Original paper

Effect of coating fillers with HEMA-phosphate copolymer on the mechanical properties of an experimental composite resin

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Abstract

Background. The water sorption and hydrolysis of silane over time can compromise the filler–resin matrix interface and cause the mechanical degradation of composite resins. The use of hydrophobic polymers for the surface treatment of fillers may improve the mechanical properties and durability of composites.

Objectives. The present study aimed to assess the effect of the surface treatment of fillers with hydroxyethyl methacrylate (HEMA)-phosphate copolymer on the mechanical properties of an experimental composite resin.

Material and methods. In this in vitro experimental study, HEMA-phosphate copolymer was synthesized and coupled with nano-silica powder. To assess the presence of the copolymer coating on the fillers, Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were performed. The fillers treated with different percentages of HEMA-phosphate copolymer were mixed with the resin matrix to fabricate experimental composites. The three-point flexural strength, microhardness and degree of conversion (DC) of 78 fabricated composite specimens were measured. Data was analyzed with the one-way analysis of variance (ANOVA) and Tukey's test.

Results. Fourier-transform infrared spectroscopy and TGA confirmed the attachment of the copolymer to the nano-silica filler for the synthesis of the composites. Group 1 (control) showed the maximum and group 6 showed the minimum hardness. Hardness decreased with an increase in the percentage of copolymer in the study groups. The maximum and minimum flexural strength and DC were noted in group 6 and the control group, respectively. Increasing the percentage of copolymer and its combination with silane non-linearly increased the flexural strength and DC of the experimental composites.

Conclusions. Increasing the percentage of HEMA-phosphate copolymer with/without silane for the coating of fillers improved the mechanical properties of the experimental composites, particularly their flexural strength and DC.

Keywords: copolymer, hydrolytic degradation, composite coupling agent, HEMA-phosphate

Highlights

- HEMA-phosphate copolymer significantly enhances composite material properties.
- Proven chemical bonding and improved material stability.
- Non-linear effect on hardness optimization for better performance.
- The synergistic combination of HEMA-phosphate copolymer and silane boosts composite performance.
- Increased durability potential for long-lasting, high-performance composites.

Introduction

Despite the advances in the formulations of composite resins observed in the past decades, their performance is still inferior to that of dental amalgam.[1–3] One major cause of failure of composite restorations is the instability of the filler–resin matrix interface over long periods of time. So far, most investigations have focused on the type and composition of fillers, the size of filler particles, or the polymerization shrinkage of composites, and the coupling agents used for bonding fillers to the resin matrix have been less commonly addressed. Following the water sorption and hydrolysis of silane, the covalent bond between silane and silica shows ionic properties, and consequently, hydrolytic degradation occurs at the filler–matrix interface, which decreases the mechanical properties of the composite and can result in its eventual degradation.[4–7] The filler–polymer matrix interface greatly influences the properties of the composite. The surface treatment of fillers with polymers possessing certain characteristics may further stabilize the interface.[8–10]

The literature is controversial regarding the types of coupling agents and the surface treatment of filler particles.[4] Grafting the polymer on the filler surface and applying a tetraethyl orthosilicate coating are among the suggested kinds of surface treatment for fillers.[4,11] Mortazavi et al. used a polymethyl methacrylate graft for dental composite nanofillers, and reported the improvement of flexural strength and better distribution of fillers in the composite resin.[12] On the other hand, evidence shows that in the surface treatment of fillers, longer polymer chains cause higher hydrolytic stabilization of the interface.[13]

Hydroxyethyl methacrylate (HEMA)-phosphate monomer, with the formulation of 2-hydroxyethyl methacrylate phosphate or ethylene glycol methacrylate phosphate, has a functional phosphate group and a HEMA group in its composition. It has been previously used in the formulation of the 7th generation bonding agent (Adper™ Prompt™ L-Pop™), since it is completely disintegrated in aqueous media and creates acidic pH for the demineralization of the enamel and dentin.[14] Foscaldo et al. used HEMA-phosphate monomer as an alternative to phosphoric acid prior to the hybridization of the 5th generation adhesives.[15] They showed that this monomer created a significantly stronger dentin interface as compared to phosphoric acid. Also, they demonstrated that the use of HEMA-phosphate as a dentin conditioner significantly decreased nano-leakage.[15] The enhanced homogenous distribution of filler particles in the composite mass and the prevention of filler agglomeration are among other advantages of applying polymer chain coatings on the surface of fillers. Due to these advantages, HEMA-phosphate-methyl methacrylate copolymer has been recently used in composite orthopedic prostheses for adhesion to the bone surfaces.[16]

Considering all the above, the present study aimed to assess the effect of the surface treatment of fillers with HEMA-phosphate copolymer on the flexural strength, Vickers microhardness and degree of conversion (DC) of an experimental composite resin. The null hypothesis was that the surface treatment of the fillers of the experimental composites with HEMA-phosphate copolymer would have no significant effect on the flexural strength, Vickers microhardness and DC of the composites.

Material and methods

In this in vitro experimental study, an experimental composite resin was first synthesized. Seventy-eight composite specimens were fabricated of the synthesized experimental composite and evaluated in 6 groups ($n = 13$). The study protocol was approved by the ethics committee at Shahid Beheshti University of Medical Sciences, Tehran, Iran (IR.SBMU.DRC.REC.1397.006).

The sample size was calculated assuming $\alpha = 0.05$, $\beta = 0.2$ and a study power of 80%. In order to obtain the correct filler weight percentage for the optimal mechanical behavior of the experimental composite, a pilot study was performed at first.

Synthesis of nano-silica composite fillers with hydroxyethyl methacrylate-hydroxyethyl methacrylate phosphate (HEMA-HEMAP) copolymer

To synthesize a specimen with 10% copolymer, 5 g of nano-silica powder (627346; Sigma Aldrich, St. Louis, USA) was added to 50 mL of distilled water in a 100-cubic centimeter beaker; 0.25 g HEMA monomer (525464; Sigma Aldrich), 0.25 g hydroxyethyl methacrylate phosphate (HEMAP) monomer (463337; Sigma Aldrich), 0.06 g tert-butyl hydroperoxide (TBHP) (as a redox initiator), and 0.03 g sodium formaldehyde sulfoxylate (SFS) (to initiate the radical polymerization of acrylate monomers) were also added to the beaker. The contents of the beaker were stirred with a magnetic stirrer (MR Hei-Standard; Heidolph Persia Co. Ltd., Tehran, Iran) at 75°C for 1 h at 500 rpm. Next, the contents of the beaker were heated in an oven (Oven Wizards, Dublin, Ireland) at 100°C for 2 h for complete desiccation and the completion of monomer polymerization. The contents of the beaker were then milled in a dual mixer/mill (SPEX™ SamplePrep 8000D; SPEX SamplePrep, Metuchen, USA), and used as such in the formulation of the experimental composite resin (Fig. 1).

Synthesis of specimens with 10% copolymer and A174 silane

The process of synthesis was the same as that explained earlier, except that in addition to HEMA and HEMAP monomers, 0.25 g A174 silane (1076730050; Merck, Darmstadt, Germany) was also added. In the process of the radical polymerization of monomers, A174 silane also participated in the structure of the copolymer (Fig. 2). During the sol–gel reaction, A174 silane bonds to the nano-silica structure with covalent bonds. In this process, the attachment of the copolymer to nano-silica becomes stronger as compared to the abovementioned synthesis without silane. The remaining steps were the same as those explained earlier. By doing so, specimens with 20% and 30% copolymer were synthesized. Specimens with 20% and 30% copolymer and 0.25 g silane were also fabricated in the same way as the 10% specimens. One group of specimens was fabricated containing only 0.25 g A174 silane acrylate monomer and 5 g nano-silica with the abovementioned synthesis protocol, to serve as the control.

Since this was an experimental study, considering the capacity of the equipment we had to synthesize and mix the experimental composites, we selected the optimal amount of filler powder and resin base that could be homogenously mixed and yield acceptable results in the pilot study. To fabricate specimens for each group of the experimental composites, the following protocol was applied: 0.66 g of modified filler powder containing nano-silica with 1.012 g resin (Table 1) were mixed manually using a mortar and a pestle for 5 min. The aforementioned values were selected by experimentation in a pilot study.[17]

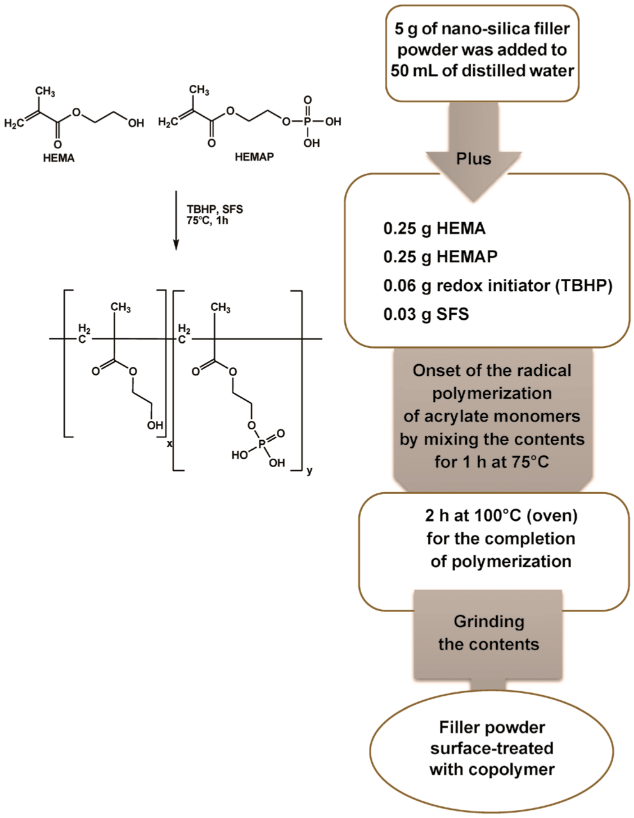

Fig. 1. Synthesis of hydroxyethyl methacrylate-hydroxyethyl methacrylate phosphate (HEMA-HEMAP) copolymer for the surface treatment of nano-silica fillers

TBHP – tert-butyl hydroperoxide; SFS – sodium formaldehyde sulfoxylate.

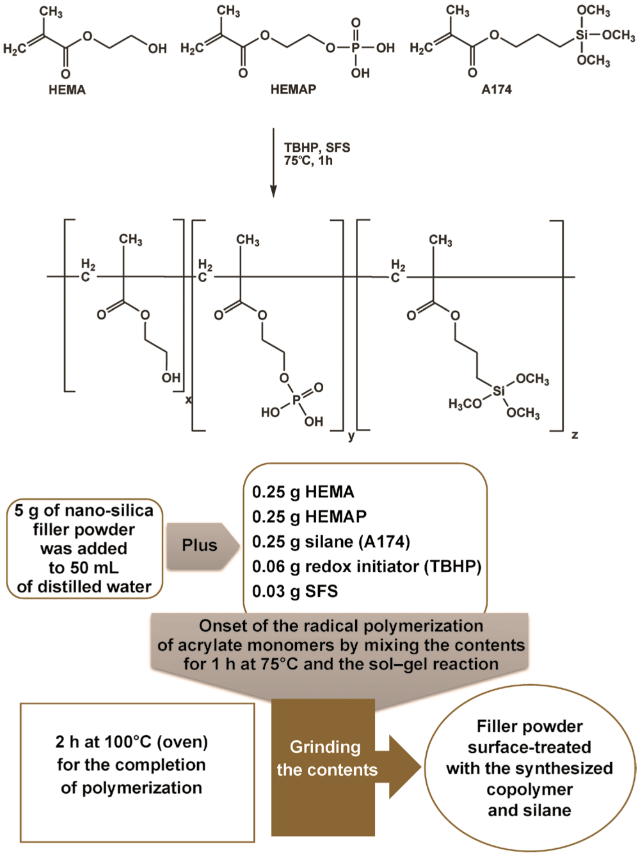

Fig. 2. Synthesis of hydroxyethyl methacrylate-hydroxyethyl methacrylate phosphate (HEMA-HEMAP) copolymer + A174 silane for the surface treatment of nano-silica fillers

Table 1. Ingredients of the resin matrix of the synthesized experimental composite resins

Material	Weight percentage [%]	Manufacturer	CAS number
Bis-GMA	48.0	Sigma-Aldrich, St. Louis, USA	1565-94-2
UDMA	25.0	Sigma-Aldrich, St. Louis, USA	72869-86-4
TEGDMA	17.0	Sigma-Aldrich, St. Louis, USA	109-16-0
TMPTMA	6.0	Sigma-Aldrich, St. Louis, USA	3290-92-4
EDMAB	2.0	Sigma-Aldrich, St. Louis, USA	10287-53-3
CQ	1.5	Merck, Darmstadt, Germany	10373-78-1
TPO	0.5	Sigma-Aldrich, St. Louis, USA	75980-60-8

CAS – Chemical Abstracts Service; Bis-GMA – bisphenol A-glycidyl methacrylate; UDMA – urethane dimethacrylate; TEGDMA – triethylene glycol dimethacrylate; TMPTMA – trimethylolpropane trimethacrylate; EDMAB – ethyl 4-dimethylaminobenzoate; CQ – camphorquinone; TPO – thermoplastic polyolefins.

For further mixing, the filler powder along with the resin were heated in a thermal box (Benchmark Scientific BSH200, Sigma Aldrich) at 56°C for 10 min to decrease the viscosity of the resin. The mixture was then transferred into a cartridge and mechanically mixed in an amalgamator (Owzan, Tehran, Iran) for 60 s at 5,000 rpm. The contents of the cartridge were manually mixed again in the dark for 5 min and placed in the amalgamator for another 60 s to obtain a homogenous mixture. Each composite was transferred into a syringe coated with aluminum foil and stored at 4°C.

The composite groups were as follows:

- group 1: Experimental composite containing the 5% silanized filler (control);
- group 2: Experimental composite containing the 10% filler coated with HEMA-phosphate copolymer;
- group 3: Experimental composite containing the 30% filler coated with HEMA-phosphate copolymer;
- group 4: Experimental composite containing the 10% filler coated with HEMA-phosphate copolymer plus the 5% silanized filler;
- group 5: Experimental composite containing the 30% filler coated with HEMA-phosphate copolymer plus the 5% silanized filler; and
- group 6: Experimental composite containing the 100% filler coated with HEMA-phosphate copolymer.

Pilot specimens were first fabricated and mechanical tests were performed on them. According to the results, groups containing 20% HEMA-HEMAP and 20% HEMA-HEMAP + silane were excluded, and replaced with the 100% HEMA-HEMAP group.

Fourier-transform infrared spectroscopy (FTIR)

To confirm the successful coating of nano-silica fillers, 0.5 g of the fillers from each study group was mixed with potassium bromide in a ratio of 1:10, condensed in the form of a disk and subjected to Fourier-transform infrared spectroscopy (FTIR) under diffused reflection (spectrophotometer 1600 series; PerkinElmer Inc., Waltham, USA).

Assessment of the degree of conversion (DC)

The DC of the control ($n = 3$) and modified ($n = 3$ from each experimental group) specimens was measured using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) (Nicolet iS10; Thermo Fisher Scientific, Waltham, USA). For this purpose, the composite was first applied into standard molds with a diameter of 8 mm and a thickness of 2 mm, and condensed with glass slides at both sides. It was then cured with a curing unit (Dr's Light AT, Good Doctors Germany, Bonn, Germany) with a light intensity of 1,470 mW/cm^2 for 20 s from both sides. One specimen was fabricated from each composite type. The absorbance peaks were recorded using FTIR (Nicolet iS10; Thermo Fisher Scientific) over a wavelength range of 650–4,000 cm^{-1} with a resolution of 4 cm^{-1}. The absorbance of the uncured specimens was also obtained under the same conditions. The DC value was calculated by estimating the changes in the peak height ratio of the absorbance intensities of the aliphatic C=C peak at 1,638 cm^{-1} and that of the internal standard peak of aromatic C=C at 1,608 cm^{-1}, in relation to the uncured material. Thus, the DC of the specimen was calculated using the following formula (Equation 1)[17]:

$$\mathrm{DC} = \left(1 - \frac{(1{,}638\ \mathrm{cm}^{-1} \div 1{,}608\ \mathrm{cm}^{-1})\ \text{after curing}}{(1{,}638\ \mathrm{cm}^{-1} \div 1{,}608\ \mathrm{cm}^{-1})\ \text{before curing}}\right) \times 100 \quad (1)$$

where:
DC – degree of conversion.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was also performed to assess the quality of the coating of nano-silica fillers with HEMA-phosphate copolymer. Prior to the synthesis of the composites, 10 mg of filler powder from each group was placed in a furnace (TGA-50; Shimadzu Corp., Kyoto, Japan) and heated up from room temperature (27°C) to 700°C at a speed of 10°C/min under nitrogen gas. A weight loss occurred due to the increase in temperature, and it was recorded as a function of temperature.

Three-point flexural strength test

For this test, stainless-steel molds measuring 25 mm × 2 mm × 2 mm were used. The composite was applied into the molds ($n = 5$), and each side was light-cured for 60 s with an intensity of 1,470 mW/cm^2. Each side was cured in three 20-second curing cycles using the overlapping technique. The specimens were then removed from the molds and stored in water at 37°C for 24 h. The three-point flexural strength test was performed according to the ISO 4049 standard,[18] using a universal testing machine (UTM) (Santam, Karaj, Iran). The distance between the 2 supports was 20 mm and load was applied at a crosshead speed of 0.75 mm/min. The maximum load was 50 N. The application of load was continued until the fracture of the specimen.[18]

Vickers microhardness test

For this test, composite disks ($n = 5$ from each group) were fabricated using stainless-steel molds with a diameter of 8 mm and a thickness of 2 mm. The specimens were fabricated as explained for the flexural strength test, and were then polished with 2,000-, 3,500- and 5,000-grit abrasive paper (Matador; Starcke, Melle, Germany). A Vickers hardness tester with a 136-degree pyramidal diamond indenter (ZwickRoell, Ulm, Germany) was used for this test. A load of 300 gf was applied for 10 s on the composite surface. Three indentations were created on the surface of each disk. The diameter of the created indentations was then measured under a microscope. The microhardness value was calculated accordingly.

Statistical analysis

Data was analyzed using IBM SPSS Statistics for Windows, v. 24 (IMB Corp., Armonk, USA). The one-way analysis of variance (ANOVA) was applied to compare the groups, while pairwise comparisons were performed with Tukey's post-hoc test. The level of significance was set at 0.05.

Results

FTIR results

The FTIR analysis of nano-silica fillers showed stretching vibrations of the Si–O–Si functional group at 1,091 cm^{-1}. Stretching vibrations of the O–H group were also noted at 3,430 cm^{-1}. Stretching vibrations of the C=O carbonyl group at 1,750 cm^{-1} confirmed the presence of the copolymer on the filler surface (Fig. 3). On the other hand, due to the presence of the hydroxyl group, the intensity of O–H vibrations slightly increased. While comparing the fillers containing HEMA-phosphate copolymer with the control group (5% silane), an increased intensity of peak at 1,240–1,310 cm^{-1} was noted, which belonged to stretching vibrations of P=O. It indicated the presence of HEMA and the HEMA-phosphate groups in the composition of the composite, as well as the OH-groups of phosphate units.

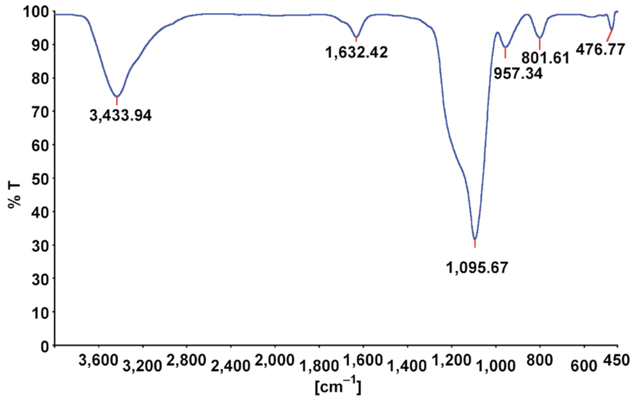

Fig. 3. Fourier-transform infrared spectroscopy (FTIR) spectrum for the control group (5% silane) fillers

The vibration peak of the C=C molecular bond in acrylate is located at 1,480–1,600 cm^{-1}. Following polymerization and the conversion of double bonds to single bonds, the intensity of this peak should decrease. This peak was not observed, which indicated the polymerization of the C=C bond with HEMA-phosphate.

In the control group (5% silane), a vibration peak at 1,750 cm^{-1} confirmed the presence of the carbonyl group (Fig. 3). Since Si–O has a chemical structure similar to silica, its related vibration peak was noted beneath the vibration peak of silica. Similarly, for the group 5 fillers, the vibration peak of Si–O was observed beneath the peak of silica (Fig. 4).

TGA results

Table 2 shows the percentages of weight loss for the specimens at each temperature range. As shown, a weight

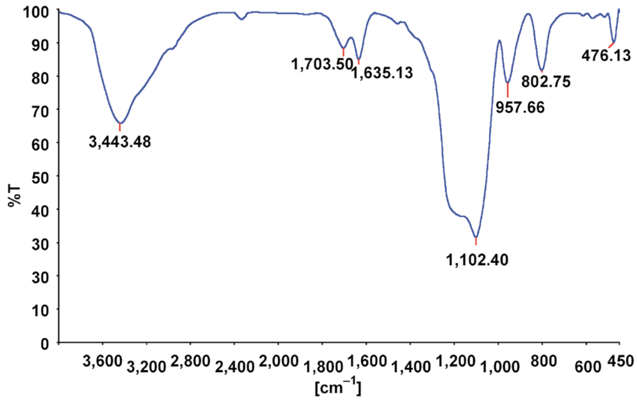

Fig. 4. Fourier-transform infrared spectroscopy (FTIR) spectrum for the group 6 fillers

Table 2. Percentages of weight loss [%] for the specimens at each temperature range

Group	Temperature ranges			
	25–175°C	175–325°C	325–475°C	475–625°C
Nano-silica*	9.20	0.90	1.54	0.79
Group 1	7.17	1.30	2.65	2.27
Group 2	9.26	1.55	3.72	2.76
Group 3	8.95	1.70	6.61	2.74
Group 4	7.48	1.12	4.65	2.99
Group 5	10.00	0.34	5.22	2.49
Group 6	6.98	5.20	13.96	1.79

Group 1 – 5% silane (control); group 2 – 10% hydroxyethyl methacrylate (HEMA)-phosphate; group 3 – 30% HEMA-phosphate; group 4 – 10% HEMA-phosphate + silane; group 5 – 30% HEMA-phosphate + silane; group 6 – 100% HEMA-phosphate.
* The weight loss of nano-silica powder alone is shown for the purpose of comparison with the weight loss of the experimental composite groups.

loss was noted at temperatures <200°C, which was attributed to the molecules physically bonded to the nanofiller surface. In other words, this weight loss was related to the loss of moisture from nano-silica powder and the water obtained from the completion of the sol–gel reaction. Another weight loss that occurred at temperatures 270–500°C indicated the presence of chemical bonds between the copolymer and nano-silica fillers (Fig. 5). Thus, the thermogram confirmed that the surface treatment of nano-silica fillers with HEMA-phosphate copolymer increased thermal stability.

Vickers microhardness test results

Table 3 shows the Vickers microhardness values for the study groups. The microhardness data had normal distribution, as confirmed by the Kolmogorov–Smirnov and Shapiro–Wilk tests. Thus, ANOVA was applied for the comparison of the groups, and revealed significant differences in their microhardness ($p < 0.05$). Thus, Tukey's test was applied for pairwise comparisons, which revealed the maximum microhardness in the composite specimens from the control group (5% silane), while the minimum microhardness was noted in group 6. The differences between groups 1 (control), 2, 3, and 6 were all significant ($p < 0.05$). Also, significant differences were noted between groups 2 and 4 ($p = 0.310$), 3 and 4 ($p = 0.000$), 4 and 5 ($p < 0.05$), and 5 and 6 ($p = 0.000$).

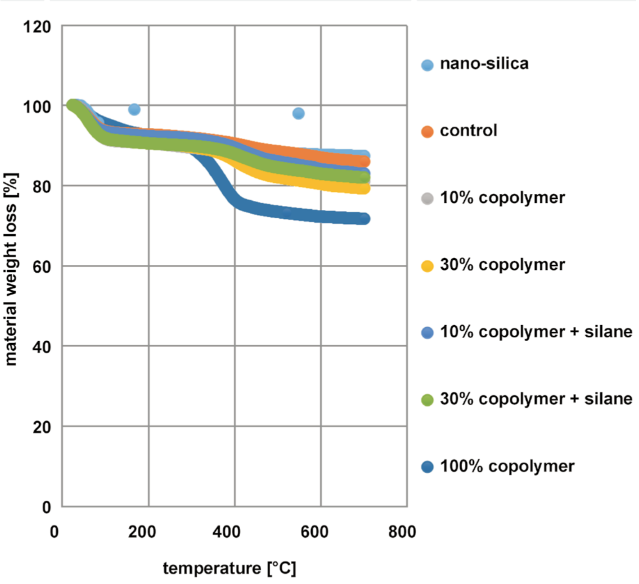

Fig. 5. Thermogravimetric analysis (TGA) diagram for the filler powder of the study groups

Table 3. Vickers microhardness values [HV] for the study groups ($n = 5$)

Group	*M* ±*SD*	min	max
Group 1^{a}	35.60 ±2.90	30	42
Group 2^{a,b}	31.67 ±1.88	29	34
Group 3^{a,c}	31.13 ±1.88	30	33
Group 4^{b,c,d}	34.67 ±2.90	30	40
Group 5^{d,e}	33.53 ±4.07	25	41
Group 6^{a,e}	30.07 ±2.02	25	33

Group 1 – 5% silane (control); group 2 – 10% hydroxyethyl methacrylate (HEMA)-phosphate; group 3 – 30% HEMA-phosphate; group 4 – 10% HEMA-phosphate + silane; group 5 – 30% HEMA-phosphate + silane; group 6 – 100% HEMA-phosphate.
M – mean; *SD* – standard deviation; min – minimum; max – maximum.
Groups with the same superscript letters showed a statistically significant difference according to Tukey's test ($p < 0.05$).

Three-point flexural strength test results

Table 4 presents the flexural strength values for the study groups. The flexural strength data was not normally distributed. Thus, comparisons were made using the non-parametric Kruskal–Wallis test, which showed significant differences in flexural strength among the groups ($p < 0.05$). Pairwise comparisons revealed significant differences between groups 1 and 5 ($p = 0.010$), and 1 and 6 ($p = 0.000$). Also, groups 2, 3 and 6 differed significantly ($p < 0.05$), group 4 showed a significant difference with regard to group 1 ($p = 0.060$), and group 5 showed a significant difference with regard to group 2 ($p = 0.050$).

Table 4. Flexural strength values [MPa] for the study groups ($n = 5$)

Group	*M* ±*SD*	min	max
Group 1^{a,b,d}	47.61 ±9.38	34.05	55.90
Group 2^{c,e}	50.88 ±11.92	36.00	68.40
Group 3^{c}	54.62 ±6.02	46.00	61.00
Group 4^{d}	62.39 ±7.22	52.95	69.50
Group 5^{a,e}	65.71 ±3.37	62.79	70.90
Group 6^{b,c}	69.46 ±5.67	62.30	75.50

Group 1 – 5% silane (control); group 2 – 10% hydroxyethyl methacrylate (HEMA)-phosphate; group 3 – 30% HEMA-phosphate; group 4 – 10% HEMA-phosphate + silane; group 5 – 30% HEMA-phosphate + silane; group 6 – 100% HEMA-phosphate.
Groups with the same superscript letters showed a statistically significant difference according to the Kruskal–Wallis test ($p < 0.05$).

Degrees of conversion

Table 5 presents the DC of the study groups. Since the DC data was not normally distributed, the Kruskal–Wallis test was applied for the comparison of the groups. It revealed significant differences ($p < 0.05$). Pairwise comparisons showed significant differences between group 1 and all other groups ($p < 0.05$), except for group 2 ($p = 0.340$). Group 2 differed significantly from groups 3, 5 and 6 ($p < 0.05$). Group 3 showed significant differences with regard to all other experimental groups ($p < 0.05$), except for group 5 ($p = 0.750$). Group 4 showed significant differences with regard to all other experimental groups ($p < 0.05$), except for group 2 ($p = 0.240$). Also, group 6 differed significantly from all other groups ($p < 0.05$).

Discussion

This study assessed the effect of the surface treatment of fillers with HEMA-phosphate copolymer on the mechanical properties of an experimental composite. HEMA-phosphate monomer breaks down into HEMA and phosphoric acid in aqueous media.[14] It has been reported that the connection of the filler with the resin matrix through short polymer chains is difficult, and such a polymer layer would often create a less stable interface.[19] Thus, attention has been directed to the use of polymers with long hydrocarbon chains instead of silane to increase the stability and durability of the coupling layer. In the present study, HEMA-phosphate copolymer was synthesized to create a polymer with a long chain. Since this copolymer has never been used in the formulation of composite resins, we first conducted a pilot study and synthesized several composite specimens in each group to find the optimal method of synthesis, with a maximum filler percentage to achieve almost ideal mechanical properties. Accordingly, the group containing fillers modified with 20% copolymer was excluded from the final analysis, since the results in this case were very similar to those for groups 1 and 2.

Table 5. Degree of conversion (DC) values [%] for the study groups ($n = 3$)

Group	*M* ±*SD*	min	max
Group 1[a]	47.6 ±2.5	45.0	50.0
Group 2[b]	51.6 ±1.9	49.2	54.6
Group 3[a,b,c]	67.5 ±1.3	66.0	68.5
Group 4[a,c,d]	56.0 ±3.0	53.0	59.0
Group 5[a,b,d,e]	70.0 ±2.0	68.0	72.0
Group 6[a,b,c,d,e]	77.0 ±1.6	75.4	78.6

Group 1 – 5% silane (control); group 2 – 10% hydroxyethyl methacrylate (HEMA)-phosphate; group 3 – 30% HEMA-phosphate; group 4 – 10% HEMA-phosphate + silane; group 5 – 30% HEMA-phosphate + silane; group 6 – 100% HEMA-phosphate.
Groups with the same superscript letters showed a statistically significant difference according to the Kruskal–Wallis test ($p < 0.05$).

FTIR analysis and TGA confirming the presence of copolymers in the composition of the synthesized composites

The chemical reactions of HEMA-phosphate copolymer with the surface of the filler were confirmed by FTIR and TGA. The vibration peak of the C=C molecular bond in acrylate is located at 1,480–1,600 cm^{-1}. Following polymerization and the conversion of double bonds to single bonds, the intensity of this peak should decrease. This peak was not observed, which indicated the polymerization of the C=C bond with HEMA-phosphate in our study. Also, the presence of a peak at 1,750 cm^{-1}, related to C=O, confirmed the presence of the copolymer on the filler surface.

Thermogravimetric analysis displays the weight loss of fillers as a function of a temperature increase.[20] The TGA of filler powder in all groups showed a reduction in the filler weight at temperatures <200°C due to the loss of water in the filler content and the unreacted coupling agent. Another drop in weight was noted at 270–500°C. The maximum percentage of reduction in the filler weight was noted in group 6 between 325°C and 475°C. The reduction in weight increased with an increase in the copolymer content, which indicated that HEMA-phosphate copolymer underwent thermal degradation at a higher temperature due to its chemical bond with nano-silica fillers.

Flexural strength analysis of the synthesized composites

Groups 2, 3 and 6 (10%, 20% and 100% HEMA-phosphate copolymer, respectively) showed significant increases in the flexural strength and DC of the composites. Another study that used HEMA-phosphate copolymer reported that it increased the mechanical strength of zinc oxide and zinc polycarboxylate cements, and decreased their solubility.[21] It appears that if the percentage of unreacted monomers in the polymer matrix of the composite is lower, the polymer network on the filler surface can improve the mechanical properties of the composite resins, such as flexural strength. Also, it occurs that long polymer chains on the filler surface create ester repulsion and overcome the Van der Waals forces between particles, preventing the agglomeration of filler particles and leading to an increase in the composite strength.[22]

DC analysis of the synthesized composites

A number of factors can affect the DC of composite resins, e.g., the cavity size, its location, the distance between the tip of the curing unit and the composite surface, the filler type, the type of curing unit, and light intensity.[23]

A review study demonstrated that the size, weight and volume of filler particles, and the filler/matrix ratio can significantly affect the DC and microhardness of composite resins.[24] In the present study, the composite specimens containing the maximum percentage of HEMA-phosphate copolymer showed the highest DC value. A lower filler/resin matrix ratio in this group, in comparison with other groups, appeared to be directly correlated with a higher DC value.[25]

The current study did not assess the rheological properties of the experimental composite resins; however, in the process of synthesis, it was noticed that filler groups with a higher percentage of copolymer (group 6) had lower viscosity and better handling, and were better mixed with the resin matrix. In other words, materials with lower viscosity have a lower filler content or contain more flowable resin monomers. A previous study demonstrated a greater movement of free radicals in the resin matrix of resin monomers with lower viscosity, which led to higher DC.[26] It has been reported that the modification of the filler surface by using oligomeric chains increases the DC of the composite as compared to composite resins with silane as the only coupling agent in their structure.[27] In the present study, increasing the percentage of copolymer increased the DC of the composite. The final polymerization of the composite involves 2 key processes: the polymerization of 60 wt% of the resin added to the filler; and an increased conversion of carbon–carbon double bonds into single bonds within the resin part of the pre-polymerized filler. Together these processes enhance the overall conversion of carbon bonds.

Microhardness analysis of the synthesized composites

The Vickers microhardness test is commonly performed to assess the mechanical properties, DC and wear properties of composite resins.[17,28,29] In the present study, the control group (5% silane) showed the maximum microhardness, while group 6 showed the minimum microhardness. The calculation of the weight fraction of the filler in the synthesized composites revealed that increasing the resin matrix decreased microhardness. Pala et al. reported similar results.[30] On the other hand, they showed an inverse correlation between microhardness and flexural strength.[30] Chung and Greener found a significant correlation between the weight fraction and volume fraction of fillers and microhardness, which confirms our findings.[31] Nonetheless, Lee et al. found a positive correlation between microhardness and flexural strength, which is different from our results.[32] However, it should be noted that they assessed the mechanical properties of denture-base acrylic resins, while we evaluated composite resins. Marovic et al. demonstrated a correlation between DC and hardness.[33] They noted that increasing the pre-polymerized filler content in the composite decreased its microhardness. On the other hand, they showed that the microhardness of the composite was more influenced by the filler content rather than DC,[33] which is in line with the results obtained in our study.

Karabela and Sideridou reported that the structure of silane used for nano-silica silanization affected the adsorption and solubility of composite resins.[34] The silane molecule has two functional ends. One end bonds to the hydroxyl groups of silica particles and the other end can copolymerize with the polymer matrix. In the present study, in the process of synthesis of HEMA-phosphate copolymer, a 3D polymer structure was created on the silica matrix upon using the redox initiator. In this process, all insoluble 3D acrylate monomers were placed on silica particles. Phosphate groups in the structure of HEMA-phosphate are attached to the silica structure via strong ionic bonds. The presence of these bonds was confirmed by the TGA of the modified filler powders.

In groups 4 and 5 (the use of silane and HEMA-phosphate copolymer), silane monomer was incorporated in the structure of the copolymer during radical polymerization, while silane monomer forms covalent bonds with the nano-silica structure during the sol–gel reaction. Obviously, the attachment is stronger when silane along with HEMA-phosphate copolymer bond to nano-silica particles, as compared to the attachment of HEMA-phosphate copolymer without silane. Ye et al. used both silane and polyethylene glycol dimethacrylate oligomer for the surface treatment of colloidal silica fillers, and observed a uniform distribution of silica particles in the urethane dimethacrylate (UDMA) matrix, which enhanced the strength.[27] This result is in line with our findings in groups 4 and 5, where a combination of silane and HEMA-phosphate copolymer was used, with the difference being that the type of copolymer was different in the 2 studies.

Thus, a combination of HEMA-phosphate copolymer and silane as filler surface treatment may result in a more stable and reliable resin matrix–filler interface. However, long-term studies are required to assess the hydrolytic and mechanical stability of the interfaces containing HEMA-phosphate copolymer, with and without a silane base, to cast a final judgment in this respect. Also, the assessment of other mechanical properties of the synthesized composites, as well as the evaluation of the mode of failure (with the use of scanning electron microscopy (SEM)), are recommended.

Conclusions

Increasing the percentage of HEMA-phosphate copolymer for the filler surface treatment of an experimentally synthesized composite, in both pure form and in combination with silane, improved its mechanical properties, particularly DC and flexural strength.

Ethics approval and consent to participate

The study protocol was approved by the ethics committee at Shahid Beheshti University of Medical Sciences, Tehran, Iran (IR.SBMU.DRC.REC.1397.006).

Data availability

The datasets supporting the findings of the current study are available from the corresponding author on reasonable request.

Consent for publication

Not applicable.

Use of AI and AI-assisted technologies

Not applicable.

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