Structured Urethane Acrylates Vs. Telechelic Urethane Acrylates Comparison in Inkjet Applications

Endrit Shurdha Ph.D.

Sartomer, Exton PA, USA

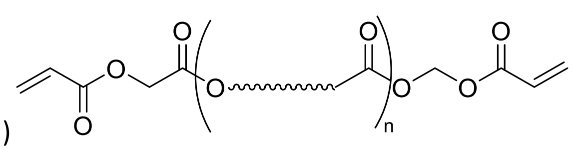
Abstract:

The current work presented here addresses differences in oligomer properties and how these properties affect inkjets ink formulation. Structured urethane acrylates have a new architectural design compared to conventional or telechelic design. The differences in mechanical properties of the final inks are shown herein. The benefits and the formulation latitude that these new type of oligomer provide will be discussed.

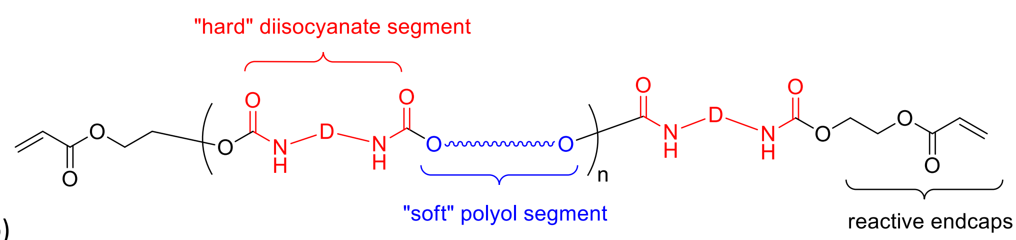
Introduction:

UV acrylate chemistry is known to be the superior performance in inkjet application thought the printing industry when compared to water based inks and solvent inks. These performance details include ease of use, no VOCs, fast curing and more. The disadvantages are the high cost and possible low migration issues depending on formulation especially with low functional monomers (f=1).

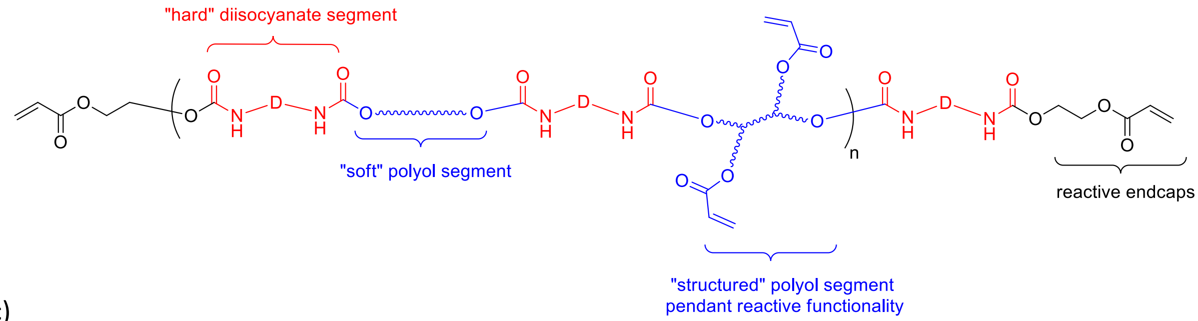
The ink formulations consist of a combination of monomers and oligomers where monomers are considered the solvents for viscosity adjustments and oligomers are considered the film formers and imbue various properties depending on the choice of backbone, which they have. A variety of materials are available to consider when preparing acrylated oligomers and in this study it will show but not limited to polyester acrylate (PEsA) compare to urethane acrylates (UA) and structural urethane acrylates (SUA) Figure 1.



a)



b)



c)

Figure 1. a) generic polyester acrylate, b) generic urethane acrylate and c) structured urethane acrylate.

Polyester acrylates consist of polyester diols reacted with acrylic acid. Telechelic urethane acrylates are the most common types of acrylates where the isocyanates are end caped with acrylated alcohols while the SUAs are urethane acrylates that contain acrylate groups along the backbone as well as at the ends giving its structure a more uniform distribution of acrylate groups. It is theorized that by employing this type of architecture one can formulate mixtures with higher toughness and hardness due to a more uniform distribution of crosslinking sites.

Experimental Section:

All the chemicals were used without any purification. UA1 and SUA1 have the same isocyanate in their structure. The same is valid for the UA2 and SUA2 pair. Brookfield viscometers LVT was used to determine the viscosity of the final product. Instron 100 N instrument was used to determine physical properties of cured films of pure resin and cured ink films that were prepared by curing 96/4 oligomer/photoinitiator blends for neat oligomers in an IMPRO unit with 400 J/in2 dose and 0.12-0.18 mm thickness. The ink samples were cured under a constant flood UV lamp for 1 min on both sides between glass slides. The final cured ink films have a thickness of 0.15-0.25 mm.

Results & Discussion:

Basic mechanical properties of the neat oligomers have been tested on an Instron instrument for thin film setup and shown in Table 1. The liquid viscosity shows an upward trend increase as you go from polyester which contain minimal to no H-bonding to urethane acrylate with some H-bonding and finishing with structural urethane acrylate with higher molecular weight oligomers and also H-bonding. The T_g of the cured films as well as the tensile strength has the same pattern as the viscosity with the lowest temperature and strength for the polyester and the highest ones for the SUAs. One interesting phenomenon to observe is that the Young's Modulus has increased drastically with SUA type architecture while still maintaining the same elongation. The crosslink density is slightly higher for the SUA which would have reduced the elongation but it is believed that because the distribution of acrylate groups along the backbone of the oligomer gives this great advantage of increased hardness without sacrificing on elongation which is a desirable trend. Note that higher functionality monomers were added to the

UAs to compensate for lack of functionality compared to the SUAs but the end result performance of the cured materials did not yield the same properties indicating that the SUA architecture has benefits and the higher performance properties are not solely attributed to higher functionality.

Oligomer	Resin Type	Functionality	Viscosity (25°C)	T_g (°C)	Tensile (psi)	Elongation (%)	Young's Modulus (psi)
PEsA	Polyester	2.0	105	26	360	13	3,000
UA1	Urethane	2.0	9,014	33	1,160	88	1,713
UA2	Urethane	2.0	5,194	39	1,380	73	2,600
SUA1	**Urethane**	**2.0-2.5**	**28,254**	**46**	**2,310**	**86**	**20,378**
SUA2	**Urethane**	**2.0-2.5**	**9,760**	**41**	**3,300**	**75**	**6,127**

Table 1. Neat oligomer physical properties.

The next step was to observe the performance of these oligomers in inkjet formulations. The simple inkjet formula consists of 59% monofanctional monomer, 15% oligomer, 15% TiO_2, 10% TPO and 1% dispersant. This ink formulation is designed to be low viscosity since that is one requirement that affects ink performance and printer performance when printing with inkjet printers. As expected from the oligomer viscosities, the ink viscosities follow similar trend where the polyester containing ink is the lowest followed by urethane acrylates and SUAs.

The inks were cured in thin films and their physical properties were tested and showed in Table 2. The ink containing the polyester acrylate is the softest and weakest film former out of the bunch.. The UA and SUA containing films show the highest toughness with superior elongation and moderate to high modulus. The only drawback to the UA and SUA performance is the high viscosity of the finished ink. Seeking to improve viscosities and better performance the structured urethane acrylates were seen as a possible solution to this issue added to a lower concentration since even by reducing the concentration there should still be room to play since the inks exhibit high modulus. Higher modulus in a finished ink combined with elongation makes for a tougher ink that can resist scuffing and scratching while still being flexible enough to undergo bending in the final printed article.

Ink	Viscosity (45°C)	T_g (°C by DMA)	Tensile (psi)	Elongation (%)	Young's Modulus (psi)	Energy at Break (J)
PEsA	6.45	37.2	1,751	178	2,544	0.61
UA1	10.8	47.5	1,885	208	2,060	0.91
UA2	9.70	40.5	1,965	201	2,584	1.08
SUA1	11.8	47.6	2,857	217	14,913	0.93
SUA2	10.3	41.4	2,477	175	22,738	1.00

Table 2. Inkjet ink cured film properties.

New inkjet inks were prepared with 10% concentration of SUAs and their properties are shown in table 3. The polyester oligomer and urethane acrylates containing inks were kept at 15% since reducing the polyester would make the finished ink film much weaker. Higher concentration of the polyester could have been used but since the properties of the polyester vs. SUAs are so drastically different it was not seen suitable to compare. The UA concentrations were not lowered in concentration because again they would be inferior to the SUAs in comparison. In this comparison study, the SUAs can be lowered in concentration since the final ink viscosities are the highest. The 33% decrease in concentration did yield lower ink viscosities for the two inks as expected and are comparable with the polyester containing ink. Even though the concentration of SUA containing inks were reduced by one third, the toughness of the inks did not reduce by the same degree. SUA oligomers would give a formulator enough formulation latitude to adjust not only for viscosity but to be able to adjust for other properties like the elongation or the modulus. The benefits of the SUA oligomers are only highlighted when the average acrylate functionality of the total formulation is the same or below the acrylate functionality of SUAs hence these oligomers are well suited for inkjet printing and other low viscosity formulations.

Ink	Viscosity (45°C)	T_g (°C by DMA)	Tensile (psi)	Elongation (%)	Young's Modulus (psi)	Energy at Break (J)
PEsA	6.45	37.2	1,751	178	2,544	0.61
UA1	10.8	47.5	1,885	208	2,060	0.91
UA2	9.70	40.5	1,965	201	2,584	1.08
SUA1	8.00	47.5	1,961	224	13,457	0.96
SUA2	6.80	39.7	2,288	232	20,800	1.77

Table 3. Inkjet ink properties of 10% concentration of SUAs vs 15% concentration of PEsA, UAs.

Summary:

A variety of oligomer backbones are compared and contrasted in inkjet formulations. It is shown that polyester acrylate oligomer yield low viscosity needed inks but suffer in their toughness. Urethane acrylates show higher toughness while suffer from higher viscosity. The SUA oligomers do show higher viscosity but are more versatile in formulation due to flexibility of amounts needed in the ink formulation without giving up toughness of the finished cure films. SUAs crosslinking density favors higher performance at lower concentrations in the final formulations.