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ORIGINAL PAPER

Physicochemical Properties, Anti-Adhesion Effect against *S. mutans*, and Resistance to Mucin Adsorption of Dental Resins Contained Synthesized Silicone Methacrylates

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Abstract
With the purpose of preparing an anti-bacterial adhesion dental resin, two silicone methacrylates (SMAs) were synthesized. After being confirmed by the FT-IR and ^{1}H-NMR spectra, the SMAs were incorporated into commonly used Bis-GMA/TEGDMA (50/50, wt./wt.) dental resin systems with an incremental series of concentrations. Physicochemical properties, anti-bacterial adhesion effect, and protein adsorption were tested. The results showed that SMAs had no influence on the double bond conversion of dental resin, and could decrease volumetric shrinkage of dental resin. Because of the increased hydrophobicity and reduced surface free energy, SMAs containing cured resin had resistance to mucin adsorption and anti-adhesion effect against *S. mutans*. However, flexural properties, water sorption and solubility of dental resin were impaired after introducing SMAs. Therefore, further research should be undertaken to improve these properties by utilizing appropriate inorganic fillers.

Keywords Dental resin · Anti-adhesion · *S. mutans* · Mucin adsorption · Physicochemical properties

1 Introduction

Dental resin composites (DRCs), which consist of methacrylate-based resin matrix and silanized inorganic fillers, have been widely used as restorative materials in dentistry due to properties such as easy handling and desirable esthetics [1]. However, compared with other restorative materials such as silver amalgam and glass ionomer cement, DRCs can accumulate more biofilm on the surface because of lacking inherent antibacterial activity [2–4], leading to a higher possibility of secondary caries, and secondary caries is considered to be one of the main reasons for clinical DRCs restoration failure in the long term [5–7]. Therefore, the reduction of biofilm formation on the surface of DRCs plays an important role in the long-term success rate of restoration.

Besides the characteristics of fillers, the properties of DRCs are mainly influenced by the monomeric composition of resin matrix [8]. For the purpose of achieving long-term biofilm inhibition, several methacrylate monomers with antibacterial groups such as quaternary ammonium have been synthesized and incorporated into dental resins as polymerizable antibacterial agents [9–11]. These agents immobilize antibacterial groups into polymeric network by covalent bonds, and thus could endow dental resins with long-last antibacterial activity [12].

Nevertheless, immobilizable antibacterial groups work only when bacteria are in contact with them, and acquired pellicle forms on the surface of DRCs which forbids contact between antibacterial groups and bacteria, thus leading to a reduction in antibacterial efficiency of the polymerizable antibacterial agents [13, 14]. The acquired pellicle is a thin protein layer formed by the absorbed biological components such as salivary proteins on DRCs surfaces [15, 16], thus a protein-repellent monomer, 2-methacryloyloxyethyl

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phosphorylcholine (MPC), was introduced into resin matrix to inhibit the formation of acquired pellicle [13–16]. Cao et al. [14] revealed that dental resin both with MPC and quaternary ammonium dimethylaminohexadecy methacrylate (DMAHDM) had stronger antibacterial effects than using DMAHDM and MPC alone.

As a reversable adhesion, bacterial adhesion is considered to be the most important step in biofilm formation [17], so modifying DRCs to be anti-adhesion against bacteria should also be an effective way to inhibit biofilm formation. In recent years, bacterial anti-adhesion coating bearing different chemical components, such as MPC and polyethylene glycol have applied onto the surface of dental materials [18, 19]. However, bacterial anti-adhesion coating might be invalidated after abrasion. Thus, it is better to modify the entire materials to be bacterial anti-adhesion.

Adhesion capabilities of bacteria have been demonstrated in conjunction with the surface physicochemical properties of biomaterials and bacterial [20–22]. It was reported that materials with low surface free energy accumulated less bacteria with high surface free energy, whereas materials with high surface free energy accumulated less bacteria with low surface energy [23]. Bacteria in early plaque such as *Streptococcus sanguis*, *V. parvula*, and *S. mutans* (*S. mutans*) are all bacteria with high surface free energy [24, 25], thus DRCs with low surface free energy might have an inhibition effect on biofilm formation through reducing bacteria adherence.

In this research, two kinds of silicone methacrylates (SMA) were synthesized and incorporated into dental resin system of DRCs with the aim of reducing surface free energy, and thereby endowing entire dental resin with anti-adhesion effect against bacteria. The influence of SMA structure and concentration on physicochemical properties, anti-adhesion effect against *S. mutans* and mucin adsorption were investigated.

2 Materials and Methods

2.1 Materials

Two types of branched amino silicone (BAS) (SF1706, methoxyl terminated amino silicone with amino content of 0.46 mmol/g; SF1708, methyl terminated amino silicone with amino content of 0.8 mmol/g.) were obtained from Momentive Performance Materials Inc., USA. Isocyanatoethyl methacrylate (IEMA), camphorquinone (CQ), and Bradford solution were purchased from the Tokyo Chemical Industry Co., Ltd., Japan. 2,2-bis[4- (2-hydroxy-3-methacryloxy-propoxy)- phenyl]propane (Bis-GMA), triethyleneglycol dimethacrylate (TEGDMA), and 2-(N,N-dimethylamino)ethyl methacrylate (DMAEMA) were purchased from Sigma-Aldrich Co., USA. Mucin from bovine submaxillary was purchased from Hefei Biomei Biotechonolgy Co., Ltd., China.

2.2 Synthesis of Silicone Methacrylates (SMA)

The synthesis route for target compounds was shown in Fig. 1. A mixture of 30 g BAS, IEMA (amount was based on the amino content of different BAS), and 50 mL pre-dried acetone was added into a glass flask and stirred at room temperature. The reaction was continued until the infrared absorbance peak of -NCO group (2270 cm-1) vanished in the FT-IR (Vector 33 Model Fourier Transform Infrared Instrument, Bruker Co., Germany) spectra of the sample that was taken from the reaction system. The SMA was obtained after removing the acetone by distillation under vacuum. The FT-IR and ^{1}H-NMR (nuclear magnetic resonance instrument, Avance AV 600 MHz, Bruker, Switzerland) spectra of SMA were taken to confirm the structure.

2.2.1 Methyl terminated silicone methacrylate (SMA-ME).

FT-IR: $\nu(cm^{-1})$ 3312, 2964, 2908, 2835, 1724, 1635, 1261, 1100, 1026, 853, 804, 702. ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 6.10–6.00 [2H, $2C\underline{H}_2$ = $C(CH_3)$- trans], 5.54–5.44 [2H, $2C\underline{H}_2$ = C(CH3)- cis], 4.24–4.06 [4H, 2-$NHCH_2C\underline{H}_2O$-], 3.48–3.32 [27H, $9C\underline{H}_3OSi$-], 3.30–2.99 [8H, 4-$NHC\underline{H}_2CH_2$-], 1.86 [6H, $2CH_2$ = $C(C\underline{H}_3)$-], 0.01–0.1 [-$Si(CH_3)_2$-].

2.2.2 Methoxyl terminated silicone methacrylate (SMA-MEO).

FT-IR: $\nu(cm^{-1})$ 3312, 2966, 2904, 2835, 1722, 1637, 1261, 1097, 1020, 853, 802, 702. ^{1}H-NMR ($CDCl_3$, 600MHZ): δ 6.10–6.00 [2H, $2C\underline{H}_2$ = $C(CH_3)$- trans], 5.54–5.44 [2H, $2C\underline{H}_2$ = $C(CH_3)$- cis], 4.23–4.07 [4H,2-$NHCH_2C\underline{H}_2O$-], 3.48–3.01 [8H,4-$NHC\underline{H}_2CH_2$-], 1.86 [6H, $2CH_2$ = $C(C\underline{H}_3)$-], 0.01–0.1 [-$Si(CH_3)_2$-].

2.3 Preparation of Experimental Dental Resin Systems

SMA containing dental resin systems were prepared according to the formulations shown in Table 1. A dental resin without SMA was prepared as a control.

2.4 Measurement of Degree of Double Bond Conversion

The degree of double bond conversion (DC) was determined by using an FT-IR spectrometer with an attenuated total reflectance (ATR) accessory. The ATR spectra were collected at a resolution of 4 cm^{-1} through 4 scans. All the samples were tested in a mold with a thickness of 2.0 mm and a diameter of 6.0 mm. First, the spectrum of the unpolymerized sample was

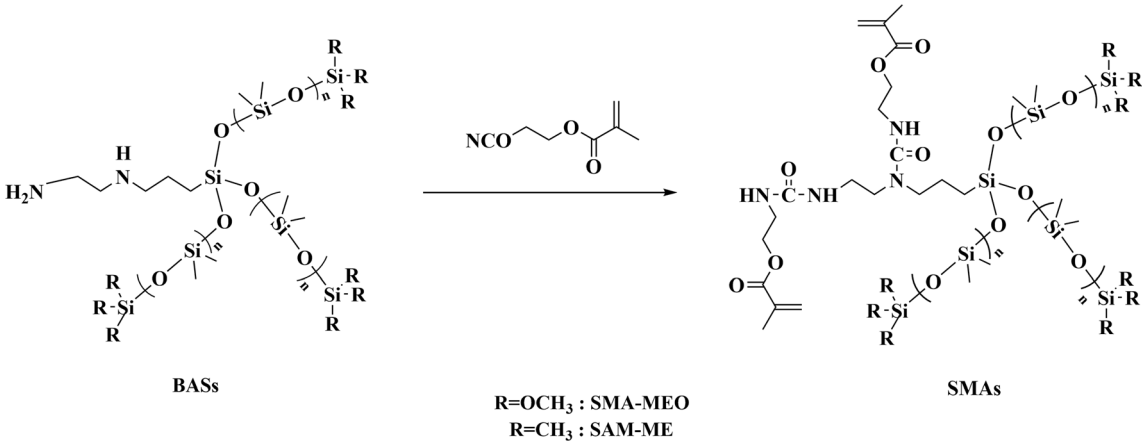

Fig. 1 Synthesis route of SMAs

measured. Then, the sample was irradiated with a visible light-curing unit (X-Cure, λ = 385–515 nm, I ~ 1000 mWcm^{-2}, Woodpecker Medical Instrument Co., Ltd., China) for 40s at room temperature. Finally, the spectrum of the polymerized sample was recorded.

In order to calculate the percentage of reacted vinyl, the absorbance intensities of the methacrylate C=C absorbance peak at 1636 cm^{-1}, which were decreased after being irradiated, and the absorption peak of phenyl ring at 1608 cm^{-1} was taken as the internal standard peak. DC was calculated from the percentage of change in the normalized methacrylate C=C absorbance intensity at 1608 cm^{-1} by using the following equation:

$$DC = \left[1 - \frac{\left(A_{C=C}/A_{ph}\right)_{40}}{\left(A_{C=C}/A_{ph}\right)_{0}}\right] \times 100\% \quad (1)$$

where $A_{C=C}$ and A_{ph} are the absorption intensities of methacrylate C=C at 1636 cm^{-1} and phenyl ring at 1608 cm^{-1}, respectively. The equation $(A_{C=C}/A_{ph})_{40}$ and $(A_{C=C}/A_{ph})_0$ refer to the normalized absorbance of the functional group irradiated for 40s and 0 s, respectively. Three replicates (n = 3) were performed for the measurement of every resin system.

2.5 Measurement of Volumetric Shrinkage

The volumetric shrinkage was determined according ISO 17304:2013(E). The specimens' densities were measured to determine volumetric shrinkage in accordance with the buoyancy method (Archimedes' principle) by using an analytical balance (FA1104J, Shunyuhengping Scientific Instrument Int., Shanghai, China) with a density test kit. The weight of the specimen was measured in air and water respectively, and the density of the samples was calculated by the following formula:

$$\rho = \frac{M_1 \times \rho_0}{M_1 - M_2} \quad (2)$$

where ρ is the individual density of the sample, M_1 is mass of the sample in air, M_2 is the mass of the sample in water medium, ρ_0 is the density of the water medium at the temperature at the respective time of measurement.

one gram of unpolymerized dental resin was used to measure the density before polymerization, and disk-shaped cured resin sized 1.0 mm × Φ15 mm was used to measure the density after polymerization. The density of cured resin was measured 24 h later after light curing.

Table 1 Composition of dental resin system with SMA-ME or SMA-MEO

Resin system	Components (wt.%)					
	SMA-ME	SMA-MEO	Bis-GMA	TEGDMA	CQ	DMAEMA
SMA-ME-10%	10	0	44.3	44.3	0.7	0.7
SMA-ME-20%	20	0	39.3	39.3	0.7	0.7
SMA-ME-30%	30	0	34.3	34.3	0.7	0.7
SMA-MEO-10%	0	10	44.3	44.3	0.7	0.7
SMA-MEO-20%	0	20	39.3	39.3	0.7	0.7
SMA-MEO-30%	0	30	34.3	34.3	0.7	0.7

Then, volumetric shrinkage (VS) was calculated according to the following formula:

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

Where ρ_u is the density of the unpolymerized specimen, ρ_c refers to the density of the polymerized specimen. Six replicates (n = 6) were performed for the measurement of each resin system before and after polymerization, respectively.

2.6 Three-Point Bending Test

Bar-shaped specimens sized 2 mm × 2 mm × 25 mm were made in half-split stainless steel moulds between transparent Mylar sheets. The resin was cured using a visible light-curing unit as mentioned above for 40 s in five separate overlapping portions from one side of the mould. Sixteen specimens were prepared for every dental resin system and divided into two groups randomly. One group was kept dry in a desiccator for 1 week before testing, and the other group was immersed in distilled water at 37 °C for one week before testing. The three-point bending test (span = 20 mm) was carried out on a universal testing machine (AGS-10KN, Shimadzu Co., Japan) at a cross-head speed of 1.0 mm/min to evaluate the flexural strength (FS) and modulus (FM) according to ISO 4049:2019(E). The values of FS and FM were directly obtained from the software of the universal testing machine.

2.7 Measurement of Water Sorption, Solubility, and Diffusion Coefficient

The resin was filled into a 1.0 mm height cylindrical stainless steel mold with a diameter of 15.0 mm followed by a transparent Mylar sheet. The resin was light cured using a visible light-curing unit as mentioned above for 40 s in twelve separate overlapping portions from one side of the mould. Five specimens (n = 5) were prepared for every dental resin system. The initial mass (M_1) of every specimen was measured using an analytical balance with an accuracy of 0.1 mg. After that, the specimens were immersed in 30 ml of distilled water at 37 °C. At fixed time intervals, the specimens were taken out, wiped to remove the excess water on the surface, and weighed to get mass (M_t). The equilibrium mass of specimens after 16 days of water immersion was defined as M_2. Finally, the specimens were dried in a vacuum oven at 60 °C until getting equilibrium mass (M_3). Water sorption (WS) and solubility (SL) were calculated by the following formula.

$$WS = \frac{M_2 - M_3}{M_3} \times 100\% \quad (4)$$

$$SL = \frac{M_1 - M_3}{M_1} \times 100\% \quad (5)$$

The water absorption and solubility of resin-based composite have been proven as being diffusion-controlled [23]. In a relatively short term (1, 3, 6 and 9 h) immersion, when $\Delta M_t / \Delta M_f \leq 0.5$ ($\Delta M_t = M_t - M_1$, $\Delta M_f = M_2 - M_1$), the diffusion coefficient of water (DCW) in resin can be calculated using Stefan's approximation [26, 27]:

$$\frac{\Delta M_t}{\Delta M_f} = \frac{4}{L}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \quad (6)$$

2.8 Measurement of Contact Angle and Surface Free Energy (SFE)

The resin was filled into a 1.0 mm height cylindrical stainless steel mold with a diameter of 10.0 mm followed by a transparent Mylar sheet. The resin was light cured using a visible light-curing unit as mentioned above for 40 s in four separate overlapping portions. Every specimen was polished using wet silicon carbide grinding paper (FEPA #4000) in a grinding machine using water as lubricant (MPD-1, Guangxiangzhiyang Instrument Ltd., Shanghai, China) to obtain a smooth surface. Subsequently, the polished specimens were ultrasonically cleaned in distilled water for 30 min to remove possible embedded grinding material. After that, specimens were dried in a desiccator before using. Six specimens (n = 6) were prepared for every dental resin system.

Distilled water and diiodomethane were used as testing liquids for surface free energy calculation. A 2 μL droplet of liquid was placed on the surface of every specimen for 20 s, and equilibrium contact angle was measured at room temperature using a contact angle meter (SDC-100, Dongguan SINDIN Precision Instrument Co., Ltd., Dongguan, China). The surface free energy was calculated using the Owens-Wendt approach and the result was directly obtained from the software company with the contact angle meter.

2.9 Assessment of Mucin Adsorption

The specimens for the mucin adsorption test were prepared with the same protocol as the specimens for contact angle measurement. Six specimens (n = 6) were prepared for every dental resin system. The amount of adsorbed mucin was determined by the Bradford method [28]. Every specimen was soaked in phosphate buffered saline (PBS) for 2 h before testing, and then immersed in a tube with 1 mL mucin solution (0.4 mg/mL) for 24 h at 37 °C. After removing the specimen, 20 mL of Bradford solution was added to the mucin solution and ultrasonically dispersed for 1 min. The absorbance of the mixed solution at a wavelength of 595 nm was recorded using a UV-vis spectrophotometer (UV755B, Shanghai Yoke Instrument Co., Ltd., Shanghai, China). The concentration of mucin solution was calculated according to the following

equation:

$$y = 1538.1x, R2 = 0.9919 \quad (7)$$

where y is the concentration of mucin solution, x is the absorbance of mucin solution with the Bradford solution.

Finally, the amount of adsorbed mucin per area (AMA) was calculated by the following equation:

$$AMA = \frac{(y_b - y_a)V}{S} \quad (8)$$

where y_b and y_a is the concentration of mucin solution before and after testing, respectively. V is the volume of tested mucin solution. S is the surface area of the specimen.

2.10 Assessment of Bacterial Adhesion

Bacterial Culture *S. mutans* (*S. mutans*, ATCC 25175) was spread on brain heart infusion (BHI) agar plates. After overnight culture at 37 °C, a single colony was collected into 15 mL centrifuge tubes with 5 mL of BHI medium and incubated under anaerobic conditions at 37 °C for 24 h. The bacterial suspension was diluted to approximately 1×10^7 CFU/mL for the bacterial adhesion assay using the McFarland Criterion.

Adhesion Assay The specimens for the bacterial adhesion test were prepared with the same protocol as the specimens for contact angle measurement. Two specimens of every dental resin system were prepared for one test, and the test was repeated in triple (totally n = 6). After being sterilized with ultraviolet rays on each side, the disc shaped specimen was placed at the bottom of 24-well cell culture plate, which was then with 1 mL of bacteria suspension. The covered plate was anaerobic incubated at 37 °C for 24 h. Subsequently, the sample was rinsed twice with PBS and moved to a 5 ml centrifuge tube containing 3 ml phosphate buffered saline (PBS). After sonication for 15 min and vortexing for 15 s to detach the adhered bacteria, 100 μL of diluted suspension was spread onto BHI agar and incubated at 37 °C in 5% CO_2 for 24 h. The colonies that grew on the BHI agar were counted to assess the ability of resisting bacterial adhesion. The amount of bacteria recovered from the surface of the control group was setting as 100%.

2.11 Statistical Analysis

One-way ANOVA were used to examine statistical differences between variables by employing SPSS 25.0 software (IBM SPSS Software, USA), followed by post hoc Tukey tests (at a significance level of $p = 0.05$).

3 Results

Fig. 2 and Fig. 3 were the FT-IR spectra and ^{1}H-NMR spectra of synthesized SMAs, respectively. All the spectra indicated that both SMAs synthesized as designed.

Table 2 exhibited the results of DC and VS. Compared with the control group, all SMAs containing resins had a similar DC ($p > 0.05$), and there was no significant difference in DC between SMAs containing resins ($p > 0.05$). All SMAs containing resins had lower VS than the control ($p < 0.05$), and VS had a trend of decreasing with the increase of SMAs content ($p < 0.05$). At the same mass fraction, SMA-MEO group had lower VS than the SMA-ME group ($p < 0.05$).

Figure 4 and Fig. 5 depicted FS and FM before and after water immersion. As shown in Fig. 4 and Fig. 5, no matter before or after water immersion, the FS and FM were in a trend of decreasing with the increasing of SMAs concentration in the resin system ($p < 0.05$), and in the same mass fraction, SMA-MEO containing cured resin and SMA-ME containing cured resin had similar FS and FM values ($p > 0.05$). After water immersion, the FS and FM of all cured resins decreased significantly ($p < 0.05$).

The results of WS, SL, and DCW were summarized in Table 3, and Fig. 6 shows the water sorption behavior of cured resins. Only cured resin with 10 wt.% of SMAs had comparable WS and SL as a control ($p > 0.05$), all the other SMAs containing cured resin had higher WS and SL ($p < 0.05$). All of the SMAs containing cured resin had higher DCW than the control ($p < 0.05$).

The results of contact angles and SFE were listed in Table 4. As shown in Table 4, in all cured resins, the control had lowest contact angles for both water and diiodomethane ($p < 0.05$), and highest surface free energy ($p < 0.05$). The contact angles for two liquids of SMAs containing cured resin were in a trend of increasing with the increasing of SMAs concentration, while surface free energy was in a trend of decreasing with the increasing of SMAs concentration.

The amount of adsorbed mucin and percentage of adherent bacteria compared with control are shown in Fig. 7 and Fig. 8, respectively. The amount of adsorbed mucin (Fig. 7) and adhered bacteria (Fig. 8) on the surfaces of SMAs containing cured resins were all lower than that on the surface of control ($p < 0.05$). Structure and concentration of SMAs had no influence on the amount of adsorbed mucin (Fig. 7, $p > 0.05$). The amount of adherent bacteria was in a trend of decreasing with the increasing of SMAs in cured resin.

4 Discussion

With the aim of reducing SFE of DRCs, the strategy of this research was to prepare resin matrix which would have low SFE after polymerization, for resin matrix is the continuous

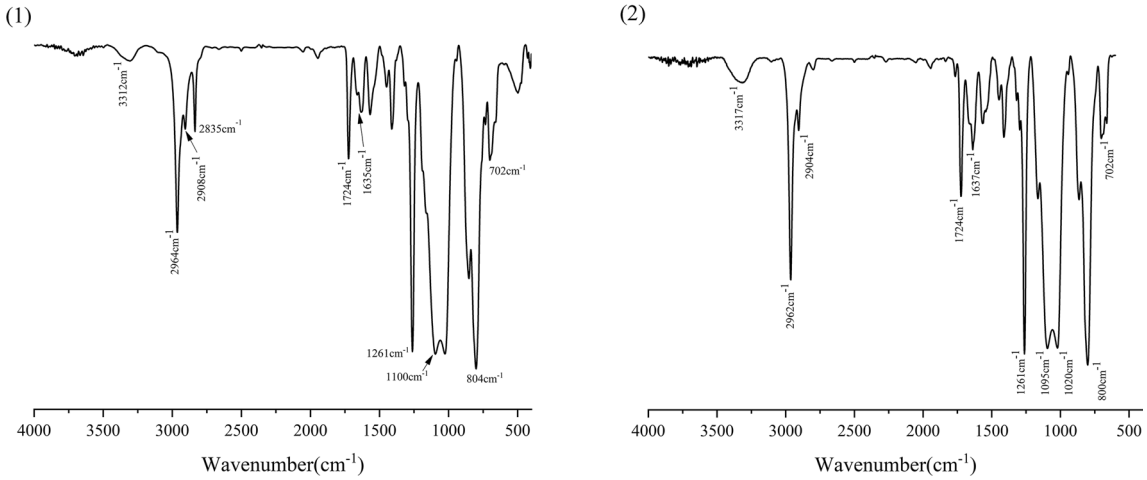

Fig. 2 FT-IR spectra of SMAs: (1) SMA-MEO; (2) SMA-ME

phase in DRCs. For this purpose, methacrylates with silicone chains were synthesized and incorporated into the commonly used resin matrix (Bis-GMA/TEGDMA), because silicone-based materials are low SFE materials that have already been used in several fields for preventing bacteria adhesion, anti-fouling, anti-graffiti, and anti-contamination [29–32].

The DC is a critical factor that determines the mechanical properties as well as other performance of methacrylate based dental materials [33]. The results of the present study indicated that the addition of SMAs had no negative effect on DC of dental resin (Table 2), both structure and concentration of SMAs had no influence on DC.

The process of polymerization of methacrylate involves the formation of covalent bonds and reduction in distance between molecules, which would inevitably cause volumetric shrinkage. The volumetric shrinkage would then lead to shrinkage stress, which could induce microleakage, marginal discoloration, postoperative sensitivity, and secondary caries in clinic, eventually causing failure of the restoration [34]. Therefore, volumetric shrinkage is a primary defect of

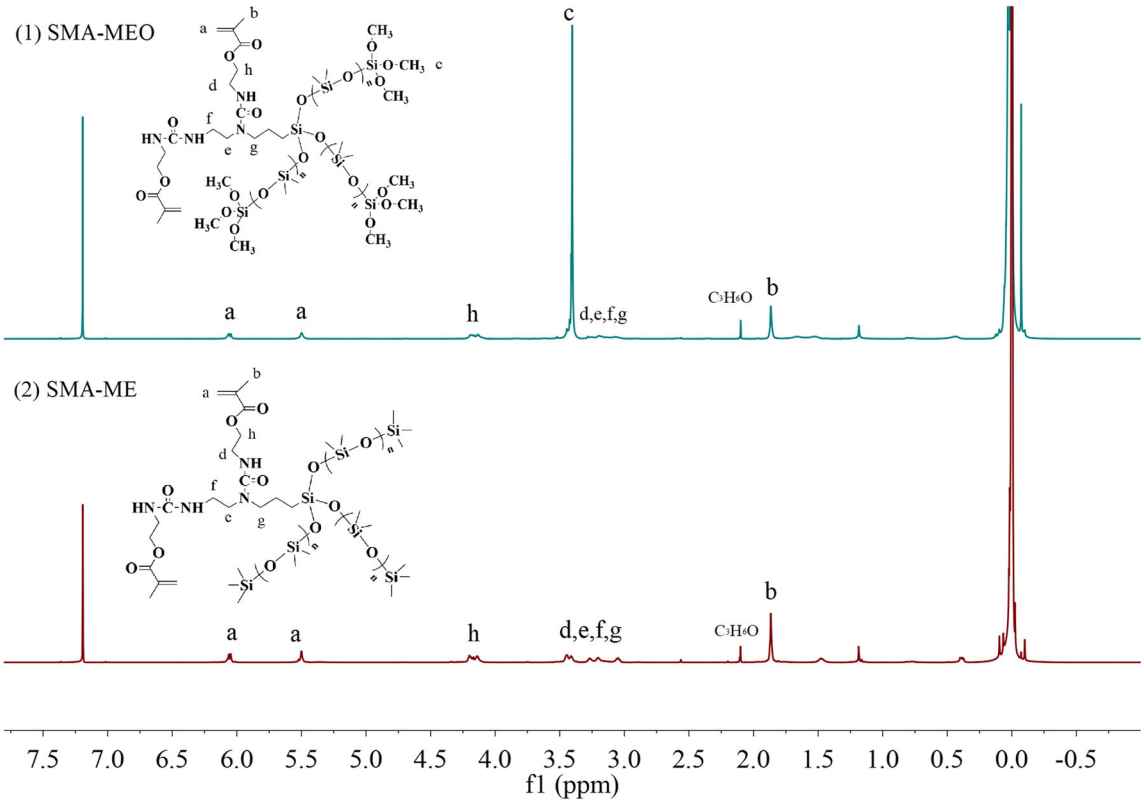

Fig. 3 ^{1}H-NMR spectra of SMAs: (1) SMA-MEO; (2) SMA-ME

Table 2 Degree of conversion (DC) and Volumetric Shrinkage (VS) of experimental dental resin system

Resin system	DC (%)	VS (%)
Control	66.5 ± 1.2^{a,A}	10.2 ± 0.3^{a,A}
SMA-MEO-10%	66.2 ± 0.9^{a}	8.1 ± 0.3^{b,*}
SMA-MEO-20%	67.2 ± 0.8^{a}	7.5 ± 0.6^{c,*}
SMA-MEO-30%	62.7 ± 1.4^{a}	6.7 ± 0.3^{d,*}
SMA-ME-10%	63.3 ± 1.9^{A}	9.1 ± 0.4^{B}
SMA-ME-20%	65.8 ± 1.5^{A}	8.8 ± 0.2^{B}
SMA-ME-30%	63.0 ± 2.9^{A}	8.2 ± 0.4^{C}

[a] The same lowercase letter indicates that there is no statistical difference between resin systems with and without SMA-MEO (p = 0.05)

[A] The same uppercase letter indicates that there is no statistical difference between resin systems with and without ME (p = 0.05)

*The asterisk refers the statistical difference between resin systems with different SMAs at the same mass ratio in resin system (p = 0.05)

methacrylate-based dental materials [35–37]. The degree of volumetric shrinkage is related to the conversion and concentration of double bonds, and studies have reported that for linear methacrylate, when one mole of C=C was converted to C-C, the corresponding volumetric shrinkage was about 22.5 cm^3 [38, 39]. Several efforts have been taken to minimize volumetric shrinkage by reducing double bond concentration while optimizing the double bond conversion [34, 39, 40]. With the same level of DC, SMAs containing dental resins had lower VS than the control (Table 2), this should be due to the molecular weight of SMAs. Comparing monomers with

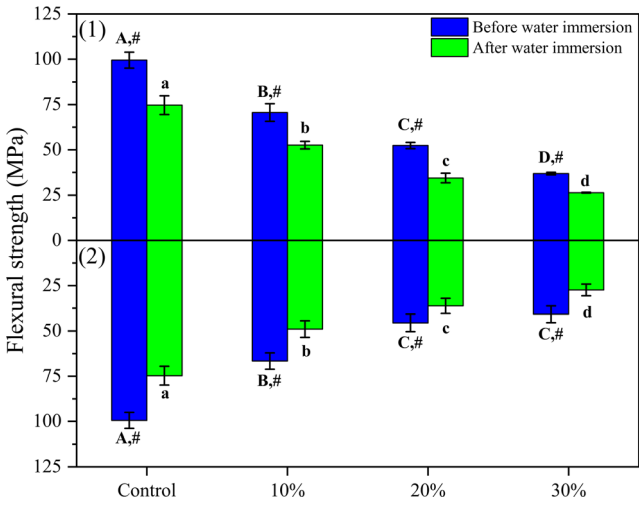

Fig. 4 (1) cured resin with SMA-MEO; (2) cured resin with SMA-ME. [A] The same uppercase letter refers to there is no statistical difference between cured resins with and without SMAs before water immersion (Tukey's test, p = 0.05). [a] The same lowercase letter refers to there is no statistical difference between cured resins with and without SMAs after water immersion (Tukey's test, p = 0.05). [#] The octothorpe indicates the statistical differences between FSs of the same cured resin before and after water immersion (Tukey's test, p = 0.05)

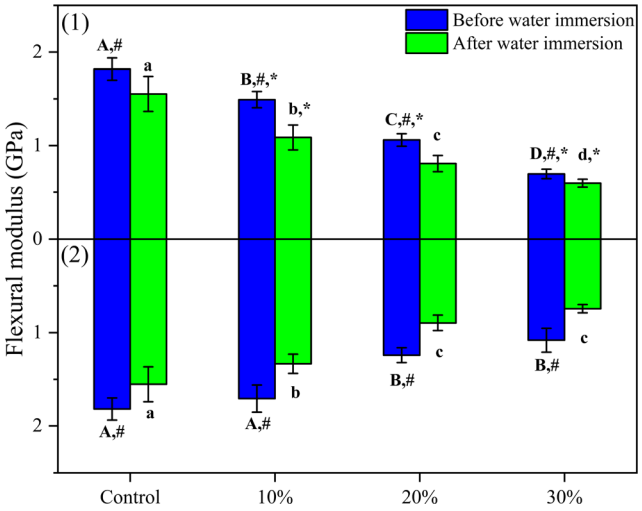

Fig. 5 (1) cured resin with SMA-MEO; (2) cured resin with SMA-ME. [A] The same uppercase letter refers to there is no statistical difference between cured resins with and without SMAs before water immersion (Tukey's test, p = 0.05). [a] The same lowercase letter refers to there is no statistical difference between cured resins with and without SMAs after water immersion (Tukey's test, p = 0.05). [#] The octothorpe indicates the statistical differences between FSs of the same cured resin before and after water immersion (Tukey's test, p = 0.05). [*] The asterisk refers to the statistical differences between cured with different SMAs at the same mass ratio in resin system (Tukey's test, p = 0.05)

the same functionality, volumetric shrinkage would decrease with the increasing of molecular weight, because high molecular weight leads to low double bond concentration [34, 40–42]. According to their amino contents, molecular weights of SMA-MEO and SMA-ME could be approximately calculated as 6832 g/mol and 4060 g/mol, respectively, which were much higher than molecular weight of Bis-GMA (512 g/mol) and TEGDMA (286 g/mol). Therefore, it also could be explained that, at the same mass fraction, why SMA-MEO containing resins had lower VS than SMA-ME containing resins.

Mechanical properties of cured resin were revealed to be associated with degree of double bond conversion and chemical structure of monomers [34, 43]. With the comparable DC, the reduction of flexural properties after adding SMAs should be due to the branched silicone chains in the structure of SMAs, which could decrease interaction between polymeric chains just like some side alkyl chains [44]. Moreover, adding SMAs into Bis-GMA/TEGDMA would decrease concentration of rigid benzene ring in a polymeric network, which could further lead to poor mechanical properties. After water immersion, the flexural properties of all cured resins were decreased because of the plasticization effect of water molecules [45]. Though mechanical properties of cured resin were reduced significantly after introducing SMAs, this phenomenon would be ameliorated after adding inorganic fillers to prepare DRCs. Because silicone chains in SMAs, especially the methoxyl terminated silicone chains in SMA-MEO, might have an effect on improving the miscibility and interface properties

Table 3 Water sorption (WS), solubility (SL), and diffusion coefficient of water (DCW) of cured resins

Resin system	WS (%)	SL (%)	DCW×10^8 ($cm^2 \cdot s^{-1}$)
Control	$4.09 \pm 0.06^{a,b,A}$	$0.73 \pm 0.09^{a,A}$	$1.49 \pm 0.10^{a,A}$
SMA-MEO-10%	3.94 ± 0.12^{a}	0.82 ± 0.11^{a}	$2.35 \pm 0.09^{b,*}$
SMA-MEO-20%	$4.15 \pm 0.04^{b,*}$	$1.38 \pm 0.08^{b,*}$	$3.14 \pm 0.21^{c,*}$
SMA-MEO-30%	$4.37 \pm 0.11^{c,*}$	$1.44 \pm 0.07^{b,*}$	$3.15 \pm 0.07^{c,*}$
SMA-ME-10%	3.97 ± 0.07^{A}	0.72 ± 0.01^{A}	1.87 ± 0.08^{B}
SMA-ME-20%	3.78 ± 0.04^{B}	1.00 ± 0.01^{B}	2.45 ± 0.19^{C}
SMA-ME-30%	3.75 ± 0.08^{B}	1.30 ± 0.05^{C}	4.44 ± 0.25^{D}

[a] The same lowercase letter indicates that there is no statistical difference between cured resins with and without SMA-MEO ($p = 0.05$)

[A] The same uppercase letter indicates that there is no statistical difference between cured resins with and without ME ($p = 0.05$)

*The asterisk refers the statistical difference between cured resins with different SMAs at the same mass ratio in resin system ($p = 0.05$)

between resin matrix and fillers. This should be proven in further study.

Compared with the control group, all SMAs containing cured resin had higher hydrophobicity (Table 4), but some of them still possessed comparable or even higher WS (Table 3). This should be attributed to the higher DCW of SMAs containing cured resin, which made the water molecules to penetrate into polymeric networks much more easily. While the higher DCW of SMAs containing cured resin was the result of increased motion of polymer chains [46], which was induced by the lower interaction between polymeric chains as mentioned above. The amount and leachability of residual monomers in cured resin determined its SL in water [47], and the amount of residual monomers is correlated with DC [48]. Though having the same DC, cured resin with more than 10 wt.% of SMAs had higher SL, since the decreased interaction between polymeric chains made the residual monomers leach out of the polymeric network easily.

The development of biofilm always starts from the initial adhesion of bacteria [20, 49, 50]. Regarding the first colonizers in biofilm, oral *streptococci* are the most prominent bacteria [49]. Among *streptococci*, *S mutans* is a main etiological factor for dental caries [51, 52], and have a greatest ability to form biofilm [53], thus *S mutans* was chosen in this work to study the anti-bacterial adhesion effect of cured resin. In addition, mucin adsorption of cured resin was also investigated in this study, because mucin is one of the main components that constitute saliva and acquired pellicle [54, 55], and has been reported that can enhance growth, biofilm formation and survival of *S mutans* [56]. Bovine submaxillary mucin was recommended as the most optimal commercially available mucin source when attempting to replicate saliva based on surface adsorption [55], so bovine submaxillary mucin was used here. The results showed in Fig. 7 and Fig. 8 indicated that SMAs could not only endow cured resin with an anti-bacterial adhesion effect, but also with resistance to mucin adsorption.

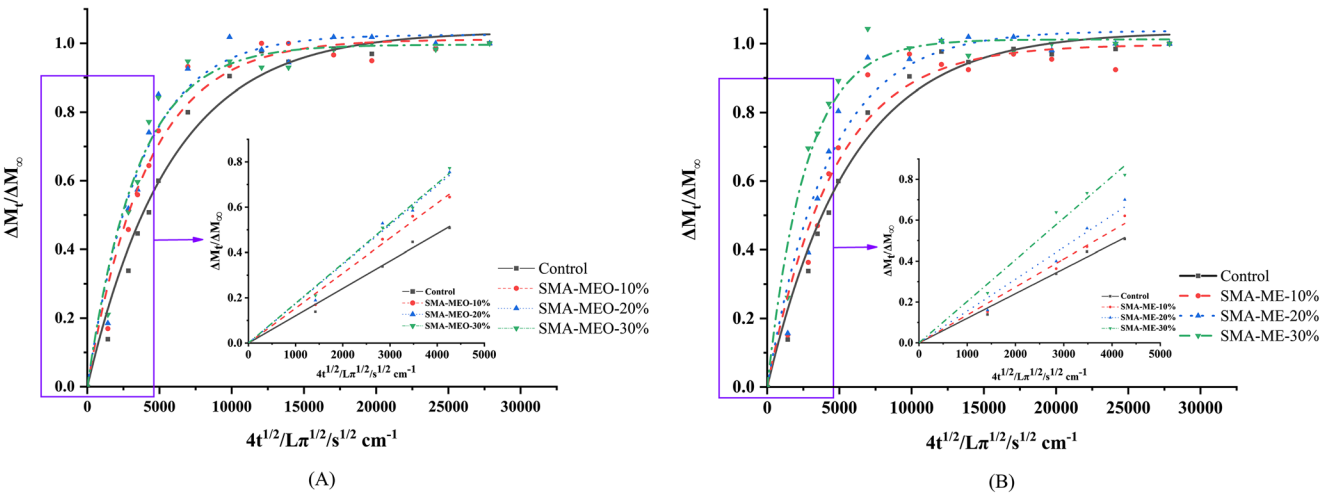

Fig. 6 Water sorption behavior of cured resins

Table 4 Contact angles and surface free energy (SFE) of cured resins

Resin system	Contact angles (°)		SFE ($mJ \cdot m^{-2}$)
	Water	Diiodomethane	
Control	$70.29 \pm 3.69^{a,A}$	$48.38 \pm 4.35^{a,A}$	$38.86 \pm 2.74^{a,A}$
SMA-MEO-10%	101.61 ± 2.29^{b}	64.70 ± 2.53^{b}	26.37 ± 1.83^{b}
SMA-MEO-20%	114.65 ± 1.53^{c}	76.97 ± 1.53^{c}	20.41 ± 1.22^{c}
SMA-MEO-30%	118.10 ± 2.74^{c}	$82.97 \pm 3.15^{d,*}$	$17.25 \pm 1.46^{d,*}$
SMA-ME-10%	100.51 ± 2.27^{B}	64.58 ± 1.66^{B}	26.20 ± 0.60^{B}
SMA-ME-20%	117.71 ± 2.48^{C}	77.40 ± 1.08^{C}	21.02 ± 0.97^{C}
SMA-ME-30%	117.31 ± 2.48^{C}	74.67 ± 1.37^{D}	22.90 ± 0.93^{C}

[a] The same lowercase letter indicates that there is no statistical difference between cured resins with and without SMA-MEO ($p = 0.05$)

[A] The same uppercase letter indicates that there is no statistical difference between cured resins with and without ME ($p = 0.05$)

*The asterisk refers the statistical difference between cured resins with different SMAs at the same mass ratio in resin system ($p = 0.05$)

It was reported that surfaces with water contact angle lower than 20° and approaching 120° exhibit a reduction in protein adsorption [29, 57]. Thus, the resistance to mucin adsorption should be mainly attributed to the increased water contact angle (Table 4) after adding SMAs. Meanwhile, the reduced surface free energy of SMAs containing cured resin (Table 4) should be the main reason of reduced adhered bacteria. According to the study of Absolom et al. [58], *S. mutans* with high surface free energy (117 mJ/m^2) [24] should adhere worse to surfaces with low surface free energy.

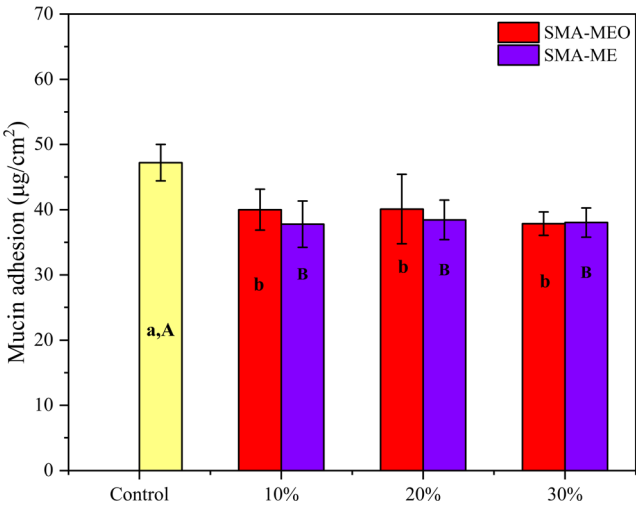

Fig. 7 The results of mucin adsorption on the surface of cured resins. [a] The same lowercase letter refers to there is no statistical difference between cured resins with and without SMA-MEO (Tukey's test, $p = 0.05$). [A] The same uppercase letter refers to there is no statistical difference between cured resins with and without SMA-ME (Tukey's test, $p = 0.05$). [*] The asterisk refers to the statistical differences between cured with different SMAs at the same mass ratio in resin system (Tukey's test, $p = 0.05$)

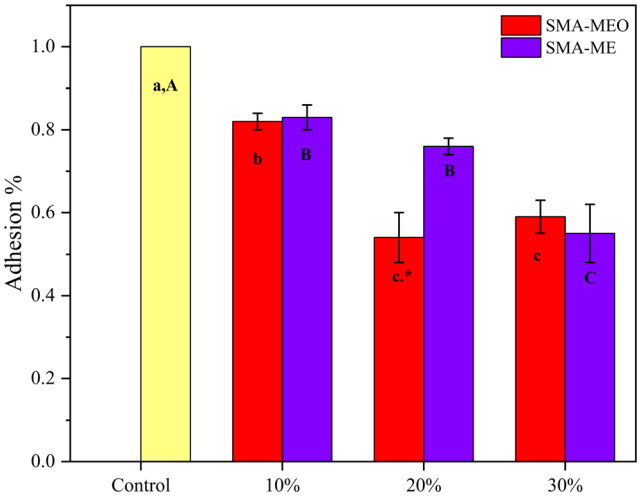

Fig. 8 The results of anti-bacterial adhesion test. [a] The same lowercase letter refers to there is no statistical difference between cured resins with and without SMA-MEO (Tukey's test, $p = 0.05$). [A] The same uppercase letter refers to there is no statistical difference between cured resins with and without SMA-ME (Tukey's test, $p = 0.05$). [*] The asterisk refers to the statistical differences between cured with different SMAs at the same mass ratio in resin system (Tukey's test, $p = 0.05$)

With the purpose of using SMAs containing resin as resin matrix of RDCs, besides improving mechanical properties, several studies should be carried out in the future, such as evaluating biocompatibility and bonding efficiency to tooth of SMAs containing DRCs.

5 Conclusion

It could be concluded that the synthesized silicone methacrylates SMAs could reduce volumetric shrinkage of dental resin, endow cured resin with an anti-bacterial adhesion effect and resistance to protein adsorption. However, the reduced flexural properties, increased water sorption and solubility after adding SMAs should be improved through incorporating suitable inorganic fillers in further study.

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Xiangya Huang: Methodology, Writing – Review & Editing.
Fang Liu: Writing – Review & Editing.
Sui Mai: Supervision, Writing – Review & Edition.
Jingwei He: Conceptualization, Supervision, Writing – Review & Edition.

Data Availability Not applicable.

Declarations

Ethics Approval Not applicable.

Consent to Participate Not applicable.

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