

Rapid Measurement of Photopolymerization Kinetic Behavior Using a Thin-Film Calorimeter

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Abstract

A thin-film calorimeter was constructed for the quantitative characterization of photopolymerizable systems. A detailed description of its assembly and mechanics of operation indicate the ease with which the instrument can be utilized. The thin-film calorimeter's linear response range is more than an order of magnitude greater than that of the photo-DSC, and is capable of measuring both smaller and larger signals more accurately. Polymerization exotherms were collected on films as thin as 2 micrometers and on commercial UV curable pigmented inks.

Introduction

Recent advances in the field of photopolymerization have focused on streamlining the technology to yield a more profitable product. For example, the development of photoinitiatorless systems,¹ discovery of ultra-fast monomers,^{2,3} and creation of efficient lamps with long lifetimes⁴ all serve to increase productivity and simplify the photopolymerization process. With these developments come exciting new applications which are often difficult to quantitatively characterize using traditional instrumentation. The construction of versatile tools which are efficient, simple to use, and inexpensive would significantly promote future technological developments.

The evaluation of polymerization kinetics has been achieved using a variety of different methods such as a change in a physical parameter (volume, modulus), real-time spectroscopy (IR and Raman), and calorimetry.⁵ Calorimetry is advantageous because it is not affected by crosslinking reactions and offers direct measurement of the polymerization rate. Photocalorimetry involves the measurement of heat evolved during a chemical reaction initiated by a photon of light. The polymerization rate is calculated assuming the amount of heat released is directly proportional to the number monomer units converted to polymer. Photo differential scanning calorimetry (photo-DSC), which measures the heat evolved from a photo-induced chemical reaction referenced against a blank, has been a commonly used instrument for examining bulk polymerization kinetics of unfilled systems. However, limitations such as poor time resolution, large sample volumes, and cost often limit its value and/or prevent its usage.

A photocalorimeter based upon a single thin-film heat flux sensor was first developed by Wisnosky and Fantazier.⁶ Minor modifications and basic applications of this technology have since been documented.^{7,8} Based on this literature, a thin-film calorimeter (TFC) was assembled in an attempt to offer solutions to the shortcomings associated with photo-DSC.

The superior time response and increased sensitivity of the thin-film sensor suggests many exciting new applications. The following report details the construction and application of a TFC.

Experimental

A schematic of the thin-film calorimeter is shown in Figure 1. A flexible thin-film heat flux sensor is attached via double sided adhesive tape onto a machined metal heat sink. Through a metal lid containing a 1 cm² hole, a UV LED lamp serves as the UV light source. The signal is filtered, amplified, and converted to a digital signal by an A/D converter board interfaced with a PC.

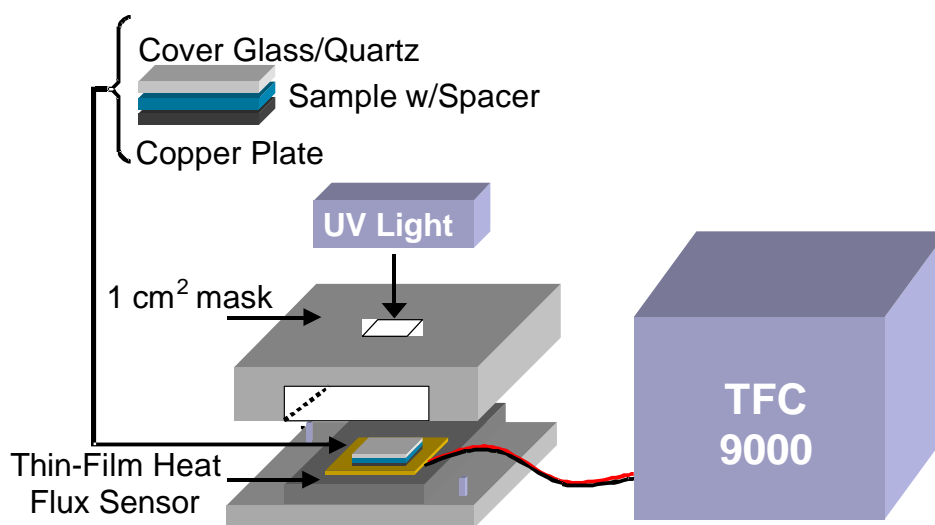


Figure 1. Diagram of the thin-film calorimeter (TFC)

A protective barrier such as aluminum (Al) or polyethylene (PE) must be used between the sample and sensor to prevent damage to the sensor. For low viscosity samples, a small amount of silica spacer (diameter determined by the user) is placed on the edges on the Al/PE protective barrier which resides atop the sensor. After a drop of sample is deposited in the center, a polyethylene film or glass/quartz cover slip is placed on top of the sample and the metal lid is clamped onto the heat sink. For high viscosity samples, sample films are solvent cast or spin coated onto the Al/PE support. The coated support is placed on the sensor and the metal lid is clamped onto the heat sink.

The materials used in this study include the monomer 1,6-hexanediol diacrylate (UCB Chemicals Corp.), the photoinitiator 2,2-dimethoxy-2-phenyl acetophenone (Ciba Specialty Chemicals) and a UV curable ink (Flint Ink Corporation). All chemicals were used as received, without additional purification. The relevant chemical structures are shown in Figure 2.

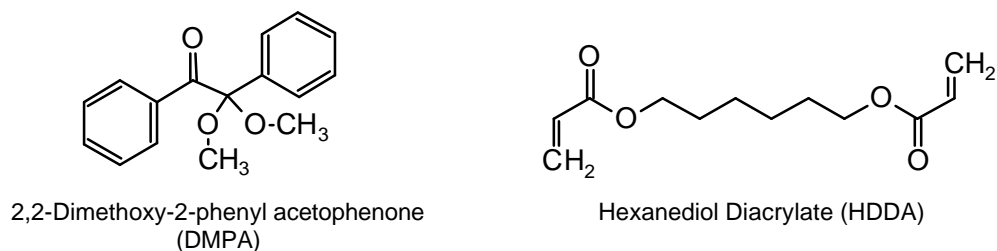


Figure 2. Chemical structures of the photoinitiator (DMPA) and monomer (HDDA).

Discussion

An advanced thin-film heat flux sensor serves as the primary component of the TFC. The sensor consists of thermopiles or measurement sites, which are connected in series and encased in a polyimide film. No external voltage or current stimulation is required to operate the sensor, and the measured heat flux (voltage output) is readable by the TFC. The TFC is interfaced with a PC through a multichannel A/D converter having 16 bit resolution and a maximum sampling rate of 100 kHz.

The major improvements of the TFC as compared to Wisnosky and Fantazier's original photocalorimeter include significantly enhanced sensor sensitivity, increased data acquisition resolution, and considerably greater sampling rates. As a result, the TFC has the ability to accurately measure a much smaller stimulus, hence making the quantitative analysis of photopolymerizable systems which evolve a small amount of heat possible. Direct implications of this phenomenon include characterization of films on the nano/micro size scale and thin pigmented UV curable ink formulations.

An instruments' sensitivity is a critical performance feature since it imposes limitations regarding the types of systems it can accurately examine. To illustrate the excellent sensitivity of the TFC, a comparison is made to the traditionally used photo-DSC. Free-radical photopolymerization kinetic equations dictate that polymerization rate is proportional to light intensity to the 0.6-0.7 power.⁵ Therefore, the linear range in a log-log plot of the polymerization rate as a function of light intensity approximates the range of heat flux that analytical tools can accurately measure. Figure 3 (a & b) clearly shows that linearity is maintained with the TFC over a light intensity range much larger than the photo-DSC when samples of HDDA with 1wt% DMPA are polymerized at various light intensities. Remarkably, the TFC is able to measure polymerization exotherms conducted at both lower and higher light intensities, which corresponds to the measurement of smaller and larger quantities of heat flux. Small quantities of heat are released in systems with low concentrations of reactive groups, as the case in many commercial applications of UV curing such as thin, clear films and pigmented inks. Large quantities of heat are released by extremely rapid polymerizing monomers and/or thick coatings.

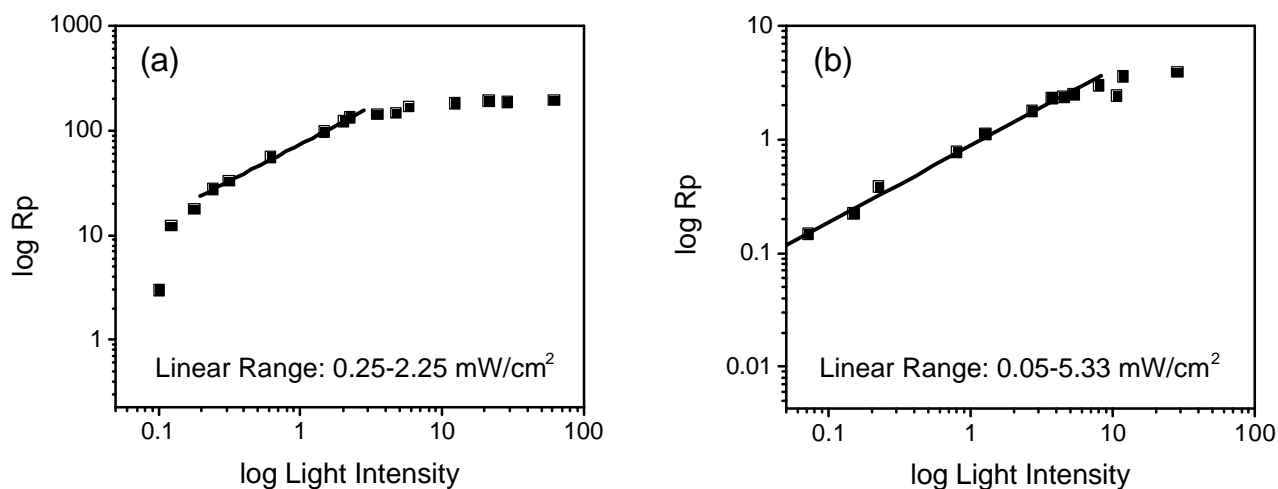


Figure 3. log-log plots of the polymerization rate (R_p) vs light intensity for 200 micron thick HDDA samples using the (a) photo-DSC and (b) TFC. All samples contain 1 wt% DMPA.

Traditionally, thin-films have been characterized using expensive spectroscopic methods which give indirect measurements of polymerization rate. Aside from its poor sensitivity, the photo-DSC is not able to examine thin-films because of the necessity to uniformly cover a DSC pan. In fact, extremely thick samples approaching 175 micrometers are needed for reproducible results. The TFC may have a significant impact on the study of thin-films because of its inherent sensitivity and ease of controlling sample thicknesses. Figure 4 depicts a series of HDDA photopolymerization exotherms on films as thin as 2 micrometers. For low viscosity samples, such as most monomeric systems, sample thickness can be controlled using glass microsphere spacers. In each of these sample thicknesses, a significant exotherm is observed demonstrating the viability of using TFC on extremely thin films.

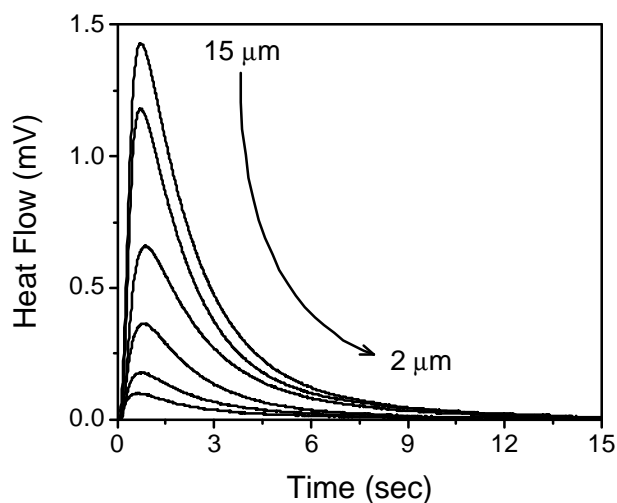


Figure 4. TFC polymerization exotherms of HDDA at various sample thicknesses. Samples contained 1wt% DMPA and were irradiated with light intensity of 50 mW/cm^2 .

Pigmented inks are an important commercial application of UV curing. Surprisingly, there is no analytical tool which can quantitatively characterize the photopolymerization rates of these systems. Pigmented UV curable coatings typically have reduced photopolymerization

rates because the pigments absorb and scatter incident UV radiation. As a consequence, the photoinitiator efficiency is decreased and application thickness is limited to thin-films. In addition, commercial UV curable inks consist of pigment dispersed in reactive oligomers. The resultant concentration of reactive groups is low and consequently small quantities of heat are released upon polymerization making characterization difficult. Figure 5(a) shows the TFC polymerization exotherm of a yellow UV curable ink formulation along with the heat evolved from the lamp system. Since the magnitude of heat generated by the polymerization exotherm is exceptionally small, the heat from the lamp system is significant and must be subtracted from the polymerization exotherm. Figure 5(b) depicts the corrected TFC polymerization exotherm of a 5 micrometer thick ink. Again, the exotherm is easily seen, which can give direct information on cure speed and reaction behavior. Since the viscosity of these oligomeric systems are high, solvent casting can be used to produce any desired film thickness.

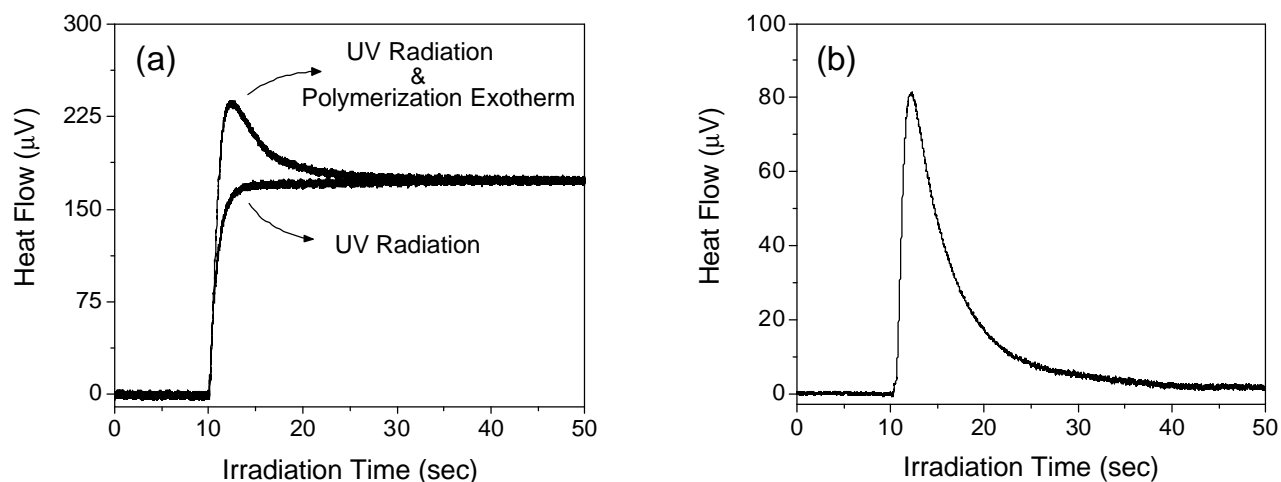


Figure 5. TFC exotherms of (a) the incident UV radiation and the polymerization of a 5 micrometer thick UV curable ink and (b) the polymerization exotherm after the heat from the UV radiation has been subtracted. Light intensity was 50 mW/cm^2

Conclusions

The operation and applicability of a thin-film calorimeter were discussed. The experiments are simple to conduct and provide accurate reproducible results. The thin-film calorimeter offers solutions to many of the short comings of photo DSC in that it is significantly more sensitive and is applicable to the study of thin-films and pigmented inks.

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