Terahertz time-domain spectroscopy for monitoring the curing of dental composites

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Abstract: We apply terahertz (THz) time-domain spectroscopy for monitoring the curing process of three different light-curing dental composites. Exact knowledge of the sample thickness is required for a precise determination of the THz dielectric parameters, as the materials exhibit shrinkage when they are cured. We find very small but significant changes of the THz refractive index and absorption coefficient during stepwise light exposure. The changes in the refractive index are correlated with changes in the density of the materials. Furthermore, the refractive index and the sample thickness are found to give the most reliable result for monitoring the curing process of the dental composites.

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1. Introduction

Light-curing dental composites are widely used in restorative dentistry nowadays. Their establishment has been fostered not only by aesthetic aspects but also by concerns about harmful effects of mercury in conventional amalgam fillings. An appropriate polymerization of the resin is essential for the success of restoration, as the degree of cure may influence the mechanical, physical and chemical properties of the materials, such as wear resistance [1], bond strength to dentin [2], solubility and biocompatibility [3,4]. Moreover, a non-uniform degree of hardening with depth can lead to inadequate cure at the interface between composite and tooth.

Commonly destructive methods or methods requiring sample preparation are applied for assessing the optimal degree of cure, such as an evaluation of the depth of cure by a scraping technique [3,4] or by micro-hardness testing [3,4]. Adequate techniques that allow for a non-destructive (ND) monitoring of the degree of cure are still rare and are therefore a current field of research.

Non-destructive methods applied for investigating the curing of dental composites are Fourier transform infrared spectroscopy (FTIR) [5,6], Raman spectroscopy [7] and ultraviolet spectroscopy [8]. Drawback of these methods is that only surface near regions are accessible, and no information from inside the layers with millimeter thickness applied for restoration is...
obtained. Differential scanning calorimetry (DSC) was used as another technique [9]. However, it requires sample preparation and represents a pure off-line laboratory method.

Further ND techniques proposed are micro-computed tomography (μCT) and parameter selective magnetic resonance imaging (MRI). μCT allows for an accurate measurement of volumetric changes due to polymerization [10,11]. However, it can hardly be applied during restoration. MRI has shown to be sensitive to the curing process in polymers, but monitoring the complete solidification in dental composites is still limited by their very short transversal relaxation times $T2^*$ [12]. Furthermore, optical coherence tomography (OCT) and low-coherence interferometry (LCI) were demonstrated to be capable of dynamic cure measurements of resins, where the refractive index and sample thickness were correlated with the degree of cure [13,14]. However, the measurements were restricted to unfilled composites or depths smaller than about 1 mm due to the limited penetration of the probing light in the near infrared. Only recently, a method with potential for clinical application based on light scattering has shown to be capable of monitoring the curing kinetics of dental composites [15]. Altogether, to date there is still a search for ND methods that allow a direct monitoring of the degree of cure throughout a dental composite during restoration.

Terahertz (THz) technology is an emerging method for the ND investigation of materials. THz radiation is located in between the infrared and microwave bands of the electromagnetic spectrum and commonly denotes frequencies from 0.1 to 10 THz (wavelengths from 3 mm to 30 µm). Many dielectric materials exhibit large penetration depths in this frequency range [16,17], and THz radiation suffers much less from scattering due to the larger wavelengths compared to, e.g., infrared radiation. In addition, THz radiation is non-ionizing and the majority of genotoxicity studies performed so far have not revealed any adverse effects to deoxyribonucleic acid (DNA) [18]. The high potential of THz technology has been demonstrated in the field of material investigation for a variety of applications. For a review refer to, e.g., [19]. In the field of biomedicine, THz technology is restricted to specific applications (e.g., [20]), as THz radiation is strongly absorbed by polar substances such as water. On the other hand, this property can be exploited for hydration measurements of tissues [21,22]. Another wide field is THz spectroscopy of bio-molecules (e.g., [23,24]). For dentistry, THz technology has already been applied to measurements of demineralized and carious enamel [25,26], also performing a comparison with microradiography and microindentation [27], or the investigation of enamel and dentin [28].

In this work, we use THz time-domain spectroscopy (TDS) for monitoring the curing of light-curing dental composites by measuring their THz dielectric parameters. In contrast to OCT or LCI, the sample thickness is no longer limited to sub-millimeter values due to the much higher penetration depth of THz radiation, allowing to assess samples with clinically relevant thicknesses of several millimeters. Beyond medical applications, light curing of polymers has been investigated by THz-TDS so far only for a three-component UV-curable epoxy resin [29], where a decrease in absorbance was observed for the cured material. For light curing of dental composites, the changes of the THz dielectric parameters are expected to be very small, as these materials commonly consist of about 70 vol. % of inorganic fillers. Only about 30 vol. % consists of the polymeric matrix, which participates in curing. However, elaborate algorithms have been developed (e.g., [30]) that allow a highly precise determination of the THz dielectric parameters.

The paper is organized as following: First, we will give a short introduction to THz-TDS and the extraction of the THz dielectric parameters. Thereafter, we will describe the employed dental composites, sample preparation and the measurement procedure. The results for stepwise curing of the different dental composites will be presented after a general characterization of the THz dielectric parameters of the samples. In the discussion of the results also the influence of the sample thickness will be investigated.
2. Materials and methods

2.1. THz-TDS and THz dielectric parameters

THz-TDS employs pulsed broadband THz radiation with the spectrum typically ranging from 100 GHz to a few THz. The measurement setup that we use is a standard free-space THz-TDS laboratory system in transmission geometry similar to the one in [16]. For generation and detection of THz radiation, we employ low-temperature grown gallium arsenide photoconductive antennas driven by a femtosecond (fs) titanium sapphire laser with sub-100 fs pulse duration at a center wavelength of 800 nm. The emitted THz radiation is collimated and focused by off-axis parabolic mirrors (OAPs), forming an intermediate focus at the position of the sample. The THz beam is transmitted through the sample and is guided towards the THz detector by another set of OAPs. THz-TDS employs a time-resolved detection scheme of the electric field amplitude of the THz pulse. For this purpose, the femtosecond laser beam is divided by a beam splitter, with one part illuminating the emitter and the other part being guided towards the detector. One of the two arms is delayed by a mechanical translation stage, introducing a variable time delay between the arriving THz pulse and the gating fs-laser pulse at the detector, thus enabling time-resolved detection. For a more detailed description of the principles of THz-TDS refer to, e.g., [31].

Data analysis is done in the frequency domain by performing a Fourier transform of the time-domain signal, yielding the frequency dependent amplitude spectrum and phase. The phase-sensitive measuring principle differentiates THz-TDS from common intensity based methods, as it allows a direct determination of the complex dielectric parameters of a material, such as the complex refractive index

\[ \tilde{n} = n + i\kappa. \] (1)

We will present the intensity related absorption coefficient \( \alpha \) instead of the extinction coefficient \( \kappa \) in our results, which are related by

\[ \kappa = \alpha \frac{c_0}{4\pi f}, \] (2)

where \( c_0 \) is the velocity of light in vacuum and \( f \) the frequency.

The frequency dependent THz refractive index \( n \) and absorption coefficient \( \alpha \) are based on the phase difference and ratio of the amplitude spectra of a reference measurement (without sample) and with a sample at the measuring position. A general difficulty for a precise determination of the THz dielectric parameters arises from the fact that \( n \) and \( \alpha \) depend indirectly proportional on the sample thickness \( d \) (e.g., [29]). Thus, wrong values will be obtained for both parameters if incorrect values of \( d \) are used. This effect has to be considered in particular for the investigation of the dental composites, as volumetric shrinkage of the material of a few percent takes place during curing, leading to changes in the sample thickness. Only a simultaneous measurement of the sample thickness circumvents erroneous values of \( n \) and \( \alpha \). Therefore, we employ a commercially available data extraction software [32] based on the method described in [30], which exploits multiple reflections inside the sample and an optimization approach in so-called quasi-space for calculating the frequency-dependent refractive index and absorption coefficient simultaneously with the exact geometrical thickness of the sample.

2.2. Dental composites

We investigate three different dimethacrylate-based, light-curing dental composites, which are Z100 from 3M ESPE, X-tra fil and Admira, both from Voco. The following material parameters are extracted from the corresponding data sheets:

- Z100 is a mixture of the resins bisphenole-A-glycidyldimethacrylate (bis-GMA) and triethyleneglycol-dimethacrylate (TEGDMA) (15.5 weight-%, 29 vol. %) with zirconium/silicon filler (84.5 weight-%, 71 vol. %) with particle sizes from 0.01 to 3.5 µm and an
average particle size of 0.6 µm. The color shade \textit{CG} (cervical grey) was available for this work.

X-tra fil is a hybrid-composite containing micro- and macro-filler systems, where the inorganic silicate fillers (70.1 vol. \%) are embedded in a matrix of bis-GMA, urethanedimethacrylate (UDMA) and TEGDMA (29.9 vol. \%). The composite is available as universal shade.

Admira contains three-dimensionally linked inorganic-organic co-polymers (Ormoceres® [33]) and dimethacrylate (bis-GMA and UDMA) monomers (22 weight-\%, 44 vol. \%), containing inorganic micro-fillers (78 weight-\%, 56 vol. \%) with a particle size of about 0.7 µm. The color shade \textit{A2} was available.

Curing of the dental composites is performed using a blue-light polymerization exposure unit (Individio Light Box from Voco, see Fig. 1(a)), which is equipped with four 9 W blue light halogen lamps (spectral range 400–500 nm) and exhibits an illuminance of about 15,000 lx, according to manufacturer’s data.

2.3. Sample preparation, measurement and data evaluation

Samples with defined geometry and surface are prepared for the THz-TDS measurements. The composite material is placed between two quartz glass plates (see Fig. 1(b)) with a thickness of around 700 µm each, which are transparent for the blue curing light and the probing THz radiation. The thickness of the composite material is adjusted by spacers to about 2 mm, which equals the thickness mainly recommended for dental restoration.

The THz-TDS setup is enclosed by a housing purged with gaseous nitrogen, preventing absorption due to the humidity of the air. The blue-light exposure unit (without the drawer) is directly attached to the housing. The sample is mounted on a motorized translation stage for fully automated positioning either inside the exposure unit or at the measuring position. Curing is done stepwise: after inserting the sample into the exposure unit for a defined time, THz measurements are performed, followed by the next exposure step. This procedure allows for an investigation of the curing process in defined steps, starting with the fully uncured material up to the completely cured dental composite.

As discussed in Chap. 2.1, a reference measurement is required for calculating the THz dielectric parameters of the sample. In order to account for any changes of the THz signal in the subsequent data analysis due to mechanical or thermal drifts, a reference is recorded directly after the sample measurement at each curing step. For statistical evaluation, a number \(N\) of sample and reference measurements is performed each time. For Z100 (the first composite investigated), \(N = 3\) for the sample and reference measurements, respectively. For the other composites \(N\) was increased to 6, improving statistics.

As the sample geometry represents a layered system, the THz dielectric parameters of the single quartz plates have to be known for an evaluation of the embedded dental composites. Therefore, first measurements of the single quartz plates only are performed. In combination with measurements of the complete sample, the data extraction software allows for a separate determination of the refractive index \(n\) and absorption coefficient \(\alpha\) of the dental composites.
As the measurements are performed in transmission geometry, the obtained THz dielectric parameters represent integral values over the sample thickness.

Prior to the calculations, data pre-processing by dc-offset removal and Blackman-windowing of the time-domain data is performed. The data extraction software provides the mean THz dielectric parameters and the corresponding statistical error, based on the Student t-distribution and the number of measurements. Unless otherwise specified, the presented statistical errors correspond to the 95% confidence interval according to the Student t-distribution throughout the paper.

3. Results

3.1. Characterization of THz dielectric parameters

First, we perform a basic characterization of the THz dielectric parameters of the uncured dental composites. Figures 2(a) and 2(b) show the frequency dependent values of $n$ and $\alpha$ of Admira, X-tra fil and Z100, respectively, from 0.3 to 1.5 THz. For Admira and X-tra fil data is clipped at 1 and 0.9 THz, respectively, as the results are limited by the dynamic range of the measurement at higher frequencies due to the larger absorption coefficients of these materials. It is noted that for X-tra fil no data of the uncured material but only after 5 s of exposure is available due to a failure in the measurement routine. However, the higher refractive index of X-tra fil is significant as $n$ changes only in the range of 1% due to curing (see Chap. 3.2).

The THz refractive indices are found to lie in a range of about 2.05 to 2.25. These values are higher than for common polymer materials [34] due to the large content of inorganic filler such as silicate glasses, which exhibit higher THz refractive indices of up to, e.g., 2.5 [35]. In order to explain the values of $n$ of the dental composites in detail, separate measurements of the matrix and filler materials and effective medium theory would be required. The THz absorption coefficient increases with increasing frequency for all three materials and is lowest for Z100. The larger absorbance for Admira and X-tra fil is presumably due to their content of UDMA, which has a highly polar structure [36]. The dotted lines indicate the very small statistical error of the measurements.

Fig. 2. (a) THz refractive index and (b) absorption coefficient as a function of frequency for the uncured materials Admira and Z100 and for X-tra fil after an exposure of 5 s, respectively. The dotted lines indicate the statistical error of the measurements.

3.2. Monitoring of curing

For monitoring the curing process of the dental composites, the frequency dependent THz refractive index and absorption coefficient of the three samples are evaluated as a function of the exposure time. As an example, the results of $n$ and $\alpha$ are shown for Z100 for exposure times from 0 to 420 s in Figs. 3(a) and 3(b), respectively. These figures already indicate changes in the THz optical constants with increasing exposure time.

The dependence of $n$ and $\alpha$ on the exposure time is evaluated in detail at a frequency of 0.6 THz, where data is not limited by the dynamic range of the measurement for all three samples.
The corresponding results are displayed in Figs. 4(a), 5(a), and 6(a), respectively. For all three dental composites, an increase of the refractive index and a decrease of the absorption coefficient are observed due to curing. For \( n \), a decrease of 0.86%, 0.59% and 1.62% is found for Z100, X-tra fil and Admira, respectively, for the cured (maximum exposure time) with regard to the uncured material. For \( \alpha \), changes of −14.7%, −5.1% and −12.6% are observed for the three composites. For X-tra fil, slightly higher real values are expected as only the data at 5 s is available (see Chap. 3.1).

In addition, the layer thicknesses received from the data evaluation software are shown in Figs. 4(b), 5(b), and 6(b), revealing the shrinkage of the dental composites during curing. We
find a shrinkage of the cured with regard to the uncured material of 2.4%, 1.5% and 4.0% for Z100, X-tra fil and Admira respectively. For X-tra fil, again a slightly higher real value is expected. The increase in d (correlated with a decrease in the refractive index) observed for Admira between an exposure time of about 100s and 200s (Fig. 6) is a clearly unphysical result. This effect is presumably due to instabilities, such as fluctuations of the phase between reference and sample signal during the measurement.

As the data evaluation software does not provide information on the error of the delivered sample thickness, its statistical error (standard deviation) is calculated from separate evaluations of pairs of the single sample and reference measurements exemplarily for a small and a large exposure time. The obtained standard deviations are given by the error bars in Figs. 4(b), 5(b), and 6(b).

4. Discussion

The observed changes of the THz dielectric constants and in particular of the refractive indices are very small, posing the question of the reliability of the results. The maximum relative statistical errors of the refractive index, $\sigma_n/n$, are 0.10%, 0.18% and 0.24% for Z100, X-tra fil and Admira, respectively, which are in all cases smaller than the observed relative changes, indicating the significance of the results. The maximum relative statistical errors of the absorption coefficient, $\sigma_\alpha/\alpha$, amount to 7.4%, 8.0% and 8.9% for the three samples. Thus, the results are considered as significant for Z100 and Admira; only for X-tra fil (starting at 5 s) the relative statistical error is larger than the change in $\alpha$.

As the sample thickness enters $n$ and $\alpha$ inversely proportional, exact knowledge of $d$ is required for a precise determination of the THz dielectric parameters. For estimating the influence of the error of $d$ on the refractive index and absorption coefficient, Gaussian error propagation is performed with the standard deviations obtained for $d$. For all three samples, the resulting errors of $n$ and $\alpha$ are smaller than their relative changes, thus confirming the significance of the obtained results.

In general, we find that the evaluation of $n$ and $d$ produces more stable results with lower statistical errors compared to the absorption coefficient. Thus, the refractive index and the sample thickness seem to be best suited for investigating the curing of dental composites.

For correlating the THz dielectric parameters with the shrinkage of the composites, linear regression of $n$ and $\alpha$ with $d^{-1}$, $d^{-2}$ and $d^{-3}$, respectively, is performed. The results show that the refractive index is highly correlated with the inverse volume $V^{-1} = d^{-3}$, with linear correlation coefficients between 0.99 and 0.97 for the three samples. This effect can be understood when $n$ is considered as a linear function of the density of the material, which increases due to shrinkage. The linear correlation coefficients are larger than for $d^{-1}$ and $d^{-2}$, which would indicate a directional dependence of shrinkage due to the geometry of the sample. On the other hand, the absorption coefficients exhibit lower correlation coefficients.
with regard to $V^{-1}$ from 0.95 to 0.60 and thus exhibit no clear linear dependence on the density of the materials. This is also visible in Figs. 4, 5, and 6, where any kink in the layer thickness is also visible in $n$ but not in $\alpha$.

The obtained results of $n$ and $\alpha$ represent integral values over the sample thickness. As curing of the dental composites starts from the illuminated surface (in our case both sides of the sample), it is expected that also inhomogeneous hardening of the sample over depth is present during curing. However, in particular the refractive index and sample thickness exhibit a distinct saturation behavior, indicating that the whole sample volume has been cured after maximum exposure times of about 50 s for all of the samples with thickness of 2 mm.

5. Conclusions

In conclusion, we have shown that THz-TDS is capable of monitoring the curing of dental composites. Although the observed changes in the THz dielectric parameters are small, they are demonstrated to be significant. We find that the changes of the refractive index are correlated with an increase in the sample density due to shrinkage during curing. Besides the refractive index, also the sample thickness appears to be a good measure for monitoring the curing process.

Further research is required to reveal the full potential of THz-TDS for monitoring the curing of dental composites, with measurements under environmental conditions, in reflection geometry and using simulation of fillings of cavities in teeth. These subsequent experiments would be a further step for THz-TDS to become a valuable tool for the investigation of new composites or even for clinical applications.

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