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Measurement of shrinkage during photopolymerization of methacrylate resins by interferometric techniques: local and global analyses

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ABSTRACT

Light based measurement techniques have largely proven its efficiency on polymer materials. In this study we describe a method based on specific optical techniques for characterization of dental composites. First, a Dynamic Speckle Pattern (DSP) global analysis was made, which allowed qualitative descriptions of the behavior of samples during polymerization from their upper surface view. This analysis is complemented with local measurements of shrinkage by means of a fiber optic Fizeau Interferometer. Second, a Time History Speckle Pattern (THSP) analysis of different samples was carried out in order to gain a better understanding of the shrinkage development as the polymerization reaction takes place. To show the virtues of these techniques, we applied them to both a commercial resin dental composite and a model resin based on methacrylate monomers. Both techniques could serve as a good comparing test protocol among different commercial resins.

Keywords: Photopolymerization Shrinkage; Fiber Optics Sensors; Interferometry; Dynamical Speckle Analysis; Dental Composites.

Introduction

Determination of volumetric shrinkage in resin curing is a topic of great significance in developing and designing new and better dental resin formulations. Polymerization reaction itself has an inherent impact on this, because this volumetric shrinkage could lead to formation of further caries in the teeth. In addition, the stored stress may generate fractures and detachments while the exothermic nature of the reaction is a parameter that should be considered to prevent damage to the dentin. More biocompatible formulations are made by loading them with glass material nano-particles in order to reduce thermal effects and improve reduction of the final volume [1-3]. Consequently, modern formulations have minimized these issues and therefore, the set of conventional methods, successfully used to measure shrinkage some decades ago, might be out of range today. Many techniques from the most diverse measurement areas have tried to address these issues such as dilatometry, bonded disk, laser interferometry, digital image correlation, etc. [4-16]. Recently, some researchers have introduced really interesting approaches that make use of computer vision [17-19], while curing light transmission, translucency and opalescence of dental composites as well as living being dentins have attracted the attention to develop better application techniques for deontology science [20-22]. Among all these techniques, those optical remain as the most efficient and recommended ones to deal with such characterization of materials, mainly due to their high resolution and their non-invasive nature [23, 24].

In this study we describe a method based on specific optical techniques for characterization of dental composites. A Dynamic Speckle Pattern (DSP) global analysis [25], which allows qualitative descriptions of the behavior of samples during polymerization from their upper surface view, is complemented with local measurements of shrinkage by means of a fiber optic *Fizeau* Interferometer (FI) [26]. In addition, a Time History Speckle Pattern (THSP) analysis [27] of diverse samples measured in pairs was carried out in order to gain a better understanding of the shrinkage development as the polymerization reaction takes place.

To show the virtues of these techniques, we applied them to a commercial resin (3M Filtek P60®) and a laboratory-made specimen. Both techniques provided useful information about the polymerization for light-curing dental composites. In addition, they could serve as a reasonable comparing test protocol among different commercial resins.

Experimental

- Materials

      The resins were formulated from blends of {2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)phenyl]propane} (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) at mass fractions 70:30 Bis-GMA/TEGDMA. Bis-GMA (Esstech, Essington, PA, USA) and TEGDMA (Aldrich, Argentina) were used as received. The resins were activated for visible light polymerization by the addition of camphorquinone (CQ) in combination with dimethylaminoethylmethacrylate (DMAEMA). CQ and DMAEMA were from Aldrich, Argentina. Model dental composites were prepared by mixing the methacrylate monomers with 27 wt% SiO_2 (Aerosil, Degussa, Germany). The structure of the monomers and photoinitiator system is shown in Fig. 1. In addition, a commercial light-cured dental composite (3M FILTEK P60®) was used for comparative purposes.
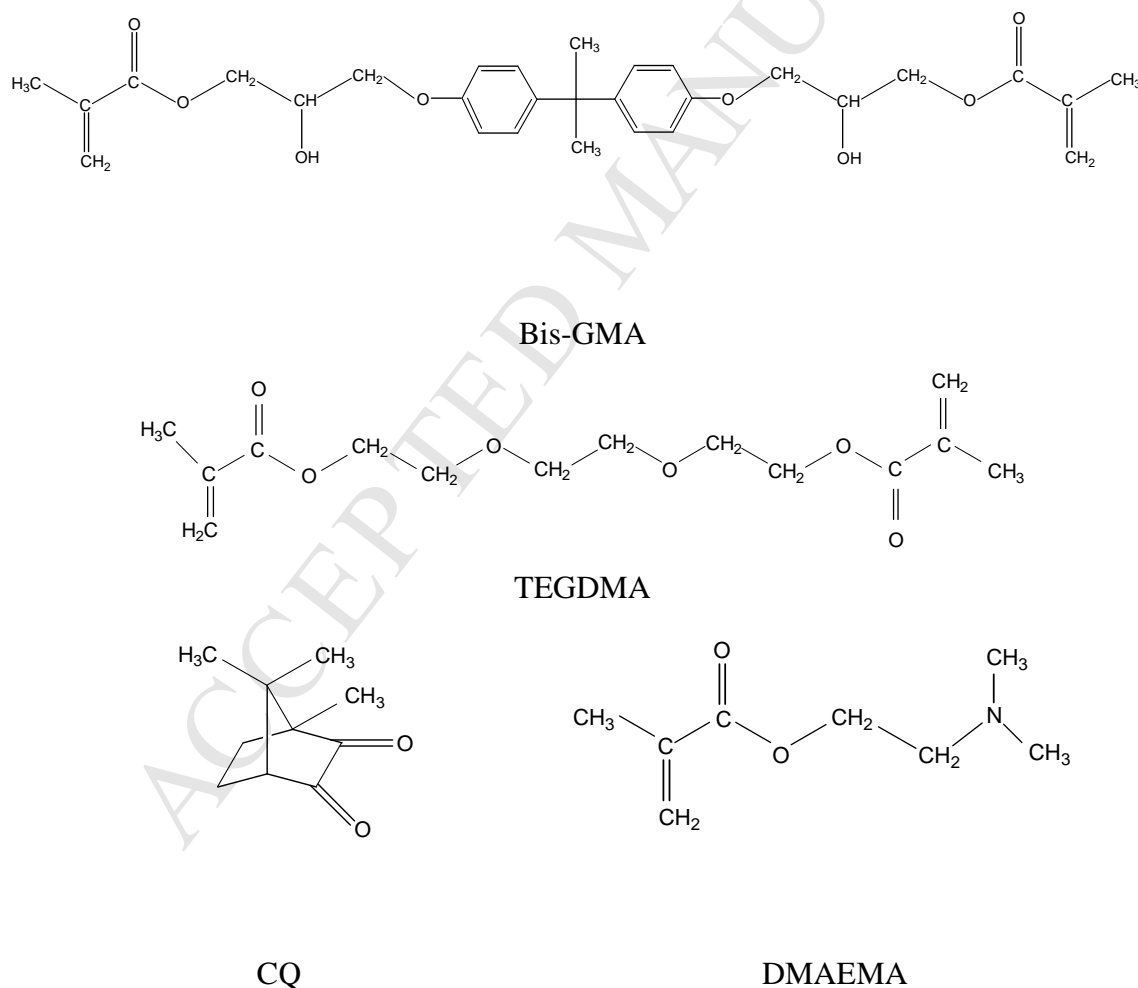

Bis-GMA

TEGDMA

CQ   DMAEMA

Figure 1: Structures of monomer and photoinitiator used in this study

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The LED used in the measurements (1W LUXEON STAR LXHL-MB1D) had a dominant wavelength at 470 nm. It was driven at 500 mA with a regulated current source (THORLABS LD500).

- Methods of characterization

For the DSP and FI measurements we used the experimental setup shown in Figure 2. This setup has a common part consisting of a 1-mm thick, 6-mm diameter rubber mould, which is adhered to a 2-mm thick glass plate. The resins were placed into the mould verifying that the upper surface of the specimens was flat and smooth before each test. The whole assembly was firmly attached on an optical table (Melles Griot) and was continuously irradiated from the bottom by the high power LED.
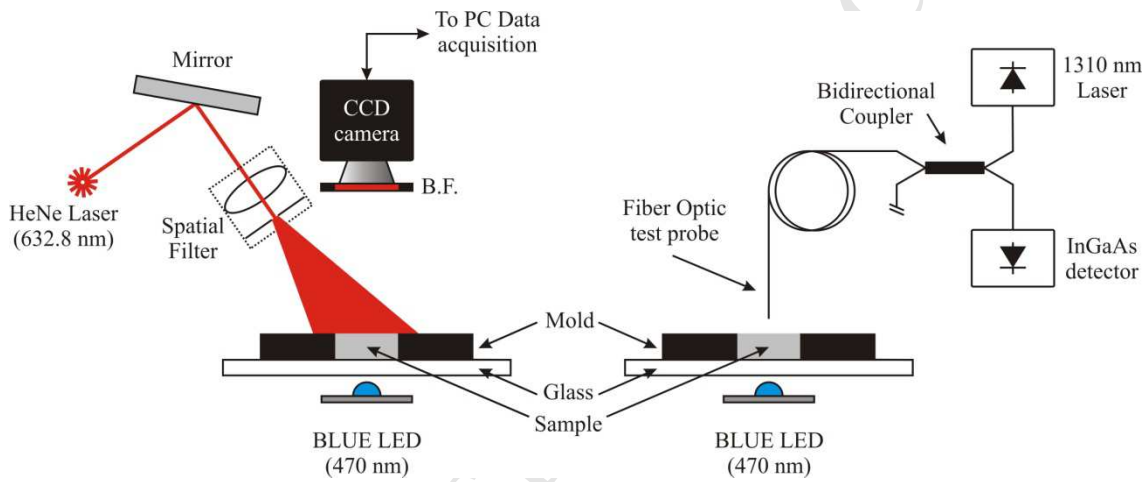

Figure 2: Experimental setup employed for: Dynamic Speckle Pattern Analysis (left) and Fiber Optic Fizeau Interferometer distance meter (right).

In particular, for the DSP global analysis (Fig. 2, left), the sample should be illuminated from above by a HeNe laser beam (MELLES GRIOT, 632.8nm/30mW), properly expanded and spatially filtered to provide a clean and uniform area of illumination, while images were registered by a CCD camera, connected to a digitizer board (MATROX PULSAR) in a PC. The acquisition was performed by recording data as sequences of 8 bits image, 300×300 pixels, stored for post-processing. The sampling frequency was 25 frames per second (fps) and 2000 samples were taken for each experience (~80 seconds). To prevent saturation of the CCD detector from the curing source, a blue filter with good attenuation up to 600 nm was placed in the path of the camera.

While using the above described scheme, a laser beam illuminated an object, and exhibited a granular diagram called *speckle pattern* due to a random interference phenomenon. Any movement present on the surface of an object resulted in a fluctuating pattern over time called dynamic speckle [25]. The characteristics of the dynamic speckle pattern could be used here to assess the

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evolution of the polymerization reaction and, in turn, the shrinkage of the resin. For the measurement of dynamic speckle activity, we propose two methods:

- *Dynamic Range Descriptor:* a pseudo-colored video applying the dynamic range descriptor [28] to 24 consecutive frames repeatedly till the end of the recorded experience, i.e. we took frames 1-25 and generated the first frame of the pseudo-colored video; then to generate the second frame we used the frames 2-26 and so on till the last frame.

- *Time History of the intensity of a Speckle Pattern* analysis (THSP): a technique that creates an image formed from fringes or stripes of 1 pixel-wide and the length of the original cut from all the frames

These methods allowed us to follow the evolution of the activity pattern throughout all the experience.

For determinations of absolute shrinkage the HeNe Laser and the Camera (Fig. 2, right) were replaced by the *Fiber Optic Fizeau Interferometer*. This is an instrument with excellent capabilities as high resolution less than a tenth of a micron, intrinsically self-calibrated due to light interference theory and it is non invasive since it does not require any physical contact to work. The shrinkage of the resins is measured from the variation of the interference cavity formed between the end of the sensor and the top surface of the resin itself. The evolution of the samples thickness is simply a voltage signal that is commonly called interferogram. In this study this signal was acquired at 100 Hz. A more detailed explanation of the technique has been previously reported [29, 30] and typical signals from the two workbenches described are shown in Fig 3.
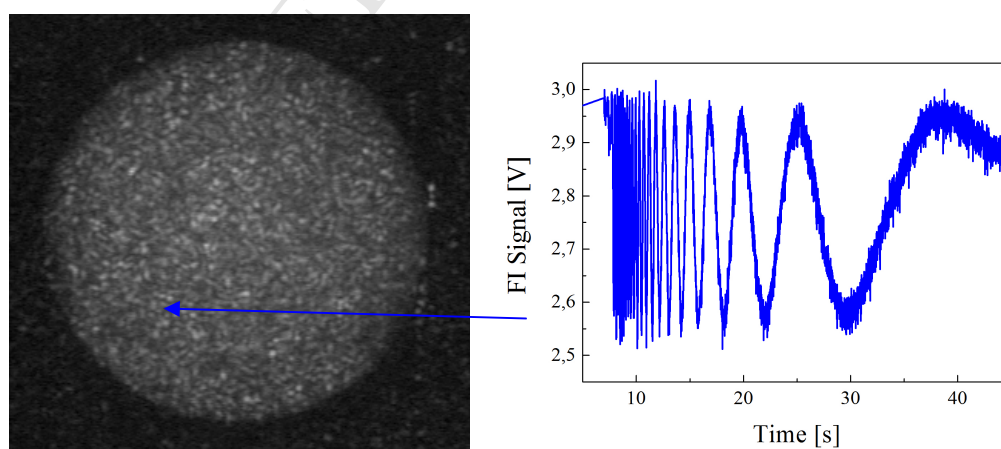

Figure 3: Typical experimental signals obtained with both techniques. Left: Speckle Pattern image of resin and mould during photocuring. Right: an interferogram for a given point on the resin surface.

Speckle activity was also processed by a THSP algorithm which gave an additional monitoring of the progress of the polymerization. In this case we prepared another rubber mould with two holes for different resins and were cured them simultaneously by means of two identical blue LED´s as depicted in Figure 4. By this setup, we were able to acquire simultaneous images during the photo-polymerization of two samples at the time on the same CCD image capture, allowing a simple and powerful way to assess the performance of both cases with the same image acquisition system.
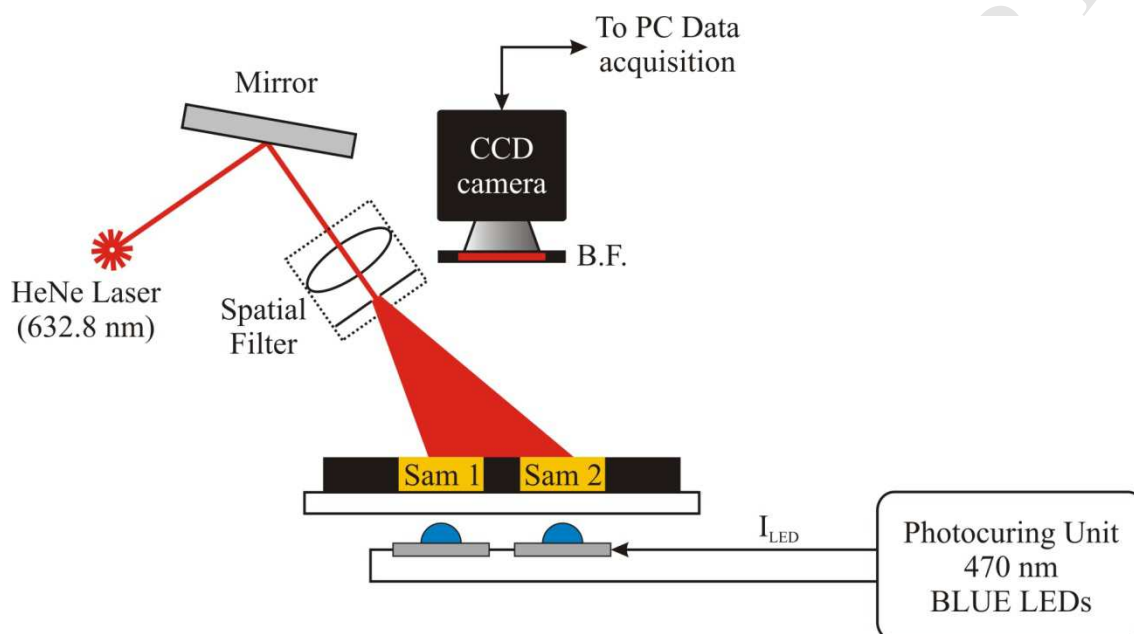

Figure 4. Setup used for THCP image analysis. By this approach two samples can be analyzed at the same time. In this case, Sam 1 was P60 3M$^{(R)}$ and Sam 2 was the laboratory-made resin labeled "B88".

To show the temporal evolution of THSP we used the Oulamara et al. method [27]. The procedure to build up a THSP image from a collection of image (i.e. recorded video file of a photocuring experience) is simple and should be interpreted as a new image in which the activity of the sample changes the gray level intensity in the horizontal direction. So, when a phenomenon shows low activity, time variations of the speckle pattern are slow and the THSP shows elongated shape. When the phenomenon is very active, the THSP resembles an ordinary speckle pattern. See Figure 5.
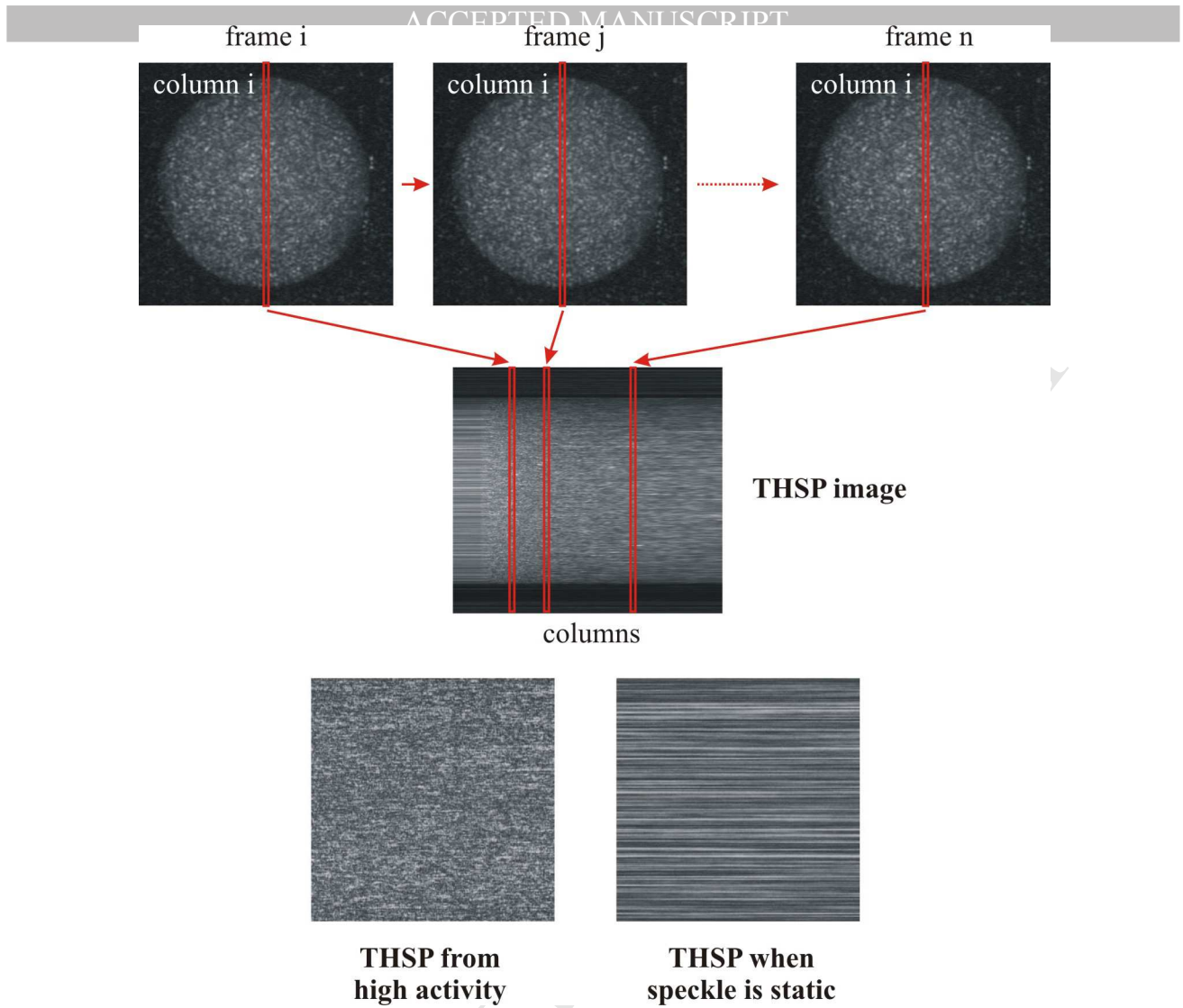
Figure 5: Temporal history of Speckle Pattern (THSP). How it is generated from a sequence of frames and its typical aspect under different situations.

Results and Discussion

In Fig. 6 (left) it is observed a snapshot of speckle pattern analysis process for a certain time "t" after the photocuring reaction started. Since this is a pseudo-colored image that assigns a scale from blue to red ranging from the lowest to the maximum activity, it was easy to deduce a little or null activity on the mould. In contrast, the different areas of activity throughout the sample under study were highlighted. According to the results of this technique, there were areas of higher activity in the center (A), while in the boundary a lower activity (C) was recorded, having a gradient of values in the middle section (A). In order to achieve more detailed information regarding these different levels of activities we applied the FI sensor at three specific points A, B and C, marked in

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Fig. 6. Interferograms produced for each measurement were demodulated and are shown in Fig. 6, right.
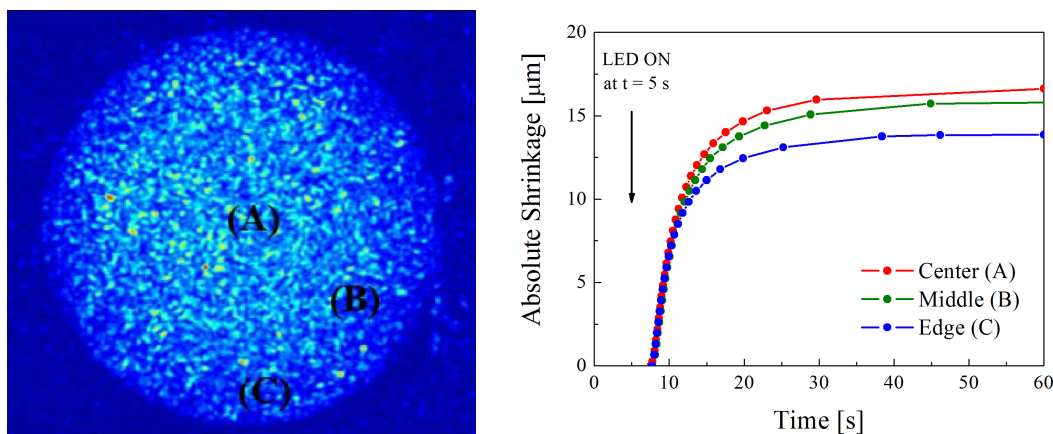

Figure 6: Processed signals from each scheme with labels for each point of interest. **Left:** Activity Speckle Pattern pseudo-colored image. **Right:** Shrinkage curves demodulated from Interferograms (see Fig. 2). LED irradiation started at *t = 5* s.

Both speckle image and shrinkage curves offer several issues of interest: the entire sample being photocured initiated shrinkage at the same time, but net volume contraction was not equal because it depended on the irradiation level. This fact is clear from the map of colors in speckle image, and quantitatively well determined by FI sensor (Table 1). It is remarkable the sensitivity of this method, taking into account that the contraction profile barely differed (about ~3 microns between the edge and the center). In addition, since the FI sensor allowed continuous monitoring of shrinkage (i.e. the interferometer cavity formed between the end fiber optic tip and the surface resin), it was possible to show the profile of polymerization shrinkage dynamic as a function of curing time (Fig. 6, right).

It is worth mentioning that shrinkage variation detected by our methods could be directly linked to the blue light source. In effect, LED irradiation was not uniform over the whole length of the sample. In Fig. 7, a plotting of typical LED distribution measured at our laboratory, enabled observing that points in the sample at the center received more photons per unit of time as it vanished toward the borders following an approximately gaussian distribution. The overall contraction along the sample exhibited a quasi-linear relation, as expected. Thermal effects by Joule heating could reach an increase 1-2 ºC due to the LED device and hence it was not significant in the scope of our study [31].
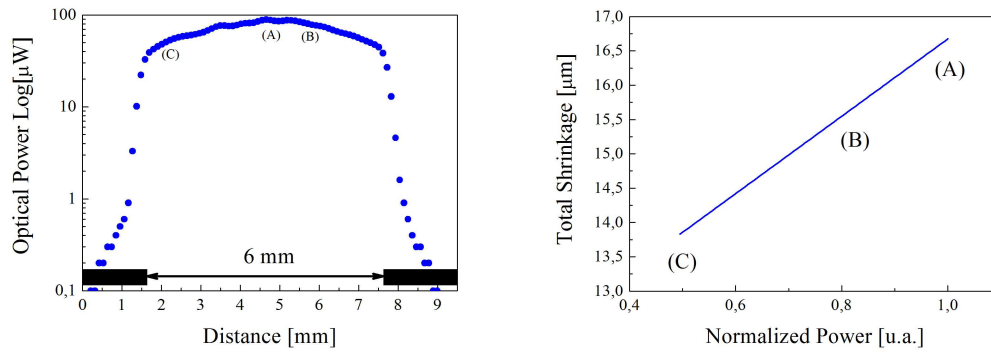
Figure 7: Left: Blue LED irradiation profile at the resin samples. The rubber mould acts as a mask that blocks light further its aperture diameter of about 6 mm. **Right:** Total shrinkage as a function of power intensities. In all cases, points **(A)**, **(B)** and **(C)** indicate where the speckle activity and absolute shrinkage were analyzed.

Sample point	Actual Thick (mm)	Net Shrinkage [μm]
Center **(A)**	1.2	16.64
Middle **(B)**	1.2	15.72
Edge **(C)**	1.15	13.81

Table 1: Total shrinkage registered by the Fiber Optic Fizeau Interferometer. Tolerances in readings: +/- 0.1mm for thickness, +/- 0.1 μm for shrinkage.
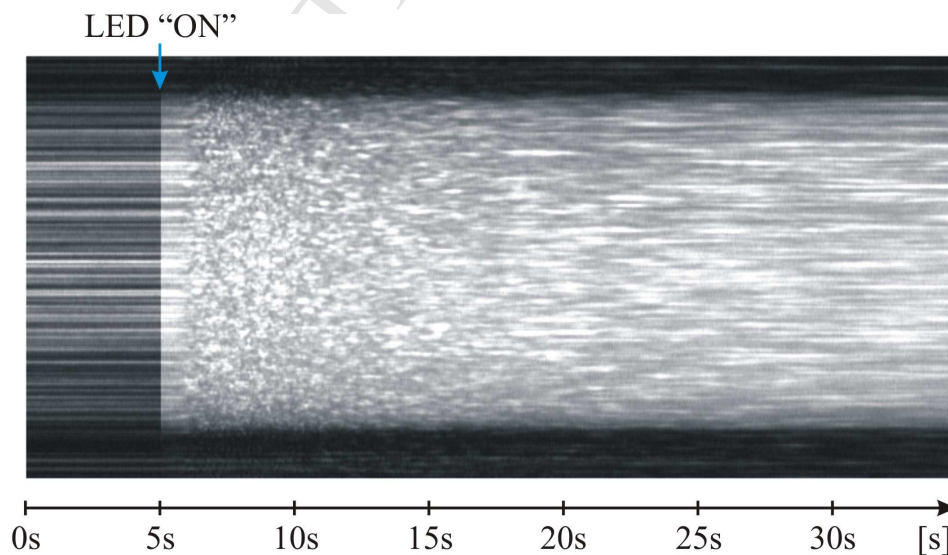

Figure 8. THCP image for 3M P60® sample corresponding to same set of images shown on the left of Fig 2.

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Fig. 8 shows a THSP image from 3M P60®. As it can be seen, no activity was registered before LED was turned on, and that may result clearly from the constant gray level pixels frame per frame resulting in horizontal lines. The same applies to the upper and lower zones representing the rubber mould borders. When light was on, the reaction initiated slightly later probably due to some inhibitor always present in commercial formulations. A high activity was present during the next 10-15 seconds that progressively decreased following the normal polymerization dynamics. Finally, the entire specimen became completely polymerized deductible by again a set of horizontal grey lines.

DSP and THSP applied to double-holed samples:

Figs. 9 and 10 show the same speckle techniques to the double mould experiment in order to compare both commercial and lab-made resins.
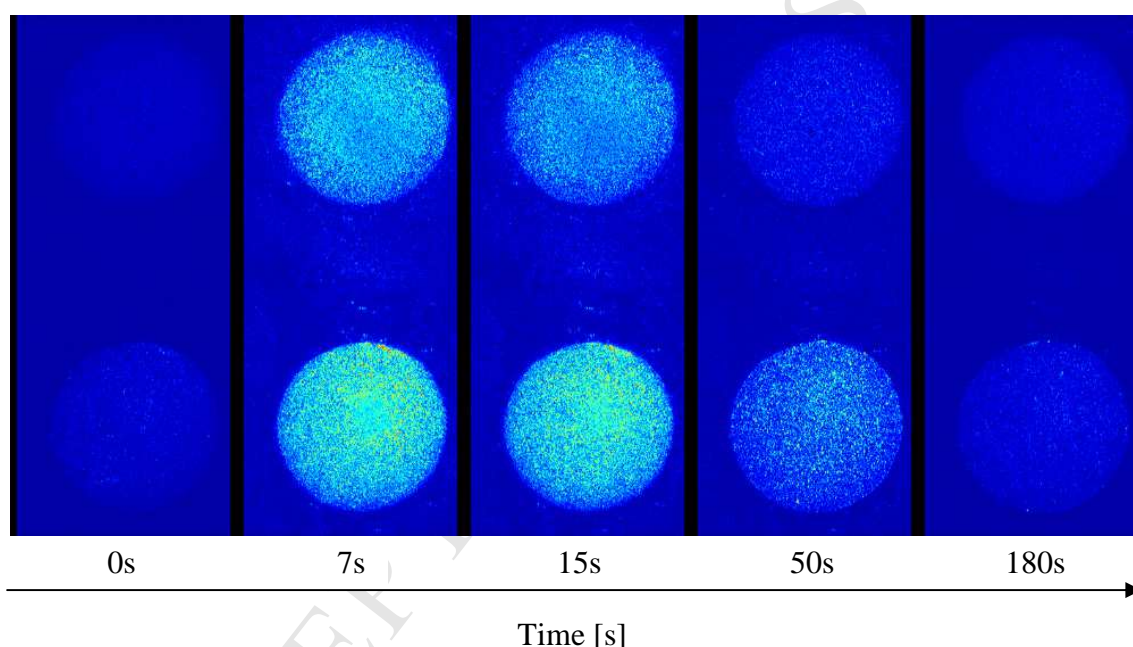

0s	7s	15s	50s	180s

Time [s]

Figure 9: Pseudocolored images extracted from the video generated with the dynamic range descriptor [25] for several moments of the double-holed photocuring reaction.

Fig. 9 shows pseudocolored images extracted from the video generated with the dynamic range descriptor applied to them, while in Fig. 10 some specific speckle images of the double-holed experiment are shown. The upper sample corresponds to 3M P60® resin while "B88" lab-made one is below.

Prior to the beginning of the photo-polymerization reaction, both samples speckle images appeared like each other and had almost null activity, evidenced by horizontal gray scale lines in Fig. 9 THSP (down) and mainly blue colored pixels in Fig. 9, for t=0s. As the LED started to

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irradiate, the speckle patterns increased in both cases with different dynamic: 3M P60® reached a vitreous state in less time than "B88" due to its formulation. In comparison to commercial 3M P60®, B88 has only glass nanoparticles and thus the polymeric reaction is more energetic, requires more time and often delivers more heat. Images (t=7s to t=50s) in Fig. 9 offer, easily and simply, the same information as a "2D" representation, while THSP denotes again that polymerization was not uniform over the entire sample. Finally, for t>150s no activities were present over the samples, i.e. horizontal gray scale lines in THSP and deep blue pseudocolored samples in Fig. 9. At this point, both resins reached the vitreous (glassy) state and hence no significant shrinkage further occurred. Complementary information could be useful from double THSP in Fig. 10.
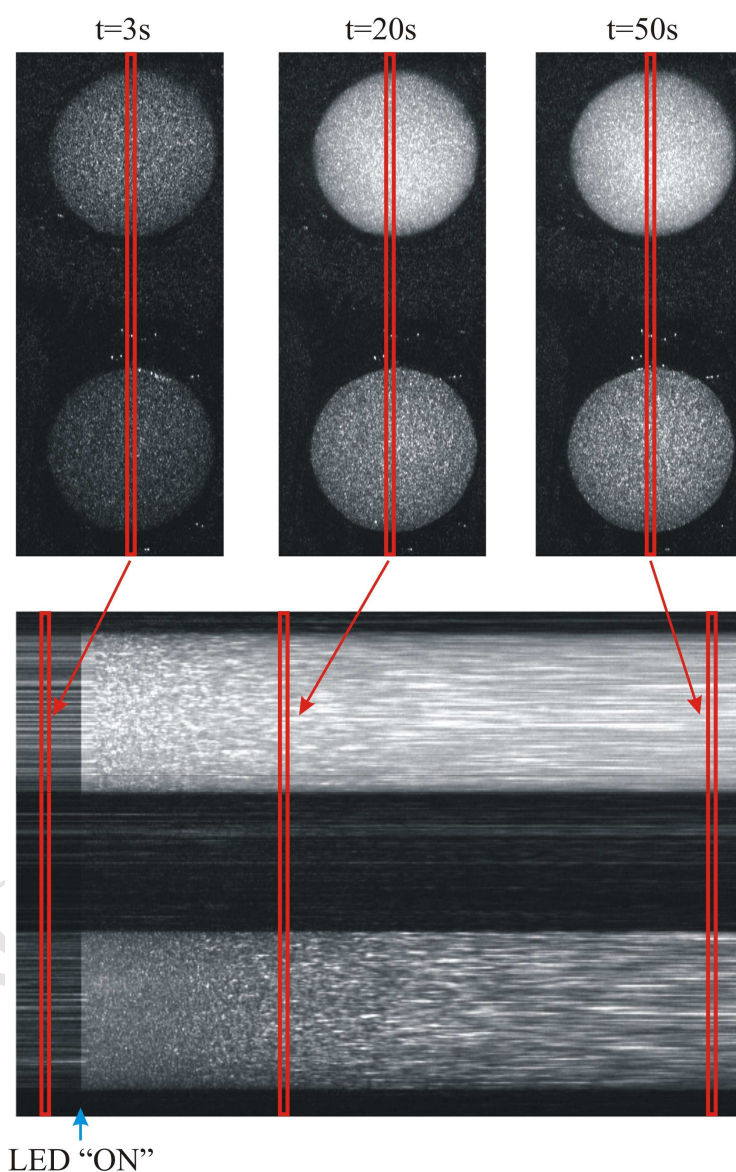

Figure 10. Up-Left: Images from samples as being cured before switching on LED, tens of seconds after photocuring initiation (slightly left from the middle) and about one minute later. **DOWN:** corresponding THSP for this experiment.

It is worth mentioning some other interesting considerations: commercial specimen began to contract to its full extent at a later time after the initiation of photocuring stage. This is probably related to some inhibitor (i.e. unknown part of the commercial formula), which must be consumed prior to allowing polymerization to occur. However, this lag is also due to a kind of inertia proper to the phenomenon of contraction itself, considered in its total volume.

Furthermore, the extent of shrinkage was obviously smaller for points far from the center. It is also remarkable the range of values being considered (only microns), and high resolution of both methods. While the dynamic speckle provided visible differences throughout the sample at a glance, the Fiber Optic Fizeau Interferometer offered quantified values at each point with submicrometer resolution.

Although polymeric reaction is an exothermic process, heating of samples is always expected. If that were the case, all the considerations and assumptions made here remain correct. Anyway, as it was mentioned before, a customer of the resin used here has minimized the impact on this issue. Certainly, we had recorded typical temperature rises close to 20-30 degrees, in earlier studies [31].

Conclusions

The THSP and dynamic range descriptor are very simple techniques and their implementation in an integrated circuit is really easy so in the future we will try to develop an instrument that could follow the photocuring reaction in real This will contribute to optimize the formulations of dental resins in order to fulfill the requirements of dental practice. With this set of optical techniques, we have demonstrated that it is possible to correlate various aspects of the photopolymerization reaction by joining their main abilities to characterize the entire sample under test. The Fiber Optic Fizeau Interferometer measurements provide quantitative information, while the assessment of dynamic speckle images gives invaluable qualitative information that, conveniently processed, allows points of agreement. It is emphasized that both methods are non invasive with high resolution, giving the specialist researcher a powerful tool that allows him to promptly reach useful conclusions. This method can be implemented with a variety of optical elements readily available, with a moderate degree of complexity on the experimental side.

Acknowledgments

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Figure Captions

Figure 1: Structures of monomer and photoinitiator used in this study

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