

Optical Study of Short-Term Polymerization Kinetics for Dental Resin Cement

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Abstract: This work shows the time behavior presented by the temperature, dilation and/or contraction strain and thickness of dual-cure dental resin cement measured by using optical techniques.

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1. Introduction

Resin cements are used as restorative materials and according to their initiation mode can be classified as chemically activated, photoactivated or dual-activated. The photo-activation is allowed by addition of a photosensitizer, usually camphorquinone (optical absorption band close to 470 nm). The cure reaction splits carbon-carbon double bonds in individual monomer molecules and allows the formation of carbon-carbon single bonds resulting in polymer chains. Part of the photoinitiator may remain unreacted due to insufficient irradiation resulting from light sources with low energy/short illumination time or even light attenuation at the photoinitiator absorption band along the resin layer depth [1]. All these parameters affect the overall shrinkage occurring during polymerization, which is proportional to the degree of conversion. The higher the rate of monomer conversion, the faster the gel point is reached, and the lower is the flow capacity of the material. The higher the degree of conversion, the bigger the composite final shrinkage and its elastic modulus, both of which contribute to higher stresses [2]. During the polymerization reaction the monomers are converted into long cross-linked polymeric chains causing a volume reduction of 1.5 – 6% [2,3]. The consequences of the volumetric shrinkage are the stress generation within restorative cavities, potentially debonding, occurrences of marginal staining, bacterial microleakage and recurrent caries [4,5]. Despite the advantage of using photoactivated dual-cure resins, temperature increase during the photoactivation have been a concern as high temperatures can damage pulpal and gingival tissues [6,7]. To solve this drawback, LEDs were introduced as promising light sources for dental treatment. However, part of the energy produced by LEDs is still converted in heat and the composite polymerization is itself an exothermic reaction. Data from literature have shown increases in the temperature inside the resin of 10 °C that can produce damage mainly in deep cavities with a thin dentin layer [7,8]. Techniques that have been used to measure resin kinetics include dilatometry, interferometry, strain gage sensors, optical scanning and direct linear displacement transducer measurements [1]. Some works focus on results obtained before and after the polymerization, comparing generated stresses, air bubbles, cracks and shrinkage percentage usually by employing in-vitro or in-vivo teeth as substrate. Previous works used the OCT ability to produce high resolution images to show the inner characteristics of the restored teeth, usually only before and after polymerization [9–11]. Fiber Bragg gratings were used to analyze dental resins by employing a stainless steel mould as substrate for sample deposition and sensor guiding [11].

In this work the polymerization of dental resin cement dual-activated was optically monitored by two fiber Bragg gratings (FBG), by Optical Coherence Tomography and spectroscopy techniques. Information about the resin temperature, contraction strain and thickness were obtained in real time measurements performed before, during and after the photoactivation.

2. Materials and methods

The AllCem dual-cure resin cement (FGM dental products) was used in this work. Resin was photoactivated by using a 500 mW/cm² blue light LED with wavelength range between 450-480 nm. Measurements performed with different techniques were carried out by using resin layers approximately 500 µm thick at the beginning of the experiment. Resin samples were photoactivated along 40 to 100 seconds (depending on the experiment) and data acquisition was performed before, during and after the resin layer deposition and photoactivation. To monitor the absorption spectra, the LED head was placed in front of the resin layer deposited between microscope slides, and the light transmitted through the resin layer was recorded in real time by a spectrometer (Ocean Optics, HR 4000). The emission spectrum of the LED was recorded before the resin deposition and was used as a reference signal for

absorption measurements. Dental resin absorption spectra were recorded every 1 second during 100 seconds. A heterogeneous system based on FBG sensors and Optical Coherence Tomography (OCT) was also used in the experiments [12]. The system combines two FBGs, employed as temperature and strain transducers with sensitivities of $(9.80 \pm 0.05) \text{ pm}/^\circ\text{C}$ and $(1.03 \pm 0.05) \text{ pm}/\mu\epsilon$, and the OCT for monitoring the evolution of the thickness during the polymerization. One FBG was positioned at approximately 1 cm above the resin sample for measuring only the room temperature. The other one was placed on an acetate sheet and was covered by the resin layer to monitor simultaneously strain and temperature inside the sample. The acetate sheet is smooth enough to allow the resin sliding due to contraction strain, allowing the FBG to measure deformations of an unbounded resin during the polymerization. The environment humidity was between 58% and 64.5% and the room temperature was $25.0 \pm 0.5^\circ\text{C}$. A super-luminescent LED (Superlum, PILOT 2, wavelength range from 1520 to 1570 nm) and an FBG interrogation monitor (Ibsen, I-MON E 512D, resolution $< 0.5 \text{ pm}$) were used to interrogate the gratings. The OCT was configured to take a transversal tomogram of a similar resin layer kept under identical environmental conditions. Air-resin and resin-substrate interfaces were determined by Gaussian fits to the interference patterns generated by reflection at these interfaces. A previous measurement performed without the resin provided the substrate spatial position used to calculate the sample thickness. Data provided by the FBGs and OCT were acquired at a sampling rate of 5 Hz.

3. Results

Fig. 1 shows longitudinal deformation and temperature changes measured by the FBG immersed into the resin.

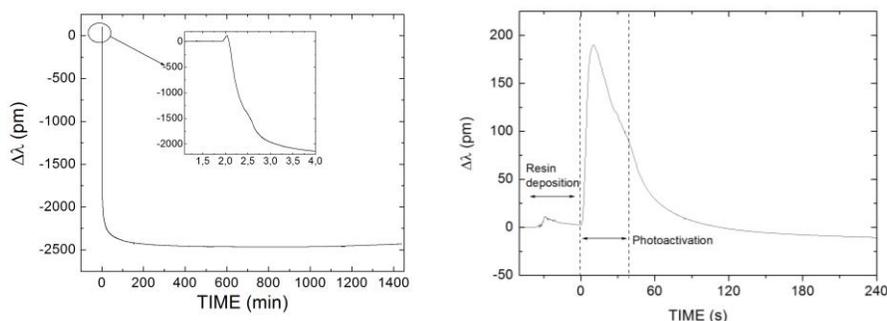


Fig. 1. (a) FBG response to both resin deformation and temperature changes during 24 hours. Inset shows the first 4 minutes, where the sample deposition and photoactivation occurs. (b) Resin temperature during the first 4 minutes. Temperature/strain cross sensitivity was avoided by covering the FBG with a thermal paste layer.

FBG wavelength shifts obtained during 24 hours related to resin deformation and temperature changes are presented in fig. 1a where the first four minutes are showed in the inset. As a result of fiber Bragg gratings cross sensitivity, the temperature increase produces positive wavelength shifts while strain contraction tends to shift the Bragg wavelength to lower values. Consequently, the magnitude of the wavelength shift do not provide individual information about the resin temperature or mechanical deformation. However, by covering the FBG with a layer of thermal paste, the strain effect can be avoided. Fig. 1b shows FBG response only to temperature changes. After 10 s from the beginning of the photoactivation, resin temperature reaches its maximum value showing an increase of approximately 18°C . This behavior is related mainly to the exothermic change associated to the polymerization plus the heat provided by the LED. Approximately 10 seconds after photoactivation had started the polymerization rate and consequently the resin temperature starts to decrease. At the end of the photoactivation, after ~ 40 s, the resin temperature decreases of approximately 11°C and after ~ 100 seconds, temperature reaches its initial value. Temperature changes related to wavelength shifts of fig. 1b allowed decoupling effects of temperature and strain visualized in fig. 1a, solving the cross-sensitivity problem inherent to the FBG sensor. A maximum deformation of approximately $2040 \mu\epsilon$, corresponding to a contraction of $2040 \mu\text{m}/\text{m}$, is observed after ~ 250 minutes. This deformation represents a total contraction of $0.2 \times 10^{-3} \%$. However, approximately 70% of the deformation occurs during the photoactivation and is related to the rate of reaction and consequently to the degree of conversion of monomers. Results obtained with the FBG sensor are consistent with those presented in the literature [13] for the degree of conversion and rate of polymerization. Additionally, resin absorption spectra, fig. 2a, show the time behavior of the camphorquinone photoinitiator consumption. Spectral changes are not observed in the 3 to 4 seconds from the beginning of the photoactivation. After that, camphorquinone absorption band centered at 470 nm decreases in intensity disappearing after 40 seconds and a band with increasing intensity is observed at lower wavelengths, ~ 455 nm. This band continues to grow with a lower rate stabilizing in intensity after approximately 80 s. Besides, a thickness reduction of approximately 5 % occurring during approximately 120 seconds after the

beginning of the experiment is detected by the OCT. Fig. 2b depicts this contraction for three independent measurements. The thickness reduction starts after the beginning of the photoactivation, as also observed to occur with strain contraction measured with the FBG and showed in fig. 1.

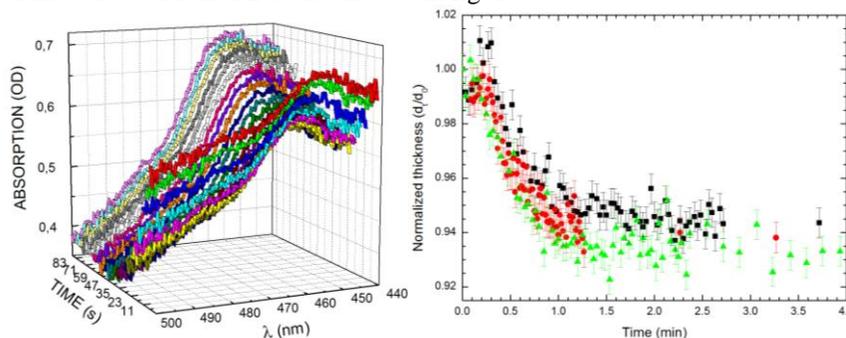


Fig. 2. (a) Resin absorption spectra acquired during and after photoactivation approximately each 4 seconds (b) Resin relative thickness measured with OCT for 3 independent experiments.

3. Conclusion

Experimental techniques employed in this work seek to characterize the kinetics of the polymerization through the acquisition of different physical parameters. FBGs sensor allowed measuring resin mechanical deformation and temperature taking the advantage of the high sensitivity and fast response time inherent to this kind of sensor. FBG sensor showed that the temperature inside the resin starts to increase exactly when the photoactivation takes place reaching its maximum value, approximately 18 °C above the room temperature, 10 seconds after the photoactivation had started. Spectral changes were observed during the first 80 seconds while the photoactivation takes place and the resin experiences important temperature changes. Resin maximum contraction is observed after ~250 minutes. However, approximately 70% of the deformation occurs during the photoactivation and is related to the rate of reaction and consequently to the degree of conversion of monomers. Measured values of thickness reduction (~5%) are consistent with previous works. The knowledge of such physical parameters in real time can be used to provide a better understanding of the polymerization process, as well as to define the ideal photoactivation that optimizes this process.

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