The evolution of the longitudinal modulus during the photo-polymerisation of a bis-GMA/TEGDMA resin by pulsed photoacoustic technique

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Abstract. A pulsed photoacoustic (PA) technique was implemented to study the evolution of the longitudinal modulus, C_{11}, during the polymerisation of a methacrylate co-monomer system, induced by UV light. A laser pulse was used as a standard source of ultrasound waves to monitor the changes in the longitudinal velocity of the acoustic signal during the photo-polymerisation (PP) a bis-GMA/TEGDMA co-monomer system (70/30 %w/w) containing camphorquinone as photo-initiator, and N,N-dimethyl-p-toluidine as reducing agent. C_{11} was determined on real time conditions after irradiating the system for predetermined periods. The kinetics of the PP reaction was also studied by infrared spectroscopy in order to compare the evolution of C_{11} with the rate of conversion of the double bounds of the methacrylate groups. The evolution of C_{11} reflects the whole polymerisation process: The technique permits to determine the transitions of the resin during polymerisation from viscous to viscoelastic state and further to a glassy polymer.

1. INTRODUCTION

In general, dental composite resins are mostly based on mixtures of dimethacrylate monomers that cure rapidly by UV light (photo-polymerisation). The monomer of many restorative dental materials is 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (bis-GMA) because its molecular structure (aromatic rings) and hydrogen bond formation (with hydroxyl groups) promote sufficient strength after the material is cured. However, its handling during dental restorations was troublesome because of its high initial viscosity [1]. In order to increase resin fluidity TEGDMA has been mixed to the bis-GMA leading also to the formation of a three-dimensional network (by crosslinking) [2]. The PP reaction involves the conversion of the double bonds (C=C) of the methacrylate groups of the bis-GMA and TEGDMA by a free radical mechanism. The degree of conversion of these C=C ranges commonly from 50 to 85 %, however only part of them are used in crosslinking, others remain in side chains, affecting the mechanical response of the dental resin and reducing its hydrolytic resistance and colour stability.

The kinetics of polymerisation and the morphology of the resulting copolymers have been studied by different techniques such as: DSC, TMA, ultrasonic wave propagation [3, 4, 5], infrared, ^{13}C-NMR, and Raman spectroscopy [6, 7, 8], plasma light [9], impulsive stimulated thermal scattering (ISTS) where real-time measurements of elastic properties during polymer processing are possible with laser acoustic techniques [10], and others [11]. From these studies, it has been suggested that network formation proceeds in two steps. The first step is characterized by formation of microgels and the second step by connection among microgels, resulting in inhomogeneous

network morphologies. It has also been suggested that depending on the molecular weight and flexibility, microgellation can be preceded by cyclization of oligomers. Generally, cyclization is more effective during the first stage of cure while excluded volume effects operate in the second stage.

We studied the PP process of a typical bis-GMA/TEGDMA system, induced by UV irradiation, by pulsed PA and infrared techniques, on real time conditions, in order to analyze the evolution of the longitudinal modulus, C_{11}. The results were compared with those of conversion, as obtained by FTIR spectroscopy under similar real time conditions. We found that the evolution of the longitudinal modulus is closely related to both the conversion and the transitions of the resin from viscous to a viscoelastic state and further to the glassy state.

2. EXPERIMENTAL

The TEGDMA monomer, the camphorquinone (CQ) used as photo-initiator, the N, N,3,5-tetramethyl aniline (TMA) used as promoter (Sigma), and the bis-GMA monomer (Polysciences) were used as received. The CQ (0.2 % w/w) was dissolved in the bis-GMA and the TMA promoter (0.3% w/w) in the TEGDMA. The two parts were mixed at 70/30 %w/w proportion to form a homogeneous reacting mixture. A Q-switched Nd:YAG laser (Continuum) at 532 nm, 10 Hz, 7 ns duration, and pulse energy about 400 µJ, was used for generating the ultrasound waves. The diameter of the irradiated spot was about 1 mm. The PA signals were recorded from the beginning to the end of each reaction. The reacting mixture was poured into thin glass moulds ($22x15x2$ mm^3). The open face of the mould with the sample inside was aligned perpendicular to the optical line. The filled mould was prepared to receive the laser pulses by placing an Al foil on the resin surface. A piezoelectric sensor (PS, 5 MHz) attached a digital oscilloscope was placed into opposite face of the mould. The PP was induced with 468-480 nm UV light by using a dental lamp (Delux, 75 mW). An optical fibre ($\Phi = 8$ mm) was used to direct the UV light through the glass mold.

A typical measurement was done as follows: The sample is irradiated for one second with the UV light, and then the PA signals are registered until they no longer change, this procedure is repeated until the sample is completely cured. The changes in the time of flight were acquired from the PA signals and both the longitudinal velocity and C_{11} were determined as a function of reaction time.

The pulsed PA technique has been widely used to investigate the chemical and physical properties of many types of samples [12], in particular, the longitudinal velocity, V_L, in the PA mode, is defined as the ratio between the sample thickness, d and the time of flight, t, of the ultrasonic wave through the sample. When the sample surface is set perpendicular to the direction of propagation of the acoustic waves, the wave propagation is regulated by the longitudinal modulus, which is related to the compressibility (K) and shear (G) module by $C_{11} = K+(4/3)G$. For low damping solids, where the attenuation of the waves across the material may be neglected, C_{11} can be obtained from longitudinal velocity, V_L, and density ρ of the sample by the following approximation: $C_{11} = \rho V_L^2$. In this case, C_{11} corresponds to the stiffness of the system. The conversion of the Bis-GMA/TEGDMA system, under the same irradiation conditions set for the PA experiments, was determined by monitoring the double bonds as a function of reaction time by FTIR spectroscopy (Nicolet spectrometer, model 510P). The detailed procedure is reported elsewhere [6]. The experiment was developed on five samples.

3. RESULTS AND DISCUSSION

Figure 1a shows the evolution of the C_{11}, for a sample subjected to a single one-second UV light shot. C_{11}^0 is the initial longitudinal modulus (before UV light irradiation) of the viscous resin. The C_{11} profile shows first the transition from viscous to viscoelastic state (in about 3 min) and is characterized by a dramatic increase in C_{11} (up to 3 GPa). Then C_{11} increases at a slower rate until a stationary state is reached (in about 13 min) where C_{11} remains almost constant. At this point, a second transition from viscous to glassy state is observed. The reaction was re-activated by applying another UV light shot for one second. The rate increased again for about 1 min and C_{11} reached a maximum value (4 GPa).

To reach maximum conversion it was necessary to irradiate the sample with other five UV light shots of one second. The evolution of C_{11} under these conditions is shown in Figure 1b together with the conversion of double bonds, obtained by FTIR under similar conditions. It is worth to notice that the evolution of C_{11} and the conversion almost follow the same pattern: an initial dramatic increase in rate after the first UV light shot, C_{11} reaches about 75 % of its maximum value while the conversion is near 40%. Then both C_{11} and conversion orient to a stationary state. This first stage of the reaction is characterized by an acceleration followed by a de-acceleration [3]. After 4 UV light shots, in spans of 13 minutes, C_{11} reached a maximum value when the sample is in the glass state. Apparently, up to this point polymerisation was completed. However, the reaction progress very slowly up to the point at which the maximum in conversion is reached in a post-curing stage.
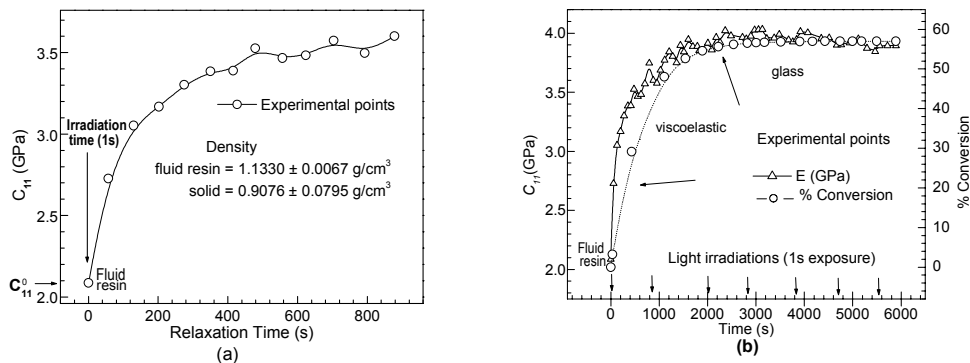

Figure 1. a) C_{11} evolution as a function of time by PA technique for a bis-GMA/TEGDMA sample 2 mm thick after a UV light shot of one second. b) Longitudinal modulus and conversion evolution during a whole PP process.

The details of the different stages shown by a bis-GMA/TEGDMA (70/60 %w/w) system can be found elsewhere [3]. Our concluding remark is that the PP reaction of a bis-GMA/TEGDMA system could be properly studied on real time conditions by pulsed PA. This work opens the possibility to study other PP reactions.

Acknowledgements

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