New Oligomers for 3D Printing Inks

Heather Francis, Ahmet Nebioglu

Dymax Corporation

Torrington, CT USA

Abstract

The present work addresses a strong market demand for oligomers for 3D printing formulations. Structure-property relationships in a new family of oligomers will be discussed. Effect of oligomers on oxygen inhibition, coefficient of thermal expansion, heat distortion temperature, shrinkage, and color stability will be revealed. Some of the formulations based on the various new oligomers are very fast curing and prone to substantially less oxygen inhibition. They demonstrate good adhesion to different substrates and possess very low water absorption characteristics.

Introduction

3D printing uses additive manufacturing processes that uses gradual creation or addition of materials to form the object. 3D printing has become a widely used method for manufacturing of prototypes in many industries including automotive, aerospace, consumer goods, and medical device industries since it produces prototypes with complex shapes relatively quickly and at a significantly lower cost than traditional methods.

Most common 3D printing methods that use light to form the desired 3D shapes are stereolithography (SLA), UV inkjet, and digital light processing (DLP). SLA uses a UV laser to crosslink a liquid resin in a specific area with a specific depth. Once the first layer of the desired object is formed, it is lowered and the liquid resin is re-applied on top of it. Successive curing of layers will form the desired object with high precision. 3D UV inkjet method works similar to a 2D UV inkjet printer. Instead of printing on paper, successive layers are printed and cured on top of a previous layer in 3D UV inkjet method. DLP uses a digital light projector to project a 2D image and cure the resin. Successive curing of the 2D images form the 3D shape desired. Compared the other methods, light intensity used in DLP is significantly lower.

Replacing traditional mass manufacturing processes with 3D printing especially in applications where only relatively small number of parts are required is of very appealing from commercial perspective. There are several challenges in front this; speed of manufacturing and meeting the material performance properties are the most important ones. From materials perspective, it has been a challenge to match performance of common plastics like PC and ABS. It is often difficult to match deformation resistance of plastics at elevated temperatures with thermoset materials. This study focused on our investigation of oligomers used in 3D printing industry and how to improve their heat distortion temperatures without giving up significantly from other performance attributes.

Experimental

All oligomers were analyzed with gel permeation chromatography (Polymer Labs PL-GPC 50 equipped with RI detector and mixed D-columns and FTIR (Perkin Elmer Spectrum 100) Viscosities were measured using a Brookfield CAP 2000+ viscometer. The oligomers were tested for potential use in 3D printing applications using a simple model formula (Table 1). Formulations were mixed using a FlackTek DAC 150.1 FVZ SpeedMixer at 3000 rpm for 2.5 minutes.

Table 1. Model Formula

(Meth)acrylate monomer	51.1%
Benzoylformic acid methyl ester (MBF)	1.9%
Benzophenone	1.7%
(2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (TPO)	0.3%
Oligomer	45.00%

Each formulation was cured UV Curing Conveyor Systems (UVCS) with 5000-EC Flood Lamps at an intensity of 300 mW/cm^{2}and 4000 mJ/cm^2 energy. The curing intensity and energy were recorded using an ACCU-CAL™ 150 radiometer.

The durometer hardness of each formulation was measured using ASTM D2240. Cure profiles of all formulations were analyzed by a Differential Scanning Calorimeter (DSC) equipped with a Dymax BlueWave® 200. After 30 seconds of isothermal stabilization at 25°C, samples were exposed to 50 mW/cm^2 intensity UV light for 15 seconds. Tensile properties were measured with Instron according to ASTM D882.Themal Analysis DMA Q800 was used to measure Heat deflection temperature (ASTM D648) and glass transition temperature (ASTM E1640).

Results and Discussion

Polyurethane acrylates are used in 3D printing formulations primarily due to the toughness they provide which is critical to obtain impact and scratch resistant objects. In order to investigate how the structure of polyurethane acrylates affect the properties that are critical for 3D printing resins, three different type of polyurethane acrylate were synthesized. Representative structure of these polyurethane acrylate (PUA) oligomers were given in Figure 1. First type is the most common type of PUA where backbone contains soft segments and hard segments, and acrylate groups are connected to the hard segment. In the second type, acrylate group is directly connected to the soft segment. Third type of PUA has 3 acrylate functionality.
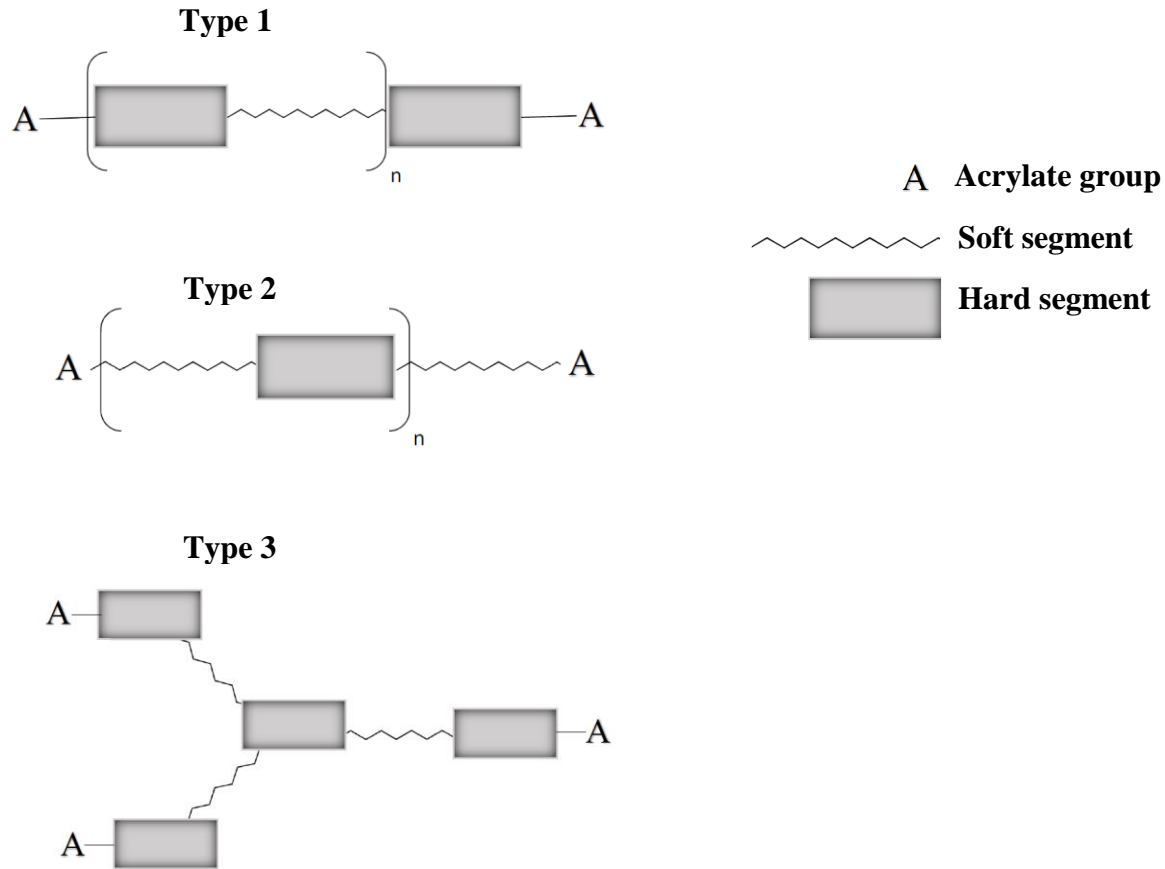
Type 1

Type 2

Type 3

A Acrylate group

~~~~~~ Soft segment

Hard segment

Figure 1. Different Types Polyurethane Acrylates

Table 1 shows the type 1 oligomers' structural description and viscosity of the model formula with the corresponding oligomer. Acrylate ratio is defined as the relative ratio of the acrylate groups within each oligomer. Soft segment ratio (SSR) and hard segment ratio (HSR) are relative length of the soft and hard segments of each oligomer respectively compared to other oligomers. According to Table 1, oligomers 1B, 1C and 1D have the same amount of HSR. With increase in SSR, viscosity of the formulations were decreasing.

Table 2 lists the physical properties of the cured formulations. Heat distortion temperature (HDT) is important for operating temperature of the printed objects, especially for non-prototype applications. Oligomers 1C and 1D gave the highest HDT, both of them had high HSR and highest acrylate amount (AR). Oligomer 1D had higher SSR, which resulted in slightly higher elongation at break and lower tensile modulus compared to 1C. Interesting result was that HDT of 1D was same as 1C although it had higher SSR. From 1B to 1C, AR and SSR were increased by about same factor, as a result HDT was increased (despite the increase in SSR). 1A provided very good elongation due to its high SSR, it can be used as an additive oligomer in objects that require relatively high elongation rates.

Table 1. Oligomers with Type 1 Structure

Oligomer	Acrylate Functionality	Acrylate Ratio (AR)	Soft Segment Ratio (SSR)	Hard Segment Ratio (HSR)	Viscosity (cP)
1A	2	1.0	67.7	1	850
1B	2	8.9	1.7	7	1000
1C	2	12.1	2.6	7	680
1D	2	12.1	9.0	7	430

Table 2. Cured Properties of the Model Formula with Type 1 Structured Oligomers

	Tensile Strength (psi)	Elongation (%)	Modulus (ksi)	HDT (ºC)	Tg (ºC)	Durometer Hardness (D)	Linear shrinkage (%)	Water Absorption (%)
1A	2000	550	20	36	31	29	0.8	0.48
1B	4200	2	130	110	131	89	0.6	0.16
1C	4400	2.7	100	124	143	86	0.87	0.2
1D	4400	3.5	90	124	145	86	0.95	0.15

Table 3 shows the type 2 oligomers' structural description and viscosity of the model formula with the corresponding oligomer. Type 2 oligomers provided significantly lower viscosities compared to Type 1 oligomers. Viscosity of the formulation with oligomer 2C was exceptionally low.

Type 2 oligomers provided lower HDT compared relatively similar SSR, HSR, and AR containing Type 1 oligomers. This might be related to hard segments' proximity to acrylate groups and hence hard segments' proximity to crosslinks in the cured material. When the hard segments are closer to crosslinks it might be harder to distort the crosslinks and therefore result in higher HDT. Type 2 oligomers also provided higher tensile strength and lower linear shrinkage values compared to Type 1 oligomers. Lower shrinkage might be due to relatively less stress formation during curing due to hard segments' proximity to the crosslinking site. Less stress build up in the material also affects tensile properties. Increase of HSR, AR and decrease in SSR seem to increase HDT. Oligomer 2A is appealing due to very low shrinkage and good balance of tensile strength and elongation.

Table 3. Oligomers with Type 2 Structure

	Acrylate Functionality	Acrylate Ratio	Soft Segment Ratio	Hard Segment Ratio	Viscosity (cP)
2A	2	8.7	1.1	11	174
2B	2	9.4	1.0	12	191
2C	2	6.8	1.6	10	88

Table 4. Cured Properties of the Model Formula with Type 2 Structured Oligomers

	Tensile Strength (psi)	Elongation (%)	Modulus (ksi)	HDT (ºC)	Tg (ºC)	Durometer Hardness (D)	Linear shrinkage (%)	Water Absorption (%)
2A	7200	6	100	74	85	82	0.4	0.18
2B	6200	5	90	80	96	83	0.46	0.17
2C	5100	3.2	100	72	88	77	0.55	0.19

Oligomers with Type 3 structure have average of three acrylate functionalities per polymer chain. It does not seem like increasing functionality of an oligomer simply improves HDT. 3A has same HSR compared to 1B, and also has relatively higher SSR and lower AR which as expected result in lower HDT than 1B. Higher functionality of 3A did not improve HDT. Oligomers 3B and 3C have significantly higher HSR and lower SSR than 3A which resulted into higher HDT. It is interesting to note that 3A has practically same Tg as 3B and 3C, but it has significantly lower HDT. This is probably due to higher amount of trapped soft segments that are relatively easier to deform at elevated temperatures.

Table 5. Oligomers with Type 3 Structure

	Acrylate Functionality	Acrylate Ratio (AR)	Soft Segment Ratio (SSR)	Hard Segment Ratio (HSR)	Viscosity (cP)
3A	3	7.6	4.1	7	949
3B	3	7.1	0.9	24	597
3C	3	5.9	1.3	21	541

Table 6. Cured Properties of the Model Formula with Type 3 Structured Oligomers

	Tensile Strength (psi)	Elongation (%)	Modulus (ksi)	HDT (ºC)	Tg (ºC)	Durometer Hardness (D)	Linear shrinkage (%)	Water Absorption (%)
3A	5000	3	110	70	118	87	0.7	0.22
3B	6000	3.2	110	99	119	87	0.64	0.18
3C	4000	2.7	80	93	114	84	0.67	0.2

Cure speed of formulations are important factor in many 3D printing applications. Relative cure speeds of the formulations were measured by photo-DSC based on time to reach gel point. Formulations with Type 2 oligomers cured relatively slowly. Type 1 oligomers cured relatively fast except very high SSR ratio oligomer (1A). Among Type 3 oligomers, 3B cured fastest probably due to lower SSR ratio.

Table 7. Relative Cure Speeds (Photo-DSC)

	1A	1B	1C	1D	2A	2B	2C	3A	3B	3C
Relative Cure Speed	1.5	2.8	3.0	2.2	1.5	1.4	1.4	1.2	2.0	1.5

Conclusion

In this paper, we have described several, new polyurethane acrylate oligomers with varying structure which may find uses in various 3D printing applications. These oligomers' physical properties have been compared in a model formula. Several oligomers provided high heat distortion temperature that might be useful in various real life usable 3D printed objects. Various structure-property relations have been explored that will lead way to tailor-made products for each 3D-printing application.