PHOTOPOLYMERIZATION REACTION RATES BY REFLECTANCE REAL TIME INFRARED SPECTROSCOPY: APPLICATION TO STEREOLITHOGRAPHY RESINS

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ABSTRACT

An advanced real time infrared technique for studying the isothermal in-situ cure of ultra-fast photopolymerization reactions has been developed. The method, referred to as reflectance real time infrared (RRTIR), involves time resolved IR analysis by reflected IR radiation while a resin sample is being exposed to a UV laser beam. The effect of factors such as chemical composition, radiation intensity, and temperature on reaction rate were determined for multifunctional acrylate resins exposed to a HeCd laser (325 nm). Isothermal cure profiles were monitored quantitatively through disappearance of the 810 cm^{-1} acrylate IR absorbance band. The dark reaction after the UV radiation was turned off also was monitored. The RRTIR method is shown to be highly effective for quantifying photopolymerization reactions in the millisecond time range.

The rate data indicate that quantitative comparisons between reactivities and conversions for different stereolithography resins are possible using this method under conditions that simulate the SLA process. Also, the data show conclusively that the reaction continues for long periods of time after initial laser exposure. This is expected to be a significant factor in the development of warpage and curl during the SLA building process.

INTRODUCTION

A reflectance real time infrared (RRTIR) technique has been developed to analyze UV curing reactions that occur in a fraction of a second. Thus it is well suited for analyzing the cure of stereolithography resins. Cure profiles are determined directly from the data that give a quantitative measure of reaction rates. The method is unique in that cure can be carried out isothermally. In this paper we consider the effect of various factors on reaction rates such as resin composition, temperature, UV exposure intensity, and exposure time. We also explore the reaction rate after termination of exposure, the so-called dark reaction. Two acrylate resins which have very different cure characteristics were analyzed. The measurements cover three different temperatures in the range from 25 to 55°C.

EXPERIMENTAL

Reflectance-Real-Time Infrared Spectroscopy

Real-time Infrared Spectroscopy (RTIR) is a relatively new method used to study the extremely fast kinetics of the laser-induced polymerization of multifunctional acrylates [1-3]. Using this method, the sample is simultaneously exposed to the photopolymerizing ultraviolet (UV) beam and to the analyzing infrared (IR) beam so that the degree of conversion can be determined at any time during and after the exposure. The RTIR method described here is a reflectance method (referred to as reflectance-RTIR or RRTIR, where the resin rests on a reflecting substrate. The initial light intensity is reduced to a smaller value after passing through the resin. The method requires thin film samples that are optically transparent.

With RRTIR it is possible to quantify a change in concentration of a reactive, functional group by monitoring the change in its IR absorbance intensity with time. For multifunctional acrylates the most convenient absorbance is the acrylate vinyl unsaturation band at 810 cm^{-1}. As reaction proceeds the absorbance intensity decreases. For quantifying the change the standard method is to ratio the unsaturation absorbance to an internal reference band that does not change and remains constant throughout the reaction.

A feature of RRTIR is that it is possible to characterize reactions that occur in a few milliseconds. The RRTIR method described here is unique because it measures accurately from 0.5 msec at 1 msec intervals and is capable of maintaining the sample at constant temperature, providing quantitative rather than semi-quantitative kinetic data. The exact systematic delay time can be measured precisely to within 25 μsec. The vinyl unsaturation band does not need to be completely isolated but can be deconvoluted if there are overlapping bands, a feature that proves important in analyzing most stereolithography resins. All data collection and analysis functions are computerized.

Experimental Apparatus

The reflectance-RTIR (RRTIR) system was constructed on an optics table. The system configuration is described in reference 4. The sample stage, shown in Figure1 consists of a brass block, teflon spacer, NaCl window (a UV/IR transparent material), and an aperture. The resin sample is placed between the NaCl window and the brass block. The brass block is a 1-inch diameter right-cylinder with a mirror-finished reflecting top surface. An aluminum block containing cooling coils with a circulating thermostatically controlled fluid is used to maintain isothermal conditions. A thermocouple attached to the center of the lower surface determines the temperature. The teflon spacers are 15 μm (0.6 mils) thick and the aperture has a 0.36 cm inside diameter. The experimental and data analysis procedures are also described in reference 4.

During an experiment reference and vinyl band spectra of the empty sample stage (including the NaCl window but not the resin) are collected. Then the "before" exposure reference and vinyl band spectra are collected. After this, a contact closure triggers the shutter to open. When the shutter opens the data acquisition board is activated. Thus the sample is exposed to UV normal to the surface using a focused HeCd laser. The laser has a wavelength of 325 nm. The "during" exposure vinyl absorbance maximum spectrum are collected at a fixed wave number (810 cm^{-1}) while the resin is continuously exposed to UV. After the "final" exposure spectra of the vinyl and reference bands are collected.

Materials and Reaction Conditions

Data were recorded for two acrylate resins for the purpose of illustrating the utility of the RRTIR method in comparing cure characteristics. In this paper we report primarily on experimental resin F61.1, a fast curing, "tough" photopolymer developed at the University of Dayton. The data for this resin are also compared with those for Cibatool XB 5081.1, a relatively slow curing resin. Reaction conditions considered included various exposure times ranging from 25 to 200 msec, different laser power levels from 95 to 238 mW/cm^2, and three temperatures from 25 to 55°C.

RESULTS AND DISCUSSION

The data in Figure 2 are typical conversion vs. time plots showing fraction cure (fraction of acrylate groups reacted) vs. time for resin F61.1. Each curve represents the results for a different exposure time at constant laser intensity (25 mW). As expected the cure level increases with exposure time. However, most of the cure occurs through "dark" reaction after laser exposure is terminated (referred to as after the cutoff time). This is illustrated more clearly in the reaction rate curves of Figure 3, which show that the rate peaks at times approaching the cutoff time but continues to be appreciable, approaching zero asymptotically at long times. We note also that the maximum chemical conversion is well below 100%, which is typical in photopolymers, particularly under short term light exposures.

Data for different light intensities at a constant exposure time show the same trend. It is well known in photopolymerizations that total exposure intensity relates to ultimate conversion with laser power and exposure time both combining to contribute to total intensity. The corresponding rate curves of show that in this case the rate curves all peak at around the same time. The effect of cure temperature is that conversion and conversion rate both increase as temperature increases.

The data of Figure 4 compare dark reaction cure profiles for F61.1 and the Cibatool XB 5081.1 resin, indicating that for given exposure cutoff times the expected extent of cure is appreciably less than that recorded for resin F61.1 under comparable conditions.

These data suggest that, particularly for slow curing resins, initial UV exposure results in a relatively low degree of cure. Most of this occurs after light exposure. The initial degree of cure is most likely "boosted" in the stereolithography process by the local temperature rise in the region of the laser spot [5]. Considerable additional cure occurs on subsequent exposures during hatch formation and through overcure when the next layer is being formed. Since vectors are attached at these stages, the additional cure will contribute to warpage and curl resulting from cure shrinkage occurring after vector attachment. Further shrinkage and warpage can occur during postcure. Resins that cure more fully on initial exposure will shrink less after vector attachment and can be expected to exhibit less warpage and curl. These conclusions are consistent with shrinkage results presented previously [6-8].

Cure Rates for Other Resins

RRTIR can be used for cure rate studies of other acrylates using methods similar to those discussed in this paper based on analysis of the acrylate vinyl IR absorbance at 810 cm^{-1}. Epoxy or vinyl ester resins also can be analyzed by keying into the appropriate reactive functional groups. In the case of epoxies, for example, disappearance of the epoxy group absorbance at 800-900 cm^{-1} can be followed. We plan in future studies to demonstrate the RRTIR method with other types of resins.

CONCLUSIONS

Reflectance-RTIR is a useful method for obtaining quantitative cure rate data for photopolymers as a function of controlled light exposure and temperature. The data obtained show that most of the cure obtained in laser scanning of stereolithography resins occurs in the dark after the laser has passed. Relatively low degrees of cure may be achieved with an initial exposure. Resins that cure quickly and achieve a high degree of cure in the initial exposure probably will exhibit less warpage and curl. RRTIR provides quantitative comparisons of cure rates for different resins.

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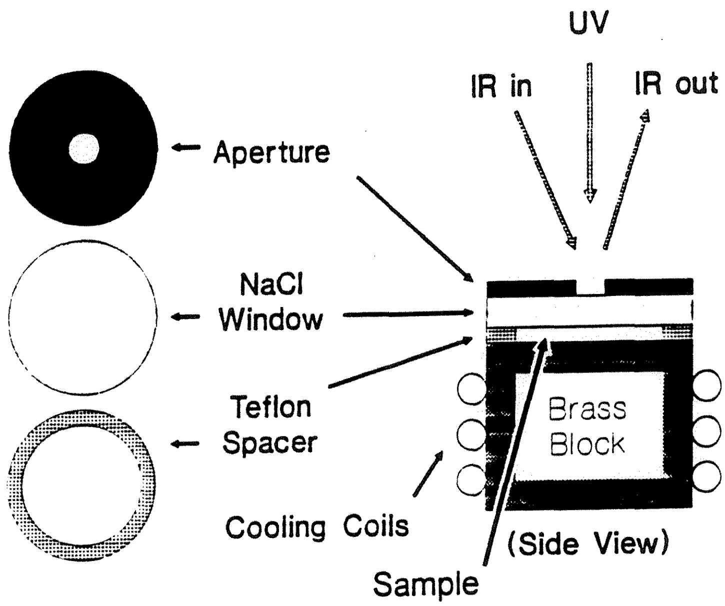

Figure 1 **Reflectance-RTIR sample stage configuration.**

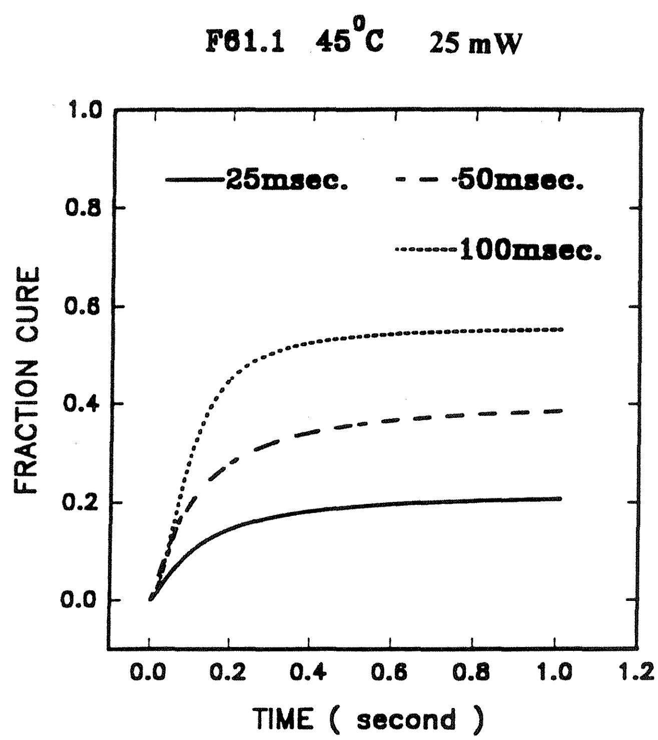

Figure 2 **RRTIR dark reaction fraction cure vs. time profiles for resin F61.1 at 45°C for 3 exposure times; laser power output 25 mW.**

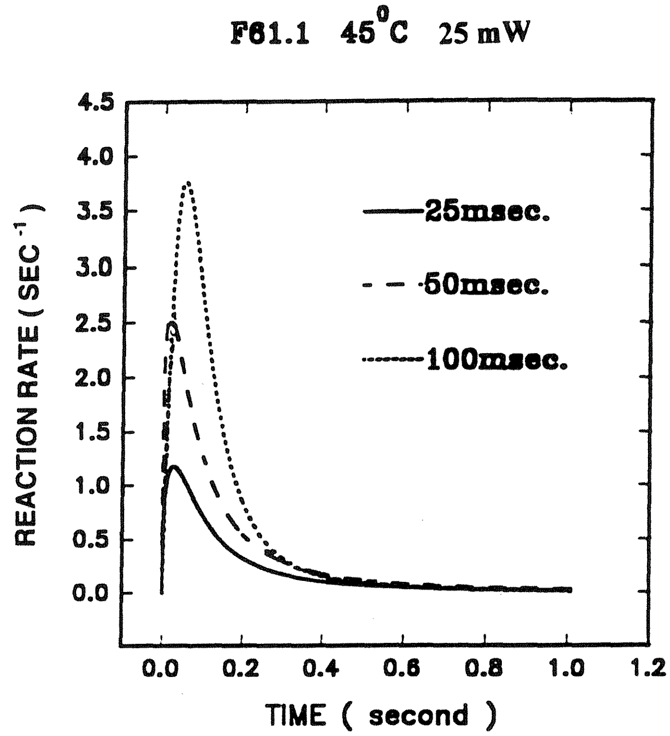

Figure 3 RRTIR reaction rate vs. time curves corresponding to data of Figure 2.

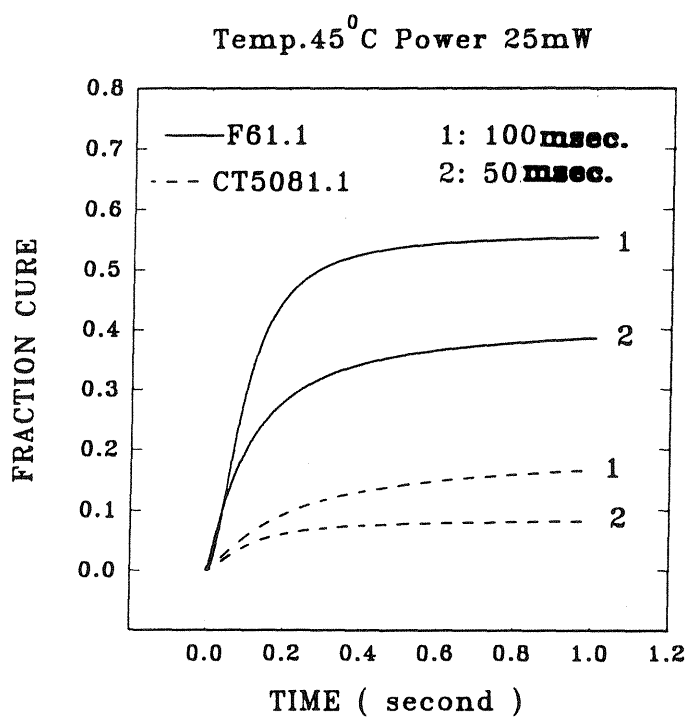

Figure 4 Comparison of RRTIR dark reaction profile curves for resins F61.1 and Cibatool 5081.1.