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Oxygen concentration and conversion distributions in a layer-by-layer UV-cured film used as a simplified model of a 3D UV inkjet printing system

Kentaro Taki[a,*], Yoshihito Watanabe[b], Tadao Tanabe[c], Hiroshi Ito[d], Masahiro Ohshima[b]

[a] *Advanced Reactive Systems Lab, Chemical and Material Engineering Course, School of Natural Systems, College of Science and Engineering, Kanazawa University, Rm. 1C416, Kakumacho, Kanazawa, Ishikawa 920-1192, Japan*
[b] *Department of Chemical Engineering, Kyoto University, Japan*
[c] *Department of Materials Science, Graduate School of Engineering, Tohoku University, Japan*
[d] *Department of Polymer Science and Engineering, Yamagata University, Japan*

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ABSTRACT

Three-dimensional (3D) ultraviolet (UV) inkjet printers represent a versatile technology for creating complex functional structures. During their operation, 3D objects are formed by repeating cycles of drawing a UV-curable resin with inkjet nozzles and then solidifying it with UV irradiation. In this study, the activity performed by a 3D UV inkjet printer was simulated by spin casting a 33 μm thick layer of UV-curable resin (containing diurethanedimethacrylate and 1-hydroxycyclohexyl phenyl ketone compounds mixed at a weight ratio of 99:1) onto a Si wafer followed by photopolymerization for 2 s at a UV irradiation of 10 mW cm^{-2}. Afterwards, the second resin layer with a thickness of 33 μm was spun-cast onto the first layer and photopolymerized under the same conditions. The conversion distribution of C=C bonds in the UV-curable resin was investigated via confocal laser Raman microscopy and numerical calculations, which took into account the kinetics of photopolymerization and oxygen inhibition reactions. The confocal laser Raman microscopy technique provided a unique distribution of the C=C bond conversion across the film depth. Thus, the conversion magnitude at a depth of 0 μm was zero and increased to 0.2 at 6 μm. Afterwards, the slope of the conversion distribution plot became moderate until the conversion reached the value of 0.43 at a film depth of 28 μm. Between the film depths of 28 and 38 μm, the conversion remained constant with a variation not exceeding 0.03. After that, the conversion value increased again, reaching the magnitude of 0.48 at a depth of 50 μm and remained constant in the region between 50 and 56 μm (with a variation not exceeding 0.04). At higher depths, the graph slope became moderate again, and the conversion value increased gradually to 0.51 at 66 μm, after which the silicon wafer was reached. As a result, two different plateaus were observed on the conversion distribution plot: between 28 and 38 μm and between 50 and 56 μm (the corresponding conversion variation in these regions was below 0.05). The obtained experimental data were in good agreement with the results of numerical calculations, which attributed the existence of the two plateaus on the plot of the C=C bond conversion distribution to the formation of an oxygen-lean point. In addition, the effects of the UV intensity, irradiation time, lamination time, photoinitiator concentration, and concentration of dissolved oxygen on the oxygen concentration and conversion distributions across the depth direction have been examined. The obtained results revealed that the increases in the UV intensity, irradiation time, and photoinitiator concentration as well as the decrease in the initial dissolved oxygen concentration effectively increased the conversion of C=C bonds in the resin film and decreased the thickness of an unpolymerized layer.

Abbreviations: I, Initiator radical; I–OO, Initiator peroxide radical; I–$\mathrm{M_n}$, Macroradical; I–$\mathrm{M_n}$–OO, Peroxide macroradical; M, Monomer; PI, Photoinitiator; $\mathrm{O_2}$, Oxygen molecule; A_p, Parameter of the Goodner-Bowman model; A_t, Parameter of the Goodner-Bowman model; $A_{\nu,}$, Absorbance measured at wavenumber ν; D_O, Oxygen diffusion coefficient; D_O0, Oxygen diffusion coefficient in monomer; f, Free volume fraction; f_a, Rational factor of Raman spectroscopy and FT–IR techniques; f_cp, Critical free volume fraction of propagation; f_ct, Critical free volume fraction of termination; f_m, Free volume fraction of monomer; f_p, Free volume fraction of polymer; $I(z)$, UV light intensity; I_0, UV light intensity at the upper film surface; [IR], Concentration of initiator radicals; k_i, Rate coefficient for the reaction of initiator radicals with C=C bonds; k_io, Rate coefficient for the reaction of initiator radicals with oxygen species; k_O, Rate coefficient for the oxygen inhibition reaction; k_p0, Rate coefficient for the propagation reaction without diffusion; k_p, Propagation rate coefficient; k_t0, Rate coefficient for the termination reaction without diffusion; k_t, Binary termination constant; H,, Film thickness; [M], Concentration of C=C bonds; [MR], Concentration of macroradicals; $[\mathrm{O_2}]_\mathrm{eqb}$, Equilibrium concentration of oxygen; [PI], Photoinitiator concentration; R,, Reaction diffusion parameter; R_i, Initiation rate; $R_{\mathrm{Si},}$, UV light reflection ratio; t, Time; T_gm, Glass transition temperature for the monomer thermal expansion coefficient; T_gp, Glass transition temperature for the polymer thermal expansion coefficient; x, Vertical coordinate across the UV light direction; x_A, Functional monomer conversion; z,, Horizontal coordinate across the UV light direction; α, Attenuation parameter for the diffusion coefficient; α_m, Thermal expansion coefficient for monomer; α_p, Thermal expansion coefficient for polymer; ϵ, Molar absorption coefficient for photoinitiator; ϕ, Quantum yield; ϕ_m, Monomer volume fraction

[*] Corresponding author.

E-mail address: taki@se.kanazawa-u.ac.jp (K. Taki).

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1. Introduction

UV-curable resins have been used for the first time in stereolithography after they were selectively solidified inside a vat by a UV laser (Kodama, 1981); they are currently becoming popular materials utilized in additive manufacturing applications (Gao et al., 2015). Some of these applications include projection-type printers, in which a UV curable resin is selectively solidified via illumination with UV or near-UV visible light through a digital light processing mirror. As a result, an object is printed through repeating cycles of illumination and lifting (Chua and Leong, 2015). Recently, the projection-type printing technique has been modified to accelerate printing times via the utilization of an oxygen inhibition reaction (Tumbleston et al., 2015). Another printing method is represented by inkjet-type printers, which are characterized by relatively low material consumption. In such printers, a UV-curable resin is selectively delivered to a desired spot, while the other printing techniques utilize resin-filled vats. The remaining content of the UV-curable resin left in the vat is typically discarded after printing to avoid contamination with the produced dust. In contrast, the inkjet-type printers are capable of storing the resin inside a reservoir tank attached to the printer head and then using it during the next printing operation. Although 3D UV inkjet printing inherently limits the choice of suitable UV-curable resins, which can be used as raw materials, it is becoming increasingly popular because of the strong demand for manufacturing of elaborate and colorful objects.

In order to produce one object layer via 3D UV inkjet printing, the following four steps must be utilized: (1) jetting a UV-curable resin from the printer head to replicate the object shape; (2) solidifying it with UV light; (3) scraping uneven areas around the object with a knife; and (4) repeating step (1) to deposit the next layer. Thus, the described process includes layer-by-layer lamination and photopolymerization steps.

UV-curable resins can be solidified via photopolymerization or UV curing. They contain photoinitiator and monomer species, such as vinyl, acrylic, and methacrylic groups. When UV light is applied to a resin, photoinitiator molecules undergo dissociation to produce free radicals, which in turn react with C=C bonds to form primary radicals. These primary radicals afterwards react with other C=C bonds of the monomer molecules (Fouassier and Lalevée, 2012).

If oxygen molecules are present in the resin, oxygen inhibition likely occurs because the primary radicals would rather react with them than with C=C bonds, forming peroxide radicals and carbonyl groups (Decker and Jenkins, 1985). The upper resin surface is usually exposed to the air oxygen; thus, if UV light with low intensity is applied (which is common during 3D UV inkjet printing), photopolymerization does not occur, and an "unpolymerized" layer is formed. This unpolymerized layer contains peroxide species, and its fluidity is identical to that of the original resin.

The second layer can be deposited on the unpolymerized layer both horizontally and vertically. A fine positional precision is difficult to achieve even when the touchdown position of the droplet released from the inkjet head is precisely controlled because it may flow away from the desired position. The conversion of C=C bonds in monomers affects the degree of volume shrinkage as well as the object strength. Therefore, in order to be able to create elaborate objects with high precision using 3D UV inkjet printers, the effects of the second layer lamination and UV irradiation on the conversion of C=C bonds in monomers and thickness of the unpolymerized layer must be investigated in detail.

The kinetics of the photopolymerization reactions utilized in stereolithography (Huang and Jiang, 2003) and projection-type 3D UV printing applications (Jariwala et al., 2011) has been examined in detail via numerical simulations. While in stereolithography a UV-curable resin is selectively photopolymerized inside a special vat, the layer-by-layer lamination and photopolymerization processes occur during 3D UV inkjet printing under air exposure, which may likely initiate the oxygen inhibition reaction. Hence, the detailed numerical simulations of the layer-by-layer lamination and photopolymerization steps can elucidate a possible mechanism of the oxygen inhibition process that affects the degree of C=C bond conversion.

Recently, the kinetic constants of propagation (k_p) and termination (k_t) have been determined for the diurethane dimethacrylate/1-hydroxycyclohexyl phenyl ketone (Irgacure 184) system using a dark polymerization technique, which utilized real-time Fourier transform infrared (FT–IR) spectroscopy to evaluate the conversion and reaction rates for methacrylate groups at different time points. The kinetic constants corresponding to conversion values between 0.15 and 0.5 were used to obtain the parameters of the Goodner-Bowman model employed for numerical simulations of the photopolymerization kinetics (Taki et al., 2014).

In this study, both the layer-by-layer lamination and UV irradiation processes were investigated experimentally and theoretically. In the experiment part, the spin casting and UV irradiation stages were sequentially combined; as a result, two laminated layers were produced. The conversion distribution of C=C bonds was obtained using a confocal laser Raman microscope. To evaluate the distribution of oxygen species and investigate the conversion geometrical resolution, a numerical calculation model developed in the previous study was utilized (Taki et al., 2014). This model was modified to take into account the rate coefficients estimated for reactions between initiator radicals, C=C bonds, and oxygen molecules as well as the UV light attenuation and conversion dependence of the diffusion coefficient (the detailed distributions of the oxygen species and conversion values were discussed after the validation of the obtained experimental results). In addition, the effects of the UV intensity, irradiation time, lamination time, photoinitiator concentration, and dissolved oxygen molecules on the distributions of the oxygen concentration, macroradical concentration, and C=C bond conversion across the resin depth direction have been evaluated.

2. Materials and methods

2.1. Materials

Diurethane dimethacrylate, a difunctional monomer with a purity of greater than 97% containing (225 ± 25) ppm of topanol inhibitor, was purchased from Sigma-Aldrich, while 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) supplied by BASF was used as a photoinitiator. All chemicals were used as received without further purification. The weight ratio between the monomer and the photoinitiator was 99:1. The UV-curable resin was prepared by mixing these two compounds together and storing for 24 h until the initiator species were completely dissolved. The obtained resin formulation was identical to that for the resin used in the previous study (Taki et al., 2014).

2.2. Layer-by-layer UV curing process

A typical commercial 3D UV printer consists of an inkjet nozzle, a UV light source, and a vertical stage (Chua and Leong, 2015; Srivatsan et al., 2016). All these components were found to be proprietary and difficult to obtain for the purpose of our study. Therefore, to analyze the 3D UV inkjet printing process in detail, a special layer-by-layer UV curing procedure has been developed (see Fig. 1). In particular, a Si wafer with dimensions of $20{\times}20\ \text{mm}^2$ was placed on a spin coater (1H−D7, Mikasa, Japan) followed by dosing the prepared UV resin and spin casting at a speed of 3000 rpm for 10 s. Subsequently, the obtained specimen was irradiated with UV light for 2 s. The light intensity measured at a wavelength of 365 nm was $10\ \text{mW cm}^{-2}$. A high-pressure Hg lamp (S2000, ExFo, Canada) without bandpass filters was used as a UV light source. The utilized UV meter (UIT−150, USHIO, Japan) exhibited high sensitivity at a wavelength of 365 nm.