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Functionalized pink $\text{Al}_2\text{O}_3\text{:Mn}$ pigments applied in prosthetic dentistry

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Abstract

Statement of problem—The color of dental polymethyl methacrylate (PMMA) is traditionally rendered by organic and inorganic pigments, which are usually not bonded to the polymer network. Functionalized ceramic pigments can be used to color PMMA allowing improved chemical interaction with the resin matrix.

Purpose—The purpose of this in vitro study was to synthesize, functionalize, and characterize pink manganese-doped alumina ceramic pigments. The hypothesis tested was that functionalized ceramic pigments would render pink coloration to a translucent PMMA without jeopardizing its mechanical properties.

Material and methods—Pink alumina powders doped with 1 mol% or 2 mol% of manganese ($\text{Al}_2\text{O}_3\text{:Mn}$) were prepared by means of a polymeric precursor method. Pigment particles were functionalized with a silica coating method followed by silanation before preparation of PMMA-based composite resins (5 wt% pigment). The color of composite resins (Fig.1% and Fig.2%) and PMMA controls (Pink and Translucent) was evaluated (CIELAB color coordinates), and their mechanical properties were tested (3-point-bending).

Results—The microstructure of the pigment particles showed approximately 55-nm nanocrystals of manganese-doped α -alumina clustered into irregular porous particles up to 60 μm . The composite resins and Pink PMMA showed similar color parameters (CIE a^* Pink=20.1, Pig. 1%=14.6, Pig. 2%=16.0, Trans=0.19 – $P<.001$; CIE b^* Pink=17.0, Pig. 1%=18.6, Pig. 2%=19.0, Trans=2.52 – $P<.001$). No statistical differences were observed in mechanical properties among groups (σ_f Pink=98.4, Pig. 1%=98.1, Pig. 2%=98.8, Trans=89.1 – $P=.136$).

Conclusions—The addition of the functionalized pink ceramic pigments to a translucent PMMA yielded similar coloration to that of the regular pink PMMA used in dentistry and did not jeopardize its mechanical properties.

INTRODUCTION

Shade matching plays an important role in the success of restorative treatments. For removable dentures, the artificial teeth and denture base should mimic the patient's original tooth features and gingival appearance.¹ Dental polymethyl methacrylate (PMMA) is available in various shades, which are yielded by the addition of oxide powders (titanium dioxide, iron oxide) and organic pigments. Determining which pigments to use and their quantities is a decision based on their optical properties, most importantly the pigment color,^{2–5} considering the wavelength range in which the light is reflected from the particles. The refractive index mismatch between pigment and resin matrix will also control opacity.⁶

The pigment powders are usually not functionalized to bond with the resin matrix.^{7–13} Therefore, the maximum quantity of inorganic pigment is limited to an amount which will not affect the material mechanical properties.^{14–17} Because of shrinkage associated with the material polymerization, a gap may be formed in the particle-matrix interface. These gaps and pores might act as stress concentration/magnification areas and reduce the load-bearing capacity of materials.^{18–20} Porosity also scatters light and reduces the material translucency.^{21–24} This limitation often makes necessary the combined use of organic pigment molecules.

The PMMA used in prosthetic dentistry may discolor over time.²⁵ Discoloration is associated with the sorption of extrinsic staining agents and more complex intrinsic processes: resin-based materials are subjected to hydrolytic degradation in the oral cavity.^{26–29} This process involves the oxidation and hydrolyses of organic components, including pigment molecules and polymerization promoters.^{30,31} The hydrolytic degradation of the polymeric matrix can lead to filler/pigment particle loss and/or degradation.^{26,32} Therefore, the use of functionalized well-bonded pigment particles^{33,34} could provide significant improvements. These include elimination of the porosity associated with nonbonded particles, reducing sorption of extrinsic staining agents and particle loss due to abrasion and the possibility of using a greater maximum quantity of inorganic pigment, thereby reducing or eliminating the need for organic pigments. Inorganic pigments prepared by doping crystalline ceramic powders^{2–4} are stable (almost inert) against chemical challenges, because with the dopant agent (chromophore centers) in solid solution within the crystalline lattice, their color does not change or fade over time.

This in vitro study was designed to synthesize, functionalize, and characterize pink manganese-doped aluminum oxide pigments and to prepare experimental PMMA-based composite resins by adding functionalized pigment particles to a translucent PMMA commonly used in prosthodontics. The hypothesis that functionalized ceramic pigments would render pink coloration to a translucent PMMA without jeopardizing its mechanical properties was tested.

MATERIAL AND METHODS

Pink alumina powders doped with 1 mol% or 2 mol% of manganese ($\text{Al}_2\text{O}_3\text{:Mn}$) were prepared by means of a polymeric precursor method. Manganese(II) nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) P.A. (lot # 1005002) and aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) P.A. (lot # DCBC5042) from Sigma-Aldrich were used to prepare the pigment powders. The powders were functionalized by immersion in a tetraethyl orthosilicate (TEOS) solution (Sigma-Aldrich, lot # STBC3383V) and heat treated for the deposition of a silica layer, followed by silanation with 3-(trimethoxysilyl)propyl methacrylate (Sigma-Aldrich). Pink nanocomposite resins were obtained by adding 5 wt% pigment powder in translucent autopolymerizing PMMA (JET; Clássico). Translucent and pink autopolymerizing PMMA (JET; Clássico) were used as controls. Therefore, 4 groups were tested: Pink, Pig.1%, Pig.2%, and Translucent (Transl.).

The nanostructured pigment powders were produced by using a variation of a previously described method.^{2,3,35,36} In this study, 0.01 M or 0.02 M manganese nitrate and 1 M aluminum nitrate were dissolved in water. Manganese/aluminum citrate forms by stirring in 3 M citric acid anhydrous (Sigma-Aldrich) at 50°C for 1 hour. Ethylene glycol (Sigma-Aldrich) was added at a 60:40 mass ratio of the citric acid/ethylene glycol. The mixture was further stirred at 80°C for 1 hour, and the temperature increased to 130°C to promote polymerization. The resin was heat treated in an atmospheric air furnace with a 10°C/minute heating rate up to 400°C dwell temperature for 1 hour, resulting in a solid black mass. This material was hand ground with a mortar and pestle. The resulting ground powder is referred to as the “precursor.” The precursor was heat treated at 10°C/minute up to 1200°C, dwelling for 2 hours in air. Various dwelling temperatures and times were also tested, resulting in pink-colored powders of distinct shades (data not shown here).

The morphology of the manganese-doped alumina particles was analyzed by scanning electron microscopy (SEM) (S3500N; Hitachi). Crystalline phases were determined by x-ray diffraction (XRD) (PANalytical X'Pert powder diffractometer) with $\text{CuK}\alpha$ radiation at 45 kV and 40 mA with a scan rate of 0.2 degrees/minute, 20 to 80 degrees, in the 2θ range, at room temperature. The average crystal size was calculated by using the Scherrer equation.³ To investigate whether the manganese dopant was in solid solution within the alumina lattice, a full-profile fitting refinement method was used,^{37,38} comparing the ceramic pigment powders and a sample of a nondoped alumina powder synthesized by the exact same method. Both spectra shifting and the lattice parameters from the powders were compared to test that hypothesis.

The manganese-doped alumina particles were coated with a silica layer following a sol–gel method described elsewhere.^{34,36} The particles were dispersed in an aqueous solution of 0.1 M hydrochloric acid P.A. (Synth). The suspension was kept in vigorous magnetic stirring for 15 minutes to control particle aggregation. TEOS was added to the suspension in the proportion of 5 mol% relative to the powder.³⁶ Vigorous magnetic stirring was maintained and the temperature increased to 60°C to evaporate the aqueous content. After drying, the particles were heat treated in an air atmosphere oven with a 5°C/minute heating rate up to 900°C dwell temperature for 2 hours.

After cooling, the powders were silanated with 5 wt% 3-(trimethoxysilyl)propyl methacrylate as described elsewhere.¹⁰ Batches of 5 g of particles were dispersed in a solution containing 0.5 g silane, 100 mL cyclohexane, and 0.1 g propylamine, all from Sigma-Aldrich. Stirring was kept up for 30 minutes at room temperature and then at 60°C for an additional 30 minutes. The suspension was transferred to a rotary evaporator at 60°C under vacuum to remove the liquid components. Finally, the powders were dried at 100°C in an incubator for 24 hours.

The PMMA was manipulated following the manufacturer recommendations in a 3:1 powder:liquid volume ratio. For the 2 experimental groups (Fig.1% and Fig.2%), a translucent shade of PMMA was used. After pouring the required volume of the PMMA monomer, 5 wt% of the pigment was added. To ensure adequate dispersion of the pigment particles, the suspension was sonicated for 1 minute before mixing with the PMMA powder. The mixture was then placed into a metallic mold (internal dimensions: 65×10×2.5 mm). Uniaxial pressing for 10 minutes was applied to remove excess material, ensure flat surfaces, and avoid bending due to polymerization shrinkage. A total of 56 bar-shaped specimens (n=14 per group) with definitive dimensions checked with a digital caliper after polishing with 2000-grit SiC abrasive papers were prepared. Immediately after polymerization and polishing, the bars were incubated in distilled water at 37°C to simulate the oral environment and stored for 24 hours for complete hydration. This study also included 2 control groups: the same translucent PMMA (without pigments) and a pink PMMA (with organic and inorganic pigments added by the manufacturer).

The specimens were tested in 3-point bending mode (50-mm span length) in a mechanical testing machine (DL500; EMIC) at 1 mm/minute crosshead speed. Flexural strength (σ_f), flexural modulus (E_f), and work-of-fracture (WoF) were calculated based on the load-deformation curves.^{39,40} After mechanical testing, 10×10×2.5-mm specimens were cut from the fragments of the bars for color measurements. CIELAB color coordinates^{41,42,43} were then evaluated for all specimens. A spectrophotometer (SP60; X-Rite) was used in reflectance mode, with an 8-mm aperture, D-65 illuminant, 10-degree observer angle, and specular component excluded (SCE). During the test, the spectrophotometer was connected to a voltage stabilizer to avoid changes in light source intensity. The equipment was calibrated by using the standard tiles provided. The specimens were evaluated on a neutral-grey background ($L^*=50$; $a^*=0$; $b^*=0$).

The 4 groups (Pink, Fig.1%, Fig.2%, and Trans) were compared with regard to their color parameters (L^* , a^* , and b^*) and mechanical properties (σ_f , E_f , and WoF). Data were

analyzed by 1-way ANOVA separately for each outcome. All pairwise multiple comparison procedures were conducted using the Tukey test ($\alpha=.05$ for all analyses).

RESULTS

Figure 1 shows the 2 manganese-doped alumina powders obtained in this study. Color difference is visually noticeable: coloration is more homogeneous for the 2% doped $\text{Al}_2\text{O}_3\text{:Mn}$. XRD showed spectra consistent with α -alumina crystalline structure, with a crystal size of around 55 nm for both powders. The percentage of manganese is below the equipment precision limit; thus, it was not quantified. Figure 2 presents the XRD spectra of a control Al_2O_3 and the 2% doped $\text{Al}_2\text{O}_3\text{:Mn}$ powders. The noticeable lower shift angle present for all peaks in the $\text{Al}_2\text{O}_3\text{:Mn}$ compared with the Al_2O_3 indicates that the manganese ions are in solid solution within the alumina lattice. This observation is further corroborated by the lattice parameters as follows: Al_2O_3 $a=4.758$ Å, $c=12.985$ Å, volume= 254.566 Å³; $\text{Al}_2\text{O}_3\text{:Mn}$ $a=4.763$ Å, $c=13.001$ Å, volume= 255.391 Å³. Note that both parameters a and c , as well as the volume of the lattice, have increased values for the doped powder, demonstrating that the manganese ions (bigger ionic radius than the aluminum) are in solid solution. Figure 3 presents the microstructure of the 2% doped $\text{Al}_2\text{O}_3\text{:Mn}$ pigment powder, which was fairly similar for the 1% doped powder. Irregular shaped agglomerates (mesostructures) of wide particle size distribution (maximum 60 μm) are seen in Figure 3A. By using high magnification, the nanostructured arrangement of the individual clusters was observed (Fig. 3B), with nanocrystals embedded into porous mesostructures (Fig. 3C).

Figure 4 shows a set of specimens (pink PMMA, composite resins with 1 wt% and 2 wt% of pigment, and translucent PMMA) over a translucent white background. The illumination direction and image capture angle were modified to better observe the apparent color and translucency of the specimens. In the top row, the light source was positioned on top of the specimen and angulated to avoid surface reflectance of light (flash artifacts). The image capture angle was oblique to the surface of the specimen in order to observe apparent color with homogeneously scattered light. The composite resin specimens appear to resemble the color of the Pink specimen, although some color differences are visually perceptible among them. In the bottom row, the light source was positioned below the background and specimen to produce transillumination. The image capture angle was perpendicular to the surface of the specimen and in line with the light beam. The modified composite resin is more translucent than the Pink specimen and more opaque than the Translucent. Such observations are corroborated by the color parameters CIELAB presented in Table 1. ANOVA for CIE L^* showed $F=57.1$, $P<.001$; for CIE a^* $F=1640.5$, $P<.001$; and, for CIE b^* $F=1082.3$, $P<.001$.

Although CIE a^* and b^* for the composite resins were statistically different compared with the Pink specimens, the extent of that difference was deemed clinically insignificant. Further, the Pink group presents the highest L^* value (Table 1), while little to no differences were observed among the composite resin groups and translucent PMMA. Table 2 presents the mechanical properties for all groups tested. ANOVA for σ_f showed $F=1.9$, $P<.136$; for E_f $F=4.8$, $P<.105$; and, for W_oF $F=0.08$, $P<.969$. The addition of 5 wt% of either pigment in the PMMA did not affect its mechanical properties.

DISCUSSION

The functionalized ceramic pigments yielded pink coloration to the translucent PMMA tested and did not jeopardize its mechanical properties. Thus the hypothesis of the study was not rejected. The pink coloration observed for the pigment powders is yielded by the presence of manganese atoms (doping-agent) within the alumina lattice.²⁻⁴ Perceptibly more homogeneous color for the 2% doped $\text{Al}_2\text{O}_3\text{:Mn}$ powder can be explained by the greater amount of the dopant, which generates chromophore centers, yielding coloration to the otherwise white alumina. Previous studies²⁻⁴ have shown that the molar percentage of dopant-agent, type of dopant (cobalt, chromium, bismuth, and molybdenum), and the temperature in which the polymeric precursor is heat-treated have significant influences in the shade of the pigment powder. The noticeable shift to lower angles observed in the XRD spectra for the $\text{Al}_2\text{O}_3\text{:Mn}$, as well as the increased values of the lattice parameters for the doped powder, confirm that the manganese ions (bigger ionic radius than the aluminum) are in solid solution^{37,38} within the alumina lattice. This ensures the chemical stability and inertness of the doped-alumina powder prepared in the present study. Such characteristics are important to minimize potential biological hazards and to guarantee the color stability of the pigment powders.

The pigment powder particles are composed of irregular shaped porous agglomerates (mesostructures) of wide particle size distribution (maximum 60 μm). The porous mesostructures show a nanostructured arrangement (55 nm). The precursor powder was obtained by hand-grinding the heat-treated polymer by using a mortar and pestle. More sophisticated mechanical grinding methods can be used to obtain a pigment powder with finer particle size.^{2,3,35} Ideally, for application in dental restorative materials, inorganic particles should have an average particle size no larger than 5 μm to ensure adequate polishing and gloss²⁹ and to improve filler packing, thereby yielding better mechanical properties.^{27,28}

The photographs of the specimens over a translucent white background had the illumination direction and image capture angle modified to better observe the apparent color and translucency of the specimens. With the light source positioned on top of the specimen and angulated to avoid surface reflectance of light (flash artifacts), the pink coloration observed for the composite resin specimens, in comparison with the translucent specimen, was solely a result of the addition of the pink pigment. The composite resin specimens appeared to resemble the color of the Pink specimen, although color differences were visually perceptible. Such observation was corroborated by the color parameters CIELAB. Such differences in color coordinates are desired to fabricate composite resins of various shades,²² meeting the esthetic demands of the intended application in prosthetic dentistry. Previous studies have reported color coordinates in the range of those reported in Table 1 for pink PMMA (a^* approximately 20, b^* approximately 12)⁴³ and translucent PMMA ($a^*=-0.2$, $b^*=2.1$)⁴² for denture base resin.

When the light source was positioned below the background and specimen to produce transillumination, the modified composite resin was clearly more translucent than the Pink specimen and more opaque than the Translucent. Accordingly, group Pink presents the

highest L* value (Table 1), while little to no differences were observed among composite resin groups and translucent PMMA. The greater translucency of the composite resins and Trans groups can explain their lower CIE L*, or luminosity, which is negatively correlated to the translucency of the material.²¹ Note that the formulation of the composite resins did not include opacifiers,²² whose use seems to be a suitable solution to increase the L* value and reduce the difference in final appearance compared with the Pink group. The L* parameter differs markedly among studies,^{42,43} which is explained by the different background colors used (black, white, or grey) and the distinct thickness/translucency of the study specimens.

Regarding mechanical properties, the flexural resistance values measured in the present study were in the midrange of those previously reported (85 to 110 MPa).^{32,33,42} The addition of 5 wt% of either pigment in the PMMA did not affect its mechanical properties. Note that before preparation of the composite resins, the pigment powder was functionalized by means of a sol-gel silica coating method. Previously published results of elemental mapping by EDS/SEM show a thin film of Si atoms on the surface of the alumina particles,³⁶ so the silica layer is not expected to significantly affect particle size. In addition, its presence allows for effective and stable silanation,³⁴ which is required for a strong bond between resin matrix and filler particles, and avoids interfacial pores that would compromise not only the mechanical properties of the composite resins^{18–20} but also their translucency.^{22–24} In the present study though, the chemical interaction of silane with the silica coated pigment particles and with the PMMA matrix was not investigated. Further studies are needed to test the hypothesis that the functionalized pigment particles are effectively and stably bonded to the PMMA matrix, even after chemical and/or mechanical aging.

The addition of well-bonded inorganic particles to a resin matrix usually results in mechanical reinforcement.^{8–17} The lack of mechanical reinforcement reflects a limitation of this study, likely related to the size of the mesoscale agglomerates. For application in dental restorative/prosthetic materials, the inorganic particles usually have an average particle size below 5 µm to ensure adequate polishing and gloss²⁹ and to improve filler packing and homogeneous distribution, thereby yielding better mechanical properties.^{27,28} However, the size of the pigment particles can be significantly reduced, even to submicrometric scale, by using mechanical grinding in the preparation of the precursor powder.^{2,3,35} Another important aspect of the mechanical properties is that the filler loading was low (5 wt.% of pigment particles) the mechanical reinforcement expected from the ceramic component did not become predominant.

The possibility of controlling the pigment color by the molar percentage of dopant-agent, the type of dopant and the temperature in which the polymeric precursor is heat-treated are advantageous not only for application in prosthetic dentistry but also may result in the development of novel materials for ocular and facial prostheses. Further research with functionalized ceramic pigments is encouraged to better understand the various potential applications. In addition, future studies should address the limitations of the present research, investigating the reproducibility of pigment color among different batches, controlling the particle size of the pigment to optimize the mechanical and optical properties

of the composites, and considering the effects of aging on the mechanical and optical properties of composites prepared with these pigments.

CONCLUSIONS

Within the limitations of the present experiment, the following conclusions were drawn:

1. The method used to prepare pink $\text{Al}_2\text{O}_3\text{:Mn}$ ceramic pigments indicates a promising strategy for the development of colored polymeric composite resins.
2. The PMMA composite resins prepared and tested showed pink similar to a regular pink PMMA, as well as comparable mechanical properties.

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CLINICAL IMPLICATIONS

PMMA colored by functionalized manganese-doped alumina ceramic powders can be produced in a multitude of shades, satisfying the esthetic demands for shade matching in prosthetic dentistry.

Figure 1.
Pigment powders. Manganese doping yielded pink coloration to alumina particles.

Figure 2.

X-ray diffraction (XRD) spectra of pure Al_2O_3 and 2% doped $\text{Al}_2\text{O}_3:\text{Mn}$ powders. Both specimens were synthesized by same polymeric precursor method, differing only in doping or not with manganese. Full-profile fitting method was used to refine spectra: Spectra collected during x-ray diffraction evaluation (Obs), calculated with refinement method (Calc), and difference between collected and calculated spectra (Dif) are presented.

Figure 3. Scanning electron micrographs of $\text{Al}_2\text{O}_3:\text{Mn}$ powder. A, Irregular-shaped agglomerates (mesostructures) of nanocrystals (original magnification $\times 300$). B, One mesostructure in detail (original magnification $\times 1000$). C, Nanocrystals within porous mesostructures (original magnification $\times 24\ 000$).

Figure 4.

Representative specimen per group over white translucent background Top row, oblique illumination and oblique image capture were used for color comparisons. Bottom row, transillumination through background with image captured perpendicular to specimen surface and in line with light beam was used to compare transluency.

Table 1

Mean (standard deviation) for CIE L*a*b* color coordinates

Group	L*	a*	b*
Pink	61.7 (0.7) ^a	20.1 (0.4) ^a	17.0 (0.4) ^b
Pig. 1%	55.2 (2.1) ^c	14.6 (1.0) ^c	18.6 (1.0) ^a
Pig. 2%	57.3 (1.5) ^b	16.0 (1.0) ^b	19.0 (1.1) ^a
Transl.	55.1 (1.3) ^c	00.2 (0.1) ^d	02.5 (0.4) ^c

Distinct letters indicate statistical differences within each color coordinate.

Table 2

Mean (standard deviation) for flexural strength (σ_f), flexural modulus (E_f), and work-of-fracture (WoF)

	σ_f (MPa)	E_f (GPa)	WoF (kJ.m ^{1/2})
Pink	98.4 (14.3)	4.8 (0.5)	1.8 (0.6)
Pigm 1%	98.1 (14.6)	5.1 (0.8)	1.9 (0.4)
Pigm 2%	98.8 (10.3)	5.0 (0.6)	1.9 (0.3)
Transl.	89.1 (9.8)	4.4 (0.3)	1.9 (0.5)

There were no statistical differences for any properties.