

Urethane Acrylate Oligomers and UV/EB Curing: A Disruptive Technology for Traditional Urethane Prepolymers



Kenneth W. Swiderski
R. David Zopf
Igor V. Khudyakov
Joseph A. Leon
Bomar, Torrington, CT USA



Introduction

Urethane acrylate oligomers are one of the major components for UV/EB (Ultraviolet light, Electron Beam and Visible light) curable coatings, adhesives, sealants and inks. UV/EB cure, in particular ultraviolet light cure of urethane acrylate oligomers, is a viable alternative to thermal cure of urethane prepolymers. Use of urethane acrylate oligomers and all aspects of the UV/EB curing market have been growing into many new applications traditionally using urethane prepolymers. These applications include cast materials and complex three-dimension objects.

Progression of the Urethane Prepolymer to the Urethane Acrylate Oligomer

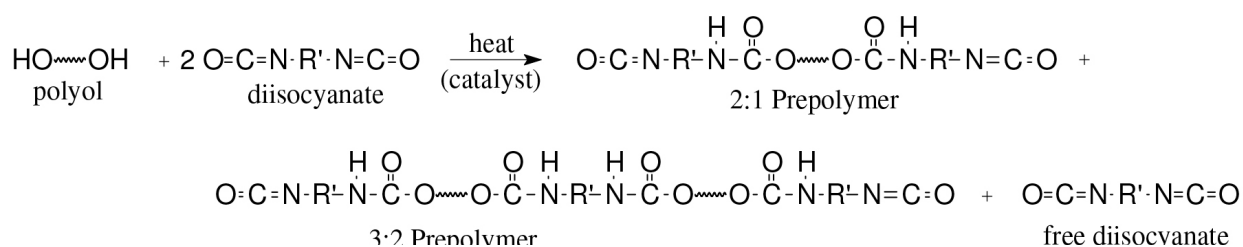
Urethane acrylate oligomer technology is based on isocyanate terminated urethane prepolymers. The term oligomer is synonymous with the term prepolymer commonly used in the urethane industry. Basically, urethane acrylate oligomers are simply formed by another synthesis step beyond urethane prepolymers. A simple change in the functionality to acrylic (a.k.a. acrylate) allows the prepolymer to become curable by ultraviolet light, visible light and electron beam.

Urethane prepolymers are well known to the urethane industry^{2,3,5} as the reaction product of a diisocyanate and a polyol, typically at a 2:1 ratio. MDI and its variants are more commonly used than TDI due to cost and lower toxicity. Due to nature of the reaction dynamics, there is almost always some amount of unreacted diisocyanate left after the prepolymer formation, a noted inhalation hazard. The isocyanate termination provides reactive sites for curing.

Urethane acrylate oligomers start with the synthesis of isocyanate terminated urethane prepolymers^{1,3,9,11,12,13}. The process is continued with a second step, reacting all of the available isocyanate groups with a low molecular weight monofunctional hydroxy bearing acrylate monomer, typically 2-hydroxyethyl acrylate (HEA). This second step is referred as end capping and is a form of blocking the isocyanate group. This differs from traditional blocking; its function is to change the type of reactive functionality to an acrylate and does not disassociate at higher temperatures. If a urethane methacrylate oligomer is desired, a methacrylate monomer is used, typically 2-hydroxyethyl methacrylate (HEMA). All of the free diisocyanate left over from the prepolymer reaction is consumed by the acrylate monomer to form a polyol free urethane acrylate monomer, this is considered the adduct of a urethane acrylate oligomer. Since all of the isocyanate is consumed during the synthesis of a urethane acrylate oligomer, concerns of toxicity from the isocyanate are eliminated. The adduct is far less hazardous than diisocyanates, though they have the potential of irritating the skin. Use of TDI is more common than MDI. TDI is preferred over MDI due to the lack of color, ease of use and the tendency to produce lower viscosity urethane acrylate oligomers. IPDI and H₁₂MDI are preferred in most applications. Most UV/EB applications add to the appearance of the finished good, the non-yellowing properties of aliphatic isocyanates are desirable.

The change from urethane prepolymer to urethane acrylate oligomer is the key to allowing urethanes to grow into a green technology. Reduced energy costs and the elimination of VOCs in coatings and low viscosity applications are paving a path to easier environmental compliance for the urethane industry.

Scheme 1. Synthesis of a Urethane Prepolymer



Moving from the Thermal Cure of Urethane Prepolymers to the UV/EB Cure of Urethane Acrylate Oligomers

Urethane prepolymers are cured with a step growth reaction between two different types of functional groups^{2,3,5}. When curing with chain extenders, a balanced ratio of chain extender to prepolymer is required to completely react all of the functional groups, isocyanate and hydroxyl (or amine). Curing with moisture technically requires the same balance, but in practice adding an excess of moisture is appropriate since it will evaporate (Except for urethane foams, not discussed in this paper). Using isocyanate prepolymers for low viscosity applications often requires the use of volatile solvents for viscosity reduction. The volatiles, VOCs, require expensive recovery systems, add to the cost of the material, require a large amount of energy to remove and can cause defects such as solvent popping. The use of these materials tends to require a large amount of equipment and floor space.

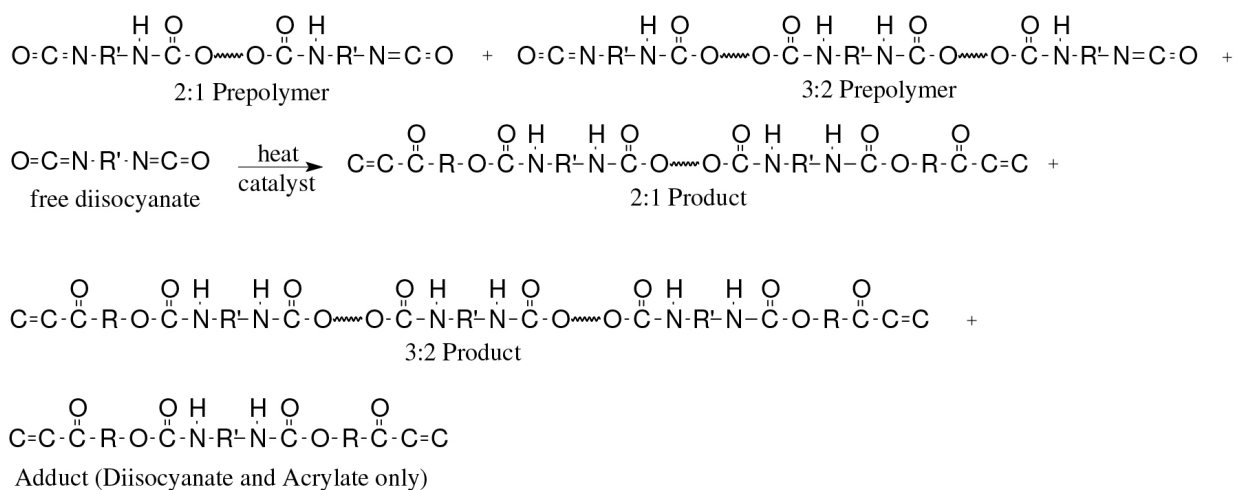
Curing with alcohols or amines, two-part urethanes, and moisture curing, one-part urethane, both require a large

amount of heat. Two-part cure, favored in cast materials, has the problem of a short pot life. These materials are mixed shortly before the point of use or immediately before the point of use with a stationary in-line mixer. Heat is often required to reduce the viscosity of the urethane prepolymer and the curative, further shortening the pot life. A mold filled with a reactive mixture can take many hours at high temperature for cure. One part cure, favored in coatings, requires the removal of VOCs before cure and a moisture saturated atmosphere. Solvent recovery systems are required. Money is spent on the part of the coating formulation that is evaporated off and eventually sent out as hazardous waste. Metal or amine catalysts are often required for a complete cure.

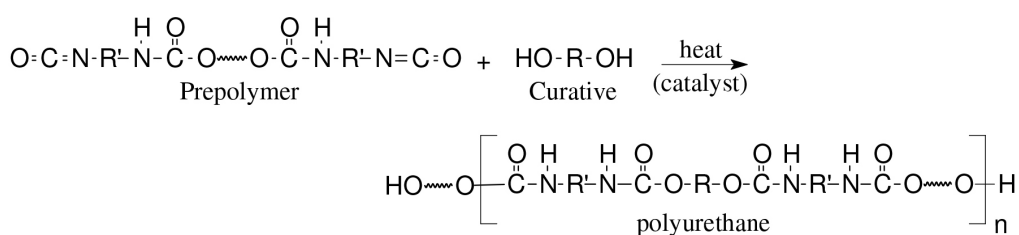
Thermal cure of urethane prepolymers is time and energy intensive. We have also mentioned in the previous paragraph the difficulty of quick mixing of reagents at elevated temperature prior to their reaction.

Urethane acrylate oligomers are cured by a chain growth reaction^{13,4,9}. UV-light excites photoinitiators, which undergo a photochemical reaction leading to free radicals. There is one species of functional group (acrylate) that reacts with itself. When curing urethane acrylate oligomers, there is no need to have a balance of another chemical in the mix

Scheme 2. Synthesis of a Urethane Acrylate



Scheme 3. Cure of a Urethane Prepolymer



(e.g. acrylate monomers). Lower molecular weight urethane acrylate oligomers can be cured without any monomer, they just require photoinitiator. Acrylate monomers; such as Hexanediol Diacrylate (HDDA), Isobornyl acrylate (IBOA) and Trimethylenep propane triacrylate (TMPTA); are still used to reduce viscosity and modify physical properties. Higher molecular weight urethane acrylate oligomers require some amount of acrylate monomer (usually 30% minimum) for thorough cure due to restricted molecular mobility.

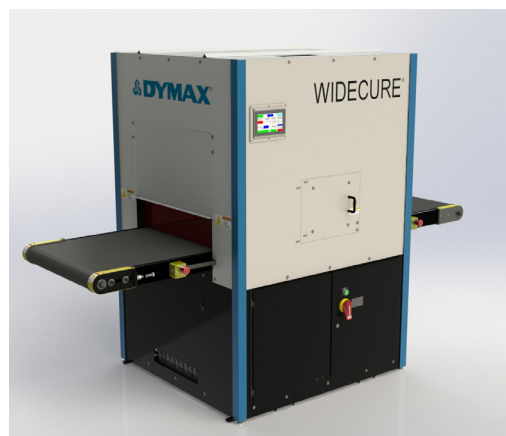
Urethane acrylate oligomers do not require any volatile solvents to reduce viscosity. Instead acrylate monomers are used as reactive diluents. The acrylate monomers become a part of the cured material. Usually, cure takes place at room temperature. Cure (photopolymerization) is an exothermic reaction. Larger articles can have a release of heat.

The equipment used for UV curing requires lower capital cost than thermal curing. Low viscosity formulations based on urethane acrylate oligomers require no solvent recovery system; close to 100% of the formulation becomes part of the cured material (no added cost of material from the solvent). UV/EB curing uses 80–99% less energy and produces reduced reject rates. Urethane acrylate oligomer formulations are cured with a choice of photoinitiator and exposed to ultraviolet light or visible light. Curing formulations with electron beam technology does not require photoinitiator.

UV/EB curing is environmentally friendly. It is considered a green technology by many. The technology dramatically reduces emissions to the environment, close to zero. UV/EB curing uses far less energy than conventional curing and can cure in seconds. There are multiple cost savings with the technology. The savings include lower reject rates, less need for floor space and lower labor costs.

Figure 1. A Typical UV Curing Conveyor System

(Courtesy of Dymax Corporation)



Applications for UV/EB curing have grown from light cured adhesives, laminating of clear substrates and two dimensional curing of coatings and inks. Many of the obstacles that kept the UV/EB market from other applications have been overcome. UV/EB is being used for coating complex three-dimensional objects, pressure sensitive adhesives, cast products and others.

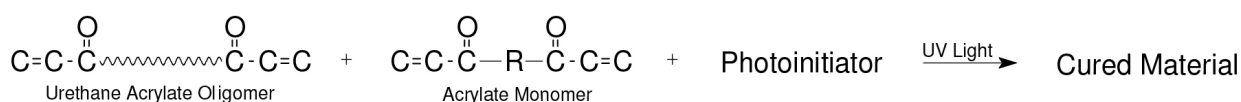
Examples of Urethane Acrylate Oligomers

Chemists familiar with formulating urethane prepolymers have the requisite knowledge to formulate urethane acrylate oligomers, allowing for a short learning curve. As with their conventional counterparts, urethane acrylate oligomers derive their properties of tensile strength, elongation, hardness, weatherability, adhesion, etc. from the interplay of polyol and isocyanate selection, with the added minor complexity of acrylate end groups.

As with thermally cured urethanes, urethane acrylate oligomer properties can range from the hard materials commonly used in wood coatings to the soft, tacky, elongative materials used in film laminating and pressure sensitive adhesives¹⁵.

In the case of BR-144B, a low-medium molecular weight polyether urethane triacrylate oligomer, the same properties

Scheme 4. Photopolymerization of a Urethane Acrylate Oligomer formulation



are achieved that a similar nonacrylated prepolymer would. BR-144B has high hardness, scratch and abrasion resistance, outdoor durability, and extensive chemical resistance.

BR-7432GB is a difunctional oligomer with a higher molecular weight, designed for both high elongation and tensile strength. This material has a lower level of unsaturation and low shrinkage upon cure, a problem with highly unsaturated urethane acrylate oligomers. BR-7432GB offers good adhesion benefits to many PSA and laminating applications. This oligomer also offers superior chemical resistance. The low shrinkage and overall toughness (defined as the combination of high tensile strength and elongation) makes this material a candidate for cast applications.

BR-3641AA¹⁴, by comparison, is a low functionality (1.3 on average), high molecular weight material with high hydrocarbon content. It provides extreme elongation and tackiness. Table 1, below, compares a selection of physical properties of these three oligomers, diluted in a common acrylate monomer.

Table 1. Properties of Urethane Acrylate Oligomers

Product*	Tg, °C (DMA)	Tensile Strength, psi	% Elongation at break	Durometer Hardness
BR-144B	56	5600	6	85D
BR-7432GB	-62	2800	550	84A
BR-3641AA	-50	206	5280	<20A

*each diluted with 30% isobornyl acrylate, and 2 phr 1-hydroxy cyclohexylphenyl ketone photoinitiator added.

A large number of urethane acrylate oligomers are available. They offer combinations of properties which vary between and beyond these extremes.

In addition, the choice of acrylate capping agent allows for some unusual modifications to a urethane acrylate oligomer. An excess of acrylate functionality, as with the ~15 acrylate groups of BR-941, results in an additive urethane acrylate oligomer which can further improve the specific properties of scratch resistance and hardness, by introducing areas of extremely high crosslink density.

Likewise, the backbone itself can be selected from unconventional chemistries, as with the silicone backbone of BRS-14320S. Here, a silicone backbone improves the properties of heat resistance and compression-set ratio in a low crosslink density oligomer. This offers the possibility of a final formulation which incorporates properties more typically associated with silicone rubber. This product also

exhibits the blend of low shrinkage and overall toughness of a candidate for cast applications.

Applications Replacing Traditional Urethane Prepolymers with Urethane Acrylate Oligomers

UV/EB technology is meeting the needs for several known commercial applications using urethane materials. Reviewing these applications, we hope to give the reader an idea of the potential for UV/EB technology within their market.

Doming resins are a well known application for UV curable materials. Flexible, low shrinkage urethane acrylate oligomers comprise the basis for a technology which has replaced thermal-cured cast caprolactone-modified polyether/isocyanate systems in many markets. The productivity achieved with rapid cure has been the strongest motivator towards a switch to UV. Markets served include standard label applications, along with decal and logo systems for interior automotive.

Thermal urethane film elastomers are seeing the transition to UV/EB technology in a variety of optical and retro-reflective assemblies. The applications include safety reflective tapes, optical displays and luminary films¹⁸⁻²¹. In high volume applications, UV/EB technology is utilized to manufacture in situ elastomeric films between 1 and 120 mils thick. UV formulations are used for the base substrate, the protective coating for the reflective assembly, or both.

Decoupage coatings are another area where UV technology is used. Thick section cure is required on mixed wood and paper decorative objects. UV coatings up to ¼ inch thick are cast and quickly cured under a UV flood system.

Form-in-place (FIP) gaskets are another commercial area where cure depths of ¼ inch or greater are common using UV/EB curing technology²². The applications include gasket systems for automotive assemblies, cell phones, edge gaskets for mold assemblies, appliances, and fuel cells.

Last, there is a growing market for field-applied UV industrial floor coatings on wood and concrete²³. In these applications, a contractor will be trained to utilize a mobile UV cure system. Urethane acrylate oligomer based coatings cure quickly, providing a fast turnaround time. Floors are put into service or refinished with minimal down time. The challenge for UV in this application is adequate cure into porous substrates and other areas shadowed from

receiving full UV exposure. To be successful in floor coating applications, a secondary cure mechanism is needed. Full cure is required up to four inches away from the nearest point of UV exposure. Allyl curatives, such as TPO¹⁷, can be used in conjunction with metal driers to give the added cure required.

The Potential and Application of Urethane Acrylate Oligomers in Cast Materials

UV curing of thick section materials has been difficult in

the past. These difficulties have held UV curing to markets requiring only a shallow cure; e.g. coatings, adhesives and inks. In the past decade, advances have been made to UV/EB technology, allowing thick section cure.

UV Stereo Lithography⁸ allows the creation of a three dimension object from a urethane acrylate oligomer formulation. This process does not require a mold. A movable platform is set in a bath full of a UV formulation. A UV laser guided by mirrors takes its instructions from a computer rendering. It creates the object layer by layer as the platform lowers progressively down. The technology is often called rapid prototyping and is commonly used by engineers during the design of various parts.

Objects thermally cured in a mold can also be cured by UV-light. It was demonstrated that with phosphine oxide photoinitiators, such as TPO¹⁷, one can UV cure thick objects by irradiating them from the top. This advance in technology is allowing the use of urethane acrylate oligomers in cast applications. These photoinitiators have also been noted for their ability to cure highly pigmented systems, a selling point of BASF.

Dual-cure systems allow urethane acrylates to cure even were UV light does not reach. Use of secondary curatives allow unattended through cure after an article is formed.

There is a report on cure depths of 25 inches by irradiating thiol-ene based formulations with UV-light from the top⁷. Through cure can be achieved on colored and black materials. This is a step growth copolymerization of thiol and vinyl groups. The vinyl groups used are both acrylate and vinyl ethers. Urethane prepolymers can be capped with both kinds of functional groups. Bomar is in the early stages of developing urethane thiol oligomers. This paper discusses time to thickness of cure in thiol-acrylate copolymerized systems. The paper shows that near full conversion of

a 10-inch-thick object took place in 21 minutes. 90% conversion (acceptable for most UV cured products) took place in 13 minutes. These cure rates are not at the near instantaneous cure time of UV coatings but are comparable to or faster than thermally cured cast products.

A paper in Radtech Report⁸ goes through the process of making custom cast mouthguards via UV Curing. Thiol-ene chemistry is used in the fabrication. The cast mouthguards show improved compression set values over traditional EVA mouthguards with appropriate energy absorption properties.

Increasing market interest is leading to the development of injection molding applications for UV curing. Urethane acrylate oligomer-based formulations can be cured in a metal mold with a UV transparent top or completely made of UV transparent material. UV light directed from the top or multiple sides can cure the injection molded item with less time and energy than thermally cured articles. The pot life of the formulations can be increased beyond a month with the requirement that it is protected from light.

Market interest has also lead to the concept of using urethane acrylate oligomers for floor mats. The UV formulation can be poured into an open mold. UV light can cure the mat from the top. The same mold used for thermal cure can be used for UV cure.

Conclusions

Urethane acrylate oligomers are an environmentally friendly progression of urethane prepolymers. They cure with less energy and do not require adding VOCs for low viscosity applications.

Urethane acrylates oligomers have a full range of properties. Oligomers can be very hard and ideal for scratch resistant coatings. Other oligomers range to very soft with elastomeric elongation, tacky cure and are ideal for PSAs. Urethane acrylate oligomers with low levels of unsaturation combined with good tensile strength and elongation are ideal for use in cast applications.

Growing innovation in UV/EB curing technology allows urethane acrylate oligomers to replace urethane prepolymers in many applications. These applications include form in place gaskets, optical films, thick section coatings and industrial floor coatings. The environmental benefits, lower toxicity, and regulatory compliance factor into the drive for replacing urethane prepolymers. This trend makes UV/EB technology a growing presence in the market place.

New photoinitiators, secondary cure systems and thiol-ene technology are bringing UV cure to cast applications. Urethane oligomers are not only limited to acrylates. Urethane vinyl ether oligomers and urethane thiol oligomers are being developed to further increase the progression of the urethane industry into UV cure of cast urethanes.

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