RELATIONSHIP BETWEEN PHOTOCHEMICAL EVENTS AND 3D PRINTING

Xavier Allonas, Boris Métral, Aymeric Champion, Adrien Bischoff,
Céline Croutxé-Barghorn, Christian Ley

Laboratory of Macromolecular Photochemistry and Engineering,
University of Haute Alsace, 3b rue Alfred Werner 68093 Mulhouse, France
xavier.allonas@uha.fr

Vat photopolymerization technologies are promising 3D printing techniques in the field of additive manufacturing, which requires high performance and affordable photoinitiating systems (PIS). If the general process is well understood and currently applied in industry, there is a clear lack of knowledge concerning the relationship between the photochemical reactivity and the photonic parameters used for 3D printing.

In this paper, a model which predicts with good accuracy the change in conversion with both time and light intensity is proposed. Cure depth experiments are conducted and the critical energy (Ec) and penetration depth (Dp) are established for the resin when a photocyclic initiating system based on safranine is used. The relationship between these parameters and the corresponding RT-FTIR results was highlighted through the role of the conversion at the gel point, allowing optimization of the formulation [1].

Another example was provided through the study of riboflavin tetrabutyrate (RFT) as Type II photoinitiator. First, its photochemical reactivity is assessed by laser flash photolysis in the absence and in the presence of an amine as coinitiator. RFT alone is able to photopolymerize the acrylate formulation at a rate which is drastically increased when the coinitiator is added. Then, the depth of light penetration (Dp) and the critical energy (Ec) to form a polymer film were measured and compared to those determined from Bouguer-Lambert-Beer law for Dp and from Stockmayer equation and photopolymerization experiments for Ec. A new proposed model is able to predict the in-depth acrylate conversion within a printed part with a relatively low input of experimental parameters. Confocal Raman microscopy is used to discuss the effect of the photobleaching of RFT in the absence of coinitiator on the photopolymerized films. Finally, it is shown that this formulation performs quite well for 3D printing with a resolution close to the best performance of the DLP printer [2].

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[1] B. Metral, A. Bischoff, C. Ley, A. Ibrahim, X. Allonas, *ChemPhotoChem*, 2019, 3, 1.

[2] A. Champion, B. Metral, A.-S. Schuller, C. Croutxé-Barghorn, C. Ley, X. Allonas, *ChemPhotoChem*, submitted.