Hard X-ray nanotomography of dental composites for wide color matching

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ABSTRACT

Caries affects billions of individuals worldwide, thus pointing out the importance of advancements in restorative dentistry. Dental resin composites yield restorations with satisfying mechanical properties, therefore the focus of development has shifted to accelerated treatments and esthetic aspects. Challenges in matching tooth color arise due to limited options, application changes, and color variations over time. Single-shade composites with the 'chameleon effect' adapt their color to the surrounding enamel by closely matching the tooth's optical spectrum, enhancing color blending. Structural color, based on light interference, contributes to this effect. The study investigates the submicron filler particles' impact on optical properties and the chameleon effect. Four single-shade dental resin composite materials were investigated. Needle-like samples about 100 μm in diameter were prepared and imaged in a scanning electron microscope. Light transmission through the materials for wavelengths between 200 and 900 nm was measured using a spectrophotometer. Three-dimensional nanotomography data were obtained through transmission X-ray microscopy at the ANATOMIX beamline, Synchrotron SOLEIL, France in both absorption and Zernike phase contrast mode with 23 nm voxel size. The real space information was complemented with small-angle X-ray scattering. These experiments revealed substantial differences in the microscopic structure of the materials. In the case of Omnichroma, the filler consists of almost identical spheres with a diameter of 260 nm while Filtek Universal exhibits polydisperse, irregularly shaped fillers. Additionally, Venus Pearl One's fillers have a polyhedral shape and a wide size distribution. Finally, the setups used did not reveal any clearly identified microstructure of the Chroma Fill composite. Although all investigated materials are known to exhibit the chameleon effect, their differences in micro- and nanostructure call into question previous hypotheses on the chameleon effect's origin from structural color. While we have now a reasonable understanding of filler morphology, size distribution and spatial arrangement, more information is needed on the exact chemical composition of filler and matrix and their interaction with electromagnetic waves, including possible nonlinear effects.

Keywords: Dental restoration, chameleon effect, nanomaterials, structural color, nanotomography, optical transmission, biomimetics, synchrotron radiation, transmission X-ray microscopy.

1. INTRODUCTION

Caries, a well-known disease, affects billions of individuals, usually requiring restorative treatments. Today, the dentists apply resin composites. The polymer matrix is strengthened by ceramic fillers and crosslinked after placement by ultraviolet light. The color matching of crown and enamel is at times improvable, especially because of color changes of the teeth over time [1]. Thus, single-shade composites have been developed. They adapt their color to the surrounding enamel reminiscent of the way chameleons shift color for camouflage, see Fig. 1. Structural coloration based on visible light interference explains the effect [2]. In contrast, the conventional filling materials feature their color from the light absorption of the employed pigments. Using the conventional fillings, the dentist needs a series of dental materials on

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stock to select the suitable one for the specific patient. The correct selection needs time and is prone to failure. Furthermore, although the dentist may choose the correct color, the patient's change of habits, such as smoking or red wine consumption, can give rise to unesthetic color difference between enamel and filling material, which may not be tolerated for front teeth.

Figure 1. The photograph in (a) shows a camouflaged chameleon that can adapt its color to the surroundings. The photograph in (b) displays a crown *ex vivo* treated with a single-shade restorative material - Omnichroma PLT (Tokuyama Dental, Tokyo, Japan). The dental filling cannot be identified.

This tomography study allowed imaging the size, the morphology, and the three-dimensional arrangement of the submicrometer-size filler particles within four commercially available materials for wide color matching. Tokuyama Dental's Omnichroma, Kulzer's Venus Pearl One, and R-dental's Chroma are known as color-matching composites, which should work for any patient. The 3M Oral Care's Filtek Universal offers a reduced shade set. The four commercially available restoration materials were not only investigated by the transmission X-ray microscope of the ANATOMIX beamline at synchrotron SOLEIL, France. In a complementary fashion, electron microscopy, small-angle X-ray scattering (SAXS) and spectrophotometry were included. Electron microscopy enabled us to visualize the surface of filler material fragments with a high depth of focus. The reciprocal-space technique SAXS allowed for the characterization of the nanostructure within a reasonable volume and the extraction of aggregate information from the illuminated volume. Finally, the optical properties, even beyond the visible range, have been studied by a spectrophotometer.

2. MATERIALS AND METHODS

2.1 Sample preparation

Four dental composites for wide color matching were selected and purchased. These filling materials were Omnichroma PLT (Tokuyama Dental, Tokyo, Japan) [3, 4], Filtek Universal (3M, St. Paul, USA) [5], ArtOral Chroma Fill (R-dental, Hamburg, Germany) [6], and Venus Pearl One (Kulzer, Hanau, Germany) [7].

For the nanotomographic measurements, the specimens should have a diameter of 100 µm or even below. For appropriate handling, a length of several millimeters is desirable. Such needle-like samples were fabricated by rolling out the material precursor. Subsequently, these precursor needles were cured applying ultraviolet light of the OptiLux 400 (Demetron Research Corporation, USA). The photographs of Fig. 2 (a) and (b) show these needles glued on the holders for the tomography measurements. The tip of each needle was characterized using an electron microscope [8] (EM-30AXN, Coxem, Daejeon, Korea; acceleration voltage set to 20 kV) with the aim to identify the best suitable tips for the limited beamtime available for the rather expensive synchrotron radiation-based tomography experiments.

Besides the entire needle samples, fragments of them, see optical micrograph of Fig. 2 (c), were glued onto a syringe tip for the tomography study.

For the SAXS measurements, thin plates with a thickness of about 0.5 mm were prepared. The uncured composite was pressed into shape with a flat metal piece. Selected samples are represented by a photograph in Fig. 2 (d).

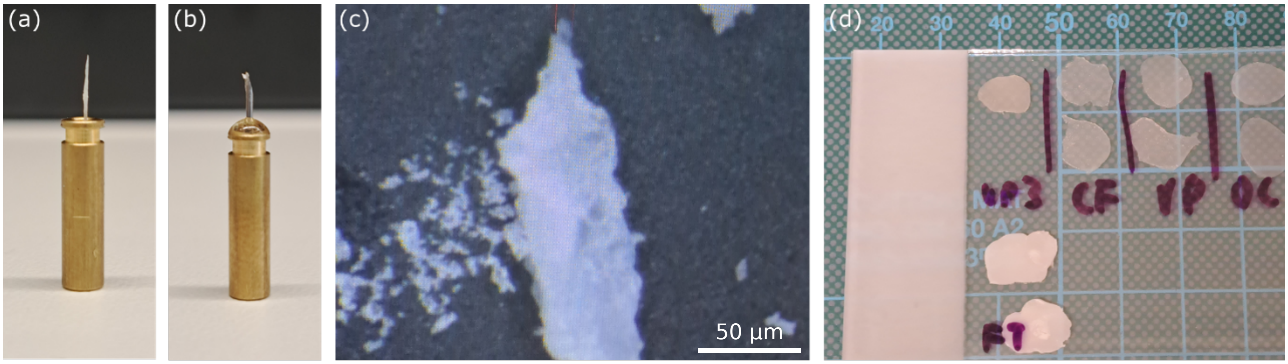


Figure 2. (a) Photograph of a needle-like sample of composite material, mounted on a brass specimen carrier (height 12.5 mm, diameter 3.15 mm, Huber Diffraktionstechnik, Rimsting, Germany) for TXM imaging, (b) photograph showing a piece of debris from breaking such a needle glued onto a metal syringe tip mounted on the specimen carrier, (c) optical micrograph of this piece of debris, and (d) photograph of an array of disk-like samples as used for optical transmittance measurements and X-ray scattering experiments.

2.2 Synchrotron radiation-based transmission X-ray microscopy imaging

Local tomograms of both the needles and the fragments were acquired with the full-field transmission X-ray microscope (TXM) at the ANATOMIX beamline, Synchrotron SOLEIL, Saint Aubin, France [9] using a photon energy of 10 keV. Five hundred projections with two seconds exposure time were acquired per scan. The tomograms consisted of 1024×1024×1024 cubic voxels of 23 nm length.

The data were reconstructed applying the standard reconstruction pipeline employed at the ANATOMIX beamline. To mitigate noise, a Paganin filter with 25-pixel width was implemented to the projections [10], i.e. a Fourier space filter with kernel $1/(1+L^2k^2), L = 25$ pixel. To increase the contrast-to-noise ratio (CNR), four consecutive scans were registered for averaging by the elastix toolbox software [11, 12].

2.3 Small-angle X-ray scattering (SAXS)

The Bruker NanoStar (Bruker AXS, Karlsruhe, Germany) served for the SAXS measurements [13]. They were performed using the K_α edge radiation of a copper source set at an acceleration voltage of 50 kV and a beam current of 0.6 mA. Specimen-detector distance was 1.075 m, and exposure time was 15 min.

2.4 Spectrophotometry

Optical transmittance [14] spectra of disk-like samples of the dental composites were acquired using the spectrophotometer [7, 15, 16] LLG-uniSPEC 2 (LLG Labware, Meckenheim, Germany). The light source is a deuterium lamp for wavelengths below 340 nm, and a tungsten halogen lamp above 340 nm [17]. The spectra ranged from 200 to 900 nm in 0.3 nm steps with the exception of Omnichroma. Here, the step was set to 0.1 nm.

3. RESULTS

3.1 Scanning electron micrographs

Electron microscopy was used to measure the tip diameters of the samples. Figure 3 shows two electron micrographs of characteristic examples from two selected dental materials. These images clearly demonstrate that diameters well below 100 µm could be reached. The images were also used to identify the most promising samples for the nanotomography measurements at the synchrotron radiation facility.

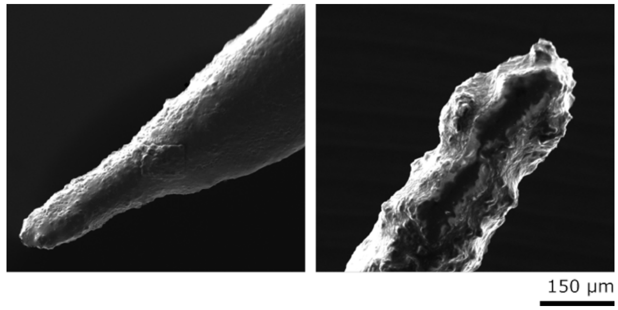


Figure 3. Electron micrographs of two selected single-shade composite materials revealing the shape of the rolled-out samples close to the tip and their surface morphology: left image – Omnichroma and right image – Chroma Fill. The length bar is used as an estimate for the tip diameters.

3.2 Synchrotron radiation-based transmission X-ray microscopy

TXM nanotomography on the four materials revealed the shape, size, and arrangement of the strongly X-ray absorbing nanometer-sized components of the composite materials, cf. Fig. 4. For each of the four selected dental materials a characteristic section of a slice is displayed.

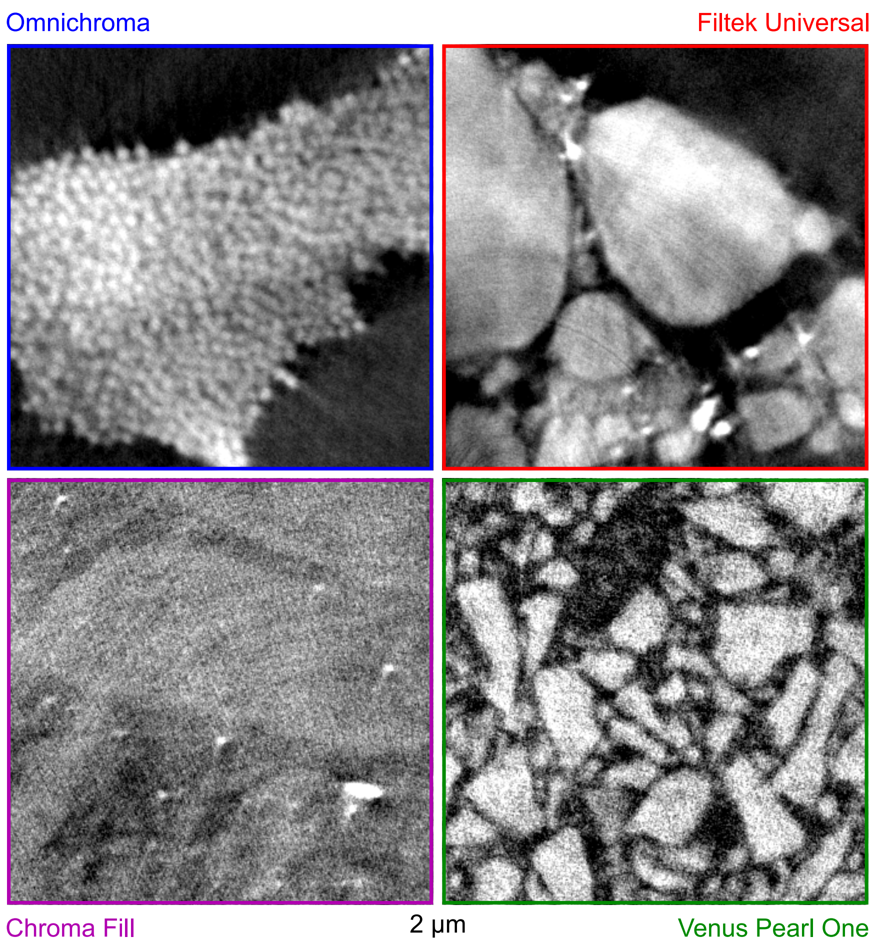


Figure 4. Selected sections of nanotomography slices of four single-shade dental restorative materials showing the sub-micrometer structure of the fillers. Omnichroma contains domains of densely packed spherical fillers. Filtek Universal shows two classes of filler particles distinct in size and X-ray attenuation. The

Chroma Fill composite exhibits sparsely distributed particles a few hundred nanometers in size. Venus Pearl One contains fillers with sharp edges and a broad size distribution.

As communicated earlier [18], Omnichroma contains ceramic spheres 260 nm in diameter. Filtek Universal possess both highly X-ray-absorbing particles about 200 nm in size and less X-ray absorbing particles up to 5 µm in size. Venus Pearl One's fillers have a variety of polyhedral shapes and show a broad size distribution ranging from tens of nanometers to several microns. In the Chroma Fill composite, some micrometer-scale structure can be made out, however the attenuation differences almost vanish in the noise. Some smaller, more highly attenuating particles are visible.

The ceramic spheres of Omnichroma are not homogeneously distributed in the samples prepared. The section of the tomography slice, shown in Fig. 5, clearly indicates the presence of air inclusions, labeled 1, the polymer matrix without ceramic spheres, labeled 2, and the composite (ceramic spheres and polymer matrix), labeled 3.

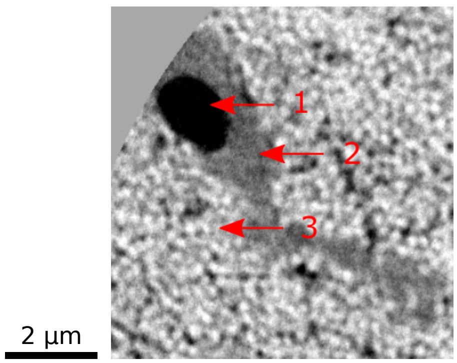


Figure 5. Section of a local nanotomography slice from Omnichroma, where the contrast differences allow identifying three phases, i.e. air inclusion (1), polymer matrix without ceramic fillers (2), and the composite with spherical filler particles surrounded by the polymer matrix (3).

3.3 Spectrophotometry

The disks are almost opaque in the ultraviolet range and more or less translucent in the visible and near-infrared range. For wavelengths between 200 and 330 nm the selected dental filling materials show a surprisingly similar transmission behavior, see Fig. 6 (a). The exception is Omnichroma with a peak of 1% transmittance at a wavelength of 267.5 nm [19], which corresponds to the diameter of the spherical ceramic fillers [18]. In the visible range, see Fig. 6 (b), the transmittance is characteristic for each restorative material selected. Whereas Filtek Universal exhibits a low transmittance associated with high light absorption over the entire range of visible light between 400 and 750 nm, the other dental composites show a linear decrease of light absorption with wavelength. Within the range of visible light from 400 to 700 nm, Venus Pearl One and Chroma Fill have a comparable slope increasing the transmittance from 7 to 14 % and 10 to 17 %, respectively. Omnichroma is more translucent with a transmittance increase from 20 to 42% for wavelengths ranging from 400 to 700 nm.

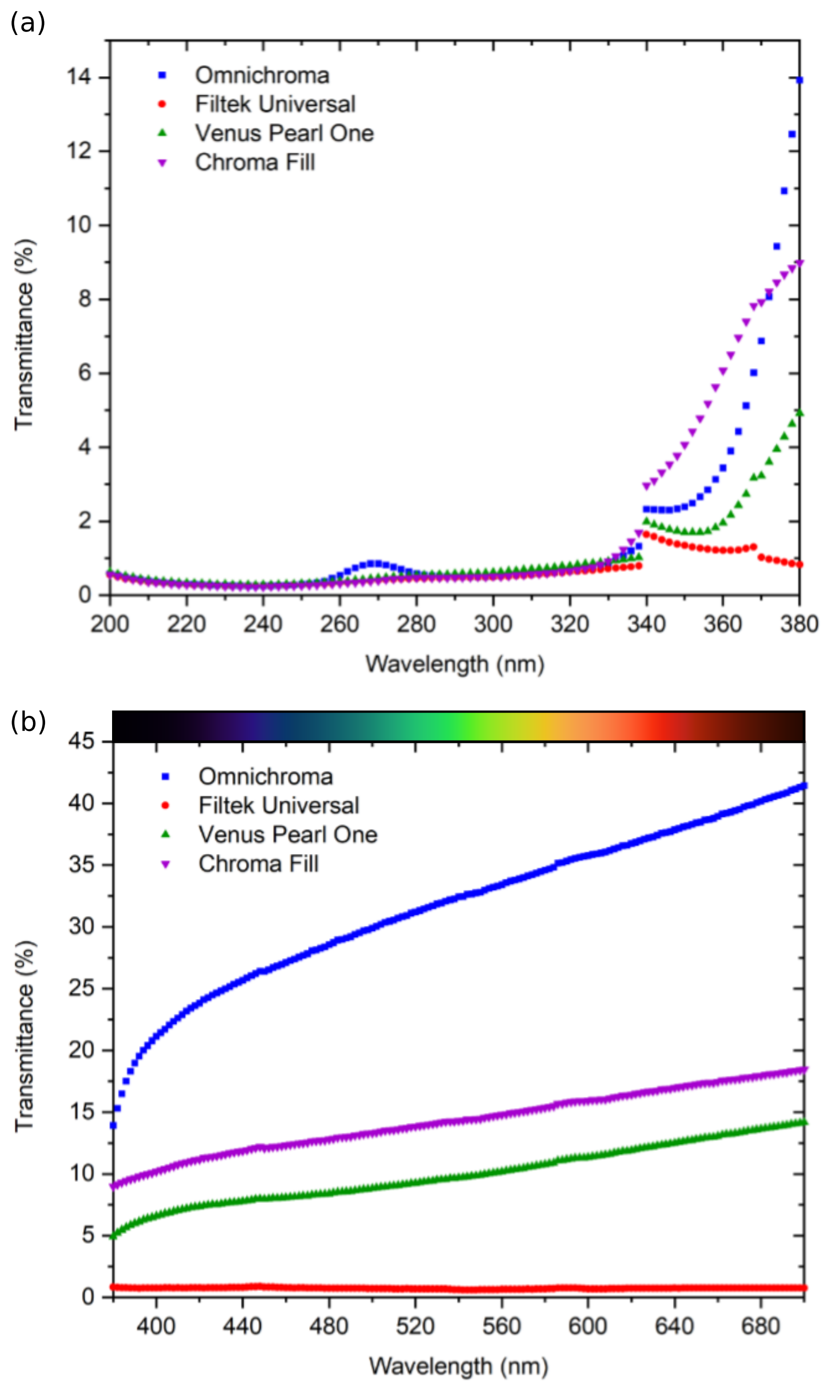
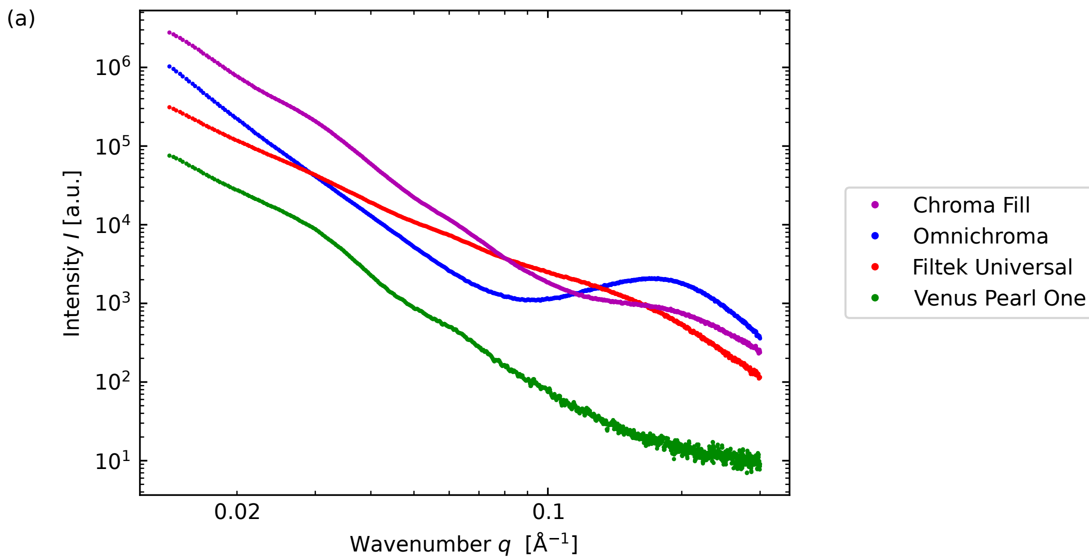


Figure 6. Transmittance spectra of disk-like samples from four selected dental composite materials. Diagram (a) shows their opaqueness by the spectra for the ultraviolet range, which contains the changeover of the lamps at a wavelength of 340 nm. Diagram (b) covers the visible range. Here, the spectra are characteristic for the four selected composites.

3.4 Small-angle X-ray scattering (SAXS)

Because the laboratory-based SAXS systems are usually designed to cover the real-space range from 1 to 100 nm, the fillers visualized by nanotomography cannot be further quantified. Nevertheless, nanostructures within this range might be uncovered in a complementary fashion to TXM.

The scattering intensity plots in Fig. 7 (a) hardly indicate the presence of highly ordered periodic nanostructures. The graphs in the diagram, however, exhibit several bumps and for Omnichroma even a prominent peak at a scattering vector of 0.2 Å^{-1}.



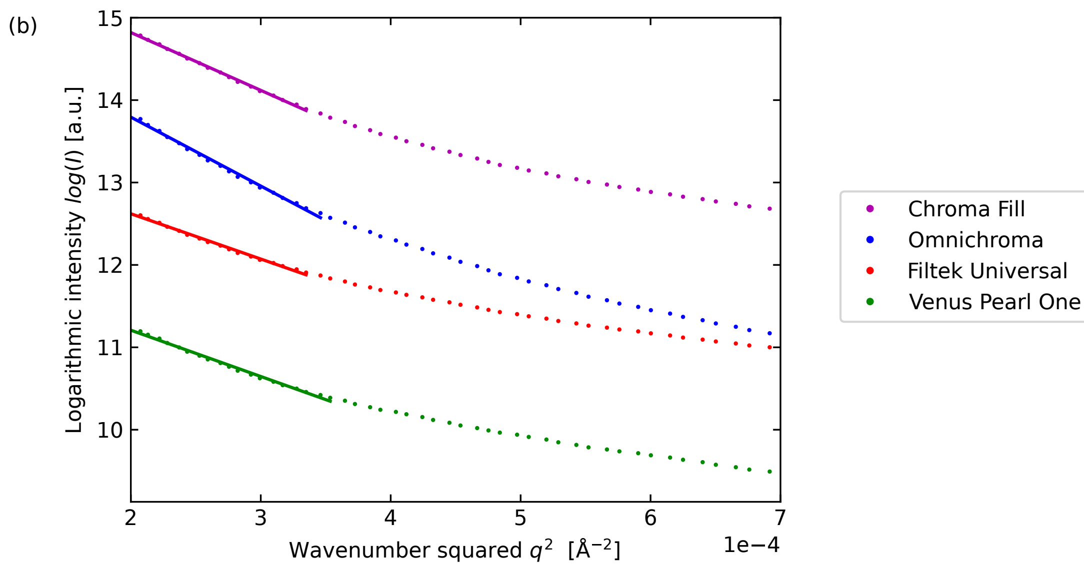


Figure 7. Results of laboratory-based small-angle X-ray scattering using disks of the composite materials listed. Diagram (a) corresponds to the *q*-plot, i.e. the azimuthally integrated scattering intensity *I* is plotted versus the scattering vector *q*. Diagram (b) is the Guinier plot. The data of the four restoration materials were not normalized with respect to the sample thickness and, therefore, just represent the intensity *I* integrated within a time period of 900 s.

Figure 7 (b) contains a diagram with Guinier plots. From the slope in this specific plot, one can derive the radius of gyration of the material components in the Guinier approximation [20]. The radii of gyration R_g found in the range between 2.0 and 3.5 $Å^{-2}$ were determined for the selected dental composites: R_g = 158 Å for Omnichroma, R_g = 128 Å for Filtek Universal, R_g = 145 Å for Chroma Fill, and R_g = 130 Å for Venus Pearl One [21].

4. DISCUSSION

The structural analysis of the transmission X-ray microscopy data from the four selected commercially available dental materials for wide color matching revealed a surprisingly wide variety of filler sizes, filler morphologies, and filler arrangements. Obviously, the chameleon effect can be gained for diverse micro- and nanostructures.

The Chroma Fill composite TXM data was more difficult to analyze, because probably the X-ray attenuation of the matrix and the filler was rather similar and, therefore, showed less or no contrast at least at their interfaces, or the resolving power of the TXM setup was not enough to visualize the structure of this composite material.

The filler materials are not always homogeneously distributed within the samples prepared. Air inclusions were detected. These findings might be due to the preparation procedure of the dental materials, which differed from the clinical application.

The light reflection at the filler-matrix interfaces determines the optical properties of the selected restoration materials. The opaqueness of Filtek Universal might be attributed to the wide variety of filler sizes and shapes, which favors light absorption. This interpretation would be in line with the presence of these interfaces for Venus Pearl One and the related absorbance, which is stronger than for Chroma Fill. The exception is again Omnichroma with the ordered 260 nm-sized zirconia-silica spheres with a narrow size distribution, which could explain the higher transmittance values especially for the larger wavelengths from yellow to red color. This structure of the Omnichroma composite, thus, adjusts the light that is transmitted in the relevant optical range and shows matching the color of neighboring enamel of the patient's tooth [22]. Further studies are necessary to obtain an improved quantitative understanding of the chameleon effect in restoration dentistry, which includes the change of the optical properties during polymerization. SAXS might be well suited to follow the ultraviolet light induced polymerization process in a quantitative fashion.

5. CONCLUSION

The chameleon effect of restoration materials for dental fillings is obtained for a wide variety of filler sizes and shapes as well as their arrangement within the polymer matrix as demonstrated by the transmission X-ray nanotomography study for the four commercial products investigated. Further research is necessary to quantify the relation between composite nanostructure and optical properties of dental filling materials for wide color matching.

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REFERENCES

[1] Joiner, A., "Tooth colour: a review of the literature," J. Dent. **32**, 3–12 (2004).

[2] Kobayashi, S., Nakajima, M., Furusawa, K., Tichy, A., Hosaka, K. and Tagami, J., "Color adjustment potential of single-shade resin composite to various-shade human teeth: Effect of structural color phenomenon," Dent. Mater. J. **40**(4), 1033–1040 (2021).

[3] Oivanen, M., Keulemans, F., Garoushi, S., Vallittu, P. K. and Lassila, L., "The effect of refractive index of fillers and polymer matrix on translucency and color matching of dental resin composite," Biomater. Investig. Dent. **8**(1), 48–53 (2021).

[4] Anwar, R. S., Hussein, Y. F. and Riad, M., "Optical behavior and marginal discoloration of a single shade resin composite with a chameleon effect: a randomized controlled clinical trial," BDJ Open **10**(1), 1–6 (2024).

[5] Akgül, S. and Gündoğdu, C., "Color Change Evaluation of Three Universal Resin Composites after Storage in Water: An In Vitro Study," J. Adv. Oral Res. **13**(2), 176–182 (2022).

[6] Humbel, M., Scheel, M., Tanner, C., Rodgers, G., Schulz, G., Carlucci, C., Von Jackowski, J., Sigron, G., Izquierdo, A., Weitkamp, T. and Müller, B., "Nano-tomography of dental composites with wide color matching," Dev. X-Ray Tomogr. XIV, B. Müller and G. Wang, Eds., Proc. SPIE **12242**, 122420Q (2022).

[7] Lucena, C., Ruiz-López, J., Pulgar, R., Bona, A. D. and Pérez, M. M., "Optical behavior of one-shaded resin-based composites," Dent. Mater. **37**(5), 840–848 (2021).

[8] Cho, K., Rajan, G., Farrar, P., Prentice, L. and Prusty, B. G., "Dental resin composites: A review on materials to product realizations," Compos. Part B Eng. **230**, 109495 (2022).

[9] Scheel, M., Perrin, J., Koch, F., Daniel, G., Giorgetta, J. L., Cauchon, G., King, A., Yurgens, V., Roux, V. L., David, C. and Weitkamp, T., "Current Status of Hard X-Ray Nano-Tomography on the Transmission Microscope at the ANATOMIX Beamline," J. Phys. Conf. Ser. **2380**(1), 012045 (2022).

[10] Paganin, D., Mayo, S. C., Gureyev, T. E., Miller, P. R. and Wilkins, S. W., "Simultaneous phase and amplitude extraction from a single defocused image of a homogeneous object.," Pt 1, J. Microsc. **206**(Pt 1), 33–40 (2002).

[11] Klein, S., Staring, M., Murphy, K., Viergever, M. A. and Pluim, J. P. W., "elastix: A Toolbox for Intensity-Based Medical Image Registration," 1, IEEE Trans. Med. Imaging **29**(1), 196–205 (2010).

[12] Shamonin, D., Bron, E., Lelieveldt, B., Smits, M., Klein, S. and Staring, M., "Fast Parallel Image Registration on CPU and GPU for Diagnostic Classification of Alzheimer's Disease," Front. Neuroinformatics **7** (2014).

[13] Bayarı, S. H., Krafft, C., İde, S., Popp, J., Guven, G., Cehreli, Z. C. and Soylu, E. H., "Investigation of adhesive–dentin interfaces using Raman microspectroscopy and small angle X-ray scattering," J. Raman Spectrosc. **43**(1), 6–15 (2012).

[14] Rocha Maia, R., Oliveira, D., D'Antonio, T., Qian, F. and Skiff, F., "Comparison of light-transmittance in dental tissues and dental composite restorations using incremental layering build-up with varying enamel resin layer thickness," Restor. Dent. Endod. **43**(2) (2018).

[15] Graf, N. and Ilie, N., "Long-term mechanical stability and light transmission characteristics of one shade resin-based composites," J. Dent. **116**, 103915 (2022).

[16] Zebic, M. L., Muric, B., Savic-Sevic, S., Dzeletovic, B., Stratimirovic, D. and Pantelic, D., "Real-time multispectral transmission of hard tooth tissues and dental composites with their heating," Dent. Mater. **39**(10), 903–912 (2023).

[17] Lab Logistics Group GmbH., "LLG-uniSPEC 2 Instruction Manual."

[18] OMNICHROMA., "Omnichroma Technical Report," Tokuyama.

[19] Humbel, M., Mattle, C., Scheel, M., Diaz, A., Jerjen, I., Lominski, R., Sterchi, R., Schulz, G., Izquierdo, A., Sigron, G., Deyhle, H. and Müller, B., "Dental composites for wide color matching," Bioinspiration Biomim. Bioreplication XII, A. Lakhtakia, R. J. Martín-Palma, and M. Knez, Eds., Proc. SPIE **12041**, 1204102 (2022).

[20] Jacques, D. A. and Trewhella, J., "Small-angle scattering for structural biology—Expanding the frontier while avoiding the pitfalls," Protein Sci. **19**(4), 642–657 (2010).

[21] Putnam, C. D., Hammel, M., Hura, G. L. and Tainer, J. A., "X-ray solution scattering (SAXS) combined with crystallography and computation: defining accurate macromolecular structures, conformations and assemblies in solution," Q. Rev. Biophys. **40**(3), 191–285 (2007).

[22] Ahmed, M. A., Jouhar, R. and Khurshid, Z., "Smart Monochromatic Composite: A Literature Review," Int. J. Dent. **2022**, e2445394 (2022).