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YbF_3/SiO_2 Fillers as Radiopacifiers in a Dental Adhesive Resin

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Abstract: The objective of this study was to evaluate the effect of functionalizing a dental adhesive resin with YbF_3/SiO_2 fillers for use as radiopacifiers. Particles of YbF_3/SiO_2 were obtained with the high-energy mechanical milling method and characterized by both physical and chemical methods. After characterization, the particles were sieved and silanized prior to being incorporated into an adhesive resin. The stability of the particle suspension was then evaluated. After light activation, the radiopacity, degree of conversion, flexural strength and elastic modulus were determined. The dental adhesive resins with 10 and 15 wt% of filler provided satisfactory radiopacity, while flexural strength and elastic modulus were not affected. The degree of conversion was statistically lower than that of the control ($p<0.05$). The method used for incorporating the tested ytterbium fluoride/silicon dioxide particles at concentrations of 10 and 15 wt% was shown to be feasible for the development of a radiopaque dental adhesive system.

Keywords: Radiopacifier; YbF_3/SiO_2; Dental adhesive resin; Composite

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Introduction

In dentistry, there have been a growing number of technological improvements in adhesive dental materials, which have become widely accepted as a result of their versatility in re-establishing the shape and function of restored teeth, with aesthetic results satisfactory to patients.

After placement, restorations should be monitored by clinical evaluations, using visual clinical inspection, radiographic exams and other diagnostic methods [1-3]. Although the composite resin should meet specific radiopacity standards in accordance with ISO and ANSI/ADA protocols [4], in most commercially available adhesive systems, the adhesive layer typically consists of a radiolucid material. This radiolucid material sometimes creates doubt, or leads clinicians to make false diagnoses of marginal gaps or secondary caries under restorations [5,6].

Dental adhesives are low viscosity composites characterized by their dimethacrylate monomer content, with low density chemical elements, such as carbon, hydrogen, nitrogen and oxygen [7]. Because radiopacity is provided by elements with high density, the addition of metal oxides with a high atomic number [8,9] is one approach to solve this problem.

However, the dispersion and stabilization of particles in suspension in a low viscosity resin represents a challenge for adhesive system development. The agglomeration of particles could cause phase separation, and the consequential loss of homogeneity in the resul-

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tant material may impair the degree of conversion and mechanical strength resulting in fractures in the hybrid layer [10,11].

The addition of silica nanofillers has been shown to produce mechanical improvements in polymers and stabilize suspensions [12]. This is partly due to the ability of silica to react with a silane agent, which in turn will promote resin-filler coupling and minimize particle-particle interaction [11], facilitating spreading. Unfortunately, silica cannot provide radiopacity or the tailored refractive index used for optimal dental composite translucency [13]. On the other hand, some elements known to be radiopaque do not have a well-established mechanism of silanization [14].

Therefore, mixed oxides with adjustable properties, such as BaO/SiO_2 [8], Ta_2O_5/SiO_2 or Yb_2O_3/SiO_2 [9], have been investigated [14] in an attempt to produce a material capable of providing radiopacity and simultaneously interacting with the resin matrix.

In addition to the improvements that can be obtained by incorporating radiopacifier fillers, the mechanical and chemical properties of the adhesive resin, such as the degree of conversion and mechanical strength, can also be modified. Thus, the aim of this study was to evaluate the effects of using milling-modified YbF_3/SiO_2 fillers as radiopacifiers in a dental adhesive resin model.

Materials and methods

Functionalization of particles

The YbF_3/SiO_2 particles were obtained by combining YbF_3 (Stanford Materials, Aliso Viejo, USA) and SiO_2 (Aerosil 380, Evonik Degussa GmbH, Weiss-Fraunenst, Germany) with mechanical milling. This process was performed using a high energy mill (PE 075, Netzsch, Pomerode, Brazil) containing polishing spheres of zirconia (Ø=2 mm) at a speed of 50 rpm for 2 h. Isopropyl alcohol was used as a lubricant. The resultant powder was dried at 50℃ until the solvent had completely evaporated.

The elementary chemical analysis of these particles was performed by energy dispersive X-ray spectroscopy (EDX; Shimadzu EDX-720, Shimadzu, Kyoto, Japan). The microstructure was characterized by scanning electron microscopy (SEM; Shimadzu SSX 550, Shimadzu, Kyoto, Japan) at 15 kV. X-ray powder diffraction (XRD; Shimadzu XRD-6000, Shimadzu, Kyoto, Japan) with Bragg $\theta/2\theta$ geometry, equipped with a graphite monochromator and using Cu Kα radiation, was utilized for the crystal structure determination. The specific surface area (SSA) was determined by the BET method (forty-point isotherm, $0.01<p/p_0<1.0$), and the pore size/volume was calculated by the BJH method with N_2 adsorption at 77K (Autosorb-1C, Quantachrome Instruments, USA).

After characterization, the particles were sieved through a 150 μm opening, silanized with a 10 wt% solution of γ-methacryloxypropyltrimethoxysilane (γ-MPTS Aldrich Chemical Co., Milwaukee, USA) in ethanol (Labsynth Ltda., Diadema, Brazil) and stored at 37℃ for 24 h until the solvent was completely evaporated. The resulting material was filtered again through sieves with 30 and 150 μm openings.

Adhesive resin formulation

The experimental adhesive resin was formulated by mixing the monomers 2, 2-bis[4-(2-hydroxy-3-methacryloyloxypropyl) phenyl]-propane (Bis-GMA-Esstech Inc., Essington, USA), 2-hydroxyethyl methacrylate (HEMA-Sigma Aldrich, Steinheim, Germany) and triethylenoglycol dimethacrylate (TEGDMA-Esstech Inc., Essington, USA) in a 50/25/25 wt% ratio. A binary light-curing system, composed of 0.4% camphorquinone (CQ) (Esstech Inc., Essington, USA) and 0.8% ethyl 4-dimethylaminebenzoate (EDAB) (Fluka, Milwaukee, USA), was added to the mixture to obtain light-activated material. The reagents were used as received without further purification.

Five experimental groups were formulated, in which the composition varied depending on the type of constituent particles (Resin 0%: without fillers; Yb:YbF_3; Si:SiO_2; YbSi:YbF_3/SiO_2 mixed without milling and YbSiM:YbF_3/SiO_2 obtained after the mechanical milling process).

These particles were incorporated into the adhesive resin in microtubes, followed by sonication for 15 min (CBU 100/1LDG, Plana TC, São Paulo, Brazil) and mechanical agitation for 3 min in an amalgamator for capsules (Dosamix, Dabi Atlante, Ribeirão Preto, Brazil), to promote dispersion of the fillers and complete mixing of the phases.

For each group, four different concentrations of load particles (wt%) were selected, according to the comparison to be carried out in the X-ray study (Yb and Si groups: 0.5%, 2.5%, 5% and 7.5%; YbSi and YbSiM groups: 1%, 5%, 10% and 15%).

In the YbSiM group, the YbF_3 content in the powder was previously determined by a pilot study ranging between 5-87 wt% and finally established at 50 wt% considering the stability of the suspended particles in the adhesive resin and the degree of radiopacity provided. The same proportion was used for the YbSi group.

Precipitation study

To evaluate the particle stability (suspension) in monomers, groups without a light activation system were placed in transparent microtubes at ambient temperature (∼20℃) and visually observed every 10 min during the first hour and once every 30 min during the subsequent 9 h. Readings were then taken every 24 h during the first seven days.

Radiopacity

Specimens measuring 5.0 mm in diameter with a thickness of 1.0±0.01 mm were produced using a silicone-based mold. Four specimens were made for each experimental group, totaling 64 samples. The specimens were light-cured for 20 s on each surface using a LED light-curing unit (Radii®, SDI, Bayswater, Australia) with an irradiance of 1400 mW/cm^2, as measured by a power meter (Ophir Optronics, Danvers, USA).

After mold removal, the thickness of the samples was measured with a digital caliper (Digimatic Caliper, Mitutoyo, Japan), and the above-mentioned measurements were verified in accordance with ISO 4049/2000 [4].

The specimens were divided into four groups, each containing a sample of each material, and placed in a periapical InSight film (Kodak, USA). An aluminum scale measuring 20×10 mm (10 steps, varying 0.5 mm per step, with an Al purity of 99.6%) and samples of human enamel and dentin (of the same thickness as the specimens) were used as the parameters for radiographic comparison. The set was fixed in an acrylic support, which was developed to standardize the focus-film distance at 40 cm with a 90° angle and irradiated with 0.4 s exposures in an X-ray device (Spectro 70X Seletronic 70 kV/8 mA, Dabi Atlante, Ribeirão Preto, Brazil). Five radiographs were taken of each group. Processing performed shortly thereafter, and the digital images of the films were obtained with the aid of a scanner at a resolution of 500 dpi (Artixscan 1100, Microtek, USA).

The relative radiopacity densitometry was measured by pixel analysis using Image J software (version 1.42q, National Institutes of Health, U.S.A.). Of the five X-rays taken, the three that had the most standardized images were selected, based on the pixel analysis of the areas on which the samples were not superimposed, which were situated at the right and left edges of the film. Three points in each sample were measured, and their mean value was used. The data were submitted to statistical analysis.

The samples of human enamel and dentin were acquired from the tooth bank of the School of Dentistry, Federal University of Pelotas, after obtaining prior approval from the Research Ethics Committee of the university.

At this point, only experimental groups that were approved in previous tests were selected for the other trials, i.e., those that simultaneously presented stability in suspension and radiopacity.

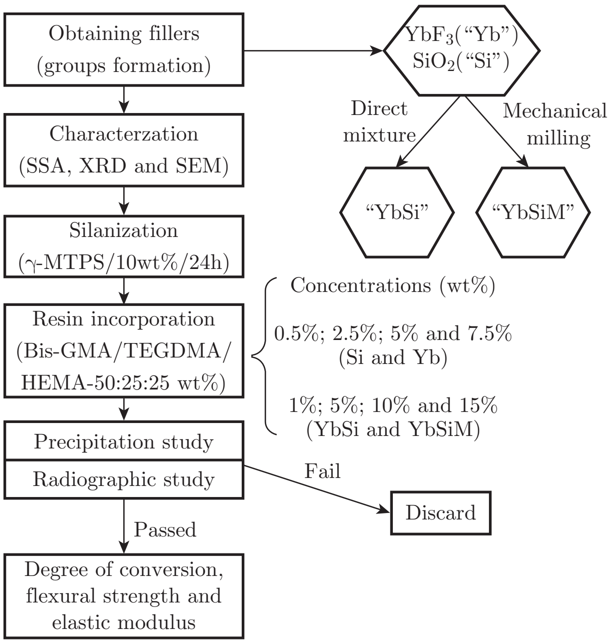

Fig. 1 Study overview.

Degree of Conversion

The degree of conversion (DC) of the experimental materials was evaluated using real-time Fourier Transform Infrared Spectroscopy (FTIR) in a Shimadzu Prestige-21 spectrometer (Shimadzu Corporation, Kyoto, Japan) equipped with an attenuated total reflectance device, which was composed of a horizontal ZnSe crystal with a 45° mirror angle (PIKE Technologies, Madison, USA). A support was coupled to the spectrometer, which fixed the light-curing unit in place and standardized the distance between the fiber tip and sample at 5 mm. Analysis was performed at a controlled room temperature of 23°C (± 2°C) with 60% (±5%) relative humidity. The sample (∼3 µl) was dispensed directly onto the ZnSe crystal, and the spectra of the uncured and cured (after 40 s of photo-activation) resins were acquired at a frequency range of 1700-1575 cm^{-1} with 12 scans at 4 cm^{-1} resolution in absorbance mode. The degree of conversion was calculated for the polymerized and unpolymerized samples, as described in a previous study [15], by considering the intensity of the carbon–carbon double bond stretching vibration (peak height) at 1635 cm^{-1} and using the symmetric ring stretching at 1610 cm^{-1} as an internal standard. Five samples of each material were analyzed.

Flexural strength and elastic modulus

The specimens (n=10), measuring 10.0 mm long ×2 mm wide ×2 mm thick, were fabricated using a stainless steel matrix. The adhesive resin was placed in the mold, and a strip of acetate was placed on the sample. The top and the bottom surfaces were light cured along their entire extension by two 20 s exposures on each side while still in the mold. The specimens were removed from the mold, polished and stored in distilled water at 37±1℃ for 24 h. The load test was conducted in a universal testing machine (EMIC® DL 500, São José dos Pinhais, Brazil) using a 100-N load cell with a crosshead speed of 0.5 mm/min until fracture. The flexural strength (σ) and elastic modulus (E) of each specimen were calculated and expressed in Mpa and GPa, respectively.

One-way analysis of variance (ANOVA), followed by Tukey's test, were used to detect statistically significant differences between groups (α=5%).

Results and discussion

EDX analysis identified the presence of YbF_3 and SiO_2 in the nanocomposite after high-energy mechanical milling. Figure 2 shows the characteristic peaks in the emission energy spectra of these elements.

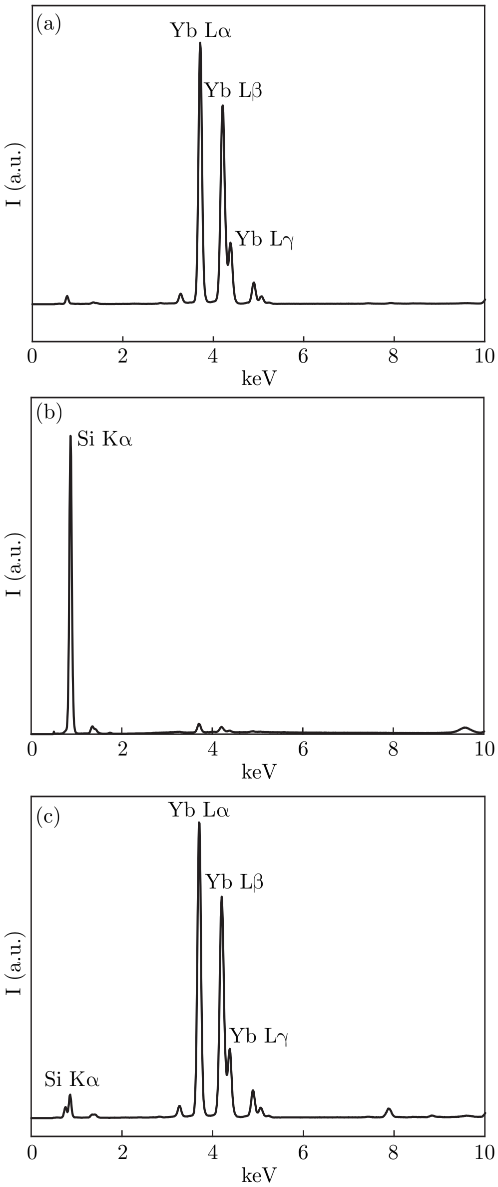

Fig. 2 EDX analysis of the (a) SiO_2, (b) Yb and (c) YbSiM groups.

Figure 3 shows typical XRD patterns for the SiO_2, YbF_3 and YbF_3/SiO_2nanocomposites. The profile analysis also shows that the silica and YbF_3 phases are in the amorphous and crystalline state, respectively. The YbF_3/SiO_2 nanocomposite system showed a cubic structure (JCPDS 74-2178) similar to that of YbF_3. The crystallite size of YbF_3 and the YbF_3/SiO_2 nanocomposite were determined using the Scherrer equation (15-17). In this study, the diffraction peak profile was fitted using a pseudo-Voigt function to calculate the full-width at half-maximum (FWHM). This analysis revealed particle sizes of 19.14 and 6.24 nm for the YbF_3 and the YbF_3/SiO_2 nanocomposites, respectively. This suggests a significant difference in the crystalline structures of the nanocomposites processed by high-energy mechanical milling (HEMM). These results indicate that the amorphization process is related to the decrease in the crystallite size [18].

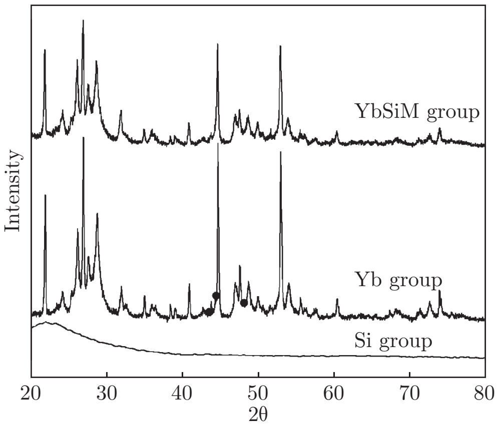

Fig. 3 XRD results of the samples.

Table 1 Specific surface area (SSA), average poro diameter (d_{pore}) and pore volume (V_p) determined by N_2 adsorption at 77 K (BET and BJH method)

Groups	SSA ($m^2 \cdot g^{-1}$)	d_{pore} (nm)	V_p($cm^3 \cdot g^{-1}$)
Si	365.7	18.5	0.9863
Yb	12.0	29.8	0.0437
YbSiM	134.6	16.9	0.6478

Figure 4 shows the N_2 adsorption/desorption isotherms obtained for SiO_2, YbF_3 and the YbF_3/SiO_2 nanocomposites. These results show a typical type II isotherm representative of a mesoporous material. Table 1 shows the specific surface area (SSA), average pore diameter, and pore volume determined by N_2 adsorption of the different samples at 77 K. An improvement

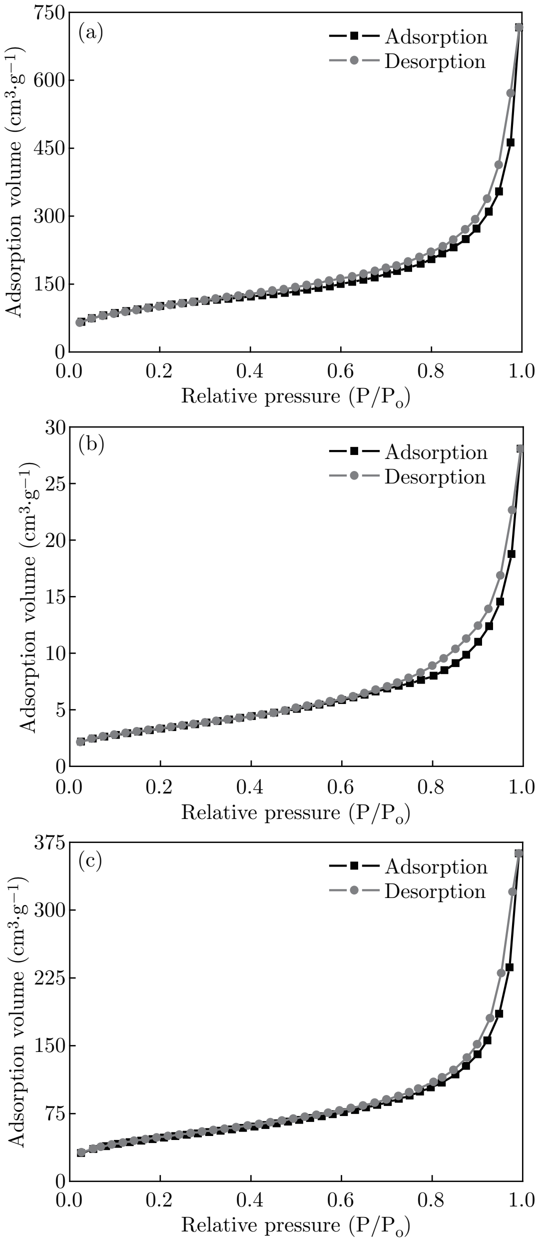

Fig. 4 Isotherms of adsorption-desorption of the (a) Si, (b) Yb and (c) YbSiM groups.

in the SSA may be associated with the mechanical milling process (16-18).

The SEM micrographs, shown in Fig. 5, clearly demonstrate a reduction in the size of the YbF_3/SiO_2 particles when compared with YbF_3, but with the formation of several agglomerations of particles.

Through visual analysis, for the functionalization of dental adhesive resin with YbF_3/SiO_2 fillers as radiopacifier, the groups containing only Si (Si), or Si combined with Yb by high energy mechanical milling (YbSiM) did not settle out of the dispersion and were stable throughout the seven days of evaluation. Precipitation was observed in the other experimental groups.

The relative radiopacity densitometry values (pixels) are shown in Fig. 6. The values for the groups containing >2.5% YbF_3 (except the 5% YbSiM group) were similar to those for the control (Al thickness of 0.5 mm), whereas the values for groups containing only silica or <2.5% YbF_3 were statistically lower than those of the control. The opposite result was observed when compared with the negative control (composite without fillers). Comparisons with 1.0 mm dentin thickness showed that all of the experimental groups tested had statistically lower radiopacity.

Based on these results, only the groups with 10% YbSiM and 15% YbSiM satisfactorily met the requirements and were submitted to the subsequent tests.

The results for the degree of conversion, flexural strength and elastic modulus are expressed in Table 2. One way ANOVA revealed no significant differences between the flexural strength and elastic modulus of the experimental groups and the control. Differences were found in the degree of conversion, as the addition of particles was found to slightly decrease these values.

In this study, the preparation of YbF_3/SiO_2 by high-energy mechanical milling, which is a well-known process used in the preparation of nanostructured metals and alloys [16], was shown to be successfully employed for the processing of ceramic materials.

Despite the ease of implementation, this technique requires optimization of a number of variables to achieve the desired product phase and/or microstructure, such as milling speed, milling time, type/size and size distribution of the grinding medium, process control agent (solvent/lubricant), and other parameters [17]. However, once these factors have been controlled, the simple execution and low cost of this method make it attractive for processing nanostructured materials [18,19]. Additional advantages of the milling process are that the particle and crystallite size can be successfully varied through the choice of milling parameters, and large amounts can be produced [20].

The analysis performed in the characterization of the YbSiM group particles showed some improvements when compared with the use of pure silica (amorphous).These improvements were in relation to the elementary precursors, such as the formation of a crystalline phase. There was an increase in specific surface area (134.6 m^2/g) in comparison with the Yb group (12.04 m^2/g), but a decrease when compared with the Si group (365.7 m^2/g). In contrast, there was better homogeneity and a significant increase in the average pore diameter of the synthesized sample, which most likely allowed better interaction with the resin, mediated by the silane agent, and agrees with the results observed in the precipitation study.

Incorporating charged particles into an adhesive resin in a dispersed and stable way is difficult due to its low viscosity. Therefore, the experimental adhesive resin was prepared without the use of solvents such as

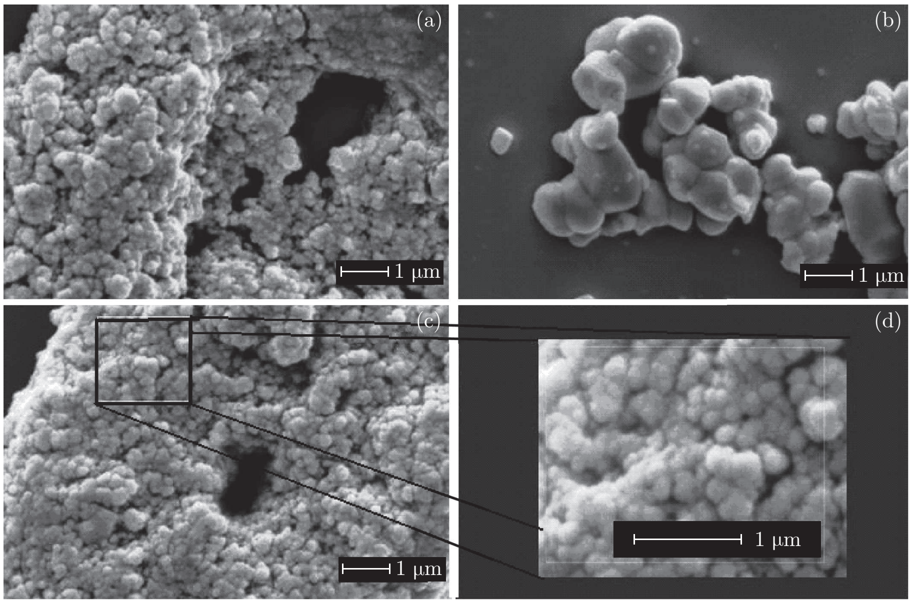

Fig. 5 SEM analysis of samples of the (a) Si, (b) Yb and (c) YbSiM groups. Inset shows detail of a selected area in the (d) YbSiM group.

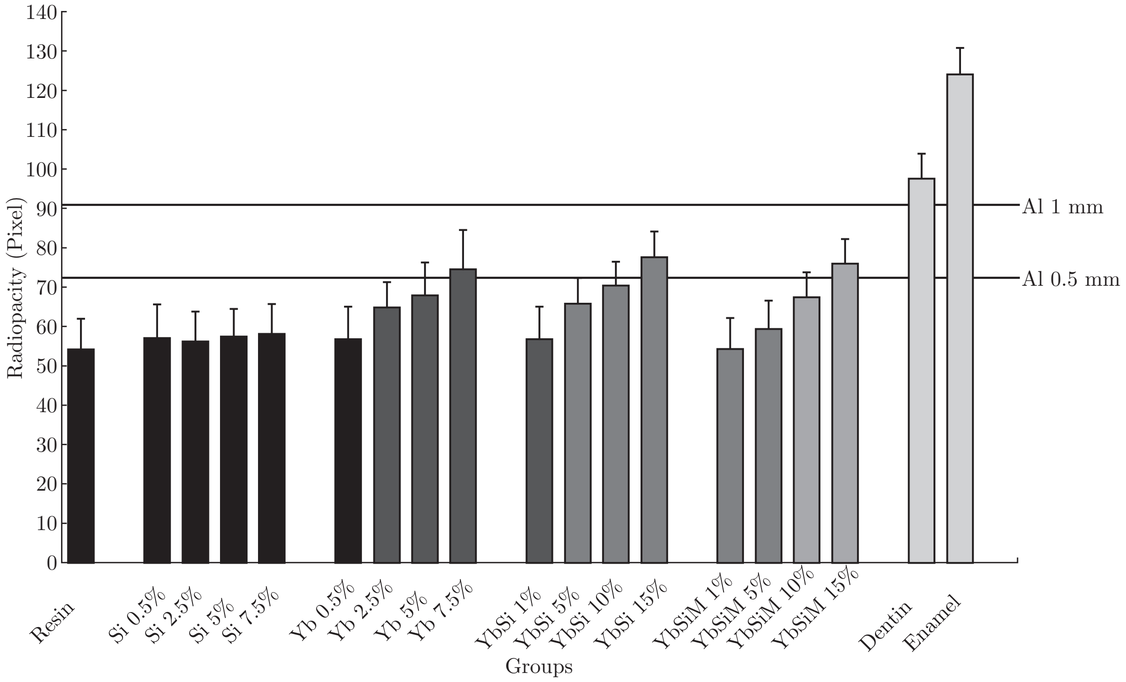

Fig. 6 Radiopacity density, in pixels, of the experimental adhesive groups evaluated with different fillers as the radiopacifier. Identical colors represent statistically similar results according to the Bonferroni t-test.

Table 2 Degree of conversion (DC), flexural strength (σ) and elastic modulus (E) means ± standard deviation for 10% YbSiM, 15% YbSiM and 0% resin

Groups	DC(%) (n=5)	σ (MPa) (n=10)	E (GPa) (n=10)
Resin 0%-Control	66.90 (±0.99) a	70.93 (±8.96)	0.92 (±0.14)
YbSiM 10%	59.70 (±3.52) b	72.82 (± 14.15)	1.01 (±0.11)
YbSiM 15%	60.38 (±1.36) b	64.40 (±14.00)	0.97 (±0.09)

Legend: Different letters after the average values represent statistically significant differences ($p<0.05$). No statistically significant differences were detected between groups for flexural strength and degree of conversion.

acetone or ethanol, which decrease viscosity [21]. This was allowed the stable incorporation of the filler but still maintained the relatively low viscosity provided by low molecular diluent monomers -HEMA and TEGDMA- which would enable it to be used, for example, as the bond resin of a two-step self-etching adhesive system.

Stabilization and surface modification of the metal oxides (filler) is crucial and was not achieved as easily as with silica [22]. The results of the precipitation study showed the ability of silica to stabilize in suspension (Si group) as well as the inability of YbF_3 to stabilize on its own (Yb group) or in the presence of only silica in the absence of a strong link between them (YbSi group). In this group, YbF_3 precipitation was easily observed due to differences in the particle colors, which did not occur in the YbSiM group, which exhibited stability. These results suggests that HEMM had an effect on the modification of these particles, most likely establishing a link between them in which, theoretically, the interaction of silica with the silane agent was able to maintain particle suspension during the observed period.

This stability is important to prevent the deposition of particles in the bottle during the storage period and, more importantly, during the quick precipitation between applications, which would require constant and efficient manual shaking. Moreover, phase separation would eventually affect radiopacity and potentially lead to a diagnostic error in further radiographic follow-ups. Furthermore, it would make the resulting material in the bottle increasingly viscous, hindering close contact with the tooth substrate, which is required to obtain the hybrid layer, consequently decreasing the bond strength.

Once stabilization was achieved, the radiopacities of the materials were evaluated. The concentration of the groups with a mixture of SiO_2 and YbF_3 (YbSi and YbSIM groups) was twice that of the groups containing only one of these elements (Si and Yb groups), suggesting an equal participation of each in the degree of radiopacity. The possibility of HEMM interfering with this characteristic could also be evaluated by means of a comparison between the YbSi and YbSiM groups.

Based on the results presented in Fig. 6, the radiopacity of pure silica is very low (Si group), verifying that YbF_3 is responsible for this feature (Yb group). The presence of silica and HEMM did not cause this type of interference because the radiopacity of the YbSi and YbSiM groups was almost the same as that of the group containing this element in the pure form (Yb group).

In the initial stages of this study, the groups of interest were selected according to their stability in suspension and radiopacity. Thus, only the groups with 10% and 15% YbSiM were selected. The degree of conversion (DC), flexural strength and elastic modulus of the resin were evaluated, and only the degree of conversion was significantly different when compared with the control group (resin without filler). This effect can be investigated by the incorporation of the particles into methacrylate monomers [11] and can be attributed to the fact that the fillers may act as light scatterers, hindering light penetration at depth, especially particles with a size that approaches the output wavelength of the light-curing unit [23]. In this study, although the addition of particles reduced the DC, the values remained at approximately 60%, which can be considered acceptable because dental composites possess a DC ranging from 43 to 75%, depending mainly on the composite composition, irradiation intensity and exposure time [22,24].

The incorporation of inorganic particles is a well-established mechanism for reinforcing polymer-based materials, as observed in studies in which the addition of nanofillers to polymer matrices improved the mechanical properties of the resulting composites [12,25,26]. However, for the results of the mechanical tests of flexural strength and elastic modulus in this study, no significant differences were found in comparison with the control group (Resin 0%).

Kemp-Scholte and Davidson have reported that thick layers of adhesive show a higher elasticity, improving the ability to withstand the stress caused by composite shrinkage during setting and additional mechanical challenges imposed on the restoration by oral dynamics as well as maintaining the proper position [26]. Labella *et al.* affirm that a thicker layer can be obtained with the addition of fillers but speculate regarding whether the increased rigidity caused by these particles could affect their ability to act as elastic buffers [10].

Thus, the following question arises when considering radiopacity: will an increase in the thickness of the adhesive layer make it even easier to confuse it with a radiographic secondary carious lesion? If the addition of particles does indeed provide an improvement in the mechanical properties and adhesion durability, it is important that these characteristics are accompanied by radiopacity, so that the durability achieved will not be interrupted, erroneously leading to a diagnosis that will require the premature and unnecessary replacement of the restorative material.

Although the radiopacity of the 15% YbSiM group did not reach 1.0 mm of Al, it was shown to have a value higher than (but statistically similar to) 0.5 mm of Al. Moreover, it was clearly observed in the radiographic examinations performed and easily distinguishable from the radiolucent area (dark background), which resembles the dark halo present in cases of secondary carious lesions. When compared with the negative control (which had minimal contrast with the radiolucent area), the radiopacity of the 15% YbSiM group was significantly higher. It should be noted that high radiopacity is not always desirable because the material can end up masking carious lesions, as occurs with amalgam [6,28].

Conclusions

The results presented herein demonstrate the possibility of a single and feasible method to obtain a polymer composite, as well as the incorporation of the tested ytterbium fluoride/silicon dioxide particles by high energy mechanical milling at concentrations of 10 and 15 wt%, for use as a radiopacifier in a model dental adhesive resin. A long observation period and the inclusion of more variables, such as temperature and storage conditions, are needed to verify that the particles are completely stable, in order to examine the potential for future clinical application of the material.

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