Fourier-transform infrared spectroscopic method for assessing sensitivity of light-curable dental restorative composites to ambient light – a pilot study

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ABSTRACT

Aim: To investigate whether Fourier transform infrared spectroscopy (FTIR) can be used to identify the point at which polymerization begins when dental restorative composites are exposed to ambient light.
Materials and methods: An FTIR spectrometer with an attenuated total reflectance (ATR) diamond accessory and a mercury-cadmium-telluride detector was used to evaluate real-time changes in the degree of conversion (DC) at a fast data collection rate (2 spectra/s). The 0.1 and 0.2 mm thick samples of three commercial composites (OmniChroma, Tetric PowerFill, and Filtek One Bulk Fill) were irradiated with white light simulating dental operating light (temperature of 4,000 K and illuminance of 8,000 lux, according to the recommendations of ISO 4049). The DC data were plotted as a function of time and the first derivative was calculated. The first time point with a non-zero value of the first derivative was considered to indicate the start of the polymerization reaction.
Results: Statistically significant differences in time of onset of polymerization were observed between the materials at both layer thicknesses ($p<0.001$) with the following material ranking: OmniChroma > Tetric PowerFill > Filtek One Bulk Fill. The highest mean values were measured for OmniChroma (161.75 s / 193.0 s) while the lowest mean values were observed for Filtek One Bulk Fill (76.0 s / 96.75 s) for 0.1 mm and 0.2 mm thick layers, respectively. Statistically significant effects of layer thickness were observed for OmniChroma ($p=0.002$) and Filtek One Bulk Fill ($p<0.001$), while Tetric PowerFill showed no significant effect of layer thickness ($p=0.350$).
Conclusions: High-speed ATR-FTIR spectrometry can be used to detect early signs of the onset of polymerization of dental restorative composites with high sensitivity and reproducibility.

KEYWORDS: Polymerization onset, FTIR spectroscopy, Dental restorative composites, Degree of conversion, Layer thickness effects

SAŽETAK:

FOURIEROTRANSFORMACIJSKA INFRACRVENA SPEKTROSKOPSKA METODA ZA PROCJENU OSJETLJIVOSTI STOMATOLOŠKIH REKONSTRUKCIJSKIH KOMPOZITA KOJI SE STVRDNJAVAJU SVJETLOM NA OKOLNO SVJETLO – PILOT-STUDIJA

Cilj: Istražiti može li se Fourierovom transformacijskom infracrvenom spektroskopijom (FTIR) identificirati točka početka polimerizacije kada su dentalni rekonstrukcijski kompoziti izloženi ambijentalnom svjetlu.
Materijali i metode: FTIR spektrometar sa smanjenom dodatkom dijamanta ukupne refleksije (ATR) i detektorom žive-kadmija-tellurida korišten je za procjenu promjena u stupnju konverzije (DC) u

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stvarnom vremenu brzim prikupljanjem podataka (2 spektra/s). Uzorci debljine 0,1 mm i 0,2 mm triju komercijalnih kompozita (OmniChroma, Tetric PowerFill i Filtek One bulk Fill) ozračeni su bijelom svjetlošću koja simulira stomatološko operacijsko svjetlo (temperatura od 4.000 K i osvjetljenje od 8.000 luksa, prema preporukama ISO 4049). DC podaci iscrtani su kao funkcija vremena i izračunata je prva izvedenica. Smatra se da prva vremenska točka s vrijednošću koja nije nula prvog derivata ukazuje na početak polimerizacijske reakcije.

Rezultati: Statistički značajne razlike u vremenu početka polimerizacije uočene su između materijala pri obje debljine sloja (p < 0,001) sa sljedećim rangiranjem materijala: Omnikroma > Tetrična PowerFill > Filtek Jedna masovna ispuna. Najviše srednje vrijednosti izmjerene su za OmniChroma (161,75 s/193,0 s), dok su najniže srednje vrijednosti opažene za Filtek One bulk Full (76,0 s/96,75 s) za 0,1 mm odnosno 0,2 mm debele slojeve. Statistički značajni učinci debljine sloja uočeni su za OmniChroma (p = 0,002) i Filtek One bulk Fill (p < 0,001), dok Tetric PowerFill nije pokazao značajan učinak debljine sloja (p = 0,350).

Zaključci: Spektrometrija brzog ATR-FTIR može se koristiti za otkrivanje ranih znakova početka polimerizacije stomatoloških restorativnih kompozita s visokom osjetljivošću i ponovljivošću.

KLJUČNE RIJEČI: Početak polimerizacije, FTIR spektroskopija, Stomatološki restorativni kompozit,Stupanj pretvorbe, Efekti debljine sloja

INTRODUCTION

Most modern resin composites for restorative dentistry are light-cured, i.e. they cure on demand by activating a dedicated curing lamp which emits blue light [1,2]. The light-activated curing of the material theoretically gives the dentist unlimited working time to adapt the material to the walls of the tooth cavity and achieve the desired shape. In practice, however, this is not the case, as the white light of the dental operating lamp contains a sufficiently high irradiance in the blue part of the visible light spectrum to trigger a premature polymerization reaction in resin composites [3]. The polymerization of multifunctional methacrylates in dental composites is a chain reaction mediated by free radicals, which, once initiated, continues to propagate on its own [4]. Due to viscosity changes in the polymerizing resin, the reaction is subject to kinetic phenomena such as autoacceleration, which means that the ongoing reaction basically accelerates itself by reducing the rate of termination through an increase in the viscosity of the reaction medium [5]. The practical consequence of this is that once the composite material stabilizers, which are essentially free-radical scavengers, are exhausted, the polymerization can proceed and reach a sufficient degree of conversion to reach the gel phase. This is the phase in which the polymer chains become entangled and cross-linked in such a way that the composite material transitions from its plastic (moldable) state to a partially elastic state [6]. For the practitioner, this means that the composite loses the consistency conducive to adaptation to the tooth cavity and further attempts by the practitioner to shape the material by applying pressure lead to cracks and fractures within the partially rubbery material. At this state, the practitioner can either ignore the fact that the material has partially set and proceed with the fabrication of the restoration with structural defects, or remove the entire increment of material and start shaping again with a new increment.

Premature curing of composite materials can be avoided by using an orange light source as a operating light, which is not absorbed by the photosensitizers in composite materials and thus does not trigger the chain polymerization reaction [7]. However, this approach has not been widely accepted in practice and most dentists continue to use high-intensity white light for restorative treatments. The problem of premature curing under white light was recognized soon after light-curing composites became established in clinical practice. Therefore, the requirement that composite materials must tolerate a certain amount of exposure to ambient light was included in the ISO 4049 standard [8]. This standard specifies the minimum requirements that a composite material must fulfill in order to be suitable for permanent restorations. Among other requirements, it requires that the material must withstand white light (temperature of 3,600-6,500 K and illuminance of 8,000 ± 1,000 lux), which is intended to approximate a dental operating light, for at least 1 minute in order to prevent premature curing. The transition to a rubbery state after simulated exposure to operating light is assessed visually by manually shear-thinning the composite between two glass plates and examining the macroscopic structure of the composite by looking for the formation of clefts and voids, which would indicate gelation. If the material remains homogeneous, gelation has not yet occurred and the material is considered to have complied with the requirement of ambient light tolerance. If any surface defects are observed, the material is considered to have failed. The ambient light sensitivity test method described above is a simplistic method for rapid screening of materials, similar to other simplified tests described in the ISO 4049 standard. The aim of the present pilot study was to investigate whether an alternative, more sensitive method with a more robust chemical background could be developed. Therefore, Fourier-transform infrared (FTIR) spectroscopy was chosen as a sensitive means of detecting small changes in the chemical structure of composite materials [9], which can be used to identify the point at which polymerization begins when the material is exposed to ambient light. FTIR spectroscopy is widely used to measure the progress and extent of polymerization in dental composites and to investigate the effects of different curing conditions on the effectiveness of polymerization [10–14]. Therefore, it was hypothesized in the present study that the same approach could be used when the composite is exposed to dental operating light to detect the onset of polymerization and quantify the length of time over which the composite tolerates exposure to ambient light.

The hypotheses were as follows: (I) the changes in the FTIR spectra allow identification of the onset of the polymerization reaction, (II) the method can be used to identify differences in tolerance to ambient light among different brands of commercial composites, and (III) variations in composite thickness affect the time of the onset of polymerization.

MATERIALS AND METHODS

In order to include different composites in the present pilot study, three materials were examined, namely an one-shade universal composite OmniChroma (Tokuyama Dental, Tokyo, Japan) [15], a bulk-fill composite Filtek One Bulk Fill, which is intended for application in 4-mm layers (3M, St. Paul, MN, USA) [16], and a bulk-fill composite Tetric PowerFill, which can be used in 4-mm layers and polymerized using high-intensity rapid light-curing (Ivoclar, Schaan, Liechtenstein) [17].

The FTIR spectra of the composites were acquired using a method previously developed for real-time monitoring of the progress of the polymerization reaction during light-curing [10–12]. This method is based on a rapid data acquisition rate of 2 spectra per second, followed by a quantitative evaluation of the gradual change in intensity of the spectral band at 1638 cm^{-1}, which corresponds to the vibration of C=C double bonds in methacrylate monomers [18]. The consumption of these bonds as polymerization progresses is reflected in a decrease in the intensity of the spectral band at 1638 cm^{-1}. This parameter has been defined as the degree of conversion (DC) and represents one of the fundamental properties of composite materials. For the calculation of the DC, an additional spectral band is used as an internal standard, usually the aromatic C=C vibration at 1608 cm^{-1}. For the composites without the aromatic core-containing monomers (for example, urethane dimethacrylate-based composites), alternative reference bands can be used as internal standard [19]. The DC is calculated from the intensities of the band at 1638 cm^{-1} and the reference band according to the following expression:

$$DC\ (\%) = \left[1 - \frac{(1638\ cm^{-1}/1608\ cm^{-1})_{peak\ height\ after\ curing}}{(1638\ cm^{-1}/1608\ cm^{-1})_{peak\ height\ before\ curing}}\right] x\ 100$$

FTIR spectra were recorded using an FTIR spectrometer (Nicolet iS50, Thermo Fisher, Madison, USA) with an attenuated total reflectance (ATR) diamond accessory and a fast liquid nitrogen cooled mercury-cadmium-telluride detector. By positioning the uncured composite specimen on the ATR crystal, DC can be recorded in situ and in real time without the need for additional specimen preparation [11]. The thickness of the composite sample was controlled using 0.1 or 0.2 mm thick glass plates as spacers and the sample was covered with a thin glass plate that negligibly attenuates white light. While the sample was irradiated with white light simulating dental operating light (temperature of 4,000 K and illuminance of 8,000 lux, according to the recommendations of ISO 4049), FTIR spectra were collected at a data acquisition rate of 2 s^{-1} for 5 minutes. The spectral range was 500-3,500 cm^{-1} and the spectral resolution was 8 cm^{-1}. Each spectrum was recorded in 4 scans. For each experimental group, 4 replicates were performed (n=4).

After plotting the DC data as a function of time, the first derivative was calculated, which represents the slope of the tangent to the DC-time curve [20]. The first time point with a non-zero value of the first derivative was considered to indicate the start of the polymerization reaction. This time was recorded with a temporal resolution of 0.5 s and used for statistical comparisons among the materials and layer thicknesses. The effects of the factors "material" and "film thickness" on the time of polymerization onset were evaluated using a two-way ANOVA. This was followed by one-way ANOVAs with Tukey post-hoc adjustment to assess the differences among the different materials and layer thicknesses. P-values below 0.05 were considered statistically significant. Statistical analysis was performed using SPSS, version 25.0 (IBM, Armonk, USA).

RESULTS

The part of the FTIR spectrum of resin composites is exemplified in Figure 1. The band at 1638 cm^{-1} corresponds to the vibration of double C=C bonds which are consumed during polymerization, while the band at 1608 cm^{-1} remains unchanged and is used as an internal standard. Monitoring changes in the intensity of the band at 1638 cm^{-1} can be used to evaluate polymerization kinetics or to identify early signs of the onset of polymerization.

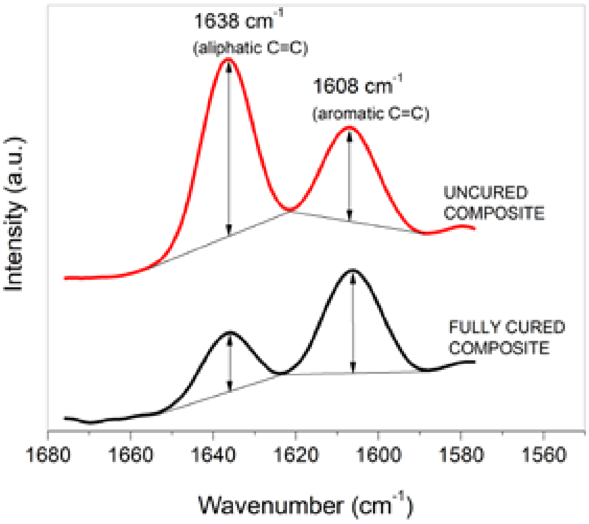

Figure 1. Spectral bands used to calculate the degree of conversion of resin composites. The comparison between the spectrum of an uncured (red) and a fully cured composite (black) is shown.

Figure 2 illustrates the real-time DC data and the data processing steps used to obtain the outcome variable termed "time of polymerization onset". Figure 2a shows the real-time DC curve obtained by plotting the DC values as a function of time with a temporal resolution of 0.5 s. The noise in the curve is caused by the noise in the FTIR spectra due to the fast data acquisition. By adjacent-average curve smoothing, the curve shown in Figure 2b is obtained. This curve contains a plateau and an inflection point indicating the onset of polymerization. To determine the start of polymerization more precisely, the first derivative of this curve was calculated and plotted in Figure 2c. A smoothed version of the derivative curve is shown in Figure 2d. The time of the inflection point of this curve was defined as the time of the onset of polymerization and used in the statistical analysis.

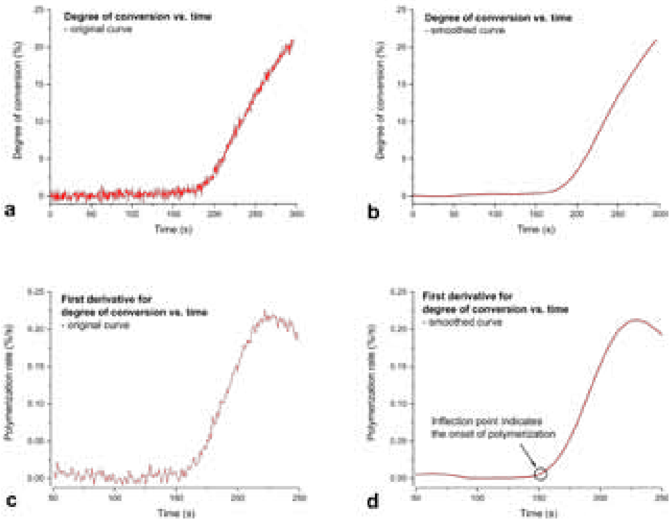

Figure 2. Visual representation of the degree of conversion data as a function of time. The original DC data vs. time curve (a) was smoothed to obtain the curve shown in (b), which was used to calculate the first derivative (c). From the smoothed derivative curve, a reading has been taken for the time of the onset of polymerization.

Figure 3 summarizes the results for the time of the onset of polymerization under dental operating light for three composite materials at two layer thicknesses. Statistically significant differences in time of onset of polymerization were observed between the materials at both layer thicknesses ($p<0.001$) with the following material ranking: OmniChroma > Tetric PowerFill > Filtek One Bulk Fill. The highest mean values were measured for OmniChroma (161.75 s / 193.0 s) while the lowest mean values were observed for Filtek One Bulk Fill (76.0 s / 96.75 s) for 0.1 mm and 0.2 mm thick layers, respectively. Statistically significant effects of layer thickness were observed for OmniChroma ($p=0.002$) and Filtek One Bulk Fill ($p<0.001$), while Tetric PowerFill showed no significant effect of layer thickness ($p=0.350$).

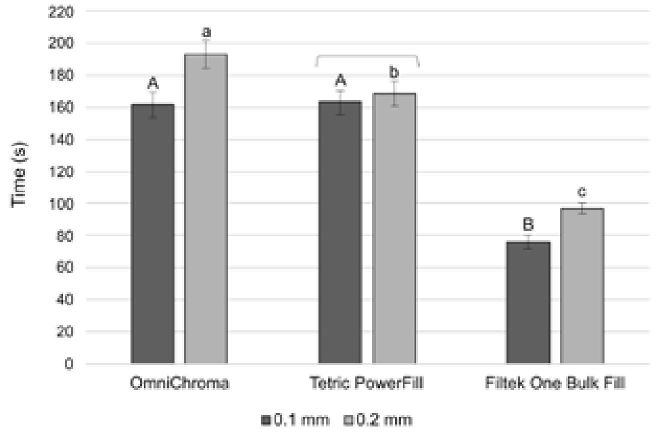

Figure 3. Time of the onset of polymerization reaction during exposure of composite materials to standardized ambient light (mean values ± 1 standard deviation). Same uppercase and lowercase letters indicate no statistically significant differences in comparisons among materials, for layer thicknesses of 0.1 mm and 0.2 mm, respectively. Square brackets indicate no statistically significant differences between two layer thicknesses for a given material. The level of significance for all comparisons was $\alpha=0.05$.

Given the low within-group data variability and large effect sizes, the observed statistical power for the between-material comparisons approached ~100%, while the observed statistical power for the comparisons between layer thicknesses was 99.1%, 13.1%, and ~100% for OmniChroma, Tetric PowerFill, and Filtek One Bulk Fill, respectively.

DISCUSSION

This pilot study showed that it is possible to determine the sensitivity of resin composites to simulated ambient light using FTIR spectrometry. The rapid recording of successive FITR spectra and the evaluation of the first derivatives of the DC-time curves enabled highly reproducible identification of the early signs of polymerization. The low coefficients of variability (i.e. the relative standard deviations) indicate a high reproducibility and the potential to achieve high statistical power even with low sample sizes. Therefore, the first hypothesis was accepted. The second and third hypotheses were also accepted, as both the material brand and the layer thickness significantly influenced the time of the onset of polymerization.

A comparison of the results of this study with the requirements of ISO 4049, which stipulates a minimum working time of 60 seconds before the start of polymerization [8], shows that all the materials tested meet this requirement. However, it should be noted that the threshold of 60 seconds in the ISO 4049 standard is defined for a substantially different phenomenon, namely the visually observable gelation of the composite material, which does not necessarily correspond to the first observable sign of the decrease in C=C bond concentration, which was used as a marker for the onset of polymerization in the present study. On the one hand, the use of FTIR may be more sensitive than the visual method described in ISO 4049, as the latter identifies gelation, which usually occurs at DC values of ~5% [21], while FTIR is able to detect effects that are almost an order of magnitude smaller (DC values of about 0.5-1.0%). On the other hand, while the ISO 4049 method identifies gelation in the uppermost part of the composite closest to the light source, the ATR-FTIR setup used in our study measures the changes in the lower part of a 0.1 or 0.2 mm thick layer. Since the light is attenuated while passing through composite materials filled with a large amount of small filler particles [22], polymerization in the bottom layer is initiated at a slower rate [20], which may actually make the FTIR method less sensitive. If this happens to be the case, the sensitivity of the FTIR method can be improved by using a thinner composite layer, which would reduce the effect of light attenuation [23]. However, there is a limit to this thinning, that is determined by the penetration of the infrared light into the sample positioned on the ATR crystal and the sampling depth associated with the method [24]. This aspect could be investigated in a further study.

The differences in the time of onset of polymerization observed among the three commercial materials can be attributed to variations in the concentration and effectiveness of the photoinitiators and stabilizers used in a particular brand of material. The exact material compositions are not disclosed by the manufacturers [25], but in general it can be assumed that higher concentrations of photoinitiators and their higher quantum yield result in the formation of more free radicals when exposed to ambient light, which then need to be neutralized by the stabilizers [26]. Therefore, the relative effectiveness of photoinitiators and stabilizers should determine the tolerance of the composite material to ambient light. Another factor that can be assumed to play a role in the sensitivity to ambient light determined by our ATR-FTIR method is the light transmittance of the composite material [27]. As mentioned above, the ATR-FTIR method is able to record the changes at the “bottom” layer of the composite adjacent to the ATR crystal. Under these conditions, the light transmission through the overlying material has a direct effect on the number of photons that can reach the bottom layer, regardless of the apparent thinness of the composite film of 0.1-0.2 mm. The ISO 4049 method is expectedly not as dependent on light transmission as it evaluates the gelation in the top layer closest to the light source. In any case, as the compositions of commercially available composite materials are only partially known, a more detailed investigation of the components responsible for the differences in tolerance to ambient light in the various brands of composite materials is not possible within the scope of the present study. Nevertheless, it can be deduced that there is a large heterogeneity among the different brands of commercially available composites, which has clinical relevance if composite materials are manipulated under operating light for extended periods of time. This is particularly notable with bulk-fill composites [28], which are used to fill the entire tooth cavity at once and therefore require a comparatively longer time to shape than conventional composites that are used in the traditional way, where small amounts of material are applied and cured incrementally.

Real-time DC measurements have been used extensively by our group in previous studies to evaluate various aspects of polymerization kinetics [10–12,20,29]. In contrast to these studies, where the main outcome parameters are the DC, maximum polymerization rate, time of maximum polymerization rate, and four exponential curve fitting-derived parameters specific to the gel and glass phases of polymerization, in the present study only the time of onset of polymerization is considered as the outcome of interest. Since polymerization under ambient light proceeds at much lower rates than the clinically relevant polymerization initiated by a narrow spectrum of blue light, typically above 1,000 mW/cm^2 [30], there was no practical value in continuing the measurements until the final DC values were reached, as this would take more than 30 minutes and thus be clinically irrelevant. Therefore, the measurements were stopped after 5 minutes regardless of not reaching the final DC values. Even shorter measurement times would be possible, because in order to obtain the time of onset of polymerization as the main outcome variable of this study, the measurement only needs to last a few minutes after the actual onset, as this is sufficient to identify the decrease of the DC-time curve as well as the first non-zero values of the first derivative calculated from this curve.

In general, the extent of methacrylate polymerization in dental composites can be evaluated based on the changes in any material property affected by polymerization. Various methods have been used for this purpose, including differential scanning calorimetry [31], microhardness [32], impedance spectroscopy [33], and even visible light spectrometry [34]. However, vibrational spectroscopies (FTIR and Raman) are considered the most direct methods to study the progress of the polymerization reaction, as they directly measure the consumption of C=C double bonds [19,35]. FTIR spectrometry has the added advantage of allowing a very high data acquisition rate with sufficient precision for the evaluation of DC in special experimental setups with an ATR accessory and a fast liquid nitrogen cooled detector [36]. This results in exceptional reproducibility and much lower within-group variability compared to other FTIR sampling methods where samples are ground and mixed with KBr [37]. Mounting the already cured specimens on the ATR crystal also has a lower reproducibility than the direct application of the uncured material in the present study, most likely due to the fact that a good contact between the rigid sample and the ATR crystal cannot be guaranteed. Therefore, the method used in the present study, that was previously developed for the evaluation of polymerization kinetics [10], is known for its unparalleled reproducibility, which also proved useful for the evaluation of the onset of polymerization in the present study.

Since this pilot study has shown that the FTIR measurements have the potential to detect the onset of polymerization under ambient light, the next step in the investigation could be to apply the ISO 4049 method to the composite specimens exposed to the same simulated ambient light as used in the setup described, and compare the outcomes to the results of this study.

CONCLUSIONS

This pilot study has shown that high-speed attenuated total reflectance Fourier-transform infrared spectrometry can be used to detect early signs of the onset of polymerization of dental restorative composites. By quantifying the time of polymerization onset as the main outcome variable, high sensitivity and reproducibility can be achieved, enabling the detection of differences among different composite brands and layer thicknesses.

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