Tantalum oxide as filler for dental adhesive resin

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The purpose of this study was to formulate and evaluate an adhesive resin with tantalum oxide. Ta_2O_5 was evaluated by scanning electron microscopy and laser diffraction. The adhesive was formulated with methacrylate monomers and photoinitiators. Ta_2O_5 was added into the adhesive at 1, 2, 5 and 10 wt%. One group remained without filler (control group). Ta_2O_5 distribution, radiopacity ($n=5$), degree of conversion (DC) ($n=3$), softening in solvent ($n=5$) and ultimate tensile strength (UTS) ($n=10$) were evaluated. Data were analyzed by one-way ANOVA and Tukey's test ($\alpha=0.05$). Spherical nanometric Ta_2O_5 was arranged in 3.35 μm particles. The groups over 5 wt% presented higher radiopacity ($p<0.05$). The DC ranged from 61.78 (± 1.19)% to 67.35 (± 1.40)%, with statistical difference from control group over 5 wt% addition ($p<0.05$). There was no difference in softening in solvent ($p>0.05$) and UTS ($p>0.05$). Tantalum oxide is a promising alternative for adhesive formulation and it could be further tested for biomimetic remineralization.

Keywords: Dental cements, Inorganic compounds, Tantalum oxide

INTRODUCTION

The wet environment of the dentin is adverse for the polymerization of methacrylate monomers, promoting an interface susceptible to degradation over time^{1,2}. In addition, an adequate cavity seal is necessary to inactivate the residual bacteria in affected dentin to stop caries progress in a minimally invasive dentistry approach³. Many modifications have been proposed in the adhesive resins to contribute to the longevity of the restorative treatments⁴⁻⁶. A current trend involves the incorporation of inorganic fillers to decrease the relative amount of organic phase, providing a higher hydrolytic stability to resin and a reliable cavity seal⁷⁻¹².

Besides physical and chemical properties, the addition of inorganic fillers may increase the radiopacity. A radiopaque adhesive resin promotes more accurate diagnosis by clinicians and the distinction of recurrent caries from restorative material¹³. The most used filler in commercial adhesives is silicon dioxide (either colloidal silica or pyrogenic silica)¹⁴. However, silica is radiolucent and must be supplemented with metal-containing glasses or minerals to be radiopaque^{14,15}. Nevertheless, glasses are susceptible to hydrolysis and degradation. To eliminate the use of glasses, one solution is to use heavy-atom compound as homogeneous filler in matrix¹⁵. Ytterbium trifluoride (YbF_3)¹¹, barium sulphate ($BaSO_4$), calcium tungstate ($CaWO_4$)¹⁶ and niobium pentoxide (Nb_2O_5)^{8,10} have been used. However, the incorporation of the inorganic filler needs to be in low concentrations in order to not compromise the wetting of the dental substrate due to high viscosity of the resin while it is possible to increase the radiopacity and mechanical properties of the material¹⁴.

Tantalum is known to be a radiopaque element¹⁷ and a biocompatible material^{10,18}. Furthermore, tantalum

metal showed bioactivity^{19,20} and affinity to phosphate groups²¹, enabling the deposition and nucleation of apatite on its surface. Tantalum oxide also showed bioactivity, inducing hydroxyapatite growth and osteoblasts attachment²¹. Tantalum oxide and metal alloys with tantalum have been used in medicine¹⁸ and in dental fields²²⁻²⁶ due to properties as high fracture toughness and high workability²⁰. Therefore, it has been studied and it was incorporated in polymer-based materials to dentistry^{15,27}. However, to the best of our knowledge, there are no reports on the use of pure tantalum oxide (Ta_2O_5) in adhesive resins. The purpose of this study is to develop an experimental adhesive resin with Ta_2O_5 in different concentrations and evaluate the radiopacity, degree of conversion (DC) and ultimate tensile strength (UTS) of the formulated adhesive resin.

MATERIALS AND METHODS

Morphological analysis of Ta_2O_5

The morphological analysis of tantalum oxide was performed by scanning electron microscopy (SEM) (JSM 6060, JEOL, Tokyo, Japan). The powder of Ta_2O_5 was placed on metallic stubs and gold-sputter coated (15–25 nm) (SDC 050, Baltec, Vaduz, Liechtenstein). The equipment was configured to 8 kV, 10,000 and 20,000 $\times$ magnification.

Particle size of Ta_2O_5

The particles of tantalum oxide was dispersed in ultrasound for 10 s with isopropyl alcohol before the analysis. Particle size was assessed by laser diffraction (CILAS 1180, Cilas, Orleans, France) according to previous study²⁸.

Experimental adhesive resin formulation

The experimental adhesive resin was formulated mixing 50 wt% bisphenol-A-glycidyl methacrylate (Bis-GMA), 25 wt% triethyleneglycol dimethacrylate (TEGDMA) and 25 wt% 2-hydroxyethyl methacrylate (HEMA). Camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (EDAB) were added as photoinitiator system at 1 mol% to all groups, according to monomer moles and 0.01 wt% Butylated hydroxytoluene (BHT). All these materials were provided by Aldrich Chemical (St Louis, MO, USA). Ta_2O_5 was subjected to a silanisation process with 5% of silane (γ -methacryloxypropyltrimethoxysilane, Aldrich Chemical) and 95% of solvent (acetone), in weight. After the silanisation process, the particles were stored for 24 h at 37°C to allow the solvent vaporization. Ta_2O_5 powder was added at four different concentrations: 1, 2, 5 and 10 wt% into the adhesive resin and one group remained without filler addition as control group. All the components were weighed using an analytical balance (AUW220D, Shimadzu, Kyoto, Japan).

The mixture (resin/particles) was hand-mixed for 5 min, sonicated for 180 s and hand-mixed again for 5 min. To perform monomer photo-activation, a light-emitting diode unit (Radii Cal, SDI, Victoria, Australia) was used. An irradiation value of 1,200 mW/cm² was confirmed with a digital power meter (Ophir Optonics, North Andover, MA, USA).

Particle distribution analysis

Adhesive resin was inserted into a cylindrical silicon matrix with 5 mm of diameter, covered by a polyester film and photo-activated (Radii Cal, SDI) for 30 s on each side. The specimens ($n=1$) were placed on metallic stubs and gold-sputter coated (15–25 nm) (SDC 050, Baltec). The distribution of the Ta_2O_5 particles in the polymer was analyzed by SEM (JSM 6060, JEOL) using 3 kV.

Radiopacity

The radiopacity of adhesive resins was evaluated according to International Organization of Standardization (ISO) 4049/2009 standards. Five specimens were produced per group ($n=5$), 10.0 mm (± 0.5 mm) in diameter and 1.0 mm (± 0.1 mm) in thickness each one. Radiographic images were obtained using a phosphor plate digital system (VistaScan, Dürr Dental, Bietigheim-Bissingen, Germany) at 70 kV and 8 mA, with 0.4 s of exposure time and a focus-film distance of 400 mm. For each film, one specimen from each concentration was positioned, for a total of five specimens per film. An aluminium step-wedge was exposed simultaneously with the specimens in all images. The aluminium step-wedge thickness ranged from 0.5 to 5.0 mm in increments of 0.5 mm. The aluminium alloy used was Al 99.12, Fe 0.47, Mg 0.41 and with <0.1 of Cu (mass%). The images were saved in TIFF format and analyzed using Photoshop software (Adobe Systems Incorporated, San Jose, CA, USA). The mean and standard deviation of the grey levels (pixel density) was measured according to previous study⁷.

DC

DC of adhesive resins was measured by fourier transform infrared spectroscopy (FTIR) with a spectrometer (Vetrex 70, Bruker Optics, Ettingen, Germany) equipped with an attenuated total reflectance device (ATR), composed of a horizontal diamond crystal with a mirror angle of 45 degrees. A support was coupled to the spectrometer fixing the light-curing unit and standardizing the distance between the fiber tip and sample in 5 mm. Data was evaluated with the Opus software (Bruker Optics), with Blackman-Harris 3-Term apodization in a range of 4,000 to 400 cm⁻¹ and a resolution of 4 cm⁻¹. The sample (uncured composite) ($n=3$) was directly dispensed on the top of the diamond crystal and photoactivated for 20 s. The analyses were performed in a room at 23°C and 60% relative humidity. The absorbance spectra were obtained before and after polymerization. The DC was calculated as showed in a previous study²⁸.

Softening in solvent

Samples (5.0 mm in diameter and 1.0 mm thick) were prepared of each experimental adhesive resin ($n=5$) and light activated for 30 s on each side. The specimens was polished before Knoop microhardness (KHN) measurements. Three indentations were made (10 g for 5 s) in each specimen (HMV 2, Shimadzu) before (KHN1) and after immersion in a solution of 50% ethanol and 50% water mixture for 2 h (KHN2). The percentage difference between KHN1 and the KHN2 values were calculated ($\Delta\text{KHN}\%$).

UTS

The adhesive resins were dropped into a metallic matrix with a hourglass design measuring 8 mm long, 2 mm wide, 1 mm thick and a cross-sectional area of 1 mm² and were covered with polyester matrix on both sides before light activation. All specimens were light activated for 30 s on each side, after polymerization, specimens were measured with a digital caliper. Hourglass shaped specimens ($n=10$) were fixed in a specific device with cyanoacrylate adhesive and loaded under tension. Tests were performed in a test machine Shimadzu (EZ-SX; Shimadzu) at a crosshead speed of 1-mm/min. UTSs were calculated according to previous study²⁹.

Statistical analysis

The normality of data was evaluated using the Shapiro-Wilktest. Statistical data analysis was performed using one-way ANOVA and Tukey's test at the 0.05 level of significance ($p<0.05$) and paired student's *t*-tests were performed between KHN1 and KHN2.

RESULTS

The morphology of tantalum oxide is shown in Fig. 1. Nanometric tantalum oxide particles with spherical shape arranged in agglomerates were observed. The analysis of particle size of Ta_2O_5 by laser diffraction showed a median size of 3.35 μm . Images of distribution of the tantalum oxide particles in the polymer are presented in Fig. 2. The

Fig. 1 Representative image of tantalum oxide. Tantalum oxide particles have 300 nanometers size, spherical shape and are clustered in agglomerates of 5 micrometers.

Fig. 2 Distribution of the tantalum oxide particles in the polymer. a: Control group; b: 1% of Ta_2O_5 ; c: 2% of Ta_2O_5 ; d: 5% of Ta_2O_5 ; e: 10% of Ta_2O_5 ; f: Agglomerate of the tantalum nanoparticles of about 3 micrometers.

radiopacity values of the experimental dental adhesives are presented in Fig. 3. The density of pixels ranged from 26.06 (± 3.55) to 50.15 (± 4.97). The groups with 5 and 10 wt% of Ta_2O_5 showed higher radiopacity than the control group ($p < 0.05$). A representative image of the radiopacity of all groups is presented in Fig. 4. The DC of the experimental dental adhesives are shown in Table 1, values ranged from 61.78 (± 1.19) to 69.96 (± 18.67). There was no statistically significant difference between control and groups with until 2 wt% of Ta_2O_5 ($p > 0.05$). A representative image of FTIR spectra from adhesive before and after the photoactivation is shown in Fig. 5. Softening in solvent results are demonstrated in Table 2. The initial microhardness values (KHN1) were similar to the control group ($p > 0.05$). The values after immersion in ethanol were lower than the initial ones for all groups ($p < 0.05$). The percentage difference between KHN1 and KHN2 ($\Delta\text{KHN}\%$) showed no statistically significant difference between all groups ($p > 0.05$). Data of UTS ranged from 57.73 (± 14.67) to 65.15 (± 18.67),

Fig. 3 Means and standard deviations of radiopacity values, in pixels, for dental adhesive resins. The reference line shows the radiopacity, in pixels, for 1 mm Al. Different capital letter indicates statistical difference ($p < 0.05$).

Fig. 4 The X-ray images showing the difference of the radiopacity between groups.

Fig. 5 The FTIR spectra images of DC of polymers. The DC is determined by variation of peaks corresponding to aliphatic ($1,640\text{ cm}^{-1}$), aromatic ($1,610\text{ cm}^{-1}$) bonds of the monomer and de polymer.

Table 1 Means and standard deviations of DC and UTS of adhesive resins

Groups	DC (%)	UTS (MPa)
0%	69.96 (± 18.67) ^A	65.15 (± 18.67) ^A
1%	67.35 (± 1.40) ^{A,B}	57.73 (± 14.67) ^A
2%	65.16 (± 1.50) ^{A,B}	62.03 (± 11.47) ^A
5%	61.82 (± 4.21) ^B	61.67 (± 14.47) ^A
10%	61.78 (± 1.19) ^B	58.43 (± 11.07) ^A

Different capital letters indicate statistical difference in the same column ($p < 0.05$).

Table 2 Microhardness value of the model adhesives before (KHN1) and after immersion in solvent (KHN2) and the variation of microhardness values ($\Delta\text{KHN}\%$)

	KHN1	KHN2	$\Delta\text{KHN}\%$
0%	18.10 (± 0.97) ^{Aa}	7.52 (± 0.73) ^b	58.32 (± 4.80) ^A
1%	18.44 (± 2.57) ^{Aa}	10.62 (± 1.01) ^b	41.15 (± 12.61) ^A
2%	20.42 (± 2.04) ^{Aa}	10.42 (± 1.99) ^b	48.42 (± 10.83) ^A
5%	20.18 (± 1.56) ^{Aa}	11.38 (± 2.26) ^b	43.26 (± 12.07) ^A
10%	20.06 (± 1.32) ^{Aa}	10.90 (± 0.72) ^b	45.38 (± 6.28) ^A

Different capital letter indicates statistical difference in same column ($p < 0.05$). Different small letter indicates statistical difference in same row ($p < 0.05$).

and showed no statistically significant difference among groups ($p > 0.05$, Table 1).

DISCUSSION

The incorporation of inorganic fillers into polymers may

enhance adhesives' mechanical properties and improve the clinical practice^{5,7-11}. It decreases the composite's organic phase and the adhesives may be more hydrolytic stable, as the water sorption occurs mainly in the organic matrix²⁹. The adhesive resin must promote the distinction of the demineralized tissue (dentin or

enamel) and the restorative material^{1,9}. The addition of radiopaque fillers to adhesives should enable the assessment on radiographs without compromising the material properties¹¹.

The tantalum oxide particles were silanized with 5% silane (γ -methacryloxypropyltrimethoxysilane) and 95% solvent (acetone). Although there is no chemical silanization, the modification of filler surface can affect the rheology of the mixture, improving the wetting of the particles by the resin matrix^{30,31}. The analysis of particle size of Ta₂O₅ was performed by laser diffraction, which showed a median size of 3.35 μ m. However, it was observed by SEM that the particles presented nanometric size of about 300 nm and were arranged in bigger particles. The laser diffraction analysis showed the size of nanoparticle agglomerates while with SEM analysis it was possible to observe not only the morphology, but also the arrangement of Ta₂O₅. Nanoparticles are prone to agglomeration due to the increase in the surface energy²⁹. Although the nanoparticles's agglomeration demonstrated also in the polymers, there was no difference in the mechanical property evaluated by UTS or in the softening in solvent among the experimental groups.

Tantalum is a transition metal with high atomic number (73), factor involved in the radiopacity of the material. Since adhesive resins are made of organic compounds, there is a gap in the commercial adhesive formulations regarding to radiopacity. In this study, from 5 wt% there was significant difference from control group ($p < 0.05$), an adhesive resin similar to commercial adhesives¹⁴. With this amount, the radiopacity achieved 1 mm Al, value comparable to 1 mm of sound dentin³². Adhesives with higher radiopacity may support the clinician the observation of recurrent caries and restoration failures, improving the accuracy of diagnostics¹⁵. To replace the use of glasses in adhesive resins, tantalum oxide could be a heavy-metal alternative since it showed to enhance the radiodensity of the experimental adhesive resin.

The DC of the aliphatic carbon double bonds to carbon single bonds is related to improving the properties of the polymer^{33,34}. The addition of 5 and 10 wt% of Ta₂O₅ influenced the DC compared to control group ($p < 0.05$). However, all groups showed values above 50%, which is in agreement with the DC of the commercial adhesives in the literature^{35,36}. The addition of fillers in an adhesive resin may change the DC³⁷, due to the decrease of light transmission in the filled resin matrix. Thus, the availability of light in the resin matrix decreased because of the higher refractive index of the filler (2.09–2.15)³⁸ than the co-monomer blend (1.47–1.59 for monomer and 1.50–1.62 for polymer)⁸, leading to lower DC of the adhesive resin³⁹. Probably it explains the statistically significant difference observed when 5 and 10 wt% of Ta₂O₅ was incorporated. Although, the higher concentrations achieved satisfactory DC, the viscosity of the material may change due to filler addition and microtensile bond strength test is necessary to be accomplished.

Initial hardness values showed no statistical difference between groups, and all groups showed a statistical reduction after solvent immersion. A reduction of DC can influence the values of microhardness⁴⁰, however the Δ KHN% values showed no statistical difference in all groups, despite reduction of DC in the addition of 5 and 10 wt% of Ta₂O₅. This may have occurred due to the secondary interactions and cross-linking present in this materials that improve the microhardness, despite the difference of the number of C=C converted⁴⁰. With the addition of inorganic fillers there is a reduction of forces of attraction between polymer chains and solvent molecules²⁹. Thus, the addition of Ta₂O₅ can be improved material properties and the softening resistance, due to the inorganic fillers are less vulnerable to degradation than organic matrix⁴¹.

The incorporation of fillers in adhesive resin may increase of the UTS^{37,42} by decreasing the cracks propagation⁴³ providing obstacles at the crack front³⁷. However, the particle clustering formation may occur and it can potentially act as stress concentration site leading to a significant decrease in bond strength³⁹. In this study, through increasing concentration of Ta₂O₅ to 10 wt%, there was no difference in UTS values for all groups ($p > 0.05$). Thus, the addition up to 10 wt% was not enough to increase this propertie but it did not produce stress concentration sites, which may improve the performance of the material face to hydrolytic degradation and microtensile bond strength in future studies.

Tantalum oxide is a radiopaque inorganic filler with low toxicity^{10,18} and bioactivity²¹. These properties are very important once the adhesive resin has directly contact with mineralized tissues (dentin and enamel). Therefore, the experimental adhesive resins with Ta₂O₅ are suitable for further tests of bioactivity and biomimetic remineralization of collagen fibers and may be an alternative material to be used after selective caries removal.

CONCLUSIONS

In the present study, the addition of 5 and 10 wt% of Ta₂O₅ into an experimental adhesive resin increased the radiopacity ($p < 0.05$) and remained the DC compatible with commercial adhesives in literature, maintaining the UTS of the material ($p > 0.05$), the initial microhardness ($p > 0.05$) and the softening in solvent ($p > 0.05$) of the adhesives. Thus, Ta₂O₅ up to 10 wt% showed to be a reliable filler for adhesive resins according to the tested properties. Therefore, tantalum oxide is a promising alternative for adhesive formulation and it could be further tested for biomimetic remineralization.

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