

Properties of Particulate Resin-Luting Agents with Phosphate and Carboxylic Functional Methacrylates as Coupling Agents

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ABSTRACT: This study investigated properties of resin-luting agents using silane [3-(trimethoxysilyl)propyl methacrylate (TSPM)], phosphoric acid methacrylate (PAM) [mono/*bis*(methacryloyloxyethyl (di)hydrogen phosphate)], or carboxylic acid methacrylate (CAM) [mono-2-(methacryloyloxy)ethyl maleate] as coupling agents between the inorganic and organic phases. Ba-B-Al-Si microparticles (3 μm) and SiO₂ nanoparticles (7 nm) were coated with TSPM, PAM, or CAM (control = no filler coating). A *Bis*-GMA/triethyleneglycol dimethacrylate comonomer was loaded with 60% mass of inorganic fillers. The properties evaluated were degree of C=C conversion (DC), flexural strength (σ), and modulus (E_f), Knoop hardness number (KHN), and film thickness (FT). Dispersion/interaction of the particles with the resin phase was assessed by scanning electron microscopy (SEM). No significant differences in DC were observed. For σ and E_f , TSPM > CAM > Control > PAM. For KHN, TSPM > CAM > PAM = Control. For FT, TSPM < Control < CAM < PAM. The SEM analysis revealed clustering of nanoparticles for all groups and better organic–inorganic phases interaction for TSPM and CAM. The use of TSPM generated agents with improved properties as compared with the acidic methacrylates, with CAM showing better performance than PAM. The use of PAM generated agents with properties usually poorer compared with the material with no coupling agent. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: biomaterials; hardness; mechanical properties; microstructure; surface modification

Received 4 January 2011; accepted 28 February 2012; published online 00 Month 2012

DOI: 10.1002/app.37627

INTRODUCTION

Dental resin-luting agents consist of a resin matrix mixed with reinforcing inorganic particles; a coupling agent mediates the bonding between these two phases. The filler–polymer interaction is expected to affect the material mainly by influencing the dispersion of the particles within the resin matrix,¹ affecting properties as monomer conversion, viscosity, and film thickness (FT). The interfacial strength is also expected to affect mechanical processes during macroscopic deformation, leading to better load transfer, toughening, and increased wear resistance.^{2,3}

The most common coupling agents in dental composites are organo-silanes.⁴ These agents contain a trialkoxysilane function on one end for bonding to the silica-containing fillers, and a methacrylate group on the other end to make the fillers compatible with the resin. The alkoxy groups of silanes are hydrolyzed into silanol groups to bond with silica through the formation of siloxane bonds,^{5,6} as shown in Figure 1. It has been suggested, however, that the breakdown of the filler–polymer

interface may be one of the main causes of failures of dental resin composites,⁷ as hydrolysis of the siloxane bonds may lead to filler dislodgement.⁸ Another limitation of silanes is the dependence on the presence of silica in the inorganic fillers. Silica is radiolucent and has been partially substituted by heavy metal-containing glasses or minerals in dental composites.⁹

Other potential coupling agents for resin composites are acidic methacrylates. Functional acidic monomers are characterized by three segments: a polymerizable group, a spacer, and an acid termination.¹⁰ It has been shown that functional groups capable of releasing one or more protons, such as carboxyl and phosphate groups, may bond to metal oxides.^{11–15} Likewise, the use of functional monomers as coupling agents could potentially allow bonding to inorganic fillers, although this effect is still unknown.

The aim of this study was to investigate fundamental properties of particulate resin-luting agents with phosphate and carboxylic functional methacrylates as coupling agents. The null-

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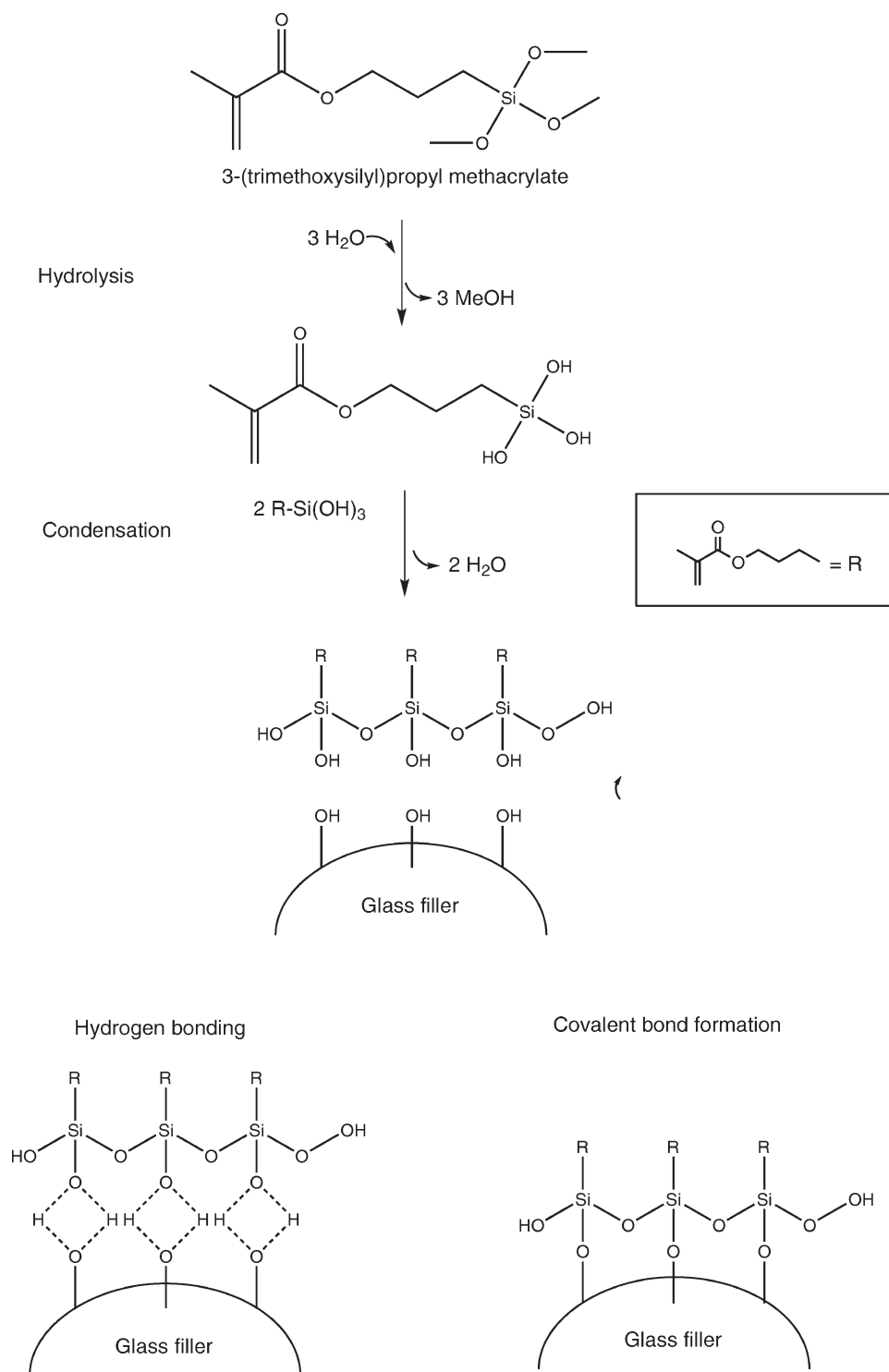


Figure 1. The reaction of TSPM with the glass filler involves four steps. Initially, hydrolysis of the methoxy label groups occurs. Condensation to oligomers follows. The oligomers then hydrogen bond with the hydroxyl groups from the filler. Finally, as the silane dries, covalent bond with the substrate is formed with concomitant loss of water.

hypotheses tested were as follows: (i) the properties of the resin-luting agents would be independent of the filler treatment, and (ii) there would be no differences in the filler–resin interaction for agents obtained using the different coupling agents.

MATERIALS AND METHODS

Reagents

The monomers 2,2-*bis*[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (*Bis*-GMA) and triethyleneglycol dimethacrylate, and the photoinitiator camphorquinone, were donated by Esstech Inc.

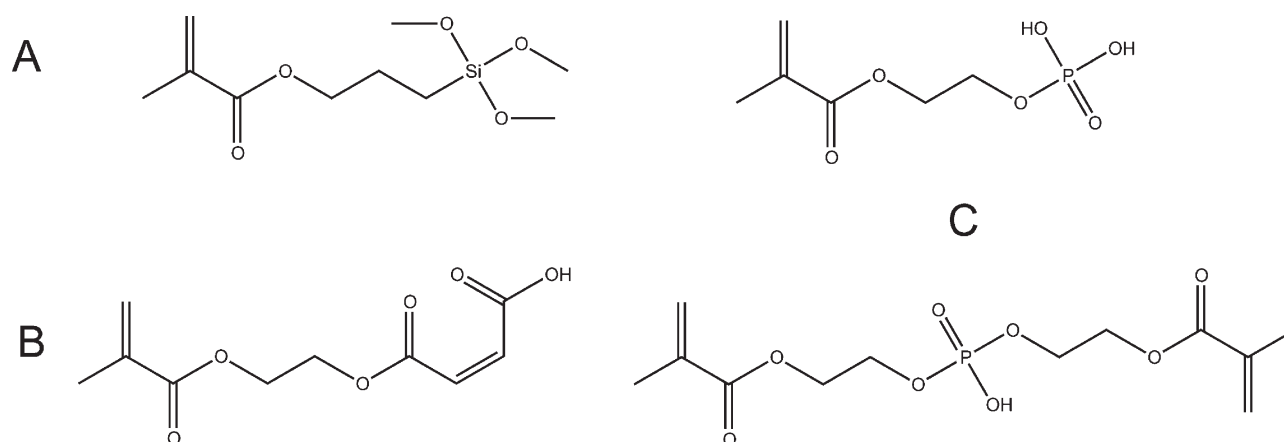


Figure 2. Molecular structure of the coupling agents used in the study: (A) TSPM; (B) mono-2-(methacryloyloxy)ethyl maleate; (C) methacryloyloxyethyl dihydrogen phosphate/*bis*(methacryloyloxyethyl) hydrogen phosphate.

(Essington, PA). The monomer 2-hydroxyethyl methacrylate, the co-initiator ethyl 4-dimethylamino benzoate, the radical scavenger butylated hydroxytoluene, the organo-silane 3-(trimethoxysilyl)propyl methacrylate (TSPM) and the carboxylic acid methacrylate (CAM) mono-2-(methacryloyloxy)ethyl maleate were purchased from Sigma-Aldrich (St. Louis, MO). All chemicals were used as received. The phosphoric acid methacrylate (PAM) was synthesized as previously described.¹⁶ Briefly, to a round bottom vessel at 0°C with methylene chloride, phosphorus pentoxide was added and the slurry stirred vigorously while 2-hydroxyethyl methacrylate was slowly added at room temperature. After filtering the product, radical scavenger was added and the methylene chloride was removed under distillation using a rotary evaporator. The product of the reaction was an equimolar mixture of the monomers methacryloyloxyethyl dihydrogenphosphate (MEP) and *bis*(methacryloyloxyethyl) hydrogen phosphate (*Bis*-MEP). The molecular structures of the coupling agents TSPM, PAM, and CAM are shown in Figure 2.

Filler Coating

Ba-B-Al-Si glass microparticles (Schott, Mainz, Germany: $d_{50} = 3 \pm 1 \mu\text{m}$) and silica nanoparticles (Aerosil 380; Degussa, Germany: 7 nm average size) were used. The particles were submitted to one of the following surface treatments, as shown in Table I: none (Control), coating with TSPM, coating with CAM or coating with PAM. The amount of coating material was set at 5% mass fraction related to the mass of the inorganic fillers. The coupling agents were diluted in a 96% ethanol–water solution. The particles soaked into the solution and left to dry at 80°C for 24 h

to assure complete solvent removal. After storage, the fillers were sieved through a 150- μm sieve.

Formulation of the Resin-Luting Agents

A model dimethacrylate comonomer based on a 1 : 1 mass ratio of *Bis*-GMA and triethyleneglycol dimethacrylate was loaded with a 0.4% mass fraction of camphorquinone, 0.8% mass fraction of ethyl 4-dimethylamino benzoate, and 0.1% mass fraction of butylated hydroxytoluene. Four resin-luting agents were obtained by loading the comonomer with a 60% mass fraction of the fillers submitted to one of the treatments described before. The filler system was added at a 59 : 1 mass ratio of micro- and nanoparticles. The particles were incorporated by intensive manual mixing followed by mechanical stirring with a motorized mixer. To assure the adequate dispersion of the filler system, the materials were submitted to a thorough sonication.

Degree of C=C conversion

The degree of C=C conversion (DC) was measured using Fourier transform infrared spectroscopy (Prestige21; Shimadzu, Tokyo, Japan), equipped with an attenuated total reflectance device ($n = 5$). The unpolymerized materials were placed direct on the attenuated total reflectance cell and the unpolymerized spectra were obtained. The readings were taken under the following conditions: 32 scan co-addition, 4 cm^{-1} resolution, and 2.8 mm/s mirror speed. Photoactivation was then carried out for 40 s using a LED unit (Radii; SDI, Bayswater, Victoria, Australia) with 600-mW/cm² irradiance. The light guide tip was positioned 2-mm away from the material. The diameter of the specimens was restricted to match the diameter of the light guide. The %DC was evaluated in the absorbance mode using a baseline technique,

Table I. Filler Treatments Tested in the Study

Filler treatment	Coupling agent ^a	Manufacturer	Group code
None	–	–	Control
Organo-silane	3-(Trimethoxysilyl)propyl methacrylate	Sigma-Aldrich	TSPM
Carboxylic acid methacrylate	Mono-2-(methacryloyloxy)ethyl maleate	Sigma-Aldrich	CAM
Phosphoric acid methacrylate	Equimolar mixture of the synthesized monomers MEP/ <i>Bis</i> -MEP	–	PAM

^aThe proposed mechanisms for the bond between the coupling agents and the inorganic glass fillers are shown in Figures 1 and 4.

considering the intensity of C=C stretching vibration (peak height) at 1635 cm^{-1} and, as an internal standard, using the symmetric ring stretching at 1608 cm^{-1} .¹⁷

Flexural Strength and Modulus

Flexural tests were performed using bar specimens with dimensions of $12 \times 2 \times 2\text{ mm}^3$ (8-mm span width). The luting agent was placed into the stainless steel/glass mold, covered with a Mylar strip and photocured using two irradiations of 40 s on each side. A three-point bending test was carried out 24 h after irradiation on a mechanical testing machine (DL500; EMIC, São José dos Pinhais, PR, Brazil), at a crosshead speed of 0.5 mm/min. Flexural strength (σ) and flexural modulus (E_f) were calculated from the load–displacement trace ($n = 20$).

Hardness

The materials were placed into cylinder-shaped metal molds (5-mm inner diameter \times 2-mm thick), covered with a Mylar strip and light-activated for 40 s on each surface. The specimens were dry stored in lightproof containers at 37°C , for 24 h, then wet-ground with 800-, 1000-, 1200- and 1500-grit SiC abrasive papers. Three readings were performed on each specimen through a microindenter (FM-700; Future-Tech, Kawasaki, Japan), under a load of 25 g and a dwell time of 5 s. The Knoop hardness number (KHN, kgf/mm^2) for each specimen was recorded as the average of the three indentations ($n = 5$).

Film Thickness

Two optically flat square glass plates, each 5-mm thick, and having a contact surface area of 200 mm^2 were used. The combined thickness of the glass plates stacked in contact was measured (reading A) with a digital caliper accurate to 0.001 mm. Then, 0.1 mL of luting agent was placed centrally between the plates, and a constant load of 150 N was carefully applied vertically and centrally via the top plate, for 180 s. After this period, light irradiation was performed for 40 s to stabilize the specimen. The combined thickness of the two glass plates and the luting agent film was measured (reading B). FT was recorded as the difference between reading B and reading A ($n = 5$).

Statistical Analysis

Data from DC, σ , E_f , KHN, and FT analyses were separately submitted to one-way ANOVA followed by the Tukey's *post hoc* test ($P < 0.05$).

Scanning Electron Microscopy Evaluation

To observe the dispersion and interaction of the filler particles within the resin phase, cylinder-shaped specimens (5-mm diameter \times 1-mm thick) were embedded in epoxy resin and wet-polished with 600-, 1200-, 1500-, 2000- and 2500-grit SiC papers and with 3-, 1-, 0.25-, and $0.1\text{-}\mu\text{m}$ diamond polishing suspensions. The specimens were coated with gold and the polished surfaces examined by scanning electron microscopy (SEM) (SSX-550; Shimadzu) at 15 kV.

RESULTS

Results for all evaluations are presented in Table II. No significant differences among the filler treatments were detected in the DC analysis ($P = 0.127$). For flexural strength, all groups presented significantly different results as compared with each other: TSPM $>$ CAM $>$ Control $>$ PAM ($P < 0.001$). Likewise, for flexural modulus, TSPM was significantly higher than CAM

Table II. Means (SD) for Degree of C=C Conversion (DC), Flexural Strength (σ), Elastic Modulus (E_f), Hardness (KHN), and Film Thickness (FT)

	Filler treatment			
	Control	TSPM	CAM	PAM
DC (%)	59.0 (0.7) ^A	54.1 (0.5) ^A	58.1 (6.2) ^A	59.7 (4.0) ^A
σ (MPa)	40 (4) ^C	107 (16) ^A	56 (12) ^B	23 (4) ^D
E_f (GPa)	1.55 (0.2) ^C	2.04 (0.2) ^A	1.72 (0.2) ^B	0.8 (0.1) ^D
KHN (kgf/mm^2)	16.8 (1.7) ^C	34.5 (2.2) ^A	23.6 (1.2) ^B	18.2 (1.4) ^C
FT (μm)	10.2 (1.8) ^C	4.2 (2.6) ^D	17.2 (3.4) ^B	38.6 (4.0) ^A

Distinct letters in a same row indicate significant differences for filler treatment ($P < 0.05$).

($P < 0.001$), which was significantly higher than the control group ($P = 0.023$); the group PAM showed again significantly lower values than all the other groups ($P < 0.001$). The group TSPM also showed significantly higher KHN than all the other groups ($P < 0.001$); CAM showed intermediate results for KHN, while the groups PAM and Control showed the lowest KHN values. For FT, all filler treatments showed results significantly different compared with each other: TSPM $<$ control $<$ CAM $<$ PAM ($P \leq 0.03$).

SEM pictures of the polished luting agent surfaces are shown in Figure 3. Nanoparticle clustering was evident for all surface treatments, although filler agglomeration was less frequent for PAM-based materials. Voids between the fillers and the organic resin matrix were observed, owing to the detachment of fillers during the polishing procedures. The areas caused by dislodgement and loss of fillers are more evident and frequent for the Control and PAM groups. The presence of these areas was less frequent for the TSPM group as compared with the other surface treatments.

DISCUSSION

The first null-hypothesis tested was rejected, as resin-luting agents with functional methacrylates as coupling agents presented a wide range of properties, usually poorer as compared with the silane-containing agent. The presence of residual acidic methacrylates is usually associated with negative effects on the DC due to the ability of functional monomers in quenching free radicals.^{18,19} Radicals terminated by an acid group are also less reactive than free radicals derived from unmodified monomers, reducing the polymerization rate.²⁰ However, treating the particles with acidic monomers had no significant effect on the DC. This finding is most likely related to the low amount of coupling agent needed to couple the organic and inorganic phases of the luting agents. A previous investigation showed that substantial reductions in DC occurred mainly in the presence of high concentration of acidic monomers, and that the effect was more stressed in self-cured materials (which show slower cure) due the deactivation of the amine coinitiator.¹⁹

Materials treated with TSPM showed better mechanical properties compared with either acidic methacrylate. This is the first time this result is described, as no previous investigation on the use of acidic methacrylates as coating agents could be found.

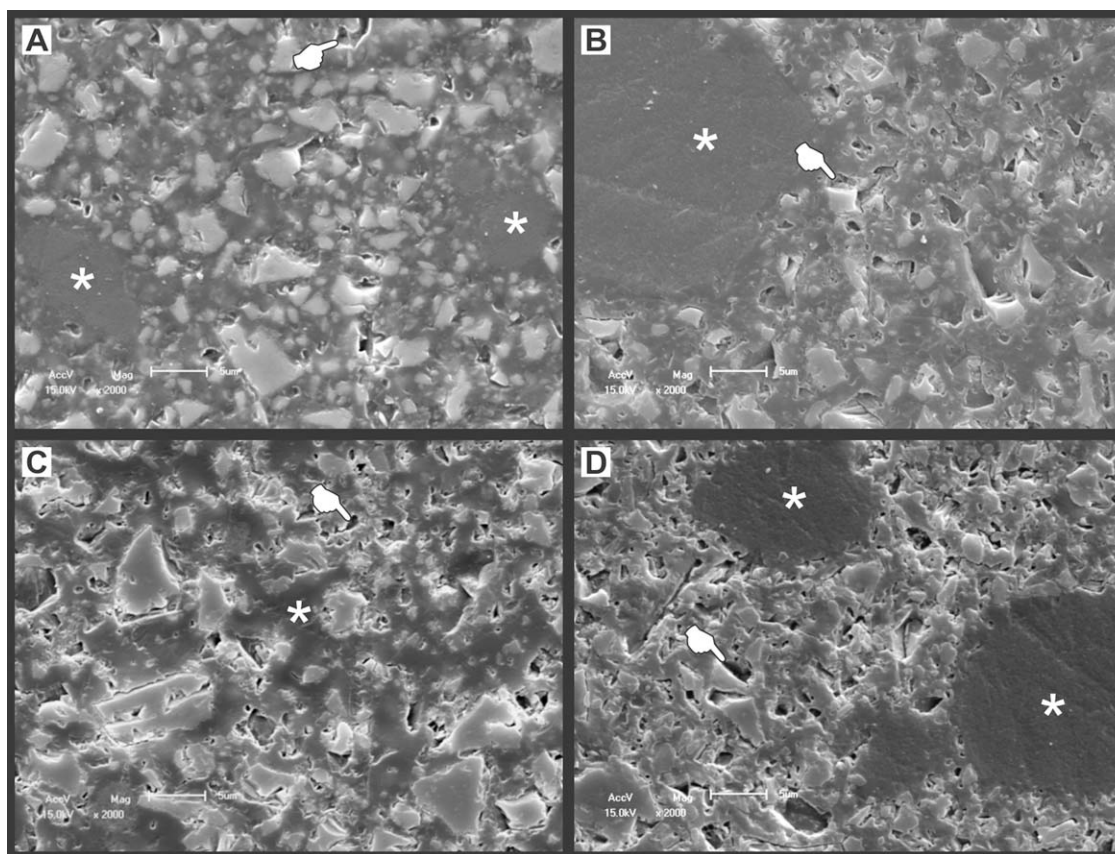


Figure 3. SEM pictures of the polished surfaces of the luting agents: TSPM (A), CAM (B), PAM (C), and Control (D). Asterisks indicate nanoparticle clustering; arrows indicate voids between the inorganic and resin phases owing to filler detachment during the polishing procedures.

Other studies have reported the beneficial effects of coating the filler particles with organo-silanes.^{3,21} This finding might be related to the fact that the bond of TSPM with the fillers relies on the formation of strong covalent siloxane bonds (Figure 1), whereas the interaction of the acidic methacrylates with fillers probably relies on a weaker ionic interaction between the acid and silanol groups (mechanism proposed in Figure 4). Comparing the results of the two functional monomers, the performance of CAM was better compared with PAM. The behavior of PAM was sometimes poorer compared with the Control group, with no coupling agent. One possible explanation for this result is that the PAM molecule has a non-reacted acid hydroxyl, which may render the monomer too acid even after coating, therefore interfering with the organic–inorganic coupling and impairing the properties of the luting agent.

The second null-hypothesis is also rejected, as voids due to filler detachment were more evident and frequent for the groups Control and PAM, suggesting poorer interaction between the inorganic and organic phases. This poorer interaction may be another cause of the deleterious effects on flexural properties and hardness observed for PAM. The lower mechanical strength observed for PAM is, however, in contrast with the findings for filler agglomeration, which was less pronounced. Particle clustering is expected to contribute to low mechanical properties because poorly connected areas may serve as spots for stress

concentration or magnification during mechanical loading. However, the present results indicate that filler agglomeration alone cannot explain the different properties observed for composites formulated with distinct coupling agents, as the material with less filler agglomeration showed the poorer mechanical properties. This is probably related to alteration in the attractive forces between the particles associated with the use of different coating materials affecting particle diffusivity and dispersability into the comonomer. The group TSPM showed the best results for all mechanical conditions; this result, in addition to the SEM analysis, indicates a better filler–resin interaction when TSPM was used as coupling agent.

During the mixing of the luting agents, variations in the interfacial chemistry caused noticeable differences in how readily the fillers could be incorporated into the resin, as well in the final consistency of the pastes. Potential increases in filler loading in composite pastes have been associated with variations in the particle surface chemistry and subsequent changes in particle–particle and particle–resin interactions.²² A significant reduction in the surface pH has been described when a silica-based ceramic was treated with acid, indicating an increase in the concentration of H^+ ions in the surface.²³ When the acidic methacrylates were used, it is possible the same effect occurred, hindering the incorporation of the fillers. As the acidity of the acidic monomers is defined by their dissociation constants ($pK_a = 10^{-5}$

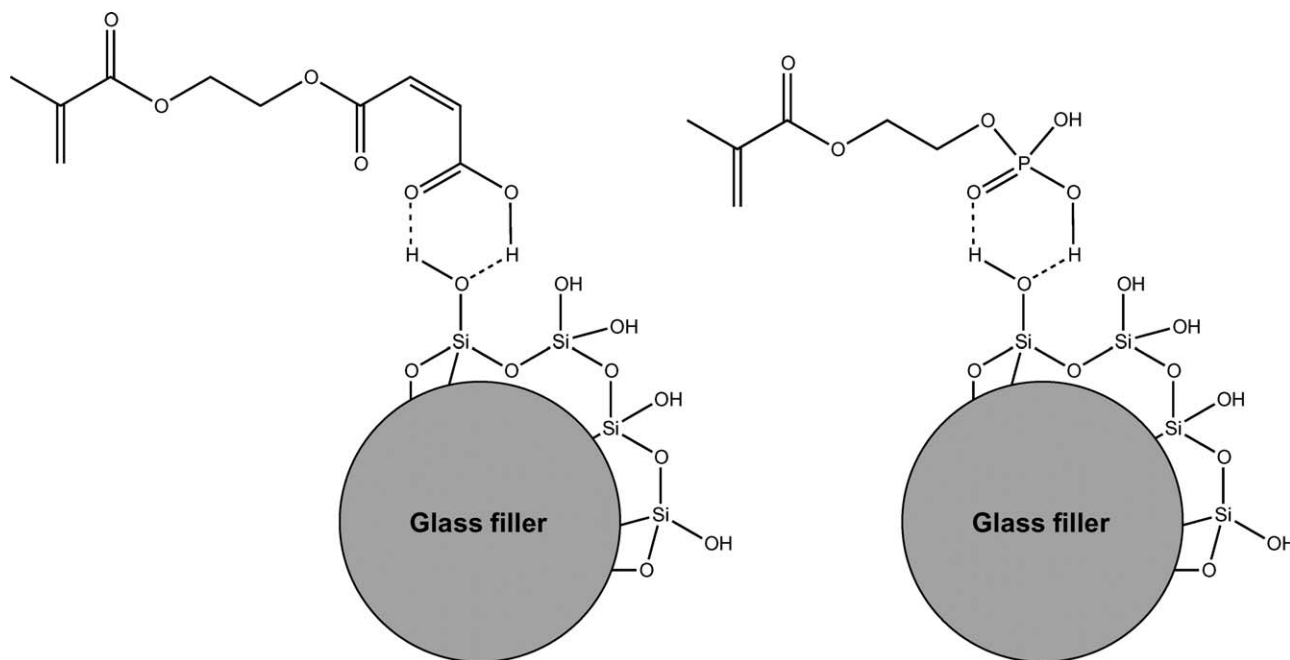


Figure 4. Proposed mechanisms for the bond between the carboxylic (A) and phosphoric (B) acid methacrylate monomers and the glass fillers based on an ionic interaction between the acid and silanol groups. Note the nonreacted phosphoric acid hydroxyl in B.

for CAM, and 10^{-3} for PAM),¹⁹ the lower pH of PAM may have enhanced this effect, causing a polarity incompatibility. A previous study have indeed described that CAM and PAM derivatives may show distinct bonding performances to metal oxides.¹³

The coating material used also influenced the FT. The lower FT for TSPM may be a result of the better wettability of the TSPM-coated particles within the resin phase. The use of silanes has been associated with a reduction in the amount of comonomer needed to incorporate a given amount of inorganic filler and obtain a given consistency.^{2,3} However, the results for FT did not follow the same trend for mechanical data; the FT for the group CAM was higher than for the Control luting agent. This finding suggests filler–resin interactions other than the wettability of the particles solely also contribute to the resulting FT of the material. Alteration in material thixotropy is another potential effect that may interfere with FT.

The data from the different tests and SEM images suggest that resin–particle interaction and their interface have a significant impact on properties of particulate resin-luting agents. Under stress loading, the connectivity of the filler with the polymer matrix is even more important than the ultimate strength of the polymer, as a good link may halt the crack propagation in the matrix surrounding the filler.²⁴ Interestingly, irrespective of the surface coating, clustering of nanofillers was always present. Although for some examples the mechanical properties of particle agglomerates can be relatively low,² the interparticle spaces are very small inside the clusters. Therefore, provided that strong connective forces between the nanofillers themselves and between the nanofillers with the resin are obtained,²⁵ these areas may have a protective effect in the structure. Poor connective forces, on the other hand, may lead the clusters to act as spots

for stress concentration within the luting agent, impairing the mechanical properties.

Although the best results were observed for TSPM, the hydrolysis of the Si–O–Si bonds and of the ester linkage that serves as the silane–resin bond is a well-known phenomenon that is expected to weaken the polymer–filler interface during aging.⁷ Therefore, other filler treatments should still be evaluated. Different concentration of acidic monomers, acidic functionalities and perhaps the combined use of organo-silanes and acidic methacrylates could be investigated. In addition, in cases where the toughness rather than the strength of the luting agent is crucial, the use of acidic methacrylates might be an approach to tune the luting agent properties.

CONCLUSION

The use of organo-silane generated a resin-luting agent with properties generally improved as compared with the acidic methacrylates, with the carboxylic derivative showing better performance than the phosphate derivative. This finding is suggested to be a result of the nonreacted acid hydroxyl in the phosphate methacrylate molecule, which may render the monomer too acid even after the coating process.

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