

Material Solutions for High Heat Resistance in 3D Printing Applications

Brendan T. McGrail

Sartomer, 502 Thomas Jones Way, Exton, PA, 19341

Introduction

Photocurable resins with heat stability comparable to conventional engineering polymers are increasingly important for the development of 3D printing materials across a wide range of end uses. Highly crosslinked acrylate formulations are commonly employed as high temperature components in traditional photocure applications, but come at a cost of shrinkage, high internal stresses, and poor mechanical properties at the service temperature, rendering them unsuitable for most applications. Methacrylates offer higher glass transition temperatures at equal functionality but have relatively low ceiling temperatures, lower reactivity, and a smaller pool of commercially available materials. The failure of these traditional photocurable (meth)acrylate resins to match the mechanical toughness of engineering thermoplastics such as polystyrene, ABS, and polyamides is well documented, but these photocurable formulations often show lower glass transition and heat deflection temperatures than engineering thermoplastics, further limiting their utility and placing applications where the use of (often brittle) high temperature thermosets beyond reach.

Herein, we present new formulation strategies to achieve photo-3D printable materials with high T_g s and HDTs alongside the mechanical properties of different classes engineering materials while retaining print accuracy and dimensional stability.

Experimental

All raw materials were acquired from commercial sources and used without further purification. All monomers and oligomers other than developmental materials highlighted herein reflect Sartomer's commercial production. Bulk curing experiments were conducted using LED sources with emission maxima at 365, 395, or 405 nm and 9W nominal power output. Samples in non-thin-film geometries were prepared by pouring liquid resin into molds conforming to appropriate ASTM and ISO standards. 3D printed samples were produced in shapes conforming to the same ASTM and ISO standards as bulk cured samples using both "closed" and "open" systems.

Tensile tests were conducted according to ASTM D638 and/or ISO 527-2(5A) using an Instron universal testing apparatus. DMA experiments were conducted between -100 and 200 °C in single cantilever geometry at 0.01% strain and 5°C/min heating rate using a TA Instruments Q800 dynamic mechanical analyzer. T_g values are reported as the highest-temperature maximum of the $\tan(\delta)$ vs. temperature curve. Heat deflection temperatures are reported according to ISO 75 method A (1.8 MPa, 61 mm distance between supports, 2°C/min heating rate). Kinetic analyses are based on time-resolved FT-IR spectra (0.5 s resample rate, 2 scans, using peaks identified in the literature for spectral assignment).

Results and Discussion

Thermoplastic-Like Materials with T_g s > 100 °C

One of most commonly discussed limitations of (meth)acrylic photopolymers is their limited toughness and impact resistance. One common approach to addressing this problem has been to formulate in a way so as to achieve a glass transition region that spans the material's useful temperature range, allowing for a mixture of glassy and rubbery dynamics to influence material properties. While this approach has yielded modest successes, traditional free-radical curing systems still show pronounced property limitations, particularly heat deflection temperatures (HDTs) of 35-50 °C and a loss of rubbery dynamics below 10-20 °C, resulting in resins that only provide mechanical utility for one to two temperature decades centered around 25 °C. Building on our earlier work to enhance the cure speed of methacrylate monomers,¹ we sought a purely radical curing system that could show useful mechanical properties over 100 °C and had showed mechanical properties genuinely comparable to engineering thermoplastics. To this end, we conducted a screening study to understand the behavior of fast curing methacrylate systems in which high molar mass urethane methacrylate oligomers provided the only crosslinking. This approach allows for comparable volume fractions of rigid, high T_g methacrylic copolymers to be combined with lower T_g oligo(urethanes) to provide thermoplastic-like toughness in a single-phase system conceptually analogous to well-known PMMA/thermoplastic polyurethane blends^{2,3} while operating in a printable viscosity range. Representative DMA thermograms at different oligomer levels are shown in Figure 1.

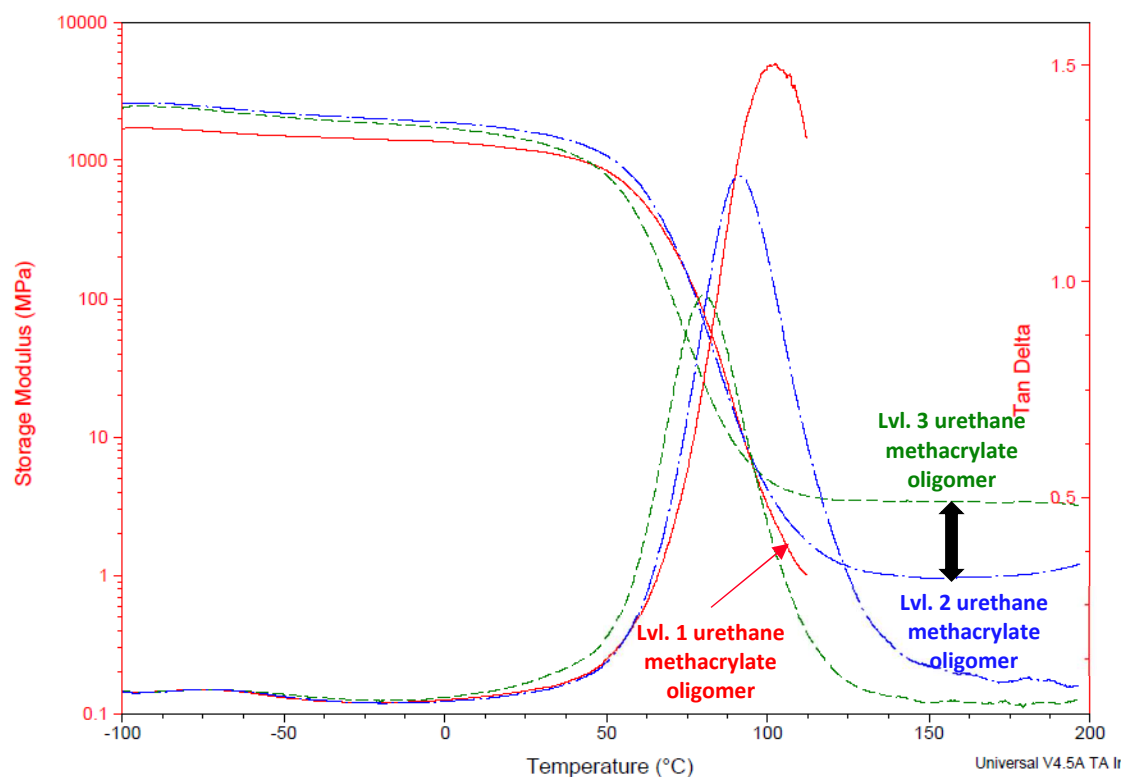


Figure 1. DMA thermograms showing partial results of a screening study of all-methacrylate systems for high T_g thermoplastic-like performance.

With preliminary results suggesting that elevated T_g s and printable viscosities remained possible even at large volume fractions of urethane oligomer, an optimization study focused on thermal and mechanical properties was conducted over a constrained monomer set. Results of particular interest are shown in Table 1 and Figure 2.

Table 1. Overview of Preliminary Optimization Study

	Ultimate Tensile Strength (MPa)	Young's Modulus (MPa)	Tensile Elongation @ Break (%)
F5	43.1 ± 1.2	610.6 ± 39.5	26.2 ± 3.1
F12	46.8 ± 0.9	601.4 ± 64.9	30.4 ± 9.4
F28	50.5 ± 1.1	800.9 ± 30.4	22.5 ± 6.9
F31	45.5 ± 0.9	596.0 ± 50.6	19.9 ± 1.6

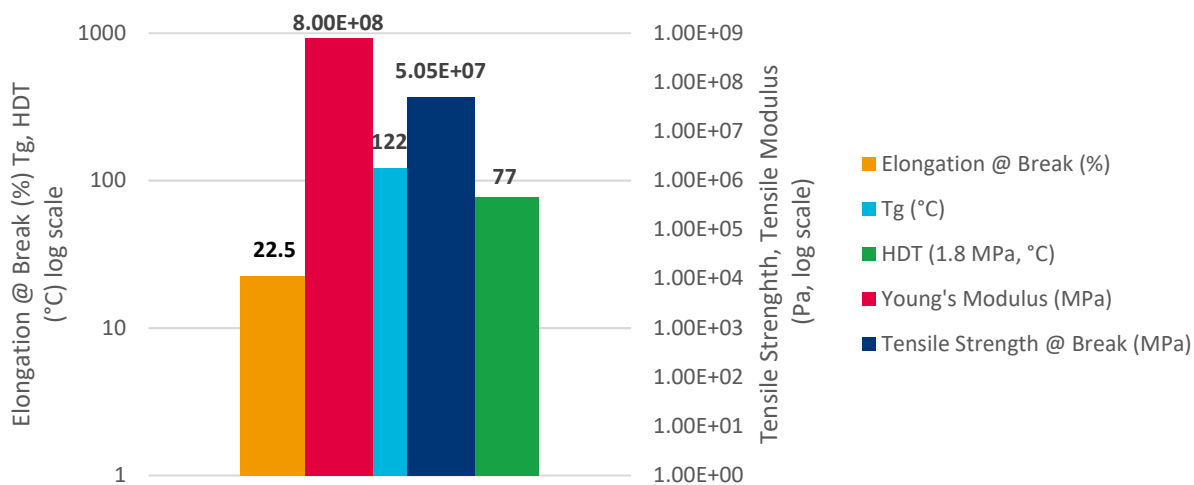


Figure 2. Summary of thermomechanical properties for Formulation 28

The partially optimized formulations all display pseudo-yield points at 10-15% strain and undergo brittle fracture at break. Typical yield stresses are approximately 35-45 MPa, with sample 28 showing a yield stress of 53 ± 1.2 MPa. The range of observed T_g s was between 65 and 125 °C (1.8 MPa HDTs between 40 and 85°C). Printed properties of the sample 28 formulation on show slight increases in tensile

modulus and tensile strength and a slight decrease in elongation at break; T_g and HDT are essentially unchanged from the bulk-cured samples. The full formulation range of this system reaches to tensile moduli of approximately 0.9-1.1 GPa, but these formulations show only modest increases in T_g with little to no increase in HDT and substantial reductions in elongation at break and tensile strength using this oligomer/monomer system, compromising part toughness. A full optimization study across a wider range of urethane oligomers and possible small-molecule crosslinkers may result in overall improvement in thermoplastic-like properties. The formulations found in this study show properties that compare favorably with injection-molded PMMA/thermoplastic polyurethane blends at DLP and SLA-printable viscosities.

High Temperature Resin Components

Unlike the case of raising T_g in thermoplastic-like resins, high rigidity and low strain-at-break are as strongly associated with high temperature engineering thermosets as they are with photocurable (meth)acrylic resins, meaning that such formulations are more likely to benefit from relatively straightforward synthetic and formulation approaches. When such traditional formulation approaches are employed, however, final resin properties often become strongly dependent on post-processing conditions due to limited diffusion of reactive centers in highly-crosslinked systems as shown in Figure 3.

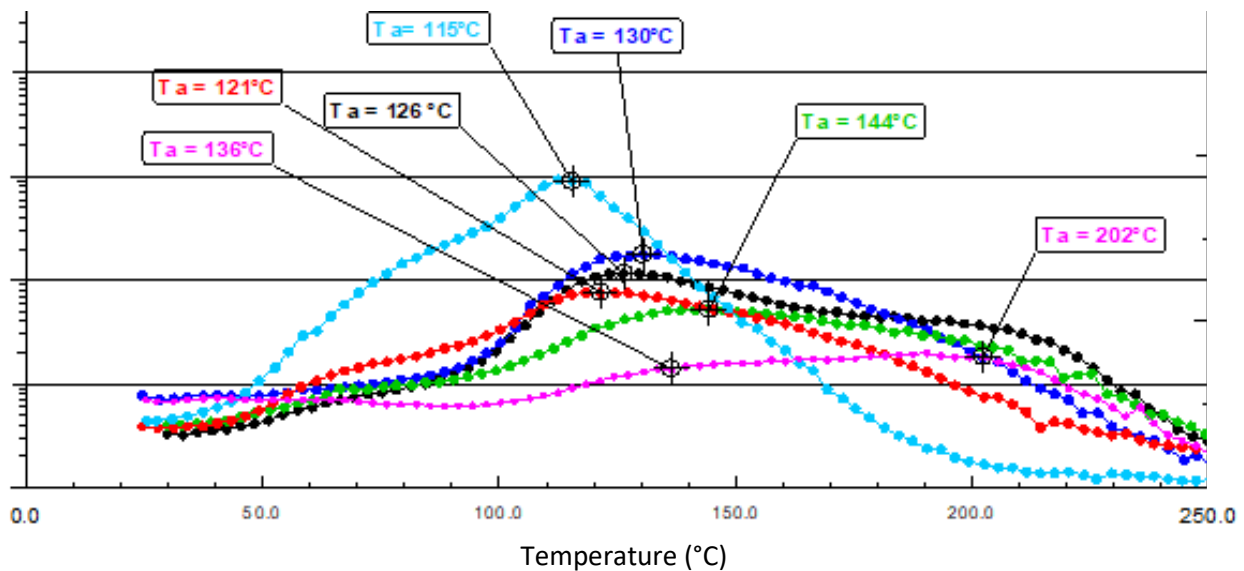


Figure 3. Dynamic mechanical thermograms showing $\tan(\delta)$ for two high-temperature formulations subjected to three different post-processing conditions.

The variability in post-processing results across different resin compositions suggests that a wide variety of combinations of properties that are most amenable to assessment through design of experiments. The variability of selected formulations as a function of post-processing is shown in Figure 4.

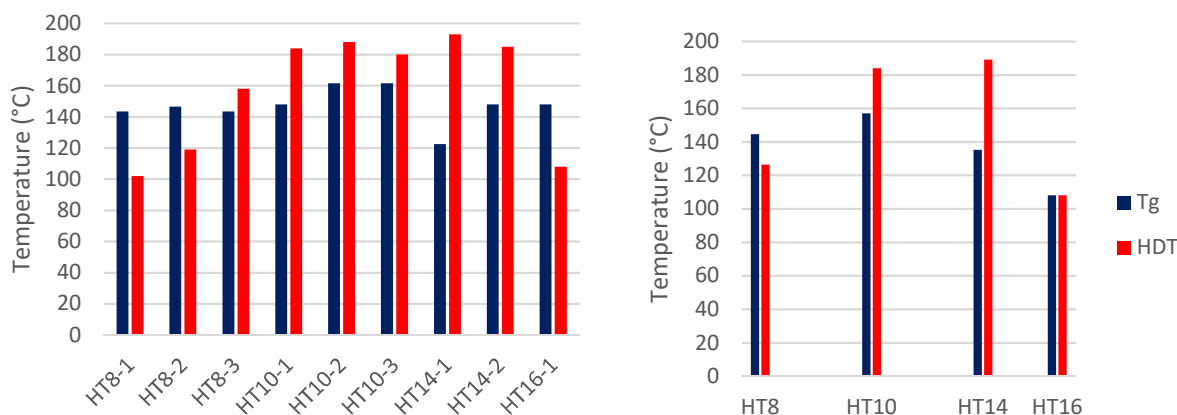


Figure 4. T_g and HDT for three high temperature formulations cured under identical conditions and post-processed under different conditions. Right: T_g and HDT for each formulation averaged across all post-processing conditions.

In aggregate, these results suggest that heat deflection temperature, rather than T_g (taken as the highest temperature maximum of the tan(δ) vs. temperature curve) is more strongly affected by post-processing conditions. Figure 3 suggests that this difference between T_g and HDT changes after post-processing is likely due to different post-processing conditions enabling different degrees of mobility of trapped reactive sites, leading to more constrained chain mobility (i.e., lowering the number of accessible modes at the lower temperature end of the tan(δ) vs. temperature curve), whereas T_g is dominated by free volume considerations across a larger temperature range. Formulations HT8, HT10, and HT16, whose thermal properties are summarized in Figure 4, are all printable on commercial SLA and DLP printers and represent modest property tradeoffs as shown in Table 2.

Table 2. Mechanical Properties of Formulations HT8, HT10, and HT16

(Printed, post-processed 65 min @ 65 °C + 120 min @ 80 °C)

	Tensile, 5A, 5mm/min						Flexural 3 pts, 2mm/min					
	Stress at break (MPa)		Elongation (%)		Young's Modulus (GPa)		Stress at break (MPa)		Deflection at break (mm)		Flexural modulus (GPa)	
	Val.	±	Val.	±	Val.	±	Val.	±	Val.	±	Val.	±
HT8	11	1	1.4	0.1	2.2	0.1	39	16	2	0.8	3.3	0.09
HT10	24	3	1.8	0.2	2.7	0.2	46	7	1.8	0.2	4.3	0.1
HT16	29	5	2.2	0.2	1.9	0.2	50	0.4	2.7	0.1	3.5	0.05

The printed parts all show high rigidity, isotropic shrinkage, and good dimensional stability once printed (no single dimension shows > 1.5% shrinkage on post cure, and thermal hysteresis averages < 1% over two 25-200°C cycles after post-processing), and are amenable to toughening using a variety of commercial products.

Conclusions

3D Printable formulations based on novel chemistries have been developed to meet needs for tough, thermoplastic-like properties with stable mechanical performance significantly above room temperature as well as true high temperature performance with T_g s and HDTs over 150°C. The formulation spaces adjacent to the described formulations have been studied to understand the ability of these formulations to be altered to meet the specific needs of end-users, specifically in terms of polymerization kinetics, thermomechanical properties, and monomer and oligomer structure.

References

1. Guichard, M.; McGrail, B.T; Wolf, W. Klang, J; Curable Compositions and Uses Thereof, WO2018219729, 2018
2. Poomali; Siddaramaiah; Suresha, B.; Lee, J.-H.; Mechanical and three-body abrasive wear of PMMA/TPU blends *Mater. Sci. Eng. A*,492, **2008**, 486
3. Schultes, K; Battenhausen, P.; Golchert, U.; Loidl, A.; Transparent TPU (thermoplastic polyurethanes)/PMMA (polymethyl (meth) acrylate) blends with improved low-temperature impact resistance, US8722788B2, **2005**