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Simultaneous measurement of polymerization stress and curing kinetics for photo-polymerized composites with high filler contents

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ABSTRACT

Objectives. Photopolymerized composites are used in a broad range of applications with their performance largely directed by reaction kinetics and contraction accompanying polymerization. The present study was to demonstrate an instrument capable of simultaneously collecting multiple kinetics parameters for a wide range of photopolymerizable systems: degree of conversion (DC), reaction exotherm, and polymerization stress (PS).

Methods. Our system consisted of a cantilever beam-based instrument (tensometer) that has been optimized to capture a large range of stress generated by lightly-filled to highly-filled composites. The sample configuration allows the tensometer to be coupled to a fast near infrared (NIR) spectrometer collecting spectra in transmission mode.

Results. Using our instrument design, simultaneous measurements of PS and DC are performed, for the first time, on a commercial composite with $\approx 80\%$ (by mass) silica particle fillers. The *in situ* NIR spectrometer collects more than 10 spectra per second, allowing for thorough characterization of reaction kinetics. With increased instrument sensitivity coupled with the ability to collect real time reaction kinetics information, we show that the external constraint imposed by the cantilever beam during polymerization could affect the rate of cure and final degree of polymerization.

Significance. The present simultaneous measurement technique is expected to provide new insights into kinetics and property relationships for photopolymerized composites with high filler content such as dental restorative composites.

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1. Introduction

Photopolymerized composites are widely used in applications ranging from electrical and optical materials, structural materials, coatings and adhesives, to various biomedical applications such as dental restoration. Photopolymerization exhibits several advantages over other polymerization techniques, including excellent spatial and temporal control, fast curing rates under ambient conditions, and solvent-free processing (non-toxic/green) [1]. As monomers polymerize to form covalent bonds during the curing process, the volume of the resulting polymers can contract by significant amount, *e.g.* as high as 12% of the volume contraction for dental resins [2]. Increasing the size or molecular mass of monomers, incorporating a larger amount of fillers, and tuning the reaction kinetics are some of the strategies to mitigate the adverse effects of polymerization shrinkage [2]; however, no approaches have been shown to fully eliminate polymerization shrinkage [3]. Further, enormous polymerization stress (PS) can develop for materials that shrink by as little as 1% owing to the high modulus of these materials and can reduce the overall material performance. For example, in polymeric dental composites, considerable PS can develop at the tooth-composite interface that may lead to debonding, further tooth decay at the interface, and/or cracking of the tooth [4]. In coatings and adhesives, stress generated may lead to surface cracking and debonding. One of the common features in photopolymerization processes is that gelation can take place very fast, *e.g.* less than a second under a high-intensity irradiation condition. Therefore, it is important to accurately follow the curing kinetics of such fast reactions for a better assessment of the performance of monomers, as well as understanding and controlling the curing process. The object of this study is to introduce new instrumentation that can continuously monitor the development of PS and curing kinetics in real-time for polymer composites with filler content as high as $\approx 80\%$ by mass during photo-cure processing.

Polymerization shrinkage and stress are dictated by complex interplay among several factors, including curing kinetics (normally characterized by the degree of conversion, DC), development of resin shrinkage and modulus associated with DC, sample dimensions, and external constraint [5,6]. Although there is generally a correlation between DC and PS, for practical purposes, DC is rarely used as a parameter to reduce PS since DC also correlates with other important material properties, *e.g.* mechanical properties [7], wear resistance [8], and the amount of leachable components [9]. Several methods have been developed to characterize PS for photopolymerized materials, including stress-strain-analyzers [10], universal testing machines (with an extensometer) with almost zero compliance [11], single cantilever devices with fixed compliance [12], and cantilever beam-based instruments (a tensometer) with adjustable compliance [13,14]. To understand reaction kinetics and PS development, it is necessary to measure these properties simultaneously. It is known that slight changes in sample configuration, irradiation, or instrumental compliance can greatly affect the properties of complex photo-polymerizable systems. Therefore, there is a strong desire to combine these measurements for the same

sample. To this end, Hsu et al. have demonstrated that Fourier Transform (FT) mid-infrared (mid-IR) spectroscopy can be coupled with a miniature cantilever system to effectively measure PS and DC simultaneously for photo-curing coatings [15]. In their study, FT-IR was collected in reflection mode; therefore, only the immediate surfaces (top few microns) were measured [16]. Later, near-IR (NIR) spectroscopy was shown to be capable of measuring double bond conversions in bulk samples in transmission mode. NIR exhibits lower molar absorptivity compared with the fundamental bands in the mid-IR region and shows two distinct peaks (6165 cm^{-1} and 4743 cm^{-1}) for C=C bond [17]. Lu et al. [18] showed that PS and DC for a limited range of composites could be determined simultaneously by combining NIR spectrometry with a tensometer. In that study, the dynamic range of the materials was limited by the instrument design (rigid beam), which reduced the sensitivity and accuracy of the instrumentation [14]. This design also required a sample with diameter of $\approx 6\text{ mm}$, which was too large for accurate collection of transmission NIR at high filler contents due to the absorption and attenuation of the IR signal intensity. Using this instrument design, Lu et al. were able to measure composites with up to 30% by mass filler content [18–20]. Many practical applications use a significantly higher amount of fillers (as high as 80% by mass [21]) to improve the mechanical, tribological, and thermal properties of the materials [22].

In this study, a tensometer constructed according to our design criteria [14] was coupled to a high-speed data acquisition NIR spectrometer to enable real-time simultaneous measurement of PS and DC for highly filled polymer composites. Since temperature rise during photo-polymerization is usually a critical parameter in determining the applicability of the material, and reaction exotherm is also associated with the curing kinetics, the evolution of exothermic temperature is measured in parallel. Due to the existence of a vast number of monomer systems, studies related to methacrylate-based composites were chosen here. A capacitive displacement sensor and data acquisition devices/programs were incorporated in our tensometer system to improve the resolution and acquisition speed of the curing kinetics. Our results indicate that the simultaneous measurement can be performed on a model highly-filled composite ($\approx 80\%$ by mass) at a high acquisition rate in excess of 10 data points per second, which gives sufficient data to accurately evaluate curing kinetics from the inception of polymerization. This higher resolution instrument also provides additional insight of curing kinetics under different degrees of constraint (achieved by adjusting sample position along the cantilever-beam of the tensometer). The null hypothesis tested was that changing the degree of constraint would have no effect on the curing kinetics, reaction exotherm, and final degree of polymerization.

¹ Certain commercial materials and equipment are identified in this manuscript in order to specify adequately the experimental and analysis procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST) nor does it imply that they are necessarily the best available for the purpose.

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