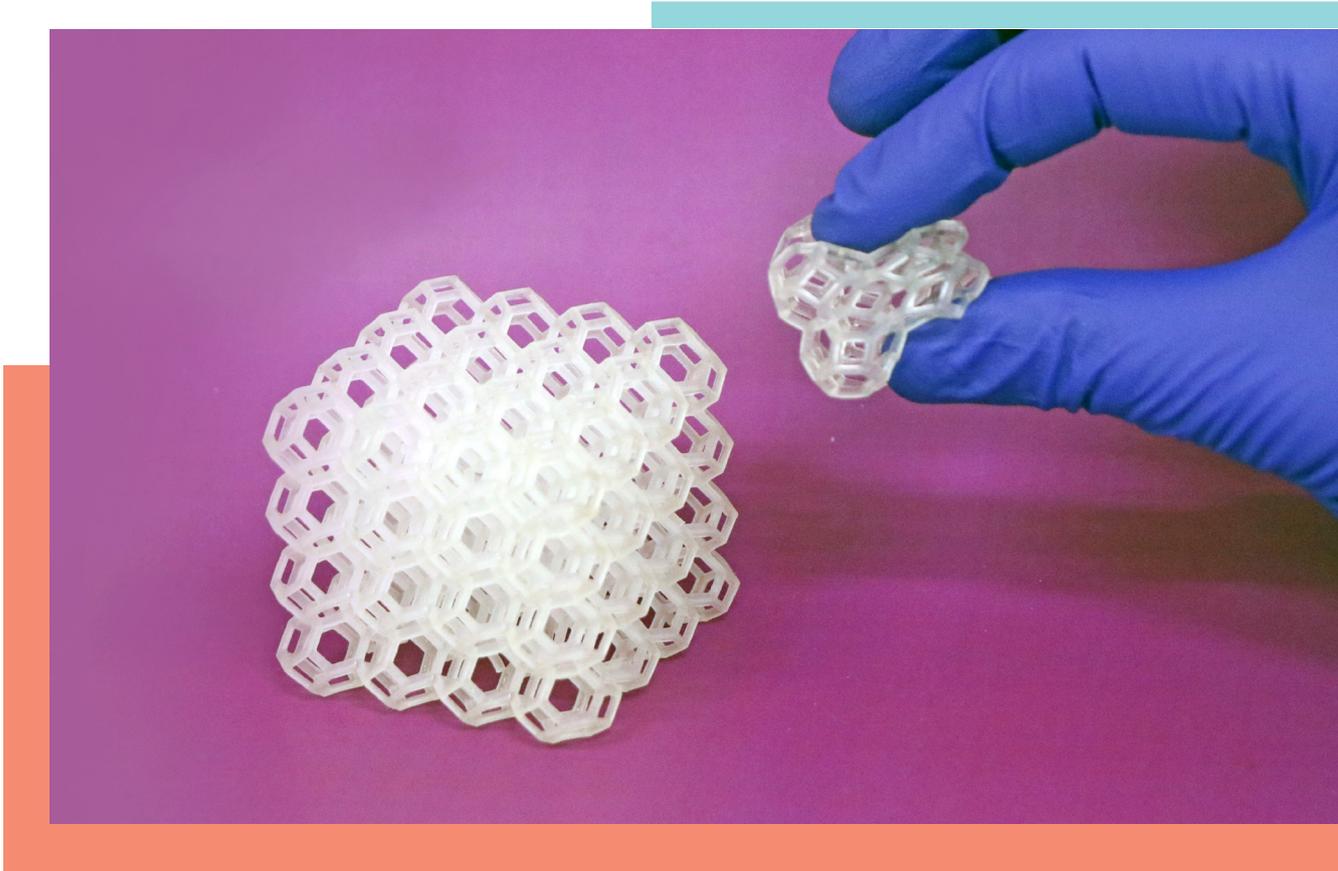


New Developments in Acrylate Oligomers for 3D Printing



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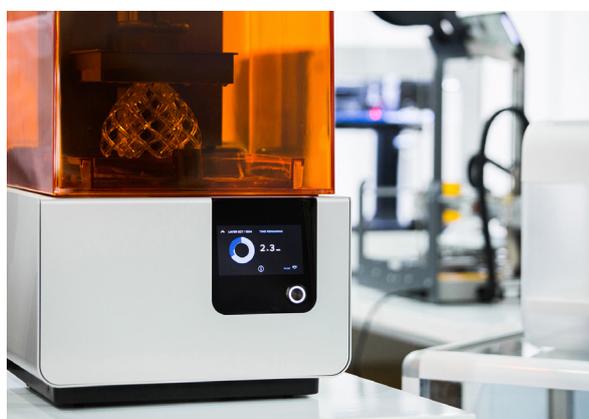
Abstract

The present work addresses a strong market demand for the next generation of oligomers for use in 3D printing, rapid manufacturing applications. Printing relatively flexible parts is often challenging for printers that require moving of the parts in x or y direction. Printability versus quick modulus increase during light curing will be discussed. Benefits of new oligomers are investigated in free-radical-curing acrylate formulations and free-radical/cationic curing acrylate/epoxy hybrid formulations. Mechanical and thermal properties of the formulations will be revealed.

Introduction

The expansion of 3D printing into rapid manufacturing applications has been coupled with an increased demand for materials with a wide variety of physical properties. Rigid materials, with high tensile strength and low elongation, are readily available, but offerings of tough, flexible materials with high elongation are more limited. Aside from the technical challenges of developing these types of materials, another potential source driving this limitation is the challenge associated with printing flexible parts with certain types of 3D printers.¹ When the printing process involves movement of parts or printer hardware in the x or y direction, as it does with some SLA or DLP type printers, forces are exerted on the part in situ that could cause an overly flexible part to move out of alignment, separate from the build platform, or even break resulting in poor resolution and failed prints. Thus, in the development of new materials for 3D printing, especially flexible ones, it becomes important to evaluate how well the material can withstand these types of forces.

Figure 1. Stereolithography (SLA) 3D Printer



This work, then, had two major goals. The first was to evaluate the mechanical properties of newly developed (meth)acrylate oligomers that have the potential to meet the demand for tough, flexible 3D printing materials. This evaluation included a comparison to materials currently on the market that are advertised as being tough or flexible. The second goal was to identify a method that would allow for an evaluation of the oligomers' ability to resist the forces that act upon parts during the printing process. This resistance, in turn, relates to printability or the probability of having a successful printing outcome. For this latter goal, both relative rate of (meth)acrylate conversion and the change in the material's complex modulus during cure were examined. These methods were used to evaluate how quickly the material's green state properties were reached and whether those properties would meet a minimum threshold required to survive the printing process.

Experimental

For this work, four urethane (meth)acrylate oligomers (UAO) of varying structures were synthesized to explore their suitability for use in 3D printing formulations, especially those designed to generate flexible shapes or parts. The oligomers were synthesized in 35–40% reactive diluent to produce a preformulated resin mixture and then further formulated into the model 3D printing formula found in Table 1. Three commercially available (meth)acrylate based 3D printing resins (CR) were also examined for comparative purposes and were used as received. The viscosity of all resin formulations was measured using a Brookfield CAP2000+ viscometer at 25 C.

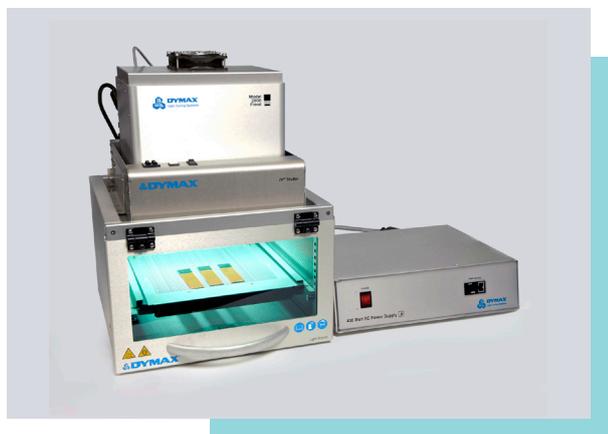
Table 1. Model 3D Printing Formulas

Component	Wt%
UAO	55.0
Reactive Monomers	40.0
Photoinitiator	3.0
Additives	2.0

Test samples of UAO based formulations were cured using a broad spectrum Dymax 2000–EC Flood Lamp (Figure 2) for four minutes at an irradiance of 50 mW/cm² as measured by a Dymax ACCU–CAL™ 50 Radiometer. Test samples of CR materials were prepared using a commercial SLA 3D printer with a reported 405 nm, 250 mW/cm² laser followed by a post-cure under the same curing conditions as the UAO

based formulations. Tensile properties of all test samples were obtained using an Instron tensile tester according to ASTM D638.

Figure 2. Dymax 2000–EC Curing System



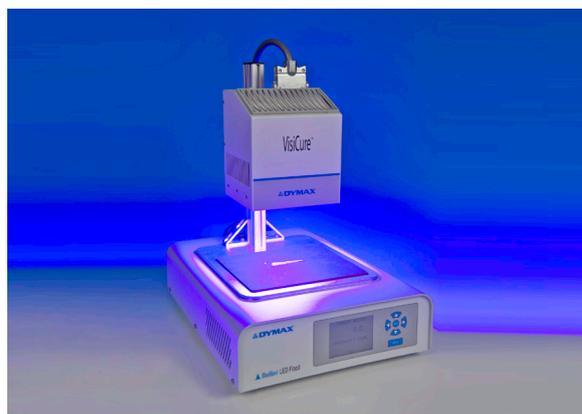
Both the heat deflection temperature (HDT) and glass transition temperature (T_g -DMA) were assessed using DMA methods per ASTM D648 and ASTM E1640 respectively. Materials were tested using a Thermal Analysis DMA Q800 with dual cantilever geometry. For HDT determination, the instrument's Controlled Force test parameters were used to apply a constant stress of 0.445 MPa. The glass transition temperature was determined using the instrument's Multi-Frequency - Strain program. Samples were equilibrated at -80°C before increasing the temperature at a rate of $5^\circ\text{C}/\text{min}$ to a maximum temperature of 75°C for HDT and 110°C for T_g -DMA. For both tests, the results were analyzed by TA Universal Analysis software. The T_g -DMA reported is the peak of the $\tan \delta$ curve.

The linear coefficient of thermal expansion (CTE) for each cured resin was measured via TMA according to ASTM E831 using a Thermal Analysis TMA Q400 set to an expansion program. While exposed to a constant force of 0.10N, samples were equilibrated at -60°C and then ramped to 250°C at a rate of $5^\circ\text{C}/\text{min}$. Data was analyzed by TA Universal Analysis software. The T_g -TMA was also measured at the point of inflection in the resulting dimensional expansion versus temperature curve.

The relative cure speed of the resins was measured using Fourier Transform Infrared Spectroscopy to determine the extent of (meth)acrylate conversion. Materials were cured at a depth of 1 mm using a 405 nm Dymax BlueWave[®] LED Flood Lamp with VisiCure[®] Emitter (Figure 3) at an irradiance of $250 \text{ m}/\text{cm}^2$ as measured by Dymax ACCU-CAL[™] 50-LED

radiometer. Resins were exposed at 5 second intervals over a range of 15 seconds and the rate of decline of the (meth)acrylate peak at approximately 810 cm^{-1} per unit time was calculated.

Figure 3. Dymax BlueWave LED Flood with VisiCure (405 nm) Emitter



The photo-rheological properties of each resin were tested using a Discovery HR-2 Hybrid Rheometer (DHR-2) using an 8mm parallel plate, UHP geometry. After allowing the instrument to equilibrate for 30 seconds, the samples were exposed to a 405 nm wavelength of light at an irradiance of $250 \text{ mW}/\text{cm}^2$ using a BlueWave LED Flood Lamp with VisiCure Emitter (Figure 3) set at a distance of 1.0 mm from the sample. Exposure times varied between 15–45 seconds depending on the sample to ensure completion of cure. Measurements of complex modulus were obtained during cure and for an additional 15 minutes after the cessation of exposure. Complex modulus is the ratio of stress to strain under oscillatory or vibratory conditions.

Results and Discussion

UAO Characterization

The structures of most UAOs are commonly generalized as being comprised of three segments: the soft and hard segments, which together comprise the main polyurethane backbone, and the (meth)acrylate functional segment that end-caps the oligomer. In large part, the bulk properties exhibited by a UAO will depend on the particular structure, position, and relative concentrations of these segments within the final oligomer.² Table 2 describes the four new UAO along these dimensions as well as reports the viscosity of the final formulation for each. The soft segment of each UAO is differentiated by type (SST) and by relative length (SSL). Broadly speaking, due to the presence of constraining intra-structural functional groups, the soft segments of Type 1 and Type 3 would tend to be more rigid than Type 2. The relative concentration of hard segments within each oligomer is depicted as the hard segment ratio (HSR). Lastly, the acrylate ratio (AR) represents the functional equivalent weight of (meth)acrylate groups for each oligomer with a further differentiation between acrylates (A) and methacrylates (M).

As would be expected from a soft and hard segment containing polyurethane backbone, the SSL is inversely related to the HSR with the shorter SSL oligomers having the highest relative concentration of hard segments and vice versa for longer lengths. Similarly expected is the proportionate relationship between the SSL and AR. As the SSL, and therefore overall oligomer size, increases, the oligomer mass per functional (meth)acrylate group correspondingly increases as well. A lower AR indicates a higher (meth)acrylate group density and should, therefore, result in a more tightly crosslinked final polymer after cure.

In terms of which of these structural elements effect the formulation viscosity, multiple variables are likely involved. UA04 resulted in the highest formulation viscosity due to the higher degree hydrogen bonding between hard segments and the relatively constrained Type 3 soft segment. The formulation based on the UA01 has a lower HSR than UA04 but also has a longer Type 1 soft segment. Taken together, these properties of UA01 resulted in a viscosity in between UA04 and the two Type 2 oligomers, UA02 and UA03. Comparing UA02 and UA03, although UA02 has a higher HSR, which would be expected to have more hydrogen bonding, the viscosity of these formulations appears to be more dependent on SSL with the larger UA03 giving a slightly higher viscosity. This may be due to the higher potential for

chain stacking in UA03's longer Type 2 soft segment that is not diluted as well by the reactive monomers in the model formula.

When compared to the viscosities of the CR materials it appears that the viscosity of all formulations should be suitable for printing with an SLA or DLP 3D printer. The measured viscosities of CR1, CR2, and CR3 were 1000, 2500, and 4500 cP respectively.

Table 2. UAO Characterization & Formulation Viscosity

	SST	SSL	HSR	AR (Type)	Form. Viscosity
UA01	Type 1	Medium	1.6	1.8 (A)	3000 cP
UA02	Type 2	Medium	1.7	1.7 (M)	2500 cP
UA03	Type 3	High	1.0	2.0 (M)	2800 cP
UA04	Type 4	Low	2.2	1.0 (A)	3500 cP

Tensile and Thermomechanical Properties

Table 3 provides the tensile properties of the four UAO and three CR materials. This data would reflect the final material properties when subjected to a post-curing step after the actual 3D printing process. As seen, with respect to % elongation all four UAOs are significantly superior to any of the CRs. The UAO with the lowest elongation, UA04, has nearly four times the % elongation of CR3, the commercial resin with the highest % elongation. Coupled with this high elongation, the UAOs also have reasonably good tensile strength and modulus, a balance that is often difficult to achieve, illustrating their toughness characteristics.

Table 3. Tensile Properties

	Tensile Strength	Elongation	Young's Modulus
UA01	19 MPa	395 %	380 MPa
UA02	18 MPa	295 %	630 MPa
UA03	16 MPa	395 %	375 MPa
UA04	30 MPa	195 %	310 MPa
CR1	40 MPa	10 %	820 MPa
CR2	27 MPa	25 %	430 MPa
CR3	4 MPa	50 %	7 MPa

The thermomechanical properties of all materials are given in Table 4. Apart from the HDT of UA03, which could not be detected at temperatures above 0 °C, all UAOs show improved thermomechanical properties compared to the

more flexible commercial resin, CR3. UA04 and to some extent UA01 are comparable in HDT, Tg, and CTE to the much less flexible CR1 and CR2. Overall, each UAO offers a unique, high elongation alternative to the three commercial resins tested with the primary differentiating properties being tensile strength and the relative flexibility or rigidity at different temperatures.

Table 4. Thermomechanical Properties

	HDT (°C)	Tg - DMA (°C)	Tg - TMA (°C)	Pre-Tg CTE (10 ⁻⁶ /°C)
UA01	47	82	48	103
UA02	36	63	42	100
UA03	<0	61	41	122
UA04	58	83	58	93
CR1	55	70	58	55
CR2	63	82	60	94
CR3	8	35	33	120

Relating the UAO properties to their structural characteristics, the tensile and thermomechanical properties correlate well to both the expected stiffness of the polyurethane backbone and degree of cross linking. UA04 has the highest tensile strength, HDT, and Tg, but lowest elongation and CTE. These properties can be attributed to its Type 3 soft segment, low SSL, high HSR, and low AR all of which result in a more rigid backbone and higher cross link density. At the opposite end is UA03 whose high SSL, Type 2 backbone, low HSR, and high AR gave the lowest tensile strength, HDT, Tg, and highest CTE. The inability to even detect an HDT for UA03 is primarily due to the high SSL. At a certain point, the SSL becomes so high that the polymer will always have areas within it that remain flexible even at low temperatures.

UA01 and UA02 are in between these two extremes. UA01 shows a higher tensile strength, HDT, and Tg than UA02 possibly the result of the slightly higher AR and a more constrained Type 1 soft segment. Interestingly, UA01 was found to have a lower elongation and modulus than UA02, but higher HDT and Tg. One potential explanation for this incongruity could be that UA02 is methacrylated rather than acrylated. The presence of methacrylate groups tends to reduce chain mobility and increase polymer rigidity. At the same time, though, methacrylates are known to cure more slowly than acrylates. If, under identical curing conditions, UA02 did not reach the same degree of (meth)acrylic

conversion, then the properties of UA02, including strength, toughness and rigidity, would be negatively affected. The lower than expected elongation for UA03, another methacrylate, despite its structural characteristics could be due to these same reasons.

Conversion Rate and Photo–Rheometry

Having identified the potentially advantageous mechanical properties of the UAO materials for 3D printing applications, the next question is whether they would be expected to experience any problems during the 3D printing process itself. To investigate this possibility, the relative (meth)acrylic conversion rate (RCR) and the change in complex modulus (G*) during cure were measured. Figure 4 illustrates an example of the data obtained from the photo–rheometer with the left– and right–hand graphs showing complex modulus and modulus rate of change, respectively, as a function of time. Together with the RCR data, Table 5 gives the numerical output of the photo–rheometric testing showing the maximum complex modulus, peak rate, and the times elapsed before reaching those points.

While both the RCR and photo–rheometric measurement of complex modulus are intended to provide some indication of how quickly the materials' green–state properties are achieved, the measurement of complex modulus has the added benefit of providing some evidence of what those properties can be. The RCR data highlights this difference and raises the probable limitation of strictly relying on conversion rates to evaluate printability as it does not necessarily correlate to material physical properties. CR1, which is the most rigid of the materials tested, had the lowest RCR and CR3, which was one of the least rigid, had the highest. All the UAO oligomers had a higher conversion rate than CR1 preliminarily suggesting that they should be printable. The acrylates, UA01 and UA04, were faster than the methacrylates, UA02 and UA03, as would be expected. The slight differences in RCR between UA01 and UA04, and between UA02 and UA03, is in line with the materials' AR with the more (meth)acrylic dense materials with in each group being faster.

Figure 4. Example of Photo-Rheometer Output

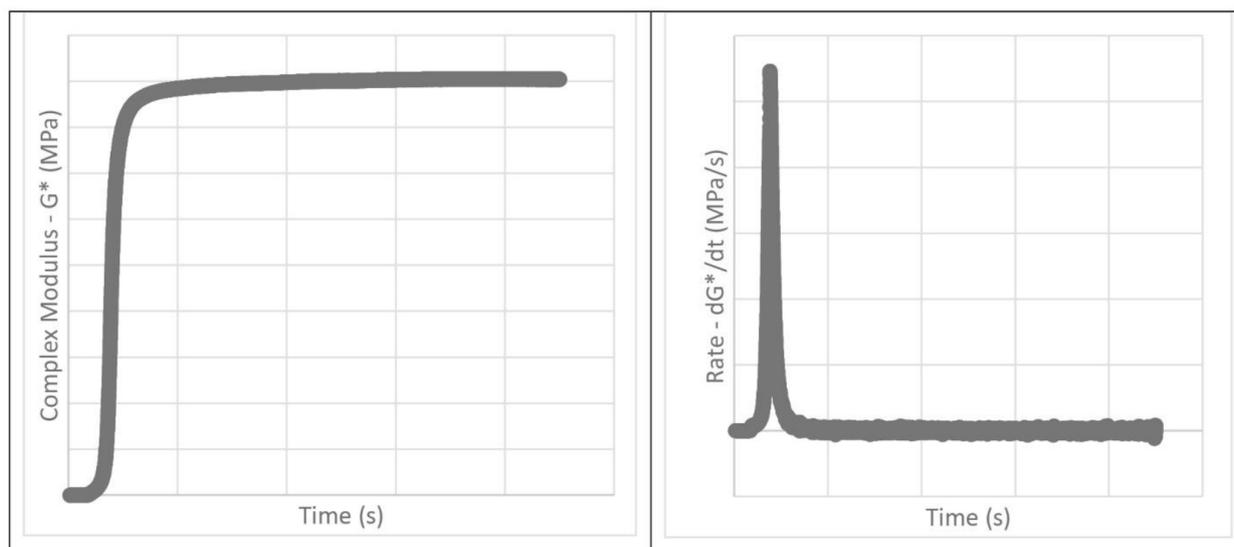


Table 5. Relative Conversion Rate and Photo-Rheometer Data

	RCR	Complex Modulus (G*)			
		Max. (MPa)	Time to Max. (s)	Peak Rate (MPa/s)	Time to Peak Rate (s)
UA01	1.9	13	100	1.5	14
UA02	1.4	9	570	0.6	40
UA03	1.1	7	710	0.2	46
UA04	2.1	13	59	3.9	13
CR1	1.0	26	102	3.1	7
CR2	2.1	41	73	6.7	8
CR3	2.4	5	150	0.3	17

The materials' complex modulus response upon exposure to light gives a much clearer picture of whether the material will reach a threshold degree of stiffness quick enough to withstand the stresses of the 3D printing process. Here, CR3 has the lowest maximum modulus, consistent with its final post-cured properties, and is the slowest of the CR materials. All the UA0 materials have a higher maximum complex modulus than CR3. This implies that they all should have the requisite amount of rigidity to survive the printing process given a long enough exposure time.

UA04 builds modulus and reaches its maximum quickest of the UA0 materials and is faster than CR1. This speed is likely related to its low SSL, Type 3 soft segment, and high HSR, providing a stiffer polyurethane backbone even before cure. Its low AR also plays a role leading to the quicker formation of a more tightly cross-linked network. UA01 is second in terms of the rate of modulus increase mirroring the structural differences between it and UA04. The maximum modulus reached is the same for both UA01 and UA04 which roughly matches the modulus observed after post-curing. This similarity could be due to the unique similarities and

differences in their soft segment structure. When compared to the results from the CR materials, both UAO1 and UAO4 appear to surpass the threshold rate of modulus increase needed for printability.

Although the maximum modulus for UAO2 and UAO4 exceeds that of CR3 and the rate of modulus increase is comparable or marginally better, the time required to reach these points is significantly longer. As with the low RCR, this sluggishness in modulus build is primarily the result of the methacrylate end groups which cure more slowly than their acrylate counterparts. Based on this data, to improve the chances of a successful print the UAO2.

and UAO4 based formulations may need adjustment to increase the rate of modulus increase or the exposure time per layer may need to be increased if allowed by the particular 3D printer

CONCLUSION

This work had two overall goals: to evaluate new, flexible polyurethane (meth)acrylate oligomers for use in 3D printing applications and to evaluate those oligomers for printability using an appropriate method. All four new oligomers showed a substantial improvement in elongation over the three comparative commercial resins. At the same time, they had reasonable tensile strengths indicating that they would be useful in 3D printing applications requiring tough and highly flexible materials. Differences in tensile and thermomechanical properties between oligomers can generally be traced to structural differences, including soft segment type, soft segment size, and hard segment concentration. The relative (meth)acrylate conversion rate

for the new oligomers was on par with the commercial resins with the acrylates showing faster conversion than the methacrylates. The rate of complex modulus increase, as it is a much more direct measurement of a material's resistance to an applied stress, was revealed as a better potential indicator of printability. In this regard, using the comparative, commercial resins as a baseline for what should be printable, the two acrylate oligomers appear to exceed the threshold rate of modulus increase to be considered printable. In contrast, formulations based on the two methacrylates, whose modulus increased at a much slower rate, may require some reformulation or printing process adjustment to produce a successful print.

References

1. "The Ultimate Guide to Stereolithography (SLA) 3D Printing." Formlabs.com. March 2017, pg. 6. Available for download at <https://formlabs.com/blog/ultimate-guide-to-stereolithography-sla-3d-printing/>.
2. See e.g. Francis, Heather and A. Nebioglu. "New Oligomers for 3D Printing Inks." UV+EB Technology. Issue 1, 2016. Available at <http://www.uvebtech.com/stories/022616/3d-printing.shtml#.WrQqMGff-PIU>.

