Oxime esters : highly efficient photoinitiators for overcoming oxygen inhibition in 3D-inkjet priting applications

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Abstract

A series of four commercially available oxime esters were studied as Type I photoinitiators. Initially, their UV-visible absorption properties were examined, revealing significant absorption in the near-UV range, with some also exhibiting absorption in the visible range. Photopolymerization kinetic studies were conducted using the Real-Time Fourier Transform Infrared (RT-FTIR) technique, employing various light sources (UV lamp, LEDs at 365 and 395 nm) for samples of 12 µm and 2 mm thicknesses under ambient air conditions. These experiments demonstrated that all four photoinitiators facilitated efficient polymerization, particularly under conditions of high oxygen inhibition (seen prominently in 12 µm thick samples under air). These oxime esters undergo a photocleavage reaction and decarboxylation, resulting in the release of carbon dioxide (Figure 1) [1]. The release of CO_2 was monitored through RT-FTIR experiments. Results indicate that the oxime esters outperformed certain common phosphine oxides, such as Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO). Molecular modeling calculations were employed to determine the enthalpy of cleavage reactions from both singlet and triplet states, revealing favorable cleavage from both energy states. Electron spin resonance spin-trapping experiments were also carried out to investigate the generation of free radicals, contributing to an understanding of the structure-reactivity relationship. Moreover, the oxime esters were tested in 3D-inkjet printing applications, displaying highly promising results with tack-free surfaces. Additionally, these oxime esters exhibit the potential for thermal initiation at moderate temperatures (150°C), offering a dual-curing behavior (Figure 1).

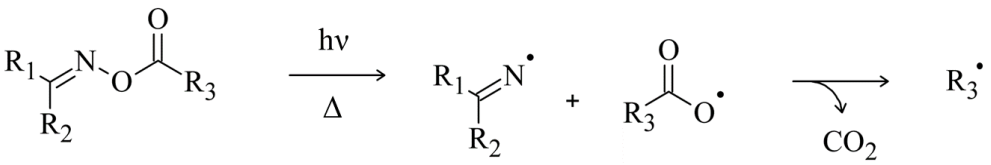

Figure 1. Mecanism of cleavage and decarboxylation of oxime esters [1]

Reference(s)

[1] Shaohui Liu *et al.*, Effect of Decarboxylation on the Photoinitiation Behavior of Nitrocarbazole-Based Oxime Esters, Macromolecules 2022 55 (7), 2475-2485