Doctoral Thesis

Nanocomposites from flame-made nanoparticles radiopaque Ta₂O₅/SiO₂ for dental adhesives and fillings

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Nanocomposites from Flame-made Nanoparticles: Radiopaque Ta$_2$O$_5$/SiO$_2$ for Dental Adhesives and Fillings

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SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZÜRICH
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presented by
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Im ersten Kapitel wurde der Einfluss der inhärenten Partikeltransparenz auf die Transparenz anorganischer/organischer Komposite untersucht. Kommerziell erhältliche Füllerpartikel mit Durchmessern von 7 nm bis 1.5 μm wurden zu Tabletten gepresst und in Flüssigkeiten unterschiedlicher Brechungsindizes getaucht. Maximale Transparenz ergab sich bei übereinstimmenden Brechungsindizes.

Silikatbasierte Oxide mit 0 – 100 gew. % Ta₂O₅-Gehalt wurden mittels Flammen-Sprüh-Pyrolyse für transparente Nanokomposite hergestellt. Der Brechungsindex der Nanopartikel wurde durch den Ta₂O₅-Gehalt mit dem der Polymermatrix in Übereinstimmung gebracht. Produktionsparameter wie Ta-Vorläufer, Lösungsmittel, Gesamtmetallkonzentration in der zu sprühenden Lösung und Ta₂O₅-Gehalt wurden auf ihren Einfluss bezüglich der inhärenten Partikeltransparenz untersucht. Der Ta-Vorläufer mit der höchsten chemischen Stabilität, das Lösungsmittel mit dem geringsten Wassergehalt und die Produktionsbedingungen mit der geringsten Metallkonzentration führten bei einem Ta₂O₅-Gehalt von bis zu 35 gew.% Ta₂O₅-Gehalt, zu einer gleichmässigen Ta-Verteilung in der Silikatmatrix. Die dabei entstandenen kristallinen Ta₂O₅-Strukturen, welche mittels TEM- und XRD-Analyse untersucht wurden, führten zu zusätzlichen Grenzflächen in den Partikeln mit unterschiedlichen Brechungsindizes, so dass die Komposittransparenz drastisch sank.

Die mechanische Belastbarkeit von Nanokompositen lässt sich durch chemische Bindungen zwischen Partikeln und Polymermatrix erhöhen. Dafür müssen die Partikeloberflächen mit organischen Gruppen, zum Beispiel γ-
-Methacryloxy-propyltrimethoxysilan, funktionalisiert werden, die während der Polymerisation mit der organischen Matrix reagieren können,. Flammensynthetisiertes Ta₂O₅/SiO₂ besass eine deutlich höhere Oberflächenazidität als reines
SiO₂. Deshalb musste der Oberflächenmodifikationsprozess so optimiert werden, dass die höchste Modifikatordichte auf der Partikeloberfläche erreicht wurde. Der gebräuchliche Katalysator Propylamin adsorbierte stark auf der Oberfläche der Mischoxide und blockierte dabei aktive Zentren der Oberfläche für die Modifikation. Funktionalisierung ohne Propylamin führte zu höheren Modifikatordichten auf der Oberfläche. Sowohl für die Mischoxide als auch für das reine Silikat war der Modifikator auf der Oberfläche stark vernetzt, was zu einer vergleichbaren hydrolytischen Stabilität des Modifikators auf der Oberfläche bei stark sauren Bedingungen führte (pH=2). Partikel, die mit auf der Oberfläche stabilen Modifikatoren funktionalisiert wurden, bilden chemische Bindungen mit der Polymermatrix während der Polymerisationsreaktion und erhöhen dadurch die Festigkeit des Komposites.

Dentalkomposite müssen von Zahndefekten wie Karies zu unterscheiden sein. Dafür muss deren Radiopazität mindestens der des Zahnschmelzes entsprechen. Komposite, die 20 gew.% Partikel (83 gew.% Ta₂O₅/SiO₂) enthalten, hatten eine höhere Radiopazität als Zahnschmelz. Die Viskosität der Suspensionen war ausreichend niedrig, so dass diese leicht zu einem dünnen Film verblasen werden konnten und in Oberflächenrauhigkeiten eindrangen. Unbehandelte Partikel zeigten stärkere Wechselwirkungen als funktionalisierte, so dass letztere mit weniger Energieeinsatz dispergiert werden konnten. Um Sedimentation zu verhindern, wurden Dispergierparameter für unbehandelte und oberflächenfunktionalisierte Partikel so optimiert, dass > 85 gew.% der dispergierten Partikel kleiner als 100 nm waren, Dentaladhäsive ohne Partikel und mit 20 gew.% Partikelgehalt hatten vergleichbare Scherfestigkeit auf Zahnschmelz und Dentin.

Flammensynthetisierte Nanopartikel sind zur Einarbeitung in Polymere geeignet und können diesen neue Eigenschaften geben, wie in transparenten, kratzfesten Kompositen oder radiopaken Dentaladhäsiven. Optimale Kompositeigenschaften können nur durch gleichzeitige Optimierung von Partikelsynthese, deren Oberflächenfunktionalisierung und Dispergierung erreicht werden. Mit
Zusammenfassung

SUMMARY

Inorganic/organic composites are used in many commodity products such as tires, coatings, paints, pastes, construction materials etc. Particles have a significant influence on the composite strength, dimensional stability, Young’s and shear modulus, wear and transparency. New functionalities of the composite like radiopacity, electrical conductance and magnetism can be added by the particles. For every application polymer refractive index, chemical composition, viscosity, hydrophobicity and transparency as well as particles size, agglomerate size, refractive index, elemental distribution, surface texture and functionalization have to be tailored. In this study, the influence of particle properties on composites for dental adhesives and fillings have been studied.

The influence of the inherent filler particle transparency on the inorganic/organic composite transparency was investigated. Commercially available particles with diameters ranging from 7 nm to 1.5 μm were pressed to tablets and immersed in liquids with different refractive indices. Filler transparency was maximum when the refractive indices of particles and liquid matched. In contrast, transparency decreased drastically for increasing refractive index mismatch. The same was determined for inorganic/organic composites. In both cases larger particles resulted in a more significant transparency decrease for the same mismatch, which was described by quantitatively. Knowing the particle
diameter, its inherent filler transparency and the refractive index mismatch of particles and matrix, composite transparencies could be predicted by using this simple method, when no differences have been found by common particle characterization techniques.

For transparent nanocomposites with 0 – 100 wt.% Ta$_2$O$_5$ containing SiO$_2$, based nanoparticles have been produced by flame spray pyrolysis. The particle refractive index was tailored by the Ta$_2$O$_5$ content to match the refractive index of the polymeric matrix. Production parameters such as Ta-precursor, solvent, total metal concentration and Ta$_2$O$_5$ content were investigated for their influence on the inherent particle transparency. The precursor with the highest stability, the solvent with the lowest water content and the production conditions with the lowest metal concentration resulted in a simultaneous Ta- and Si-precursor combustion leading to a high Ta-dispersion in the SiO$_2$ matrix for up to 35 wt.% Ta$_2$O$_5$ content. The onset of crystalline structure formation as observed by TEM and XRD resulted in additional interfaces in the particles with mismatching refractive indices therefore leading to a dramatic composite transparency decrease.

Nanocomposites containing particles that are chemically bound to the polymeric matrix exhibit high strength. Therefore, particles have to be surface functionalized with organic groups that can react with the organic phase during polymerization as γ-methacryloxypropyltrimethoxysilane. Flame-made Ta$_2$O$_5$ containing SiO$_2$ exhibited a significantly higher surface acidity than pure SiO$_2$. So that, surface-functionalization conditions had to be tailored for the highest surface modifier density on the particle surface. The commonly used catalyst propylamine strongly adsorbs on the mixed oxide particle surface and blocks active sites for surface functionalization. Surface modifications without propylamine resulted in higher surface modifier density on the particles. Modifiers were crosslinked on the particle surface for the Ta$_2$O$_5$/SiO$_2$ and pure SiO$_2$ resulting in the comparable hydrolytic stability of the modifier under severe conditions (pH=2). Particles containing 0 – 100 wt.% Ta$_2$O$_5$ with stable functional surface
groups enable the chemical bonding to the organic matrix during polymerization.

Dental composites have to be distinguishable from tooth defects such as caries. Therefore, the radiopacity of the composite has to be comparable to that of enamel. Composites containing 20 wt.% filler (83 wt.% Ta₂O₅/SiO₂) exhibited higher radiopacity than enamel with low viscosity, enabling easy spreading and penetration onto surface roughness of the dental adhesive film during application. Dispersion parameters have been studied for untreated and surface functionalized particles, exhibiting stronger particle/particle attraction in methacrylate monomers for untreated than for functionalized particles. So that two-step dispersion with centrifugal mixing and ultrasonication resulted in more than 85 wt.% of the agglomerates smaller than 100 nm which will not sediment during storage. Unfilled and 20 wt.% filler (untreated and functionalized) containing adhesives had comparable shear strength on enamel and dentin.

Flame-made particles are potentially attractive materials to be incorporated in organic matrices for the addition of new functionalities to the polymer such as transparent, scratch resistant composites or radiopaque dental adhesives. It has been demonstrated that particle processing must be tailored for every production step, synthesis, functionalization and dispersion, for optimal composite performance. Flame spray pyrolysis is capable for manufacture of non-agglomerated nanoparticles with controlled refractive index, radiopacity, elemental distribution and particle morphology. With surface functionalization particle surface properties can be adjusted by the functional groups and the modification process resulting in organophilic surfaces with functional groups, that can participate in the polymerization of the organic matrix. Particle size distribution in the monomer mixture and suspension properties can be tuned by the dispersion method and its process parameters ranging from non-agglomerated primary particles which were present in the monomer to the designed formation of particle networks in the liquid with unique mechanical properties.
Abstract

The transparency of metal oxide containing polymeric composites was correlated to its filler transparency using a new method based on light microscopy analysis. Filler particles were pressed into filler tablets from which fragments were submerged in different refractive index liquids. Transparencies of different particulate materials with diameters from 0.007 - 1.5 \( \mu \text{m} \) were investigated. The transparencies depended on light absorption of the solid, filler particle size and refractive index mismatch of filler and liquid. A correlation between filler transparency and the transparency of filler containing polymers (composites) was established. The method allows to predict the composite transparency for any filler particle size and any filler particle/polymer refractive index mismatch. Manufac-
turing-caused, batch-wise quality differences in transparency of the same filler material showed similar transparency trends for filler/liquid and filler/polymer transparencies when no quantitative difference was found by nitrogen adsorption, XRD, DRUV-Vis, DRIFTS and SEM analysis.

Introduction

Polymers containing metal oxide particulate fillers (organic/inorganic composites) are used in many commodities such as dental restoration materials as well as tires, inks and scratch-resistant coatings.\cite{1} Fillers typically are added to improve mechanical, optical, electrical or chemical properties of polymers for increased performance in specific applications.\cite{1} Light transparent polymer/filler composites replace common polymers in optoelectronics,\cite{2} wear resistant coatings\cite{3} and light emitting devices (LEDs).\cite{4} For example, in scratch-resistant, transparent coatings, fillers increase the mechanical strength of the polymer without sacrificing the initial transparency of the unfilled polymer.\cite{3} In dental applications, fillers can increase the radiopacity (x-ray absorption) of composite restorations facilitating distinction between natural teeth and artificial fillings.\cite{5} For dental composites high visual transparency is required which is a result of light absorption and scattering in the visible wavelength range. Visual transparency depends on filler particle size, refractive index mismatch of filler and polymer, filler homogeneity, filler content, wavelength and inherent filler transparency.\cite{6-9}

Both polymer and embedded fillers lead to absorption effects while light scattering occurs at any interface with differences in refractive index such as filler/polymer\cite{9} and inhomogeneities in the fillers themselves.\cite{6} Therefore, matching the refractive index of polymers with that of homogeneous fillers results in maximum composite transparency by minimizing scattering.\cite{6} As a result, filler properties such as refractive index have to be tailored to that of the
host polymer matrix. Testing and optimizing composite transparency is an elaborate, multi-step process including several composite preparation steps. Commonly, composite transparency is measured by UV-Vis spectrophotometry, requiring large sample volumes for every composite.\textsuperscript{[10]}

Recently a method was presented for measuring the refractive index of particulate materials applying the Becke-line method while only milligrams of nano- to micron-sized fillers were used\textsuperscript{[6, 7]} This method is used here to determine the inherent filler transparency by measuring the transparency of fillers in liquids of various refractive indices. Filler transparency was determined in the visible light range as required for most applications. That way for a given inherent filler transparency, filler particle size, refractive index mismatch and preparation conditions, the composite transparencies could be predicted. Filler/liquid transparencies could be correlated to filler/polymer composite transparency, enabling a prediction of composite transparency for a given filler/polymer combination by the fast Becke line refractive index measurement. Even deviations in the manufacturing-process of the fillers which lead to transparency deviations that are difficult to identify with common filler characterization methods have been quantified by the Becke line refractive index measurement and correlated to the final composite transparency.

Experimental

The visual appearance of fillers that are typically used in dental applications are shown in Table 1.1. Fillers made by milling of under-cooled melts\textsuperscript{[11]} and by flame aerosol technology\textsuperscript{[12]} were compared. Micron-sized Ba-glasses obtained by milling had nominal contents of 55 wt.% SiO\textsubscript{2}, 25 wt.% BaO, 10 wt.% B\textsubscript{2}O\textsubscript{3}, 10 wt.% Al\textsubscript{2}O\textsubscript{3} while flame-made nanofillers consisted almost of pure SiO\textsubscript{2} (> 99.999 wt.%). Monomer solutions that resemble the ones commercially employed in dental applications have been used here as composite matrix.
Table 1.1. Silica ($\rho = 2.2 \text{ g/cm}^3$) or Ba-glass ($\rho = 2.73 \text{ g/cm}^3$) produced by flame aerosol synthesis (Degussa) or milling (Schott). Fillers produced in the gas phase exhibited a homogeneous appearance, while mechanically ground fillers exhibited dark spots possibly from contamination.

<table>
<thead>
<tr>
<th>Name</th>
<th>Production method</th>
<th>SSA [m$^2$/g]</th>
<th>BET-equivalent filler size</th>
<th>Refractive index [a.u.]</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerosil 380</td>
<td>aerosol</td>
<td>380</td>
<td>7 nm</td>
<td>1.49</td>
<td>homo.</td>
</tr>
<tr>
<td>OX 50</td>
<td>aerosol</td>
<td>49</td>
<td>55 nm</td>
<td>1.49</td>
<td>homo.</td>
</tr>
<tr>
<td>Ba-glass$^1$</td>
<td>milling</td>
<td>5.8</td>
<td>0.4 μm</td>
<td>1.53</td>
<td>inhom.</td>
</tr>
<tr>
<td>Ba-glass</td>
<td>milling</td>
<td>3.1</td>
<td>0.7 μm</td>
<td>1.53</td>
<td>inhom.</td>
</tr>
<tr>
<td>Ba-glass</td>
<td>milling</td>
<td>2.2</td>
<td>1.0 μm</td>
<td>1.53</td>
<td>inhom.</td>
</tr>
<tr>
<td>Ba-glass</td>
<td>milling</td>
<td>1.5</td>
<td>1.5 μm</td>
<td>1.53</td>
<td>inhom.</td>
</tr>
</tbody>
</table>

$^1$ four different batches of this Ba-glass were investigated.

**Filler Characterization**

The specific surface area (SSA, m$^2$/g) of the fillers was determined from the adsorption of nitrogen at 77 K using the BET method (Micromeritics Tristar 3000, 5-point isotherm, $0.05 < p/p_0 < 0.25$). X-ray diffraction (XRD) analyses were performed using a Bruker D8 Advance diffractometer with $2 \theta$ from 20° to 50° (step size 0.03°, scan speed 0.60°min$^{-1}$, Cu-Kα radiation). Diffuse-reflectance infrared Fourier-transform spectra (DRIFTS) were recorded on a Harrick Praying Mantis diffuse reflectance unit of a FTIR instrument (Bruker, Vektor 22). The reaction chamber of the FTIR is equipped with KBr windows, heating control and a gas flow system. The filler samples were mixed 1:5 with KBr particles (>99.5%, Fluka) and dehydrated in argon (Pan Gas, > 99.999 %, 5 ml/min, 200°C, 1 h). For each spectrum 512 scans were collected at 50°C at a resolution of 2 cm$^{-1}$ against a pure KBr particles background. Diffuse reflectance UV-Vis spectra (DRUV-Vis) were collected on Cary 500 (Varian). In this case the filler was mixed 1:5 with BaSO$_4$ (>97.5%, Riedel-de-Haën) and measured against a pure barium sulfate background at 600 nm/min and a step size of 1 nm.
*Filler Tablet Preparation and Characterization*

The ceramic filler was pressed into round filler tablets with a fixed diameter of 13 mm. The applied pressure and specific volume ranged from 74 to 740 MPa and 0.5 to 2.5 mm$^3$/mm$^2$, respectively, while 370 MPa and 1 mm$^3$/mm$^2$ was used as standard unless otherwise stated (filler density reported in Table 1.1).\(^6,7\)

The resulting thickness of the pressed filler tablet was measured by mounting a fragment of the filler tablet on the stage of a microscope (Zeiss, Axioplan) in reflectance mode. Focusing on the stage surface and subsequently on the upper surface of the filler tablet resulted in a difference in the vertical position of the stage which was measured by a micrometer being equivalent to the filler tablet thickness. For each material, three filler tablets were prepared and from each filler tablet three different fragments were measured.

The refractive index of the fillers was measured by the Becke-line method, relying on the difference in the filler/matrix refractive index which leads to patterns around the tablet fragment for certain analysis conditions.\(^7\) The series of index matching liquids (Cargille Laboratories Inc.) ranged from refractive indices of 1.4 to 1.7 with 0.004 intervals. A NaD filter was used to assure a measurement at a wavelength of 589 nm. For filler transparency determination the disk-like fragments were mounted between two glass slides and the gap between these was filled with index matching oil. The half automated microscope (Zeiss, Axioplan Imaging) ensured standardized measuring conditions (optical and mechanical settings) for all samples. Operating the microscope in transmittance mode, images were taken by a digital camera (Zeiss, AxioCam HR), ensuring linear signal/light intensity dependence. The digital images were evaluated for their grayness (black = 0 and white = 256, image size 1.3 mm$^2$). Histogram analysis of the pixel grey values was carried out using Igor Pro (WaveMetrics Inc., Version 4.0). For statistical evaluation, selected filler transparency measurements were repeated for at least three different filler tablets at several filler/liquid combinations. Image regions which were not covered by the filler
tablet fragment served as reference for maximum transparency thereby excluding refractive index mismatch effects between the glass slides and the refractive index liquid.\cite{13} Differences in the tablet thickness and therefore the adsorption by the matrix liquid could be neglected, since the preparation procedure ensured the same path of light through the solid for all fillers regardless of its size and density. The reported filler extinction was defined as the mode of the pixel grey value histogram. From this the filler transparency was estimated:

\[
\text{filler transparency}[\%] = 100 - \text{filler extinction}[\%]
\] (1.1)

Filler tablet morphology was examined by scanning electron microscopy (SEM, Hitachi, S-900) after platinum sputtering (2 nm).

**Polymer and Composite Synthesis and Characterization**

The influence of refractive index mismatch of polymer matrix and Barium glass (Ba-glass) filler on composite transparency was investigated mixing chemically identical fillers with different particle sizes with the monomer solutions. Five different monomer solutions with mixtures of Bisphenol A Glycidyl-dimethacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) were used. Their refractive indices were adjusted by the Bis-GMA weight fraction ranging from 10 to 85 (Figure 1.1). The Ba-glass filler/monomer ratio was 30:70 (by weight). The suspensions were activated with light curing initiators such as 0.3 wt.% camphorquinone (CC) and 0.6 wt.% N,N-Cyanoethyl-Methyl Anilin (CEMA). For investigation of filler transparencies of different Ba-glass batches, a monomer solution of Bis-GMA, Urethane-dimethacrylate (UDMA) and TEGDMA at a weight ratio of 43:37:20 (initiated with 0.3 wt.% CC and 0.6 wt.% CEMA) was mixed with fillers (70:30 by weight) with same particle size of 380 nm (0.4 μm) and chemically identical composition.

The composites were polymerized with a dental curing unit (Ivoclar Vivadent, Astralis 10, 1100 mW/cm², 20 seconds). The composite transparency was meas-
ured at 1 mm sample thickness (diameter of 20 mm) with a Minolta Spectrometer (CT-310) in comparison to water. Prior composite transparency analysis the refractive indices of unfilled polymers fragments (0.5 mm disk thickness), have been measured by Becke-line method (see above, Figure 1.1).

**Figure 1.1.** Polymers from five different monomer solutions have been prepared, containing different Bis-GMA and TEGDMA weight fractions. Polymerization increased the refractive index compared to the monomer solution resulting in a linear dependence on the Bis-GMA content.

For describing the transparency dependence of various filler particle / matrix combinations, the facet model has been applied. It was assumed that light is scattered at dielectric interfaces such as particle and matrix. Light transmittance decreases by absorption were neglected and only intensity reduction by scattering was taken into account. Particles are made out of facets that scatter the light (Figure 1.1). Light incidents on facets of the particles $\theta_i$ that can be tilted from the optical axis $\theta_f$. In this case the average light direction is the same as the opti-
cal axis so that $\theta_i = \theta_f$. Using Snell’s law, scattered light propagates with a certain angle to the facet $\theta_i$ and the optical axis $\alpha$ (Equation 1.2).

$$n_i \times \sin(\theta_i) = n_i \times \sin(\theta_t)$$

(1.2)

**Figure 1.2.** Schematic of the facet model. Light incidents the facet with the angle $\theta_i$. The facet is tilted by $\theta_f$ from the average measurement direction ($z$, facet normal: $n$). Light is transmitted at an angle $\theta_t$. The maximum collection angle $\alpha$ is indicated. In this case, the scattered light beam would not have been collected.
From reflection coefficients of light with normal and parallel electric vectors to the plane ($r_n$ and $r_p$, Equation 1.3), total reflection ($R$, Equation 1.4) was determined.[14]

$$r_n = \frac{\cos(\theta_t) - \frac{n_1}{n_2}\times\cos(\theta_i)}{\cos(\theta_t) + \frac{n_1}{n_2}\times\cos(\theta_i)}$$

$$r_p = \frac{\cos(\theta_t) - \frac{n_1}{n_2}\times\cos(\theta_i)}{\cos(\theta_t) + \frac{n_1}{n_2}\times\cos(\theta_i)}$$

(1.3)

$$R = \frac{1}{2} \left( |r_n|^2 + |r_p|^2 \right)$$

(1.4)

Only light with angles $\alpha$ lower than the maximum detectable angle from the optical axis ($1^\circ$) were accounted for transparency.

$$\alpha = \theta_t - \theta_f \quad \text{for } n_1 > n_2$$

$$\alpha = \theta_t + \theta_f \quad \text{for } n_1 < n_2$$

$$\alpha = 0 \quad \text{for } n_1 = n_2$$

(1.5)

Probability densities of local slopes were assumed to follow a Gaussian distribution and $\sigma$ therefore represents the width of the slope of the facet angle distribution.[15] Light is scattered at planar, randomly oriented facets of arbitrary orientation represented by the single correlation length $L$.[16]

$$P(s) = \frac{L}{\sigma} \times \frac{1}{2\sqrt{\pi} \cos^2(\theta_f)} \times \exp \left[-\left(\frac{L\times\tan(\theta_f)}{2\sigma}\right)^2\right]$$

(1.6)

Transparency was calculated from transmitted light within the minimum and maximum facet tilt.

$$T = \int_{\theta_f,\min}^{\theta_f,\max} (1 - R) \times P(\theta_f) \, d\theta_f$$

(1.7)

Filler and composite transparencies were normalized to the maximum transparency at matching refractive indices, which was then called transmittance.
Changes in filler/liquid and composite transparency for different refractive index mismatches were fitted with this facet model by adjusting the dimensionless parameter $L/\sigma$\textsuperscript{[14]} by minimizing the total error between data and model. The model does not take multiple scattering into account. Multiple scattering will result in arbitrary scattering in the plane normal to the incoming light, so that the average light direction is unchanged. This showed no effect on the correlation obtained between the filler in liquid and the composite. By using the same particles to determine the filler and composite $L/\sigma$ influences of particle shape and morphology could be neglected. However comparisons between different particle sizes should only be done with great care when the material and manufacturing methods are the same.

Results

Monomer solutions with five different Bis-GMA and TEGDMA mass ratios have been polymerized and the refractive index of these pure polymers have been measured by the Becke-line method (Figure 1.1). The refractive index of the polymer increased linearly with increasing Bis-GMA content. Small Bis-GMA contents influence the refractive index more significantly after polymerization (slope > 1, Figure 1.1) as a result of the different reactivity of the two monomers. This is consistent with literature\textsuperscript{[17]}

Figure 1.3 shows the light extinction distribution that passed through a pure filler tablet submerged within a liquid of identical refractive index of 1.53 (solid lines). Ba-glass fillers (Schott, 5.8 m$^2$/g, 0.4 μm) with identical filler particle size and composition but from different production batches exhibited different extinction modes as indicated by high and low transparency. The mode of these filler extinction distributions was used to quantify the filler transparency.

Figure 1.4 shows the filler transparency as a function of thickness or volume (from 81 up to 351 μm for 0.5 to 2.5 mm$^3$/mm$^2$) of the high transparency Ba-
glass filler (Figure 1.3). The thickness of the filler tablets was adjusted by two methods: a) by the filler tablet volume (0.05 to 0.25 mm$^3$/mm$^2$) at constant filler tablet diameter and pressure (d=13 mm, 370 MPa, triangles) and b) by the applied pressure during filler tablet preparation (74 to 740 MPa) at constant filler tablet diameter and filler volume (d=13 mm, 1.0 mm$^3$/mm$^2$, circles). Apparent filler tablet density ranged from 61% (74 MPa, Figure 1.4, right inset) to 87% (740 MPa, Figure 1.4, left inset). The increase in filler tablet preparation pressure decreased its thickness by 40% from 164 to 114 μm without affecting the measured transparency significantly (less than 5%, Figure 1.4). The smaller filler tablet volume (0.05 mm$^3$/mm$^2$) resulted in lower apparent densities (62%) than the largest filler tablet volume (0.25 mm$^3$/mm$^2$, 71%, respectively).

![Figure 1.3. Measured light extinction of two Ba-glass filler tablets with identical filler particle size (0.4 μm, 5.8 m$^2$/g) in matching refractive index liquid (n = 1.532, solid lines). Filler extinction was determined from the mode of the extinction distribution indicated by the dotted vertical lines.](image_url)
Figure 1.4. The reported filler (0.4 μm, 5.8 m²/g) transparency in matching refractive index liquids (n = 1.532) depended weakly on the applied pressure during filler tablet production (circles, constant pellet volume of 1 mm³/mm², pressure ranged from 74 MPa to 740 MPa and was stepwise increased by a factor of two). The SEM images (insets) show a slight difference in the overall packing morphology for an applied pressure of 740 MPa (left) and 74 (right). Increasing the solid volume of the filler tablet from 0.05 to 0.25 mm³/mm² while keeping its diameter and pressure constant at 370 MPa (triangles), reduced the filler tablet transparency in excellent agreement with Lambert-Beer-Law (solid line).

The effect of filler/matrix refractive index mismatch was investigated for two silica (n = 1.49) and four Ba-glass (n= 1.53) fillers with average particle sizes ranging from 7 nm to 1.5 μm. Filler tablet fragments were immersed in various refractive index liquids to achieve a defined refractive index mismatches ranging from -0.08 to 0.08 (Figure 1.5, only 0.7 and 1.0 μm Ba-glass fillers are shown). Maximum filler transparency for all fillers was observed when matching refractive index between filler and liquids. Small mismatches in the refractive index reduced the transparency for all fillers resulting in a symmetrical bell shaped curve (Figure 1.5). This effect is much less pronounced for nanofillers. The
transparency of the fumed silica filler (7 nm, Aerosil 380) decreased approximately 5% for the largest refractive index mismatch of ±0.08. The transparency of a larger fumed silica filler (55 nm, OX50) had the same maximum filler transparency for matching refractive indices as the 7 nm fumed silica filler (Aerosil 380) but showed 15% filler transparency decrease for a maximum refractive index mismatches of ±0.08. The filler transparency of Ba-glass with an average filler particle size of 1.0 μm was reduced from 91% for matching refractive indices to approximately 9% for a refractive index mismatch of ±0.08. Differences in the maximum filler transparency at matching refractive indices resulted from the inherent filler transparency.

Figure 1.5. Splinters of filler tablets in liquids with matching refractive indices exhibited the highest transparency compared to mismatching filler/liquid combinations. Larger derivations in filler/liquid refractive indices decreased the filler transparency. The filler particles size has a significant influence on the transparency in case of refractive indices mismatches. Filler transparencies at matching filler/liquid refractive indices correspond to the inherent filler transparencies.
In Figure 1.6 filler/liquid transparencies were normalized to the maximum transparency. The transmittance data for different refractive index mismatches were fitted using the facet model by adjusting the parameter $L/\sigma$. The transmittances predicted by the facet model decreases with increasing filler/liquid mismatch. The fitting parameter $L/\sigma$ reflects the dimensionless ratio of surface roughness to a correlated surface length. Large $L/\sigma$ values indicate smooth surfaces and result in high transparencies even for large refractive index mismatches. While rough surfaces result in small $L/\sigma$ values which results in high transparencies only for closely matched filler/liquid refractive indices. The agreement between the theoretical fit with the experimental data was good over the entire refractive index mismatch range ± 0.08.

**Figure 1.6.** Filler transmittances for different filler/liquid mismatches and filler particle sizes (symbols) have been fitted with the facet model by adjusting the parameter $L/\sigma$ (solid lines). Filler transparencies have been normalized to the filler transparency at matching filler/liquid refractive index.

Figure 1.7 shows the measured composite transmittance for three Ba-glass ($n = 1.53$) fillers. The composite transparency strongly depends on the refractive
index mismatch for filler particles in the size range of 0.4 to 1.5 \( \mu \text{m} \). Differences in the maximum composite transparency resulting from the inherent filler transparencies were eliminated by the normalizing the mode of the composite transparency to 1. All polymer/filler composites were less transparent for larger refractive index mismatches while this effect was more pronounced for the filler with a larger average particle size. The composite transmittances were fitted with the facet model. The agreement with the experimental data was good.

\[ \frac{\text{n}_{\text{polymer}}}{\sigma} \]

\[ \text{data \hspace{1cm} model} \]

\[ \triangle 0.4 \mu \text{m} \hspace{1cm} - - - - \]

\[ \triangledown 0.7 \mu \text{m} \hspace{1cm} --- \]

\[ \circ 1.5 \mu \text{m} \hspace{1cm} \ldots \ldots \]

\[ n_{\text{polymer}} \text{ a.u.} \]

\[ 1.48 \hspace{1cm} 1.5 \hspace{1cm} 1.52 \hspace{1cm} 1.54 \hspace{1cm} 1.56 \]

\[ \text{composite transmittance, a.u.} \]

\[ 0.0 \hspace{1cm} 0.2 \hspace{1cm} 0.4 \hspace{1cm} 0.6 \hspace{1cm} 0.8 \hspace{1cm} 1.0 \]

\[ n_{\text{polymer}} - n_{\text{filler}} \text{ a.u.} \]

**Figure 1.7.** Fillers in polymers with closely matching refractive indices exhibited the highest composite transparency. As in the case of filler transmittances (Figure 1.6) the experimental data (symbols) was fitted with the facet model (lines).

Figure 1.8a shows the dimensionless parameter, \( L/\sigma \), for different filler particle size of the Ba-glass filler/liquid and composite systems. \( L/\sigma \) were obtained by fitting filler/liquid (Figure 1.6) and filler/polymer (Figure 1.7) transmittances with the facet model. Increasing the filler particle size from 0.4 \( \mu \text{m} \) to 1.0 \( \mu \text{m} \) resulted in a decrease of the dimensionless parameter from 2.7 to 0.7 (value for
Figure 1.8. a) The dimensionless surface roughness parameter $L/\sigma$ decreased with increasing particle size for the filler and the composite transmittance for filler particle sizes from 0.4 to 1.5 μm. b) Composite $L/\sigma$ was correlated to the filler $L/\sigma$ by linear approximation.
1.0 μm not shown). Increasing the filler particle size further to 1.5 μm did not change the dimensionless surface roughness parameter significantly (0.65). The decrease of surface roughness (0.7 to 0.3) with increasing filler particle size (0.4 to 1.5 μm) was also observed for the composite transmittance. The parameter $L/\sigma$ of the filler/liquid system was linearly correlated to the $L/\sigma$ values of the composites (Figure 1.8a). Each data point represents the average of 27 measurements.

Figure 1.9 corroborates the correlation of the filler transparency and resulting composite transparency for four batches of Ba-glass with a filler particle size of 0.4 μm (5.8 m$^2$/g). Filler and composite transparencies ranged from 78 up to 92 % and from 39 to 51 %, respectively, while fillers with a high inherent trans-

\textbf{Figure 1.9.} Direct correlation of filler transparency with the final composite transparency shown for four different Ba-glass batches. Although the Ba-glass batches cannot be distinguished in their chemical or physical properties they showed different filler transparencies. Microscope images (insets) show filler tablets suspended in matching refractive index liquid. Both fillers exhibited inhomogeneities of the material (dark dots) while the difference of filler transparency (brightness of the sample) is evident by eye.
Chapter 1: Filler/Composite Transparency

Transparency resulted in highly transparent composites. Images of filler tablet fragments suspended in a liquid with matching refractive index (1.53) are shown in Figure 1.9. Dark spots were present for highly and less transparent materials. It should be noted that the reported filler transparency does only represent the mode of the grayness histogram (Figure 1.3) and does not take tail effects (dark spots) into account.

Discussion

*Filler Transparency*

Light extinction by scattering at the filler/liquid interfaces can be excluded for matching refractive indices of filler and liquid. Therefore, light extinction is a result of absorption in the liquid and fillers only. Since the intensity of transmitted light through the pure liquid was determined experimentally, light extinction can be related directly to inherent filler properties. For a constant specific solid volume the average path of light through the solid is equivalent for all materials and filler transparencies are comparable. The smallest tablet volumes (e.g. 0.5 mm$^3$/mm$^2$) may have resulted in an inhomogeneous filler tablet thicknesses or less dense packing. Therefore, the increase in thickness from 0.5 up to 2.5 mm$^3$/mm$^2$ is slightly lower (4.3) than the theoretically value of 5 (Figure 1.4). The relation between filler transparency and the specific volume followed Lambert-Beer law (solid line).$^{[18]}$ All filler tablets had low transparencies in air which increased substantially after submerging into a liquid with matching refractive index regardless of the filler tablet preparation pressure. Despite the fact that higher preparation pressures led to an increased packing density, filler transparency did not change significantly with preparation pressure indicating a comparable accessibility of the remaining voids by the fluid or monomers. It is worth noting that fillers manufactured using aerosol methods showed a homogeneous appearance (Figure 1.5 inset) in the microscope (resolution: 1 μm). Fillers
manufactured by milling exhibited inhomogeneities visible with the light microscope as dark spots (Figure 1.9 insets). Filler tablets with a homogenous appearance showed a narrower extinction distribution (smaller geometric standard deviation) than fillers with an inhomogeneous appearance (Figure 1.3).

**Filler/Matrix Transparency**

An increase in refractive index mismatch between filler and matrix resulted in an increase of scattering at the filler/matrix interface,\(^{[19]}\) thereby decreasing the transparency of the filler/liquid and filler/polymer systems.

In this study the filler particles are either much smaller (silica filler) or larger (Ba-glass filler) than the wavelength of the visible light. The nano-sized fumed silica fillers (5 – 50 nm) scatter light according to Rayleigh-Gans theory.\(^{[20]}\) From Rayleigh theory it is known that the extinction coefficient increases with increasing filler particle size and filler/matrix refractive index mismatch. Therefore, the measured transparency decreases for larger filler particles (Figure 1.5).\(^{[21]}\) For nano-sized filler particles, remaining air in the voids would have introduced interfaces with a high refractive index mismatch thereby reducing the transparency by scattering. But SiO\(_2\) nanofillers of 7 nm and 50 nm exhibited maximum transparencies in most cases, indicating only a small influence of this mechanism (Figure 1.5).

The micron-sized Ba-glass fillers have preferential scattering directions (Mie scattering). Here, the filler particle size is comparable or larger than the light wavelength and therefore, light can be scattered at each facet of a filler particle. In this case the facet light scattering model was used to correlate the experimental results of the filler and composite transparency on filler/matrix mismatch (Figure 1.5 and Figure 1.6). The model was originally developed for the refractive index analysis of rough solids, where the dimensionless surface roughness determines the transparency depending on the refractive index mismatch.\(^{[15]}\) Since light passes more interfaces inside the filler tablet/composite than at the
surface, surface effects of the filler tablet or composite have been neglected. Inside the pressed filler tablet or the composite individual filler particles are randomly oriented. Light is scattered at interfaces of arbitrary orientation while the facet size cannot be larger than filler particles size itself. The packed filler particles (in the filler tablet and composite) form interface structures to the surrounding matrix that are mainly determined by their size. Larger filler particles resemble therefore higher surface roughness. In composites the filler particles are not as closely packed as in the pressed filler tablets so that the virtual roughness of the filler particles distributed in the polymer is increased leading to lower dimensionless surface roughness parameters (Figure 1.8). Even though dimensionless surface roughness was decreased in the composites compared to the filler/liquid system, the two roughnesses are well correlated by a linear approximation (Figure 1.8b). The facet model is mostly applied to the transparency of solids with rough surfaces [14] and has recently been used for the reflectance of composites containing particulate fillers [22] while in this study it is extended to correlate the transparency of filler containing composites.

It should be noted that the facet model was originally derived based on Snell’s law. Even though the particles are in the dimension of the wavelength the maximum in transparency with regard to particle size of the filler/liquid and filler/polymer systems can be described. These correlations hold for all particle systems tested, some of which are outside the geometric assumptions of Snell’s law. The interpretation of surface roughness obtained with Snell’s law cannot be related directly to the physical parameters L and σ since facets and even particles are smaller than the wavelength.

The measured composite transparencies can be predicted from the transparency of the filler tablet fragments submerged in corresponding refractive index liquids (Figure 1.9). Furthermore the composite transparency for any filler particle size and any filler particle/polymer refractive index mismatch can be predicted by the two correlation functions obtained in Figure 1.8 and Figure 1.9.
This requires only information on the specific surface area and the filler’s maximum transparency. High filler transparencies resulted in high composite transparencies. Uncertainties of the presented correlation might result from the higher viscosity of the monomer in comparison to the refractive index liquid. The monomer might not have completely wetted the filler particles leading to gas enclosures and therefore additional optical interfaces or tail effects which were not taken into account by the filler transparency measurement.

**Transparency Quality Control**

Fillers with the same specification but from different batches exhibited different filler and composite transparencies (Figure 1.9 insets). These Ba-glass batches were investigated for their physical/chemical properties. Filler morphology such as crystallinity has a significant influence on the final composite transparency. Crystallites in an amorphous matrix result in interfaces inside the filler that scatter the light and thereby reduce the transmitted light intensity.\(^{6, 7}\) XRD patterns of the different Ba-glass batches clearly showed a broad hump from 2 \(\theta = 20 – 35^\circ\) without any distinct peaks, typical for amorphous SiO\(_2\)-based materials, but no significant differences were detected. Contamination can result in light adsorption in the visible and near-visible light region, which then decreases the inherent filler transparency. All fillers appeared to be white, indicating no adsorption in the visible light range. DRUV-Vis spectroscopy exhibited no detectable absorption in the visible and near-visible light region. Wavelengths below 230 nm were absorbed by both materials mainly because of the silica absorption at these wavelengths.\(^{23}\) Contamination and elemental distribution were analyzed by Fourier Transform Infrared Spectroscopy. DRIFTS measurements. Absorption bands of Al\(_2\)O\(_3\)\(^{24}\) at 700 cm\(^{-1}\) and SiO\(_2\) bands at 800 and 1000 - 1200 cm\(^{-1}\) were detected,\(^{25}\) but no significant differences between the low and high transparency materials were quantified. Therefore fillers in industrial manufacturing must be tested directly for their transparency and cannot rely
only on standard material characterization before incorporated in the monomer. Filler producer can make fast and easy transparency tests with the presented method having little knowledge of the final composite production and thereby ensure a high quality of their products. But transparencies can only be compared for fillers with the same particle size from comparable manufacturing methods. This has a significant influence on the maximum transparency of the composite.\[21\]

Conclusions

It was shown that the inherent filler transparency has a significant influence on the composite transparency. Fillers with high inherent transparency resulted in composites with higher transparencies. Matching refractive indices of filler and liquid/polymer are less important for filler particles much smaller than the wavelength of light (nanofillers) in comparison with micron-sized fillers. Determining filler transparency has been shown to be an inexpensive and fast method for batch quality control of particulate products before further manufacturing. Furthermore, filler transparency and particle size can be used to predict composites transparencies for any particle size/refractive index mismatch combination.

References


CHAPTER TWO

Flame-made Ta$_2$O$_5$/SiO$_2$ particles with controlled refractive index and nanocomposite transparency

Abstract

Mixed Ta$_2$O$_5$-containing SiO$_2$ particles, 6 – 14 nm in diameter, with closely controlled refractive index, transparency and crystallinity were prepared by flame spray pyrolysis (FSP) at production rates of 6.7 – 100 g/h. The effect of precursor solution composition on product filler (particle) size, crystallinity, Ta-dispersion and transparency was studied by nitrogen adsorption, x-ray diffraction, light microscopy, HRTEM, and DRIFTS analysis. Emphasis was placed on the transparency of the composite that was made with Ta$_2$O$_5$/SiO$_2$ filler and dimethylacrylate. Increasing Ta$_2$O$_5$ crystallinity and decreasing Ta-dispersion on SiO$_2$ decreased both filler and composite transparencies. Powders with identical
specific surface area (SSA), refractive index (RI) and Ta₂O₅-content (24 wt.%) showed a wide range of composite transparencies, 33 – 78 %, depending on filler crystallinity and Ta-dispersion. Amorphous fillers, high Ta-dispersion and matching RI with that of the polymer matrix showed the highest composite transparency, 86 %. That composite contained 16.5 wt.% filler containing 35 wt.% Ta₂O₅ having, thus, optimal radiopacity for dental fillings.

Introduction

Dental fillings made of composite organic monomers and ceramic fillers (particles) are used for tooth shaded dental restoration of anterior lesions and small - medium sized defects in the posterior region. This is a result of the excellent esthetic properties of these fillings as well as health concerns with amalgam fillings regarding mercury release. Therefore, the relation of filler properties to composite characteristics such as radiopacity, tensile strength, hardness, shrinkage, wear and transparency have been intensively studied in the last few years.

High radiopacity, a property conventionally provided by the ceramic filler, is needed for x-ray detection of the filling. For nanocomposites of organic monomers including Ta₂O₅ or TiO₂ particles, excellent radiopacity was observed for ceramic filler loadings of 60 – 80 wt.%. However, the tensile strength of composites containing Ta₂O₅ particles below 100 nm decreased at high (≤ 30 wt.%) filler content. Grafting the particle surface enhanced particle bonding with the polymer matrix and increased tensile strength (TiO₂, 1 – 3 μm) and hardness (SiO₂, 40 nm).

The polymerization shrinkage of restorative composites during curing depends on filler content and contributes to formation of a marginal gap which can cause secondary caries. Using smaller filler particles the attainable filler content is lower than using larger ones, and this increases the composite polymeri-
The composite wear, however, is significantly lower for nano- than for micron-size particles. High initial transparency of the dental filler is desired as the opacity of dental filling is adjusted to the patient’s tooth color by opaque additives. Excellent composite translucence was observed when matching the polymer and ceramic refractive indices (RI). The RI of mixed oxides can be controlled over the range of the RI of its components. In this regard Ta$_2$O$_5$/SiO$_2$ gives a broad range of RI while the Ta presence provides the radiopacity. Mixed Ta$_2$O$_5$/SiO$_2$ has no absorption band in the visible spectrum and can have a high transparency as desired in dental applications.

Commonly mixed Ta$_2$O$_5$/SiO$_2$ of high SSA is made by sol-gel preparation, templating and impregnation. A challenge in these wet preparation processes is the simultaneous reaction of Ta- and Si-precursors. High reactivity of the Ta-precursor causes faster hydrolysis and condensation of Ta$_2$O$_5$ compared to SiO$_2$. Then Ta$_2$O$_5$ crystallites are formed lowering the transparency of the ceramic material. Differences in Ta-precursor water sensitivity and solvent water content alter the atomic distribution, morphology and even the catalytic performance of the product particles. High dispersion of Ta within the SiO$_2$ matrix is achieved with up to 48 wt.% Ta$_2$O$_5$ content. Wet preparation methods result in porous ceramics consisting of hollow network structures with pores smaller than 8 nm. Blending such porous materials into the polymer results in heterogeneous with irregular composite properties lowering composite performance.

Dry, flame-made particles can be dispersed uniformly in a polymer matrix (e.g. dimethacrylate) increasing the elastic modulus of the resulting composite. Recently conventional flame processes for manufacturing of commodities (e.g. carbon black, pigments, optical fibers) have been extended for production of nano-sized mixed oxides or even metal-ceramic particles by flame spray pyrolysis (FSP), a highly versatile and scalable technique. The control of the FSP parameters with respect to the resulting product properties has been investi-
gated extensively.\textsuperscript{[24]} For example, production of solid nano-sized or hollow micron-sized particles can be controlled by the metal oxide precursor and solvent compositions as well as by the liquid to gas feed ratio to the spray flame.\textsuperscript{[25]} The RI of these materials can be controlled by the Ta\textsubscript{2}O\textsubscript{5} content of SiO\textsubscript{2} as in manufacturing of optical fiber performs.\textsuperscript{[26]} Here FSP is used for production of Ta\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} filler (particles) with closely controlled particle size and RI. The pure filler and its composite (with dimethacrylate) transparencies are characterized and related to intrinsic ceramic properties such as crystallinity and elemental distribution (dispersion).

Experimental

Precursor Preparation

Tantalum butoxide (butox, Aldrich, > 98 \%), tantalum ethoxide (ethox, Aldrich, > 99.98 \%) or tantalum tetraethyl-acetylacetonate (TEAA, Strem, > 99.99 \%) and tetraethoxysilane (TEOS, Fluka, > 98 \%) were used as tantalum and silicon precursors, respectively. Appropriate amounts of the precursors were diluted or dissolved under nitrogen either in pentane (Fluka, > 98 \%), hexane (Fluka, > 95 \%), dodecane (Fluka, 90 - 95 \%), xylene (Fluka, > 96 \%) or a 5:2 mixture by volume of 2-ethylhexanoic acid (2EHA, Fluka, > 99 \%) / toluene (Fluka, > 99.5 \%). The total (Ta & Si) metal concentration was varied from 0.5 to 4.5 M in the precursor solutions. For the maximum concentration, 4.5 M, only the metal precursors without any solvents were used. The weight fraction of Ta\textsubscript{2}O\textsubscript{5} in the product powder was defined as

\begin{equation}
\text{wt.\% } \text{Ta}_2\text{O}_5 = \frac{\text{mass (Ta}_2\text{O}_5)}{\text{mass (Ta}_2\text{O}_5) + \text{mass (SiO}_2)} \times 100
\end{equation}

and ranged from 0 – 83 wt.\%. Standard (std) precursor conditions were 0.5 M total metal concentration of Ta-butoxide and TEOS in hexane (Ta/Si = 0.086)
and 24 wt.% \( \text{Ta}_2\text{O}_5/\text{SiO}_2 \). They were selected as such because they resulted in nearly optimal nanocomposite transparency at high radiopacity.

**Filler Synthesis by Flame Spray Pyrolysis (FSP)**

Mixed tantalum oxide silica powders were produced in a laboratory scale flame reactor.\(^{[27]}\) A concentric two-phase nozzle (capillary inner/outer diameter 0.42 / 0.71 mm) and annulus (outer diameter 0.95 mm) was used to spray the metal-containing liquid mixture. The annular gap area (maximum 0.25 mm\(^2\)) of the dispersion gas (\( \text{O}_2 \), Pan Gas, 99.95\%) was adjusted to achieve a 1.5 bar pressure drop. In all experiments, a syringe pump (Inotec, RS 232) fed 5 ml/min of the precursor solution into the flame through the innermost capillary, where it was dispersed into fine droplets by 5 l/min \( \text{O}_2 \) through the first annulus. The spray was ignited by a circular premixed flame (inner diameter 6 mm, slit width 10 \( \mu \text{m} \)) of \( \text{CH}_4 \) (1.1 l/min, Pan Gas, 99.5\%) and \( \text{O}_2 \) (2.5 l/min). Additional \( \text{O}_2 \) sheath (3.5 l/min) was supplied through a ring of sinter metal (inner/outer diameter 11 / 18 mm). All gas flow rates were controlled by calibrated mass flow controllers (Bronkhorst). The production rate ranged from 6.73 g/h for pure silica (0.5 M) to 100 g/h for 24 wt.% \( \text{Ta}_2\text{O}_5/\text{SiO}_2 \) (4.5 M). The powders were collected by a vacuum pump (Busch SV 1025 B) on a glass microfibre filter (Whatman GF/D, 25.7 cm in diameter).

The combustion enthalpy density (\( \Delta_c h \), kJ/g\(_{\text{gas}} \)) of the flame was determined by calculating the specific combustion enthalpy (\( \Delta_c \hat{h}_i \), kJ/ml\(_{\text{liquid}} \)) for full combustion (products: \( \text{CO}_2 \), \( \text{H}_2\text{O} \), \( \text{Ta}_2\text{O}_5 \) and \( \text{SiO}_2 \)) of the reactants divided by the specific mass (\( \dot{m}_i \), g\(_{\text{gas}}\)/ml\(_{\text{liquid}} \)) of evolving gases during combustion,

\[
\Delta_c h = \frac{\sum \hat{x}_i \times \Delta_c \hat{h}_i}{\sum \hat{x}_i \times \dot{m}_i},
\]

where \( \hat{x}_i \) is the volume fraction of reactant \( i \) in the precursor solution.\(^{[28]}\)
Chapter 2: FSP-made, Radiopaque Ta$_2$O$_5$/SiO$_2$

*Inorganic - Organic Composite Synthesis and Characterization*

The composite was prepared by treating the surface of the ceramic nanoparticles filler with $\gamma$-methacryloxypropyltrimethoxysilane to improve the bonding with the monomer matrix. After mixing bisphenol-A-glycidyldimethacrylate, urethane dimethacrylate and decandiol dimethacrylate at a ratio of 4:3:2 (by weight), 0.3 wt.% camphorquione and 0.6 wt.% N,N-cyanoethylmethylanilin were dissolved in the monomer solution. Filler Ta$_2$O$_5$/SiO$_2$ were added to the above mentioned monomer mixture and stirred under vacuum to form the composite containing 16.5 wt.% of the filler. The composite was polymerized with a dental curing unit (Ivoclar Vivadent, Astralis 10, 1100 mW/cm$^2$) with curing time of 20 seconds. The composite transparency was measured at 1 mm sample thickness (diameter of 20 mm) with a Minolta Spectrometer (CT-310) in comparison to water. The polymer matrix had an RI of 1.53.

*Particle Characterization*

Specific surface areas (SSA, m$^2$/g) of the materials were determined from the adsorption of nitrogen at 77 K using the BET method (Micromeritics Tristar 3000, 5-point isotherm, 0.05 < $p/p_0$ < 0.25). Assuming spherical, monodisperse primary particles with homogeneous density, the average BET-equivalent particle diameter, $d_{BET}$, is

$$d_{BET} = \frac{6}{SSA \times (x_{Ta_2O_5} \times \rho_{Ta_2O_5} + x_{SiO_2} \times \rho_{SiO_2})},$$

where $x_i$ the mass fraction of Ta$_2$O$_5$ or SiO$_2$ and $\rho_i$ the density of pure Ta$_2$O$_5$ (8.2 g/cm$^3$) or amorphous SiO$_2$ (2.2 g/cm$^3$). HRTEM images were taken with a CM30ST microscope (Philips, LaB6 Cathode, 300kV, point resolution 0.2 nm). Particles were disposed dry onto a carbon foil supported on a copper grid. XRD measurements were performed using a Bruker D 8 Advance diffractometer with 2$\theta$ from 10$^\circ$ to 70$^\circ$ (step size 0.03$^\circ$, scan speed 0.60$^\circ$min$^{-1}$, Cu-K$\alpha$ radiation).
For all optical experiments with ceramic fillers 3.5 mm$^3$ of the material was pressed by 370 MPa into a round tablet (13 mm in diameter). RI and transparency tests of the tablets were carried out on a Zeiss Axioplan light microscope. A disc-like fragment of the pressed tablet was mounted on a microscope slide. The transparency images were taken by a camera (Panasonic, WV-CD50) at 2.5x/0.075 magnification (Zeiss, Plan Neofluar) operating the microscope in transmittance mode. For comparison, a fragment of the standard (std) material is shown in every image. Then RI of the glasses were measured by the Becke line method. The series of index matching oils (Cargille Laboratories Inc.) ranged from 1.4 to 1.7 with 0.004 intervals and from 1.7 to 1.8 in 0.01 intervals. A NaD filter was used to assure a measurement at a wavelength of 589 nm.

Diffuse reflectance IR fourier transform spectra (DRIFTS) were recorded on a Harrick Praying Mantis diffuse reflectance unit of a FTIR instrument (Bruker, Vektor 22). The reaction chamber is equipped with KBr windows, a heating control and a gas flow system. The diluted samples (1:50 KBr) were outgassed (room temperature, 1 h) and dehydrated in argon (Pan Gas, > 99.999 %, 5 ml/l, 200°C, 1 h). For each spectrum 512 scans were collected at room temperature at a resolution of 2 cm$^{-1}$ against a KBr background. The spectra were fitted by five Gaussians with the multipeak fitting package of Igor Pro (Version 4.0, WaveMetrics Inc.). The Gaussians were shifted by fitting a polynomial baseline (third degree) to the spectrum. For some spectra the deconvoluted areas of specific peaks were negligible, so that less than five peaks were necessary for the fitting. The relative Ta-dispersion was estimated by the formula:

$$relative\ Ta-dispersion = \frac{area(Ta-O-Si)}{area(Si-O-Si)} \times \frac{molar\ fraction(Si)}{molar\ fraction(Ta)}$$  \hspace{1cm} (2.4)

and the deconvoluted areas for Ta-O-Si at 943 – 958 cm$^{-1}$ and Si-O-Si at 1076 – 1097 cm$^{-1}$.[29]
SAXS measurements of the powders were performed using as pinhole Bonse-Hart camera\(^{[19]}\) with an experimental setup at the European Synchrotron Radiation Facility.\(^{[30]}\) The radii of gyration of the agglomerates and the fractal dimension were determined by the unified fit method.\(^{[31]}\)

**Results and Discussion**

*Ta\(_2\)O\(_5\)/SiO\(_2\) Synthesis*

Flame spray pyrolysis of precursor solutions having a 0.5 M total metal concentration (Ta-butoxide and TEOS, solvent: hexane) resulted in Ta\(_2\)O\(_5\)/SiO\(_2\) particles with 0 – 100 wt.% Ta\(_2\)O\(_5\) content (composition) and high SSA (51 - 380 m\(^2\)/g). The average BET-equivalent diameter of these particles ranged from 6.4 to 14.4 nm (Figure 2.1). Doping pure silica (261 m\(^2\)/g) with less than 5 wt.% Ta\(_2\)O\(_5\) led to a steep increase of the SSA with a maximum (380 m\(^2\)/g) at 2.4 – 4.7 wt.%. Beyond this, the SSA decreased constantly down to 51 m\(^2\)/g for pure Ta\(_2\)O\(_5\). The corresponding d\(_{\text{BET}}\) decreased for small Ta\(_2\)O\(_5\) contents down to 6.4 nm compared to pure SiO\(_2\) (10.4 nm). A further increase of the Ta\(_2\)O\(_5\) content resulted in larger particles up to 14.4 nm for pure Ta\(_2\)O\(_5\) (Figure 2.1). A steep decrease of the d\(_{\text{BET}}\) has been observed also for flame-made ZnO containing SiO\(_2\).\(^{[32]}\) Interaction of Ta\(_2\)O\(_5\) with SiO\(_2\) during particle formation within the flame could change the SSA so drastically since independent formation of these oxides would cause insignificant SSA changes at these low Ta\(_2\)O\(_5\) contents. It should be noted that Ta\(_2\)O\(_5\)/SiO\(_2\) does not form any silicates.\(^{[33]}\) The homogeneous particle morphology and the average particle size of the powder was validated by TEM images (Figure 2.1 inset).
Results and Discussion

Figure 2.1. Small Ta$_2$O$_5$ contents have a profound effect on the powder SSA (squares) which increased drastically, reached a maximum at 3.6 wt.%, and decreased constantly for higher Ta$_2$O$_5$ contents. The SSA is decreased as the particle diameter increased and by the increase of the material's density with increasing Ta$_2$O$_5$ content. The corresponding average BET-equivalent diameter (circles) decreased, following Equation 2.3. The TEM image inset shows the homogeneous morphology of the 24 wt.% Ta$_2$O$_5$/SiO$_2$ powder and indicates an average primary particle size below 10 nm.

The RI was controlled by changing the Ta$_2$O$_5$ content (Figure 2.2). Materials with RI ranging from 1.44 (pure SiO$_2$), which is close to the theoretical value of 1.46,[11] to more than 1.8 (40 mol% or 83 wt.% Ta$_2$O$_5$) were made. For the latter material, the RI exceeded the maximum RI of the matching oils (1.8). The RI increase can be divided in two regions: For 0 – 0.25 mol% (0 – 1.8 wt.%) Ta$_2$O$_5$ content, the RI increased steeply, while for higher Ta$_2$O$_5$ contents (2 – 30 mol%) the RI increased linearly following Appen’s law. The RI increase for bulk (pellets)[12] Ta$_2$O$_5$/SiO$_2$ is larger than the one measured here. This indicates that the RI can be affected by the particle size through the dielectric constant.[34] The nominal and the measured material’s composition are in the range of the mixing
accuracy in flame processes\textsuperscript{[22]} Therefore, a reduced RI by a possible loss of Ta\textsubscript{2}O\textsubscript{5} from the present nanoparticles compared to the larger ones of Satoh\textsuperscript{[12]} can be safely excluded. The sharp RI increase for small Ta\textsubscript{2}O\textsubscript{5} contents coincided with the steep SSA increase as seen in Figure 2.1. The powders that exhibited the highest SSA belong to the transient region between the steep and the rather linear increase of the RI (Figure 2.2). For small Ta\textsubscript{2}O\textsubscript{5} contents, the Ta-concentration at the particle surface might be higher than the bulk of the material as will be shown by Ta-surface dispersion measurements. This resulted in a steep increase of the RI. After this surface phenomenon of the RI, the concentration in the bulk of the particle increased leading to the expected linear (Appen’s law) increase of the RI.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.2.png}
\caption{The RI (squares) increased (solid line) with Ta\textsubscript{2}O\textsubscript{5} content. Appen’s law for bulk structures (broken line) results in slightly different RI than the current data. At low Ta\textsubscript{2}O\textsubscript{5} contents (inset) the RI increased more steeply than for high contents.}
\end{figure}
Results and Discussion

Effect of Precursor and Solvent Composition and Concentration

Metal precursors and solvents can have a profound influence on the characteristics of product mixed oxides made by sol-gel techniques\(^{[15]}\) and FSP\(^{[35]}\). Therefore, three different Ta-precursors (Ta-ethoxide, Ta-butoxide, and Ta-tetraethylacetylacetonate, (Ta-TEAA)) and five different solvents (pentane, hexane, dodecane, xylene and 2-ethylhexanoic acid/toluene, 5:2 by volume) have been investigated. Table 2.1 summarizes their effect on SSA, RI and combustion enthalpy density for Ta\(_2\)O\(_5\)/SiO\(_2\) powders made at otherwise standard conditions. Any combination of Ta-precursor and solvent hardly affected the product SSA and RI at these rather constant specific combustion enthalpies (9.7 – 10.4 kJ/g\(_{\text{gas}}\)). Small differences were caused by slight experimental variation. The SSA and RI of the powders from Ta-TEAA/hexane and Ta-TEAA/2-EHA/toluene were statistically validated by three experiments. The arithmetic standard deviation was 20 m\(^2\)/g and 15 m\(^2\)/g, respectively. The RIs varied by \(\forall\) 0.01 for both precursor combinations. RI The All precursors were stable enough to avoid decomposition on the droplet surface during the FSP process and formation of hollow, egg-shell like particles of \(\mu\)m size\(^{[25]}\) as verified by TEM.

Particle formation is influenced by the metal precursor concentration as it affects directly particle growth rates by coagulation as it was shown with TiO\(_2\)\(^{[36]}\) and SiO\(_2\)\(^{[19]}\) for fast sintering. Therefore the 24 wt.% Ta\(_2\)O\(_5\)/SiO\(_2\) standard was produced at total metal concentration of 0.5 - 4.5 M in the precursor liquid corresponding to particle production rates from 11.1 g/h (0.5 M) to 100 g/h (4.5 M). Figure 2.3 shows that the SSA (squares) decreased from 255 m\(^2\)/g (0.5 M) to 98 m\(^2\)/g (4.5 M) as observed in previous studies\(^{[23, 37]}\). The product RI (circles), however, was not significantly influenced by the different SSAs. Small deviations are attributed to experimental variations as the data scatter randomly around the average of 1.532 (horizontal line).
Table 2.1. Comparison of the SSA, RI and combustion enthalpy density ($\Delta_h$) for flame-made tantalum oxide-silica powders containing about 24 wt.% Ta$_2$O$_5$ from different Ta-precursors and solvents. The SSA and RI were not influenced significantly by the Ta-precursor or solvent composition as all powders were made at similar $\Delta_h$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ta-precursor</th>
<th>SSA  (m$^2$/g)</th>
<th>Ref. index (RI)</th>
<th>Combustion enthalpy density (kJ/g$_{gas}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>Ta-butoxide</td>
<td>258</td>
<td>1.54</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>Ta-ethoxide</td>
<td>250</td>
<td>1.53</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>Ta-butoxide</td>
<td>255</td>
<td>1.52</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>Ta-TEAA</td>
<td>268</td>
<td>1.52</td>
<td>10.4</td>
</tr>
<tr>
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<td>Ta-butoxide</td>
<td>255</td>
<td>1.54</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>Ta-ethoxide</td>
<td>266</td>
<td>1.53</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>Ta-butoxide</td>
<td>264</td>
<td>1.53</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>Ta-TEAA</td>
<td>268</td>
<td>1.53</td>
<td>10.1</td>
</tr>
<tr>
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<td>Ta-butoxide</td>
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<td>1.54</td>
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<td></td>
<td>Ta-TEAA</td>
<td>269</td>
<td>1.52</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Ta$_2$O$_5$/SiO$_2$ Transparency

Figure 2.4 compares the transparency through the greyness of powder tablet fragments that were produced with different a) Ta-precursor, b) solvent, c) total metal concentration or d) Ta-content. All precursor solutions deviated from the standard solution in a single parameter, indicated in the images. The surface texture of the fragments originated from the production process of the tablets. Dark spots or lines in the images came from glass fibres that have been introduced during powder separation from the filter. With light shining through the samples, fragments with high (or low) transparency appeared light (or dark) in the image. Having the same RI and SSA (except for Figure 2.4d), powders made
from different Ta-precursors and solvents exhibited very different transparencies (Figure 2.4a,b).

Figure 2.3. The SSA (squares) of the 24 wt.% Ta$_2$O$_5$ in SiO$_2$ powder decreased with increasing total metal concentration in the precursor solution. The RI (circles) of the material is not influenced by the SSA in the range from 98 m$^2$/g to 255 m$^2$/g.

Precursors$^{[25]}$ and solvents$^{[35]}$ can have significant influence on the structure$^{[25]}$ and thermal stability$^{[35]}$ of FSP-made particles having the same SSA. The specific surface areas of most of the powders were rather similar (Table 2.1). Therefore, the interfaces which the light has to pass on its way through the tablet fragment are comparable. The volume of the ceramic particles (filler) used for tablet preparation was kept constant for all measurements. Therefore, the light path through the solid material is comparable for all samples. Voids can only be filled with air that may not lower the overall transparency. Si-O-Ta bonds have no absorption band in the visible light spectrum, thus powders with low Ta-content diminish the light intensity by absorption.$^{[13]}$ For dental and possibly
other applications, the transmittance of these particles is important. Therefore, the proportion of absorbed and reflected light is of minor interest.

Figure 2.4. Pressed powder tablet fragments made with different a) Ta-precursor, b) solvent, c) total metal concentration in the precursor liquid, and d) Ta$_2$O$_5$ content. All images contain a 24 wt.% Ta$_2$O$_5$ reference sample (std: Ta-butox, hexane, 0.5 M) for consistent comparison. Light or dark fragments showed a high or low transparency, respectively. While the powder transparency was changed significantly by these parameters, the SSA and RI were not (Table 2.1).

The transparency reduction with increasing precursor concentration (Figure 2.4c) can be understood by the associated increasing particle size (Figure 2.3).
Likewise, $\text{Ta}_2\text{O}_5$ crystallites in the $\text{SiO}_2$ matrix decreased the transparency as observed for sol-gel-made $\text{Ta}_2\text{O}_5$-containing $\text{SiO}_2$.\cite{12} Increasing the $\text{Ta}_2\text{O}_5$-content lowered the material’s transparency as $\text{Ta}_2\text{O}_5$ crystallites were formed. This was verified with XRD analysis of all Figure 2.4 powders in Figure 2.5. The broad peak of amorphous $\text{SiO}_2$ and $\text{Ta}_2\text{O}_5$ could be observed for all the samples. Compared to pure $\text{SiO}_2$, all $\text{Ta}_2\text{O}_5$ containing samples showed a second broad hump from $40^\circ$ to $70^\circ$ attributed to amorphous $\text{Ta}_2\text{O}_5$. For some powders small orthogonal $\text{Ta}_2\text{O}_5$ crystallites could be observed (especially Figure 2.5d at 76 wt.% $\text{Ta}_2\text{O}_5$). Generally powders with small crystallites (XRD intensity peaks slightly above the noise level) corresponded to powders with reduced transparency. Crystallites have a higher density and RI than amorphous $\text{Ta}_2\text{O}_5$ so that they scatter light, thereby decreasing the transparency.\cite{12} The degree of crystallinity in the XRD patterns (Figure 2.5) corresponded nicely to the decreased transparency observed in Figure 2.4.

The powder crystallinity can be correlated also with the Ta-precursor stability. For wet-phase made $\text{Ta}_2\text{O}_5$-containing $\text{SiO}_2$, it has been observed that the Ta-precursor reacted fast with residual water.\cite{15} The hydrolysis and consecutive condensation to hydroxides may have aided the formation of Ta-O-Ta bonds. Ta-butoxide reacts slower with water than Ta-ethoxide.\cite{17} Furthermore, the residual water in the solvent of the precursor solution influenced the crystallinity of the resulting material as observed for the wet phase preparation.\cite{17} Different amounts of a hydrolysis catalyst in the solvent altered the crystallinity of wet-made TiO$_2$ particles by resembling the crystalline phase in the molecular structure.\cite{38} Here, substituting hexane with the more hydrophilic TEOS increased the residual water in the precursor solution resulting in a lower filler transparency (Figure 2.4c). Apparently, increasing the solvent hydrophobicity reduced the crystallinity of $\text{Ta}_2\text{O}_5$ resulting in higher filler transparency (Figure 2.4b). Increasing the $\text{Ta}_2\text{O}_5$ content did not change the XRD pattern up to about 45 wt.% (Figure 2.5d), where the first $\text{Ta}_2\text{O}_5$ crystallites were observed (the standard, 24
wt.%, is at Figure 2.5a, butox (std)). Increasing the Ta₂O₅-content raised its peak intensity indicating increased crystallinity. These results agree with data from wet-made Ta₂O₅/SiO₂ xerogels that segregated at 48 wt.% content.¹⁸

Figure 2.5. XRD patterns of Ta₂O₅/SiO₂ powders made by varying a) tantalum precursor, b) solvent, c) total metal concentration in the precursor liquid and d) Ta₂O₅ content. For every material only the indicated parameter was changed in comparison to the standard production (std: tantalum butoxide, hexane, 0.5 M, 24 wt.% Ta₂O₅/SiO₂). Except for the Me-concentration in the liquid, all parameters influenced the powder crystallinity.

Figure 2.6 shows HRTEM images of 24, 45, 76 wt.% Ta₂O₅-containing silica from standard solutions (Ta-butoxide in hexane, 0.5 M). All samples consist of solid nanoparticles in agreement with nitrogen adsorption (Figure 2.1). The 24 wt.% Ta₂O₅-containing particles were amorphous which is confirmed by the electron diffraction insert. The 45 wt.% Ta₂O₅ sample was mainly amorphous.
but exhibited small crystalline regions as shown also in the inset with the two white dots in the periphery of electron diffraction. Formation of small crystallites with increasing oxide content has been observed also for the FSP-made ZnO/SiO$_2$ particles.$^{[32]}$ Silica with 76 wt.% Ta$_2$O$_5$ led to large crystalline structures as shown by the lattice fringes within the amorphous domains. The rings and multiple white dots in the electron diffraction inset confirm crystallite formation. These images corroborate the XRD data (Figure 2.5). TEM images and SAXS measurements confirmed the homogeneous particle size distribution. Therefore the presence of large particles was excluded. SAXS measurements revealed the presence of agglomerates with radii of gyration ranging from 100 – 300 nm.

Figure 2.6. HRTEM images of 24, 45 and 76 wt.% Ta$_2$O$_5$ in SiO$_2$ (standard, Ta-butox, hexane, 0.5 M). The lowest Ta$_2$O$_5$ content is amorphous, while at higher Ta$_2$O$_5$ content, the formation of crystalline Ta$_2$O$_5$ regions can be observed. The inset electron diffraction images confirm the increasing crystallinity observed by the XRD (Figure 2.5d).

Tantalum Dispersion

Figure 2.7 shows DRIFT spectra of 0, 24, and 76 wt.% Ta$_2$O$_5$-containing SiO$_2$. The absorption band at 809 – 829 cm$^{-1}$ gives the symmetrical Si-O-Si stretching$^{[15]}$ while the bands at 1076 – 1097 cm$^{-1}$ and 1182 - 1202 cm$^{-1}$ come from asymmetrical Si-O-Si stretching. The band at 635 – 671 cm$^{-1}$ is characteristic for the Ta-O-Ta absorption spectrum.$^{[15]}$ An increase (compare 24 wt.% and
76 wt.% $\text{Ta}_2\text{O}_5$ samples) of the absorption band (Ta-O-Ta) at $\sim 660 \ \text{cm}^{-1}$ is caused by the formation of $\text{Ta}_2\text{O}_5$ crystallites as it was observed by XRD (Figure 2.5d) and HRTEM (Figure 2.6) of the corresponding materials.

![DRIFT spectra of 0, 24, and 76 wt.% $\text{Ta}_2\text{O}_5$ containing $\text{SiO}_2$. The spectra were fitted with five Gaussians (one for each vibration mode). An example of the fitting procedure is shown for the 24 wt.% $\text{Ta}_2\text{O}_5$-containing $\text{SiO}_2$, where the Ta-O-Si and the Si-O-Si vibration bands have been identified and extracted.](image)

Tantalum oxide containing $\text{SiO}_2$ exhibited an absorption band at 943 – 958 cm$^{-1}$ that is neither present in pure $\text{SiO}_2$, or $\text{Ta}_2\text{O}_5$, nor the mechanical mixture of the two materials and was observed already in sol-gel-made materials.$^{[15]}$ For increasing $\text{Ta}_2\text{O}_5$ content, this absorption band was shifted to smaller wavenumbers$^{[15]}$ indicating a decrease of bond interaction. The resulting fit for the 24 wt.% $\text{Ta}_2\text{O}_5$ sample is shown in Figure 2.7 (24 wt.% fit). The weighted proportion of the areas of the two absorption bands at $\sim 960 \ \text{cm}^{-1}$ and $\sim 1080 \ \text{cm}^{-1}$ was calculated by equation 2.4 to estimate the Ta-dispersion in silica.$^{[29]}$ The better the dispersion of Ta in $\text{SiO}_2$ matrix the more Ta-O-Si bonds exist in the material and the larger is the area of the $\sim 960 \ \text{cm}^{-1}$ absorption band. For less
than 7 wt.% Ta$_2$O$_5$, the intensity of the Ta-O-Si peak was near the signal’s noise so the peak area determination was difficult.

Figure 2.8 shows that the relative Ta-dispersion of the mixed ceramic did not change for small Ta$_2$O$_5$ contents indicating an accumulation of Ta-atoms at the surface of the particles similar to Figure 2.1. After this surface effect, the Ta-dispersion decreased hyperbolically with increasing Ta$_2$O$_5$ content as observed for sol-gel derived TiO$_2$- containing SiO$_2$.\cite{39} Increasing the Ta$_2$O$_5$ content resulted in less Ta-O-Si structures and lower Ta-dispersion indicating that Ta atoms associate preferentially with each other than with Si. The Ta-dispersion values can only be compared relatively to each other as the absolute absorbance of each DRIFTS band is unknown.

Materials made from Ta-butoxide in hexane (0.5 M, squares) exhibited the highest Ta-dispersion. Measuring the same sample twice resulted in a deviation of the relative Ta-dispersion in the range of the symbol size as indicated for the 24 wt.% data point. Changing the Ta-precursor to Ta-TEAA (triangles tip top), the solvent to 2 EHA/toluene (triangles tip bottom), or the Ta-precursor to Ta-TEAA and the solvent to 2 EHA/toluene (diamonds) resulted in a lower Ta-dispersion in the SiO$_2$ matrix. In these powders small Ta$_2$O$_5$ crystallites were observed in the XRD (Figure 2.5) so that they contained even less Ta-O-Si bonds than the standard amorphous particles, explaining the observed lower Ta-dispersion.

The materials with the highest transparency (Figure 2.4) exhibited the highest Ta-dispersion by DRIFTS. Likewise, the lowest dispersion was observed for powders made with Ta-butoxide in pure TEOS (circles, 4.5 M) that exhibited the lowest transparency even though it was amorphous (Figure 2.5c). Favoured by the high Me-concentration in the flame, Ta-O-Ta structures were formed lowering the relative Ta-dispersion in SiO$_2$. Another possibility for detecting atomic compositions could have been electron energy loss spectroscopy (EELS). How-
ever, Ta and Si having similar adsorption edges making impossible such distinction with EELS.

![Graph showing Ta dispersion vs. TaO5 content]

**Figure 2.8.** Starting with a rather high Ta-dispersion at small TaO5 contents in SiO2, the dispersion decreased at higher ones as Ta atoms associated more with each other than with Si. Using high Me-concentrations (circles) or Ta-TEAA as precursor (triangles tip top, diamonds) and/or 2EHA/toluene (triangles tip bottom, diamonds) as solvent reduced the Ta-dispersion below that made at standard conditions (squares).

**Nanocomposite Transparency**

Silane-treated powders with different TaO5 contents were added as fillers to the methacrylate-based monomer solution resulting in nanocomposite resins after polymerization. Figure 2.9 shows that the composite transparency increased from 78 % for 15 wt.% TaO5 content in SiO2 made at standard conditions (squares) up to 86% for 35 wt.% TaO5 content. A further increase of the Ta2O5 content reduced the composite transparency. Increasing the Ta2O5 content up to 35 wt.% of the mixed oxide increased its RI (Figure 2.2) and reduced the RI mismatch with the polymer matrix resulting in a higher composite transparency. A maximum was reached for identical organic-inorganic RI. For higher
Results and Discussion

Ta$_2$O$_5$ contents the RI mismatch and the powder crystallinity increased reducing the composite transparency.

![Composite Transparency Graph](image)

**Figure 2.9.** Influence of the Ta$_2$O$_5$ content in the Ta$_2$O$_5$/SiO$_2$ filler on the transparency of the polymer-particle blend (dental composite, 16.5 wt.% filler content). All blends from standard powders (squares) below 40 wt.% Ta$_2$O$_5$ have a high transparency (> 78 %). It increased slightly with increasing Ta$_2$O$_5$ loading, reached a maximum (86 %) at 35 wt.% Ta$_2$O$_5$ content and decreased steeply above that. Three reference samples (Ta-TEAA triangles, tip top, 2EHA/toluene, triangles tip bottom, 4.5M, circles) which exhibited a lower filler transparency (Figure 2.4) exhibited also a significantly lower composite transparency.

Changing the precursor from Ta-butoxide to Ta-TEAA (triangles tip top), the solvent from the hexane to 2 EHA/toluene (triangles tip bottom) or the total metal concentration from 0.5 M to 4.5 M (circles) resulted in a significantly lower composite transparency (Figure 2.9). The 24 wt.% Ta$_2$O$_5$ materials had the same RI as shown in Table 2.1 and Figure 2.3. Therefore, differences in the mismatch of the RI from the polymer matrix and the ceramic filler, which decrease the transparency$^{[1]}$ can be excluded. All materials in Figure 2.9 had the same SSA (except for the 4.5 M concentration, Table 2.1) so that the transpar-
ency was not influenced by the filler particle size. All ceramic fillers that exhibited a lower transparency (Figure 2.4) had Ta$_2$O$_5$ crystallites and/or a lower Ta-dispersion (Figure 2.7 and Figure 2.8) resulting in lower composite transparencies. The agglomerate’s radius of gyration was determined by SAXS and ranged from 100 – 300 nm for the investigated powders. The fractal dimension is in the range of 2 – 2.5.

Commercially available nanocomposites contain 60 - 80 wt.% ceramic filler. However, 16.5 wt.% filler content as used in this study was sufficient for transparency determination of the nanocomposite and optimization of the filler properties. The ceramic filler with 35 wt.% Ta$_2$O$_5$ content resulted in both high transparency and radiopacity[7] which is preferred for enhanced caries and x-ray detection. Adding 16.5 wt.% ceramic filler to the monomer resulted in transparencies for the standard material that are equivalently high as adding 7.9 wt.% or 3 wt.% SiO$_2$ to copolymerized allyl glycidyl ether with CO$_2$[40] or to polyurethane[41] and 1 wt.% montmorillonite to an epoxy resin.[42] Increasing the filler content decreased the composite transparency in all 3 studies so that a superior transparency of the present materials would be expected for equal filler content.

Standard methods involve mechanical mixing of SiO$_2$ and radiopaque materials in such composition that the ceramic filler mixture matches the refractive index of the polymer. These methods may lead to contamination of the product by attrition from the processing apparatus and the filler that may lead to reduced transparency by locally mismatching RIs. In contrast, the FSP process leads to atomic mixing inside each individual particle, thereby reducing the particle/polymer refractive index mismatch resulting in a high composite transparency. Additionally this process leads to synthesis of ceramic particles of high purity as it is used routinely in manufacture of optical fibers with controlled refractive index profile across their radius.[26]
Conclusions

Silicas containing 0 – 83 wt.% Ta₂O₅ of SSA of 78 - 380 m²/g were made by flame spray pyrolysis. The RI of these particles could be controlled from 1.44 to more than 1.80 by the Ta₂O₅ content. The Ta-precursor, solvent and particle size did not influence the RI for the Ta₂O₅/SiO₂ filler containing 24 wt.% Ta₂O₅. Excellent composite transparency was observed for high transparencies of the filler itself. The composite transparency increased for Ta₂O₅ contents in the ceramic filler up to 35 wt.% in the material made at standard conditions (Ta-butox as precursor, hexane as solvent with total metal concentration in the precursor liquid of 0.5 M). For higher Ta₂O₅ contents, the composite transparency decreased drastically. High composite transparency is attributed to high powder (filler) transparency, amorphous mixed ceramic oxides, high dispersion of Ta within the SiO₂ matrix and matching RI between filler and polymer. Composites with a high Ta₂O₅ content in the particles (35 wt.%) coupled with a high transparency (86 %) are best for dental restoration applications for optical caries detection and x-ray detection of the filling.

References


T. F. Morse, *US 6546757 B1*, **2003**.


CHAPTER THREE

Surface functionalization of radiopaque Ta$_2$O$_5$/SiO$_2$

Abstract

Mixed Ta$_2$O$_5$/SiO$_2$ nanoparticles are attractive for their high radiopacity as transparent dental fillers and even for bone replacement. The effect of Ta$_2$O$_5$ content on surface acidity of flame-made Ta$_2$O$_5$/SiO$_2$ particles was studied by NH$_3$ temperature programmed desorption (TPD). Emphasis was placed on the influence of particle composition on surface functionalization by a common surfactant, $\gamma$-methacryloxypropyltrimethoxysilane (MPS). Such surface modified particles were analyzed by thermogravimetric analysis, $^{13}$C- and $^{29}$Si-NMR and FT-IR spectroscopy. Compared to pure silica, Ta$_2$O$_5$/SiO$_2$ particles exhibited significantly higher surface acidity, thereby facilitating functionalization of their surface hydroxyl groups without a catalyst (e.g. $n$-propylamine, PA). The surface modifier structure was only slightly influenced by the Ta$_2$O$_5$ presence com-
pared to pure SiO$_2$. The long term hydrolytic stability of such surface modified Ta$_2$O$_5$/SiO$_2$ particles was comparable to pure silica up to 80 days at 22 °C indicating stable bonding between particle surface and modifier.

Introduction

Nanocomposites of inorganic particles in polymer matrices are widely used in dental restorative materials.[1] The particles have a significant influence on composite properties such as strength,[2] dimensional stability,[3] Young’s and shear moduli,[4] wear[5] and transparency[6]. For every application, polymer matrix refractive index, chemical composition, viscosity, hydrophobicity and transparency[7] as well as filler particle size,[8] agglomerate size,[9] refractive index, elemental distribution,[6] surface texture,[10] and functionalization[11] have to be tailored. Composites for dental fillings must exhibit, among other characteristics, high mechanical strength to minimize the risk of failure. Particles do not typically form any covalent bonds with the polymer matrix during polymerization.[12] As a result, particles act as voids in the matrix when stresses are applied[13] reducing composite strength.[2] To overcome this, particles are functionalized or modified by organic molecules covalently bonded to their surface. Such surface modifiers often contain silicon alkoxide groups bound to the surface by at least one Si-O-Si bond[14] and have a functional group such as C=C that can polymerize.[8]

One of the common surface modifiers is MPS containing a functional methacrylate and three methoxy groups. Polar solvents can adsorb on the particle surface and block the silane coupling reaction.[15] Surface functionalization is enhanced significantly when amines are added as bases.[16] In combination with PA, non-polar solvents contribute to the highest bonding densities between surface modifier and particles. The use of amines enhances the coupling without depositing thick layers of silane-oligomers.[17] Temperatures in the range of 30 –
110 °C enhance surface functionalization yields and grafting.\textsuperscript{[18]} Decreasing particle size results in higher surface functionalization density but delays that process.\textsuperscript{[8]}

Different surface arrangements of MPS on SiO\textsubscript{2} particles have been reported: Physically adsorbed MPS results in the weakest bonding and can be removed easily by washing.\textsuperscript{[19]} When covalent bonds are formed, MPS can either be parallel or normally oriented to particle surface. In parallel arrangement, methacrylate oxygen can form hydrogen bonds with surface silanol groups\textsuperscript{[19]} while in normal, MPS can be highly crosslinked\textsuperscript{[14]} interacting with their organic tails and forming a ladder structure.\textsuperscript{[20]}

Surface functionalization has been studied mostly for pure metal oxides\textsuperscript{[21]} and in particular for silica.\textsuperscript{[14]} Using other oxides such SnO\textsubscript{2}, Sb/SnO\textsubscript{2},\textsuperscript{[21]} Al\textsubscript{2}O\textsubscript{3},\textsuperscript{[14, 22]} ZrO\textsubscript{2}, TiO\textsubscript{2}\textsuperscript{[22]} and PbO\textsuperscript{[23]} resulted in different reaction kinetics by the formation of Me-O-Si bonds. Depending on particle morphology and elemental distribution, grafting may lead to different quantities of surface modifier bound to the surface and different types of modifier/particle bonds.\textsuperscript{[22]} The influence of surface properties on functionalization of silica-based mixed oxides is not well understood yet.

In dental formulations typically particles are dispersed in monomer liquids and the resulting suspensions are stored for long time till use. To ensure suspension stability, particle surface functionalization has to be monitored over long storage periods under severe conditions. Surface modifiers forming crosslinked networks with particles have exhibited better hydrolytic storage than with single covalent bonds.\textsuperscript{[24]} Decreasing the solution pH during storage drastically reduces the hydrolytic stability.\textsuperscript{[24]} With MPS in cyclohexane and PA as base, surface functionalized SiO\textsubscript{2} particles exhibited higher fraction of retaining such bonds than other polar and non-polar solvents after washing.\textsuperscript{[25]}

In dental nanocomposites, filler particles fulfill multiple purposes. Some metal oxides and especially silica cannot provide radiopacity or the tailored re-
fractive index for optimal dental composite translucency. Therefore mixed oxides such as BaO/SiO$_2$,[26] Ta$_2$O$_5$/SiO$_2$[6] or Yb$_2$O$_3$/SiO$_2$[27] with adjustable properties have been explored.

Here mixed Ta$_2$O$_5$/SiO$_2$ and pure SiO$_2$ particles were produced by flame spray pyrolysis (FSP),[28] a versatile process for gas-phase synthesis of high purity nanoparticles. Their size and extent of agglomeration was controlled by the flowrate and composition of the FSP liquid precursor and dispersion gas.[29] Upon collection, particles were surface functionalized and characterized by NH$_3$ temperature programmed desorption, thermogravimetry, FTIR, $^{13}$C-, and $^{29}$Si-NMR spectroscopy and related to their surface acidity and bonding structure.

Experimental

Particle Synthesis and Characterization

Tantalum butoxide (Aldrich, > 98%) and tetraethoxysilane (TEOS, Fluka, > 98 %) were used as tantalum and silicon precursors, respectively. Appropriate precursor amounts were mixed with hexane under nitrogen. The total (Ta & Si) metal concentration was kept constant at 0.5 M in these solutions. The Ta$_2$O$_5$ weight fraction in the product powder ranged from 0 – 100 wt.%. Mixed Ta$_2$O$_5$/SiO$_2$ powders were produced in a laboratory scale FSP reactor as described elsewhere.[6] The production rate ranged from 9 g/h for pure SiO$_2$ to 33 g/h for pure Ta$_2$O$_5$. The powders were collected by a vacuum pump (Busch SV 1025 B) on a glass microfibre filter (Whatman GF/D, 25.7 cm in diameter).

The specific surface area (SSA, m$^2$/g) of the FSP-made particles were determined by N$_2$ adsorption at 77 K using the BET method (Micromeritics Tristar 3000, 5-point isotherm, 0.05 < p/p$_0$ < 0.25). Assuming spherical, monodisperse primary particles with homogeneous density, the average BET-equivalent particle diameter, d$_{BET}$, is
Experimental

\[ d_{\text{BET}} = \frac{6}{SSA \times (x_{Ta_2O_5} \times \rho_{Ta_2O_5} + x_{SiO_2} \times \rho_{SiO_2})}, \]  

(3.1)

where \( x_i \) is the mass fraction and \( \rho_i \) the density of pure Ta_2O_5 (8.2 g/cm³) or SiO_2 (2.2 g/cm³).

Surface acidity was measured by temperature-programmed NH₃ desorption (ASAP 2010, Micromeritics). Such samples (∼200 mg) were pressed, crushed and placed in a U-shaped glass tube, kept in 5vol.% O₂/He at 500 °C (PanGas, 10 °C/min) for 30 min for full oxidation and combustion of residual carbon, cooled to 50 °C, flushed first with 1 vol.% NH₃/Ar (PanGas, 90 min), and then with pure He (PanGas, >99.999%, 120 min) and finally heated to 900 °C (10 °C/min). Evolving gases are monitored on a mass spectrometer (Thermostar, Pfeiffer Vacuum, SEM and emission mode) and for evaluation the signal for m/z = 16 was used. The stronger signals m/z = 17 and 18 could not be used since desorbing H₂O influences them. Analysis conditions were chosen after tests with different heating rates during NH₃ desorption so that mass-transfer limitations were excluded.[30]

Surface Functionalization and Nanocomposite Preparation

For surface functionalization, 1 g of flame-made nanoparticles was immersed in 200 ml cyclohexane (Fluka, >99.5 %). From the specific surface area of the particles and assuming the highest reported OH density (4.6 #OH/nm²) of pure silica, resulted in the highest possible OH quantity in dispersion, though flame-made particles usually contain 3.3 or less # OH/nm².[31] The amount n-propylamine added was thrice that corresponding to that of OH groups (PA, Fluka, >99 %) in the dispersion and refluxed at 70 °C for 15 min.[18] The surface modifier MPS (Fluka, >98 %) amount added was twice the corresponding one to the OH group concentration. The dispersion was kept at 70 °C at reflux for 24 h. After surface functionalization, particles were separated from solution by cen-
trifugation (Rotina 35, Hettich, 9000 rpm, 15 min), washed with 200 ml cyclo-
hexane and redispersed once, centrifuged again (same conditions) and dried
overnight in ambient conditions. Drying or wetting (dionized water) the particles
prior to surface functionalization did not change significantly the surface func-
tionalization density.

Untreated and surface functionalized 76 wt.% $\text{Ta}_2\text{O}_5/\text{SiO}_2$ particles were dis-
persed (0.5 wt.% particles) in a 2-hydroxethyl-methacrylate (HEMA, Ivoclar
Vivadent, > 98 %) : glycerol-dimethacrylate (GDMA, Ivoclar Vivadent, > 85 %)
mixture (1:1) with 1 wt.% camphorquinone as curing agent. Suspensions were
ultrasonicated (Vibracell VCX 600, Sonics & Materials Inc., 600 W, 20 kHz,
50s, 13 mm tip) and ~3 mm thick samples were polymerized by a blue light
lamp (Heliolux GT, Vivadent, 100 W, >5 min).

**Characterization of Surface Functionalization**

Nanocomposites were cut with a microtome (Ultracut E, Reichert-Jung) in
thin slices (<100 nm thickness). HRTEM images of nanocomposites containing
untreated and surface functionalized particles were taken with a CM30ST mi-
croscope (Philips, LaB6 Cathode, 300kV, point resolution 0.2 nm). Thermogra-
vimetric analysis (TGA/SDTA851°, Mettler Toledo) was used to determine the
volatile mass of particles after surface functionalized. Samples were placed in an
$\text{Al}_2\text{O}_3$ pan (900 μl) and heated to 1000 °C (20 °C/min) in an $\text{O}_2$ flow (50 ml/min,
PanGas, >99.999%). The mass loss was corrected by the mass change of the
empty $\text{Al}_2\text{O}_3$ pan.

Fourier transform IR spectra (FT-IR) were recorded in transmittance mode
(Bruker, Vektor 22) from KBr (Fluka, >99.5%, 300 mg, stored at 115 °C)
pressed tablets containing ~6 mg particles. For each spectrum, 512 scans were
collected at room temperature at a resolution of 2 cm$^{-1}$ against a KBr back-
ground. The methacrylate spectra (1800 – 1550 cm$^{-1}$) were fitted by four Gauss-
sians with the multipeak fitting package of Igor Pro (Version 5.03, WaveMetrics
The Gaussians were shifted by fitting a polynomial baseline (third degree) to the spectrum. The Si-O-Si absorption band at ~800 cm\(^{-1}\) was used for reference peak fitted with a single Gaussian (range: 860 – 720 cm\(^{-1}\)).\(^{[32]}\) The normalized methacrylate absorption was calculated accordingly

\[
\text{norm. methacrylate absorbance} = \frac{\text{area}(1720 \text{ cm}^{-1}) + \text{area}(1700 \text{ cm}^{-1})}{\text{area}(800 \text{ cm}^{-1})} \times \frac{\text{moles (Si)}}{\text{moles (Ta + Si)}} \quad (3.2)
\]

The solid-state CP-MAS \(^{13}\text{C}\) and \(^{29}\text{Si}\) NMR spectra were obtained on a Bruker Avance 400 spectrometer operating at 100.6 and 79.5 MHz and spinning rate of 4000 Hz with cross polarization of 2.0 ms and relaxation delay of 1 and 4 s, respectively. Generally 3000 – 16000 transitions were accumulated. The chemical shifts were expressed with to respect the signal of tetramethylsilane.

Surface functionalized particles were tested for hydrolytic stability over prolonged periods of storage. Such particles were dispersed in a deionized water/ethanol (Scharlau, >99.8%) (1/1) mixture with pH=2 adjusted by HCl (Fluka, >36.5%). After exposing the particles for different time-periods to these conditions, they were centrifuged, washed in an ethanol/water (1/1) mixture and dried as described in surface functionalization.

Results and Discussion

Surface Properties and Functionalization Conditions

Figure 3.1 shows the NH\(_3\) temperature programmed desorption patterns corresponding to the surface acidity of Ta\(_2\)O\(_5\)/SiO\(_2\) particles of various Ta\(_2\)O\(_5\) contents. While FSP-made SiO\(_2\) showed slight acidity, as observed by the peak at 90 – 240 °C, Ta\(_2\)O\(_5\)/SiO\(_2\) and pure Ta\(_2\)O\(_5\) exhibited at least two convoluted peaks. For example, the addition of 7 wt.% (1 mol.%) Ta\(_2\)O\(_5\) increased remarkably the acidic sites as indicated by extending this band, at least, up to 500 °C. This is comparable to wet-made Ta\(_2\)O\(_5\)/SiO\(_2\) with NH\(_3\) desorption bands ranging
from 100 – 500 °C.\textsuperscript{[33]} Pure Ta$_2$O$_5$ has high acid strength.\textsuperscript{[34]} The incorporation of large Ta atoms having an average coordination number of 6.5\textsuperscript{[35]} into the SiO$_2$ matrix having a Si coordination number of 4 is responsible for the observed surface acidity.\textsuperscript{[36]}

Figure 3.1. Temperature programmed desorption analysis showed a narrow NH$_3$ desorption peak below 200 °C for pure SiO$_2$ (0 wt.% Ta$_2$O$_5$). The addition of 7 wt.% Ta$_2$O$_5$ (1 mol%) contributed to such a shoulder at 250 - 450 °C. With increasing Ta$_2$O$_5$ content, the intensity of the latter increased up to 35 wt.% Ta$_2$O$_5$. As a result, Ta$_2$O$_5$-containing particles have far more acidic strength than pure SiO$_2$.

Above 35 wt.% (6.8 mol.%) Ta$_2$O$_5$ content, that high temperature desorption peak area increased only slightly up to pure Ta$_2$O$_5$. This implies that at these Ta$_2$O$_5$ contents the OH-groups on the Ta$_2$O$_5$/SiO$_2$ surface resemble the ones on pure Ta$_2$O$_5$. Flame-made particles had a higher fraction of acidic surface sites than impregnated, wet-made ones of high surface area\textsuperscript{[33]} but comparable to those made hydrothermally.\textsuperscript{[37]}

Functionalization conditions were optimized for pure SiO$_2$: Adding more than twice the amount of surface modifier MPS corresponding to the maximum of
surface silanol groups (4.6#/nm²)[38] and more than 3 times the amount of PA at 70 °C for more than 24 h did not increase surface functionalization yield (determined by TGA and FTIR, not shown here). Therefore 1/2/3 OH/MPS/PA was chosen to be the standard surface functionalization conditions here. Over-stoichiometric concentrations of surface modifier did not result in additional layers by steric hindrance.[22]

Surface functionalization had no significant influence on the particle size distribution as observed by TEM analysis (not shown). The MPS which can form Si-O-Si bonds by condensation of its methoxy groups might have formed particle bonds which could have therefore increased the average agglomerate size.[39] Neither liquid/particle separation nor centrifugation had influenced, however, the particle size distribution. These FSP-made particles exhibited significantly smaller agglomerate sizes than commercially available SiO₂ (Aerosil 200, Degussa) with comparable primary particle diameters. This can be attributed to the lower concentrations and shorter high-temperature residence time of FSP-made particles than those made in commercial reactors.[40]

The functionalization efficiency of pure SiO₂ and 76 wt.% Ta₂O₅/SiO₂ was analyzed by thermogravimetric analysis (Figure 3.2). Particles (untreated) or immersed in just pure cyclohexane (cC₆), or in cC₆ and PA (PA/cC₆), or in cC₆ and MPS (MPS/cC₆), or their mixture (MPS/PA/cC₆) exhibited different functionalization efficiency. Untreated particles represent as-prepared FSP-made samples (190 m²/g). Their mass was reduced significantly up to 150 °C, as physically adsorbed H₂O was released.[31] For 76 wt.% Ta₂O₅/SiO₂ the mass loss was significantly lower, arising from their lower specific surface area (108 m²/g) than pure SiO₂ or their different hydroxyl acidity (electron distribution in the OH-group). During TGA no significant amounts of CO₂ or hydrocarbons could be detected by a mass spectrometer, indicating the low carbon content of untreated samples.
Figure 3.2. Mass loss of powders during TGA. Pure SiO$_2$ and 76 wt.% Ta$_2$O$_5$/SiO$_2$ were surface functionalized with cyclohexane (cC$_6$), with cC$_6$ and n-propylamine only (PA/cC$_6$), the surface modifier only (MPS/cC$_6$) and under standard conditions with PA and MPS (MPS/PA/cC$_6$). The presence of PA drastically increased the functionalization yield on pure SiO$_2$ particles while had hardly an effect on Ta$_2$O$_5$/SiO$_2$ as the latter had far more acidic sites than SiO$_2$.

For materials treated by adding only solvent (cC$_6$) or base and solvent (PA/cC$_6$) significant mass loss was observed at 480 – 580 °C and 450 – 520 °C for SiO$_2$ and Ta$_2$O$_5$/SiO$_2$ particles, respectively (Figure 3.2a,b). Weight losses in
these ranges were attributed to silanol condensation during heating. Addition of PA (PA/cC₆) did not change significantly the mass loss evolution indicating that PA may not strongly adsorb on the SiO₂ particle surface. When functionalizing pure SiO₂ with MPS but without PA (Figure 3.2a: MPS/cC₆), a steep mass loss at 290 – 325 °C was observed. This mass loss increased significantly when PA was added (Figure 3.2a: MPS/PA/cC₆). When Ta₂O₅/SiO₂ was functionalized only with MPS (Figure 3.2b: MPS/cC₆), mass loss occurred over a broader temperature (230 – 560 °C) and showed a smoother mass loss with increasing temperature than pure SiO₂. Adding PA (Figure 3.2b: MPS/PA/cC₆) resulted in actually a slightly smaller mass loss than without PA (Figure 3.2b: MPS/cC₆).

For surface functionalized particles no 2-step TGA mass loss (at ~250 °C and ~550 °C) was observed as for sol-gel-made 30 nm silica. Differences in surface acidity between pure SiO₂ and Ta₂O₅/SiO₂ as observed in Figure 3.1 might lead to different accessibilities, bond types or stabilities between particles and surface modifier. While only weak acidic sites (low temperature TPD) are present on pure silica (Figure 3.1), the Ta₂O₅/SiO₂ contains a broad range of acid strengths which might lead to differences during TGA. The PA being adsorbed as base on strong acid sites of the Ta₂O₅/SiO₂ surface might reduce the functionalization yield compared to that without PA.

**Quantification of Surface Functionalization**

Figure 3.3 compares FTIR spectra of pure liquid MPS and PA as well as untreated and surface functionalized 35 wt.% Ta₂O₅/SiO₂ particles at standard conditions (MPS/PA/cC₆). The untreated particles exhibited the typical IR bands of Si-O-Si (∼1198, ∼1081 and ∼800 cm⁻¹)[⁶] and Ta-O-Si (∼947 cm⁻¹)[⁴¹]. Silanol surface groups showed a broad IR band at about 3750 to 2800 cm⁻¹ (silanol groups) and a band for surface H₂O at ~1620 cm⁻¹. After functionalization (MPS/PA/cC₆), additional peaks appear: absorption bands at 3030 – 2840 cm⁻¹ correspond to non-specific C-H bonds. These can be found, however, in the
spectra of liquid PA and MPS (Figure 3.3). The peak at ~1720 cm\(^{-1}\) corresponds to the methacrylate functional group which is the most intense MPS absorption band. Only traces of the most intense PA absorption band at ~670 cm\(^{-1}\) could be found. The intensity of the broad silanol absorption band (~3700 - 2700 cm\(^{-1}\)) decreased after surface functionalization indicating a reduction of free silanol groups.\(^{[25]}\)

**Figure 3.3.** FTIR spectra of liquid (broken lines) surface modifier (MPS) and base n-propylamine (PA) as well as those of untreated and surface modified 35 wt.% Ta\(_2\)O\(_5\)/SiO\(_2\) powders (solid lines). For normalization, the tetrahedral Si-O-Si peak at 800 cm\(^{-1}\) was used.

Figure 3.4 shows FTIR spectra of a) pure SiO\(_2\) and b) 76 wt.% Ta\(_2\)O\(_5\)/SiO\(_2\) at the functionalization conditions of Figure 3.2. The spectra of untreated, or treated with just pure cC\(_6\) or PA/cC\(_6\) did not differ significantly for both particle compositions. Only traces of C-H bonds at wavelengths of ~3030 – 2840 cm\(^{-1}\) were observed for these samples (not shown) indicating that only small amounts of organic matter remained on the particle surface after functionalization and washing as seen by TGA (Figure 3.2a,b). When pure SiO\(_2\) was functionalized
with MPS but without PA (MPS/cC₆), a methacrylate peak appeared at ~1700 cm⁻¹ indicating formation of hydrogen bonds between the MPS C=O and SiO₂ surface silanol groups. The absorption intensity, however, was much lower than SiO₂ functionalized at standard conditions (MPS/PA/cC₆), which had an additional peak at ~1720 cm⁻¹ corresponding to liquid MPS (Figure 3.3). Less hydrogen bonds can result from the higher surface functionalization yield resulting in a higher coverage of MPS on the particle surface, thereby leaving less space for parallel arrangements of the modifier molecule to the particle surface. The PA can also enhance the cross-linking of the surface modifier by exchanging methoxy with hydroxyl groups.

Silanol concentration of the surface modifier stayed always low, so that grafting or condensation must be faster than hydrolysis. These surface modifier oligomers formed by condensation need only to be anchored at the particle surface by a single bond. Therefore most of these MPS molecules being farther away from the particle surface than directly attached molecules do not form hydrogen bonds. Since the increase of MPS concentration did not increase the surface functionalization yield, the attached oligomers cannot be the dominating type of attached modifiers.

The IR spectra of both particle compositions functionalized at standard conditions (MPS/PA/cC₆, Figure 3.4a,b) exhibited a convoluted peak consisting of two bands at ~1700 cm⁻¹ and ~1720 cm⁻¹. The latter corresponded to pure MPS (Figure 3.3, pure MPS). Bound to the particle surface, the organic tail of MPS can have different arrangements. Sticking into e.g. an organic liquid or together with other tails, the C=O groups do not form any hydrogen bonds resulting in the band at ~1720 cm⁻¹. Whereas when the MPS is arranged parallel to the surface, the C=O groups can form hydrogen bonds with surface hydroxyl groups resulting in a shift of the absorption band to ~1700 cm⁻¹, that is not present in pure MPS! The ratio of these IR band intensities indicates the dominant surface functionalization mode (normal or parallel). Low yields will lead to such parallel
arrangements (~1700 cm\(^{-1}\)). With increasing yield, a smaller fraction of organic
tails can directly interact with the particle surface and therefore lead to an in-
crease of the non-shifted IR band (~1720 cm\(^{-1}\)). The bands at ~1640 cm\(^{-1}\) and
~1620 cm\(^{-1}\) correspond to C=C bonds of the surface modifier and free H\(_2\)O on
the particles, respectively, but were not taken into account for the quantification.
When Ta\(_2\)O\(_5\)/SiO\(_2\) was functionalized without PA (Figure 3.4a, MPS/cC\(_6\)) both
methacrylate absorption bands at ~1720 cm\(^{-1}\) and ~1700 cm\(^{-1}\) were present
(Figure 3.4a) in contrast to pure silica (Figure 3.4a). The addition of PA resulted
in a slightly lower absorption intensity as a lower mass loss was observed by
TGA (Figure 3.2b). The stronger surface acidity of Ta\(_2\)O\(_5\)/SiO\(_2\) than SiO\(_2\) facili-
tates surface functionalization of the mixed oxide. The PA might adsorb stronger
on the surface of Ta\(_2\)O\(_5\)/SiO\(_2\) particles as NH\(_3\) was released from them at higher
temperatures during TPD than from SiO\(_2\) particles (Figure 3.1). Thereby the PA
might block the active sites for functionalization of the Ta\(_2\)O\(_5\)/SiO\(_2\) surface.

To quantify surface functionalization, the methacrylate absorption bands were
fitted (Figure 3.5) and peak areas were normalized by the tetrahedral Si-O-Si
peak (~800 cm\(^{-1}\)) with respect to the Si-content (Equation 3.2).\(^{[32]}\) The sum of
the ~1720 cm\(^{-1}\) and ~1700 cm\(^{-1}\) absorption bands was used to quantify surface
functionalization. The FTIR spectra in the methacrylate absorption region
(1800 – 1550 cm\(^{-1}\)) of the functionalized particles could be fitted well by four
Gaussians and a baseline (fit, broken line, Figure 3.5). The area ratio of the two
methacrylate absorption bands (~1720 cm\(^{-1}\) and ~1700 cm\(^{-1}\)) and the tetrahedral
SiO\(_2\) absorption band (~800 cm\(^{-1}\)) normalized by the Si-content results in the
normalized methacrylate absorbance (Equation 3.2, Figure 3.6).
Figure 3.4. Surface functionalization conditions had a significant influence on the FTIR spectra of the powders. While the untreated, the in pure cyclohexane (cC₆) and cyclohexane and n-propylamine (PA/cC₆) immersed particles showed only the free surface H₂O absorption band around ~1620 cm⁻¹ for pure silica and 76 wt.% Ta₂O₅/SiO₂. The addition to cyclohexane resulted in the two methacrylate C=O (~1720 and ~1700 cm⁻¹) and the C=C (~1640 cm⁻¹) absorption bands.
Figure 3.5. Quantification of surface functionalization for $\text{Ta}_2\text{O}_5/\text{SiO}_2$ in the methacrylate absorption region: Two methacrylate C=O ($\approx 1720$ cm$^{-1}$ and $\approx 1700$ cm$^{-1}$), the carbon double bond ($\approx 1640$ cm$^{-1}$) and free surface $\text{H}_2\text{O}$ ($\approx 1620$ cm$^{-1}$) absorption bands matched (broken line) the measured IR spectra (upper solid line).

Pure silica had the highest normalized methacrylate absorbance (0.8) but Figure 3.6 shows that it remained almost constant (scattering between 0.4 – 0.5) for $\text{Ta}_2\text{O}_5/\text{SiO}_2$. Increasing the MPS concentration above 20 mmol/l did not increase the functionalization yield for 35 wt.% $\text{Ta}_2\text{O}_5/\text{SiO}_2$. The MPS reacts with the particle surface till all accessible active sites are covered. Surface-attached MPS might crosslink but does not react with solution MPS indicating that condensation which might form oligomers of MPS[19] did not occur since this would have increased the TGA mass loss with increasing MPS concentration (not shown here).
Results and Discussion

Figure 3.6. Methacrylate absorbance of $Ta_2O_5/SiO_2$ (determined as in Figure 3.5) as function of $Ta_2O_5$ content at standard functionalization conditions using 20 mmol/l of MPS (triangles) and for 35 wt.% $Ta_2O_5/SiO_2$ as a function of MPS concentration (circles).

Functional Structures: C- and Si-Moieties

Figure 3.7 shows schematics of possible silicon sites at the particle and attached surface modifier molecule:[14] $Q^4$ represents Si inside the particle (siloxane, middle) while $Q^2$ and $Q^3$ correspond to Si at the particle surface with 2 (geminal) and 1 (free) hydroxyl groups, respectively (lower left). Surface modifier Si can be bound to the particle surface in many different ways. These sites are commonly abbreviated by $T^i$ where $i$ represents the number of next $\text{–O-Si}$ moieties. Linking with $i = 1$-$3$ bonds with the particles surface are called mono-, bi- or tridental bonding modes (Figure 3.7, upper left).[14] The surface modifier can either be arranged in linear, planar or shell type structures on the particles (upper right) or as oligomers of surface modifier attached to the particle surface.
by few bonds (lower right). Having similar focal environments, these Si types cannot be readily distinguished by NMR analysis. Values in the legend correspond to expected $^{29}\text{Si}$ shifts $\delta$ of the different types in NMR spectroscopy.$^{[14]}$

![Figure 3.7. Schematic of the different Si structures at the particle (Q) or surface modifier molecules (T). The $i$ refers to the number of O-Si groups bound to a Si atom. Surface functionalization can result in T$^i$ moieties which correspond to different structures.](image)

Untreated particles with different Ta$_2$O$_5$ content were analyzed using $^{29}\text{Si}$ CP-MAS NMR spectroscopy (Figure 3.8a). For pure SiO$_2$ (0 wt.% Ta$_2$O$_5$) the broad but structured peak could be deconvoluted into three Gaussian shaped bands at $\delta = -91$, -99 and -108 ppm, respectively. These are attributed to Q$^2$, Q$^3$ and Q$^4$ Si-sites present, with Q$^3$ (one free hydroxyl group) showing the highest intensity. It should be mentioned that this does not reflect the quantitative distribution among these sites as in cross-polarization only sites in short distance to protons are registered i.e. only those close to the surface. For 76 wt.% Ta$_2$O$_5$ content (Figure 3.8a), a broadened peak could be observed$^{[37]}$ whose shape could be approximated by a single Gaussian centered at $\delta = -99$ ppm. This broadening could
arise from the unresolved overlap of Si-resonances. As such, the Q\textsuperscript{3} peak in SiO\textsubscript{2} is expected to split into peaks from HOSi(OSi)\textsubscript{3}i(OTa)\textsubscript{i}, i = 1-3 which are secondarily slightly shifted one to the other. By incorporating Ta\textsuperscript{5+} cations into the particle, the number of next –OSi moieties per Si\textsuperscript{+4} cation (average radius of ~40 pm) is reduced and additional defects are introduced by the larger Ta\textsuperscript{5+} cation (average radius of ~80.5 pm) thereby increasing the Q\textsuperscript{2} signal intensity.[44]

Since surface functionalization leads to new Si-O-Si bonds between the MPS siloxanes and particle surface, the amount of surface OH-groups is reduced (Figure 3.8b). A decrease in the Q\textsuperscript{2} and Q\textsuperscript{3} signal intensity is expected that is accompanied with an increase of the Q\textsuperscript{4} signal intensity for both pure SiO\textsubscript{2} and 35 wt.% Ta\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2}.[14] The surface grafting also led to additional δ peaks ranging from ~40 ppm to ~70 ppm (Figure 3.8b). These peaks correspond to T\textsuperscript{i} bonding sites of covalently attached surface modifier. While mainly T\textsuperscript{2} and T\textsuperscript{3} signals were observed for surface functionalized pure SiO\textsubscript{2}, the T signals seemed to be shifted towards T\textsuperscript{1} for increasing Ta\textsubscript{2}O\textsubscript{5} content. For pure Ta\textsubscript{2}O\textsubscript{5}, the strongest bands are resonances in the region of T\textsuperscript{1} and T\textsuperscript{2} Si-types. This showed the high interconnection between surface modifier molecules on the particle surface since no Si-O-Si bonds could have been formed to the surface. The T\textsuperscript{0} peak (δ = ~42 ppm), representing the Ta-O-Si bond and lying close to the T\textsuperscript{1} peak cannot be clearly distinguished\textsuperscript{[45]} as for antimonytinoxide\textsuperscript{[21]} and alumina.\textsuperscript{[22]}
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Figure 3.8. $^{29}$Si NMR spectra show only $Q^2$, $Q^3$ and $Q^4$ Si sites and a broadening of the Si peak with increasing Ta$_2$O$_5$ content in the untreated powder (a). After standard surface functionalization (b), up to three new Si types ($T^1$, $T^2$ and $T^3$) were identified for pure SiO$_2$ and Ta$_2$O$_5$/SiO$_2$ while no $Q^i$ Si-moieties appeared for pure Ta$_2$O$_5$ particles.

For different Ta$_2$O$_5$ contents, $^{13}$C NMR spectroscopy revealed the typical MPS and PA peaks (Figure 3.9). Every peak in the spectrum corresponds to a different type of carbon in these two molecules (Figure 3.9 a-h for MPS and k for PA). Regardless of Ta$_2$O$_5$ content, functionalized particles resulted in
similar NMR spectra. The generally low intensity of the methoxy group resonance (a at $\delta = 53$ ppm) indicated either a high degree of interconnection of MPS or a bi/tridental bonding to the surface as observed for surface functionalization in a polar solvent$^{[14]}$ or prior hydrolysis of MPS.$^{[15]}$ Note that the intensity of that methoxy peak decreased as the Ta$_2$O$_5$ content increased to the point that vanishing amounts of SiOCH$_3$ groups were detected for pure Ta$_2$O$_5$. This observation brings us back to the interpretation of the $^{29}$Si NMR spectrum (Figure 3.8b). The T$^1$ prototypes shown systematically in Figure 3.7 have to be complemented as follows: The spectral region attributed to T$^2$ sites contain not only silicon of the RSi(OSi)$_2$(OCH$_3$)$_2$ type but also RSi(OSi)$_2$(OTa)$_i$, those of T$^1$ contain RSi(OSi)(OCH$_3$)$_2$$_i$(OTa)$_i$, $i=0 - 2$.

**Figure 3.9.** $^{13}$C NMR analysis of functionalized pure SiO$_2$ and Ta$_2$O$_5$ and mixed Ta$_2$O$_5$/SiO$_2$ showed that almost all carbon species of the original surface modifier molecules were present. Only the signal from the methoxy groups whose stoichiometry depends on the surface functionalization type was significantly lower.
Chapter 3: Surface Functionalization of Ta$_2$O$_5$/SiO$_2$

The second component present on the particle surface consists of PA (k in Figure 3.9), likely present in its propylammonium form. With increasing Ta$_2$O$_5$ content and the corresponding surface acidity (Figure 3.1), the concentration of PA and propylammonium increased as well ($\delta = 42 - 44$ ppm). Washing the materials for 24h in a 1:1 mixture of water and CH$_3$OH did not alter the $^{13}$C NMR spectra and it must be concluded that PA resides mostly on hydrophobic sites which are hardly accessible by solvents. As PA is not required for surface functionalization of mixed Ta$_2$O$_5$/SiO$_2$ particles, functionalization solely by MPS could be recommended as it is indicated also in Figure 3.2b and Figure 3.4b.

Hydrolytic Stability

During storage of filler particles - monomer mixtures before processing, the surface modifier should not be hydrolyzed. Such hydrolysis would reduce its ability to bond with the organic matrix thereby leading to a reduction of the mechanical properties of the nanocomposite. Therefore surface functionalized SiO$_2$ and 35 wt.% Ta$_2$O$_5$/SiO$_2$ particles were stored under severe conditions (pH=2) and tested for the remaining surface modifier as a function of time (Figure 3.10). Following the procedure of Figure 3.5, calculated FTIR absorption spectra were normalized to the IR absorption intensities of the freshly surface functionalized particles (Figure 3.4 and Figure 3.5: MPS/PA/cC$_6$, rel. methacrylate absorbance = 1).

For short storage times, the methacrylate on the particle surface decreased by ~25% (Figure 3.10) for both pure SiO$_2$ and Ta$_2$O$_5$/SiO$_2$. Storing pure SiO$_2$ in water for 17 days resulted in a comparable removal (20 %) of surface modifier.$^{[25]}$ Storing the surface functionalized particles up to 80 days under such conditions did not decrease the amount of modifier from the particle surface for either material. In the first few days either physically adsorbed modifier molecules or bonds of the modifier that can be easily hydrolyzed are removed. The bonds that remain stable after the first days seem not to hydrolyze during longer storage
times. The Si-O-Ta and Si-O-Si bonds appear to have a high stability\cite{46} so that the hydrolytic stability is not significantly influenced by the type of particle surface. Most likely, MPS is attacked at the ester bond which results in a decrease of the methacrylate absorption band after washing.\cite{47}

![Graph showing relative methacrylate absorbance over hydrolytic stability test duration](image)

**Figure 3.10.** Exposing the functionalized particles to severe conditions (pH=2) resulted in an initial reduction of the two FTIR methacrylate absorption bands for pure SiO\(_2\) and the mixed oxide but remained constant thereafter. Most of the particle/surface modifier decoupling took place in the first few days regardless of particle composition resulting in similar surface modifier contents on the particle surface.

When 76 wt.% Ta\(_2\)O\(_5\)/SiO\(_2\) was tested for its hydrolytic stability, the absorption intensity of the tetrahedral Si-O-Si band was too weak to be used as standard, so that the intensities could not be quantified as before (Figure 3.5). FTIR spectra clearly exhibited the presence of methacrylate groups remaining on the surface after hydrolysis. For the freshly functionalized particles, the ~1720 cm\(^{-1}\) adsorption band, representing the methacrylate without hydrogen bonds, is more intense than that at ~1700 cm\(^{-1}\). The intensity of the ~1720 cm\(^{-1}\) band decreased after hydrolysis with respect to the intensity of the ~1700 cm\(^{-1}\) band as observed
after washing with acetone (Figure 3.11, dotted line) or for mica with tetrahydrofurane. After storing the particles for 79 days in solution, the two methacrylate absorption band intensities decreased with respect to the C=C band which can result from partial hydrolysis of the methacrylate bonds. Functionalized Ta₂O₅/SiO₂ particles showed high hydrolytic stability that was mainly determined by the surface modifier stability for long storage at severe conditions.

![FTIR spectra](image)

**Figure 3.11.** FTIR spectra of the surface functionalized 76 wt.% Ta₂O₅/SiO₂ immersed for 79 days in an ethanol/water solution (pH=2). All samples exhibited the two methacrylate absorption bands at ~1720 cm⁻¹ and ~1700 cm⁻¹. When immersed for 2 days, the intensity ratio of these IR bands changed drastically, but only slightly afterwards during 79 days of storage.

Conclusions

Flame synthesis of Ta₂O₅/SiO₂ resulted in particles with increased surface acidity similar to that of pure Ta₂O₅. This influenced significantly the functionalization of Ta₂O₅-containing SiO₂ particles. While the addition of functionalization catalysts such as n-propylamine (PA) facilitated surface functionalization of
pure SiO₂, it reduced that of Ta₂O₅/SiO₂ particles by blocking their active sites. For silica, distinct differences in the bond arrangement of the MPS surface modifier on the particle surface functionalized with and without PA could be observed by FTIR and NMR. This may suggest that PA may not be used for surface functionalization of radiopaque Ta₂O₅/SiO₂ and possibly for other silica-based mixed oxide particles. Except for pure silica, the surface functionalization yield scaled with the surface area. Particle surface properties had a significant influence on the Si moieties, indicating that particles form either bi/tridental or crosslinked structures of the surface modifier. Hydrolytic stability is not determined by the particle surface but by the stability of the ester bond of the MPS surface modifier resulting in comparable stabilities for pure SiO₂ and Ta₂O₅/SiO₂.

References

Chapter 3: Surface Functionalization of Ta$_2$O$_5$/SiO$_2$


CHAPTER
FOUR

Dispersion of radiopaque Ta$_2$O$_5$/SiO$_2$ nanoparticles in methacrylic monomers

Abstract

Objectives: Radiopaque dental adhesives (DA) of low viscosity were made by forming stable suspensions of weakly agglomerated Ta$_2$O$_5$/SiO$_2$ nanoparticles with primary particle size of about 10 nm.

Methods: The particles were prepared by one-step flame-spray pyrolysis. Particles were functionalized with $\gamma$-methacryloxypropyltrimethoxysilane (MPS) and dispersed in a methacrylic monomer matrix by centrifugal mixing and ultrasonication. Particle size distributions were analyzed by X-ray disc centrifugation of suspensions and TEM analysis of the cured composites, while average primary particle size was obtained by N$_2$ adsorption and X-ray diffraction.
Results: The dispersion method affected the aggregate size distribution of both untreated and surface functionalized particles in these suspensions. The influence of particle content on suspension viscosity, aggregate size distribution and Ta$_2$O$_5$ content on radiopacity was investigated. The shear bond strength of such radiopaque particle-containing adhesives on enamel and dentin was comparable to that of the particle-free reference adhesive.

Significance: Flame-made Ta$_2$O$_5$/SiO$_2$ nanoparticles can be introduced readily into dental adhesives as they form quite stable suspensions. Viscosity stayed low even after adding radiopaque particles up to 20 wt.%. The resulting composites had radiopacities comparable to that of enamel facilitating their distinction from marginal gaps. Bond strength was not significantly influenced by the presence of particles in the adhesive.

Introduction

Secondary caries is a major reason for replacing composite restorations.[1]. During polymerization, and most notably aging, composite fillings shrinkage leads to stress between composite, adhesive, and dental hard tissue.[2]. Shrinkage stress promotes marginal gaps and increases the risk of cariogenic bacteria penetration and deterioration of the tooth structure.[3] [4]. Secondary caries may be detected visually by the discolorations at the tooth/filling interface though often X-ray photographs are required to safely discriminate such lesions from stained margins.[5] Radiographs rely on the difference in radiopacity between healthy dental tissue, cariogenic hard tissue and filling material. Modern composite filling materials commonly contain radiopaque components, such as Sr- or Ba-glass fillers, making them easily distinguishable by X-ray from the tooth.

The onset of secondary caries in dentin often leads to rapid tissue degradation.[6] Therefore, dental fillings are often removed upon detection of a dark halo in X-ray photographs to prevent the spreading of secondary caries in the den-
The interpretation of X-ray photographs and the decision to renew a dental restoration strongly depends on the dentist’s level of experience. Advances in X-ray photography have improved resolution down to ~ 100 μm nowadays that is expected to reach 30 μm in the near future.

Due to their low radiopacity, most current dental adhesives however easily give misinterpretable halos on X-ray photographs. This is especially the case if application to the cavity surface has not resulted in sufficiently thin (~200 μm) films before polymerization. By such error of judgment, dental fillings are often unnecessarily replaced and healthy tooth tissue is needlessly damaged. Though the influence of particles on dental adhesive properties has been studied intensively, such studies usually employ oxides with low radiopacity, such as silica with low contrast between dental adhesive and tooth. To enable the safe distinction between marginal gap and thick adhesive layers adhesives containing radiopaque particles with radiopacities higher than dentin or enamel will be demanded.

To facilitate good wetting and high bond strength, adhesives have to exhibit high affinity towards hydrophilic (tooth) and hydrophobic (filling) substrates, high mechanical strength (Young’s and shear moduli) and durability. An adhesive formulation requires careful adjustment of chemical composition, viscosity and hydrophobicity. For filled compositions, particle characteristics such as primary particle, aggregate and agglomerate sizes, surface characteristics and elemental distribution affect the final material characteristics. Mechanical durability of filled materials can be affected by particle structure, filler content and especially filler surface functionalization. Polymerizable filler coatings allow formation of covalent bonds with the polymer matrix during curing, thereby distributing mechanical and thermal stresses. Particle addition decreases polymerization shrinkage of the adhesive materials and thereby helps reduce internal stresses and the risk of gap formation.
Though dental filler particles are typically made from undercooled melts, dry aerosol routes offer products of higher purity (e.g. for optical fibers\textsuperscript{[23]}) by fewer process steps. Flame spray pyrolysis (FSP) in particular is a highly versatile method for synthesis of mixed oxides such as SiO$_2$-based Ta$_2$O$_5$\textsuperscript{[18]} and Yb$_2$O$_3$\textsuperscript{[24]} for dental fillers. For this reason, FSP has been used in production of such nanoparticles with controlled size, refractive index, composition, transparency\textsuperscript{[18]} and homogeneous distribution.\textsuperscript{[24]} Such particles have been shown to exhibit particle surface/modifier bonds of comparable hydrolytic stability as pure SiO$_2$\textsuperscript{[18]} while their composites have exhibited similar or higher radiopacity and mechanical strength than commercial fillings.\textsuperscript{[24]} Flame-made particles with closely controlled characteristics have been well dispersed in polymer matrices resulting in non-agglomerated structures\textsuperscript{[25, 26]} of smaller aggregate size than commercial SiO$_2$.\textsuperscript{[26]}

In dental monomer mixtures agglomerate size has to be minimized to avoid particle settling during storage.\textsuperscript{[27]} The direct preparation of nanoparticles in their latter matrix still faces technical challenges, so that particles commonly are made and dispersed in two steps.\textsuperscript{[28]} To achieve primary nanoparticle dispersion, high dispersion energy is necessary\textsuperscript{[29]} as with ultrasonication\textsuperscript{[30]} or solution expansion at high pressure drop.\textsuperscript{[31]} Increasing dispersion energy serves to significantly decrease agglomerate size by breaking down soft agglomerates but is ineffective against hard aggregate.\textsuperscript{[31]} Ultrasonication may be limited, however, by the contamination arising from sonotrode.\textsuperscript{[30, 31]} Dual asymmetric centrifuge mixing allows desagglomeration by submitting the actual liquid to high shear forces while greatly reducing the probability of contamination. Surface functionalization can help to prevent the reagglomeration of highly dispersed particles by steric or electrostatic stabilization.\textsuperscript{[32]} Though nanoparticles derived from BaO,\textsuperscript{[33]} TiO$_2$, ZrO$_2$\textsuperscript{[34]} and Ta$_2$O$_5$\textsuperscript{[35]} have been employed to increase radiopacity, the functionalization of these materials surface is not well understood compared to that of commonly used SiO$_2$ fillers.
Here, the application of untreated and surface modified mixed Ta$_2$O$_5$/SiO$_2$ nanoparticles containing 35 - 83 wt.% Ta$_2$O$_5$ is investigated for synthesis of dental adhesives with radiopacities greater than that of dental hard tissues. So up to 20 wt.% of such nanofillers were dispersed in a dental adhesive by ultrasonication and centrifugal mixing. Particle size distributions were determined at various dispersion conditions using an X-ray disc centrifuge and TEM analysis. Adhesive properties of the unfilled and particle containing polymers to dentin and enamel were determined by shear bond strength measurements.

**Experimental**

*Particle Synthesis, Characterization and Functionalization*

Tantalum butoxide (Aldrich, > 98%) and tetraethoxysilane (TEOS, Fluka, > 98 %) were used as tantalum and silicon precursors, respectively. Appropriate precursor amounts were mixed with hexane under nitrogen to give solutions with 0.5 M of total metal (Ta + Si) concentration (Ta + Si). Mixed tantalum oxide silica particles\[18\] were produced in a laboratory scale FSP reactor.\[18\] The Ta$_2$O$_5$ weight fraction in the product powder ranged from 35 – 83 wt.%.

The specific surface area (SSA, $m^2/g$) of these particles was determined by N$_2$ adsorption at 77 K using the BET method (Micromeritics Tristar 3000, 5-point isotherm, 0.05 < $p/p_0$ < 0.25). Assuming spherical, monodisperse primary particles with homogeneous density, the average BET-equivalent particle diameter was calculated with the mass fractions of Ta$_2$O$_5$ and SiO$_2$ and density of pure Ta$_2$O$_5$ (8.2 g/cm$^3$) and SiO$_2$ (2.2 g/cm$^3$). Particles were surface functionalized with $\gamma$- methacryloxypropyltrimethoxysilane (Fluka, > 98%) in cyclohexane (Fluka, >99.5%) at 70 °C for 24 h with 95 wt.% collection yield.\[36\] Functionalized particles were dried overnight at 10 mbar and 22 °C.
Suspension Preparation and Characterization

Untreated and surface functionalized particles were dispersed in a typical dental adhesive (DA) monomer mixture (1 and 20 wt.% filler content) containing 15 wt.% 2-hydroxyethyl-methacrylate (HEMA, Degussa, > 98%), 10 wt.% 2-[4-(dihydroxyphosphoryl)-2-oxa-butyl]-acrylic-acid-ethyl-ester (DHPAE, synthesised[37] > 96%), 35 wt.% (1-methylethyldiene)-bis-[4,1-phenyleneoxy(2-hydroxy-3,1propanediyl)]-bismethacrylate (Bis-GMA, Esschem, > 80%), 20 wt.% glycyl-dimethacrylate (GDMA, Degussa, > 85%) and 20 wt.% ethanol (Fluka, >99.8%). For TEM and bond strength analysis 1 wt.% camphorquinone (Rahn, >99%) and 0.5 wt.-% ethyl-p-(dimethylamino)benzoate were added as curing agents.

The particles were dispersed in the DA matrix after premixing with a spatula by ultrasonication (Vibracell VCX 600, Sonics & Materials Inc., 600 W, 20 kHz, 13 mm tip, 0.1 s pulse, 0.9 s pause, 70% amplitude) and/or by dual asymmetric centrifugal mixing (Speed mixer DAC 150 FVZ, Hausschild, 3000 rpm, 10 min). Dispersion energies by ultrasonication ranged 17 – 600 MJ/m³, while centrifugal mixing was determined to introduce 9 MJ/m³ by the temperature increase during mixing (ΔT = 9.6 °C). Absence of heat transfer to the surroundings, exclusive heat generation by liquid shearing and a heat capacity of 0.9 kJ/kg for the dental resin were assumed.[38] Unless otherwise stated, 83 wt.% Ta₂O₅/SiO₂ nanoparticles dispersed by 10 min centrifugal mixing followed by 300 MJ/m³ ultrasonication were used as standard suspension conditions.

The viscosity of particle-free and particle-containing DA solutions was determined by a rotational rheometer (Anton Paar Physica Rheometer, MCR 300) with a double-gap couette geometry (DG267, DIN 54453) at 23 °C. The shear viscosity of these solutions were determined for shear rates ranging from 0.1 – 1000 1/s with a logarithmic ramp. Inter-particle spacing for monomodal, ideally dispersed particles was calculated by:
Experimental

\[
\frac{\text{inter} - \text{particle distance}}{\text{particle diameter}} = \frac{1}{2} \times \left[ \frac{\phi_{\text{rcp}} = 0.64 \times x_p \times \rho_M}{x_p \times \rho_M + (1-x_p) \times \rho_P} \right]^{1/3} - 1 \tag{4.1}
\]

where \(\phi_{\text{rcp}}\) represents the volume fraction of random close-packing, \(x\) the mass fraction and \(\rho\) the density. Indices M and P indicate monomer matrix and particles, respectively.\[39\] The DA monomer density was determined as 1.045 g/cm\(^3\) by a Calculating Density Meter (Anton Paar AG, DMA 55).

The particle size distributions in DA suspensions (20 ml) containing 1 wt.% filler were obtained by an X-ray scanning disc centrifuge\[40\] (Brookhaven Instruments, BI-XDC) at 6000 rpm (up to 2000 g) for 4 h. Suspensions containing 20 wt.% particles were prepared for centrifugation by dilution and manual agitation immediately before measurement. The viscosities of suspensions containing 1 wt.% untreated (68 mPa s) and functionalized fillers (72 mPa s) at 0.1 s\(^{-1}\) shear rate were used for particle size distribution analysis. The density of 83 wt.% Ta\(_2\)O\(_5\)/SiO\(_2\) (7.2 g/cm\(^3\)) was corrected to 6.7 g/cm\(^3\) for functionalized particles (\(~8\) wt.% surface modifier, \(\rho \approx 1\) g/cm\(^3\)).\[18\] The detection limit for particle sizes at these conditions was \(~30\) nm. Mass mean diameters (MMD) in suspension were related to dispersion energy by:

\[
\text{mass mean diameter} = C \times (\text{dispersion energy})^{-b} \tag{4.2}
\]

with \(C\) and \(b\) as fitting parameters.\[30\]

Nanocomposite Preparation and Characterization

Samples for TEM analysis (~3 mm thick) were polymerized by a blue light lamp (Heliolux GT, Vivadent, 100 W, > 5 min). HRTEM images of 20 wt.% filler containing nanocomposites were prepared after microtoming (Ultracut E, Reichert-Jung, < 100 nm thickness) using a CM30ST microscope (Philips, LaB6 Cathode, 300kV, point resolution 0.2 nm). The conversion of C=C bonds before
and after polymerization was obtained by transmission Fourier transform IR spectroscopy (FTIR, Bruker, Vektor 22, 1 scan, 2 cm⁻¹ resolution). A thin film of unfilled and filled monomer mixtures (20 wt.% filler content) was placed on a KBr tablet (Fluka, > 99.5 %, 300 mg, stored at 115 °C) for FTIR analysis. Spectra were recorded against a KBr background.

Shear bond strength of unfilled and filled DA on enamel and dentin was determined on bovine incisors. For each material, 5 bovine incisors were ground with SiC paper (P1000 grit) to expose enamel or dentin and the unfilled and filled adhesives (20 wt.% filler content) applied after substrate etching with a 37% phosphoric acid etching gel (Total Etch, Ivoclar Vivadent). Composite cylinders (4 mm diameter) (Tetric EvoCeram, Ivoclar Vivadent) were prepared upon the adhesive in two increments on the Teflon cavity (4 mm diameter) according to manufacturer’s instructions. Samples were stored in water at 37 °C for 24 h. Shear load was applied according to ISO/TS 11405 using a universal testing machine (Zwick Z010, Zwich-Roell, Ulm, Germany) and a crosshead speed of 0.8 mm/min. Stress-strain curves were evaluated by testXpert V9.0 (Zwick-Roell). The X-ray radiopacity of DA composites with a defined thickness was compared to an aluminum calibration wedge. Radiograph films (Kodak Insight Dental Film) were exposed to X-rays (70 keV) of a Gentex Oralic DC.

Results and Discussion

Suspension Viscosity

Dental adhesives were applied to an appropriately conditioned tooth surface providing a layer between dental hard tissue (enamel and dentin) and composite material. The DA’s viscosity must be carefully controlled to allow application of an adequately gauged adhesive layer (~200 μm) and facilitate penetration of DA into tubuli, intertubular dentin and the enamel etch pattern.
Figure 4.1 shows the viscosity of unfilled and particle containing DA suspensions (83 wt.% Ta$_2$O$_5$/SiO$_2$, $d_{\text{BET}} = 10$ nm) after dispersion at standard conditions. The viscosity of the unfilled DA (42 mPa s) was increased rapidly to 68 and 72 mPa s when 1 wt.% untreated and functionalized fillers, respectively, were added. Increasing the particle content up to 15 wt.% resulted in a linear increase to 107 and 121 mPa s (not shown) for untreated and functionalized particles, respectively. Up to this filler content particles did not show any significant change in viscosity for different shear rates and were Newtonian liquids with other DAs.[22] At 20 wt.% filler content, however, a rather viscosity (135 mPa s) was obtained for suspension containing functionalized fillers (Figure 4.1). In contrast, a slight shear thinning behavior (160 mPa s at 1 s$^{-1}$ and 134 mPa s at 100 s$^{-1}$) was observed for untreated filler containing suspensions (Figure 4.1).

**Figure 4.1.** The viscosity of unfilled DA was constant from 0.1 to 1000 s$^{-1}$ shear rate. Adding 1 wt.% untreated and functionalized filler to the DA resulted in a steep increase of viscosity that was constant, however, for all shear rates. When 20 wt.% filler was added, the viscosity increased further and was shear rate independent for functionalized particles whereas untreated particles exhibited slight shear thinning from 170 (0.1 l/s) to 120 mPa s (1000 l/s).
For 1 wt.% of evenly dispersed equal-sized particles, the inter-particle distance (Equation 4.2, 3.6 particle diameters, Figure 4.2) effectively suppresses, limits or prevents their attractive interactions during shearing. Increased filler contents, however, lead to significantly reduced inter-particle spacing (0.9 particle diameters for 20 wt.%), thereby increasing the number of particle collisions and suspension viscosity. At low shear rates, particle-particle interactions are determined by Brownian motion whereas at high shear rates particle collisions are dominated by shearing\cite{42} that leads to filled solutions’ thixotropic behavior.

![Graph showing inter-particle spacing vs. particle content](image)

**Figure 4.2.** The inter-particle spacing for evenly dispersed, particles is strongly influenced by particle content in the monomer mixture (Equation 4.1). Using 83 wt.% $\text{Ta}_2\text{O}_5$ in $\text{SiO}_2$ that has a significantly higher density ($7.2 \text{ g/cm}^3$) than pure silica ($2.2 \text{ g/cm}^3$) would result in significantly higher inter-particle spacing than for pure silica. For 20 wt.% filler content the inter-particle spacing is 0.42 particle diameters for pure $\text{SiO}_2$ and 0.83 for 83 wt.% $\text{Ta}_2\text{O}_5$/$\text{SiO}_2$ filler.

Suspension viscosity is determined by inter-particle attraction and the extent of network formation.\cite{43} Hydrophilic surfaces of untreated particles promote
network formation in the DA matrix by inter-particle hydrogen bonding (4 - 40 kJ/mol for SiO\textsubscript{2}).\textsuperscript{[44]} In contrast, functionalization of the particle surface by methacrylate groups mitigates the formation of particle networks and lowers suspension viscosity by amplifying filler - matrix compatibility. The low inter-particle spacing and tendency for network formation leads to thixotropy as observed in Figure 4.1 with 20 wt.% untreated filler containing suspensions in contrast to functionalized ones.\textsuperscript{[45]} At higher shear rates (shear rate > 100 l/s), particle collision occurs regardless of surface functionalization and untreated and functionalized particles give similar viscosities (Figure 4.1, 20 wt.% filler content).

\textit{Dilute Suspension Dispersion}

To avoid sedimentation during suspension storage, particulate matter in organic matrices requires high levels of dispersion.\textsuperscript{[27]} To keep agglomerate particle diameters below 100 nm\textsuperscript{[46]} that prevents effective sedimentation, dispersion conditions have to be optimized. Figure 4.3a shows cumulative particle size distributions of 1 wt.% untreated filler in DA after dispersion by ultrasonication at 17 – 600 MJ/m\textsuperscript{3}. The particle fraction below 500 nm increased continuously with rising energy input. With increasing energy, the particle fraction below the detection limit of the X-ray disc centrifuge (~30 nm) increased significantly from ~20 % (17 MJ/m\textsuperscript{3}) up to ~50 % (600 MJ/m\textsuperscript{3}) of filler content. Mass mean diameters showed a linear reduction with increasing dispersion energy (log-log diagram, Figure 4.3b) as with commercial Aerosil 90 and 200.\textsuperscript{[30]} The mass mean diameter of FSP-made particles did not level off for high dispersion energies,\textsuperscript{[30]} indicating aggregates smaller than 35 nm. Mass mean diameters here depended solely on dispersion energy and not on energy density, dispersion time and particle content.\textsuperscript{[30]}
Figure 4.3. a) Particle size distributions of suspensions containing 1 wt.% untreated filler, which were dispersed by ultrasonication 17 – 600 MJ/m³. b) The mass mean diameter decreased from 55 to 33 nm with indicating the decreasing agglomerate size of these FSP-made particles. Mass fractions of fine particles (< 100 nm) increased from 58 to 79 wt.%. 
Different dispersion methods such as high-pressure drop, rotor/stator and ultrasonication resulted in similar power constants but significantly different prefactors $C$ in Equation 4.2\textsuperscript{[29]} whereas ball milling of SiO$_2$ resulted in a comparable energy dependency\textsuperscript{[47]}. The fine particle content increased significantly from 30 % (17 MJ/m$^3$) to 58 % (60 MJ/m$^3$) and then more slowly to 79 % (600 MJ/m$^3$). This increase shows that a significant increase of the fine particle content requires a dramatic increase of the dispersion energy. Such dispersion energies may pose problems by increased product contamination.

Figure 4.4. Dispersion of 1 wt.% untreated filler by centrifugal mixing (mix.) and ultrasonication (sonic.) in DA monomer mixture significantly influenced the particle size distribution. Centrifugal mixing alone (dotted line) resulted in the lowest particle contents below 500 nm. For particles dispersed by centrifugal mixing and ultrasonication (300 MJ/m$^3$) and vice versa, particle size distributions resulted in similar trends. But for the centrifugal mixing-ultrasonication sequence (solid line), the fine particle content ($<$ 100 nm) is larger and the fine particle size distribution mode (30 – 50 nm) is larger and finer than the opposite sequence (dot-broken line).

Figure 4.4 depicts the influence of dispersion method on the particle fraction of 1 wt.% untreated filler containing DA suspensions. Particles dispersed by
centrifugal mixing for 10 minutes (mix.) exhibited only a low content of fine particles (37 % of filler content) due to insufficient dispersion energy. Shearing alone is thus inadequate to rupture the strong hydrogen bonds between particles and provide nano-particulate dispersions.\[^{44}\] In contrast, the much higher dispersion energy achieved by two-step dispersion (centrifugal mixing, mix., and ultrasonication, sonic.) gave significantly smaller particles.

Figure 4.5 shows particle size distributions of suspensions containing 1 wt.% functionalized filler dispersed by centrifugal mixing (mix.) and/or ultrasonication (sonic.) with the same conditions as for the untreated particles in Figure 4.3a and Figure 4.4. Dispersion of functionalized particles by centrifugal mixing resulted in 72 % fine particle (< 100 nm) content (mix., dotted line), as compared to 37 % by untreated filler (Figure 4.4). Particles dispersed by ultrasonication exhibited more than 70 % fine particle contents with more than 60 % of particle matter below the detection limit of the X-ray centrifuge. Two-step dispersion by ultrasonication and centrifugal mixing resulted in slightly larger fractions of 60 – 500 nm particles compared to ultrasonication alone. From all assessed methods, centrifugal mixing and ultrasonication gave best results in terms of fine particle fraction (91 %) and particle contents below the instrument detection limit of 30 nm (86 %). Functionalized fillers gave similar or slightly finer dispersions than untreated ones with the same dispersion method as with Aerosil 200.\[^{48}\] Particle functionalization assists dispersibility by inhibition of interparticulate hydrogen bonds and promoting the particle - matrix interaction.\[^{49}\]
Results and Discussion

Figure 4.5. Suspensions containing 1 wt.% functionalized filler have been dispersed by centrifugal mixing (mix.), ultrasonication (sonic., 300 MJ/m\(^3\) and 2 x sonic., 600 MJ/m\(^3\)) and the combination of both (sonic. & mix. and mix & sonic.). The dispersion method and their sequence in two-step dispersion influenced the particle size distribution. All methods resulted in fine particle (< 100nm) contents > 70 wt.%.

Dense Suspension Dispersion

Figure 4.6 compares particle size distributions of suspensions containing 20 wt.% untreated and functionalized filler dispersed by centrifugal mixing and ultrasonication. As in dilute suspensions (Figure 4.4 and Figure 4.5), dense ones containing functionalized particles exhibited higher fine particle contents than those with untreated particles. Even for 20 wt.% solid content, particle size distributions exhibited comparable or slightly lower fine particle contents than the 1 wt.% filler containing suspensions.
Figure 4.6. Particle size distribution in suspensions containing 20 wt.% untreated (dotted line) and functionalized filler (solid line), that were dispersed by centrifugal mixing and subsequent ultrasonication (300 MJ/m³). Dispersing the functionalized particles resulted in smaller agglomerates than untreated ones but comparable particle modes at 35 – 40 nm.

Table 4.1 summarizes fine particle contents of suspensions containing 1 and 20 wt.% fillers that were dispersed by centrifugal mixing and ultrasonication with 9 – 600 MJ/m³ energy. In general, dispersion of functionalized particles led to comparable or higher fine particle contents in suspension than dispersion of untreated particles. Only centrifugal mixing of functionalized fillers, in contrast to untreated particles, resulted in comparable fine particle contents with ultrasonication even though dispersion energies differ significantly (9 and 300 MJ/m³).

Even though the functionalized fillers were mixed with the DA monomer mixture by a spatula before dispersion, macroscopic lumps (< 1 mm) were observed after ultrasonication, in contrast to untreated fillers with their open structure[18] which facilitated DA penetration into inter-particle voids. Therefore, highest dispersion of untreated particles may be achieved by ultrasonication
alone, whereas functionalized particles are best dispersed in a two-step process by centrifugal mixing for fragmentation of large particle lumps and subsequent ultrasonication for micron- and nanometer-agglomerate fragmentation.

**Table 4.1.** Fine particle content of 1 and 20 wt.% untreated and functionalized fillers containing suspensions. Particles have been dispersed by centrifugal mixing and ultrasonication (300 and 600 MJ/m\(^3\)). Fine particle contents are strongly dependent on the dispersion method and surface functionalization.

<table>
<thead>
<tr>
<th>filler content</th>
<th>dispersion method</th>
<th>dispersion energy (MJ/m(^3))</th>
<th>&lt; 100 nm fraction (wt.%):</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt.% mixing</td>
<td>9</td>
<td>37</td>
<td>72</td>
</tr>
<tr>
<td>1 wt.% sonication</td>
<td>300</td>
<td>75</td>
<td>73</td>
</tr>
<tr>
<td>1 wt.% sonication</td>
<td>600</td>
<td>79</td>
<td>83</td>
</tr>
<tr>
<td>1 wt.% sonication &amp; mixing</td>
<td>309</td>
<td>73</td>
<td>76</td>
</tr>
<tr>
<td>1 wt.% mixing &amp; sonication</td>
<td>309</td>
<td>77</td>
<td>91</td>
</tr>
<tr>
<td>20 wt.% mixing &amp; sonication</td>
<td>309</td>
<td>78</td>
<td>86</td>
</tr>
</tbody>
</table>

TEM images show 20 wt.% untreated (Figure 4.7, top) and functionalized fillers (bottom) dispersed by centrifugal mixing and ultrasonication (left) and single centrifugal mixing (right) embedded in a DA polymer matrix. These images corroborate particle size distributions determined by X-ray centrifugation (Figure 4.5). For two-step dispersion, homogeneous distributions of nano-sized particles of were formed (left). Surface functionalization slightly reduced agglomerate sizes, though centrifugal mixing (right) resulted in large (micron-sized) particle-clusters of nanoparticles and nano-sized agglomerates.

Filler functionalization increased the fine particle content (Figure 4.6, right bottom) in comparison to untreated fillers (right top). Flame-spray-made particles here exhibited significantly smaller agglomerate sizes than commercially
available SiO$_2$ (Aerosil 200, Degussa).$^{30, 48}$ This can be attributed to the lower particle concentrations and shorter high-temperature residence times in the FSP than in commercial reactors.$^{50}$

![Figure 4.7](image)

**Figure 4.7.** Images of composites containing 20 wt.% untreated (top) and functionalized (bottom) fillers. Particles have been dispersed by ultrasonication and centrifugal mixing (left) and by just centrifugal mixing (right). Two-step dispersion resulted in smaller and lump-free agglomerates than by pure centrifugal mixing regardless of particle functionalization. The latter contributed to even smaller agglomerates.

**Adhesive Radiopacity**

To allow a dental practitioner to safely distinguish marginal gaps from thick layers of adhesives on X-ray photographs, the radiopacity of the adhesive has to be stronger than that of the surrounding dental hard tissue. Figure 4.8 shows the
Results and Discussion

Radiopacity of composites containing 20 wt.% untreated (triangles) and surface functionalized (circles) Ta$_2$O$_5$/SiO$_2$ fillers as a function of Ta$_2$O$_5$ content. Low Ta$_2$O$_5$ contents (35 wt.%, untreated, 72 % Al) resulted in radiopacities below those of dentin (125 % Al) and enamel (160 % Al).\cite{51} Increasing Ta$_2$O$_5$ contents resulted in higher radiopacities than those of dental hard tissue. Since the attenuation coefficient of Ta$_2$O$_5$ (0.86 m$^2$/kg)\cite{52} is higher than that of SiO$_2$ (0.022 m$^2$/kg)\cite{53} at 70 keV energy, the radiopacity is determined by the Ta$_2$O$_5$ content. Particle surface-modification gave slightly lower radiopacity (circles) (Figure 4.8) than untreated particles. Even then the radiopacity was higher than that of enamel for 20 wt.-% filled adhesives containing functionalized 83 wt.% Ta$_2$O$_5$/SiO$_2$ particles (Figure 4.8).

![Graph showing radiopacity of composites](image_url)

**Figure 4.8.** Radiopacity was determined for composites containing 20 wt.% fillers with 35–83 wt.% Ta$_2$O$_5$ content in comparison to an equally thick aluminum sample. Increasing the Ta$_2$O$_5$ content significantly increased the radiopacity. For 40 mol.% (83 wt.%) Ta$_2$O$_5$ content composites exhibited higher radiopacity than dentin and enamel. Surface functionalized particles exhibited slightly lower radiopacities than untreated ones.
**Polymerization and Adhesion Strength**

The IR spectra of thin films as applied to dental cavities of unfilled and 20 wt.% filler containing DA were analyzed before and after polymerization (not shown). The degree of double bond conversion was independent of filler presence, indicating the little influence of particles on polymerization as shown for 20 wt.% ZrO₂/SiO₂ fillers (600 nm) in photoactivated resin-based composites.\(^{[54]}\) Whereas higher filler contents up to 75 wt.% resulted in a significant decrease of C=C bond conversion for nano- (30 – 75 nm SiO₂)\(^{[55]}\) and micron-sized fillers (600 nm).\(^{[54]}\)

Table 4.2 shows the shear strength of unfilled and 20 wt.% filler containing DA on dentin and enamel. The shear strength on enamel are significantly higher (22 – 27 MPa) than on dentin (14 – 16 MPa). Even though the shear strength of unfilled DA was slightly higher on dentin and lower on enamel, variations are still within the experimental error for both surface types as indicated by the geometric standard deviation. Numbers in brackets indicate cohesive failure when samples failed by crack formation in the natural tissue rather than rupture of the adhesive. Adhesion strength strongly depends on preparation conditions\(^{[56]}\) and depends significantly on the exact details of the application protocol. As a result, comparison of absolute values with literature is hardly possible. Although one important parameter that significantly influences adhesion strength is the degree of C=C bond conversion\(^{[57]}\) which was similar regardless of particle addition and their surface nature and therefore gave comparable bond strength.

The Ta₂O₅ content of particles significantly influences inter-particle spacing (Figure 4.2), since the density of Ta₂O₅ is 3.7 times higher than silica. Addition of comparable weight fractions of particles will therefore lead to much smaller inter-particle spaces for pure SiO₂ than for Ta₂O₅ containing particles with a corresponding viscosity increase. Particle size has an additional effect on suspension viscosity which can be increased 18 times by reducing the particle diameter.
from 75 to 30 nm at constant particle content. Moreover, manufacturers must consider other factors that might influence composite properties: High radiopacity as obtained by high Ta$_2$O$_5$ contents is desirable. The chemical nature of the employed surface modifiers may also greatly influence dispersion properties. The particle refractive index can be suitably tailored by variations of the Ta$_2$O$_5$ / SiO$_2$ ratio, which offers access to transparent composites preferable for dental restorations. To achieve the optimum balance of properties, Ta$_2$O$_5$ content and functionalization have to be determined in this multi-dimensional parameter space.

Table 4.2. Shear strength of unfilled and 20 wt.% filler (83 wt.% Ta$_2$O$_5$/SiO$_2$) containing DA on dentin and enamel. Shear strengths are significantly higher on enamel than on dentin. Even though shear strength is slightly lower for the filled adhesives on dentin and slightly higher on enamel, the adhesion strength variation for all samples is within the experimental error for both surfaces types.

<table>
<thead>
<tr>
<th>adhesive</th>
<th>dentin</th>
<th>enamel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>adhesion strength (MPa)</td>
<td>cohesive failure</td>
</tr>
<tr>
<td>unfilled</td>
<td>16.1 (4.0)$^a$</td>
<td>3</td>
</tr>
<tr>
<td>filled, untreated</td>
<td>14.8 (5.5)</td>
<td>3</td>
</tr>
<tr>
<td>filled, functionalized</td>
<td>13.7 (5.4)</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$geometric standard deviation

Conclusions

Radiopaque Ta$_2$O$_5$/SiO$_2$ filler particles made by FSP have been dispersed in a methacrylic matrix to give adhesive materials with radiopacity higher than dentin and enamel and excellent adhesive strength. The dentin and enamel bond strength of a 20 wt.% filled adhesive is comparable to that of the unfilled dental
adhesive (DA), while viscosity is only slightly higher than the unfilled monomer. Particle dispersion methods have to be chosen according to particle/particle attraction, particle/liquid interaction and powder morphology. Untreated filler particles can be dispersed by ultrasonication, in which mass mean diameters only depend on dispersion energy. Surface functionalized fillers have to be pre-dispersed e.g. by centrifugal mixing for fragmentation and wetting of micron- to millimeter-sized particle lumps and subsequently dispersed by ultrasonication. By this two-step dispersion approach, more than 85 % by mass of total surface functionalized filler content (20 wt.% filler content) were below 100 nm, forming stable suspensions impervious to sedimentation during storage. Untreated particles exhibited stronger particle attraction than surface functionalized particles. The latter were separated sterically by the surface modifier thereby giving the particles organophilic properties and facilitating their dispersion and storage.

References


It has been shown that flame spray pyrolysis is a powerful tool for the synthesis of mixed oxide nanoparticles. Silica containing $\text{Ta}_2\text{O}_5$ has unique properties such as adjustable radiopacity and chemically very inert/non-toxic characteristics making it attractive for other medical applications. Particles with an adjustable refractive index and high purity and can also be used in optical fibers as they should lead to little attenuation during wave propagation. Furthermore, $\text{Ta}_2\text{O}_5$ has a very high dielectric constant so that these nanoparticles can be applied in capacitors. The high surface acidity of these particles makes an application as catalyst in alkylation and esterification reactions possible.

The influence of production conditions such as solvent and precursor on the transparency of nanoparticles has been studied. Production range for maximum transparency was 10 g/h in the laboratory flame reactor, which is too low for an industrial production of these particles. Particle homogeneity might decrease with increasing production rate resulting from longer residence times in the high temperature zone so that elements can segregate. Large scale production pa-
parameters have to be optimized to achieve equal particle properties as from the laboratory scale reactor. For continuous production of high quality particles, the reactor should be a closed system to ensure that no contaminations can decrease particle/composite performance. Furthermore, controlled temperature profiles can result in particle characteristics that need longer residence times in the hot temperature zone.

After particle production, particles are commonly collected on filters. For application in suspensions, untreated nanoparticles are then dispersed in liquids to fine agglomerates of primary particles, which is a very energy-intense process step. Process intensification by collecting airborne particles directly after synthesis in the liquid with stabilizing properties might reduce the dispersion energy for nanosuspensions. The liquid could be sprayed into fine droplets in co-flow direction of the particle-laden gas stream thereby collecting the agglomerates. Suspension droplets could be separated from the gas, which contains fewer particles, by a cyclone.

In this study, particles have been surface-functionalized by classical wet-phase chemistry. Thereby the advantage of the high accessibility because of the high inter-particle porosity was lost after the process. In this case, particles have been dispersed in monomers for composites, so that low porosity might result in slightly higher dispersion energies. When the particles are used for other applications such as sensors or adsorption material, this unique powder property of flame-made particles, the high porosity, is lost irreversibly. Therefore particles should be functionalized in the gas phase (Figure 5.1). By surface modification with fluidized beds, particles would retain most of the high porosity and the continuous restructuring of soft agglomerates would ensure the functionalization of the complete particle surface. Nevertheless the fluidization nanoparticles and their agglomerates is more challenging than for commonly used micron-sized particles. Because of their unique porosity (appearant density) and surface forces (lying outside the Geldart- and Reh-Diagram), these particles have to be agitated
mechanically or sonically for fluidization, to prevent plug rising of the whole bed and channeling in the bed.

Figure 5.1. Schematic and image of a fluidized bed for nanoparticles. Important parameters that characterize the fluidized bed can be monitored by the pressure drop over the bed (PI). To overcome the adhesive forces nanoparticles, the fluidized bed has to be agitated, e.g. by a motor (M).

Besides radiopacity, more functions can be added to composites by particle incorporation. Antibacterial properties, for example, can be achieved by the production of silver-containing Ta₂O₅/SiO₂ particles with silver forming small clusters on the particle surface or the functionalization of the particle surface with bio-active molecules. When marginal gaps are formed during the polymerization of the dental filling, the antibacterial properties of the filler containing dental
adhesive might inhibit bacterial growth in the narrow fissure because of the close contact. Flame spray pyrolysis has the potential to produce a vast variety of high-quality, nanoparticulate and nanostructured materials such as oxides, halides, phosphates and pure metals and combinations of those. This can lead to completely new composite properties for electrical, chemical, biological, mechanical and magnetic applications.
APPENDIX A

Independent control of metal cluster and ceramic particle characteristics during one-step synthesis of Pt/TiO$_2$

Abstract

Rapid quenching during flame spray synthesis of Pt/TiO$_2$ (0 - 10 w.t% Pt) is demonstrated as a versatile method for independent control of support (TiO$_2$) and noble metal (Pt) cluster characteristics. Titania grain size, morphology, crystal phase structure and crystal size were analyzed by nitrogen adsorption, electron microscopy and x-ray diffraction, respectively, while Pt-dispersion and size were determined by CO-pulse chemisorption. The influence of quench cooling on the flame temperature was analyzed by Fourier-transform infrared spectroscopy. Increasing the quench flowrate reduced the Pt-diameter asymptotically. Optimal quenching with respect to maximum Pt-dispersion (~60 %) resulted in
average Pt-diameters of 1.7 to 2.3 nm for Pt-contents of 1 to 10 wt.%, respectively.

Introduction

Noble metals dispersed on ceramic particles are important in sensors, electronics and most notably in catalysis. The size of the noble metal cluster has a profound influence on the material performance e. g. for structure sensitive reactions,[1] and sensor sensitivity.[2] Though typically these materials are made by multi-step wet-chemistry processes, recently, flame technology has been used for one-step synthesis of Pt, Pd, Ag and Au nanoparticles on various nanostructured supports such as Al₂O₃,[3, 4] SiO₂[5] and TiO₂.[5-7] The as-prepared materials exhibit a high external specific surface area (40 – 320 m²/g) with a high degree of crystallinity and an excellent noble metal dispersion. The large external surface area makes them attractive for mass transfer limited reactions such as in chiral catalysts[3] and high temperature applications. The addition of noble metals does not influence usually the ceramic support characteristics as metal precipitation follows that of the ceramic support.[5] Up till now, the flame-made noble metal cluster size could be controlled only by its initial precursor concentration at constant production conditions.[5] At a given noble metal concentration, the support and noble metal particle sizes change concurrently by varying the process parameters (e. g. flame enthalpy content through the oxidant or fuel composition).[4] Therefore, decoupling the noble metal cluster size control from that of the ceramic support has been a challenge in one step flame synthesis of mixed metal-ceramic particles.

This can be achieved by manipulation of flame cooling during particle formation. Non-agglomerated silica[8] and titania[9] particles with reduced primary particle sizes can be made by increasing the cooling rate through increasing the oxidant flow. External electrical fields to the flame induce ionic winds that in-
crease flame cooling and reduce product primary particles.\textsuperscript{[10, 11]} Quenching the entire flame through a critical flow nozzle can also rapidly reduce the flame temperature resulting in non-agglomerated particles and even titania suboxides.\textsuperscript{[12]} Another possibility for controlled quench cooling is the direct radial injection of cold air from a quench ring into a vapor-fed flame at a given height.\textsuperscript{[13]} The specially arranged nozzles create a swirl-stabilized upward flow with limited disturbance upstream of the quenching ring and introduce additional oxygen into the flame ensuring complete oxidation of the precursor and simultaneously decreased the product primary particle size. Radial quench cooling has – apart from the original study on quench cooling of vapor-fed flame synthesis \textsuperscript{[13]} – been demonstrated for flame spray synthesis of pure TiO\textsubscript{2}.\textsuperscript{[14]}

Here, the application of radial quench cooling method is explored for decoupling the metal dispersion from the ceramic particle size during Pt/TiO\textsubscript{2} synthesis by the highly versatile flame spray pyrolysis process. The Pt/TiO\textsubscript{2} is selected for its broad application in catalysis such as photocatalytic\textsuperscript{[15]} and hydrogenation reactions\textsuperscript{[16]} and the relatively simple crystallinity of TiO\textsubscript{2} compared to other supports such as Al\textsubscript{2}O\textsubscript{3}. The role of the quenching location on the particle characteristics of Pt/TiO\textsubscript{2} is investigated systematically at constant flame enthalpy content, titanium concentration, dispersion gas flow and solvent composition but variable quench gas flow and platinum content.

Experimental

\textit{Precursor Preparation and Flame Synthesis}

Powders were produced in a laboratory scale spray flame reactor (Figure A1).\textsuperscript{[17]} A concentric two-phase nozzle (capillary inner/outer diameter 0.41 / 0.72 mm) and annulus (outer diameter 0.97 mm) was used to spray the metal-containing liquid mixture. The annular gap area of the dispersion gas (O\textsubscript{2}, Pan Gas, 99.95\%) was adjusted to achieve a 1.5 bar pressure drop at the nozzle.
In all experiments, a syringe pump (Inotec, RS 232) fed 5 ml/min of the precursor solution into the flame through the innermost capillary, where it was dispersed into fine droplets by 5 l/min O₂ flowing from the first annulus. The spray was ignited by a circular premixed flame (inner diameter 6 mm, slit width 10 μm) of CH₄ (1.5 l/min, Pan Gas, 99.5%) and O₂ (3.2 l/min). An additional O₂ sheath (5 l/min) was supplied through a ring of sinter metal (inner/outer diameter 18/34 mm). All gas flow rates were controlled by calibrated mass flow controllers (Bronkhorst). The production rate of pure TiO₂ was 15.6 g/h, while when adding 10 wt.% platinum this increased to 17.2 g/h.

Titanium iso-propoxide (Aldrich, 97 %) and platinum (II) acetyl-acetonate (Strem Chemicals, 98 %) were used as titanium and platinum precursors, respectively. Appropriate amounts of the precursors were diluted and dissolved in a 11:5 (by volume) mixture of xylene (Fluka, > 98.5 %) and acetonitrile (Fluka, > 99.5 %). The Ti concentration was kept constant (0.67 M) for all experiments. The nominal Pt-weight fraction ranged from 0 – 10.

The combustion enthalpy density (kJ/ggas) was calculated from the ratio of the specific combustion enthalpy (kJ/mlliquid) of the reactants and by the specific mass (ggas/mlliquid) of the evolving gases at complete combustion conditions (products: CO₂, H₂O, TiO₂ and Pt). All experiments were carried out at a constant combustion enthalpy density of 9.1 kJ/ggas, neglecting the additional quench gas flow.

A 2 cm long water-cooled quench ring (inner/outer diameter 41/51 mm) with eight evenly distributed gas outlets in its inner annulus (diameter 1 mm each) was placed axially downstream from the nozzle (Figure A1). Quench gas with a total flow rate ranging from 0 - 50 l/min was injected radially into the flame spray, though most of the experiments were carried out at 40 l/min unless otherwise noted. As in the original design, the gas outlet nozzles of the quench ring are directed 10° away from the center line of the ring and pointing downstream by 20° to reduce upstream flame distortions (Figure A1 inset). This is es-
sentential in order to enable well defined studies of the influence of quench cooling on the product properties without disturbing the entire flame zone. The ring was internally cooled by flowing 0.83 l/min water (7°C). The quench ring distance above the burner-nozzle (BQD) was varied from 2 to 12 cm. The product powders were collected by a vacuum pump (Busch SV 1025 B) on a glass microfibre filter (Whatman GF/D, 25.7 cm in diameter).

![Burner with quench cooling device. The water-cooled quench ring injects cooling gas from eight almost vertical nozzles, specifically directed to give an upwards-directed, swirling flow with intimate mixing with the hot product gas of the flame. Its distance between the burner nozzle and quench ring (BQD) was adjusted from 2 – 12 cm.](image)

**Figure A1.** Burner with quench cooling device. The water-cooled quench ring injects cooling gas from eight almost vertical nozzles, specifically directed to give an upwards-directed, swirling flow with intimate mixing with the hot product gas of the flame. Its distance between the burner nozzle and quench ring (BQD) was adjusted from 2 – 12 cm.

**Temperature Measurements and Particle Characterization**

The gas temperature in the spray flame was measured by non-intrusive Fourier transform infrared (FTIR) emission/transmission spectroscopy.[19] The spec-
trometer (Bomem Inc., Model MB157) operated over a spectral range of 6,500 to 500 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\) and 4 mm IR-beam.\(^{[20]}\) Transmission and emission (radiance) spectra were collected with a MCT detector. The zero position above the burner was set, when half of the signal was blocked by the burner nozzle. Path correction spectra for the emission measurements were taken with a black body cavity in place of the burner nozzle. The background spectrum for transmission was taken with oxygen (dispersion, flamelet and sheath) flowing but without the presence of CH\(_4\) and spray droplets. The spray flames were measured by 512 scans for one transmission and emission spectra, respectively, which were radiance-corrected.\(^{[20]}\) Average flame temperatures were estimated using the emission/transmission and the normalized radiance procedures for hot CO\(_2\).\(^{[19]}\) The temperatures shown here were averages from both procedures representing the average flame temperature in the line of sight through the center of the flame.\(^{[20]}\) For validation of the spray flame temperatures, measurements at some heights were carried out three times.

HRTEM images and electron diffraction X-ray (EDX) pattern were taken with a CM30ST microscope (Philips, LaB6 Cathode, 300kV, point resolution 0.2 nm). Particles were disposed onto a carbon foil supported on a copper grid. A high-angle annular dark field (HAADF) detector was used for scanning transmission electron microscopy (STEM). Specific surface areas (SSA, m\(^2\)/g) of the materials were determined from the adsorption of nitrogen at 77 K using the BET method (Micromeritics Tristar 3000, 5-point isotherm, 0.05 < p/p\(_0\) < 0.25). A Bruker D 8 Advance diffractometer was used for X-ray diffraction (XRD, Cu-K\(\alpha\) radiation, step size 0.03°, scan speed 0.60° min\(^{-1}\)) measurements. For determination of the anatase and rutile crystal size, XRD pattern were fitted by TOPAS 2 (Bruker AXS) with the Rietveld method (anatase: ICSD 63711, rutile: ICSD 39167) from 2 theta = 21° - 31° covering the most intensive signals of both crystal structures using a linear background.\(^{[5]}\)
Platinum dispersion was determined by CO-pulse chemisorption (Micromeritics Autochem II 2920). Prior to each measurement the samples were reduced in H₂ (20 ml/min) at 300°C for 0.5 h and then flushed with He (20 ml/min) at 300°C for 1.5 h. Carbon monoxide (10% in He, 0.5 ml) was pulsed into a He flow (50 ml/min) at 45°C while its concentration was monitored by a TCD detector. For calculating the Pt-dispersion an adsorption stoichiometry of Pt/CO = 1 was assumed. The amount of residual carbon in the powder was determined (Micromeritics Autochem II 2920) by heating the particles in O₂ (20 ml min⁻¹, Pan Gas, 99.999%) up to 900°C with 10°C min⁻¹ and monitoring the evolving CO₂ and CO with a mass spectrometer (ThermoStar, Pfeiffer Vacuum). The mass spectrometer signal arising from CO was hardly above the noise level, so that only the signal corresponding to CO₂ was taken account for determination of the carbon content. Subsequent to each experiment a pulse of 1.56*10⁻⁵ mole CO₂ (Pan Gas, 99.9%) was measured for calibration.

Results and Discussion

Spray Flame Characterization

Nanostructured Pt/TiO₂ particles containing 0 – 10 wt.% Pt were produced by combustion of the appropriate precursor solutions without the quench ring (unquenched flame) and with it injecting 40 l/min (unless otherwise stated) at various burner-quench-ring distances (BQD, quenched flame). Figure A2 shows the axial temperature profiles of the pure TiO₂ producing unquenched (squares) and quenched spray flame at BQD = 6 cm (circles). The temperature profile of the flamelets (triangles) that ignite and sustain spray combustion (without the ignited spray) is also shown in Figure A2. The maximum flamelet temperature was 2000°C close to the burner but dropped drastically above 0.6 cm to approximately 500°C at 4 cm by mixing with the surrounding gas. In contrast,
the maximum spray flame temperature was 2300°C up to a height of 5 cm. Droplets containing solvent and

![Graph showing temperature profiles of flame spray](image)

**Figure A2.** Temperature profiles of the flame spray at standard conditions (squares), with quench ring installed at 6 cm (circles, 40 l/min), and without precursor feed (triangles). The quenched flame showed a constant temperature region of 2000°C upstream of the quench ring, whereas downstream, the temperature was about 800 – 1000°C lower than for the unquenched flame.

precursor continuously evaporate and supply the fuel for combustion resulting in a rather constant temperature up to about 5 cm (Figure A2, squares). This evaporation region is observed also in classic fuel spray combustion. It is attributed to fuel mass transfer limitation that slows the combustion and prolongs the high temperature region. The distinctive constant temperature region can be shortened, for example, by increasing the oxidant flow. This dilutes the fuel accelerating mass transfer and results in earlier maximum flame temperatures and faster cooling rates. After droplet evaporation and fuel (solvent) combustion, the flame temperature decreases similar to gas-fed flames.
The applied line-of-sight FTIR analysis averages the CO$_2$ temperatures throughout the spray flame. In contrast, spatially resolved flame temperature profiles can be obtained by tomographic reconstruction of radial resolved line-of-sight FTIR measurements, as demonstrated for a premixed gas-fed flame reactor. It was shown that FTIR analysis gives slightly lower temperatures than the ones obtained by coherent anti-Stokes Raman scattering at the centerline of the flame. In the case of the presented spray flame the maximum flame width of approximately 3 cm was too small for tomographic reconstruction with a 4 mm IR beam. It should be noted that radial temperatures in spray flames can differ up to 800°C. Steep temperature gradients are especially observed at low heights above the burner, where the centerline temperature is lowered because of evaporating droplets, resulting in the highest temperatures slightly off center.

Quenching the flame at BQD = 6 cm (Figure A2, circles) lowered the flame temperature by 300°C upstream of the quench ring (2 – 4 cm) and by 800 – 1000°C downstream. The high momentum of the cooling jets, which flow in a distinct, upwards-swirling pattern, entrain cold gas into the flame upstream (below) of the ring as it has been seen also with vapor-fed flames quenched by a critical flow nozzle which also resulted in a temperature reduction upstream of the quenching device. Originally, the radial quench cooling method was developed for a flame synthesis unit with evaporated metal precursor fed as a gas jet to a flat premixed flame. In that system no differences in temperature profile (with/without quench cooling) was observed below the quenching level as this particular flame setup had been operated with a quartz chimney surrounding in the flame reaction zone and no external air could be withdrawn into the flame zone.

After the injection of quench gas (BQD = 6 cm), the flame temperature was 1000°C at 6.5 cm resulting in a cooling rate of 310 K/cm. Without quenching, the flame temperature drops at 1000°C much further downstream at approximately 12 cm above the burner, with a cooling rate of 170 K/cm. Thus using the
quench ring decreases substantially the high temperature residence time of the particle.

**TiO₂ Particle Characterization**

Figure A3 shows the influence of the BQD on the specific surface area (SSA) of both pure (squares) and 5 wt.% Pt-containing TiO₂ (circles). Figure A3 also shows TEM image of pure, solid TiO₂ particles size made without (left) and with the quench ring at 6 cm BQD (right). The particles have a homogeneous morphology and rather spherical shape for both conditions.[⁵] The highly crystalline structure of the TiO₂ particles was corroborated by the intense electron diffraction pattern (Figure A3 TEM insets). Only few necks from sintering could be observed, indicating mostly non-agglomerate particles. Quenching the flame at 6 cm had no significant influence on the morphology, crystallinity and size of the TiO₂ particles. All powders exhibited high SSAs, above 76 m²/g. Quenching at 8 cm or larger BQDs did not affect the SSA significantly compared to the un-quenched flame (BQD = 4). Lowering the quench ring from 8 to 4 cm increased the SSA as shortened residence times in the hot temperature zone resulted in smaller primary particles. It should be noted that the dependence of the SSA as a function of BQD is dramatically different than that of vapor-fed flames quenched by a critical flow nozzle. For small BQDs below 4 cm the SSA of pure TiO₂ decreased from a maximum of 138 m²/g to 120 m²/g. Quenching may have extinguished the spray flame prematurely. In fact, as Figure A2 shows at lower positions than BQD = 4 cm the temperature is rather constant by continuous droplet evaporation and combustion till BQD = 6 cm. It is quite likely that at BQD < 5 cm precursor was not fully consumed in the flame and TTIP oxidation may have taken place further downstream resulting in some very small particles.[²⁵]
Results and Discussion

Figure A3. Influence of the BQD (40 l/min) on the SSA of pure (squares) and 5 wt.% Pt/TiO₂ (circles). The specific surface area increased for small BQDs, reached a maximum at 4 cm and decreased for larger distances. BQDs above 8 cm led to a comparable SSA with respect to the unquenched flame (∞). The addition of platinum has not significantly altered the SSA of the powder made at any BQD.

Figure A4 compares the crystal size of anatase and rutile with the average BET-equivalent diameter for flames producing 5 wt.% Pt/TiO₂ and quenched at different BQDs. Peak broadening in the XRD pattern (not shown) confirmed the presence of nanoscale anatase and rutile crystallites ranging from 14 – 23 nm and 5.0 – 11.0 nm, respectively. The average BET-equivalent diameter lies in-between the anatase and rutile crystal size indicating predominantly single crystal particles consistent with TEM (Figure A3, inset). Large crystallites for BQDs below 4 cm might result from particle growth by surface reaction of TTIP. All powders contained large fractions of anatase as seen for TiO₂ made with gas-fed flames. Despite quenching, the anatase content remained in the range of 80 – 88 wt.% regardless of the BQD distance (not shown). In contrast, gas-fed flame quenched by the critical-flow nozzle resulted in TiO₂ with higher rutile content.
because of the reduced excess of oxygen in the nozzle. Nozzle-quenching of gas-fed flames resulted in substoichiometric TiO$_{2-x}$ showing a blue color and a fraction of rutile up to 85 wt.%. In contrast cooling with the quenching ring here provided enough oxygen and sufficient high temperatures for the full oxidation of the titanium, so that - except for the lowest BQD - all powders appeared white without change of the crystalline composition. Only for BQD = 2 cm the powder appeared to be slightly yellow, indicating soot or Ti-suboxides from incomplete combustion of organic matter as analyzed by temperature programmed reduction. While the material made at BQD = 2 cm contained 2.5 wt.% carbon the unquenched powder had 0.6 wt.% carbon content.

Quenching the spray flame downstream of 8 cm had little influence on the TiO$_2$ particle morphology (Figure A3), SSA (Figure A3) and crystallinity (Figure A4). Consequently, the primary particle growth of TiO$_2$ must have terminated upstream and therefore quenching above that height had little influence on the TiO$_2$ particles. Quenching the gas-fed flames at increasing burner-nozzle distances resulted in a continuous decrease of the SSA because of the increased residence time in the high temperature zone (> 1600°C). Spray-made TiO$_2$ particles have shorter residence times at high temperature resulting in much higher SSA at comparable production rates.

Adding Pt to TiO$_2$ did not affect the SSA of particles made at any BQD in the quenched and in the unquenched flame (Figure A4). The support SSA was independent from the noble metal content also for flame-made Au/TiO$_2$, Au/SiO$_2$, Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$. 
Figure A4. The TiO$_2$ anatase (squares), rutile (circles) and BET average diameter (triangles) for 5 wt.% Pt/TiO$_2$ as a function of the employed burner quench-ring distance (BQD). Quenching the flame below BQD = 3.5 cm resulted in larger crystals that may have formed by condensation of unreacted TiO$_2$ precursor and subsequent surface growth.

Pt Cluster Characterization

Figure A5 shows STEM images of 5 wt.% Pt/TiO$_2$ made without quenching at a) high and b) low magnification as well as quenched at BQD of c) 2 cm and d) 8 cm. Quenching the flame at 2 cm resulted in an inhomogeneous bimodally-sized Pt-cluster a few larger than 50 nm and many below 10 nm (Figure A5c). STEM images for powders made with BQD = 4 cm exhibited also a bimodal Pt-cluster size distribution (not shown). The maximum found Pt-cluster size was 50 nm compared to 200 nm for particles obtained with BQD = 2 cm. Quenching at BQDs $\geq$ 8 cm led to a homogeneous Pt-cluster morphology (Figure A5d) similar to the unquenched flame (Figure A5a), both of a few nanometers in diameter and below the XRD detection limit even for Pt-contents up to 10 wt.%.

Energy dispersive X-ray analysis (EDX, not shown) of all powders showed the
presence of Pt beside the visible Pt-clusters (white regions). Even though the flame temperature was below the Pt-boiling point\textsuperscript{[26]} and Pt-pressure was super-saturated, the homogeneous particle size distribution and the absence of large particles confirmed the gas-to-particle production route for platinum at large BQDs (Figure A5a, b and d). Agglomerated noble metal particles were not found in the images (Figure A5b).

The inhomogeneous particle size distribution of Figure A5c may result from droplets that were not fully evaporated and combusted by quenching the spray flame at this low height above the burner. The temperature after quenching might not be sufficiently high for complete droplet evaporation of the Pt-precursor, which causes a part of the Pt to remain in the evaporating droplet. Therefore, the last part of platinum material is converted to large particles by what in principle is spray drying and thermal decomposition. Bimodal particle size distributions have been observed for flames with low enthalpy content\textsuperscript{[18]} and precursors of low thermal stability.\textsuperscript{[27]} Spraying pure noble metals from aqueous solutions resulted in bimodal particle size distributions because of the insufficient evaporation energy and temperature.\textsuperscript{[28]} Characteristic sintering times of airborne Pt-clusters at these temperatures indicate that the time in the temperature region is adequate for full coalescence.\textsuperscript{[29]} Typical Sauter mean droplet sizes of an equivalent spray nozzle to the one used in this study are about 10 $\mu$m for ethanol as solvent.\textsuperscript{[17]} Nevertheless a detailed calculation of droplet-particle dynamics is needed to resolve this as it has been done for pure ZrO\textsubscript{2} synthesis by flame spray pyrolysis.\textsuperscript{[30]} A 10 $\mu$m solution droplet of 1.45*10\textsuperscript{-2} mol/l Pt-concentration without any Pt-evaporation would result in a dense 500 nm Pt-cluster. For simultaneous solvent-precursor evaporation, theoretically a 650 nm droplet would result in the largest Pt-cluster observed in the STEM images (BQD = 2 cm, 5c) which are approximately 200 nm. This and the decreasing maximum Pt-cluster size corroborates that the droplets, from which the large Pt-
Results and Discussion

Cluster come from, had partially evaporated supporting the observed bimodal Pt-cluster size distribution.

Figure A5. Pt/TiO₂ particles made without quenching (a and b) and quenched at BQD = 2 cm (c) and 8 cm (d). The Pt-clusters show bright spots on these STEM images. All images except for b) are at the magnification of image a). Quenching at 2 cm led to a bimodal Pt-cluster morphology with particle sizes of a few nm and above 20 nm (c). Not quenching (a) or quenching the flame at 8 cm (d) or higher resulted in Pt-clusters of homogeneous morphology. The STEM images b) – d) corroborate a Pt-cluster size of a few nanometers.

Figure A6 shows that the BQD can affect considerably the Pt-dispersion for 5 wt.% Pt/TiO₂ ranging from 40 to over 60 % (filled squares). Figure A6 shows
also the average Pt-cluster diameter (open symbols) obtained from the Pt-dispersion data for 2.5 wt.% (circles) and 5 wt.% (squares). The Pt-dispersion exhibited a maximum of about 63% at 8 cm BQD. At 12 cm BQD the Pt-dispersion was equivalent to that of the unquenched flame (BQD = 4), indicating that Pt-cluster growth has stopped at about 12 cm BQD (1000°C unquenched flame). A low Pt-dispersion resulted from the bimodal Pt-cluster size distribution at small BQDs. Large Pt-cluster (e.g., 50 nm, Figure A5c) contain a considerable fraction of Pt that was not accessible for CO-chemisorption, thereby decreasing the overall Pt-dispersion. With increasing quenching height, precursor droplets fully evaporate, releasing platinum in the gas-phase. Increasing the BQD above 8 cm led to a decrease of the Pt-dispersion. This can be attributed to a slower cooling of Pt-vapor and lower supersaturation that favors nucleation of fewer and larger particles on the surface of the TiO₂ by either gas-to-particle conversion or by surface diffusion and rearrangement.

Therefore, quenching at 8 cm led to the smallest Pt-clusters of 1.8 nm in diameter. Precursor droplets have evaporated fully at this height (Figure A1) and homogeneous or heterogeneous nucleation was enhanced by the high cooling rate of the quench ring that resulted in higher supersaturation. In contrast to the XRD and the STEM analysis, for which the Pt-clusters were too small for quantitative evaluation, the CO-chemisorption results confirm the influence of the quenching on the average Pt-cluster size. A minimum of Pt-cluster size at BQD = 8 cm was found also when Pt/TiO₂ was made with 2.5 wt.% Pt-content (Figure A6, circles). For smaller BQDs the average Pt-cluster size is independent of Pt content, resulting in similar particle sizes for 2.5 wt.% and 5 wt.% Pt-content. This indicates that the temperature history of the aerosol determines its size characteristics rather than the Pt-content suggesting heterogeneous Pt-cluster formation on TiO₂.
Results and Discussion

Figure A6. Pt-dispersion (filled squares) and Pt-clusters size (open symbols) as a function of burner quench ring distance (BQD) for Pt/TiO\textsubscript{2} content 2.5 wt.% (circles) and 5 wt.% Pt (squares) made by flame spray pyrolysis of precursor sprays. Quenching at 8 cm led to the highest Pt-dispersion and therefore the smallest average Pt-diameter. The average Pt-cluster diameter was inferred from the Pt-dispersion.

Figure A7 shows that increasing the quench gas flow rate decreases the average Pt-cluster size at BQD = 8 cm. The higher the quench gas flow rate, the higher was the cooling rate leading to a higher supersaturation of platinum in the flame and to a decrease of its surface mobility on the TiO\textsubscript{2} support. This effect, however, is limited up to about 30 l/min and flow rates above 30 l/min did not further reduce the Pt-diameter. As expected from Figure A3 and Figure A4 the TiO\textsubscript{2} characteristics are not affected by increasing the quench gas flow rate 0 – 50 l/min at this BQD. The Pt-cluster size can be controlled from 1.8 to 3.0 nm by the quench gas flow at this BQD independently of that of the TiO\textsubscript{2} support. This was achieved by the judicious placement of the quench ring at a BQD where the formation of the substrate TiO\textsubscript{2} had been completed.
Figure A7. The Pt-cluster size as a function of the quench gas flow rate for synthesis of 5 wt.% Pt/TiO$_2$ in a spray flame quenched at a burner quenching distance of 8 cm. Increasing the quench gas flow rate up to 30 l/min led to a decrease of the average Pt-diameter. The higher the quench gas flow rate, the higher was the cooling rate leading to a higher supersaturation of platinum in the flame and to a possible decrease of its surface mobility on the TiO$_2$ support.

Figure A8 compares the increase in Pt diameter with increasing Pt-content (1 – 10 wt.%) for the unquenched (squares) and quenched spray flame (40 l/min O$_2$, BQD = 8 cm, circles). For the unquenched flame, the Pt-cluster size increased from 1.7 to 3.3 nm for 1 to 10 wt.% Pt. For the quenched flame, the Pt-cluster size increased from 1.7 to 2.3 nm over the same increase in Pt-content. For the latter flame, the Pt-sizes were drastically reduced for all contents larger than 1 wt.% resulting in excellent Pt-dispersion at these high Pt-contents. The increase in the noble metal particle size with its precursor concentration is consistent for many flame-made noble metal/ceramic composites.$^{[3,5,6,31]}$ At the same time, note that the SSA of TiO$_2$ made in both flames was rather constant (90 – 100 m$^2$/g; Figure A3). For 1 wt.% Pt-content, 66 % (1.7 nm) of the total Pt are available for chemisorption regardless of quench gas as probably the Pt-clusters
are too small and near their critical size. For comparison, full accessibility is achieved theoretically for approximately 1.1 nm Pt-clusters when every Pt-atom is on the surface, assuming no blocking by the contact with the TiO$_2$ surface.

*Platinum Cluster Formation*

TiO$_2$ particles and Pt clusters stop growing in different regions of the flame as observed for Au/TiO$_2$ composite.$^{[5]}$ Titania particles are formed probably first, then platinum forms on these particles. In addition, the encapsulation of Pt-clusters in the TiO$_2$ matrix is very unlikely for such a high dispersion that can be qualitatively confirmed by STEM analysis. The reason for obtaining such a high Pt-dispersion for high Pt-contents includes different physical mechanisms. Pt-clusters might be nested at steps and kinks on the highly stepped surface of the TiO$_2$ particles that offer many of these preferred nucleation sites. Platinum was supersaturated in the flame and Pt-clusters were formed by homo- or heterogeneous nucleation upon cooling. Partial oxidation of the platinum resulting in the formation of PtO might additionally reduce the mobility on the TiO$_2$ surface.$^{[32]}$ The average Pt-clusters size made by both unquenched and quenched (Figure A8; BQD = 8 cm) flames was slightly above the average particle size, $d_{\text{Pt}} = 1.7$ nm (at 20% of Pt-monolayer), that has been observed for Pt-clusters made in ultra high vacuum (UHV) on anatase.$^{[33]}$ The 1 – 10 wt.% Pt-content corresponded to 2 – 20% of a Pt-monolayer on top of TiO$_2$. For these monolayer fractions, an almost linear increase of the average noble metal particle diameter on TiO$_2$ surfaces has been observed in UHV,$^{[34]}$ similar to Figure A8. Platinum and TiO$_2$ exhibit strong metal-support interaction (SMSI) that influences CO-adsorption.$^{[35]}$ The consistency of the two methods, STEM images and CO-chemisorption, for the Pt-cluster diameter determination indicated that the SMSI effect, that decreases the chemisorption of CO, may not be that significant.
Figure A8. Increasing the Pt-content resulted in an increase of the average Pt-cluster diameter for the quenched (40 l/min) and the unquenched flame. The average Pt-cluster size increased with the Pt-content under both conditions. Producing Pt-cluster at unquenched conditions resulted in larger Pt-cluster than for quenched flame or Pt-contents higher than 1 wt.%.

Changing the production conditions such as dispersion gas flow, liquid flow or concentration will alter not only the noble metal particle size but also the support properties such as particle size\cite{3} and thermal stability.\cite{36} For noble metals forming oxides on the ceramic support in the flame, the quench ring can lead to enhanced noble metal dispersion. Therefore, an independent particle size control of ceramic support and noble metal particles is possible by efficient quench cooling of the flame spray process without other changes in production conditions that can give undesired change on the support particle crystallinity of specific surface area.
Conclusions

A simple and easy-to-operate radial quench cooling method has been successfully applied in one-step flame spray synthesis of Pt/TiO$_2$ particles. This results in closely and independently controlled Pt-dispersion without changing the TiO$_2$ substrate properties. The particle size of the supporting ceramic (TiO$_2$) can be controlled by the standard flame spray pyrolysis parameters such as precursor, composition and concentration, liquid feed rate, oxidant dispersion gas flow rate, while the particle size of the expensive noble metal (Pt) can be controlled by rapid quenching at various heights and cooling rates. Inhomogeneously sized noble metal particles were obtained when the residence time upstream of the quenching level was insufficient for complete droplet evaporation. This resulted in a change of the particle formation mechanism from one droplet-to-gas-to-particles to that of one droplet-to-one particle. However, quenching the flame after droplet evaporation resulted in well-dispersed Pt-clusters on the TiO$_2$ surface.

For high Pt-contents (10 wt.%) the average Pt-clusters size was significantly reduced by 30%, i.e. from 3.3 nm to 2.3 nm by quenching. In contrast, the TiO$_2$ support properties such as SSA, morphology and crystal structure were not significantly influenced by quenching at this position in the flame zone. It has been shown that radial quenching at various axial positions gives direct control of the noble metal size independently of the properties of the ceramic support. This enables the production of tailor-made noble metal particle sizes at any noble metal content coupled with thermally stable, nano-sized ceramic supports suitable for applications such as catalysts or sensors. A maximum Pt-dispersion was obtained by quenching at the position of complete droplet evaporation. This dispersion corresponds to Pt-cluster sizes that are usually obtained by costly and complex ultra-high vacuum processes. As a conclusion, the combination of radial quench cooling and flame spray synthesis is an efficient and simple method
of producing complex materials of desired properties, which normally require numerous process steps by using conventional synthesis methods such as ultra high vacuum processes, impregnation or precipitation. This has direct implication on catalyst and sensor manufacture and performance.

References


Abstract

Gap formation because of shrinkage during polymerization is a major issue of composite fillings resulting in bacteria penetration and secondary caries formation. Antibacterial properties of dental adhesives can be obtained by adding Ag⁺-releasing nanoparticles to the polymer matrix. Nanoparticles containing 83 wt.% Ta₂O₅/SiO₂ and 0 – 100 wt.% Ag were produced by flame spray pyrolysis. Crystal size, structure, particle size and silver morphology were analyzed by XRD, BET and UV/Vis-spectroscopy. The accessibility of Ag was determined by the decomposition of methylene blue under UV-radiation. Nanoparticles contain non-crystalline Ag for contents below 10 wt.% and crystalline above 50 wt.%.

Powders containing up to 5 wt.% Ag are white. Ag is accessible on the particle surface. The obtained nanoparticles are potentially attractive for combining radiopaque and antibacterial properties in dental applications.
Introduction

Dental polymer-ceramic composite filling materials often replace classical restorations like amalgam especially in the anterior mouth region mainly because of their better aesthetics. Unfortunately, composite fillings shrink during polymerization and form gaps between the adhesive and the tooth which is the major reason for the replacement of composite fillings. Shrinkage can be reduced by the addition of particles to the polymer matrix which also increases the radiopacity of the composite filling when the particulate matter contains high proton number elements such as Ba,[1] Ta,[2] or Yb.[3] Additionally, the mechanical properties and durability of these composite can be increased. By adjusting the refractive index of the particles in mixed oxides, the transparency of the composite can be tailored. In addition to mechanical and optical properties biofunctions such as antibacterial properties can be incorporated into the composites which reduce the likelihood of secondary caries formation. In contrast to glass-ionomers and amalgam which can release metal ions and fluorides, respectively, composite fillings do not exhibit antibacterial properties.[4] Antibacterial effects can be achieved by releasing metal ions from the composite, immobilizing or mixing organic agents into the polymer matrix or a low pH of the composite itself. Whereas agents mixed into the matrix[4] and monomer mixtures with a low pH[5] leach out fast, these materials only have short-term antibacterial properties. Immobilized agents have long-lasting effect but need direct contact with the bacteria.[4] Therefore, composites that continuously leach out small amounts of metal ions can have the advantage of a long-lasting antibacterial effect that is not confined to the adhesive surface.[6, 7]

In the present work nanoparticles of 83 wt.% Ta₂O₅/SiO₂ with a varying amount of Ag were produced by flame spray pyrolysis and analyzed with respect to their size and morphology. The Accessibility of Ag was investigated by the degradation of methylene blue under UV-radiation.
Experimental

Flame-Synthesis of Ag-Containing Ta$_2$O$_5$/SiO$_2$

Tantalum butoxide (Aldrich, > 98%) tetraethoxysilane (TEOS, Fluka, > 98 %)[2] and silver acetate (Fluka, > 99%)[8, 9] were used as tantalum, silicon and silver precursors, respectively. Appropriate precursor amounts were mixed with hexane (Fluka, > 99.5 %) under nitrogen. The total (Ta, Si & Ag) metal concentration was kept constant at 0.5 M in these solutions. The weight ratio of Ta$_2$O$_5$ and SiO$_2$ was kept constant at 83:17. The Ag weight fraction in the product powder ranged from 0 – 100 wt.%. Particles[2] were produced in a laboratory scale flame spray pyrolysis (FSP) reactor as described elsewhere.[10]

Particle Characterization

The specific surface area (SSA, m$^2$/g) of the FSP-made particles was determined by N$_2$ adsorption at 77 K while using the BET method (Micromeritics Tristar 3000, 5-point isotherm, 0.05 < p/p$_0$ < 0.25). For spherical, monodisperse primary particles with homogeneous density, the average BET-equivalent particle diameter (d$_{\text{BET}}$) was calculated with the mass fractions of Ta$_2$O$_5$ and SiO$_2$ and the density of pure Ta$_2$O$_5$ (8.2 g/cm$^3$), SiO$_2$ (2.2 g/cm$^3$) or Ag (10.5 g/cm$^3$). XRD measurements were performed using a Bruker D 8 Advance diffractometer with 2\(\theta\) from 10$^\circ$ to 70$^\circ$ (step size 0.03$^\circ$, scan speed 0.60$^\circ$min$^{-1}$, Cu-K\(\alpha\) radiation). Crystal sizes of Ta$_2$O$_5$ and Ag were determined with Topas 2.0

Optical absorption spectra were measured with a UV-VIS NIR spectrophotometer (Varian Cary 300, range: 900 – 190 nm, scan speed: 300 nm/min, resolution 0.5 nm) with 1 wt.‰ (0 – 10 wt.% Ag) and 0.01‰ (50 and 100 wt.% Ag) particles in distilled water.

Ag-Accessibility

The accessibility of Ag on the particle surface was measured with respect to the degradation of methylene blue (MB).[9] Particles (24 mg) were dispersed in
80 mL of 10 ppm aqueous solution. The 100 mL beaker containing the suspension was placed on a magnetic stirrer to ensure full suspension throughout the experiment. The decomposition of MB was conducted under UV-light (single 8 W UV tube, Benda, at 366 nm) and at room temperature. The UV tube was positioned horizontally 1 cm above the top of the beaker, respectively 2.5 cm above the liquid surface. Each experiment was conducted for 1 h. Every 10 min, 3 ml of the solution were taken to monitor the degradation of MB by measuring its intensity in the UV/Vis-spectrophotometer (at 665 nm) in a liquid cuvette configuration with distilled water as reference.

Results and Discussion

Particle Crystallinity and Size

Figure B1 shows XRD patterns of 83 wt.% Ta$_2$O$_5$/SiO$_2$ with Ag-contents ranging from 0 – 100 wt.%. Pure 83 wt.% Ta$_2$O$_5$/SiO$_2$ exhibited as well an amorphous structure, represented by two broad humps (20 – 42° and 42 – 70°) as crystalline hexagonal Ta$_2$O$_5$(horizontal rhombus).\(^{[11]}\) The weight fraction of crystalline Ta$_2$O$_5$ decreased significantly for Ag-contents up to 10 wt.%, resulting in more amorphous structures. No crystalline Ag could be detected (detection limit: 3 nm). For 50 wt.% Ag, no crystalline Ta$_2$O$_5$ was detected, but crystalline, cubic Ag was present (vertical rhombus).\(^{[12]}\) The spraying of 100 wt.% Ag resulted in pure cubic Ag crystals.
Results and Discussion

Figure B1. Pure Ta$_2$O$_5$/SiO$_2$ (0 wt.% Ag) exhibits hexagonal Ta$_2$O$_5$/SiO$_2$ and amorphous SiO$_2$. With increasing Ag-content the crystalline Ta$_2$O$_5$ content decreased. At Ag-contents of more than 50 wt.%, metallic cubic Ag crystals were present in the patterns.

The increase of the Ag-content from 0 – 10 wt.% resulted in a slight increase of the SSA from 80$^{2}$ to 95 m$^2$/g (Figure B2), which corresponds to a decrease of the $d_{\text{BET}}$ from 11 to 9 nm. For more than 10 wt.% Ag-content, the SSA dropped significantly, which resulted in larger particles possibly originating from the lower sinter temperature of Ag in comparison to the Ta$_2$O$_5$/SiO$_2$. Crystal diameters of Ta$_2$O$_5$ (0 – 10 wt.% Ag, $d_{\text{XRD},Ta_2O_5}$) are slightly larger than $d_{\text{BET}}$, indicating single crystal particles that might have some surface roughness. Even though the content of crystalline Ta$_2$O$_5$ decreased significantly (Figure B1), crystal sizes decreased only slightly from 14 to 13 nm. For more than 10 wt.% Ag-content, Ag crystal sizes ($d_{\text{XRD},Ag}$) match the $d_{\text{BET}}$ increase.
Figure B2. The specific surface area slightly increased up to 10 wt.% Ag and dropped above 10 wt.% Ag. Crystal diameters of Ta₂O₅/SiO₂ are slightly larger than \( d_{\text{BET}} \) (0 – 10 wt.% Ag) and good agreement is obtained for Ag-contents above 50 wt.%.

Light Absorption

The Change of the Ag content resulted in a change of powder coloration (Figure B3). Here, 1 wt.% particles were dispersed in water. Up to 5 wt.% Ag-content, particles were white. An Ag-content of 10 wt.% resulted in a slightly orange/red coloration of the powder. When 50 wt.% Ag or more were added, the dispersion had an opaque black appearance. \(^9\)
Results and Discussion

Figure B3. Particles (1 wt.%o) dispersed in H₂O. Coloration shifted from white (≤ 5 wt.% Ag) over red/orange (10 wt.%) to black (≥ 50 wt.%)

Transmission spectra of dispersion that contain 1 wt.% particles (0 – 10 wt.% Ag) were normalized (horizontal dashed line, Figure B4). The addition of 0.1 wt.% Ag did not change the transmission spectrum in comparison to pure 83 wt.% Ta₂O₅/SiO₂. Particles containing 5 wt.% Ag resulted in a slightly higher transparency over the whole spectrum. When adding 10 wt.% Ag, a broad absorption band with low intensity (370 – 530 nm) was identified as for the 50 wt.% Ag-containing sample (0.01 wt.% shifted), indicating the formation of Ag-clusters.[9] Since the clusters were not visible in the XRD pattern, cluster size must be below the detection limit of the XRD. Pure Ag-particles (shifted) exhibited a slightly shifted absorption band (340 – 440 nm) towards smaller wavelengths in comparison to 50 wt.% containing Ag. This might have resulted from the influence of the 83 wt.% Ta₂O₅/SiO₂ on the Ag-electron configuration.
Appendix B: Ag-Containing Ta₂O₅/SiO₂

Figure B4. Up to 5 wt.% Ag-content the spectrum did not change significantly. At 10 wt.% Ag-content the onset of a metal Ag-absorption band is visible. Above 10 wt.% Ag-content metallic Ag-absorption bands are clearly visible (380 – 550 nm).

Ag-Accessibility on the Particle Surface

The degradation of MB was determined by the absorption intensity at 665 nm.⁹ Pure MB without particles and with pure 83 wt.% Ta₂O₅/SiO₂ did not show any decrease of MB concentration under UV-radiation (Figure B5). In contrast to that, MB degrades when Ag is present and this indicates some Ag accessible on the particle surface facilitating the leaching of Ag⁺-ions. Quantitative statements regarding the Ag-amount on the particle surface cannot be made with respect to Ag that is distributed in the 83 wt.% Ta₂O₅/SiO₂ matrix.
Conclusions

Nano-sized 83 wt.% Ta₂O₅/SiO₂ particles have been synthesized with Ag-contents ranging from 0 – 100 wt.% by a single production step. Up to 5 wt.% Ag-content particles had a white coloration, which can be attributed to the absence of Ag-clusters in and on the particles. Some silver is accessible, so that these particles (e.g. 5 wt.% Ag / 83 wt.% Ta₂O₅/SiO₂) combine radiopacity, whiteness and antibacterial properties which makes them attractive for dental adhesives.

References


Modifier configurations of modifier on the particle surface have been characterized by $^{29}\text{Si}$ NMR spectroscopy. The 35 wt.% Ta$_2$O$_5$/SiO$_2$ exhibited significantly more modifier (cC$_6$/MPS) without the catalyst (PA) in the modification suspension (Figure C1) than with the catalyst (cC$_6$/PA/MPS). In contrast to FTIR spectroscopy (Figure 3.4), when the orientation of the modifier could be determined, NMR spectroscopy showed that the $T^2$ / $T^3$ ratio was slightly higher for cC$_6$/MPS modification conditions than for cC$_6$/PA/MPS. This indicated that a stronger increase of RSi(OSi)$_2$(OCH$_3$) types in comparison to RSi(OSi)$_3$ types when more MPS is present on the surface.
Figure C1. $^{29}$Si-NMR spectra of surface functionalized particles exhibited significant differences of the surface modifier for varying functionalization conditions.

Figure C2 shows the $^{13}$C NMR spectra of pure SiO$_2$ (bottom), Ta$_2$O$_5$ (top) and 35 wt.% Ta$_2$O$_5$/SiO$_2$ for the same modification conditions used in Chapter 3. Pure SiO$_2$ that has just been dispersed in cC$_6$/PA exhibited a strong peak at $\delta = 42$ ppm indicating the adsorption of PA on the surface (pure cC$_6$ did not show any peaks). When SiO$_2$ was modified with cC$_6$/PA/MPS, this peak disappeared due to the replacement of PA by MPS on the particle surface. In contrast to this 35 wt.% Ta$_2$O$_5$/SiO$_2$ and pure Ta$_2$O$_5$ exhibited this PA assigned peak for cC$_6$/PA/MPS conditions, which is not present for cC$_6$/MPS treated particles and can be attributed to the stronger adsorption of PA on the acidic 35 wt.% Ta$_2$O$_5$/SiO$_2$ and Ta$_2$O$_5$ surfaces (Figure 3.1).
Figure C2. $^{13}$C-NMR spectra of pure SiO$_2$ (bottom), 35 wt.% Ta$_2$O$_5$/SiO$_2$ (middle) and pure Ta$_2$O$_5$ (top) exhibited the influence of surface functionalization conditions on the C-moieties present on the particle surface.

Washing cC$_6$/PA/MPS treated particles in a H$_2$O/methanol solution (1:1) for 24 h at room temperature did not significantly decrease the intensity of the PA peak ($\delta = 42$ ppm). The intensity of this peak increased whereas the methoxy peak ($\delta = 53$ ppm) decreased with increasing Ta-content in the particles as observed for the freshly surface functionalized particles (Figure 3.9). That PA remained on the particle surface even after washing proved the strong bond between the catalyst and the particles which did not break during MPS surface modification.
Figure C3. $^{13}$C-NMR spectra shown for surface functionalized particles with Ta$_2$O$_5$-contents ranging from 0 – 100 wt.% that have been stored in a H$_2$O/methanol solution (1:1) for 24h. Te increase of the Ta$_2$O$_5$-content resulted in a significant increase of PA present on the particle surface after washing

Polymerization Analysis

FTIR spectra of an unfilled and 20 wt.% particle-containing adhesives (untreated and surface functionalized, cC$_6$/MPS) before and after polymerization are shown in Figure C4. The addition of particles (untreated and surface functionalized) did not result in any significant change of the spectra in comparison to the unfilled material. The absorption band around 1635 cm$^{-1}$ is characteristic for C=C bonds. After polymerization the C=C bond almost disappeared, which indicated a high degree of C=C bond conversion during polymerization. Particles did not lead to a lower conversion of these bonds, which resulted in comparable polymerization energies for the unfilled and particle-containing adhesives (Table C1). Energies for particle-containing adhesives were slightly higher
(135 kJ/kg) than the theoretical ones for the unfilled adhesive (123 kJ/kg), which might originate from experimental errors and insufficient dispersion of the particles. Comparable C=C bond conversion and similar polymerization energies corroborate the comparable shear strength of the composites for all materials (Table 4.2).

**Figure C4.** FTIR spectra of unfilled and 20 wt.% particle-containing (83 wt.% Ta$_2$O$_5$/SiO$_2$) adhesives before and after polymerization. The absorption band at 1635 cm$^{-1}$ relates to C=C bonds present in the sample. The addition of as-prepared (untreated) and surface functionalized (cC$_6$/MPS) particles resulted in comparable conversions of C=C bonds after polymerization like the unfilled adhesive.
Table C1. Energies released during the blue-light induced polymerization of an unfilled dental adhesive and adhesives containing 20 wt.% untreated and surface functionalized (cC₆/MPS) particles (83 wt.% Ta₂O₅/SiO₂). The value in brackets represents the energy released by 80% of the unfilled adhesive, which is equivalent to the monomer mass in the filled materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Polymerization energy [kJ/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>unfilled</td>
<td>153.9 (123.2)³</td>
</tr>
<tr>
<td>untreated</td>
<td>135.1</td>
</tr>
<tr>
<td>cC₆/MPS</td>
<td>135.4</td>
</tr>
</tbody>
</table>

Particle Distribution

Figure C5 (left) shows an overview of the adhesive polymer with its two interfaces to the dentin and the filling. At the top the hard tissue dentin is visible. In the upper middle section the tubuli that have been filled with the adhesive composite can be distinguished. They have a higher durability than the dentin in the sample preparation technique, so that they protrude from the rest of the sample. The lower middle section shows the adhesive composite layer that was formed on the dentin. The filling is shown at the bottom of the image.

The interface of the adhesive composite and the filling is shown in the blow-up (Figure C5, right). The nanoparticles are well dispersed to small agglomerates or even primary particles in the dental adhesive (20 wt.% particles, 83 wt.% Ta₂O₅/SiO₂) as observed for the model composites in Chapter 4 (Figure 4.7). The filling contained micron-sized particles and the particle content was significantly higher than in the adhesive. The interface of the composites is seamless. Nanoparticles are present in the voids between the filler particles close to the adhesive. The non-reacted inhibition layer on top of the adhesive that is present after adhesive polymerization resulted in a mixture of these composites during filling application.
Particle Distribution

Figure C5. Electron microscopy images show dentin/adhesive and adhesive/filling interfaces (left). Whereas the filling (right bottom) contained micron-sized particles, flame-made nanoparticles exhibited high dispersion in the adhesive (right top).

Electron microscopy images of an axial (left) and radial (right) cut of dentin with composites containing 20 wt.% untreated (left) and surface functionalized (cC₆/MPS, right) particles (83 wt.% Ta₂O₅/SiO₂) are shown in Figure C6. The viscosity of the adhesive suspension (Figure 4.1) was sufficiently low so that during adhesive application the composites penetrated into the tubuli of the dentin. Particles are well dispersed regardless of surface functionalization.

Figure C6. Adhesives containing untreated (left) and surface functionalized particles (right) penetrated the tubuli in the dentin during the adhesive application.
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Refereed Articles


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**Presentations**

H. Schulz, B. Schimmöller, S. E. Pratsinis, J. Zimmermann, S. Klapdohr, U. Salz, "From nanoparticles to nanocomposites: Tailoring flame-made Ta$_2$O$_5$/SiO$_2$ and its processing", Oral Presentation at the Partec2007, March 27$^{th}$-29$^{th}$, 2007, Nuremberg, Germany

H. Schulz, S. E. Pratsinis, H. Rüegger, J. Zimmermann, S. Klapdohr, U. Salz, "Surface functionalization of Ta$_2$O$_5$/SiO$_2$ for filler/polymer composites in dental applications", Oral Presentation at the Partec2007, March 27$^{th}$-29$^{th}$, 2007, Nuremberg, Germany

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B. Schimmöller, R. Tschentscher, H. Schulz, S. E. Pratsinis, A. Bareiss, A. Reitzmann, B. Kraushaar-Czarnetzki, "Ceramic foams directly-coated with flame-made $V_2O_5/TiO_2$ for synthesis of phthalic anhydride", Poster Presentation at the Partec2007, March 27th-29th, 2007, Nuremberg, Germany


A. Camenzind, A. Teleki, H. Schulz, N. Theyencheri, G. Beaucage, S. E. Pratsinis, "In-situ SAXS Measurement of $SiO_2$ nanoparticle growth in diffusion flames", Oral Presentation at the Partec2007, March 27th-29th, 2007, Nuremberg, Germany


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