

Development of Dual-curing Thermoset Materials using a Novel UV-initiated Mechanism Suitable for 3D Printing Applications

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Abstract

This technology is focused on development of a series of highly functional dual-curing thermoset resins for additive 3D printing application. The typical materials that are used in 3D printing are associated with significant challenges such as low inter-layer adhesion, poor mechanical strength of the product, and low chemical resistance. Presence of multiple functionalities provides the opportunity of two consecutive curing mechanisms. By leveraging the advantage of UV/EB curing technology and photo-blocked catalysts, rapid strength build-up could be achieved after application of each layer and exposing it to UV light (Rapid cure). After application of multiple layers, the secondary curing (dark cure) will take place under appropriate conditions without the need for any additional exposure to UV, heat or moisture. By completion of the secondary curing mechanism, a strong inter-layer adhesion (increased up to 230%) and toughness could be achieved due to covalent bonding between and within the applied layers. These features could make this technology a unique option to produce high-performance items using additive 3D printing.

Keywords: Dual curing, UV, Photo-latent catalyst, 3D printing, adhesion

1. Introduction

3D printing has started to emerge in various industries as a promising replacement for conventional production processes. It is used for fabricating a wide range of structures and complex geometries from three dimensional model data. The process is referred as additive manufacturing (AM) because it is generally consisted of successive application of thin layers on each other followed by various methods of post-treatment. 3D printing was mainly used by the designers in order to obtain prototypes for the actual objects that needed to be produced before mass production. That was because the process was relatively rapid and cost effective. Moreover, the capability of product customization is another major advantage of 3D printing specially in fields such as biomedical, dentistry, and cosmetics. The use of 3D printing could minimize the additional expenses that are present in the process of developing a new product [1]. Although many materials including metals and ceramics could be produced using AM methods, polymers and composites have emerged as the main material of choice due to wide range of properties (e.g. impact resistance, flexibility, resilience), cost-efficiency, and also being versatile for use in different 3D printing processes. Depending on the application method, polymers for AM could be thermoplastic filaments, reactive monomers (cured under appropriate conditions such as UV light), resin or powder [2,3].

3D printed polymeric objects are generally applied by two common methods. In fusion deposition method (FDM), the material input is usually a thermoplastic polymer, which is heated above its glass transition temperature in a heated container and then extruded continuously through a nozzle. The extruder head or the build plate moves in different direction to deposit the patterns. Once cooled down, the green strength will be obtained by inter-diffusion of layers [4]. Stereolithography (SLA) is another common method in which UV light or electron beam (EB) are used in order to cure a thermoset formulation containing photo-polymerizable compounds (mainly acrylic and epoxy) and photo-initiators. After application of the layers, UV light will be

exposed to the areas designated by the pattern to instantly cure them into hard structures. The unreacted materials will then be filtered out by ultrasonication or solvent immersion [5,6].

Products obtained by these methods have become a popular choice in many industries such as automotive, aerospace, sales, and medicals [7,8]. However, there are some challenges associated with AM methods in order to be able to shift from prototyping to products. For 3D printed objects using the FDM method (or other methods that use thermoplastic materials), once the layers get cooled down, the diffusion of the two layers will be limited and the extent of diffusion varies at different positions. This leads to problems such as low speed, poor adhesion, incontinuity of properties, inferior toughness and low flexibility/hardness balance [9,10]. By using UV curable methods and thermosetting systems, while the rapid curing and higher strength could be achieved, the printed materials are still inferior in terms of mechanical properties and inter-layer adhesion. A post-treatment such as heating or additional UV curing may be needed for some printed parts in order to achieve the desired mechanical performance [11,12]. Recently, solutions such as incorporation of adhesion promoters and nano-fibers, chemically modification of thermoplastic copolymers, and controlling the cure extent of UV curable materials and conducting a post curing have been introduced in order to address the drawbacks of 3D printed products [13–15]. Chemical crosslinking between the layers is another interesting option that could possibly act efficiently to improve the properties. Crosslinking involves the formation of either noncovalent or covalent bonds between polymer chains [16]. However, so far the non-covalent bonding has been found to be not as effective and covalent bonding between functional groups of the layers could bring up additional challenges such as pot-life and viscosity build up [17,18]. Our research group has recently come up with a series of highly functional low viscosity materials that could potentially have multiple functionalities which some could be instantly cured using UV radiation and others could be cured using a suitable crosslinker at ambient conditions

[19,20]. Moreover, usage of photo-latent catalysts for curing of isocyanates and hydroxyls, curing of silanes, and acetoacetate/acrylate crosslinking have been well established over the past few years [21–23].

In this work, series of UV-curing formulations with multiple functionalities in their structure has been developed. Presence of these functionalities enables the material to have a dual curing mechanism. By leveraging the advantage of UV/EB curing technology and photo-blocked catalysts, rapid strength build-up (green strength) could be achieved after application of coating layer and exposing it to UV light. In addition to this, photo-latent catalyst present in the system, was activated and triggered the reaction between remaining functionalities of the system at ambient conditions. This secondary curing (dark cure) did not require any additional curing condition (e.g. UV, heat, moisture) and could occur after all of the 3D printing layers were applied. The scheme of the curing mechanism is presented in **Fig.1**. The properties of layers including flexibility, impact resistance, mechanical properties and pull-off adhesion were studied using various standard test methods with and without incorporation of secondary curing.

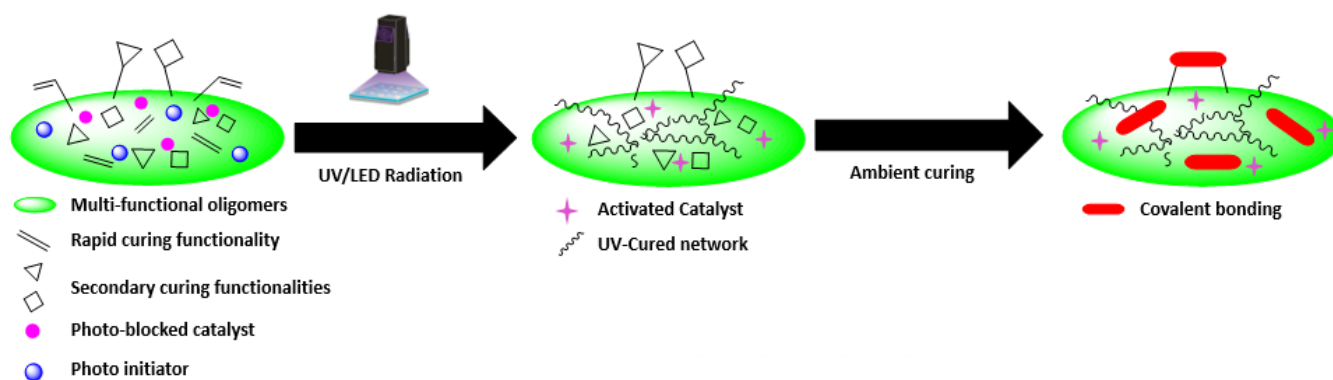


Fig. 1: Schematic overview of curing mechanism of materials used in this study

2. Materials and methods

2.1 Materials and oligomers

Cold rolled steel panels with iron phosphate pretreatment with dimensions of 3" × 6" were supplied by Q-panel. It was used as the substrate by which high adhesion could be obtained after application of materials. Two series of photo base generators (PBG) were used as catalyst. 2-isopropylthioxanthone (ITX) was also used as a photo-synergist in conjunction with the photoinitiators. Ethyl alcohol, n-butanol, acetone and tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Desmodur N 3390A and Joncryl 924 were also received from Covestro and BASF, respectively and used as components of NCO/OH crosslinking. Trimethylolpropane triacrylate (TMPTA) from Allnex and Evonik's Vestamin A139 were used as acrylate and amine crosslinkers. Alkoxysilanes precursors containing different backbones with varying functionality were synthesized by modification of amino silanes with organic compounds. Moreover, an acetoacetate/hydroxyl functional non-isocyanate polyurethane oligomer was synthesized according to the chemistry described in earlier studies. Due to the ongoing intellectual property-related reasons, their detailed structure and characterization are not presented here.

2.2 Formulation and application of materials

In order to demonstrate the effect of additional crosslinking mechanism on properties of the films, three different chemistries were prepared as shown in **Fig. 2**. For chemistry 1, an acetoacetate functional material was mixed with TMPTA in the presence of 3 wt.% of PBG catalyst followed by addition of the components of isocyanate and polyols together with PBG as the photo-blocked accelerator. The mixing was done shortly before application. In chemistry 2, a similar approach to chemistry 1 was used with the difference that instead of physical mixing, the prepolymer (AA-NI-PUPO) already contained the acetoacetate and hydroxyl functionalities. Before application, the isocyanate crosslinker and PBG were added to the mixture of prepolymer and TMPTA. In chemistry 3, an organic-inorganic silane compound was mixed with PBG catalyst and acetoacetate compound. The moisture blocked amine was then added to the mixture

before application. It should be noted that chemistries 1 and 2 are considered as a 2-component formulations while chemistry 3 could be a one component stable formulation if it is stored in dry conditions.

After preparation of the materials, three consecutive layers with a wet film with thickness of around 6 mils each were applied on CRS substrate and the films were exposed to UV radiation after applying each layer. Panels were passed 3 times under a Fusion UV system with an H-bulb (Loctite ZETA 7415) with the conveyor belt speed set to 12 feet/min and energy density of $\sim 0.70 \text{ J/cm}^2$. In order to compare the properties of dual cure systems with conventional ones, for each chemistry, two formulations were prepared. Formulation 1 consisted of only the rapid curing mechanism whereas the second formulation contained entire formulation. Samples were then kept at room temperature for 24h before testing.

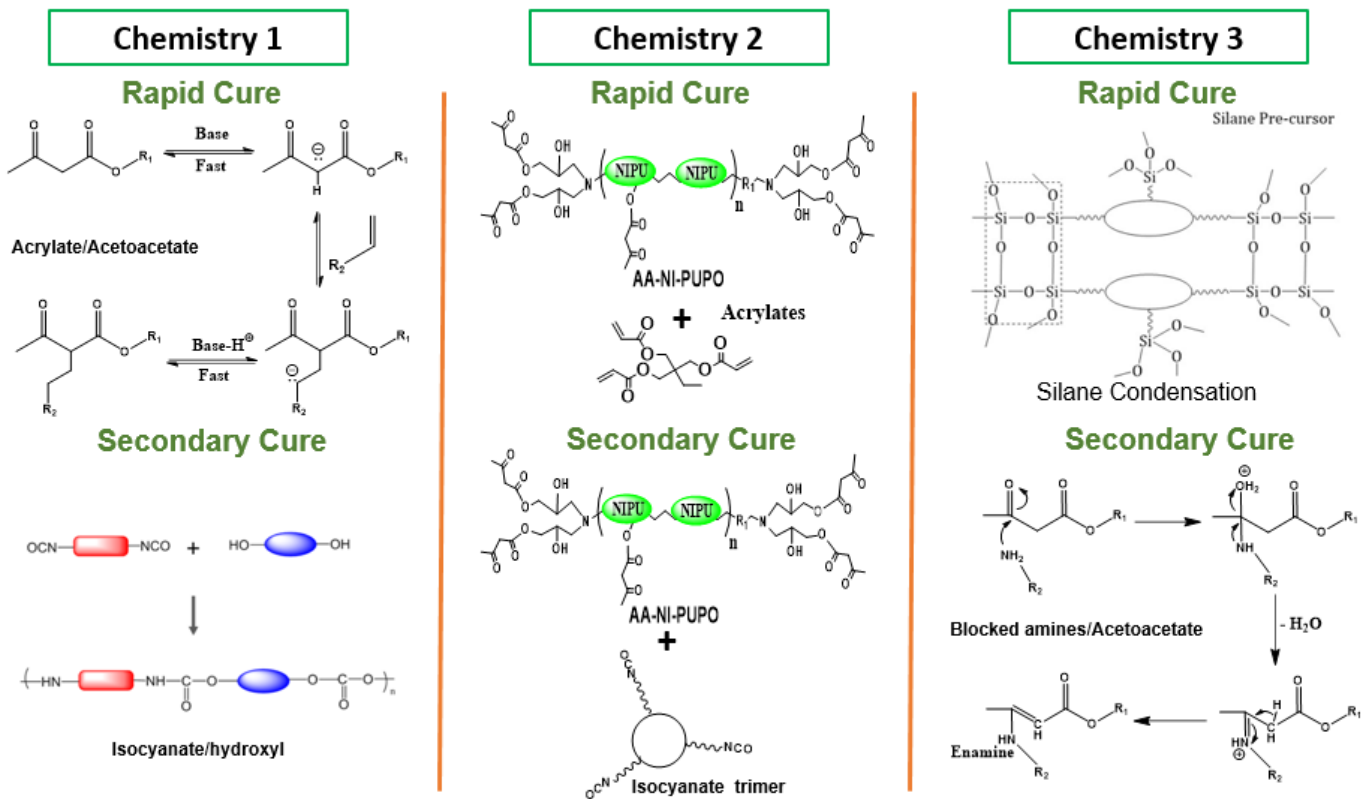


Fig. 2: Schematic overview of chemistries used in the printing material formulations

2.3 Test methods

The hardness properties of the coatings were determined using pencil and König pendulum methods according to ASTM D3363 and ASTM D4366, respectively. Flexibility and load distribution property of the coatings were evaluated by conical mandrel and impact tester as per ASTM D522 and ASTM D2794, respectively. Impact resistance was measured on the impact tester with a maximum height of 40 inches and a load of 4 lb. The resistance of samples to MEK double rubs was also evaluated by ASTM D4752 method. In order to assess the adhesion of the layers, pull-off adhesion of the samples was measured according to ASTM D4541 using a DeFlesko ATA50 PosiTest kit. The force used to detach the dollies from the coated substrate was recorded in MPa. Finally, the static mechanical properties (e.g. elongation%, and tensile strength) were measured with Universal Galdabini tensile testing machine and the crosshead rate was set at 50 mm/min.

3. Results and discussions

In order to obtain a proof of concept for the proposed dual-cure systems, three different chemistries using synthesized model compounds were used. Acetoacetylated compounds were synthesized by reaction of corresponding polyols with acetoacetates. For each chemistry, the rapid curing mechanisms were studied as the sole component of materials and were coded as formulation 1. By addition of the secondary cure mechanism, formulation 2 was prepared and compared to the first formulation in terms of various properties. Both formulations of each chemistry got tack-free after radiation of UV. This was a positive finding as for the second formulations, the uncured components did not show any negative impact on development of rapid green strength. Despite the properties such as hardness, and chemical resistance were

initially negatively affected, but the properties started to form over the course of time. **Table 1** represents the general properties of materials coated as three consecutive layers on CRS substrate after 24h of storage at room temperature.

Generally, it was observed that addition of the secondary cure, could adjust the balance of hardness and flexibility properties of the systems. For chemistries 1 and 3, the first formulations were relatively hard as a brittle film was obtained for chemistry 1 with failure in mandrel flexibility test and had a very low impact resistance. The fact that in chemistry 3, the first formulation could pass the flexibility test might be due to the rigid structure of siloxane linkages. On the other hand, for chemistry 2, the first formulation showed a very good impact resistance and flexibility. However, it was lacking in terms of hardness and MEK double rubs (40). By addition of the second crosslinker, the hardness and MEK double-rub values increased (from 35 to 80 in mandrel and 40 to 110) while still passed flexibility and 120 in.lb of impact resistance was achieved. After application of each layer and UV irradiation, the photo base generators in the formulation will be activated. This will result into immediate crosslinking of the functionalities involved in rapid curing (i.e. click chemistry reaction of acrylates and acetoacetates and silane condensation). Moreover, the continuous reaction between the remaining functional groups will be triggered by the activated catalyst in chemistries 1 and 2, and the water generated by condensation of silanes in chemistry 3. Over the course of time, completion of the secondary curing without the need for additional UV, heat, or moisture (known as dark cure), will lead to a dense and highly inter-connected network and increased crosslinking density. This could be responsible for balanced properties and increased toughness of the materials.

Table 1: General properties of layers obtained from different chemistries. Formulation 1: containing only the rapid cure system, Formulation 2: Containing rapid and secondary systems

	Chemistry 1		Chemistry 2		Chemistry 3	
	Formulation 1	Formulation 2	Formulation 1	Formulation 2	Formulation 1	Formulation 2
Pencil Hardness	8H	6H	4B	H	3H	HB
Pendulum hardness	140 ± 10	105 ± 5	35 ± 5	80 ± 5	85 ± 5	70 ± 5
MEK Double-Rub	>300	>300	40 ± 5	110 ± 5	>300	90 ± 5
Flexibility (1/8 in)	Fail	Pass	Pass	Pass	Pass	Pass
Impact resistance (in.lb)	<20	80	>160	120	60	>160

* Total DFT=15 mils

Another important goal of this research was to investigate the effect of addition of dark cure technology on the inter-layer adhesion of the AM materials. In order to do so, pull-off adhesion test was utilized as a tool to generate observations. Three consecutive layers of each formulation were applied on iron phosphate pretreated panels. UV radiation was done after application of each layer. This will simulate the process of AM 3D printing. After 24h of storage at room temperature (to let the dark cure to proceed), pull-off dollies were attached on the substrate according to ASTM standards and the force needed to detach them was recorded and summarized (mean value of three measurements) in **Fig. 3**.

It is evident in the figure that the bond strength values were significantly increased from formulation 1 to 2 for each chemistry. For instance, the adhesion value increased from 1.26 to 4.23 MPa (235%) for the third chemistry. It should be noted that the adhesion of a single layer of all formulations was in a similar range compared to the adhesion values of dual-curable three-

layer systems (Red bars). Therefore, the lower values for adhesion of three layers could be attributed to any deficiency or lack of bondings between the layers. Higher adhesion values of chemistries 2 and 3 could also be attributed to the interaction of urethane and silane functionalities within and between the layers as well as with the CRS substrate. To better understand the effect of additional curing mechanisms on inter-layer adhesion, the digital images of detached samples were analyzed (**Fig. 4**). The type of film detachment could clearly provide an estimate of the inter-layer adhesion. Specially for the last two chemistries, the type of failure in pull-off test was a cohesive failure in first formulations. Signs of delamination of the top layers from their underneath ones clearly suggested that the bonding between the layers could resist and transfer more than a certain amount of force (values in blue bars in Fig. 3). On the other hand, the type of failure was in the form of adhesion failure for second formulations and as mentioned earlier, the values were close to that of a single layer system. This clearly shows that the inter-layer bonding caused by the dark cure, could provide enough uniformity and strength to the material in order to maintain the adhesion between the applied layers. For chemistry 1, the adhesion failure in formulation 1 could be due to brittleness of the systems rather than inter-layer adhesion.

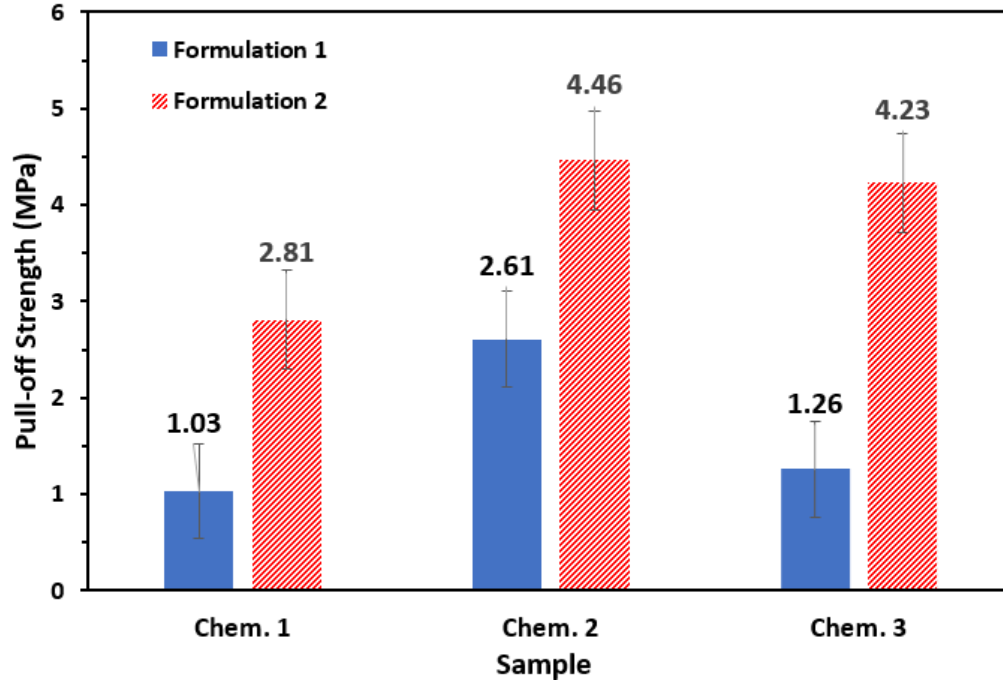


Fig. 3: Pull-off strength of 3-layer coating samples applied layer-by-layer followed by UV radiation

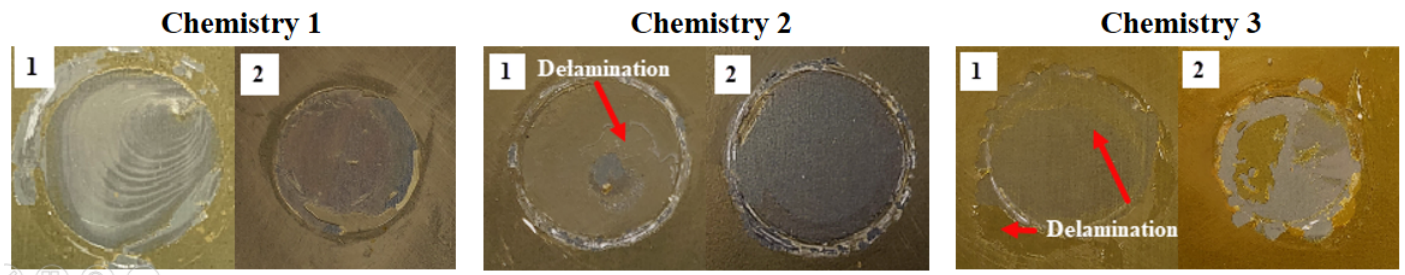


Fig. 4: Digital images of pull-off test for 3 layer coating samples

The mechanical properties of three-layer coating systems were also studied using the tensile testers. Free films which were obtained by AM method with total thickness of 1 mm were tested using the tensile machine and the elongation% at break and the tensile strength (maximum of load divided by the cross-section area) were summarized in **Table 2**. It should be noted that although the direction of pulling during the test was in perpendicular direction of the applied

layer, it could provide us with valuable information about the extent of network formation within the layers and the elasticity and toughness of the materials. For chemistry 1, due to the brittleness of the free films, no meaningful data could be generated. Results clearly showed that by incorporation of the additional crosslinking mechanism, the elongation of the free films were increased by more than double compared to the first formulations. In addition to that, the tensile strength of the samples also increased suggesting that the samples exhibited better elastic properties. In fact, the additional covalent bonding between and within the layers causes the samples to express more resistance to deformation as well as more force required to break the chains apart. This could be a great advantage for the 3D printed materials to produce products with comparable mechanical properties with respect to conventional production methods.

Table 2: Elongation% and tensile strength value of 3-layer coating samples obtained from tensile test

	Chemistry 1		Chemistry 2		Chemistry 3	
	Formulation 1	Formulation 2	Formulation 1	Formulation 2	Formulation 1	Formulation 2
Elongation %	-	64	56	114	42	105
Tensile strength (MPa)	-	2.64	0.68	1.35	1.04	1.71

4. Conclusions

A novel series of photo-latent superbase were found to efficiently cure different chemistries such as silanes, michael addition of acetoacetates and acrylates, and typical NCO/OH (urethane) chemistry. By usage of multi-functional oligomers dual curing materials could be achieved leading to a high-performance material after exposure of the coatings to UV radiation and short

storage at room temperature. Building on this technology, we aimed to develop a material suitable for additive manufacturing 3D printing as a one-component (1K) or two-component (2K) formulation. Results revealed that appropriate balance of flexibility, hardness and chemical resistance, enhanced inter-layer adhesion of materials and improved elasticity and mechanical properties could be achieved by proper design of oligomers and formulation.

5. Acknowledgements

Authors would like to thank International Ultraviolet Association (IUVA) and chemical suppliers mentioned in materials section for supporting this research.

6. References

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