

***In-situ* photo-polymerization study of Si-(bis-GMA)/TEGDMA by correlations of PA signals**

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Abstract. The photo-polymerization reaction of Si-(bis-GMA)/TEGDMA (a bis-GMA modified with silyl groups and mixed with TEGDMA) has been studied by pulsed photoacoustic (PA) and FTIR techniques. The light from a pulsed laser is focused on the surface of the sample for both to activate the chemical reaction and generate PA signals. The *in-situ* acquisition of the PA signals, during photo-polymerization (PP), in consecutive way, permits to follow changes in its physical properties. The structural changes during polymer formation are recovered by a numerical procedure based on correlation coefficients r_i . This numerical procedure, applied to digitally recorded PA signals, allows the construction of a PP profile dr_i/dT_i , and permits to detect the phase transitions during the whole process including the gel region. The obtained results are in agreement with those obtained from the FTIR analysis, under similar conditions.

1. INTRODUCTION

Acrylic dental polymer networks are obtained by photo-polymerization, PP, of dimethacrylate monomers. During PP, two-phase transitions occur: Liquid to viscoelastic and viscoelastic to glass. 2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (bis-GMA) is widely used in dental composites because of its good mechanical properties [1]. However, its high viscosity makes difficult resin handling [2]. This problem is overcome by mixing bis-GMA with reactive diluents like TEGDMA: triethylene glycol dimethacrylate [3]. The resulting copolymer absorbs water after implantation. However, TEGDMA affects the mechanical properties [4]. To surpass this problem, bis-GMA has been modified by substituting its hydroxyl groups with silyl groups, $(\text{H}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{Si}-)$, as described elsewhere [5]. The resulting silylated monomer, Si-(bis-GMA), is used to prepare the photoactivated dental resin and to be able to study the PP reaction. A procedure to acquire the PA signals in real time conditions and to process the signals by using correlation coefficients is discussed. The pulsed PA technique has been used to find out the chemical and physical properties of the materials [6]. The pulsed laser light is used here for both to activate the chemical reaction and to follow *in-situ* the change in physical properties, measured through the variation of the time-of-flight Δ from PA signals as the reaction moves forward.

This numerical procedure, programmed in MathLab[®] and applied to the digitally recorded PA signals, is used for the construction of a PP profile dr_i/dT_i and also to visualize in graphic form the phase transitions during the PP process, including the gel region. Equation 1 relates PA signal with the optic-thermo-elastic parameters [7]. The laser pulses activate the reaction and the acquired signal is related to the absorption coefficient of the photo-initiator. The detected PA signal results from the non-irradiative process that takes place after excitation of the photo-initiator. Dividing the PA signal by the laser pulse energy E_o ,

$$X_i(t) = \frac{PA}{KE_o} = \left[\frac{\beta(T_i)}{\rho(T_i)Cp(T_i)} \right] (1 - 10^{-A}), \quad (1)$$

where K is the instrumental constant that includes the transducer response, β is the volume expansion coefficient, ρ is the density, Cp is the heat capacity, and the exponent A is the material absorbance. In our case, these optic-thermo-elastic parameters should be as a function of reaction time T .

The set of normalized time stories $X_i(t)$, $i = 1, 2, 3, \dots, M$, includes all phases developed during polymer formation. Here M is the number of signals acquired at successive times T_i as the reaction moves forward, until complete polymerization is reached.

To visualize the main transitions during the reaction, it is necessary to apply a numerical procedure to the digitally recorded PA signals in order to build the reaction profiles r_i and dr_i/dT_i .

The $\{X_i(t), T_i\}$ forms M pairs, namely $(X_1, X_1), (X_1, X_2), (X_1, X_3), \dots, (X_1, X_M)$. By holding (X_1, X_1) as the reference or initial condition ($r_1=1$) the serial correlation coefficient between X_1 and X_i is given by

$$r_i = \frac{\sum (X_1 - \bar{X}_1)(X_i - \bar{X}_i)}{\sqrt{\sum (X_1 - \bar{X}_1)^2 \sum (X_i - \bar{X}_i)^2}} \quad (2)$$

\bar{X}_1 is the mean of the first X_i or initial condition, and \bar{X}_i are the mean of the subsequent signals.

The serial coefficients, $\{r_i\}$, plotted against T_i yield a profile of the reaction trends and the transitions occurring during the reaction. In order to determine the transformation time range it is usually adequate to evaluate the numerical differentiation from r_i profile, dr_i/dT_i .

2. EXPERIMENTAL

Materials: Si-(bis-GMA), TEGDMA, camphorquinone (CQ) as photo-initiator, N,N,3,5-tetramethyl aniline (TMA) as promoter. The Si-(bis-GMA) (69.5%) is mixed with the CQ (0.2%) and TEGDMA (30%) with the TMA (0.3%). The mixture was poured in thin glass moulds.

The pulsed laser (Panther OPO, laser light tunable) features are wavelength 480 nm (UV), 10 Hz, 7 ns pulse width, and 3 mJ per pulse. The laser energy is measured by using a Joule-meter (Laser Precision). The diameter of the irradiated spot is about 4 mm. The output of a fast photodiode receiving a part of the laser beam is used to trigger the oscilloscope. The PA signal is detected with a small piezoelectric transducer at 5 MHz. The signals are recorded by a digital oscilloscope of 500 MHz (Tektronik TDS540D). Typical method: A train of 20 seconds of laser pulses is applied to the sample and the PA signal is averaged during this time, this procedure is repeated up to the end of the reaction.

The PP kinetic of Si-(Bis-GMA)/TEGDMA monitor by FTIR spectroscopy (Nicolet 510P-FTIR) by measuring the dimethacrylate double bonds conversion η as a function of T is analyzed. The sample is placed in the spectrometer and is illuminated with an optical fibre connected to a dental lamp (Delux, 200mW, $\lambda = 468-480$ nm). Typical method: After a one second UV-light pulse, the optical fibre is blocked. Then, a FTIR spectrum is obtained for about 40 s [8]. This procedure is repeated until the sample is completely polymerized.

3. RESULTS AND DISCUSSION

The polymerization kinetics is proportional to conversion of double bonds, η , and the viscoelastic behaviour can be related to conversion rate: $p = d\eta/dT_i$, [9]. The properties of the dynamic system are then proportional to the parameters η , p , (from FTIR) and Δ , r_i , dr_i/dT_i (from PA).

Figure 1 shows the behaviour of η and Δ during the PP, four stages are depicted. In Stage I, η raises rapidly because of chain growth. In Stage II, η continues increasing due to chemical crosslinking and the system turns heterogeneous because of macrogel formation. In Stage III, η increases slowly as expected because the macrogels bond, forming a homogeneous viscoelastic solid. In Stage IV, the material becomes a glassy polymer because of extensive crosslinking. Also, in Stage I the Δ increases with viscosity but in the following stages (II-IV) it decreases asymptotically because the elastic modulus raises as the PP proceeds.

The normalized profiles, p and dr_i/dT_i , vs. T are shown in Figure 2. Here, p takes the typical form; observe that its profile is similar to that of Δ in Figure 1. The profile of dr_i/dT_i indicates the stage transitions undergone by the reaction system in each stage (Figure 2).

Observe first the transition from viscous fluid to viscoelastic fluid (minimum in Stage II); second, the transition from viscoelastic fluid to viscoelastic solid (end to Stage II), including the critical region, p_c (gel region); third, the transition from viscoelastic to glass occurring at the end of Stage III, from that point dr_i/dT_i remains constant. Observe also that the time scale of each stage is the same in both figures.

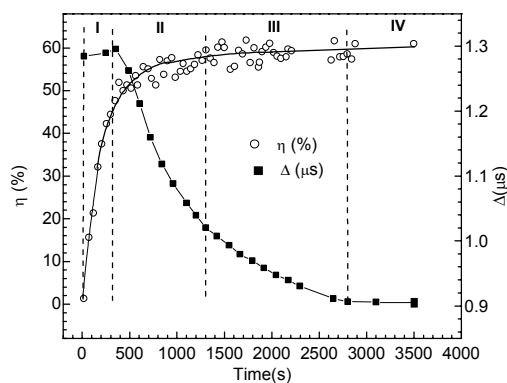


Figure 1. Variation of time-of-flight Δ , and conversion of double bounds η during the PP process.

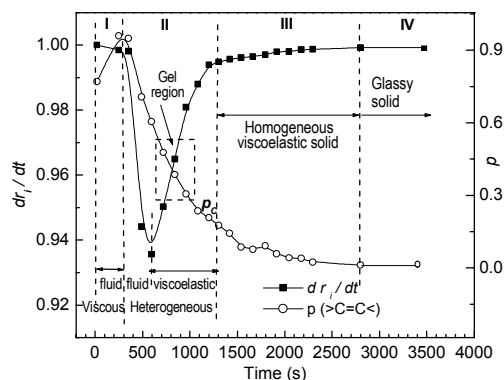


Figure 2. The dr_i/dT_i from r_i profile and evolution of conversion rate of double bonds p during the PP process.

4. CONCLUDING REMARKS

The photo-polymerization of Si-(bis-GMA)/TEGDMA has been studied by pulsed photoacoustic and FTIR techniques. The pulsed PA method is useful for studying *in situ* the PP process of bis-GMA. The PP of Si-(bis-GMA)/TEGDMA is characterized by two main transitions: Fluid to viscoelastic and viscoelastic to glass with the corresponding changes in physical properties. The photo-polymerization profile dr_i/dT_i permits to visualize the state transitions during the process including the gel region. These results are in agreement with the kinetic data obtained by FTIR under similar conditions.

Acknowledgements

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