ARKEMA

Technical bulletin

SARTOMER®

Structured urethane acrylates

Authors
Endrit Shurdha, Ph.D.

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INTRODUCTION

Acrylated urethane oligomers[1,2] (urethane acrylates, "UA") have found use in a host of UV/EB/thermal cure applications ranging from wood coatings to electronics adhesives. Such oligomers leverage the general benefits of urethane polymers with highly reactive acrylate end groups. The "hard" urethane segments provide adhesion and cohesive strength via hydrogen bonding, while the "soft" diol-derived segments provide flexibility and toughness. Traditionally, the radically reactive acrylate groups are structurally located at the ends of the molecule to yield telechelic (end-functional) materials as shown in Figure 1.

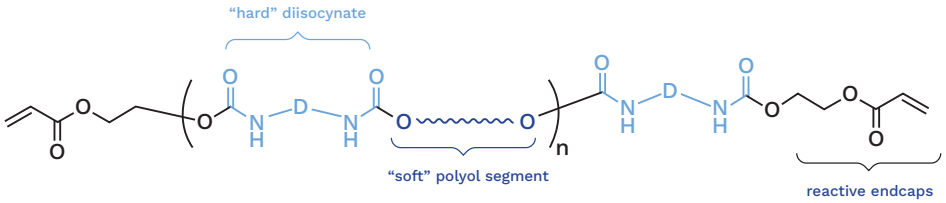

Figure 1: Traditional Telechelic UA Oligomer Structure

There are limitations to this telechelic oligomer architecture. Being end-functional, the oligomer backbone molecular weight is inversely proportional to the crosslink density one can obtain with the material. Although multifunctional acrylate crosslinkers are commonly used to modulate formulated product crosslink density, there are benefits to having more latitude in the oligomer structure as well. For example, some applications would seek to minimize multifunctional monomer levels in a formulated product, but in order to attain high crosslink density, their use is often unavoidable. If one uses very low molecular weight (MW) telechelic oligomers in order to raise crosslink density, mechanical properties derived from the urethane backbone structure itself may suffer.

In order to reduce this oligomer MW/crosslink density tradeoff, Arkema has developed new "structured" UA oligomer architectures.[3] As shown in Figure 2, this synthetic scheme allows for the incorporation of acrylate functionality pendant to the oligomer backbone in addition to at its ends. The synthetic approach is quite simple and versatile, and can be used to develop new UA materials as well as to modify familiar, useful UA oligomers by adding pendant structured functionality.

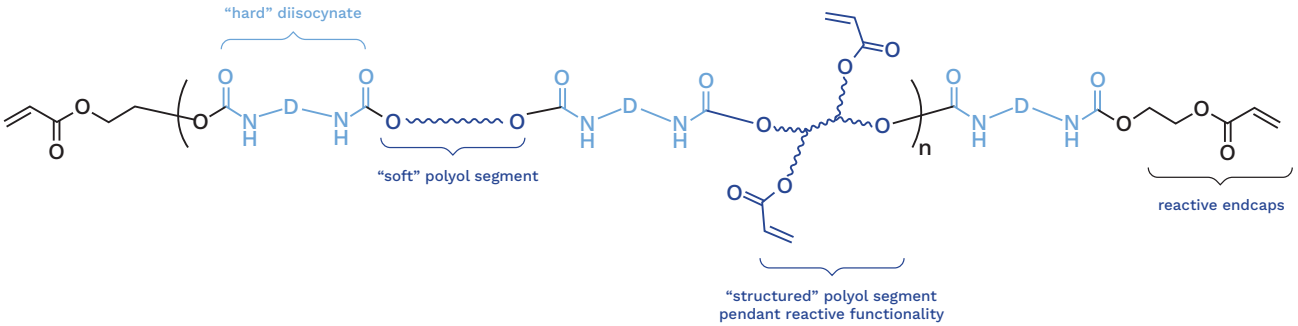

Figure 2: "Structured" UA Oligomers with Pendant Acrylate Functionality

The structured oligomer architecture allows higher MW backbones to be utilized while maintaining relatively high acrylate equivalent weights in the oligomer itself. The pendant groups can produce more even, homogenous crosslinking in energy-cured formulated products, since the acrylate groups are more evenly distributed along the polymer length vs. traditional telechelic analogs and vs. the use of multifunctional additives. This more even spacing of crosslinkable groups, and thus more homogenous crosslinked structure, can open the door to interesting and beneficial cured mechanical properties.

As described below, Arkema has studied the material properties of a range of these oligomers on their own and within simple formulated systems. Various options are under study, ranging from totally new polymers to simple "structuring" of commercial product offerings. A comparison of Sartomer® CN991 UA resin to its "structured" analog (SUA) is described hereafter.

RESULTS AND DISCUSSION

As a starting point for studying the properties of the new oligomers with pendant architectures, basic mechanical properties were compared to analogous telechelic molecules. In typical comparisons, the MW is held approximately constant, and as such the structured architectures represent elevated levels of acrylate functionality with the placement of that additional functionality along the backbone of the oligomer as opposed to at its ends as shown above schematically in Figure 2.

A typical comparison can be made between Sartomer® commercial telechelic CN991 aliphatic urethane acrylate resin (UA) and its "structured" analog CN9600 (SUA), as shown in Table 1.

PHYSICAL PROPERTY OF COMPARISON OF CONVENTIONAL UA VS. SUA

Sample	Viscosity (25°C), cP	Tensile strength (psi)	Elongation (%)	Young modulus (psi)	Tg (°C)
CN991	10,700	1,160 ± 145	88 ± 4	1,733 ± 360	33
CN9600	28,254	3,918 ± 179	86 ± 4	20,378 ± 4,090	46

Table 1: Physical properties of liquid and cured oligomers CN991 (UA) and CN9600 (SUA)

Procedure:

- The viscosities were measured with an S31 spindle at 25°C on a Brookfield DV-II+ viscometer.
- Cured films of both oligomers were cured on an INPRO Technologies curing unit with 2x400 W/in^2 lamps at 50 ft/min speed.

The viscosity of the CN991 was observed to be lower compared to CN9600, which could be expected due to a higher molecular weight that comes from the introduction of pendant functionality along the oligomer backbone of CN991. Higher Tg for the SUA product is as well expected due to higher functionality and higher crosslinking capability of the SUA polyurethane oligomer compared to the conventional UA oligomer. The rest of the physical properties of the cured films have the expected trends with the SUA matrix displaying the likely higher tensile strength and Young's modulus. The elongation values were expected to be lower for the SUA structure due to its higher overall crosslink density, but interestingly it was found that elongation was not affected significantly in contrast to the modulus and tensile strength values. This phenomenon shows that the SUA cured material is tougher (higher tensile strength with similar elongation) than the conventional CN991 oligomer.

Two viscosity studies were also performed comparing CN991 to CN9600 with three monomers/diluents. The first study showed the reduction of viscosity when comparing CN991 and CN9600 diluted with SR454. The SR454 has a room temperature viscosity of 64 cP. Dilution with 10% monomer shows a drastic decrease of viscosity of the CN9600, as shown in Figure 3. The diluted oligomers with small concentration of monomers (5-10%) show similar physical properties as the neat oligomers. Therefore, the capability to lower the viscosity while maintaining similar cured film physical properties would allow the usage of the SUA-type oligomers in applications that are more viscosity-sensitive such as thin coatings or inkjet inks.

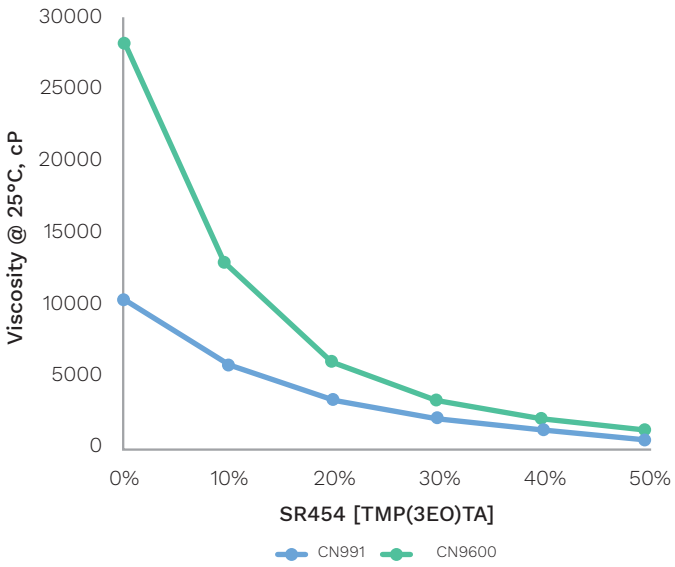

Figure 3: Viscosity curve comparison of CN991 vs. CN9600 diluted with SR454

Next, three different monomers were examined. Monofunctional SR420 (TMCHA), difunctional SR9003B (PONPGDA) and trifunctional SR454 [TMP(3EO)TA] were used to prepare viscosity curves with CN9600. The room temperature viscosities of the monomers are as follows: SR420 3 cP, SR9003B 17 cP and SR454 64 cP. Therefore, the viscosity curves of CN9600 show similar reduction trends for all three monomers as seen in Figure 4.

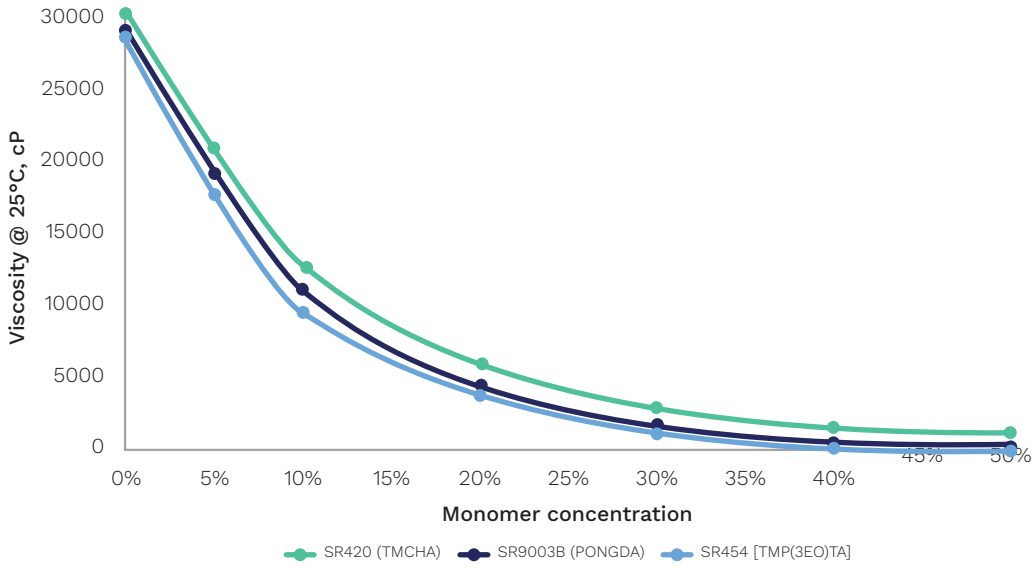

Figure 4: Viscosity curves of CN9600 diluted in SR420, SR9003B and SR454

APPLICATION DATA COMPARISON OF CN991 VS. CN9600 IN INKJET FORMULATIONS

Urethane acrylates are commonly used in a variety of applications such as wood coatings, pressure sensitive adhesives, printing inks, etc. This publication conducted an inkjet ink application comparison of the cured ink film properties between CN991 and CN9600. The ink formulation that was used comprised: 15% TiO2, 15% oligomer, 59% monomer, 1% dispersant, and 10% TPO. A second formulation was prepared with concentrations as follows: 15% TiO2, 10% oligomer, 64% monomer, 1% dispersant, and 10% TPO.

Procedure:

- The viscosity of the wet ink was measured in a Brookfield DV-II+ viscometer with S18 spindle at 45°C.
- The cured ink films were prepared with a UV flood lamp (713.4 mW/in2 UVA and 677 mW/in2 UVV) for 1 min with a film thickness averaging 0.22 mm.

Table 2 shows the physical properties of the wet ink and the cured films.

Inkjet ink	Viscosity (45°C), cP	Tensile strength (psi)	Elongation (%)	Young modulus (psi)
CN991 15% loading	10.8	1,885 ± 386	208 ± 16	2,060 ± 561
CN9600 15% loading	11.8	2,857 ± 120	217 ± 7	14,913 ± 580
CN9600 10% loading	8.0	1,961 ± 156	224 ± 27	13,457 ± 635

Table 2: Application data comparison of CN991 vs. CN9600

The wet ink viscosity shows a higher value by 1 cP between the CN991 ink and the CN9600 ink. This higher viscosity was expected due to the higher viscosity of the CN9600 as shown in the previous section. It is also observed that the viscosity of the ink drops to 8.0 cP when the oligomer concentration is dropped to 10%. Thus, ladder studies could be performed to obtain the same viscosity range for the final ink. The decrease of the oligomer by 5% was performed to demonstrate the physical properties of the cured films between the 33% lower oligomer content ink of CN9600 and the original CN991 ink.

As seen from the application data comparison, the cured film properties of the formulations containing the 15% oligomer level show significant differences in the tensile strength, with about 33% higher values for the CN9600 formulation. The elongation measurement for the 15% oligomer loading display similar values, while the Young's modulus shows a 7-8x increase for the CN9600-based formulation. These values indicate that the CN9600 creates a tougher film compared to CN991. When the concentration of the CN9600 is reduced to 10% in the last ink formulation, the tensile strength measurement decreased to values similar to the CN991 ink formulation. Elongation also remains in the same range. However, it can be seen that the Young's modulus of the formulation containing only 10% of CN9600 remained over five times higher than the benchmark formulation containing 15% CN991. This result shows that the toughness of the cured ink remained high compared to the CN991 formulation even though the oligomer concentration was reduced to 10%. The higher acrylate functionality and higher molecular weight of CN9600 increases the viscosity of the neat oligomer, but formulated viscosity targets can be achieved with lower oligomer concentration while still obtaining improved mechanical properties as shown in Table 2. Structural modifications of the SUA oligomers are facile and can be requested depending on the target properties that need to be achieved.

SUA: Controlling Polymer Architecture

SUMMARY

Arkema has developed a new class of materials, structured urethane acrylate oligomers. With a first focus on telechelic CN991 for inkjet applications, the structured analog version, CN9600, displays higher viscosity, higher functionality and higher toughness. The application data comparison shows the same trend as the pure oligomer properties, where the structured urethanes show tougher, stronger cured films compared to conventional the telechelic urethanes like CN991.

ABOUT THE AUTHOR

Endrit Shurdha, PhD

Endrit, Senior Technical Service Engineer, has been with Arkema since December 2018 working in the Sartomer® resins, Graphic Arts division. His previous experience includes ink formulation with special effects pigments (thermochromic and photochromic) in UV, solvent and water-based media. He has a background in organic and inorganic chemistry materials synthesis and characterization.

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Arkema Inc.
502 Thomas Jones Way
Exton, PA 19341
T (+1) 610.363.4100
Sartomer.exto-development@sartomer.com
sartomer.com

Headquarters: Arkema France
420 rue d'Estienne d'Orves
92705 Colombes Cedex
FRANCE
T +33 (0)1 49 00 80 80

arkema.com