



Effect of a red-shifted benzotriazole UV absorber on curing depth and kinetics in visible light initiated photopolymer resins for 3D printing



Robert Bail^a, Ji Yoon Hong^b, Byung Doo Chin^{b,*}

^a Center for Photofunctional Energy Materials (CPEM), Department of Creative & Convergent Manufacturing Engineering (CCME), Dankook University, Yongin 16890, Republic of Korea

^b Department of Polymer Science and Engineering, Dankook University, Yongin 16890, Republic of Korea

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ABSTRACT

We have investigated the effects of a red-shifted UV absorber in projection-microstereolithography operating under blue visible light (405 nm). A 2-(2-hydroxyphenyl)-benzotriazole derivative (Tinuvin[®] CarboProtect[®]; CarboP) was introduced as an absorbing additive. A remarkable decrease of the curing depth from over 800 μm in the pristine resin to 65 μm at 0.2 mol% CarboP was observed, while the polymerization and build times were somewhat increased. Microfluidic channels were accurately fabricated with the modified resin whereas the pristine photopolymer did not form any precise patterns. This demonstrates potential applications of modified UV absorbers in visible light initiating resins for precise 3D printing.

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Introduction

Projection-microstereolithography (PMSL) is a 3D printing technique based on the spatially controlled solidification of a photopolymer resin upon interaction with a digitally modulated pattern from a stationary beam of UV or blue visible light (Fig. 1) according to layer profiles determined from an STL file [1]. When an array of light spots is projected onto the surface of the resin, the light propagates within each illuminated voxel in direction of the beam and provides the activation energy to initiate the selective photopolymerization reaction in presence of a suitable photoinitiator [2].

The thickness of the cured layer is a key parameter in the PMSL process and depends on the interactions between the light beam and resin mixture [3]. This interrelationship can be easily controlled using small amounts of a suitable UV or light absorber [4]. If the maximum absorbance peak of the absorber matches the wavelength profile emitted by the light source, the concentration required for effective cure-depth control can be as low as 0.1 wt% [5].

Benzotriazoles are widely used as light stabilizers to minimize the detrimental effects of long-term exposure of organic materials in polymer components and coatings to UV radiation [6]. However,

some polymers require additional protection from irradiation in the low end of the visible region (380–420 nm) to maintain their long-term optical and mechanical properties [7]. It was demonstrated that substituting a 2-(2-hydroxyphenyl)-2H-benzotriazole moiety by a thioether group leads to a shift in the absorption peak toward the visible range by at least 20 nm in comparison to non-substituted benzotriazoles [8].

Light-emitting diodes operating in the blue visible range have emerged as an alternative light source for PMSL-based 3D printers in recent years while this is accompanied by the need to adjust the light sensitivity of the applied resin systems [9]. This applies not only to photoinitiating systems but also to all other additives that affect the light-material interactions in the resin. The aim of the presented study is to investigate the effectiveness of a red-shifted, benzotriazole-based UV absorber as a color-neutral additive for cure-depth control in a transparent resin in combination with a stereolithography process operating under blue visible light.

Experimental procedure

A prepolymer resin was prepared by dissolving 60 mol% diurethane dimethacrylate (UDMA) in 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TPA) cross-linkers. Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAP0) was utilized as the photoinitiator (Table 1). The photopolymerizable

* Corresponding author. Tel.: +82 31 80053587.

E-mail address: bdchin@dankook.ac.kr (B.D. Chin).

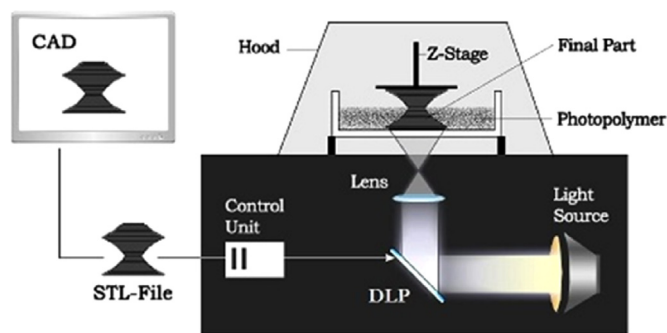


Fig. 1. Schematics of projection-microstereolithography.

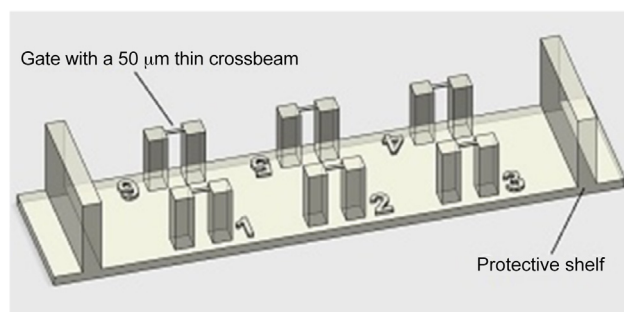


Fig. 2. Test part geometry used for cure-depth analysis.

resin was then split into five samples and a red-shifted 2-(2-hydroxyphenyl)-benzotriazole derivative (Tinuvin[®] CarboProtect[®]) was added as the UV/vis light absorber at concentrations of 0.00, 0.02, 0.05, 0.10, and 0.20 mol%. The acrylates and the initiator were purchased from Sigma–Aldrich Korea Ltd. and used as received. The absorber was received as a gift from BASF Company Ltd., South Korea. An overview of the resin components used in this study is provided in Table 1.

To determine the UV/vis absorbance profiles, the benzotriazole derivative was dissolved in acetonitrile (MeCN) at molar concentrations identical to those used in the resins. Samples from each solution were placed in the quartz cell (12.5 mm path length) of a spectrophotometer (PerkinElmer Lambda 950). The spectral absorbance of wavelengths from 250 to 450 nm was measured in steps of 1 nm and the absorbance spectra were generated for each absorber concentration by plotting absorbance [AU] vs. wavelength. The molar extinction coefficients (ϵ) were calculated for the operating wavelength of the 3D printer using the Beer–Lambert law.

All test parts were 3D-printed on a PMSL-based desktop printer (Asiga[™] Freeform Pico 2, Zydex Pty Ltd., Australia) with an LED light source (405 nm) and a projector resolution of 1280 × 800 pixels (WXGA). The projector brightness was set to 20 ± 0.5 mW/cm² intensity and the burn-in exposure time was adjusted to 8 s. The pixel size (X; Y) was factory-set to 39 μm and the layer height (Z) was kept constant at 50 μm. The built parts were removed from the build plate with a scraper, cleaned in an ultrasonic ethanol bath and air-dried.

A test part featuring six identical small gates with a 50 μm thin crossbeam located on top as illustrated in Fig. 2 was built in each absorber concentration eight times, with the standard exposure time being gradually reduced from 4 s to 0.5 s in steps of 0.5 s. The beam heights were determined under a polarized optical microscope (Olympus BX51) at 10× magnification. The average for each absorber concentration ($n = 6$) was plotted against the exposure time to obtain the working curve expressing the cure depth as a function of the penetration depth (D_p) and both actual and minimum exposure time (t ; t_0) [10].

The kinetic reaction parameters for the resin samples were determined using a TA Q2000 DSC equipped with a photocalorimetric add-on. The beam from a mercury lamp (Omnicure 2000, 200 W) was filtered to 400–500 nm and set to an intensity

20 ± 1.0 mW/cm². The resin samples (5 ± 0.2 mg) were conditioned in an isothermal nitrogen atmosphere at 25 °C for 1.0 min and then irradiated for 3 min, followed by a settling phase of 1 min. From the calorimetric plots, the time to reach the maximum heat of polymerization (t_{max}), the degree of cross-linking (DC), and the initial polymerization rates (R_p) were determined.

The theoretical enthalpy $\Delta H_{0,i}$ for each monomer (i) was derived by multiplying the number of reactive sites per mole by the theoretical enthalpy for n-butyl acrylate model compounds [11]. The DC was calculated as the ratio of the overall heat of reaction (ΔH_p) to the theoretical heat for 100% conversion of the resin ($\Delta H_{0,p}$). To calculate $\Delta H_{0,p}$ a method described by Ullrich et al. was adjusted to the resin composition used [12]. Following the same method, the initial polymerization rates (R_p) in [mol L⁻¹ s⁻¹] were calculated using the maximum peak height [h_p , in (W/mg)] in the calorimetric plot for each resin. The material constants used in this calculation are given in Table 1.

The possibility of unbound monomer residues and processing additives being released from the solidified resin upon contact with a liquid was investigated for two different solvent types: A cube with a nominal edge length of 4.1 mm was built in the resin mixture containing 0.5 mol% BAPO and 0.2 mol% CarboP applying the exposure time as derived in the cure depth experiments. With these printer settings, an actual surface area of $A = 100 \pm 2$ mm² and a volume of 68 ± 2 mm³ per specimen were achieved. The resin cube was immersed in a vial filled with 1.5 ml solvent and left in laminar flow conditions created by gentle mixing. After incubation for 24 h, the resin specimen was removed from the solvent sample. This experiment was carried out in quintuplicate ($n = 5$) at 20 °C in tetrahydrofuran (THF) and, for comparison, at 37 °C in deionized water (H₂O_{di}). Controls containing THF and known amounts [mol] of CarboP, BAPO and the acrylates (UDMA, HDDA, TPTA), respectively, were also prepared.

The solvent samples and controls were analyzed for residues of CarboP, BAPO, and the three monomers using HPLC (Agilent 1260 Infinity, detection limit 100 ppm). A 35 μl aliquot was taken from each sample and dissolved in the mobile phase (70/30 MeOH/MeCN) before separation in a C18 stationary column. Chromatograms were generated for each control solution and for the samples (THF and H₂O_{di}) after incubation of the resin cubes. The identities of the leached-out analytes were derived from the

Table 1
Materials used in the prepolymer resin and their properties.

Molecular name of the constituent	Abbrev.	M [g/mol]	ρ [g/ml]	$\Delta H_{0,i}$ [kJ/mol]	Concentrations [mol%] ^a
Diurethane dimethacrylate	UDMA	470.56	1.11	156.0	60.0
1,6-Hexanediol diacrylate	HDDA	226.27	1.01	156.0	29.5
Trimethylolpropane triacrylate	TPTA	296.32	1.10	234.0	10.0
Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide	BAPO	418.46	1.19	–	0.5
2-(2-Hydroxyphenyl)-benzotriazole	CarboP	560.00	1.16	–	0.0

^a In the prepolymer resin before adding the UV/vis absorber.

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