

The Impact of Oxygen on Photopolymerization Kinetics

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The inability of free radical photopolymerizations to overcome oxygen inhibition has limited their applicability or forced the use of expensive inerting equipment. It is thus essential to understand the kinetics and mechanisms of oxygen inhibition to achieve successful products using free radical photopolymerizations. An unsteady-state, one-dimensional kinetic model that incorporates heat and mass transfer, and spatial effects was developed to study the effect of oxygen inhibition on free radical photopolymerizations. The effect of sample thickness and oxygen concentration on oxygen inhibition was analyzed using modeling and FT-IR spectroscopy. Additionally, the effect of dissolved oxygen concentration on the bulk mechanical properties of the polymer was studied.

Introduction

Photopolymerization of multivinyl monomers is a widely accepted and growing process.¹⁻³ Countless products are produced utilizing photopolymerization including paints, coatings, adhesives, inks, microelectronics, optical materials, dental resins, and more recently, three-dimensional stereolithography and holographic recordings.^{1-3,5-8} The extensive uses and applications of photoinitiated polymerization are due to its many advantages over other polymerization processes including that they are rapid, have reduced energy requirements, readily occur at room temperature, and are low cost.^{2,4,9} The polymerizations are spatially and temporally controllable as the initiating light is resolvable in both space and time, respectively.⁸ Additionally, the initiation rate is dictated by the choice of photoinitiator (*i.e.* its molar absorption coefficient, quantum yield, and efficiency), light intensity, and temperature. In photopolymerizations the monomer is often polymerized in bulk, eliminating the need for environmentally hazardous solvents. Finally, if multivinyl monomers are used, then crosslinking of the resulting polymer occurs, imparting unique physical properties to the product.⁶ Unfortunately, despite all of these benefits there still exist many limitations, including oxygen inhibition and attenuated penetration of the light source into the sample.¹⁰⁻²¹

The goal of this study was to improve the understanding of the inhibitory effect of oxygen on the photopolymerization of multifunctional monomers. Free radical photopolymerization transforms a multifunctional monomer into a crosslinked macromolecule by a chain reaction initiated by reactive species.¹ The initiating reactive species is formed by a photoinitiator absorbing the incident light and photocleaving into initiating radicals. The initiating radicals combine with available monomer, forming primary radicals that subsequently propagate through additional monomer units to create a three-dimensional polymer network.^{1,22,23} Unfortunately, molecular oxygen inhibits several steps in this reaction pathway, reducing the overall effectiveness of the polymerization.

Molecular oxygen is known to inhibit free radical polymerizations by reacting with initiator, primary, and growing polymer radicals to form peroxy radicals (Figure 1).^{16-18,24,25} The peroxy radicals are more stable and do not readily reinitiate polymerization, and thus, the oxygen essentially terminates or consumes radicals.⁸ If oxygen is present, an induction time will be observed since the polymerization cannot proceed until nearly all of the dissolved oxygen is consumed.⁸ At high concentrations or in very thin films, oxygen scavenges all of the radicals in the polymerization, and thus, inhibits or severely retards the polymerization. In thin

films, oxygen inhibition is more important as oxygen readily diffuses back into the sample. In thicker films, the lower depths of the film polymerize, while the top layer remains “tacky” as the oxygen inhibits the surface reaction. The unpolymerized top layer reduces surface and optical properties.^{18,26}

Several techniques have been utilized to combat the effects of oxygen inhibition. The use of high intensity irradiation sources increases the initiation rate by increasing the production of primary radicals such that it becomes much greater than their consumption by oxygen. Another alternative is to polymerize the samples in an inert environment, whereby the oxygen is eliminated from the polymerization^{18,25}. There are also several methods that include the addition of molecules to reduce the inhibitory effect of oxygen. Decker developed a method whereby the dissolved oxygen in a monomer system was consumed prior to and during polymerization using a dual-initiation method with the addition of an oxygen singlet generator and acceptor molecule.^{16,17} Furthermore, the addition of thiols and amines to monomer systems is known to decrease the deleterious effects of oxygen.^{25,27-29}

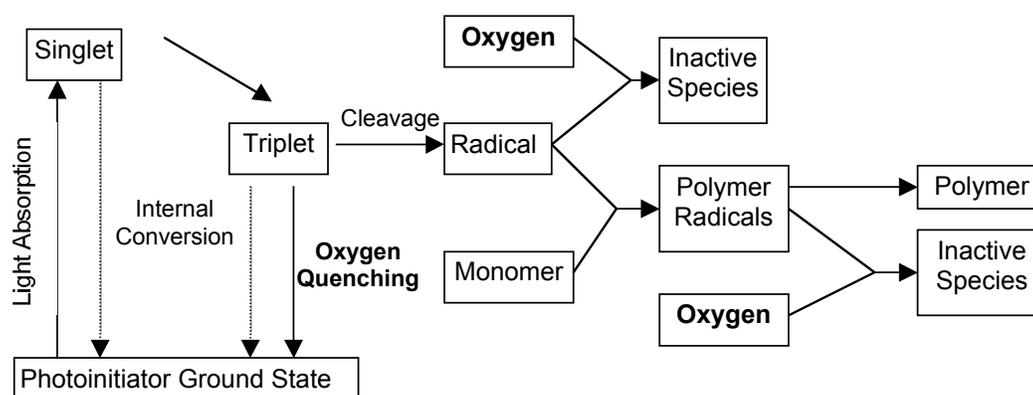


Figure 1. Different possible deactivation pathways of excited species (Scheme from Reference 1)

Due to the immense interest in and importance of the photopolymerization process, it is of great importance to understand fully the impact of oxygen on photopolymerization as a means to combat its inhibitory effects. Past research has documented the effect of oxygen, primarily focusing on the polymerization rate reduction.^{7,20,26,30,31} Additionally, Chong *et al.*²¹ and Krongauz *et al.*²⁰ developed early kinetic models that simulated specific effects oxygen had on photopolymerization kinetics. However, an extensive, in-depth study has not been conducted into the impact of oxygen on photopolymerization kinetics and the resulting polymer structure. Thus, in this study, a better understanding of the inhibitory effect of oxygen will be obtained through systematic experimental probing and comparison of experimental results with simulation prediction.

Procedure

Materials. The monomer used in this investigation was 1,6-hexanediol diacrylate (Aldrich, Milwaukee, WI, USA). The polymerizations were performed with the initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorne, NY). For the oxygen concentration determination procedure, dimethylantracene (DMA) and 5,10,15,20-Tetraphenyl-21H,23H-

porphine zinc (ZnTPP) were used (Aldrich, Milwaukee, WI, USA). All materials were used as received.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectroscopy (Nicolet Model 760 Magna Series II FTIR, Nicolet, Madison, WI) was used to obtain extents of polymerization and to examine the polymerization kinetics of the monomer systems studied. A horizontal transmission apparatus (HTA) accessory was used to enable mounting of the samples in a horizontal orientation for FTIR measurements. The HTA has a controlled polymerization atmosphere, thus allowing the samples to be exposed to nitrogen or various concentrations of oxygen. The monomer conversion was determined from the change in absorbance of the [C=C] double bond peak. In the mid-IR range this peak was at 1608-1647 cm^{-1} , and in the near-IR range the peak was at 6207-6122 cm^{-1} .

Irradiation. For FTIR spectroscopy experiments, a UV light source (Ultracure 100SS 100 Watt HG short-arc lamp, EFOS, Mississauga, Ontario, Canada) equipped with a liquid light guide and bandpass filter (365 nm) was used to irradiate the monomer mixtures.

Dynamic Mechanical Analysis (DMA). DMA (Perkin Elmer DMA7e, Norwalk, CT, USA) was performed to investigate the glass transition temperature and storage modulus in our polymer systems. The polymer samples were of uniform size (13.5 x 2.5 x 9 mm^3). DMA was performed over a temperature range of -30 - 150°C , with a ramping rate of $5^\circ\text{C}/\text{min}$ using extension mode (sinusoidal stress of 1 Hz frequency). Monomer samples were bubbled with argon, 1%, 5%, 10%, or 21% oxygen for 15 minutes and then immediately polymerized with $1\text{mW}/\text{cm}^2$ while monitoring the conversion with near-IR spectroscopy.

Ultra-Violet Visible Spectroscopy (UV-Vis). UV-Vis spectroscopy was used to obtain the extent of consumption of DMA to determine the equilibrium oxygen concentration in the monomer. The UV-Vis spectrometer (Perkin Elmer Lambda 40 UV/Vis Systems, Perkin Elmer, Shelton, CT) monitored the DMA absorption at 380nm during the reaction of singlet oxygen and DMA to form a complex.

1-D Comprehensive Photopolymerization Model. A 1-D unsteady-state, one-dimensional kinetic model that incorporates heat and mass transfer, and spatial effects was previously developed.^{32,33} The model was applied in this study to further investigate experimental systems using the experimental parameters and environmental conditions in the simulation.

Results and Discussion

Several variables that affect the extent to which oxygen inhibits free radical photopolymerization are of interest to study. These include varying the initiation rate, oxygen concentration, and sample thickness. However, to study these effects, we must be able to quantify experimentally both the oxygen concentration in our monomer system, as well as our sample thickness. Thus, initial work focused on developing methods to quantify these variables.

A photochemical method was employed to determine the equilibrium oxygen concentration in HDDA in environments with varying oxygen concentration.³⁴ The chemical scheme, in Table 1, used excited ZnTPP to convert the dissolved oxygen into the excited

singlet state, then trapped the singlet oxygen using DMA. By monitoring the conversion of the DMA into its complexed peroxide form at 380 nm with UV spectrophotometry, the concentration of the dissolved oxygen was determined. The DMA conversion is directly proportional to oxygen concentration, and thus Figure 2 shows the data for the equilibrium dissolved oxygen concentration in environments with 21, 15, 10, 5, and 1% oxygen.

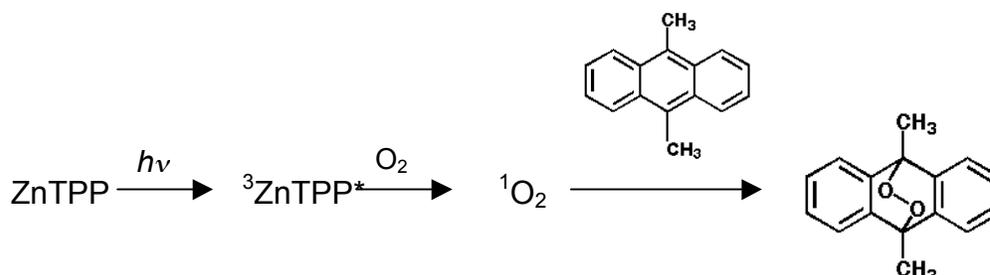


Table 1. Photochemical scheme used to determine the equilibrium oxygen concentration in monomers.

A method was developed to determine the film thickness by producing a calibration curve correlating the film thickness to the acrylate carbon-carbon peak area. Films of known thickness were produced using plastic shims, then the peak area monitored using FTIR spectroscopy. Figure 3 shows the calibration curve obtained.

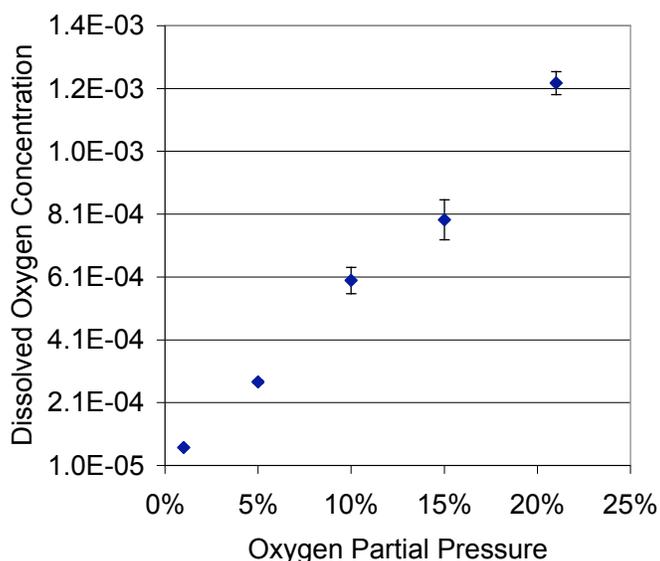


Figure 2. Equilibrium dissolved oxygen concentration in 1,6-hexanediol diacrylate (HDDA) at different atmospheric partial pressures of oxygen. (Averaged over 4 runs, with a $K_H = 5.7 \times 10^{-3}$ mol/L atm)

Using this information, we were able to describe and investigate fully the effect of oxygen concentration, as well as sample thickness on the impact of oxygen inhibition. Figures 4 and 5 show that as sample thickness increases, the overall monomer conversion also increases. This result is an artifact of the experimental method, as FTIR spectroscopy reads an average absorbance throughout the film. Thus, in reality, the top layer of each film still remains largely unpolymerized due to the constant flux of oxygen into the sample. However,

the thicker the film, a greater percentage of the film has less oxygen diffusing into it, and thus more polymerization occurs. Therefore, the overall average conversion in the film appears higher.

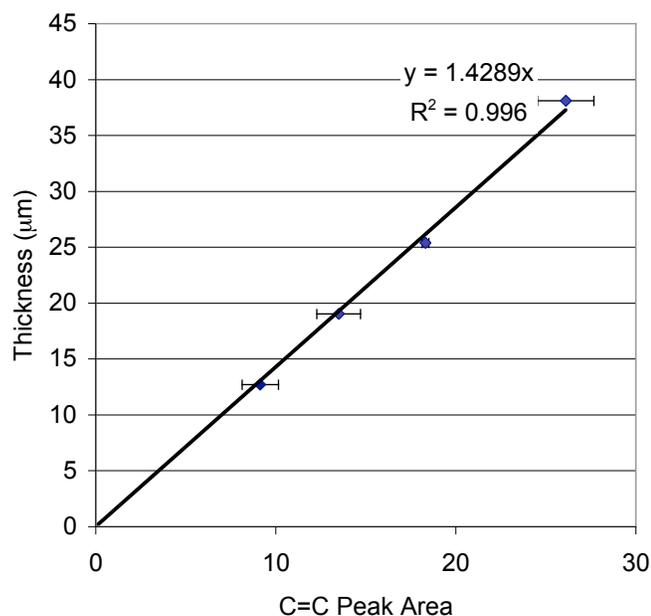


Figure 3. Calibration curve for sample thickness versus C=C peak area (peak region: 1648.866 cm^{-1} , 1604.511 cm^{-1}) for HDDA. (Averaged over 6 runs)

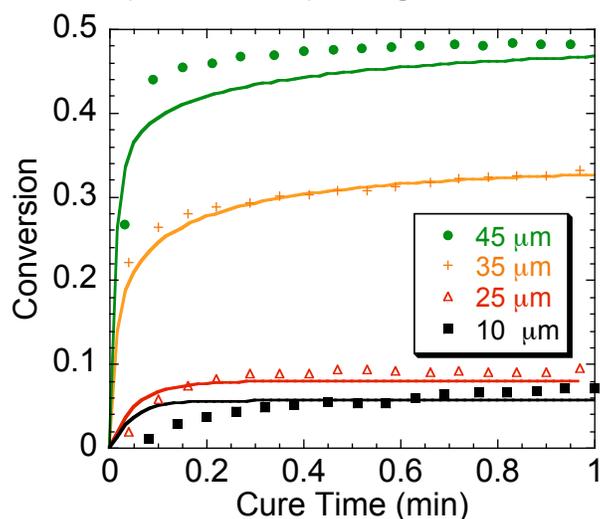


Figure 4. Conversion versus cure time for non-laminate films of HDDA with 0.1 M DMPA, and irradiated with 30 mW/cm^2 in air. The solid lines represent model predictions, and the data points represent data obtained with FTIR spectroscopy.

Additionally, Figures 5 and 6 show the effect increasing oxygen concentration has on the inhibition of the polymerization. Since oxygen is first order in the inhibition reaction, as oxygen concentration is increased, not only will the rate oxygen consumes radicals proportionally increase, but the amount of radicals necessary to consume all of the oxygen increases. This feature results in an increased inhibition time, reduced polymerization rate, and reduced conversion. Figure 6 shows the inhibition time of HDDA in air for varying initiator

concentrations. As the initiator concentration is increased, the inhibition time decreases due to the increase in initiation rate. This result is important, as the polymerization cannot begin until the polymerization rate competes with the inhibition rate. The majority of the oxygen must be consumed before polymerization proceeds as the inhibition rate constant is $\sim 10^6$ greater than the propagation constant.

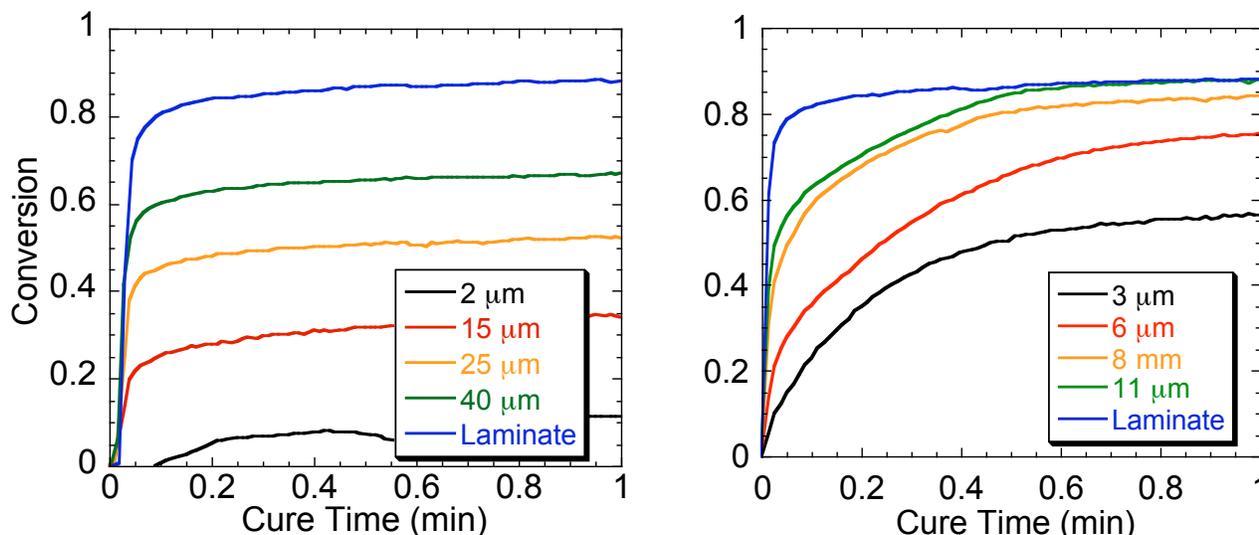


Figure 5. Conversion versus cure time for non-laminate films of HDDA with 0.1 M DMPA, and irradiated with 30 mW/cm². The left graph is in a 5% oxygen environment while the right is in a 1% oxygen environment.

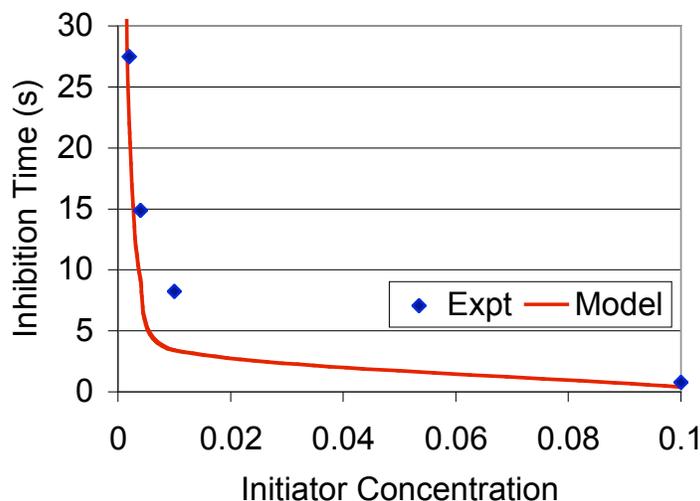


Figure 6. Inhibition time versus initiator concentration for HDDA with DMPA samples equilibrated with air then laminated. Model simulations are shown by the line, and experimental data by points. The samples are 15 μm thick, and were irradiated with 5 mW/cm².

Furthermore, the effect of the initial dissolved oxygen concentration on the resulting polymer structure was investigated. Figure 7 shows that as the initial oxygen concentration was varied from 0- 10^{-3} M, no significant difference in the glass transition temperature or storage modulus was observed. This result can be explained by the fact that any radicals produced in

the beginning of the polymerization will very rapidly consume the initial oxygen present in the monomer. The peroxy radicals subsequently formed will not propagate and will remain short-chained species. The concentration of these short-chained peroxy radicals will be no greater than the 10^{-3}M , much less than the final concentration of polymer chains. Thus, their effect on the final mechanical properties of the polymer should be negligible.

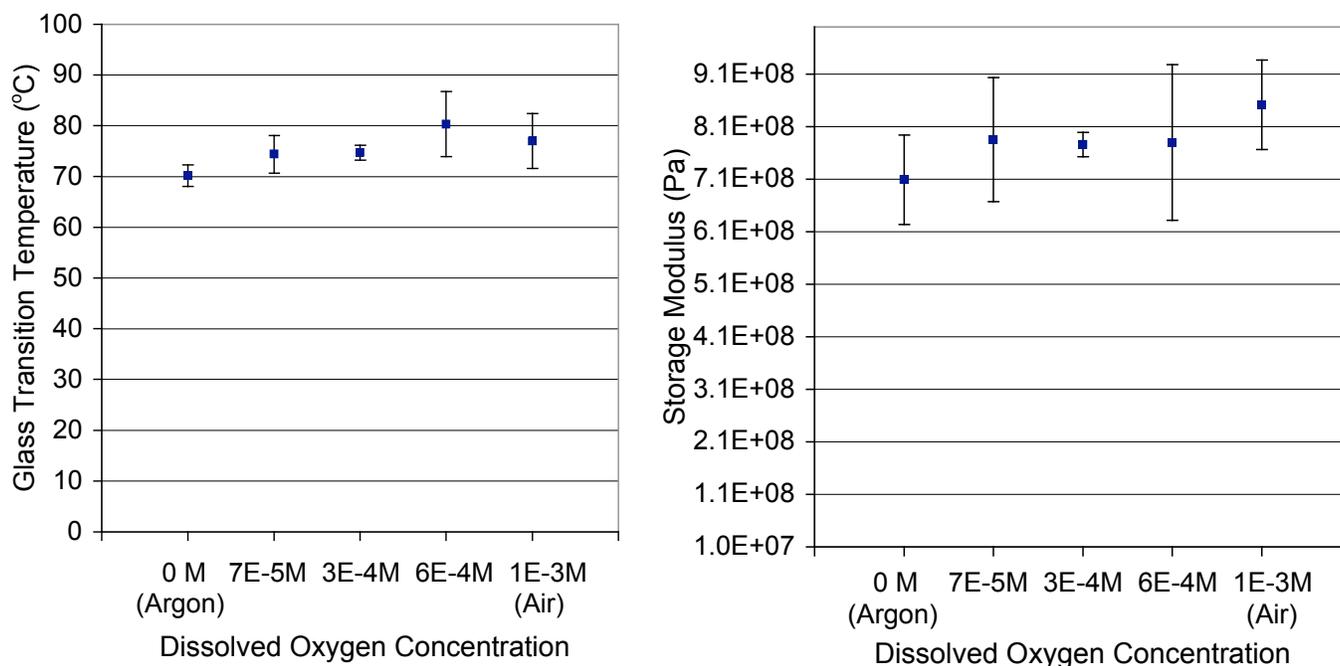


Figure 7. The glass transition temperature (left) and storage modulus (right) of HDDA polymer samples with various initial dissolved oxygen concentrations.

Conclusion

The effect of sample thickness and oxygen concentration on oxygen inhibition was analyzed using modeling and FT-IR spectroscopy. It was found that as the thickness of the film was increased, the overall average conversion increased due to the lack of oxygen diffusion to the lower depths of the film. Similarly, as the concentration of oxygen was increased, the extent of oxygen inhibition increased. The polymerization rate and overall monomer conversion decreased due to the increase in oxygen flux into the monomer film. Additionally, the effect of dissolved oxygen concentration on the bulk mechanical properties of the polymer was studied. It was found that the initial dissolved oxygen concentration had negligible effect on the glass transition temperature and storage modulus of the resulting polymer film. This is due to the very small concentration of short-chained species formed in comparison to the large concentration of polymer chains.

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