

## The benefits of cationic and cationic / free radical hybrid curing for 3D applications

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A wide variety of 3D printing technologies are now available based on several very different mechanisms of printing. The focus of this paper will be, photocured stereolithographic systems and the advantages brought by the polymerisation of epoxides and oxetanes by cationic polymerisation to this field.

The photocured resin systems employed in 3D printing technologies have typically used acrylate and methacrylate monomers and oligomers. These systems have many advantages a wide selection of resins is available which can be used to give a diverse range of mechanical, physical and chemical properties in the printed parts.

The drawbacks of acrylate-based systems in 3D printing applications are the high level of shrinkage and the viscosity of the resins. The shrinkage which occurs on polymerisation of an acrylate is inherent to the conversion from a double to a single bond and is proportional to the degree of unsaturation in the resin.(1) Levels of shrinkage can be as high as 20% by volume,(2) although much lower levels of shrinkage are often seen for high molecular weight oligomeric acrylates with low degrees of unsaturation. Typical ranges of shrinkage for commonly used acrylate resins would be in the range of 6-13%.(3) The use of these oligomeric resins can be limited in some 3D printing applications, by their high viscosity. Industrial applications often use inert fillers, such as silica, in their formulation. As the filler does not shrink this can help reduce the percentage shrinkage of the whole system. However, this does not change the amount of shrinkage in the resin system and the total amount of filler that can be added will reach a limit when other material properties start to suffer.(4) In many 3D printing applications, where resin viscosity is key to the resolution of parts that can be printed, the introduction of silica, which would have a large effect on the flowability and viscosity of the resin is not a viable option. Hence addition of fillers cannot always solve the shrinkage problem.

An alternative polymerisation mechanism based on the ring opening of epoxide and oxetane functionalities, by cationic photoinitiators can allow a significant reduction in the levels of shrinkage compared to acrylate systems.(5) Cationic resin systems will also open up new properties not available from the polymerisation of acrylates. Although it is possible to use cationic polymerisation alone, the combination of acrylate and epoxide chemistries into one free radical/cationic hybrid system can provide benefits to the system which could not be achieved with either technology alone. (6)

Cycloaliphatic epoxides such as UviCure S105 and UviCure S128 (Figure 1) give much lower levels of shrinkage [3-4 %] compared to acrylate oligomers and have low viscosities (S130 ca. 300 mPa.s S128 ca. 600 mPa.s). By using special additives, it is possible to achieve cationic polymerisations of cycloaliphatic epoxides with zero shrinkage.(7) In many 3D printing applications viscosity is key to improving resolution. These difunctional resins are able to produce highly crosslinked systems with good mechanical properties, low shrinkage and high  $T_g$ . The use of UviCure S105 alone will produce a

very hard polymer, which may be unsuitable for some applications. The adipate based S128 has a longer more flexible backbone which can help provide flexibility of the cured polymer.

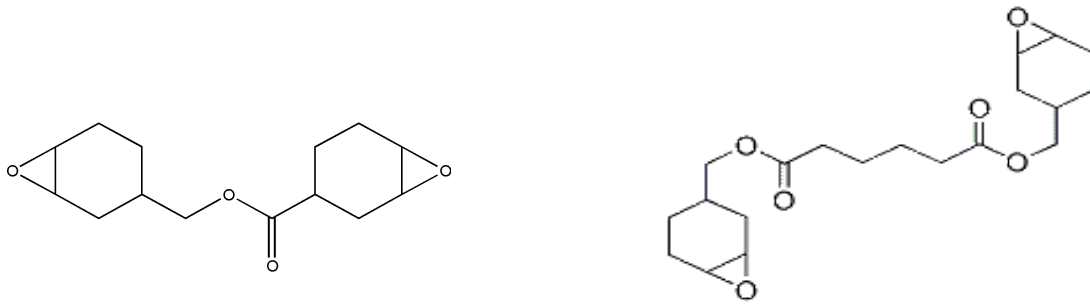


Figure 1 - Structures of difunctional cycloaliphatic epoxide resins. (Left) S105 (Right) S128.

Cationic polymerisations also employ a range of additives that can be used to broaden the properties available from the systems. Monofunctional oxetanes such as UviCure S130 and UviCure S140 (Figure 2) have viscosities in the range of 5-10 mPa.s and can be used to reduce the viscosity of resin formulations to ranges suitable for a range of applications.

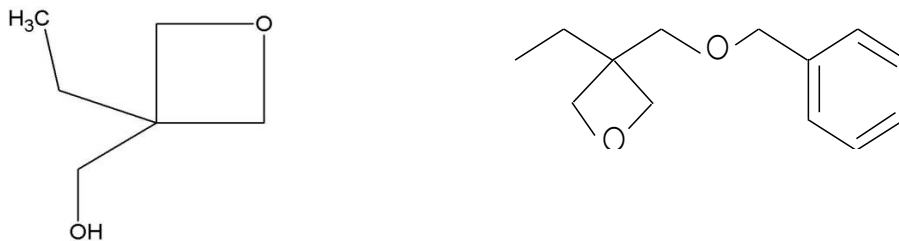


Figure 2 - Structures of monofunctional oxetane resins. (Left) S130 (Right) S140.

Increasing concentrations of monofunctional resin will also reduce the crosslink density and improve flexibility in the cured article. In addition to these benefits UviCure S130 can also have a dramatic increase on the rate of conversion of epoxy bonds as a result of chain transfer reactions from the hydroxyl functionality. (8,9)

Further modifications to the properties of the cured system can be made by adding difunctional oxetane resins such as S150 and S160 which can help increase toughness.

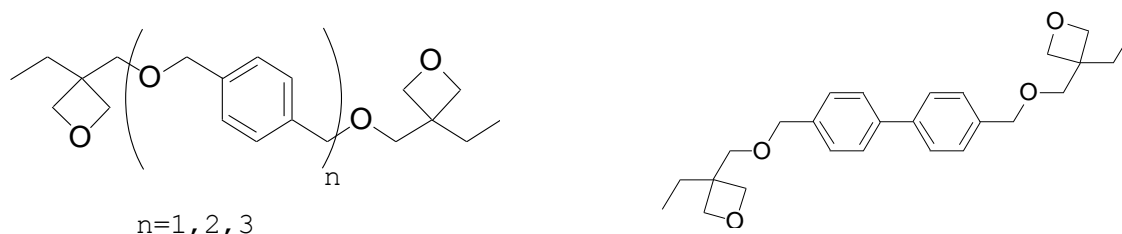


Figure 3 - Structures of difunctional oxetane resins. (Left) S140 (Right) S150.

The cycloaliphatic epoxide and oxetane resins have good compatibility with common acrylate resins but further increases in the compatibility of these systems can be made by the introduction of hybrid resins, such as, UviCure S170 (Figure 4). This hybrid resin contains oxetane and methacrylate functionalities which are polymerizable by cationic and free radical polymerisation respectively.

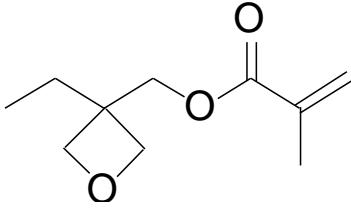


Figure 4 - Structure of oxetane methacrylate hybrid molecule (S170).

Data collected from real time FTIR (Figure 5) shows that methacrylate and oxetane functionalities of UviCure S170 are consumed during the polymerisation. It is possible to formulate the system so that the rate of polymerisation is similar for both the cationic and free radical components. When polymerised in a hybrid formulation similar rates of polymerisation of the two networks will help improve the compatibility of the growing polymer networks and reduce phase separation.

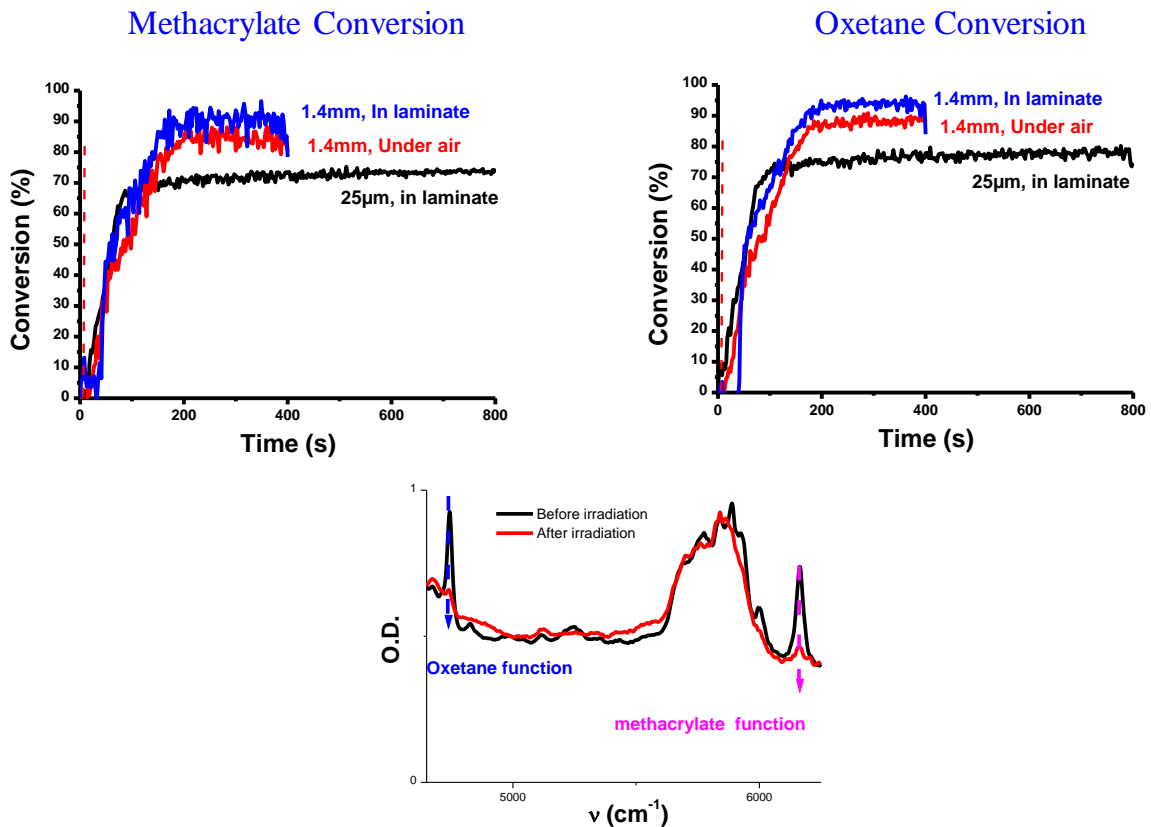


Figure 5 - FTIR data showing the conversion of oxetane functionalities ( $4700-4790\text{ cm}^{-1}$ ) and methacrylate functionalities ( $6117-6223\text{ cm}^{-1}$ ) of UviCure S170 using G1 based photoinitiating system upon exposure to the LED@405 nm ( $I \sim 230\text{mW/cm}^2$ )

Phase separation often has a negative effect on mechanical properties and can result in hazy or opaque polymers. In most applications this is highly undesirable and improving the compatibility between resin systems must be achieved. Figure 6 shows the crosslinking of S170 between the growing acrylate and epoxy networks.

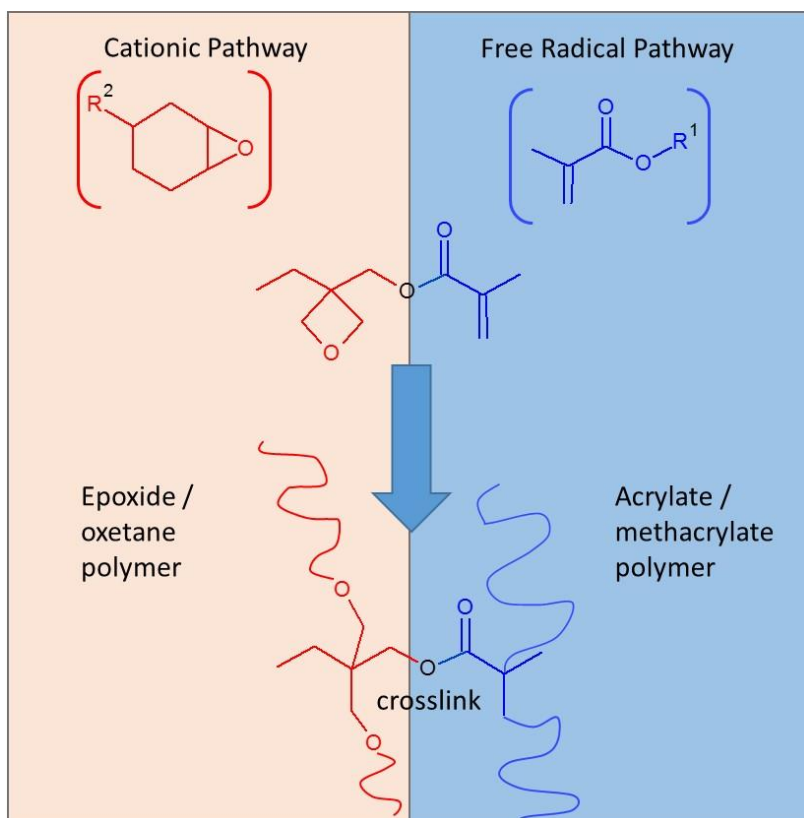


Figure 6 – A schematic diagram showing the reaction of S170 in a hybrid system containing epoxide and methacrylate to give a crosslink between the two polymer networks

Crosslinking between the two otherwise separate, polymer networks improves the compatibility by forming a chemical link between the growing polymer networks.

Photoinitiators used in cationic polymerisation are typically onium salts and most commonly  $\text{PF}_6^-$   $\text{SbF}_6^-$  salts of sulfonium and iodonium cations. Under UV irradiation these photoinitiators decompose to produce a strong acid which will initiate ring opening polymerisation. Figure 7 shows the decomposition of a typical Iodonium salt photoinitiator, SpeedCure 938. A similar mechanism occurs for the sulfonium salt based cationic photoinitiators.

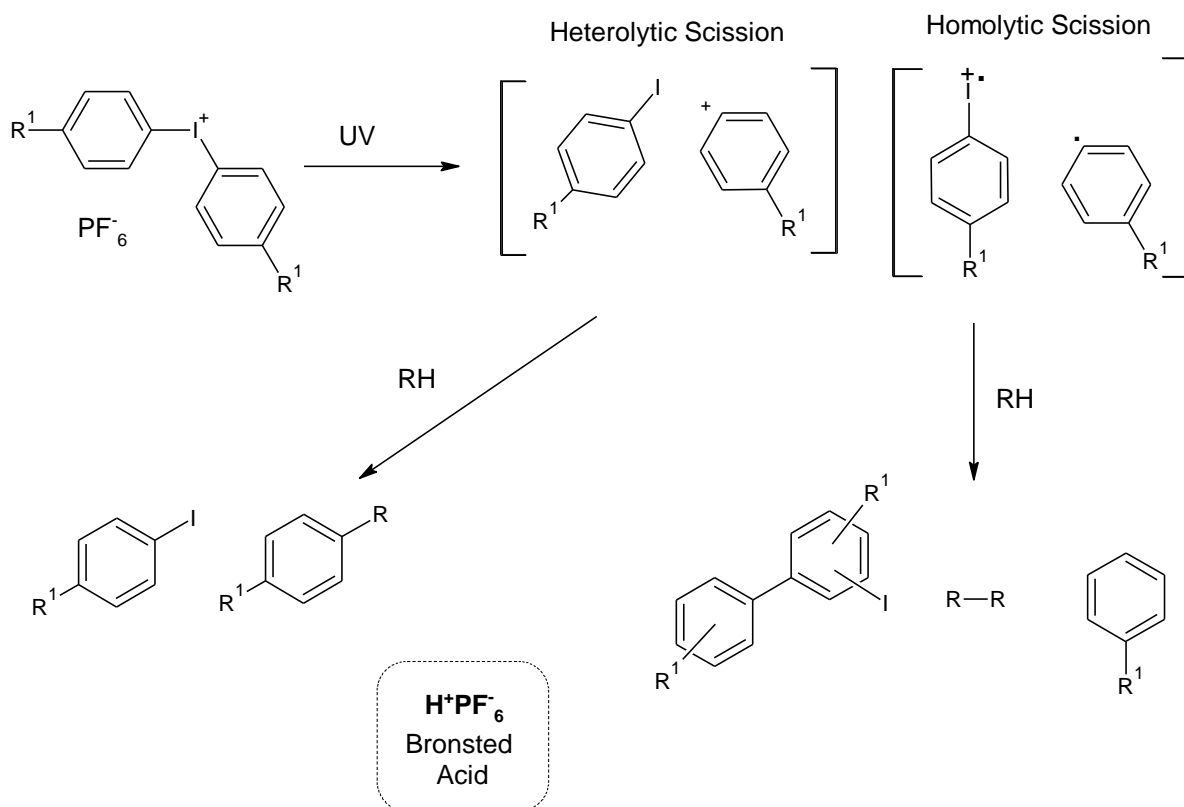


Figure 7 - Mechanism of photo decomposition of iodonium salt by heterolytic scission and homolytic scission resulting in formation of the active species, the Bronsted acid and a range of other decomposition products.

Onium salts have good compatibility with common free radical photoinitiators and can work synergistically with many Type I and Type II photoinitiators. Although, a synergistic effect is possible with many short wavelength absorption photoinitiators, 3D printing applications typically use long wavelength LED lamps. As such, it is important to identify LED relevant photoinitiating systems for cationic polymerisation in 3D printing applications.

The method of sensitisation in cationic polymerisation is quite different to free radical. Sensitisers such as CPTX operating by a charge transfer mechanism rather than energy transfer which is typical in sensitisation of free radical initiators. Type I photoinitiators such as Speedcure TPO can also be used as a long wavelength sensitizer working via a Free Radical Promoted Cationic Polymerisation which is reported in the literature.(10)

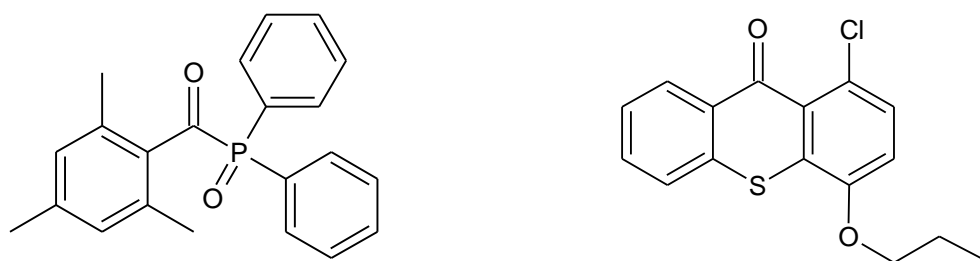


Figure 8 - Structures of Speedcure TPO (left) and SpeedCure CPTX (right)

These types of sensitisation are significantly more efficient using iodonium salts rather than sulfoniums. The lower reduction potential of iodonium salts means they can be more easily reduced by an excited state type II photoinitiator or by a radical from a decomposed Type I photoinitiator.

The reduced Iodonium decomposed to form the active species. This process is not efficient with sulfonium salts. (11,12)

Recent developments have shown that a three-component system using an iodonium salt, N-vinylcarbazole and the photoactive copper complex "G1" can produce reactive species under low intensity LED irradiation, simultaneously initiating acrylate and epoxide polymerisation via one catalytic initiation cycle.(13–15)

The long wavelength absorption of the copper complex, "G1," (ca 380 nm) means that this photoinitiator system is ideal for curing under low intensity LED irradiation conditions. This has significant benefits for safety as well as reducing the running costs of equipment as high power lamps and mercury lamps are not required.

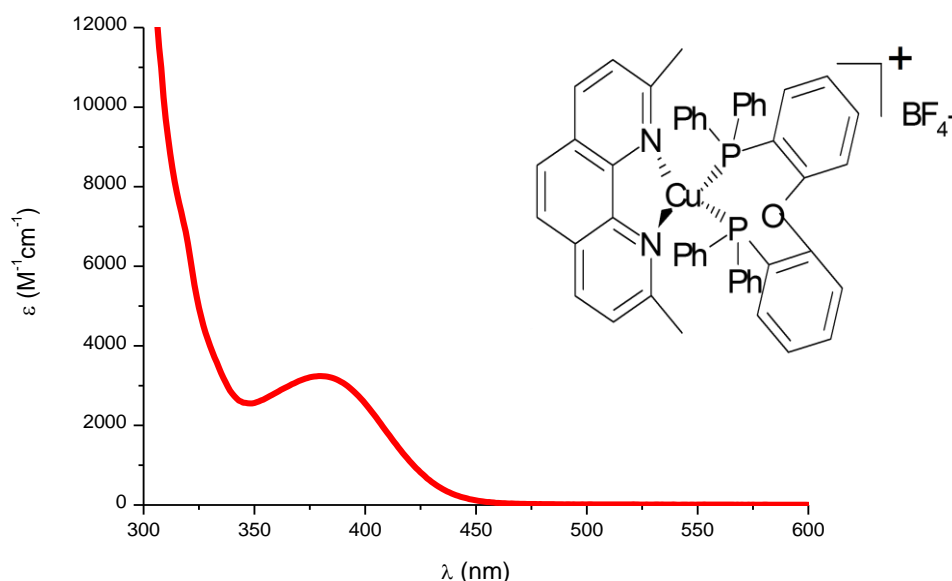


Figure 9 - The structure of the photoactive copper complex (G1) and its associated UV-vis absorption spectrum. Peak absorption ca. 380nm.

The mechanism of initiation (Figure 10) uses three components; G1 – the photoactive component which absorbs the light, an iodonium salt – the oxidising agent, N-vinyl carbazole (NVK) – the reducing agent. Together, these three components produce a catalytic cycle which regenerates "G1" and produces multiple reactive species capable of initiating the polymerisation of epoxide and acrylate simultaneously and with similar cure rates.

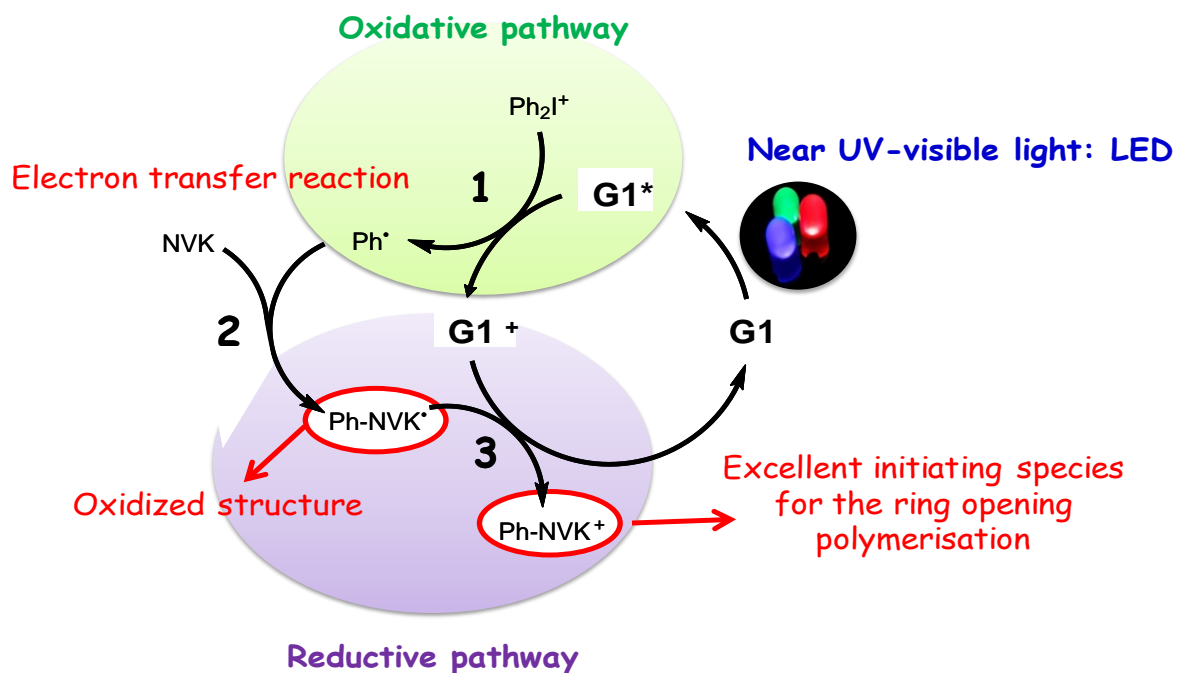


Figure 10 – Mechanism for photoredox catalysis cycle of three component system containing G1, NVK (N-vinylcarbazole) and Iodonium salt (SpeedCure 938)

Testing of the three component G1 photoinitiator system in 3D printing of a cycloaliphatic epoxide based resin system (Figure 11) and in a hybrid formulation (Figure 12), using LED projector@405 nm (Thorlabs, 110 mW/cm<sup>2</sup>) has shown fast cationic curing with reduced shrinkage compared to free radical systems. Optical microscopy and profilometry experiments show that structures can be printed in cationic resin and hybrid resin with good resolution.

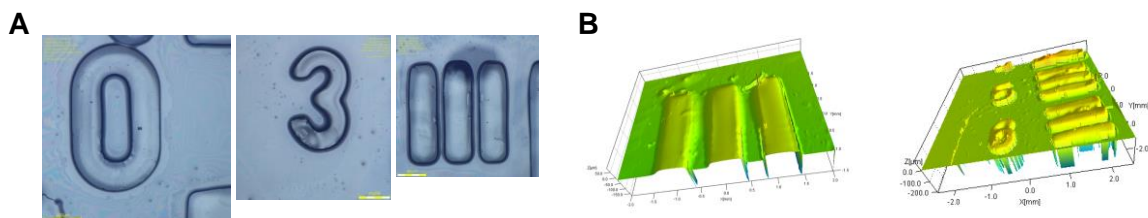


Figure 11 - Cationic photopolymerization experiments using a LED projector @405nm: (A) number and patterns using G1/SC 938/NVK in cationic resin, (B) Characterization in 3D by profilometry observed by using a numerical optical microscopy

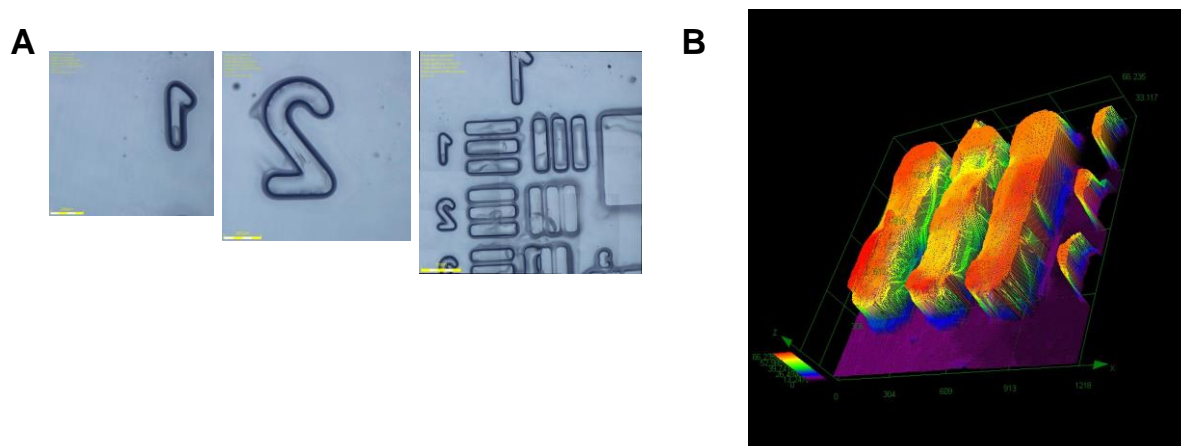


Figure 12 - Hybrid photopolymerization experiments using a LED projector @405nm: (A) number and patterns using G1/SC 938/NVK cationic resin /TMPTA blend (70%/30%), (B) Characterization in 3D by profilometry observed by using a numerical optical microscopy

This simultaneous polymerisation mechanism could be hugely beneficial in the advancement of curing of hybrid free radical/cationic formulations, providing benefits such as, low shrinkage, low oxygen and moisture inhibition, new physical properties which could be very important in 3D printing.

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