

Absorption cross-sections of Disperse Orange 13 and Irgacure 784 determined with mask projection vat photopolymerization

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ABSTRACT

It is necessary to understand the photoinitiated curing process, which occurs in vat photopolymerization resins during exposure, to develop high quality end products. Usually a curable resin contains photosensitizers, crosslinkable monomers and neutral absorbers, which have different roles in the curing process. The photosensitizer initiates the process by absorbing a photon and creating a chain initiator species, which causes the monomers to polymerize, crosslink and form a solid shape. While a photoinitiator is essential to achieve curing, a neutral absorber is required to control the cure depth. Short cure depth results in thin layers and high resolution end products, whereas large cure depth increases manufacturing speed. Thus, information about the absorptive properties of both the initiator and the absorber is crucial for the development of additive manufacturing techniques that are based on photoinitiated curing. To investigate these absorptive properties, a working curve method is applied with a mask projection vat photopolymerization apparatus to determine the absorption cross-sections of Irgacure 784 and Disperse Orange 13 and compare the results to ones obtained with spectrophotometry. With both methods, the results for each substance are within the same order of magnitude, but photobleaching seems to affect the vat photopolymerization results.

1. Introduction

Photopolymerization is a light induced polymerization reaction, which forms polymer chains or three-dimensional networks. Researchers and industries have become increasingly more interested in photopolymers since their discovery in the late 1960s [1]. Photopolymers are applied for dental restoratives, holography, data storage, inks, curable sealants, integrated optics, vat photopolymerization (VP) and other additive manufacturing methods [2–9]. In the curing process, the monomers and oligomers in the resin polymerize, crosslink and form a rigid network polymer. Controlling the curing process is a fundamental requirement for every vat photopolymerization system, since the parts are made by stacking selectively cured layers of resin.

The curing process can be controlled through careful choice of photoinitiators, neutral absorbers and their quantities. The role of a photoinitiator is to absorb incident radiation and then undergo chemical transformation producing a chain of initiator species, whereas the role of a neutral absorber is to limit the amount of available energy for polymerization reactions. Adding a neutral absorber, which usually is a dye, to a resin greatly reduces the polymerized thickness and thus makes curing thin layers possible [10]. The thinner the layers the

higher the resolution is in VP processes, since the vertical resolution is determined by the cure thickness. The choice of a photoinitiator and a neutral absorber depend on the operation wavelength, since the absorbing efficiency of these species change with wavelength. Thus, one has to know the absorption range and strength of these additives, to be able to build, for instance, an efficient mask projection vat photopolymerization (MPVP) system.

Mask projection vat photopolymerization is a modified VP technique where a mask projection system replaces the laser light source and scanning device of an vector scan VP system. In MPVP a liquid crystal display or a digital-micromirror device produces a cross-sectional pattern of a part and each layer is cured in one single exposure according to the pattern [7,11]. Although, the irradiate-to-cure principle may seem straightforward, the curing process itself with different compounds and additives is a complex process and a hot research topic [12–18].

In this paper an MPVP system is used to investigate how well the absorption cross-sections of one photoinitiator and one neutral absorber, namely Irgacure 784 and Disperse Orange 13 (DO13), can be determined with a working curve method. More precisely, it is investigated whether the absorption coefficient in the working curve

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model can be divided into products of concentration and absorption cross-section of individual absorptive species. Since the reactions of multiple absorptive features are excluded in spectrophotometry analysis, the working curve model would be an alternative approach to give more information about the investigated material. While Irgacure 784 is quite a well researched substance in the field of photoinitiation, there is only little information about DO13 [19–22]. The results obtained from the MPVP measurements are compared to those from spectrophotometry for final validation.

2. Materials and methods

The objective of this research is to investigate the absorptive properties of a resin containing Irgacure 784 and Disperse Orange 13 with MPVP at wavelengths 410 and 500 nm. The measurements were performed with a self-developed MPVP apparatus and a commercial Thermo Helios Beta spectrophotometer. The following sections will explain the measurement methods in detail.

An MPVP setup usually consists of a projection system, mirrors, resin vat, elevator, platform and computer. However, in the research setup presented here, there is no platform and a narrow bandpass filter, which has a full width at half maximum value of 10 ± 2 nm, was added to control the operation wavelength. In the bottom-up MPVP approach presented in Fig. 1, the light comes through the bottom surface of the glass slide and then cures the resin according to the projected image, which here was rectangular with an area of 40 mm^2 .

The resins in the MPVP measurements consisted of three components: Trimethylolpropane trimethacrylate (polymerizable monomer), Irgacure 784 (photoinitiator) and Disperse Orange 13 (dye). The photoinitiator concentration was kept at 1 wt%, while the dye content varied from 0 to 0.4 wt% in nine different mixtures. The mixtures were done by weighing the amount of photoinitiator and dye on a digital scale and then adding the monomer into a sample bottle with the powders. To achieve homogeneous solutions, the mixtures revolved in a rotating mixer overnight.

The curing experiments were done by filling the resin vat of the MPVP system with resin and projecting a rectangular image onto the bottom surface of the vat. After the exposure, excess liquid resin was removed and the thickness of the cured layer was measured with a micrometer screw gauge [23]. For the working curve method, one has to repeat the measurement with different exposures and measure the cure depth for each exposure value. This measurement process was done for each mixture at operation wavelengths 410 and 500 nm.

The working curve method, which is based on the Beer–Lambert law of absorption, has a fundamental role in characterizing resins in VP and is often given in the form

$$C_d = D_p \ln \left(\frac{E_{max}}{E_c} \right), \quad (1)$$

where C_d is cure depth, D_p penetration depth, E_{max} maximum exposure at the resin surface and E_c the critical energy required to initiate the

curing process [24]. The absorption cross-section can be determined from the D_p value of the resin, since the absorption coefficient α is the inverse of D_p and α is the sum of absorbing components as presented in the following equation

$$\frac{1}{D_p}(\lambda) = \alpha(\lambda) = \sum_i \alpha_i(\lambda) = \sum_i \rho_i \sigma_i(\lambda), \quad (2)$$

where ρ_i and σ_i are the number density and absorption cross-section of an individual absorbing feature, respectively [25]. In this research the resin consists of three components: monomer, initiator and neutral absorber. Thus the equation is

$$\alpha_{tot} = \alpha_{mon} + \alpha_{ini} + \alpha_{abs} = \rho_{mon} \sigma_{mon} + \rho_{ini} \sigma_{ini} + \rho_{abs} \sigma_{abs}. \quad (3)$$

Since most monomer species do not absorb light (this assumption will be verified later for Trimethylolpropane trimethacrylate), the total absorption cross-section (α_{tot}) is affected only by the neutral absorber and initiator species. For a resin with only monomer and initiator components, the absorption cross-section of the initiator can be obtained, as the slope from a plot of α_{ini} vs. ρ_{ini} , since σ_{mon} and ρ_{abs} are zero. When the resin contains absorbing dye features, the absorption coefficient of the neutral absorber is the difference between α_{tot} and α_{ini} and the absorption cross-section of the dye is obtained as the slope from a plot where α_{abs} is presented as function of ρ_{abs} as described in

$$\alpha_{abs} = \alpha_{tot} - \alpha_{ini} = \rho_{abs} \sigma_{abs}. \quad (4)$$

In spectroscopy, the absorption cross-section of a substance can be determined with absorbance measurements of samples, which have varying contents of absorbing species. The absorbance depends on the absorption coefficient (α) of the substance and the path length as follows

$$A = -\log T = -\log e^{-\alpha z} = \alpha z \log e, \quad (5)$$

where T is transmittance and z path length. Since α is the product of σ and ρ the equation becomes

$$A = \sigma \rho z \log e. \quad (6)$$

The absorption cross-section (σ) is then gained as the slope when A is plotted vs. $\rho z \log(e)$.

Samples for the spectrophotometer measurements were prepared by dissolving different amounts of Trimethylolpropane trimethacrylate, DO13 or Irgacure 784 into acetone. The absorbances of the samples were then measured with the spectrophotometer in glass cuvettes, whose path lengths were either 1, 2 or 10 mm, and the results were scaled to correspond to 10 mm path length for easier comparison.

In total, 24 mixtures (15 for spectroscopy and 9 for MPVP) were prepared and in addition to the 15 measurements with the spectrophotometer, 70 curing experiments were conducted with the MPVP system. The measurement data is presented in the following sections in tables and figures, in which the linear fits have been made with the least square method and the final result values are presented with standard deviation.

3. Results

3.1. Mask projection vat photopolymerization

The absorption cross-sections of Irgacure 784 and DO13 were determined by performing the working curve method for each resin sample with different concentrations of DO13. In the working curve method, the cure depths of a resin are inserted into a semi-log graph as function of exposure and the slope values equal to the penetration depths (see Eq. (1)). The working curves for DO13 are presented in Fig. 2 and all the penetration depth values are collected in Table 1.

Based on the slopes of the left most fits in Fig. 2(a) and (b), the penetration depth values for a Trimethylolpropane trimethacrylate solution with 0 wt% of DO13 and 1 wt% of Irgacure 784 are

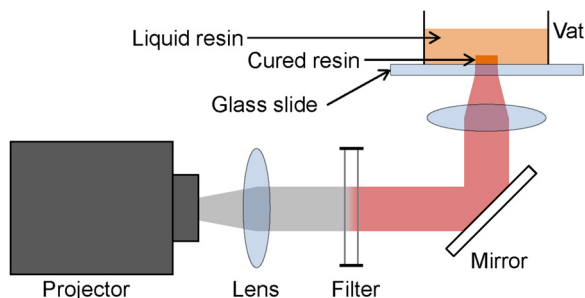


Fig. 1. The experimental setup to investigate the cure depth with various exposures.

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