacterial biofilms [9]. Further, nano-pillars based on cicada wings exhibit effective bactericidal activity [10].

Micro/nano-patterning has been applied to modify dental material surfaces containing titanium [11], zirconia [12], silica [13], alumina [14], and apatite cement [6] to control their cellular responses. Micro-textured grooves on the surface of dental titanium implants (Laser-Lok; BioHorizons, Atlanta, GA, USA) promote adhesion with soft tissue or connection to bone because of the specific patterns of fibroblasts or osteoblasts [15, 16]. Recently, dental composite resins (CRs) have been investigated for micro/nano-patterning. In a study by Frenzel et al., dental CRs

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were patterned to estimate the effect of saliva-coated surface microstructures—cubes, linear trapezoids, and flat pyramids—on their microbial adhesion properties [17]. The number of attached bacteria changed according to the size and type of the microstructure. Our previous paper described a flowable CR that was patterned by the submicro-molding method using a plastic thin-film mold [18]. The resulting grooves with submicrometer-scale dimensions improved attachment and regulated the alignment of human gingival fibroblasts. Flowable CR patterning could be used to effectively seal the space between soft tissues. The flowable CR also afforded protection against microorganism invasion.

Surface designs and materials selection influence the functions of curable dental materials. Variation of patterns on dental material surfaces could result in a wider range of dental applications. Although the patterning of titanium, zirconia, or CR has been reported, patterning of other curable dental materials is still an area to be explored. Further, patterning on the curved surface of a real or an artificial tooth with curable dental materials has not been investigated. In this study, we investigated patterning with various types of curable dental materials via micro/nano-molding as a screening trial. We used typical curable dental materials such as CR, acrylic resin, varnish, adhesive resin, restoration, sealer, cement, tooth desensitizer, and gypsum with a cyclo-olefin polymer (COP) film mold or silicone rubber-mold. We also tried patterning on the curved surface of an artificial tooth with flowable CR.

2. Materials and Methods

2.1. Preparation of COP- and PDMS-replica molds

COP- or silicone rubber-replica molds were prepared according to methods previously reported [6, 18]. The silicon master molds were purchased from Kyodo International, Inc. (Kawasaki, Japan). The nine areas of 5 × 5 mm^2 used in this study were patterned with pillars, holes, and grooves/ridges with widths of 2 μm, 1 μm, and 500 nm, and a height of 1 μm. The COP film is often used as a replica mold for patterning [19-21]. COP replicas of molds were prepared by heat-pressing a COP film (ZF14-188, 188 μm thickness, ZEON Corp., Tokyo, Japan) with the silicon master mold using a compact heating press (AH-1TC, ASONE Corp., Osaka, Japan) at 165 °C for 4 min under a pressure of 2 MPa. Upon peeling off the COP film, the COP replica mold was obtained. The PDMS prepolymer (KE-106 and CAT-RG, 10:1 mix; Shin-Etsu Chemical, Tokyo, Japan) [22] was cast against the above-mentioned replica COP mold and degassed under vacuum. The PDMS was then heat-cured at 60 °C for 12 h, and then at 150 °C for 30 min. Upon peeling off the cured polymer, the PDMS replica mold was obtained.

2.2. Patterning of curable dental materials

2.2.1. Self-curing adhesive resin restoration (Bondfill SB)

Bondfill SB (Sun Medical Co., Ltd., Shiga, Japan) [23] was mixed in a mixing dish for 30 s with a brush using six drops of the monomer liquid, three drops of the catalyst solution, and one small scoop of the powder, as recommended by the manufacturer. The paste was applied to the replica COP mold or PDMS mold and covered with a cover glass treated with a ceramic primer (GC Corp., Tokyo, Japan). They were slightly pressed and incubated at 25 °C for 30 min, 1, 2, 3, 6, or 12 h. Upon carefully peeling off the cured polymer, the patterned Bondfill SB was obtained.

2.2.2. Self-curing acrylic resin (Tray Resin)

Tray Resin (Shofu Inc., Kyoto, Japan) was mixed in a polyethylene bag using 0.5 mL of the monomer liquid and 1.4 g of the polymer powder for 1 min, as recommended by the manufacturer. The paste was applied to the PDMS replica mold and covered with an acryl frame and a cover glass. They were incubated at 25 °C for 2 h. Upon peeling off the plastic films and drying for 30 min, the patterned Tray Resin was obtained.

2.2.3. Flowable composite resin (Estelite Flow Quick)

Flowable CR Estelite Flow Quick (Tokuyama Dental Corp., Tokyo, Japan) was patterned by the method described previously [17, 18]. Approximately 100 mg of flowable CR paste was applied to a cover glass treated with a ceramic primer (GC Corp.). Subsequently, the paste was applied on the COP replica mold and pressed with a 5 mm transparent acrylic block. Light curing was carried out for 20 s using an LED light curing unit (JetLite 5000, J. Morita Corp., Tokyo, Japan). Upon carefully peeling off the COP film, the patterned flowable CR was obtained.

2.2.4. Composite resin (Beautiful NEXT)

CR Beautiful NEXT (Shofu Inc.) was patterned according to a procedure similar to that of the flowable CR.

2.2.5. Light-cured varnish (PRG Barrier Coat)

PRG barrier coat (Shofu Inc.) [24] was mixed on a mixing pad with a tip using one drop of Active liquid and one specific container of Base for 30 s, as recommended by the manufacturer. The paste was applied to the COP replica mold and covered with a cover glass treated with a ceramic primer. They were slightly pressed and light-cure incubated at 25 °C for 2 h. Upon carefully peeling off the COP film, the patterned PRG barrier coat was obtained.

2.2.6. Self-curing adhesive resin (Super-bond C&B)

Super-Bond C&B (Sun Medical Co., Ltd.) [25, 26] was mixed in a mixing dish for 30 s with a brush using six drops of the monomer liquid, three drops of the catalyst solution, and one small scoop of the powder, as recommended by the manufacturer. The paste was applied to the COP replica mold and covered with a cover glass treated with a ceramic primer. They were slightly pressed and incubated at 25 °C for 2 h. Upon carefully peeling off the COP film, the patterned Super-bond was obtained.

2.2.7. Resin-based endodontic sealer (MetaSEAL Soft)

MetaSEAL Soft (Sun Medical Co., Ltd., Shiga, Japan) [27] was mixed on a mixing pad for 30 s with a spatula using three drops of the liquid and one scoop of the powder, as recommended by the manufacturer. The paste was applied to the replica COP mold and covered with a cover glass treated with a ceramic primer. They were slightly pressed and incubated at 25 °C for 2 h. Upon carefully peeling off the COP film, the patterned MetaSEAL was obtained.

2.2.8. Light-cured resin reinforced glass ionomer restorative (Fuji II LC EM)

Fuji II LC (GC Co.) [28] was mixed for 1 min on a mixing pad with a spatula using 1.0 g of the liquid and 3.0 g of the powder, as recommended by the manufacturer. The paste was applied to the PDMS replica mold and covered with a cover glass. They were slightly pressed. Light-curing was carried out for 20 s with an LED light curing unit (JetLite 5000) and then incubation was carried out at 25 °C for 2 h. Upon carefully peeling off the PDMS mold, the patterned Fuji II LC was obtained.

2.2.9. Glass ionomer restorative (Fuji IX GP)

Fuji IX (GC Co., Tokyo, Japan) [29] was mixed for 1 min on a mixing pad with a spatula using 1.0 g of liquid and 3.6 g of the powder, as recommended by the manufacturer. The paste was applied to the PDMS replica mold and covered with a cover glass. They were slightly pressed and incubated at 25 °C for 2 h. Upon carefully peeling off the PDMS mold, the patterned Fuji IX was obtained.

2.2.10. Tooth desensitizer (Teethmate® Desensitizer)

Teethmate® Desensitizer (Kuraray Noritake Dental, Tokyo, Japan) [30] was mixed for 15 s in a mixing container with a brush using two drops of the liquid and one large scoop of the powder, as recommended by the manufacturer. The paste was applied to the PDMS replica mold and

covered with a cover glass. They were slightly pressed and incubated at 25 °C for 2 h. Upon carefully peeling off the PDMS mold, the patterned Teethmate® Desensitizer was obtained.

2.2.11. Apatite cavity lining cement (New Apatite Liner Type II)

New Apatite Liner Type II (Dentsply-Sankin Corp., Tokyo, Japan) [31] was mixed for 40 s on a mixing pad with a spatula using 1.0 g of liquid and 2.5 g of the powder, as recommended by the manufacturer. The paste was applied to the PDMS replica mold and covered with a cover glass. They were slightly pressed and incubated at 25 °C for 2 h. Upon carefully peeling off the PDMS mold, the patterned New Apatite Liner Type II was obtained.

2.2.12. Hard gypsum (New Plastone)

New Plastone powder (GC Corp.) [32] and water were mixed for 60 s in a rubber bowl with a spatula using 100 g of the powder and 24 mL of water, as recommended by the manufacturer. The gypsum paste was applied on the PDMS replica mold in an acryl flame. They were slightly pressed and incubated at 25 °C for 24 h. Upon carefully peeling off the PDMS mold, the patterned gypsum was obtained.

2.2.13. Agar impression materials (Dentloid Pro)

Dentloid Pro stick (Dentronics Co. Ltd., Tokyo, Japan) [33] was set into a syringe. The syringe was warmed up to 100 °C and retained at 60 °C in a conditioner. The resulting agar sol was applied on the COP mold in an acryl flame. They were slightly pressed and incubated at 25 °C for 30 min. Upon carefully peeling off the COP mold, the patterned agar was obtained.

2.2.14. Alginate impression material (Aroma Fine Plus)

Aroma Fine Plus (GC Corp.) [34] was mixed for 30 s in a rubber bowl using 8.4 g of the powder and 20 mL of water. The alginate paste was applied to the PDMS replica mold in an acryl flame. They were slightly pressed and incubated at 25 °C for 30 min. Upon carefully peeling off the PDMS mold, the patterned alginate was obtained.

2.2.15. Silicone impression material 1 (Exafine® Injection Type)

Exafine® Injection Type (GC Corp.) [35] was mixed for 30 s on paper using equal volumes of base and catalyst, as recommended by the manufacturer. The brown silicone paste was applied to the COP film mold in an acryl flame. They were slightly pressed and incubated at 25 °C for 5 h. Upon carefully peeling off the COP mold, the patterned Exafine® was obtained.

2.2.16. Silicone impression material 2 (JM Silicone Regular)

JM Silicone Regular (Morita Corp.) [36] was mixed for 30 s on paper using equal volumes of base and catalyst, as recommended by the manufacturer. The blue silicone paste was applied to the COP film mold in an acryl flame. They were slightly pressed and incubated at 25 °C for 5 h. Upon carefully peeling off the COP mold, the patterned JM Silicone was obtained.

2.3. Patterning of flowable CR to the curved surface of artificial tooth

Flowable CR (Estelite Flow Quick) [18] was applied near the cervical portion of an artificial tooth (Shofu Inc.). The flowable CR was covered with a COP thin film mold (ZF14-040; 40 μm thickness, ZEON Corp.) and pressed with a plastic positioning instrument (Transparent Cervical Matrices, Hawe-Neos Dental, Bioggio, Switzerland). Light-curing was carried out for 20 s using an LED light curing unit (JetLite 5000). Upon carefully peeling off the COP mold, the patterned flowable CR on the artificial tooth was obtained.

2.4. Characterization of the surface of patterned dental materials

Characterization of the surface of patterns was carried out by the previously described methods [18]. The patterned dental materials were coated with Pt-Pd using a sputtering apparatus (E-1030; Hitachi High-Tech Fielding Corp., Tokyo, Japan). The surface morphologies of the

patterns were observed using a scanning electron microscope (SEM; S-4000; Hitachi High-Tech Fielding Corp.). The surface topographies of the PDMS mold and the impression material patterns were analyzed with a 3D laser scanning confocal microscope (VK-X200; Keyence Corp., Osaka, Japan).

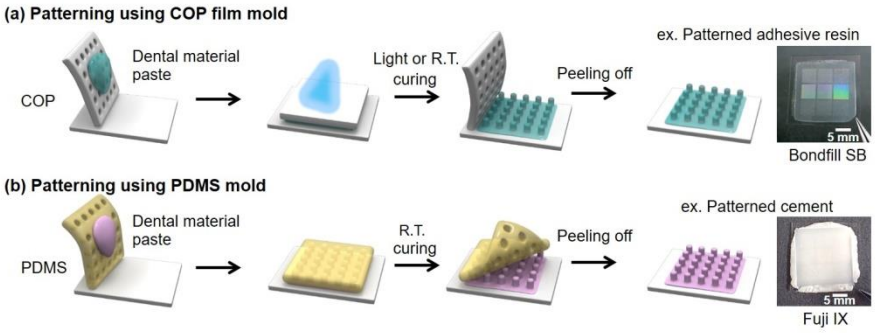

Fig. 1. Preparation of patterned-dental materials via micro/nano-molding. Patterning was using (a) COP film mold, or (b) PDMS mold.

3. Results and discussion

3.1. The effect of curing time on patterning of Bondfill SB

We investigated the patterning of curable dental materials via micro/nano-molding as a screening trial. First, the effect of the curing time on pillar patterning of Bondfill SB using the COP film mold was investigated, as shown in Fig. 1a and Fig. 2. Figure 2 shows the SEM images of the pillars transferred by the COP film mold having holes with diameters of 0.5 μm and depths of 1.0 μm each, according to the curing time. For about 30 min of curing time, the formation of pillars was not observed because of the insufficient extent of polymerization. For 1- and 2-h cures, approximately normal-shaped pillars with diameters of approximately 0.5 μm and heights of approximately 1 μm were observed. The Bondfill SB pillars cured for 1- or 2-h were easily peeled off from the COP film mold due to the softness of the pillars because polymerization was not complete at this stage. For 3 h cure, slightly longer pillars with a height of approximately 2 μm were observed. For 6 h cure, longer pillars were observed and approximately half of the pillars were missing. The elongation of Bondfill SB pillars was similar to the elongation phenomena of polystyrene nano-pillars during thermal nanoimprinting [37, 38]. The elongated polystyrene pillars were formed by the adhesion force against mold during demolding. In this study, it was difficult for pillars cured for 3 h to be peeled off from the mold because polymerization proceeded further and the pillars became harder. For 12 h cure, nearly all the pillars were lost during demolding. These results suggested that the proper curing time for the patterning of Bondfill SB pillars using a COP film mold was 1 to 2 h. Therefore, it is important to select adequate curing time for the formation of normal-shaped patterns, depending on the type of curable dental material.

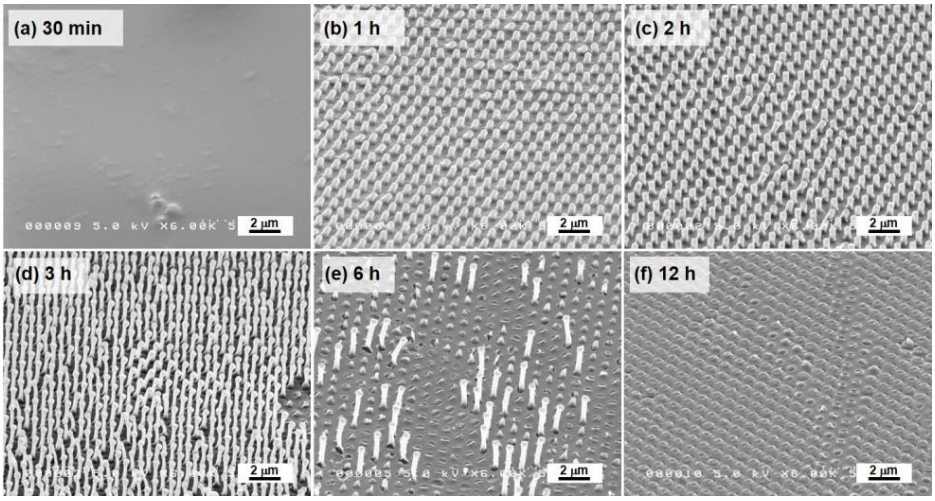

Fig. 2. SEM images of pillar patterns with Bondfill SB at different curing times at a 45° tilt angle. Bondfill SB was cured for (a) 30 min, (b) 1 h, (c) 2 h, (d) 3 h, (e) 6 h, and (f) 12 h using a COP film mold. The size of holes in the mold was 0.5 μm diameter and 1 μm depth.

3.2. The effect of mold type on patterning of Bondfill SB

We investigated the effect of the mold type, i.e., the COP film mold and PDMS mold, on the patterning of Bondfill SB for 2 h curing, as in Fig. 1. Figure 3 shows the typical pattern transferred when COP film molds (having holes, pillars, and grooves with a diameter or width of 0.5 μm and height of 1 μm) and Bondfill SB are used. SEM images revealed that the patterned COP film mold had fine hole, pillar, and groove shapes, as shown in Figs. 3a-c. Although the pattern transferred by the COP mold with holes consisted of slightly longer pillars of Bondfill SB after 2 h curing (Fig. 3d), the COP mold with the pillars and the grooves transferred the corresponding fine shapes (Figs. 3e and f). The Bondfill SB pillars were extended during peeling off from the COP film mold because of their weaker strengths than those of holes and grooves, even when polymerization was not complete after 2 h curing. Nevertheless, the COP film mold has advantages such as moderate strength, high detachability, and high resistance to organic solvents for the micro/nano-molding of dental materials. Figure 4 shows typical transfer of patterns of PDMS molds having holes, pillars, and grooves (with a diameter or width of 0.5 μm and height of 1 μm) to Bondfill SB. SEM images revealed that the patterned PDMS mold had fine holes as shown in Fig. 4a, whereas pillar and groove shapes of the PDMS mold were broken or deformed, as shown in Figs. 4b and c. PDMS pillars and grooves have weaker strengths than holes, and so PDMS pillars and grooves tore off, fell down, or neighboring patterns stuck together [39-41]. Thus, the PDMS mold with 0.5-μm-diameter holes transferred fine Bondfill SB pillar patterns. However, the PDMS mold with 0.5-μm-diameter pillars and grooves could not transfer the corresponding fine shapes. In patterning at a larger scale, PDMS molds with pillars and grooves with a diameter of 2 μm and height of 0.5 or 1 μm could transfer the corresponding pattern to Bondfill SB (data not shown). Therefore, it may be difficult for a PDMS mold to fabricate fine holes and grooves at 0.5 μm diameter or width and 1 μm height scale on Bondfill SB. However, it is easier for Bondfill SB pillars to be peeled off from PDMS hole molds than from COP film hole molds due to the softness of PDMS. These results suggested that the PDMS mold was suitable for patterning pillars with Bondfill SB while the COP film mold was suitable for patterning holes and grooves with Bondfill SB at the 0.5 μm scale. In future, we will investigate the preparation of harder PDMS molds to avoid pattern loss and to prepare patterns below the 0.5 μm scale.

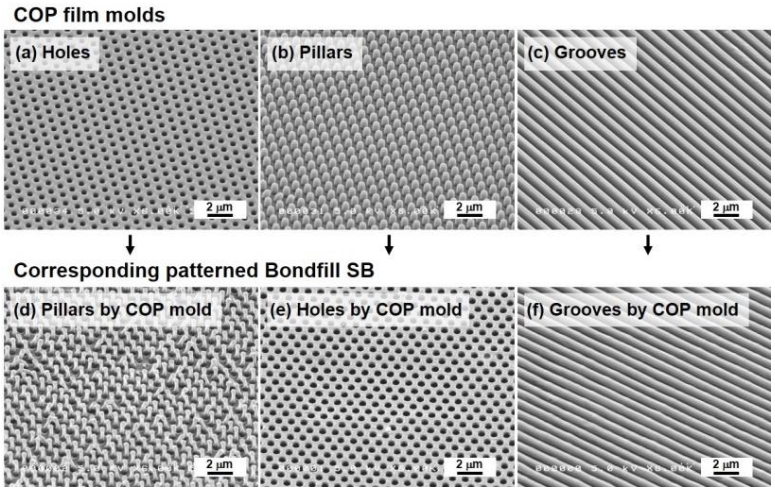

Fig. 3. Typical pattern transfer from COP film molds to Bondfill SB. SEM images of (a) holes, (b) pillars, or (c) grooves have 0.5 μm diameter or width and 1-μm height or depth of COP film molds at a 45° tilt angle. SEM images of (d) pillars, (e) holes, or (f) grooves of the corresponding patterned Bondfill SB after 2 h curing by COP film molds at a 45° tilt angle.

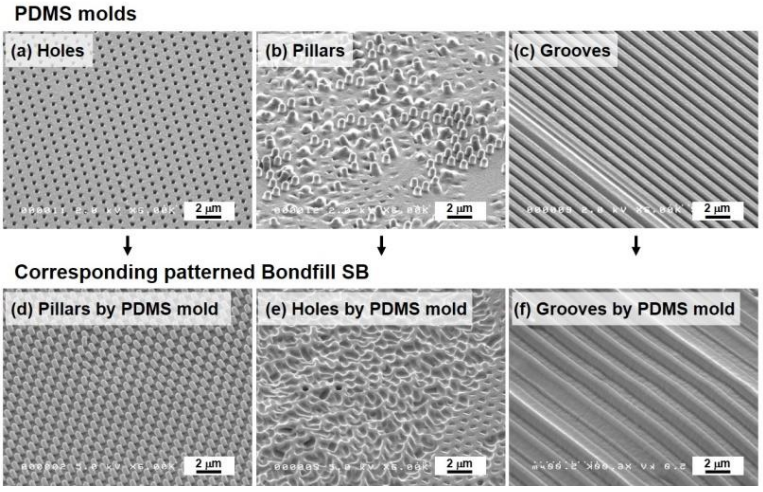

Fig. 4. Typical pattern transfer from PDMS molds to Bondfill SB. SEM images of (a) holes, (b) pillars, or (c) grooves have 0.5 μm diameter or width and 1-μm height or depth of PDMS molds at a 45° tilt angle. SEM images of (d) pillars, (e) holes, or (f) grooves of the corresponding patterned Bondfill SB after 2 h curing using PDMS molds at a 45° tilt angle.

3.3. Patterning of curable dental materials via molding: a preliminary screening trial

We investigated the patterning of various types of curable dental materials such as CR, acrylic resin, varnish, adhesive resin, restoration, sealer, cement, tooth desensitizer, and gypsum. Figure 5 shows the SEM images of pillared dental materials patterned using a mold with holes of diameter 0.5 μm and depth of 1 μm. Organic polymer patterns such as flowable CR, CR, and acrylic resins gave fine pillar structures, as shown in Fig. 5a-h. The flowable CR gave the finest pillar structure because it can enter the small spaces of the hole mold due to its high flow properties (Fig. 5a). However, typical CR gave short pillar structures because it could not enter the small spaces of the hole mold due to its low flow properties (Fig. 5b). The patterning of Tray Resin, PRG Barrier Coat, MetaSEAL, Super Bond C&B, Bondfill SB, and Fuji II LC gave fine pillar structures (Figs. 5c to h). Interestingly, some of the MetaSEAL pillars stuck to each other (Fig. 5g

arrow). The MetaSEAL pillars deformed and stuck to each other by adhesion due to their softness [40, 41]. The flow properties of curable dental material paste are important factors for submicrometer-patterning. Additionally, the usage of a COP film mold is effective for patterning with flowable CR due to its oxygen barrier properties, as previously reported [18]. However, a preferable mold for the patterning of curable dental materials depends on material type. The COP film mold is more effective for patterning in organic polymers.

When patterning inorganic substances, the glass ionomer cement Fuji IX GP gave fine pillar structures (Fig. 5i), whereas the apatite cements Teethmate® Desensitizer, New Apatite Liner, and gypsum New Plastone gave short pillars (Figs. 5j-l). Patterned gypsum was porous and consisted of gypsum crystal needles. Interestingly, gypsum pillars were observed on a gypsum crystal and were short and slightly thick with a diameter of ~0.7 μm (Fig. 5l). The formation of pillars of diameter 0.7 μm on gypsum crystal in this study disagreed with the formation of gypsum grooves with a width approximately 1 to 2 μm over entangled gypsum crystals [42]. Small pillars can be formed on a gypsum crystal. However, a compact and smooth surface of gypsum will be needed for patterning at the submicro- or nano-scale because the typical gypsum surface is porous at the micro-scale. Further, it is more difficult to pattern cements than to pattern resins. When peeling off from the mold, the pillars of cement and gypsum were easily broken because of their brittleness. Therefore, the PDMS mold is usually effective for patterning of cements or gypsum due to its softness.

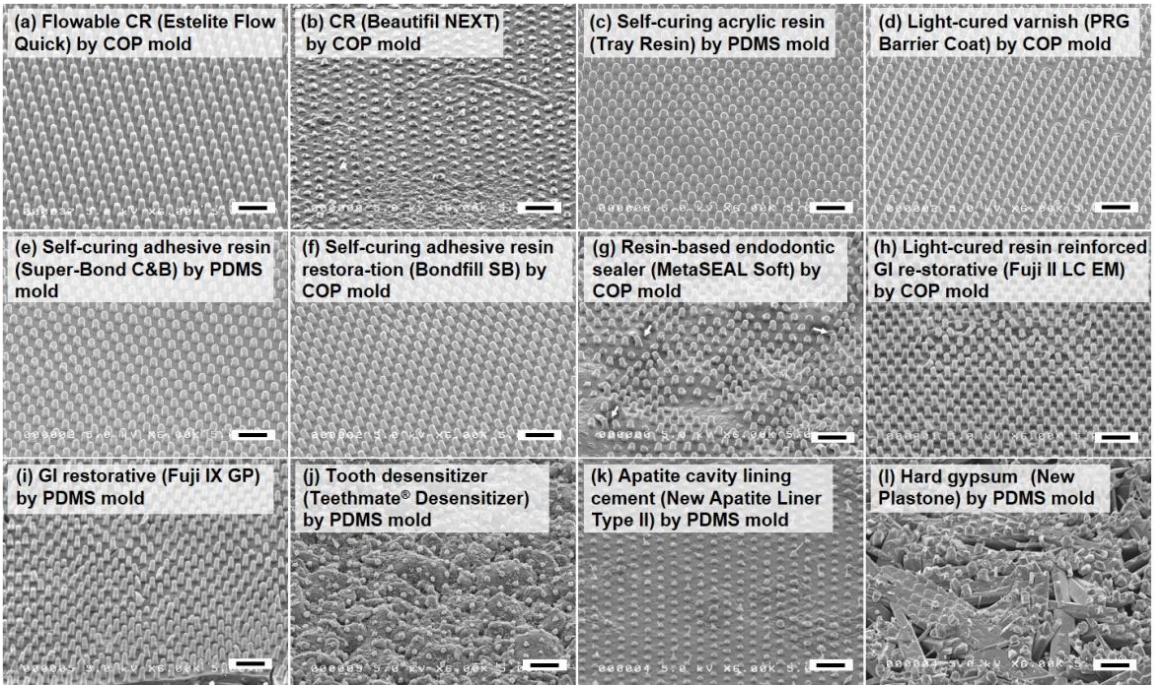

Fig. 5. SEM images of pattern-curable dental materials at a 45° tilt angle. The materials were patterned with a mold having holes of 0.5 μm diameter and 1 μm depth. The black scale bar indicates 2 μm. CR: composite resin, GI: glass ionomer. Arrows indicate stuck pillars.

Further, we investigated patterning on the dental impression materials. Figure 6 shows laser microscopy images of the surfaces of patterned agar and alginate, and SEM images of silicone impression materials using a COP film mold having holes with a diameter of 0.5 μm and depth of 1 μm. As it is difficult to observe the surface morphologies of the hydrocolloid impression materials by SEM due to their high water content, their surfaces were observed using a laser microscope. First, to estimate the effect of pillar size, dental agar Dentloid Pro was patterned using a COM film mold having holes with diameters of 2, 1, and 0.5 μm and a height of 1 μm

(Figs. 6a to c). Although fine pillars on patterned agar were not observed, very short rounded pillars were observed. The heights of the agar pillars patterned by the hole molds with diameters of 2, 1, and 0.5 μm were approximately 0.26, 0.12, and 0.01 μm, respectively. Patterning with alginate Aroma Fine Plus using the COP mold with a diameter of 0.5 μm exhibited a similar trend to agar, as in Fig. 6d (data of 2 and 1 μm not shown). Agar and alginate have high water contents. Significant volume shrinkage occurs when the solvent is evaporated. Further, their polysaccharides molecules would leave the hole space of the mold during gelation or crosslinking. Reproducibility of dental alginate and agar was lower than of the silicone impression materials. Generally, surface reproduction by alginate or agar from a mold could reproduce about 15 to 30 μm V-shaped grooves [43, 44]. Although the shape of ~0.5 μm groove reproduced with alginate and agar was not fine in this study (Figs. 6c and d), 2 μm grooves with agar or alginate were distinguishable as the groove shape was similar to the Fig. 6a pillar shapes (data not shown). These results suggested that patterning at the 0.5 μm scale using agar and alginate dental impression materials was difficult. The dental silicone impression materials Exafine® Injection Type and JM Silicone Regular did not display fine pillar structures (Figs. 6e and f). Although their 0.5 μm pillars were prepared by patterning, they were too soft to stand on and fell down or got torn off during demolding. Similar to alginate and agar, the pillars at the 2 μm scale of both silicones were distinguishable (data not shown). In a previous study, the reproduction of fine grooves by dental silicone Elite double was achieved at approximately 1.5 μm and a height of 65 nm [45]. Derrien et al. reported that dental silicone Provil was able to reproduce inverted V-shaped ridges with 1 μm wide and 1 μm high [42]. These results suggest that patterning of low aspect patterns or stable shaped patterns might be reproducible on dental silicone impression materials. In the future, harder silicone impression materials are needed for patterning at submicrometer or lower scales.

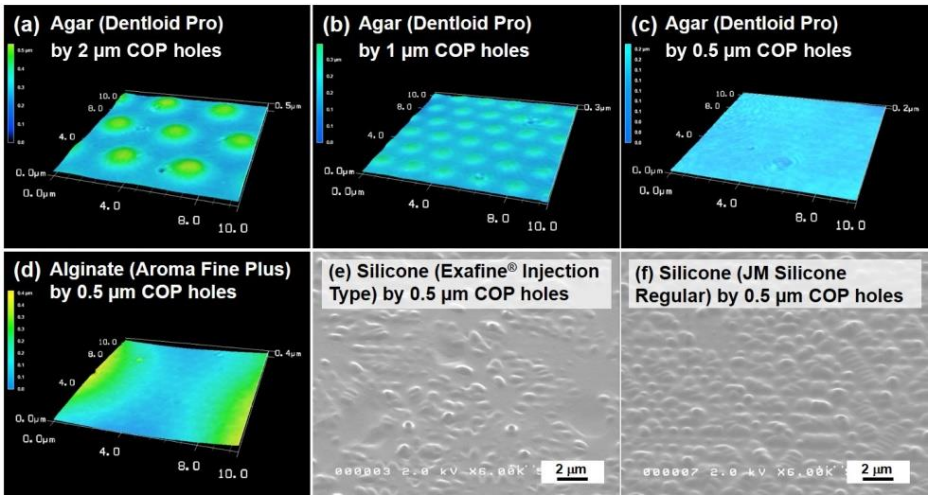

Fig. 6. Laser microscopy and SEM images of patterned-dental impression materials at a tilt angle. Laser microscopy images of Dentloid Pro agar patterned using a COP mold having holes with (a) 2 μm, (b) 1 μm, or (c) 0.5 μm diameter and 1 μm depth, and (d) Aroma Fine Plus alginate patterned using a COP mold has holes with 0.5 μm diameter and 1 μm depth. SEM images of (e) Exafine silicone, and (f) JM Silicone patterned by COP mold have holes with 0.5 μm diameter and 1 μm depth.

3.4. Patterning of the curved surface of artificial tooth

Finally, we investigated patterning on the curved surface of an artificial tooth with flowable CR for an assumed dental application to adhere gingival cells strongly, as in Fig. 7. First, flowable CR was applied on the artificial tooth, as in Fig. 7b. Patterned COP thin film with 44 μm

thickness and width of 3 mm was easily curved along the curved surface of the artificial tooth due to its flexibility (Fig. 7c). The flowable CR was pressed with a plastic positioning instrument. The flowable CR was easily spread due to its high flow property. After 20 s of light curing, (Fig. 7d), flowable CR was easily cured at the surface near the patterned COP film because COP films have a high oxygen barrier property. Figure 7f shows a SEM image of the resulting fine grooved structure with a width of 0.5 µm. As a result, we achieved patterning of a curved surface on the artificial tooth with flowable CR using a flexible COP thin film. Further, groove direction or combination with other patterns could be controlled by the designed pattern molds.

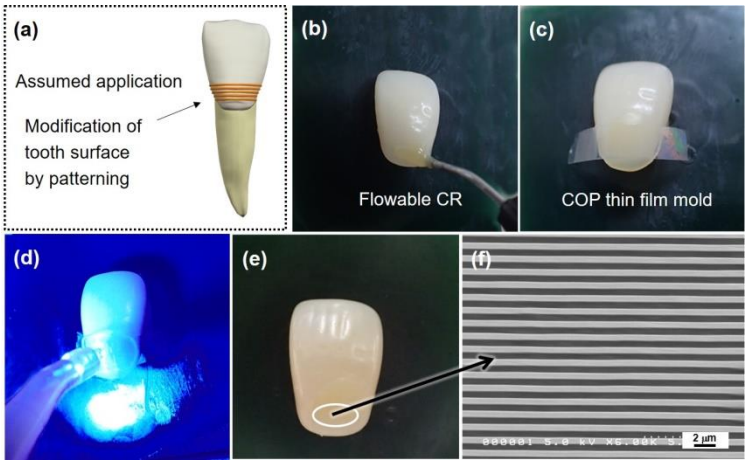

Fig. 7. Patterning of the curved surface of an artificial tooth with flowable composite resin (CR). (a) Assumed application, (b) application of flowable CR on artificial tooth, (c) covering with patterned COP thin film mold, (d) pressing and light curing, (e) the resulting patterned artificial tooth, and (f) SEM image of the groove pattern with 0.5 µm width and 1 µm height on the surface of the artificial tooth.

4. Conclusions

We investigated patterning with various types of curable dental materials via micro/nano-molding as a screening trial. The COP film mold was suitable for patterning of holes and grooves with Bondfill SB, while the PDMS mold was suitable for the patterning of pillars with Bondfill SB at the 0.5 µm scale. Nearly all of the curable dental materials used in this study without impression materials could be patterned using a COP film mold or PDMS mold that had holes, pillars, and grooves with a diameter or width of 0.5 µm and a height of 1 µm. An adequate curing time and selection of mold types depending on the type of curable dental material are important for the formation of normal-shaped patterns.

Our next step will be to estimate the stability of the patterns in culture conditions or the oral cavity environment, and to design functional patterns with dental material depending on the applications. Further, we will try to develop dental materials having faster curable patterning properties and biocompatibility. Finally, we achieved patterning on the curved surface of an artificial tooth with flowable CR (Fig. 7a). Our patterning method can be used to effectively seal soft tissue and dental materials to protect against microorganism invasion [46, 47]. In the future, we will apply this molding method to the surface pattering of the natural tooth.

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