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Low Viscosity Urethane Oligomers that Function as Reactive Diluents

To meet real world needs in the marketplace, a formulator must develop practically and commercially viable photopolymer systems. Effective UV-curable formulations are achieved by carefully selecting a mix of raw materials leading to the desired end results. For most UV-curable (meth)acrylate-based systems, monomers act as a reactive diluent in a formulation. Their primary function is to dissolve solids such as the photoinitiator and tune the formulation viscosity for the selected applications. Targeting a specific viscosity is critical for many applications.

Many desirable high-performance oligomers have unacceptably high viscosities for applications such as inkjet which typically require formulation viscosities of less than 75 cps. When the use of high-viscosity oligomers is critical to achieve certain properties, a formulator must resort to high-dilucency monomers to adjust final viscosity of the system to the suitable range.

To achieve low viscosity targets, monomers may need to be used at relatively high levels in the final formulation. As expected, there is a price to be paid when a low viscosity monomer is used to reduce the overall viscosity of a formulation that requires the properties of, for example, a high-performance but viscous urethane acrylate. It is commonly understood by formulators that the amount of monomer required to significantly reduce the formulation viscosity could result in a decrease in the impact of the oligomer properties.

An example of this can be seen in Table 1. In this experiment, a simple UV-curable formulation was made based on a trifunctional urethane acrylate. For the control, the urethane acrylate was cured using TPO as the photoinitiator. This results in a formulation with a viscosity of 6,290 cps and good mechanical properties. In this example, the viscosity exceeds the requirements of the desired application method. The usual approach would be to dilute the oligomer with a low viscosity monomer. Using 1,6-Hexanediol Diacrylate (HDDA) as the monomer of choice, two formulations were prepared with HDDA at 20% and 40% of the formulation. As expected, the viscosity was lowered substantially from the original 6,290 cps to 356 cps at 20% HDDA and 76 cps at 40% HDDA. However, at the same time the tensile strength was significantly reduced along with the tensile modulus. Clearly, the addition of the HDDA monomer had a direct and undesirable impact on the cured formulation properties.

Table 1 – Impact of viscosity reduction with a common monomer (HDDA) on mechanical properties of a formulation

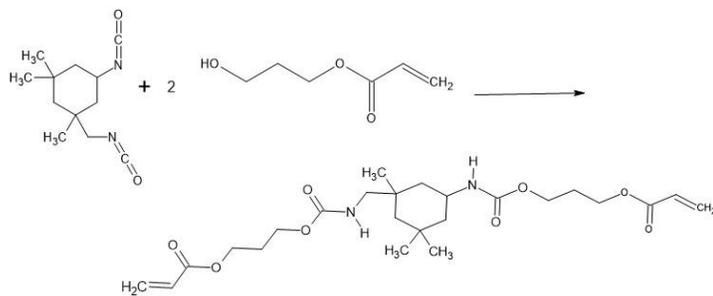
	Control	Dilution A	Dilution B
Trifunctional Urethane Acrylate	97	77	57
HDDA		20	40
TPO	3	3	3
Viscosity (cps @ 120° F)	6290	356	76
Tensile Strength (MPa)	19	8	9
Tensile Modulus (MPa)	1768	1584	1235
Elongation (%)	2.3	1.4	2.8

Low-Viscosity Urethane di(meth)acrylate Preparation and Properties

To support several ongoing formulation projects, it was critical to have a reactive diluent monomer that will lower the viscosity of the fully formulated resin yet maximize the inherent mechanical properties of the base urethane oligomer. It was also important that this molecule be difunctional to have sufficient crosslinking in the cured photopolymer. After considering different possible solutions, the optimum approach was one that was both simple but elegant. In this approach, the goal was to design a urethane (meth)acrylate that exhibited the desirable properties typical of a urethane backbone but with an exceptionally low viscosity along with good diluent properties.

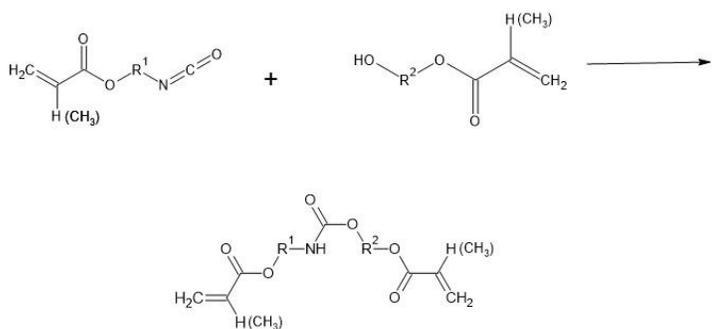
Perhaps the most common approach to making a urethane (meth)acrylate is the reaction of an appropriate isocyanate with a hydroxy containing acrylate or methacrylate (Figure 1). Higher molecular weight molecules can be made by adding polyols to extend the core structure. While the range of isocyanates, polyols and hydroxy (meth)acrylates that are commonly used is somewhat limited, the ability to vary three different components results in a wide range of urethane (meth)acrylates with a corresponding variation in properties. However, a sufficiently low viscosity urethane (meth)acrylate synthesized using this classic route was not found.

Figure 1 – Common synthesis method for production of urethane (meth)acrylates



To minimize hydrogen bonding, a major factor contributing to the high viscosities of many urethane (meth)acrylates, a modified approach to making the desired low viscosity urethane (meth)acrylate was used. As can be seen in Figure 1, the common method to synthesize urethane (meth)acrylates results in a molecule with two urethane linkages. To minimize the hydrogen bonding, an oligomer was made with a single urethane group in its backbone. A generic reaction scheme to make a difunctional urethane methacrylate that contains a single urethane group is shown in Figure 2.

Figure 2 – Synthesis of a difunctional urethane (meth)acrylate with a single urethane functional group



The properties of a low viscosity urethane dimethacrylate (LVU) made by the route shown in Figure 2 are listed in Table 2.

Table 2 – Physical properties of a representative low-viscosity urethane dimethacrylate (LVU)

Properties	LVU	Comments
Appearance	Liquid	
Color	1	APHA
Viscosity	115	cps@77°F
Purity	>99%	
Inhibitor Level	880 ppm	BHT
Acid Value	< 0.2	mg KOH/g
% Moisture	< 0.1%	
Specific Gravity	1.15	g/ml
Refractive Index	1.485	
Tg	74.6	°C (DMA)

The property of particular interest is the very low viscosity of the product. While the lower viscosity does look promising, the key question would be if LVU performs as an effective reactive diluent and to what extent the use of LVU may detract from the inherent properties of a base oligomer.

To answer these questions, the experiment shown in Table 1 was repeated with LVU substituted for HDDA. The formulation and results are shown in Table 3. A simple UV-curable formulation was made based on a trifunctional urethane acrylate. As in the initial experiment, the control was the urethane acrylate cured using TPO as the photoinitiator. This gave a formulation with a viscosity of 6,290 cps and good mechanical properties. Instead of using HDDA as the monomer, two formulations were prepared with LVU at 20% and 40% of the formulation. In this case, the viscosity was reduced significantly from the original 6,290 cps to 1,143 cps at 20% LVU and 395 cps at 40% LVU. What is important to note is that unlike in the experiment that used HDDA as the reactive diluent, when LVU was used at 40%, the tensile strength only decreased slightly to 14 MPa. Comparatively, HDDA at 40% causes a large drop in tensile strength to 9 MPa. Interestingly, the tensile modulus with LVU improved to 2,155 MPa when compared to the decrease to 1,235 MPa with HDDA. This increase likely reflects the substitution of a more rigid crosslinked HDDA system for that of a more flexible urethane system.

Table 3 – Impact of viscosity reduction with LVU on mechanical properties of a formulation

	Control	Dilution A	Dilution B
Trifunctional Urethane Acrylate	97	77	57
LVU		20	40
TPO	3	3	3
Viscosity (cps @ 120° F)	6290	1143	395
Tensile Strength (MPa)	19	18	14
Tensile Modulus (MPa)	1768	2126	2155
Elongation (%)	2.3	3.2	2.1

The improvements resulting from the substitution of a traditional monomer like HDDA with an optimized material like LVU are clearly demonstrated in Figures 3 - 5. In Figure 3, the viscosity reduction that comes with the use of LVU closely tracks that of the viscosity reduction observed with HDDA. However, Figures 4 and 5 illustrate that unlike with HDDA, LVU does not lead to as large a penalty in cured properties and can even improve properties in some cases.

Figure 3 – Comparison of viscosity reduction between HDDA and LVU

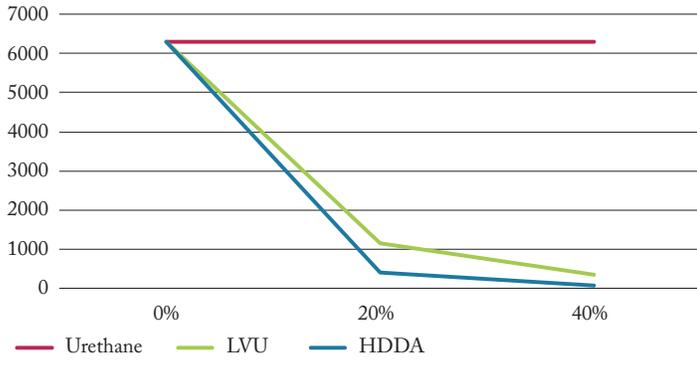


Figure 4 – Comparison of effects of addition of HDDA or LVU on tensile strength

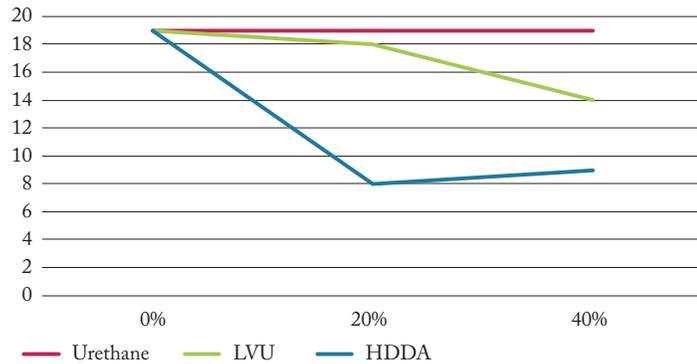
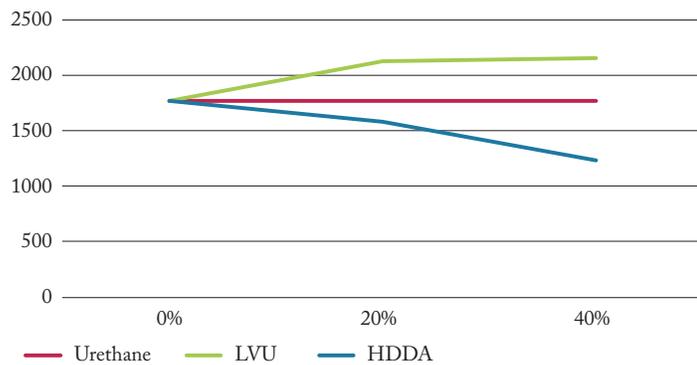


Figure 5 – Comparison of effects of addition of HDDA or LVU on tensile modulus



Applications

The formulation shown in Table 3 is simplified to serve as a direct comparison to the formulation in Table 1. Except for very few situations, this simplified formulation would not be sufficient to meet the final product performance or application requirements in most commercial situations. To evaluate the performance of LVU type materials in commercial applications, a series of experiments were run in which the LVU shown in Table 2 was substituted for a part or the entire amount of a component in a non-proprietary commercial formulation. The formulations with and without LVU were applied and tested using the appropriate application and test procedures. The test conditions and test protocols are listed in Table 4.

Table 4- Test protocols for application-specific formulations

Test	Reference
Viscosity	Brookfield DV-II Pro
Specific Gravity	ASTM D1475
% Cure	FTIR IRSPIRIT - Diamond ATR
MEK Double Rubs	ASTM D4752
Pencil Hardness	ASTM D3363
3D DLP Mechanical Properties	ASTM D638

Laminating Adhesive

The first application evaluated is a UV-Curable Laminating Adhesive. Laminating Adhesive formulations tend to be relatively simple with the blend of oligomers and monomers building the structure of the adhesive and the adhesive properties coming mainly from the tackifying resins. The formulations used in this experiment are shown in Table 5. In this situation, LVU replaced the Epoxy Acrylate/TPGDA monomer used to crosslink the photopolymer. The epoxy acrylate will lend some rigidity to the cured adhesive.

Table 5 – Laminating adhesive formulation with LVU substitution

	Control	LVU
Epoxy Acrylate /25% TMPPTA	28.5	
LVU		28.5
PEA	49.2	49.3
TPO	2	2
OB+	0.015	0.015
Tackifying Resin	20	20
XC-SB302 (Stabilizer)	0.1	0.1

The results in Table 6 demonstrate that the substitution of the low viscosity urethane LVU has equal performance to the control regarding the peel test. At the same time, the overall formulation viscosity is significantly lower. This could be an advantage when it comes to designing the application method for the adhesive. In addition, the cured urethane-based adhesive will likely result in some additional flexibility to the cured adhesive. However, this was not measured in this experiment.

Table 6 – Effects on laminating adhesive formulation properties of LVU substitution

	Control	LVU
Viscosity (cps@65°F)	516	140
Specific Gravity (g/mL)	1.2	1.19
Cure Speed (fpm)	70	70
% Cure (FTIR)	92.8	93.6
Peel Testing 4 mil PET to 0.5 mil OPP	Destructive	Destructive

Testing done using a Fusion UV 600 H bulb

Inkjet Printing

Digital printing or printing on demand is one of the fastest categories of printing today. This robust growth is due in part to the good economics when it comes to short printing runs along with the ability to customize each printed image if needed. A well-known example of digital printing is the ubiquitous ink jet printer found in many homes and offices. A key attribute of inkjet inks is the requirement for the ink to be sufficiently low in viscosity so that it can be jetted. Many inks use either water or an organic solvent to lower the viscosity. This can cause problems with the water allowing the jetted ink dot to expand on the paper thus lowering the resolution and print quality or the organic solvent releasing VOC into the air.

A satisfactory solution to these problems is the use of a UV-curable ink to both minimize VOC and, because of its fast cure with UV energy, to also increase the print quality. With the need to have a low viscosity to allow the formulation to jet, the use of LVU to reduce the viscosity of an inkjet formulation was examined. The blue inkjet test formulations are shown in Table 7. The control formulation is based on UDMA (CAS# 72869-86-4) with a blend of monomers required to sufficiently lower the viscosity. For this experiment, the UDMA was replaced with an equal weight of LVU. The monomer blend was not modified.

Table 7 – Inkjet formulation with LVU substitution

	Control (wt. %)	LVU (wt. %)
Urethane Dimethacrylate CAS# 72869-86-4	22	
LVU		22
PEA	28.9	28.9
HDDA	44.4	44.4
TPO	1.1	1.1
PTZ	2.2	2.2
BDK	1.1	1.1
Blue Pigment	0.2	0.2

The results are shown in Table 8. In this case, a suitable inkjet test rig was not available, so the inkjet formulations were drawn down on Leneta cards.

When compared to the control, the LVU-based formulation gave a small improvement on the MEK Double Rubs. More importantly, the LVU lowered the viscosity from 39.9 cps to 21.6 cps. While this decrease in viscosity might not seem large, the lower ink viscosity is significant as it could result in improved jetability and more options when it comes to inkjet print heads.

Table 8 – Effects on inkjet formulation properties of LVU substitution

	Control	LVU
Viscosity (cps@70°F)	39.9	21.6
Specific Gravity (g/mL)	1.07	1.07
Coating Method	Draw Down	Draw Down
Cure Speed (fpm)	96	95
MEK Double Rubs	10	13

Testing done using a Fusion UV 600 H bulb

Plastic Spray Coating

A common application method for UV curable industrial coatings is by aerosol spray. Whether the substrate is plastic, metal or wood, a UV curable spray coating can be found across a wide range of applications. The use of higher molecular weight (MW) oligomers such as urethane acrylates is critical to give the coating the optimum properties required by the market needs. Unfortunately, the high MW oligomers that contribute to the required cured coating performance tend to have high viscosity. Similar to the need for an inkjet ink to have a low viscosity to properly jet, a spray coating must also have a low viscosity to spray though not as low as typically required for an inkjet ink.

To evaluate the suitability of using LVU to control the viscosity of a spray coating, the formulations for a plastic spray coating were prepared as shown in Table 9. The control formulation is based on a Trifunctional Polyether Aromatic Urethane Acrylate. In this case, LVU replaced the oligomer as an equivalent weight percent.

Table 9 – Plastic spray coating formulation with LVU substitution

	Control (wt. %)	LVU (wt. %)
Trifunctional Polyether Aromatic Urethane Acrylate	39	
LVU		39
HDDA	33	33
GPTA	17	17
Triethanolamine	2	2
TPO	3	3
BP	4	4
CPK	1	1
BYK333	1	1

The results are shown in Table 10. Both coatings were applied using a HVLP (High Volume, Low Pressure) spray system. The physical properties such as the pencil hardness and MEK double rubs were essentially the same. However, there was a noticeable difference in the appearance of the coating. The control formulation resulted in a coating with an unacceptable orange peel surface while the formulation containing LVU gave a smooth, glossy surface. The lower formulation viscosity of the LVU based formulation allowed the applied coating to level out which gave a good appearance after cure. The higher viscosity of the control did not allow surface leveling to take place.

Table 10 – Effects on plastic spray coating formulation properties of LVU substitution

	Control	LVU
Viscosity (cps) @70° F	132	37.2
Coating Method	HVLP Spray	HVLP Spray
Coating	Orange Peel	Good
Pencil Hardness	3H	3H
MEK Double Rubs	16	15

3D Printing (DLP)

3D printing/additive manufacturing continues to be one of the fastest growing platforms for the manufacturing sector, offering opportunities for more efficient material and energy use, recycling, and novel and disruptive capabilities to produce complex forms. UV curable (such as DLP) printing is considered the high-end technology choice for additive manufacturing due to its high resolution, strength in the Z-axis, and the ability to customize resins among other positive features. It is especially important for the additive manufacturing formulators to be able to draw upon the wide-ranging acrylate and methacrylate toolbox to produce a cured photopolymer with the required properties. However, many of the interesting oligomers available are unable to be considered due to their high viscosity. With 3D printing technology such as DLP, inkjet, etc. having upper viscosity limits, a route to achieving the maximum properties at the lowest possible formulation viscosity is critical.

As demonstrated in the earlier simplified experiment using an oligomer with either HDDA or LVU (Tables 2 & 3), the results suggest the use of LVU could serve to reduce the formulation viscosity while at the same time enhancing the properties of the cured resin. A 3D printing resin formulation designed for DLP printing was selected. UDMA (CAS# 72869-86-4), a commonly used urethane dimethacrylate, was selected as the base oligomer. As UDMA has a viscosity of 8,000 cps @77° F, it is necessary to use HDDA as a reactive diluent to lower the viscosity so that the formulation could be printed. In one variation, the HDDA was replaced by an equal amount of LVU. A second test formulation was also prepared in which the LVU was substituted for an equal amount of UDMA. The formulations are listed in Table 11.

Table 11 – 3D printing DLP formulations with LVU substitution

	Control	LVU 1	LVU 2
Urethane Dimethacrylate CAS# 72869-86-4	70	70	43.2
LVU		26.8	26.8
HDDA	26.8		26.8
TPO	3	3	3
OB+	0.2	0.2	0.2

The properties of the resin formulations and the printed test pieces are listed in Table 12. In this case, the substitution of LVU for HDDA (LVU 1 formulation) resulted in an increase in viscosity. It was still printable but was at the upper limit for the printer that was used. The clear advantage to using LVU as a replacement for a typical monomer can be seen in the tensile strength, modulus and % elongation numbers. The tensile strength of the sample with the replacement of HDDA (LVU 1) showed a significant increase in the tensile strength going from 55 mPa to 73 mPa. In addition, the tensile modulus and % elongation also slightly increased. This increase may not be significant and might not be detected in the final application. As it is critical in Additive Manufacturing to have the optimum mechanical properties of the printed part for most applications, the replacement of a monomer with LVU could determine whether the formulation is viable for the end use.

Interestingly, the best results were obtained with the formulation that replaced part of the UDMA with LVU and retained HDDA (LVU 2 formulation). Significantly, the resin formulation viscosity was reduced from the Control viscosity of 413 cps to 163 cps which noticeably improved the printability of the formulation. The tensile strength was reduced slightly from that seen with LVU 1 (71 mPa) but was still significantly higher than the control (55 mPa). While the tensile modulus was slightly decreased and the % elongation slightly increased over the control formulation, these results may not have a noticeable impact in a commercial application.

Table 12 – Effects on 3D printing DLP formulation properties of LVU substitution

	Control	LVU 1	LVU 2
Viscosity (cps)	413 @74°F	1200 @77°F	163 @72°F
Density (g/ml)	9	9.1	9.04
% Cure	86.5	87.5	95.3
Tensile Strength (mPa)	55	73	71
Tensile Modulus (mPa)	3339	3359	3291
Elongation %	2.7	3.5	4

The overall focus of this paper was to demonstrate the positive impact from the replacement of typical monomers with LVU type oligomers. However, the results obtained from the LVU 2 experiment in Table 12 indicate that the substitution of LVU for oligomers in a formulation while keeping at least some of the monomers could result in a formulation that improved the processability while potentially increasing some of the mechanical properties of the cured photopolymer.

Summary

Typically, low viscosity monomers act as a reactive solvent or diluent in a formulation. Their principal function is to dissolve solids such as the photoinitiator and tune the formulation viscosity for the selected applications. However, most common low viscosity monomers tend at best to add little performance properties to the final cured coating or ink. Typically, monomers detract from the desired properties of the oligomers in the formulation after the formulation is cured. A series of low viscosity urethane oligomers has been developed that can serve as efficient diluents in UV curable systems. These urethane (meth)acrylates not only serve as efficient diluents but could also have minimum impact on the performance of other higher molecular weight oligomers in the formulation. A series of application formulations were tested that demonstrated the advantages of replacing some or all the monomers used with an LVU. In at least one case, improvements were noted when part of the oligomer used was also substituted with LVU. The described low viscosity urethane (meth) acrylates should prove extremely useful in applications where low viscosity formulations are important such as inkjet, spray coating and 3D Printing/Additive Manufacturing.

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