

Toughening Oligomer Review for 3D Printing

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Abstract

The use of (meth)acrylate monomers and oligomers in 3D printing has been a practiced art since the early days of stereolithography. New requirements for tougher materials have been placed on UVEB materials to offset traditional manufacturing in some niche markets. Urethane (meth)acrylates have been a staple in providing tough coatings, adhesives and composite resins and in this study we explore their utility as the main binder in a 3D printable formulation. A benchmarking study of various oligomer structures was performed, with a focus on their performance in tension and more specifically impact resistance.

Introduction

Recent advances in additive manufacturing (commonly referred to as 3D Printing) equipment has recently highlighted the limitations of thermosetting materials. Time scales for printing objects have decreased dramatically where, process time scales compete with some of the traditional thermoplastic manufacturing. With processing speeds comparable to thermoplastic processing, scientists and chemists are now focused on toughening of thermosetting materials to provide materials that can withstand the rigors of consumer goods.³

Acrylic chemistries have held their place as critical components in 3D printable resins since the industries infancy. Their rapid cure rates and extensive structure range provides a property space that has allowed formulators to develop rigid, flexibly and elastomeric-like mimics to traditional materials. While acrylics have their benefits, they are not without limitations. As the industry demand for higher modulus and lower shrinkage resins, hybrid and dual cure systems have grown to common place. Hybrid systems featuring acrylic chemistries providing vitrification while secondary cationic systems provide toughening quickly became the industry leader and leads the class in terms of performance.²

While these hybrid systems have excellent benefits, there are some tradeoffs. Cationic initiated systems requiring initiation with onium salts tend have limited lifetimes and show moisture sensitivity.⁵ Once initiated, cationic networks show continual polymerization even after the light source has been removed¹ and can lead to viscosity and property drift over time. The aromatic components providing high modulus performance tend to yellow over time, limiting the extended use for finished goods. In spite of having an intricate network of polymer matrices, they are also still plagued by poor impact performance and keep the industry limited to prototyping applications. To enable 3D Printing to grow

into producing industrial or consumer level foods, material scientists must deliver a more robust line of materials that can withstand the rigors of typical thermoplastics.

While hybrid curing approaches elegant interpenetrating network formation (IPN) are popular approaches to toughening⁴, incorporation of specific oligomers is an easy alternative to deliver toughness into a final network. Formulation chemists can relate to the observed rules of mixing for thermosetting formulations. Increasing amounts of particular oligomers push the matrix response from a cross-linked methyl methacrylate (MMA) network to behaving more like the particular oligomer. Oligomer designs with specific backbones can leverage the backbone behavior into the final matrix of the cured system. Whether its incorporation of a polyester oligomers for improved pigment compatibilities, or reliance on epoxy acrylates for abrasion resistance addition of oligomers leverage their structure properties directly into the cured matrix. Toughening mechanisms are not outside the traditional formulator’s approach and toolbox in this manner.

The most relevant oligomer for improving impact resistance of 3D printable formulations are oligomers base on urethane (meth)acrylates. These materials have historical significance of raising the bar for UVeB chemistry providing higher extensibility and improved strength to radiation curable formulations. With focused developments on resins for additive manufacturing the urethane (meth)acrylate based formulations will leverage their rapid cure times with mechanical properties closely aligned with thermoplastic urethanes.

Experimental

A study was developed to determine trends in oligomer structure and molecular weight with the materials ability to absorb high speed forces. Urethane (meth)acrylates were chosen to study differentiation between molecular weight and backbone structure because of their historical tough nature and their ease of customization. Specific backbones ranged in molecular weight from 500-2000 g/mol and were comprised of polyether and polyester based polyols. By examining each of these structures in table 1 we were able to determine their ability to dissipate energy when subjected to quick impacts as per ASTM D256.

Paper Designation	Description	Polyol Type	MW range	Tg
TCDMDA	Acrylate Monomer			
CTFA	Acrylate Monomer			
PROM ¹	Acrylate Monomer			
PEtUA1	Aliphatic Urethane Acrylate	polyether	500	
PEtUA2	Aliphatic Urethane Acrylate	polyether	1000	
PEtUA3	Aliphatic Urethane Acrylate	polyether	1500	
BPAPeT	Bisphenol A Based Polyester Acrylate	polyester	500	
PEsUA1	Aliphatic Urethane Acrylate	polyester	500	
PEsUA2	Aliphatic Urethane Acrylate	polyester	1000	
PEsUA3 ¹	Aliphatic Urethane Acrylate	polyester	1500	

Table 1. Materials of interest, and specific notes therein. ¹Material was not TSCA listed during this development.

In an effort to target high impact performance, our formulation strategy targeted traditional thermoplastic properties and is outlined in table 2. To simulate thermoplastic behavior, materials were selected to deliver moderate to high modulus values, reasonably high glass transition points with low

functionality. The design should promote component and backbone driven enhancements over the rigidity provided by the acrylic network. CTFA (cyclic triformal acrylate) was preferred over isobornyl (meth)acrylate or other cyclic monomers since it offered a moderate glass transition point and excellent diluency capacity. TCDMDA (tricyclodecane dimethanol diacrylate) also provided diluency for the toughening oligomers, but also leveraged its dense cyclic structure to provide a highest glass transition point with two crosslinking sites. PROM is a monomer in development designed to specifically target high impact resins and was incorporated in the study to push performance.

Component	phr	Purpose or Structure
Sartomer Monomer Blend	60	Held constant to supply effect
Sartomer Oligomer	40	Varies to study effect
Additive and Cure Package		
BASF Irgacure® 819	+0.5	Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide
BYK 088	+0.5	Defoaming Agent

Table 2. Formulation to study specific oligomer structures with the Additive and Cure Package added to a 100 parts of resin outlined with the components.

The study was carried out in a ladder fashion, whereas monomer type and concentration was maintained while the oligomer was simply switched out to provide a new sample. The primary evaluation resided in the materials resistance to impact according to ASTM D256. Secondary and supporting data involved tensile testing according to ASTM D638 and the materials response to mechanical and thermal stresses under Dynamic Mechanical Analysis. Impact and tensile properties highlight room temperature response of the materials while the DMA analysis can elucidate the mechanism by which the material is responding to the stress.

Samples were prepared for each ASTM in accordance to the dimensions outlined in each standard. Samples were further cured with two passes on a Fusion UV System 600W/in V lamp at 100 feet per minute.

Sample preparation for impact testing is outlined in figure 1. ASTM D256 Notched IZOD samples sheets of 1/8" were cast between sheets of glass and cut to size 2 1/2" x 1/2" using a wet saw. Notches were produced into the IZOD specimen with a Zwick/Roell manual notcher from and allowed to rest for 24 hours. A 1 Joule hammer was used on a HIT5.5P Zwick/Roell Impact Tester to measure the impact resistance of a sample population (n=5) where the average energy to break in J/m was recorded.

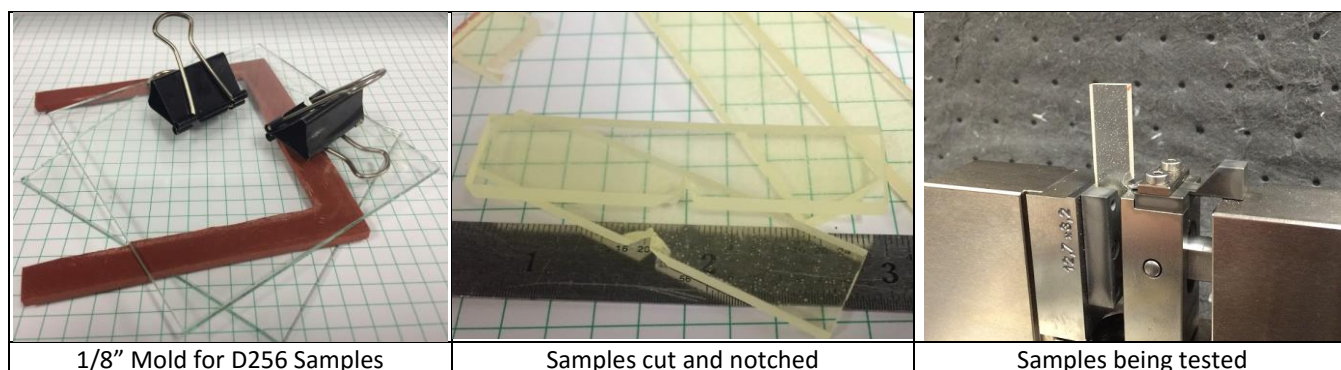


Figure 1. ASTM D256 Notched IZOD Impact Resistance, sample preparation and test fixture.

ASTM D638 Type IV Tensile samples preparation was performed according to figure 2 and were cured in a silicon mold at 1/8" thickness and allowed to rest for 24 hours before stressed to break with a 10kN on an Instron 5966 Tensile Testing Frame. Four parameters were recorded for consideration; strength, elongation, modulus and the area under the curve which we refer to as toughness.



Figure 2. ASTM D638 Tensile Properties of Plastics, sample preparation and test fixture.

Results

Oligomer Types and Trends

Oligomer type plays a pretty large role in the outcome of impact performance for UVEB cured materials. Depending on the rigidity of material between our acrylic functional groups the oligomer either stiffens or softens our network. Figure 3 demonstrates the difference between low molecular weight polyether, polyester urethane oligomers and a BPA based polyester oligomer. Figure 4 outlines the elongation of each of these formulations tested in tension.

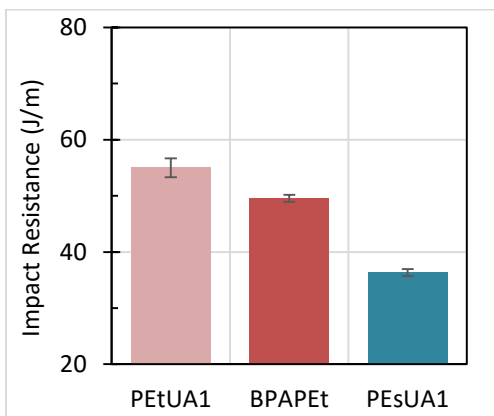


Figure 3. IZOD Impact resistance of various low MW oligomers.

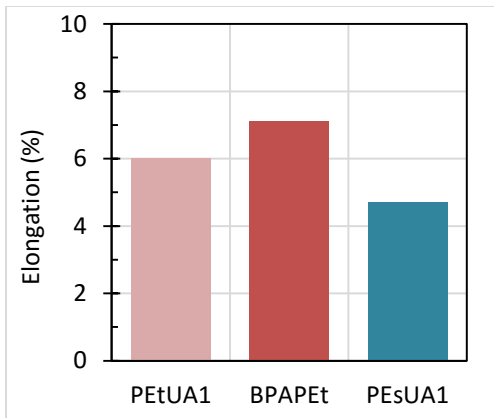


Figure 4. Elongation with various low molecular weight oligomers

Interesting to note that regardless of the main oligomer used in the formulation, the resulting networks did not show a significant response in elongation. The result should be considered a direct effect of the oligomer molecular weight more than the contribution of any backbone interactions. In contrast to the elongation values, there was a material preference when samples were subjected to the impact test. PEtUA1 allowed for larger energy dissipation as opposed to the other samples, which may be attributed to its low Tg polyol and the ability for it to conform during impact. PEsUA1 simply didn't have the flexibility within the nodes to dissipate the same amount of energy as either the polyether or BPA based materials.

Molecular Weight

The molecular weight of the oligomer component further effects the materials ability to dissipate energy. Larger molecular weight between crosslinks will typically yield higher degrees of elongation for UVeB cured parts and subsequent reductions in modulus. Figure 5 outlines observed molecular weight trends for each oligomer and their response to tensile stress.

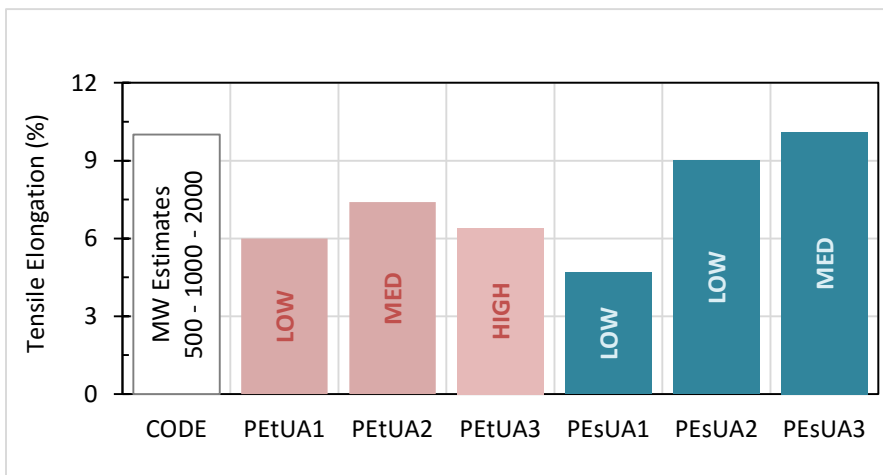


Figure 5. Tensile elongation for polyether and polyester based urethane (meth)acrylates across molecular weight.

The trend with the polyester based formulations directly supports the traditional formulating techniques for increasing elongation. Higher molecular weight oligomers and a reduction in crosslinks, allows for larger chain stretching, molecular mobility and rearrangement. Unfortunately our polyether

based urethanes did not demonstrate increase in elongation with molecular weight increases. The low Tg of the soft segments of these oligomers contributes to an overall weakening. Had phase separation been observed we may've benefited from these low Tg domains, however the complete miscibility of these materials suggests an overall weakening of the resultant network. The consequences of each trend for the polyesters and polyethers can be taken into consideration with the resultant resistance to impact on figure 6.

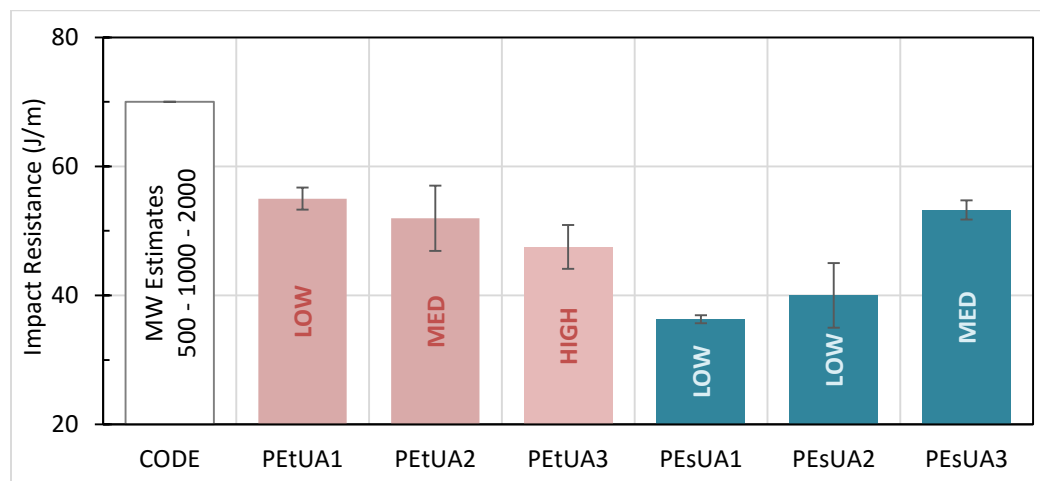


Figure 6. IZOD Impact resistance of polyether and polyester based urethane (meth)acrylates across a molecular weight range.

There are clear trends in molecular weight driving impact resistance. Each oligomer demonstrates a distinct trend and is in direct contrast with each other. Polyether based formulations dominate the performance for impact resistance in the low molecular weight regime and we observed a decrease in impact performance as the molecular weight increased through the samples. We attribute the decrease in impact again, to overall weakening as the concentration of this low Tg portion of the network increases.

Polyester based formulations demonstrated an increase in impact resistance as molecular weight of the oligomer increased. Here we attribute the heightened impact resistance to the increased contribution of polyester behavior into the network. In contrast to the polyether trends, incorporating polyester base urethanes provide an overall tougher network that can absorb a larger amount of energy before breaking. This is further exhibited in an overall toughening as shown in Figure 7 as an increase in tensile properties.

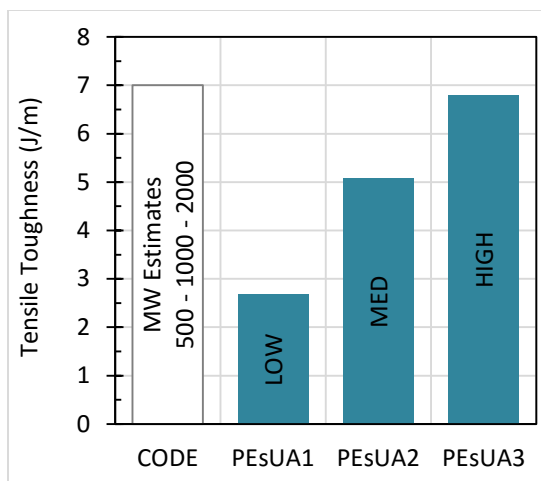


Figure 7. Tensile toughness of the polyester urethanes with increasing molecular weight.

Conclusion

Acrylic and (meth)acrylate resins have been used in 3D printing resins and can deliver the toughness required by consumer goods. Formulation properties can be predictably determined by particular selection of oligomer structure and molecular weight. High modulus and impact resistant formulations have the capability to mimic some traditional thermoplastics for manufacturing of consumer goods. Preference for material development would be on high molecular weight polyester based urethane (meth)acrylates. Continued developments will explore much more diverse chemistries and new toughening mechanisms.

Works Cited

1. Cho, Jung-Dae, and Jin-Who Hong. "UV-initiated free radical and cationic photopolymerizations of acrylate/epoxide and acrylate/vinyl ether hybrid systems with and without photosensitizer." *Journal of Applied Polymer Science* 93.3 (2004): 1473-1483.
2. Decker, Christian, T Nguyen Thi Viet, D Decker, E Weber-Koehl. "UV-radiation curing of acrylate/epoxide systems." *Polymer*, Volume 42, Issue 13, June 2001, Pages 5531-5541.
3. Jaroslaw Kotlinski, (2014), "Mechanical properties of commercial rapid prototyping materials." *Rapid Prototyping Journal*, Vol. 20 Iss 6 pp. 499 – 510.
4. Kumar, Sandeep. "Reinforcement of Stereolithographic Resins for Rapid Prototyping with Cellulose Nanocrystals." *ACS Appl. Mater. Interfaces* 2012, 4, 5399-5407.
5. Takimoto, Yasuki. "Comparative advantages and drawbacks of radical and cationic polymerization in UV curing." *Radiation curing in polymer science and technology* 3 (1993): 269-99.