

Effect of immersion in various media on the sorption, solubility, elution of unreacted monomers, and flexural properties of two model dental composite compositions

Yujie Zhang · Jingwei Xu

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Abstract Immersion in various media has different effect on the properties of dental composites, such as sorption, solubility, elution of unreacted monomers, flexural strength, and flexural elastic modulus. In the present work, the effect of immersion in various media and the relationship between the variation of these properties and the components of dental composite were investigated. Two model dental composites were immersed in three different media—distilled water, artificial saliva, and ethanol/water, respectively, for a certain time. Their sorption, solubility, flexural strength, and flexural elastic modulus were tested according to the international standard. Elution of unreacted monomers was analyzed by using high performance liquid chromatography (HPLC) and the surface morphology of samples after immersion was observed using scanning electron microscope (SEM). The results showed that the effect on properties depended on the immersion media where ethanol/water had the most significant effect and these properties were related to the components of dental composite.

1 Introduction

Dental composites generally consist of resin matrixes, inorganic fillers, and coupling agent. As dental restorative

materials, dental composites are becoming more and more popular because of their strength, rapid polymerization, and aesthetic appearance. However, dental composites have water sorption in wet oral environment, and some negative effect occurs along with this sorption, such as softening of the resin matrixes, release of some substances (unreacted monomers, impurities of monomers, additives, degradation products [1–5]), and leaching of the filler ions [6–7]. These released substances may stimulate the growth of bacteria around the restoration, promote allergic reaction, lead to secondary caries [5, 8–11], and depress the biocompatibility of dental composites [12]. It has been suggested that the long-term exposure to these substances may damage our health [13]. Water sorption can also accelerate the degradation of dental composites [4, 14] and do harm to the physical/mechanical properties such as tensile strength, flexural strength, flexural elastic modulus, and wear resistance [4, 11, 15–19], which occur essentially due to the following two reasons: first, hydrolytic breakdown of the bond between silane and filler particles and filler–resin matrix debonding ultimately; second, softening of dental resins through the plasticizing action of water [20]. However, moderate water sorption has a positive side effect: relieving some of the internal stresses created during polymerization shrinkage [7], compensating of polymerization shrinkage [21, 22], and improving marginal sealing [23, 24].

Bisphenol A glycol dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA) are widely used as monomers of dental composites. The selection of monomers strongly influences the polymerization, reactivity, mechanical properties, and water sorption [5, 25].

The qualitative and quantitative methods for the analysis of unreacted monomers and degradation products include gas chromatography (GC) [26], high performance liquid

Y. Zhang · J. Xu (✉)
Changchun Institute of Applied Chemistry, Chinese Academy
of Sciences, Changchun 130022, P.R. China
e-mail: jwxu@ciac.jl.cn

Y. Zhang
Graduate University of Chinese Academy of Sciences,
Beijing 100039, P.R. China

chromatography (HPLC) [5, 26–32], gas chromatography/mass spectrometry [33–36], and electrospray ionization/mass spectrometry [5, 13], in which HPLC is more often used.

The effect on physical/mechanical properties and the results of toxicity testing of dental composites are variable with different immersion media [37]. These immersion media include culture medium, distilled water, artificial saliva and solution of ethanol/water [4–5, 37, 38], in which the solution of 75% ethanol/water recommended by US FDA was used as a food/oral simulating liquid.

The effect of some immersion media on the properties, such as water sorption, solubility, flexural strength, flexural elastic modulus, and the elution of unreacted monomers were individually studied. A systematic study about the effect of immersion media on properties of dental composite, however, is still necessary. The purpose of this article was: (1) to study the effect of different immersion media on these properties systematically; (2) to investigate the relationship between the variation of these properties and the components of dental composite; and (3) to observe the morphology of dental composite after immersion.

2 Materials and methods

2.1 Materials

Bisphenol-A-glycidyl dimethacrylate (BisGMA), triethyleneglycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA), camphorquinone (CQ), and ethyl 4-dimethylaminobenzoate (EDMAB) were purchased from Aldrich without further purification and their structures are shown in Fig. 1. Six percent silane-treated BaAlBSiO₄ glass was from Schott, Germany (mean particle size 0.7 μm, Lot# Sil 1529).

The compositions of two model dental composites were shown in Table 1.

2.2 Immersion media preparation

Three different immersion media used in this study were: (1) distilled water, (2) artificial saliva, and (3) 75:25 v/v ethanol/water solutions. The artificial saliva was an aqueous solution prepared with 0.4 g/l NaCl, 0.4 g/l KCl, 0.795 g/l CaCl₂·2H₂O, 0.69 g/l NaH₂PO₄·H₂O, 0.005 g/l Na₂S·9H₂O, and 1.0 g/l CO(NH₂)₂ [2].

2.3 Sorption and solubility

A specimen disc with 15 mm in diameter and 1.0 mm in thickness was fabricated in a stainless steel mold between

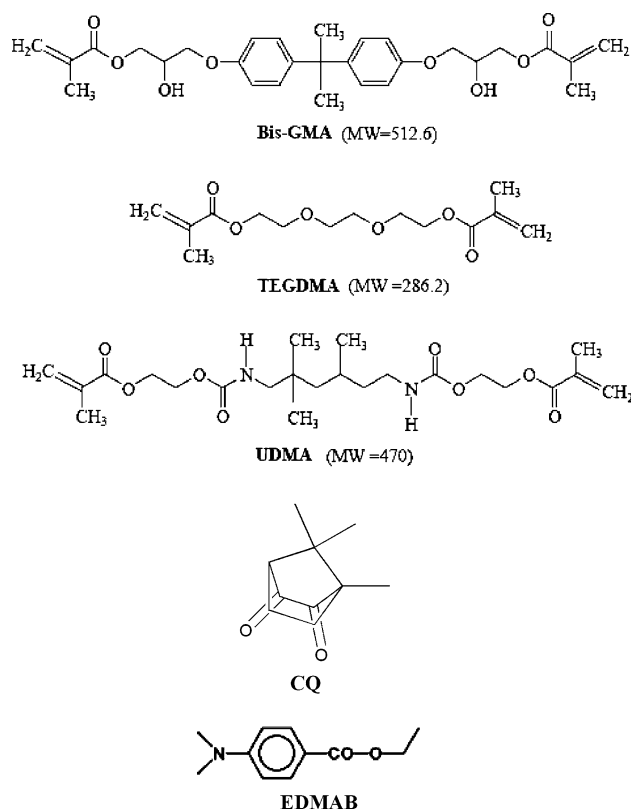


Fig. 1 Structure of materials used in the study

Table 1 Compositions of two model dental composites in experiment

Component	Dental composite 1 (wt.%)	Dental composite 2 (wt.%)
BisGMA	17.25	17.25
TEGDMA	7.5	3.75
UDMA	0	3.75
CQ	0.125	0.125
EDMAB	0.125	0.125
Silane-treated BaAlBSiO ₄	75	75

two glass slides covered with polyethylene film. It was light-cured for 100 s on each side with the pulse model of Astralis 7 dental photo curing unit (Vivadent Company); during the curing an overlapping procedure was used. Nine specimen discs were prepared for each model dental composite. All specimens were placed in a desiccator containing freshly dried silica gel at 37°C for 48 h. Then they were stored in a desiccator at 23°C for 1 h and weighed with a calibrated electronic balance (a resolution of 0.1 mg). This drying cycle was repeated until a constant mass (m_1) for each disc was attained. Three groups (each group contains three discs) were randomly distributed among the three different immersion media at 37°C for

storing, and each disc was periodically weighed until a constant weight (m_2) was attained. Then all the specimens were removed from the immersion media and replaced in the desiccator at 37°C until a constant weight achieved. They were subsequently dried at 60°C for 24 h and then reweighed for the last time (m_3).

Water sorption (W_{sp}) and solubility (W_{sl}) were calculated using the following equations, respectively:

$$W_{sp} (\%) = (m_2 - m_1)/m_1$$

$$W_{sl} (\%) = (m_1 - m_3)/m_1$$

2.4 Release of dental monomers

Three groups (each group contains three discs) of each model dental composite fabricated using the same method mentioned above were, respectively, immersed in the three media in the vials that contain 10 ml media solution at 37°C for a month. Solution samples taken from sealed vials were analyzed at predefined time intervals: 3, 6 and 24 h, 4, 7 and 30 days by Waters 600E HPLC (Milford, MA, USA) with a Symmetry Columns (C18, 5.0 μ m, 4.6 mm \times 150 mm) and Waters 2487 Dual λ Absorbance UV Detector. CH₃CN 70%/H₂O 30% was taken as the mobile phase. Two hundred and ten nanometers was used as the detection wavelength. The flow speed was 1 ml/min and 5 μ l was injected at room temperature each time.

The standard solutions of BisGMA, UDMA, and TEGDMA in methanol were made to identify and quantify the monomers released into different immersion media.

2.5 Flexural strength and flexural elastic modulus

A three-point bending test was used to evaluate the flexural strength and the flexural elastic modulus of the specimens according to the international standard [39]. The specimen (25 mm \times 2 mm \times 2 mm) was fabricated in a stainless steel mold between two glass slides covered with polyethylene film. It was light-cured for 80 s on each side with the pulse model of Astralis 7; during the curing an overlapping procedure was used. Sixty specimens were prepared for each model dental composite and three groups (20 samples as a group) were placed in three different immersion media at 37°C, respectively. Flexural strength and flexural elastic modulus of specimens were determined, respectively, at 24 h and 2 weeks storing time by using universal testing machine (Instron 1121, UK) at a crosshead speed of 0.5 mm/min with 20 mm between the two supports. Half specimens were used for each test.

2.6 Statistical analysis

The results were analyzed and compared by using one-way ANOVA with TUKEY's test at the significance level of 0.05.

2.7 Scanning electron microscope

XL30 FEG scanning electron microscope (SEM) was used to analyze the surface morphology of the samples that were immersed in different media for a month. A section of the sample was mounted on an aluminum stub and sputter-coated with gold before examination. SEM photomicrographs were obtained with an accelerating voltage of 20 kV.

3 Results and discussion

3.1 Sorption and solubility

Sorption and solubility of dental composites are affected by many factors, for example, the hydrophilicity of the polymers and cross-linking density of the network [33]. Relationships between sorption of two model dental composites and time in three different immersion media over 42 days are represented in Figs. 2 and 3, respectively. The values of sorption and solubility are given in Table 2.

The specimens immersed in distilled water and artificial saliva showed a similar behavior. In ethanol/water, more time was needed to reach the maximum sorption and then sorption began to decrease, which maybe due to the continual release of unreacted monomers and inorganic fillers. Moreover, the maximum sorption value in ethanol/water is

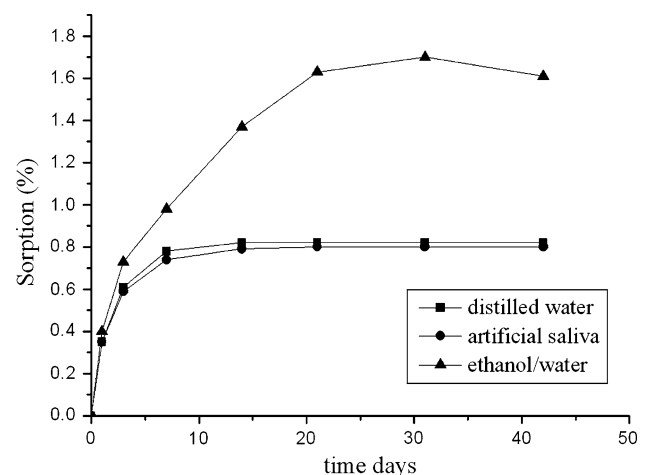


Fig. 2 Sorption values of dental composite 1 in three different immersion media over 42 days

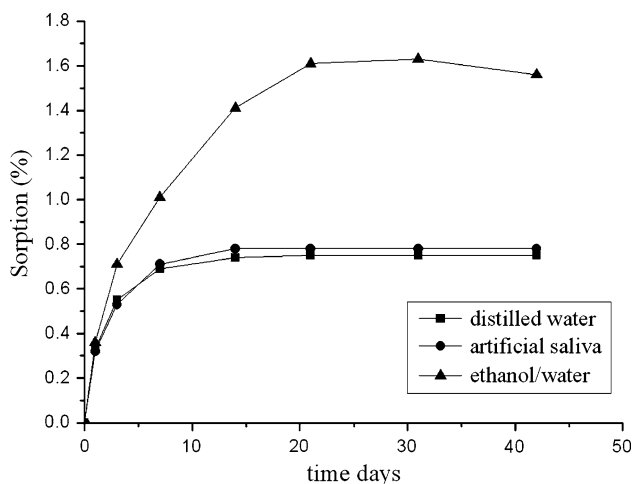


Fig. 3 Sorption values of dental composite 2 in three different immersion media over 42 days

much higher than those in distilled water and artificial saliva, which should be due to the easier penetration of ethanol into the resin matrix. The sorption values of dental composite 1 are a little higher than those of dental composite 2 in three immersion media because of the higher hydrophilicity of TEGDMA. Solubility values of dental composite 2 are higher than those of 1, which is mainly due to lower degree of conversion.

The highest solubility values of the two model dental composites are in ethanol/water and the solubility values in artificial saliva are a little higher than those in distilled water, which are consistent with other studies [40]. When ethanol/water was used as immersion media, more

components were eluted and the air voids in dental composites formed, which may lead to acceleration of solubility [36].

3.2 Release of dental monomers

TEGDMA, UDMA, and BisGMA were eluted in turn under the experimental conditions with the retention time at 4.6, 5.5 and, 6.4 min, respectively (Fig. 4). The quantification of the eluted monomers is based on integration of all peaks simultaneously and three standard curves of peak area versus monomer concentration of the three monomers are shown in Fig. 5.

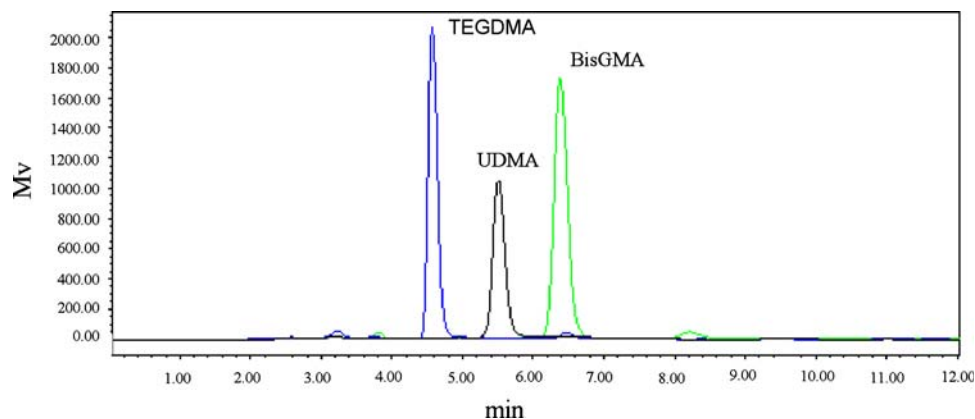
The amounts of eluted monomers from the two model dental composites in three immersion media at different time are shown in Tables 3 and 4, respectively. The amount of eluted monomers in ethanol/water is the highest, second in distilled water and third in artificial saliva for both dental composites. It is known that BisGMA, TEGDMA, and UDMA can be dissolved in ethanol. Ethanol penetrated the resin matrix and swelled the polymer network, which promoted the release of unreacted monomers.

Normally the amount of eluted monomers increases with time. Some abnormal behavior, however, was observed. The amounts of eluted monomers showed no rule in both distilled water and artificial saliva, for example, the amount of eluted Bis-GMA from dental composite 1 increased with time and that of eluted TEGDMA increased first and decreased after with time; the change of the amount of eluted Bis-GMA from dental composite 2 is the same as

Table 2 Composites: sorption and solubility in three different immersion media

	Dental composite 1 distilled water	Dental composite 1 artificial saliva	Dental composite 1 ethanol/water	Dental composite 2 distilled water	Dental composite 2 artificial saliva	Dental composite 2 ethanol/water
Sorption (%)	0.82 (0.04)	0.8 (0.03)	1.7 (0.06)	0.75 (0.08)	0.78 (0.05)	1.63 (0.04)
Solubility (%)	0.08 (0.02)	0.14 (0.03)	0.28 (0.07)	0.08 (0.03)	0.15 (0.04)	0.31 (0.09)

Fig. 4 The retention time of HPLC peaks of TEGDMA, UDMA, BisGMA under the experimental conditions



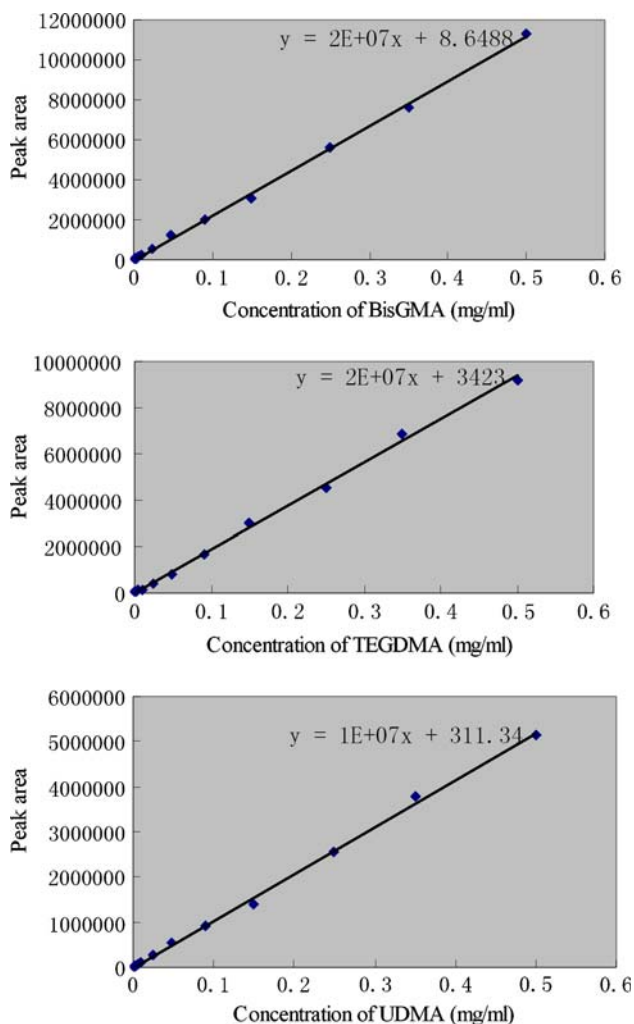


Fig. 5 Standard curves of peak area versus monomer concentration for the three monomers

that from 1; the amount of eluted TEGDMA from dental composite 2 decreased with time in distilled water and increased with time in artificial saliva, more strangely, after about 7 days the eluted monomers in distilled water and artificial saliva could not be detected by HPLC, which may result from the hydrolyzation of the monomers by water. UDMA disappeared in 6 h, which suggested that the hydrolysis rate of UDMA should be much higher than those of Bis-GMA and TEGDMA. All eluted monomers, however, were stable in ethanol/water, the reason is not clear.

When TEGDMA in dental composite 1 was partly replaced by UDMA in 2; the viscosity of the resin matrix increased, which led to lower degree of conversion and more unreacted monomers in dental composite 2. So more eluted monomers were found in the solution of dental composite 2. In ethanol/water, the amount of eluted Bis-GMA from dental composite 2 is twice that from 1. Besides the lower degree of conversion, the other reason should be

Table 3 Mean cumulative release of monomers from dental composite 1 in three different immersion media (wt./wt.-%)

		Bis-GMA	TEGDMA
Distilled water	3 h	0.0016 (0)	0.0132 (0.0031)
	6 h	0.0020 (0)	0.0151 (0.0021)
	24 h	0.0021 (0)	0.0159 (0.0017)
	4 days	0.0020 (0)	0.0160 (0.0032)
	7 days	–	0.0058 (0.0015)
	30 days	–	–
Artificial saliva	3 h	0.0012 (0)	0.0083 (0.0019)
	6 h	0.0014 (0)	0.0098 (0.0013)
	24 h	0.0018 (0)	0.0101 (0.0021)
	4 days	0.0023 (0)	0.0059 (0.0009)
	7 days	–	–
	30 days	–	–
Ethanol/water	3 h	0.0512 (0.0026)	0.0205 (0.0034)
	6 h	0.0616 (0.0031)	0.0227 (0.0027)
	24 h	0.0813 (0.0042)	0.0261 (0.0019)
	4 days	0.1096 (0.0053)	0.0312 (0.0038)
	7 days	0.1205 (0.0082)	0.0327 (0.0045)
	30 days	0.1806 (0.0102)	0.0422 (0.0052)

that lower density network [11] of dental composite 2 benefited the diffusion of ethanol and then led to more eluted monomers.

With the same amount of UDMA and TEGDMA in dental composite 2, the amount of eluted TEGDMA was lower than that of UDMA in ethanol/water, which may mean that more unreacted UDMA existed in dental composite 2.

For the two model dental composites, the amounts of eluted TEGDMA in distilled water and artificial saliva are higher than that of BisGMA. However, the case is reverse in ethanol/water. The possible reason is that the solubility of BisGMA in organic solvent is higher than that in water or saline solution.

3.3 Flexural strength and flexural elastic modulus

The flexural strength and flexural elastic modulus values of the two model dental composites (Table 5) have no difference in the three immersion media at the first 24 h. However, they decreased significantly after 2 weeks and more decrease was observed in ethanol/water. The reason should be that first, as a kind of plasticizer, water decreased the toughness of dental composites and impaired the flexural strength and flexural elastic modulus; second, hydrolytic breakdown of the bond between silane and filler particles resulted in filler–resin matrix debonding; third, release of unreacted monomers further lowered the

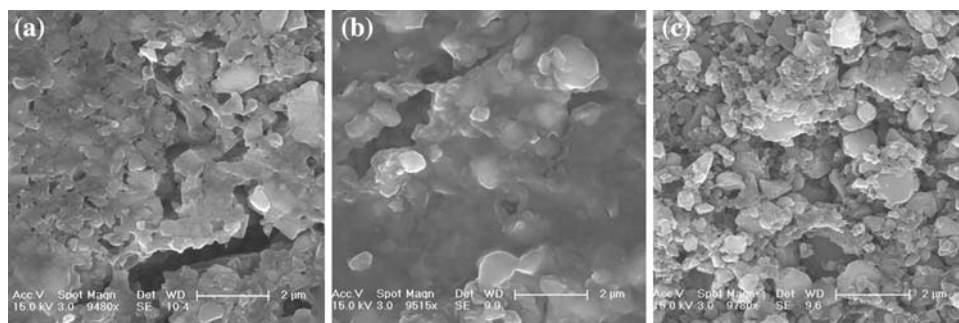
Table 4 Mean cumulative release of monomers from dental composite 2 in three different immersion media (wt./wt.-%)

		Bis-GMA	TEGDMA	UDMA
Distilled water	3 h	0.0019 (0)	0.0092 (0.0022)	0.0015 (0)
	6 h	0.0022 (0)	0.0079 (0.0016)	–
	24 h	0.0022 (0)	0.0078 (0.0018)	–
	4d	0.0031 (0)	0.0066 (0.0015)	–
	7d	–	0.0037 (0.0009)	–
	30d	–	–	–
Artificial saliva	3 h	0.0016 (0)	0.0044 (0.0010)	0.0012 (0)
	6 h	0.0017 (0)	0.0054 (0.0012)	–
	24 h	0.0020 (0)	0.0059 (0.0016)	–
	4d	0.0025 (0)	–	–
	7d	–	–	–
	30d	–	–	–
ethanol/water	3 h	0.0965 (0.0045)	0.0128 (0.0032)	0.0342 (0.0026)
	6 h	0.1240 (0.0078)	0.01629 (0.0021)	0.0413 (0.0035)
	24 h	0.1821 (0.0056)	0.0196 (0.0026)	0.0597 (0.0042)
	4d	0.2240 (0.0084)	0.0237 (0.0041)	0.0830 (0.0038)
	7d	0.2524 (0.0109)	0.0283 (0.0035)	0.1012 (0.0066)
	30d	0.5163 (0.0120)	0.0385 (0.0051)	0.2001 (0.0075)

Table 5 Values of flexural strength (FS) and flexural elastic modulus (EM) of two dental composites in three different immersion media for 24 h and 2 weeks

	Dental composite 1 distilled water	Dental composite 1 artificial saliva	Dental composite 1 ethanol/water	Dental composite 2 distilled water	Dental composite 2 artificial saliva	Dental composite 2 ethanol/water
<i>FS (MPa)</i>						
24 h	98.03 (11.2)	105.3 (10)	91.5 (13.5)	100.2 (13.5)	108.9 (15.3)	94.9 (9.8)
2 weeks	83 (5.2)	87 (6.5)	38.5 (4.6) ^a	76 (4.5)	86 (5.3)	36 (3.8) ^a
<i>EM (GPa)</i>						
24 h	10.3 (0.7)	10.1 (0.6)	9.2 (0.4)	10.1 (0.5)	9.8 (0.3)	8.3 (0.3)
2 weeks	9.8 (0.3)	9.45 (0.4)	7.6 (0.5) ^a	9.55 (0.5)	9.45 (0.3)	7.3 (0.2) ^a

^a Significant differences from others at the same time for two dental composites and three immersion media, $P < 0.05$

Fig. 6 The surface morphology of dental composite 2 after immersion in three media for a month. (a) In distilled water; (b) in artificial saliva; and (c) in ethanol/water

integrality of samples. Ethanol can penetrate the resin matrix fully, which resulted in more eluted monomers and much more impairing of the flexural strength. Flexural strength value of dental composite 2 decreased seriously than that of 1 in three immersion media, which was resulted from the higher solubility value and higher amount of eluted monomers.

3.4 Scanning electron microscope

The surface morphology of dental composites containing UDMA after immersion in three different media for a month is shown in Fig. 6. Figure 6(a) is the sample in distilled water, (b) in artificial saliva, and (c) in ethanol/water. It is clear that the sample in ethanol/water was

degraded seriously, next in distilled water and the last in artificial saliva. These results consist with that of flexural strength.

4 Conclusions

The results of this study showed that: (1) effect on the properties of dental composites depended on the immersion media where ethanol/water had the most significant effect; (2) dental composites with different components have different sorption, solubility, flexural strength, and amounts of eluted monomers even in the same immersion media.

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