

Enhanced anti-bacterial adhesion effect of FDMA/SR833s based dental resin composites by using 1H,1H-heptafluorobutyl methacrylate as partial diluent

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ABSTRACT

With the purpose of further reducing surface free energy to achieve better anti-bacterial adhesion effect of fluorinated dimethacrylate (FDMA)/tricyclo (5.2.1.0) decanedimethanol diacrylate (SR833s) based dental resin composites (DS), 1H,1H-heptafluorobutyl methacrylate (FBMA) was used to partially replace SR833s as reactive diluent. According to the degree of substitution, the obtained resin composites were marked as DSF-1 (20 wt.% of SR833s was replaced by FBMA), DSF-2 (40 wt.% of SR833s was replaced by FBMA), and DSF-3 (60 wt.% of SR833s was replaced by FBMA). Bisphenol A glycidyl dimethacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) based resin composite (BT) was used as control. The influence of FBMA concentration on double bond conversion (DC), contact angle, surface free energy, anti-bacterial adhesion effect against *Streptococcus mutans* (*S. mutans*), volumetric shrinkage (VS) and shrinkage stress (SS), flexural strength (FS) and modulus (FM), water sorption (WS) and solubility (SL) were investigated. The results showed that FBMA addition could reduce surface free energy from 44.6 mN/m for DS to 32.9 mN/m for DSF-3, and lead to better anti-bacterial adhesion effect (the amounts of adherent bacteria decreased from 2.03×10^5 CFU/mm² for DS to 6.44×10^4 CFU/mm² for DSF-3). The FBMA had no negative effects on DC, VS, SS, WS, and SL. Too high a concentration of FBMA reduced FS and FM before water immersion, but the values were still higher than those of BT.

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1. Introduction

Due to lack of antibacterial properties of dental resin composites (DRCs), pathogenic bacteria such as *Streptococcus mutans* (*S. mutans*) can easily accumulate on their surface of DRCs, resulting in a high risk of secondary caries [1, 2]. With the aim of reducing bacterial accumulation on the surface, the DRCs can be modified to be bactericidal and to have an anti-bacterial adhesion effect [3]. However, bactericides might influence the balance of oral microbiome which is important to general health [4], thus endowing DRCs with an anti-bacterial adhesion effect seems a safer method.

According to surface thermodynamics, in oral condition, cariogenic bacteria such as *S. mutans* have difficulty in adhering to surfaces with low surface free energy because of their own high surface free energy

[5, 6]. Furthermore, a previous study showed a linear relationship between the amount of adherent *S. mutans* and hydrophobicity and surface free energy [7]. Therefore, several methacrylates that can increase hydrophobicity and reduce surface free energy have been incorporated into the resin matrix of DRCs. Tong et al. [8] synthesized two kinds of silicone dimethacrylates (SMA-ME and SMA-MEO) and added these into a Bisphenol A glycidyl dimethacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) resin with the aim of preparing anti-bacterial adhesion resins for DRCs. The results showed that silicone dimethacrylates could effectively endow cured resin with an anti-bacterial adhesion effect against *S. mutans* by increasing hydrophobicity and reducing surface free energy. Unfortunately, addition of the silicone dimethacrylates seriously compromised the mechanical properties of the cured resin. In

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our previous research, Zhang et al. [9] synthesized a fluorinated dimethacrylate (DFMA) and mixed it with the reactive diluent tricyclo (5.2.1.0) decanedimethanol diacrylate (SR833s) to form a resin matrix. The resulting DRC had anti-bacterial adhesion effect against *S. mutans* as well as mechanical properties superior to those of Bis-GMA/TEGDMA based DRC. Nevertheless, there were still a certain amount of bacteria attached on the surface of the DFMA/SR833s based DRC.

If the surface free energy of DFMA/SR833s based DRC could be reduced further, an improved anti-bacterial adhesion effect might be achieved. For this purpose, 1H,1H-heptafluorobutyl methacrylate (FBMA) was used to partially replace SR833s as reactive diluent. There are two reasons for choosing FBMA as diluent in this study. One is that $-CF_3$ is more effective in reducing surface free energy than $-CF_2-$ [10]; with the same mass fraction, shorter fluorocarbon chains could introduce more $-CF_3$. The other reason is that 2,2,2-trifluoroethyl methacrylate and 2,2,3,3,3-pentafluoropropyl methacrylate, which have shorter fluorocarbon chains than FBMA, have very low boiling point, making them unsuitable for use as diluent in DRC. The hypothesis of this study was that the use of FBMA as partial diluent reduces the surface free energy of DFMA/SR833s based DRC, reducing anti-bacterial adhesion.

2. Materials and Methods

2.1. Materials

Bis-GMA, TEGDMA, SR833s, camphorquinone (CQ), 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA), and 3-(trimethoxysilyl)propylmethacrylate (γ -MPS) were purchased from Sigma-Aldrich Co. (St. Louis,

MO, USA). FBMA was purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). The fluorinated dimethacrylate DFMA (Fig. 1) was synthesized as described previously [9]. Silanated dental glass fillers (SCHOTT® UltraFine, GM27884, 6% silane, 0.7 μ m) were purchased from SCHOTT AG (Mainz, Germany).

2.2. Preparation of dental resin composites

The components of the resin matrix for each DRC were weighed and mixed according to the proportions shown in Table 1. Subsequently, the resin matrix and silanated glass fillers were mixed with a mass ratio of 30 wt./70 wt. using a high-speed mixer (ZD-T600C, Shenzhen Zhidi Technology Int., Shenzhen, China) at a speed of 2800 rpm until a uniform DRC was obtained.

2.3. Measurement of particles distribution in DRCs

The DRC was filled into a half-split stainless-steel mold (2 mm \times 2 mm \times 25 mm) that was placed on a Mylar sheet. Then, the DRC was covered with another Mylar sheet followed by a glass slide. The DRC was light-cured using a visible light-curing unit for 20 s (Kerr Demi Ultra) in six separated overlapping portions. The prepared sample was then brittle broken in liquid nitrogen. After gold spraying, the particles distribution on the fresh section was observed using a scanning electron microscope (SEM, Merlin, Zeiss, Germany) with an operating voltage of 5 KV.

2.4. Measurement of double bond conversion (DC)

The DC was investigated using FT-IR spectroscopy (Thermo Scientific Nicolet iS50, Thermo Fisher

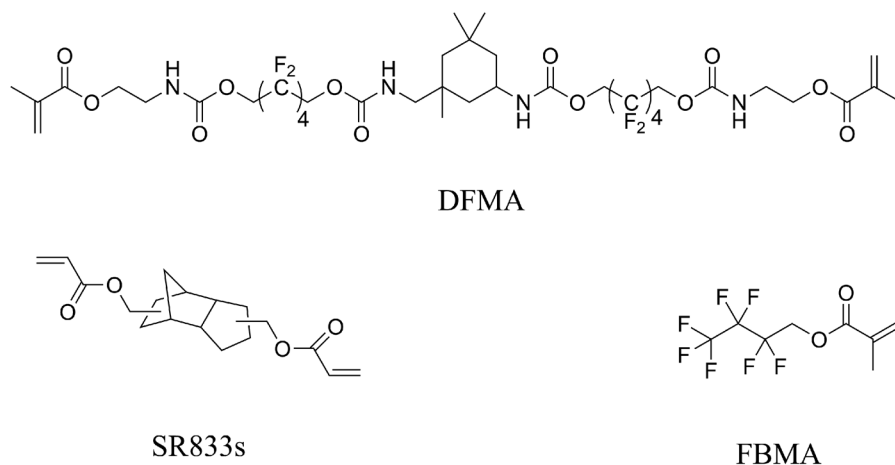


Figure 1. Structures of DFMA, SR833s, and FBMA.

Table 1. Components of the resin matrix for each dental resin composite

DRCs	Components (g)						
	Bis-GMA	TEGDMA	DFMA	SR833s	FBMA	CQ	DMAEMA
BT	49.3	49.3	0	0	0	0.7	0.7
DS	0	0	49.3	49.3	0	0.7	0.7
DSF-1	0	0	49.3	39.44	9.86	0.7	0.7
DSF-2	0	0	49.3	29.58	19.72	0.7	0.7
DSF-3	0	0	49.3	19.72	29.58	0.7	0.7

Scientific Inc., Waltham, USA) with an ATR mold at room temperature of 25°C. The FT-IR spectra were recorded with 4 scans at a resolution of 4 cm⁻¹. The DRC sample was applied into a cylindrical mold (d = 4 mm, h = 2 mm), which was placed directly on the ATR crystal, and covered with a Mylar sheet followed by a glass slide. At this point, a spectrum of the uncured sample was recorded. The sample was then light-cured from the top using a visible light-curing unit with an irradiance of 850 mW/cm² (Kerr Demi Ultra, Kerr Corporation, Orange, CA, USA) keeping the light-curing tip in direct contact with the glass slide followed by recording of a second scan. The DC was calculated from the methacrylate C=C peak at 1636 cm⁻¹, and normalized against the carbonyl C=O peak at 1720 cm⁻¹ according to formula (1)

$$DC(40) = \left[\frac{1 - (A_{C=C} / A_{C=O})_{40}}{(A_{C=C} / A_{C=O})_0} \right] \times 100\% \quad (1)$$

where $A_{C=C}$ and $A_{C=O}$ are the absorbance intensities of the methacrylate C=C at 1636 cm⁻¹ and the carbonyl group at 1720 cm⁻¹, respectively. $(A_{C=C}/A_{C=O})_0$ and $(A_{C=C}/A_{C=O})_{40}$ are the normalized absorbance of the functional groups at the radiation times 0 and 40s, respectively. The measurement of each DRC was repeated five times (n = 5).

2.5. Measurement of volumetric shrinkage and shrinkage stress

2.5.1 Volumetric shrinkage (VS)

The VS of the DRCs was measured by the difference in density before and after being cured through an analytical balance (FA1104, Shunyuhenping Scientific Instrument Int., Shanghai, China) with an accuracy of 0.1 mg equipped with a density test kit. The sample was weighed in air and in water separately, and the density of the sample (ρ) was calculated according to formula (2)

$$\rho = \frac{M_a \times \rho_w}{M_a - M_w} \quad (2)$$

where M_a and M_w are the weights of the sample in air and in water, respectively. ρ_w is the density of water at the exact measurement temperature. Densities of the sample before and after curing were all measured three times (n = 3).

The VS of DRC was then calculated according to formula (3)

$$VS = \frac{\rho_c - \rho_b}{\rho_c} \times 100\% \quad (3)$$

where ρ_b and ρ_a are density of sample before and after being cured, respectively.

2.5.2. Shrinkage stress (SS)

Shrinkage stress was determined according to the method used in previously [11]. Two 4 cm long glass rods with a diameter of 6 mm were fixed in a universal testing machine (Z010, Zwick-Roell GmbH & Co., KG, Ulm, Germany). The surfaces of the rods were ground with a 180-grit carbide sandpaper and treated with γ -MPS before use. The uncured DRC was filled into the gap between two rods and the height of specimen was fixed to 1 mm thick. The specimen was then irradiated by two visible light-curing units from two sides simultaneously for 20s. The shrinkage force was monitored and recorded for 5 min at room temperature. The SS was calculated by dividing the shrinkage force with the cross-sectional area of the glass rod. For every DRC, the measurement was repeated eight times (n = 8).

2.6. Measurement of contact angle and surface free energy

The DRC was applied into a 1.0 mm thick cylindrical stainless-steel mold with a diameter of 10.0 mm, and then covered with a Mylar sheet followed by a glass slide. The DRC was light-cured using a visible light-curing unit for 20s (Kerr Demi Ultra) in three separated overlapping portions. After curing, the sample was removed from the mold and polished on silicon carbide grinding paper (FEPA #4000) in a grinding machine (MPD-1, Guangxiangzhiyang

Instrument Ltd., Shanghai, China) using water as lubricant to obtain a smooth surface. Subsequently, the polished sample was cleaned ultrasonically in distilled water for 30 min, and then dried in a desiccator before being tested. Six samples were prepared for each DRC ($n = 6$).

The liquid contact angle on the surface of each sample was measured using sessile drop technique at room temperature with a video contact angle system (SDC-100, Dongguan SINDIN Precision Instrument Co., Ltd., Dongguan, China). A 2- μ L droplet of liquid was dropped onto the surface of the sample, and the contact angle was obtained after the droplet had stabilized on the surface for 20 s. Distilled water and diiodomethane with known surface free energy were used to investigate the surface free energy of sample, and the value was directly calculated from the software of the machine through Owens-Wendt approach.

2.7. Bacterial adhesion test

Sample preparation. The samples for the bacterial adhesion test were prepared using the same protocol as the samples for the contact angle test. Eight samples ($n = 8$) were prepared for each DRC.

Bacterial culture. *S. mutans* (*S. mutans*, ATCC 25175) was cultured in brain heart infusion (BHI) broth and adjusted to 1×10^7 CFU/mL using the McFarland Criterion. The bacteria suspension was then diluted in BHI to 1×10^6 CFU/mL.

Adhesion assay. Each prepared DRC sample was sterilized with ultraviolet rays for 1 h and transferred into one well of a 24-well culture plate with 1 mL of bacteria suspension (1×10^6 CFU/mL). After 24 h of anaerobic incubation at 37°C, the samples were removed, gently washed twice with phosphate-buffered saline (PBS) and vortexed vigorously to collect the adherent bacteria from the surface. Subsequently, 100 μ L of diluted suspension was spread onto BHI agar and anaerobically incubated at 37°C for 24 h, after which the colonies that grew on the BHI agar were counted to assess the amount of adherent bacteria.

2.8. Measurement of flexural strength (FS) and modulus (FM)

The DRC was filled into a half-split stainless-steel mold (2 mm \times 2 mm \times 25 mm) that was placed on a Mylar sheet. Then, the DRC was covered with another Mylar

sheet followed by a glass slide. The DRC was light-cured using a visible light-curing unit for 20 s (Kerr Demi Ultra) in six separated overlapping portions. Sixteen samples were prepared for each DRC and randomly divided into two groups. These two groups were used to evaluate FS and FM before and after water immersion. For aging, every sample was immersed in 30 mL of distilled water and stored at 37°C for one week. The FS and FM of each sample were investigated using a three-point bending test (span 20 mm) in a universal testing machine (AGD-10KN, Shinmadzu Corporation, Kyoto, Japan) at a cross-head speed of 1.0 mm/min. The FS and FM were obtained directly from the software of the machine.

2.9. Measurement of water sorption (WS) and solubility (SL)

The DRC was filled into a 1 mm thick cylindrical stainless-steel mold with an internal diameter of 15 mm and covered with a Mylar sheet followed by a glass slide. The DRC was light-cured using a visible light-curing unit (Kerr Demi Ultra) for 20 s in nine separated overlapping portions. Five samples were prepared for each DRC ($n = 5$). The dry weight (M_i) of the cured sample was measured using an analytical balance with an accuracy of 0.1 mg. Subsequently, each sample was immersed in 30 mL of distilled water and stored at 37°C. At fixed time intervals, each sample was removed from the water, blotted dry, weighed and then returned to the water until an equilibrium mass (M_e) was obtained. Finally, all samples were dried at 60°C under vacuum and weighed every three days until constant mass (M_f) was obtained. The WS and SL of DRC were then calculated according to formulae (4) and (5)

$$WS = \frac{M_e - M_f}{V} \quad (4)$$

$$SL = \frac{M_i - M_f}{V} \quad (5)$$

where V is the volume of the sample.

2.10. Statistical analysis

All results were statistically analyzed with analysis of variance (ANOVA) at $p < 0.05$ significance level by IBM SPSS Statistics (Version 21, IBM Co., New York, USA). Subsequent multiple comparisons were all conducted using Tukey's post hoc analysis, except for the results of FM and SL which were conducted using Dunnett's T3 post hoc analysis.

3. Results

The SEM pictures of fracture sections are shown in Fig. 2, and shows an even distribution of inorganic fillers in DRCs for all five DCRs in the observed area, indicating that fillers and resin matrix were well mixed.

The results of DC, VS, and SS for DRCs are summarized in Table 2. As can be seen, all DRCs had similar DC ($p > 0.05$). Compared with BT, all the fluorinated methacrylate containing DRCs had lower VS ($p < 0.05$) and SS ($p < 0.05$). The VS and SS showed a tendency to decrease with the increasing of FBMA concentration in resin matrix, but the differences in VS and SS between DS and DSF-1, and the difference in SS between DSF-2 and DSF-3 were not significant ($p > 0.05$).

Table 3 shows the results of the contact angle measurements on the surface of DRCs for each of the two different liquids as well as the surface free energies of the DRCs. The BT had the significantly lowest contact angles ($56.1 \pm 3.1^\circ$) and highest surface free energy ($52.9 \pm 1.4 \text{ mN/m}$) ($p < 0.05$). The contact angles increased (from $99.2 \pm 3.1^\circ$ (DS) to $117.9 \pm 1.9^\circ$ (DSF-3) for water, while from $36.9 \pm 1.5^\circ$ (DS) to $62.6 \pm 1.5^\circ$ (DSF-3) for diiodomethane) with increasing FBMA concentration in resin matrix, while the surface free energy decreased (from $44.6 \pm 1.6 \text{ mN/m}$ (DS) to $32.9 \pm 1.2 \text{ mN/m}$ (DSF-3)) with increasing FBMA concentration. However, the contact angles of water on the surface of DSF-2 and DSF-3 were statistically similar ($p > 0.05$).

The amount of bacteria recovered from the surface of the DRCs are shown in Fig. 3. As can be seen, fluorinated methacrylate containing DRCs had significantly lower amounts of adherent bacteria ($p < 0.05$) on the surface than BT ($3.97 \pm 0.82 \times 10^5 \text{ CFU/mm}^2$). The amount of adherent bacteria seemed to decrease (from $2.03 \pm 0.31 \times 10^5 \text{ CFU/mm}^2$ (DS) to $6.45 \pm 3.64 \times 10^4 \text{ CFU/mm}^2$ (DSF-3)) with increasing FBMA concentration.

Figure 4 depicts the FS (Fig. 4(A)) and FM (Fig. 4(B)) of the DRCs before and after water immersion. Before water immersion, DS ($132 \pm 7 \text{ MPa}$) and DSF-1 ($135 \pm 12 \text{ MPa}$) had statistically similar FS ($p > 0.05$) which was significantly higher than that of BT ($119 \pm 7 \text{ MPa}$) ($p < 0.05$). DSF-2 ($123 \pm 11 \text{ MPa}$) and DSF-3 ($118 \pm 6 \text{ MPa}$) both had statistically similar FS as BT ($p > 0.05$), while only DSF-3 had significantly lower FS than DS ($p < 0.05$). The FS of all DRCs decreased significantly following water immersion ($p < 0.05$). Compared with BT ($76 \pm 7 \text{ MPa}$), all fluorinated methacrylate containing DRCs had higher FS ($p < 0.05$), except for DSF-2 ($85 \pm 5 \text{ MPa}$), which had statistically similar FS as BT ($p > 0.05$). Only DSF-2 had significantly lower FS ($p < 0.05$) than DS ($102 \pm 9 \text{ MPa}$), while all the other FBMA containing DRCs had similar FS ($98 \pm 14 \text{ MPa}$ for DSF-1, and $90 \pm 13 \text{ MPa}$ for DSF-3) ($p > 0.05$) as DS. Before water immersion, all fluorinated methacrylate containing DRCs had significantly higher FM than BT ($6.83 \pm 0.80 \text{ GPa}$) ($p < 0.05$), and all FBMA containing DRCs ($10.46 \pm 0.21 \text{ GPa}$ for DSF-1, $9.66 \pm 0.64 \text{ GPa}$ for

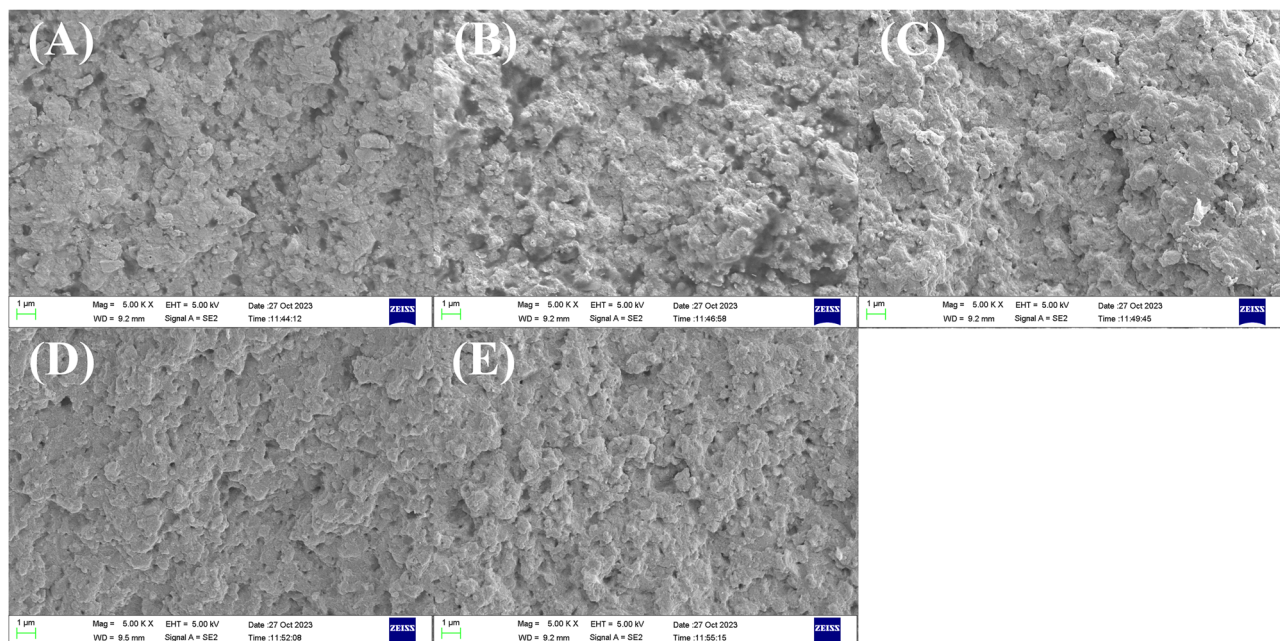


Figure 2. The fracture section morphology of DRCs. (A) BT; (B) DS; (C) DSF-1; (D) DSF-2; (E) DSF-3.

Table 2. Results of double bond conversion (DC), volumetric shrinkage (VS), and shrinkage stress (SS) of DRCs

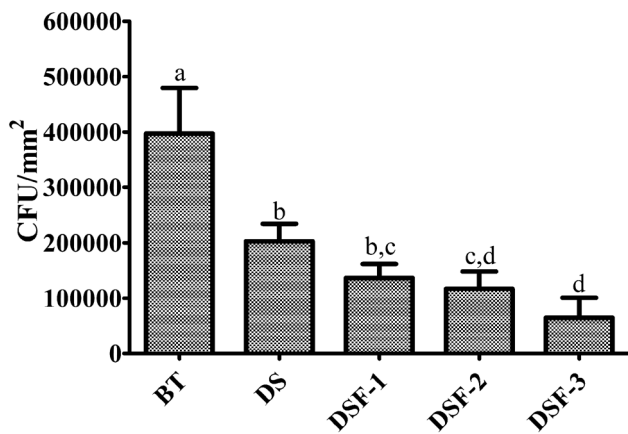
DRCs	Properties		
	DC (%)	VS (%)	SS (MPa)
BT	54.1 ± 1.3 ^a	5.30 ± 0.04 ^a	3.20 ± 0.25 ^a
DS	52.7 ± 3.2 ^a	4.42 ± 0.19 ^b	2.09 ± 0.12 ^b
DSF-1	53.7 ± 3.6 ^a	4.55 ± 0.18 ^b	2.00 ± 0.18 ^b
DSF-2	51.2 ± 3.1 ^a	4.04 ± 0.05 ^c	1.61 ± 0.25 ^c
DSF-3	51.4 ± 3.3 ^a	3.55 ± 0.37 ^d	1.48 ± 0.25 ^c

^aIdentical lower-case letters indicate no statistical difference between values within a column ($p=0.05$)

Table 3. Results of contact angle and surface free energy of DRCs

DRCs	Contact angle (°)		Surface free energy (mN/m)
	water	diiodomethane	
BT	56.1 ± 3.1 ^a	19.3 ± 3.5 ^a	52.9 ± 1.4 ^a
DS	99.2 ± 3.2 ^b	36.9 ± 1.5 ^b	44.6 ± 1.6 ^b
DSF-1	105.6 ± 2.9 ^c	44.1 ± 0.8 ^c	42.4 ± 1.4 ^c
DSF-2	113.3 ± 2.8 ^d	52.4 ± 1.2 ^d	39.6 ± 1.2 ^d
DSF-3	117.9 ± 1.9 ^d	62.6 ± 1.5 ^e	32.9 ± 1.2 ^e

^aIdentical lower-case letters indicate no statistical difference between values within a column ($p=0.05$)

**Figure 3.** The amounts of *S. mutans* recovered from the surface of dental resin composites. Identical lower-case letters indicate that there was no significant difference in the amounts of *S. mutans* between the different groups ($p=0.05$).

DSF-2, and 9.36 ± 0.34 GPa for DSF-3) had higher FM than DS (8.16 ± 0.64 GPa) ($p < 0.05$). DSF-3, which had the highest FBMA concentration, had lower FM than DSF-1 ($p < 0.05$). After water immersion, FM of all DRCs had also decreased significantly ($p < 0.05$). All fluorinated methacrylate containing DRCs had statistically similar FM (6.92 ± 0.87 GPa for DS, 8.56 ± 0.91 GPa for DSF-1, 8.26 ± 0.29 GPa for DSF-2, and 8.40 ± 1.40 GPa for DSF-3) ($p > 0.05$), which were higher than the FM of BT (5.04 ± 0.28 GPa) ($p < 0.05$).

Figure 5 presents the WS and SL results of the DRCs. As shown, all fluorinated methacrylate containing DRCs had statistically similar WS (16.5 ± 0.2 μg/mm³ for DS, 15.9 ± 0.9 μg/mm³ for DSF-1, 16.0 ± 0.5 μg/mm³ for DSF-2, and 16.4 ± 0.6 μg/mm³ for DSF-3) ($p > 0.05$) that were significantly lower than that of BT (32.6 ± 1.7 μg/mm³) ($p < 0.05$). Likewise, the SL of all fluorinated methacrylate containing DRCs (11.3 ± 0.6 μg/mm³ for DS, 11.3 ± 1.1 μg/mm³ for DSF-1, 14.2 ± 0.5 μg/mm³ for DSF-2, and 12.0 ± 1.4 μg/mm³ for DSF-3) were also lower than that of BT (20.8 ± 1.8 μg/mm³) ($p < 0.05$). Among the FBMA containing DRCs, only DSF-2 had higher SL ($p < 0.05$) than DS, while the other two DSF DRCs had similar SL ($p > 0.05$) as DS.

Figure 5 presents the WS and SL results of the DRCs. As shown, all fluorinated methacrylate containing DRCs had statistically similar WS (16.5 ± 0.2 μg/mm³ for DS, 15.9 ± 0.9 μg/mm³ for DSF-1, 16.0 ± 0.5 μg/mm³ for DSF-2, and 16.4 ± 0.6 μg/mm³ for DSF-3) ($p > 0.05$) that were significantly lower than that of BT (32.6 ± 1.7 μg/mm³) ($p < 0.05$). Likewise, the SL of all fluorinated methacrylate containing DRCs (11.3 ± 0.6 μg/mm³ for DS, 11.3 ± 1.1 μg/mm³ for DSF-1, 14.2 ± 0.5 μg/mm³ for DSF-2, and 12.0 ± 1.4 μg/mm³ for DSF-3) were also lower than that of BT (20.8 ± 1.8 μg/mm³) ($p < 0.05$). Among the FBMA containing DRCs, only DSF-2 had higher SL ($p < 0.05$) than DS, while the other two DSF DRCs had similar SL ($p > 0.05$) as DS.

4. Discussion

Fluorine is an effective atom to produce low free-energy surfaces due to its high electron negativity, small atomic radius, and low polarizability [12, 13]. It was reported that the surface free energy decreased depending on the chemical composition of the polymeric materials in the sequence -CH₂->-CH₃->-CF₂->-CF₂H->-CF₃ [10]. Consequently, in this study, DS had significantly lower surface free energy than BT, and when SR833s was replaced by FBMA, the surface free energy of DRC decreased further. As a result of reduced surface free energy, the anti-bacterial adhesion effect against *S. mutans* of DRC was enhanced. Therefore, the hypothesis of this study can be accepted. During our research, it was found that replacing SR833s with FBMA would increase the viscosity of DRC, and that DRC became too viscous to be handled when more than 60% of SR833s was replaced by FBMA. Thus, SR833s was replaced only partially by FBMA.

When the components of the resin matrix changed, the properties of DRC would be expected to vary. Though FBMA can enhance the anti-bacterial adhesion effect, its mono-methacrylic structure might influence the properties, especially the mechanical properties, of the DRC. Thus, it is necessary to investigate the influence of FBMA on the physicochemical properties of DRC.

The DC is a crucial property that determines many other properties of DRCs, such as shrinkage properties, mechanical properties, water sorption and solubility [14–16]. Though the mono-methacrylate structure of FBMA would be expected to decrease cross-link density of DRC, which is beneficial for achieving higher DC [17], the DC did not significant change after replacing SR833s with FBMA. This could be attributed to the specific properties of the fluorine atom that makes the fluorocarbon chain be bulky and rigid [13], which may decrease the mobility of the

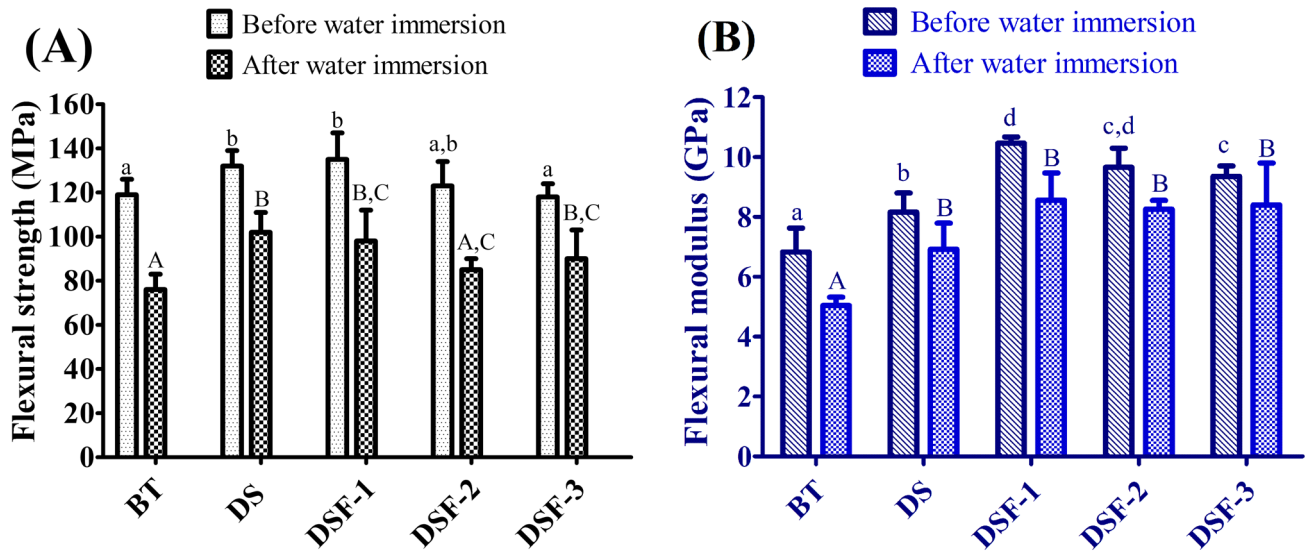


Figure 4. The results of flexural strength (A) and modulus (B) before and after water immersion of dental resin composites. Identical lower-case letters indicate that there was no significant difference in flexural strength or modulus between the different groups before water immersion ($p=0.05$), while identical upper-case letters indicate that there was no significant difference in flexural strength or modulus between the different groups after water immersion ($p=0.05$).

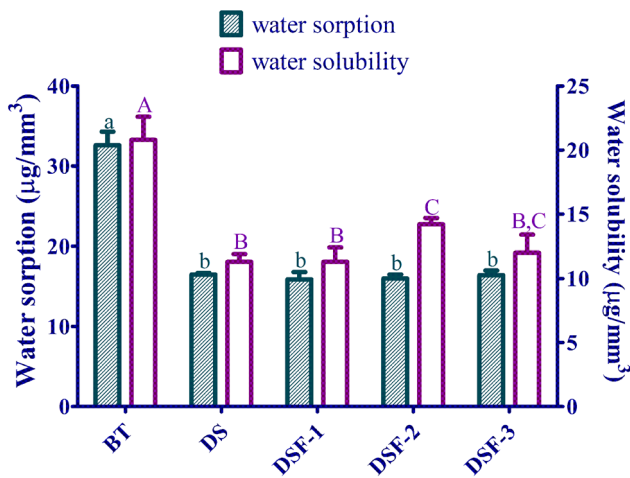


Figure 5. The water sorption and solubility of dental resin composites. Identical lower-case letters indicate that there was no significant difference in water sorption between the different groups ($p=0.05$), while identical upper-case letter indicate that there was no significant difference in water solubility between the different groups ($p=0.05$).

polymer chain and interfere with the polymerization. This phenomenon was also found in the other research [7].

As an inherent drawback of methacrylate-based DRCs, volumetric shrinkage and accompanied stress can induce secondary caries, microleakage, marginal discoloration, and postoperative sensitivity [18, 19]. The extent of VS was reported to be positively correlated with double bond conversion and double bond concentration of DRCs [20, 21]. With the same functionality, double bond concentration decreased with the

increasing of molecular weight [22]. In this research, all DRCs had similar double bond conversion (DC), thus double bond concentration of the monomers used played an important role for VS. Compared with the monomers used in BT, FDMA (1056.8 g/mol) has higher molecular weight than Bis-GMA (512.6 g/mol), and SR833s (304 g/mol) has higher molecular weight than TEGDMA (286.3 g/mol), thus DS had lower VS than BT. Though FBMA (268 g/mol) has lower molecular weight than SR833s, its mono-methacrylate structure causes a lower double bond concentration (3.73×10^3 g/mol) than SR833s (6.58×10^3 g/mol), and VS decreased with the increasing of FBMA in resin matrix. SS showed the same trend as VS, which was expected as the magnitude of shrinkage stress is associated with the extent of volumetric shrinkage [23, 24].

In harmony with a previous study, DS had higher FS and FM than BT [9]. Replacing SR833s by FBMA might have led to reduced cross-link density of DRC, but DSF-1 and DSF-2 still had comparable FS and higher FM than DS. This might be due to the bulky and rigid fluorocarbon structure in FBMA that could have a reinforcement effect on the polymeric network. When 60% of SR833s was replaced by FBMA, the reinforcement effect of the fluorocarbon structure was offset by the excessive reduction in cross-link density, thus FS and FM of DSF-3 became lower than FS and FM of DSF-1. After water immersion, FS and FM of all DRCs decreased because of the plasticization effect of water molecules [25]. However, all fluorinated methacrylate containing DRCs had higher retention

rates of FS (76.8% for DS, 72.6 for DSF-1, 69.5% for DSF-2, 76% for DSF-3) and FM (84.7% for DS, 81.8% for DSF-1, 85.5% for DSF-2, 89.7% for DSF-3) than BT (63.3% for FS, 73.9% for FM), as a sign of higher water resistance, probably due to their lower WS.

The WS of a DRC is related to the hydrophilicity [26] and cross-link density [27] of its resin matrix. The BT had the highest WS because of its lowest hydrophobicity. Using FBMA to replace SR833s could increase hydrophobicity and decrease cross-link density of the DRCs. The former would reduce the WS while the latter would increase the WS, and these two effects offset each other, resulting in all fluorinated methacrylate containing DRCs having similar WS. The SL of DRCs was influenced by the amount of unreacted monomers and the hydrophilic character of the monomers [28]. Compared with BT, the lower SL of fluorinated methacrylate containing DRCs is probably due the hydrophobic character of the monomers used as all DRCs had similar DCs.

Based on all the above results, FBMA containing DRCs showed the potential to be applied in the clinic due to its lower volumetric shrinkage, shrinkage stress, and better anti-bacterial adhesion effect, which can help in reducing the risk of secondary caries. Moreover, its better water resistance is beneficial for achieving long-term service in the clinic. Future research must now investigate biocompatibility and adhesive ability to teeth of FBMA containing DRCs.

5. Conclusion

By partially replacing SR833s with FBMA in the DFMA/SR833s resin matrix, DRCs with reduced surface free energy and enhanced anti-bacterial adhesion effect could be obtained. With the concentrations used in this study, FBMA had no influence on double bond conversion and water solubility, but could reduce volumetric shrinkage and shrinkage stress of DRCs. However, too high a FBMA concentration led to reductions in flexural strength and modulus, although the resulting DRCs still had higher flexural strength and modulus than the Bis-GMA/TEGDMA based DRC.

Disclosure of Interest

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References

- [1] Auschill TM, Arweiler NB, Brex M, et al. The effect of dental restorative materials on dental biofilm. *Eur J Oral Sci.* 2002;110(1):1–9. doi: [10.1046/j.0909-8836.2001.101160.x](https://doi.org/10.1046/j.0909-8836.2001.101160.x).
- [2] Beyth N, Domb AJ, Weiss E. An in vitro quantitative antibacterial analysis of amalgam and composite resins. *J Dent.* 2007;35(3):201–206. doi: [10.1016/j.jdent.2006.07.009](https://doi.org/10.1016/j.jdent.2006.07.009).
- [3] He J, Lassila L, Garoushi S, Vallittu P. Tailoring the monomers to overcome the shortcomings of current dental resin composites-review. *Biomater Investig Dent* 2023;10(1):2191621.
- [4] Kilian M, Chapple ILC, Hannig M, et al. The oral microbiome-an update for oral healthcare professionals. *Br Dent J.* 2016;221(10):657–666. doi: [10.1038/sj.bdj.2016.865](https://doi.org/10.1038/sj.bdj.2016.865).
- [5] Uyen M, Busscher HJ, Weerkamp AH, et al. Surface free energies of oral streptococci and their adhesion to solids. *FEMS Microbiol Lett.* 1985;30:103–106. doi: [10.1111/j.1574-6968.1985.tb00993.x](https://doi.org/10.1111/j.1574-6968.1985.tb00993.x).
- [6] Quirynen M, Marechal M, Busscher HJ, et al. The influence of surface free energy and surface roughness on early plaque formation. *J Clin Periodontol.* 1990;17(3):138–144. doi: [10.1111/j.1600-051x.1990.tb01077.x](https://doi.org/10.1111/j.1600-051x.1990.tb01077.x).
- [7] He J, Stenhagen ISR, Dragland IS, et al. Preparation of a fluorinated dental resin system and its anti-adhesive properties against *S. mutans*. *Dent Mater.* 2023;39:402–409. doi: [10.1016/j.dental.2023.03.009](https://doi.org/10.1016/j.dental.2023.03.009).
- [8] Tong H, Liao M, Huang X, et al. Physicochemical properties, anti-adhesion effect against *S. mutans*, and resistance to mucin adsorption of dental resins contained silicone methacrylates. *Silicon.* 2022;14:5835–5845. doi: [10.1007/s12633-021-01344-5](https://doi.org/10.1007/s12633-021-01344-5).
- [9] Zhang S, Liao M, Liu F, et al. Preparation of Bis-GMA free dental resin composites with anti-adhesion effect against *Streptococcus mutans* using synthesized fluorine-containing methacrylate (DFMA). *J Mech Behav Biomed.* 2002;131:105263. doi: [10.1016/j.jmbbm.2022.105263](https://doi.org/10.1016/j.jmbbm.2022.105263).
- [10] Liu X, Yang G, Lipik VT. Effects of fluorine atoms amount and fluorinated acrylic chain length chemical attached to hydroxyl groups on the hydrophobic properties of cotton fabrics. *Mod Chem Appl* 2017;5:1.
- [11] He J, Garoushi S, Vallittu PK, et al. Effect of low-shrinkage monomers on the physicochemical properties of experimental composite resin. *Acta Biomater Odontol Scand.* 2018;4:30–37. doi: [10.1080/23337931.2018.1444488](https://doi.org/10.1080/23337931.2018.1444488).
- [12] Tokuda K, Ogino T, Kotera M, et al. Simple method for lowering poly(methyl methacrylate) surface energy with fluorination. *Polym J.* 2015;47:66–70. doi: [10.1038/pj.2014.91](https://doi.org/10.1038/pj.2014.91).
- [13] Kovalchuk NM, Trybala A, Starov V, et al. Fluoro- vs hydrocarbon surfactants: Why do they differ in wetting performance? *Adv Colloid Interfac.* 2014;210:65–71. doi: [10.1016/j.cis.2014.04.003](https://doi.org/10.1016/j.cis.2014.04.003).
- [14] Dewaele M, Truffier-Boutry D, Devaux J, et al. Volume contraction in photocured dental resins: The shrinkage-conversion relationship revisited. *Dent Mater.* 2006;22(4):359–365. doi: [10.1016/j.dental.2005.03.014](https://doi.org/10.1016/j.dental.2005.03.014).

- [15] Aljabo A, Xia W, Liaqat S, et al. Conversion, shrinkage, water sorption, flexural strength and modulus of re-mineralizing dental composites. *Dent Mater*. 2015;31(11):1279–1289. doi: [10.1016/j.dental.2015.08.149](https://doi.org/10.1016/j.dental.2015.08.149).
- [16] Moldovan M, Balazsi R, Soanca A, et al. Evaluation of the degree of conversion, residual monomers and mechanical properties of some light-cured dental resin composites. *Materials*. 2019;12(13):2109. doi: [10.3390/ma12132109](https://doi.org/10.3390/ma12132109).
- [17] Lu H, Stansbury JW, Nie J, et al. Development of highly reactive mono-(meth)acrylates as reactive diluents for dimethacrylate-based dental resin systems. *Biomaterials*. 2005;26:1329–1336. doi: [10.1016/j.biomaterials.2004.04.041](https://doi.org/10.1016/j.biomaterials.2004.04.041).
- [18] Boaro LCC, Gonçalves F, Guimarães TC, et al. Polymerization stress, shrinkage and elastic modulus of current low-shrinkage restorative composites. *Dent Mater*. 2010;26(12):1144–1150. doi: [10.1016/j.dental.2010.08.003](https://doi.org/10.1016/j.dental.2010.08.003).
- [19] Soares CJ, Faria-e-Silva AL, Rodrigues Mdp, et al. Polymerization shrinkage stress of composite resins and resin cements-what do we need to know? *Braz Oral Res*. 2017;31(suppl):e62. doi: [10.1590/1807-3107BOR-2017.vol31.0062](https://doi.org/10.1590/1807-3107BOR-2017.vol31.0062).
- [20] He J, Liu F, Vallittu PK, et al. Synthesis of dimethacrylate monomers with low polymerization shrinkage and its application in dental composites materials. *J Polym Res*. 2012;19:1–9. doi: [10.1007/s10965-012-9932-3](https://doi.org/10.1007/s10965-012-9932-3).
- [21] Goldman M. Polymerization shrinkage of resin-based restorative materials. *Aust Dent J*. 1983;28(3):156–161. doi: [10.1111/j.1834-7819.1983.tb05272.x](https://doi.org/10.1111/j.1834-7819.1983.tb05272.x).
- [22] He J, Liao L, Liu F, et al. Synthesis and characterization of a new dimethacrylate monomer based on 5,5'-bis(4-hydroxyphenyl)-hexahydro-4,7-methanoindan for root canal sealer application. *J Mater Sci: Mater Med*. 2010;21:1135–1142.
- [23] Braga RR, Ballester RY, Ferracane JL. Factors involved in the development of polymerization shrinkage stress in resin-composites: a systematic review. *Dent Mater*. 2005;21:962–970. doi: [10.1016/j.dental.2005.04.018](https://doi.org/10.1016/j.dental.2005.04.018).
- [24] Schneider LF, Cavalcante LM, Silikas N. Shrinkage stresses generated during resin-composite application: a review. *J Dent Biomech*. 2010;2010:131630.
- [25] Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. *Dent Mater*. 2006;22:211–222. doi: [10.1016/j.dental.2005.05.005](https://doi.org/10.1016/j.dental.2005.05.005).
- [26] Liu X, Wang Z, Zhao C, et al. Synthesis, characterization and evaluation of a fluorinated resin monomer with low water sorption. *J Mech Behav Biomed Mater*. 2018;77:446–454. doi: [10.1016/j.jmbbm.2017.09.026](https://doi.org/10.1016/j.jmbbm.2017.09.026).
- [27] Arima T, Hamada T, McCabe JF. The effect of cross-linking agents on some properties of HEMA-based resin. *J Dent Res*. 1995;74:1597–1601. doi: [10.1177/00220345950740091501](https://doi.org/10.1177/00220345950740091501).
- [28] Gajweski VES, Pfeifer CS, Fróes-Salgado, NRG, et al. Monomers used in resin composites: degree of conversion, mechanical properties and water sorption/solubility. *Braz Dent J*. 2012;23:508–514. doi: [10.1590/s0103-64402012000500007](https://doi.org/10.1590/s0103-64402012000500007).