Photothermal radiometric determination of thermal diffusivity depth profiles in a dental resin

P. Martínez-Torres¹, A. Mandelis² and J. J. Alvarado-Gil¹

¹Department of Applied Physics, CINVESTAV-Unidad Mérida, Antigua Carretera a Progreso Km. 6, 97310, Mérida, Yucatán, México.
²Center for Advanced Diffusion-Wave Technologies (CADIFT), Department of Mechanical and Industrial Engineering, University of Toronto, 5 King’s College Road, Toronto, Ontario, M5S 3G8, Canada.

E-mail: jjag@mda.cinvestav.mx

Abstract. The depth of curing due to photopolymerization in a commercial dental resin is studied using photothermal radiometry. The sample consists of a thick layer of resin on which a thin metallic layer is deposited guaranteeing full opacity of the sample. In this case, purely thermal-wave inverse problem techniques without the interference of optical profiles can be used. Thermal profiles are obtained by heating the coating with a modulated laser beam and performing a modulation frequency scan. Before each frequency scan, photopolymerization was induced using a high power blue LED. However due to the fact that dental resins are highly light dispersive materials, the polymerization process depends strongly on the optical absorption coefficient inducing a depth dependent thermal diffusion in the sample. It is shown that using a robust depth profilometric inverse method one can reconstruct the thermal diffusivity profile of the photopolymerized resin.

1. Introduction

In recent years photothermal techniques have been applied successfully to the nondestructive study of broad classes of materials [1]. Specifically, photothermal radiometry (PTR) is one of the most important non-contact remote nondestructive thermal-wave sensing techniques. Reconstruction methodologies based on photothermal techniques have been extensively used with various systems since the development of a thermal diffusivity depth profiling algorithm based on the concept of Hamilton-Jacobi thermal harmonic oscillator [2]. One such application is the non-destructive evaluation of case hardness in steels under different heat treatments [3]. Recently novel dental resins have been developed which can be cured with blue light, exhibiting low shrinkage during the photopolymerization process [4]. One of the most popular techniques to characterize the degree of polymerization of those dental resins is hardness testing. Several authors have found that the tested cured composite resins present gradual decrease of microhardness as depth increases and this decrease is more evident for depths beyond 2 mm [5].

In this paper the thermal diffusivity depth profile of partially cured dental resins is studied using PTR. The samples were coated on one side with an opaque thin layer of gold. Thermal waves were induced on the sample through illumination of this coating with a modulated light source. Photopolymerization was induced upon illumination of the opposite (non-coated) side with non-
modulated blue light. A one dimensional depth reconstruction model for an opaque sample was used to obtain the thermal diffusivity as a function of depth. It was found that thermal diffusion is extremely sensitive to the degree of curing in the resin.

2. Materials and Methods
The experimental frequency-domain PTR system is shown in figure 1. A 20-W laser modulated at frequency $f$ using a high power laser driver was focused onto the sample surface. The infrared radiation emitted by the optically excited sample surface was collected and collimated by two paraboloidal mirrors and then focused onto a liquid-nitrogen-cooled HgCdTe detector. The detector had an active area of 1 mm$^2$ and spectral bandwidth of 2–12 µm. An antireflection coated germanium window with a transmission bandwidth of 2–14 µm was mounted in front of the detector to block any radiation from the laser. The PTR signal was sent to a SR830 digital lock-in amplifier. The lock-in amplifier received and demodulated the preamplifier output, provided amplitude and phase of the PTR signal that was recorded as a function of frequency in a PC. Frequency scans from 4 to 800 Hz with a laser beam size of 5 mm were performed on the dental resin composite samples before curing and after partial curing. The laser spot size was expanded in order to generate one-dimensional thermal-waves.

A commercial dental resin (Alert Condensable Composite, shade A3) manufactured by Pentrol Clinical Technologies, LLC, was used for the reconstruction of the thermal diffusivity depth profile. The resin composite samples were packed into a cylinder 1 cm of diameter and 2 mm high. A glass slide was placed on top and bottom surfaces of the cylinder and gentle pressure was applied to force excess resin material to overflow and obtain flat surfaces. Then, the glass slides were removed and one of the flat surfaces of the sample was gold coated by sputtering deposition until films ca. 100 nm thick were obtained. The gold coated samples were mounted on the PTR system to obtain the thermal profiles in the backward emission configuration. First a frequency scan of un-polymerized sample was performed. Afterwards, the partial polymerization of the dental resin was induced by applying 30 mW/cm² of a high power blue light LED (457 nm) for 3 min on the opposite surface of the gold coating. This UV light was partially absorbed when going through the resin generating a gradual spatial profile of polymerization in the sample. A new frequency scan in the same frequency range as the intact sample was done for the partially polymerized sample.

![Figure 1. Schematic diagram of the PTR experimental setup.](image)

3. Theory
The thermal harmonic oscillator formalism used for the inverse problem methodology of depth profiling of inhomogeneous solids with arbitrary continuously varying thermal diffusivity profile was developed by Mandelis et. al. [2]. Considering that the curing light enters into the sample on the opposite face of the substrate, and that the light is partially absorbed by the resin producing an inhomogeneous system, it is reasonable to assume that a gradual change in the thermal diffusivity is
generated (in addition to a similar change in the optical properties; however the present work involves
only the thermal property profile probed from the coated side).

It is assumed that the thermal diffusivity follows a simple functional dependence of the form
\[ \alpha_s(x) = \alpha_0 \left( 1 - \Delta e^{-x} \right)^2, \]
with \( \Delta = 1 - \left( \frac{\alpha_0}{\alpha_\infty} \right)^{\frac{1}{2}} \) (1)
such that \( \alpha_\infty = \alpha_s(\infty), \alpha_0 = \alpha_s(0) \). \( q \) is a constant that determines the rate of thermal diffusivity growth for \( \alpha_0 < \alpha_\infty \), or decay for \( \alpha_0 > \alpha_\infty \). This arbitrary profile is there only for convenience purposes and its coefficients can vary with frequency so as to give best fits to experimental data curves. Using the superposition principle in solving the thermal-wa ve boundary-value problem and constraining the resultant expression for different boundary conditions, the surface temperature of a semi-infinite inhomogeneous medium has been shown to be
\[ T(0, \omega) = \frac{Q_0}{2\sigma_j k_0} \left[ 1 - \frac{1}{4} R_\infty \exp(-\sigma_\infty J_\infty) \right] \]
where
\[ J_\infty = \frac{1}{2q} \ln \left( \frac{\alpha_\infty}{\alpha_0} \right), \quad R_\infty = \frac{k_0 \sigma_\infty}{k_j \sigma_\infty}, \quad \sigma_\infty = (1 + i) \frac{\omega}{2\alpha_\infty} \] (3)
\( k_0 \) is the thermal conductivity of the surface layer, \( Q_0 \) is the incident heat flux, \( \sigma_\infty \) is the complex wave number and \( \omega = 2\pi f \) represents the angular modulation frequency. The theoretical values of amplitude and phase are calculated with
\[ T(0, \omega) = \left| A(\omega) \right| e^{i\phi(\omega)}, \]
where \( A(\omega) \) is the thermal-wave amplitude and \( \Delta \phi(\omega) \) is the phase at angular frequency \( \omega \). At each modulated frequency, the PTR amplitude and phase are used to calculate \( (\alpha_\infty, q) \) using Eqs. (2)-(4), where \( \alpha_0 \) represents the known bulk thermal diffusivity before curing. The actual profile is updated at each frequency by recalculating new parameters of \( \alpha_\infty \) and \( q \). Arbitrary depth profiles may be reconstructed by numerically determining the optimal pair of \( \alpha_\infty \) and \( q \) so that the reconstructed profile results in the experimentally observed thermal-wave signal amplitude and phase data. Therefore at each \( \omega_j \), a system of two equations and two unknown parameters is solved. The detailed description of the inversion method can be found elsewhere [2].

4. Results and Discussion

Figure 2 shows the PTR signal amplitude ratio and phase difference of the partially cured sample normalized with respect to the signal before curing in order to eliminate the detector response. Variations in this amplitude ratio and phase difference with frequency are related to the change in the thermal diffusivity with depth due to the inhomogeneous degree of polymerization in the sample. Visual inspection showed that before curing the sample surface was smooth and the distribution of the packing dental resin into the holder-sample was uniform. The lower frequency limit was dictated by the requirement that heat diffusion in the sample is one-dimensional (non lateral effects are taken into account) and the upper limit was set so that surface effects would not interfere with the measurement.

Before normalizing, each experimental frequency response curve was smoothed, fitted with a ninth degree polynomial. Using this result, a set of 700 points in the same frequency range was generated. Smoothing is necessary for eliminating noise and reducing the effects of random errors, because the algorithm used to obtain the thermal diffusivity depth profile is very sensitive to the signal-to-noise ratio [2]. Using the transmission-PTR-measured thermal diffusivity of the bulk dental resin before curing \( (\alpha_0 = 0.0027 \text{ cm}^2\text{s}^{-1}) \), it was possible to reconstruct the thermal diffusivity depth profile of the partially cured samples, figure 3. As can be seen, when the depth varies from 10 to 130 \( \mu \)m, both reconstructed thermal diffusivity profiles first decrease, then increase with depth. The increased bulk diffusivity can be related to a decrease in monomer density (low diffusivity) and a consequent increase of the polymeric chains (higher diffusivity) due to curing induced by the blue UV light which was shone from the opposite side [6]. However, the minima observed at ca. 20 – 30 \( \mu \)m from the coated
surface, figure 3, are most likely due the fact that this surface is highly reflective and a higher curing blue light fluence is trapped than the bulk causing a local maximum in polymeric chain density (and the concomitant higher diffusivity) in the immediate vicinity of the coating.

Figure 2. (A) Normalized PTR signal amplitude. (B) Normalized PTR signal phase for a typical sample partially cured.

Figure 3. Thermal diffusivity as a function of depth for partially cured dental resin samples.

5. Conclusions
We have shown the ability of PTR to evaluate the photopolymerization of dental resins by a curing UV light and its potential as a noncontact, nondestructive quality control methodology for near surface evaluation of the curing process. From the PTR measurements of gold coated dental resin samples in the back-scattering configuration, we reconstructed the depth profiles of the thermal diffusivity of the cured resin, using the one-dimensional thermal harmonic oscillator inversion technique up to a depth of 120 μm. The profiles were found to be consistent with the known physics of resin polymerization and the creation of long polymeric chains from the shorter monomers.

References
[1] D Almond and P Patel, Photothermal Science and Techniques (Chapman and Hall: London, 1996).
[2] A Mandelis, S B Peralta, Jan Thoen 1991 J. Appl. Phys. 70 1761
[3] M Munidasa, F Funak, and A Mandelis 1998 J. Appl. Phys. 83 3495
[4] K Kyu-Choi, J L Ferracane, T J Hilton, D Chaklton 2000 J. Esthet. Dent. 12 216
[5] J C Ciccone-Nogueira, M C Borsatto, W C Souza-Zaroni, R Pereira Ramos and R G Palma-Dibb 2007 J. Appl. Oral. Sci. 15 305
[6] J P Fouassier, Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications (Cincinnati, OH: Hanser Gardner, 1995)