Unique UV Urethane Adhesives, Coatings and Encapsulants

Now Compete with Conventional Urethanes for Military and Space Applications

By Joseph F. Vaccaro

For years, adhesives made from UV technology have been used abundantly and successfully in lower technology/price sensitive commercial applications where rapid UV cure meant higher output and lower processing costs. However, for the significantly more demanding space and military applications, rapid cure rates are not as important as performance requirements. A combination of requirements such as extreme temperature cycling, outgassing, hydrolytic stability, low modulus, low glass transition temperature (Tg), high elongation, complete cure in shaded areas, and adhesion to difficult gold, ceramic, glass and plastic substrates, have been traditionally met by conventional thermoset urethane adhesives. That is because up until recently, UV technology has had a tendency to yield adhesives, which are brittle, high in modulus, high in Tg, and low in elongation. Importantly, they also fail the NASA outgassing requirements for space environments.

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Recently, the military and space industries have been under intense budgetary and competitive pressures to increase manufacturing efficiencies and reduce processing times and costs. These industries are now seeking out faster curing, more production-friendly material technologies such as snap-cure thermosets and UV-cured adhesives, coatings and encapsulants. Industry leaders such as Boeing, Northrup Grumman, Raytheon, and Lockheed Martin have approached specialty formulators to develop the next generation of rapid-cure adhesives, coatings, and encapsulants with performance characteristics that compete with the conventional urethane systems.

In this article, a basic comparison of conventional versus acrylated urethane technology will be discussed. In addition, the application requirements, recent developments, and test results of next generation UV products will be compared to a long-time industry standard urethane adhesive/coating.

Background and Technology Comparison

Conventional polyurethane elastomer technology has been field proven to be very successful and versatile for military and space applications. In fact, many MIL specifications have been written around this technology. Adhesives, coatings and encapsulants utilizing this chemistry provide excellent performance properties such as toughness, flexibility, elongation, low Tg, low modulus, hydrolytic stability, etc. Because of these inherently good qualities, it made sense to use the urethane backbone and adapt it to a UV-curing "format."

Polyurethanes were, indeed, found to be easily adaptable to UV cure. By reacting isocyanate prepolymers with small, active OH-containing acrylated monomers (for example, hydroxyethyl acrylate or methacrylate) the active N=C=O group of the prepolymer was replaced by a terminal acrylate functionality. Therefore, instead of the prepolymer reacting with polyols, amines or water to form conventional urethanes/ureas, the acrylated end groups were free to be polymerized rapidly by free radicals generated from the appropriate photoinitiators.

The early developments of urethane acrylates yielded adhesives/coatings that were brittle, with high Tg, high modulus and low elongation. Even today most urethane acrylate systems still do not approach the flexibility and elongation that conventional flexible urethane systems possess. Although other factors may be involved, there appear to be, as noted by Martin[1], two main reasons for this—inherent molecular structure and crosslink density.

First of all, the molecular structure or morphology of polyurethane polymers will be discussed. However, the discussion will be basic and limited to polyol cured, flexible low modulus polymers/structures, which are more apropos to the subject matter of this paper. For an in depth study of polyurethane chemistry including the various reactions with water, polyols, and amines to produce very flexible to very rigid products, references such as *Polyurethanes: Chemistry and Technology* by Saunders and Frisch, Vols. I and II, John Wiley and Sons, and *Reaction Polymers* by Gum, Riese, and Ulrich (editors), Hanser Publishers, are good resources to use. Many more sources are available as this chemistry is well documented.

Flexible urethane elastomers consist of mainly two segmented structures—long flexible polyol chains, usually called the "soft segment," and relatively short rigid polyurethane/polyurea-based linkages called the "hard segment." The soft segment usually has a Tg below -40°C and the hard segment has a Tg above +70°C. According to Woods[2], the characteristic properties of the resultant elastomer "depend largely upon secondary or hydrogen bonding of polar groups in the polymer chains." Hydrogen bonding between NH groups and the C=O (carbonyl) groups within the polyurea/polyurethane hard segments is strong, causing the hard segments to agglomerate into "domains within structures having long flexible chains." In other words, a two-phase structure of hard and soft segments is formed.

The challenge is to balance the hard and soft segments within the dual phase to develop the desired properties of the formulated urethane elastomers. This balancing act is possible for two-component urethanes by using a high-molecular weight prepolymer containing a partially adducted isocyanate and polyol moieties, which then can be crosslinked with selected low-molecular weight polyols or amines. The hard urethane segments or linkages would then form the hard segment domain during cure. However, for UV-cured urethane acrylates, this process of attaining the two-phase structure is not easily possible with only the acrylate functionality. Until recently, attaining the properties of conventional urethanes has been difficult to achieve.

The second issue to be addressed is crosslink density. Again, this discussion will only deal with flexible polyol-cured urethanes versus polyurethane oligomers, which are completely acrylated and cured with blends of mono and multi-functional monomers to achieve the desired handling and physical properties.

Conventional soft, flexible, high-elongation urethanes are mainly linear in structure and possess a relatively low degree of branching, which can be regulated by choosing the proper polyol/polyisocyanate precursors, which themselves are branched to a degree. Martin [3] states, "as a measure of the crosslink density of a cured

Diagram 1

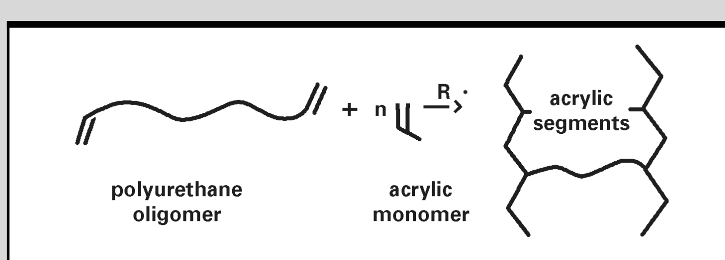


CHART 1

Properties of a flexible aromatic urethane acrylate oligomer diluted 25% with a monofunctional monomer, isobornyl acrylate (IBOA) compared to those properties of the same oligomer diluted 25% with the difunctional HDDA

Product	Viscosity Cps@ 25°C	Shore Hardness	Tg (°C)	Tensile strength	Elongation %	Young modulus @ 25°C psi
CN 972*, diluted 25% with IBOA (monofunctional) Acrylated/UV-cured	8000	80A	-31	300	96	500
CN 972*, diluted 25% with HDDA (difunctional) Acrylated/UV-cured	3000	98A	-28	500	38	2000
Uralane 5753-A/B ** Conventional Standard [4]	6000	55A	-60	350	250	650

*products and data from Sartomer Company **Uralane 5753-A/B a registered trademark of Vantico

conventional polyurethane network, the (average) equivalent weight per branch point in the crosslinked polymer network, (designated as) Mc, will typically vary from 2,000 for a flexible coating to about 25,000 for a (very) soft elastic material." He goes on to show that by contrast, for a UV-cured formulation, the higher molecular weight oligomer contains at least two terminal acrylate groups, which upon curing/co-polymerizing with the lower molecular weight monomers become the branch points for the network. He shows (Diagram 1) that the structure is usually not linear and more highly branched.

Due to viscosity/handling considerations, high molecular weight oligomers, which impart flexibility and elongation, need to be diluted 25-50% with low viscosity, low-molecular weight monomers having mono-, di-, tri-, or higher functionality. The higher the functionality of the monomer, the lower the Mc, the higher the crosslink density resulting in higher tensile strength, lower elongation, higher Tg, higher hardness and a more rigid product.

Using a mathematical model, Martin shows that for a 50/50 blend of difunctional oligomer of 1,000 molecular weight and the difunctional monomer 1,6 hexanediol diacrylate, HDDA, (molecular weight 226) the Mc, which he relates directly to crosslink density, would be only 184. Even if the oligomer was of a molecular weight of 4,000, this model would yield an Mc of only 214, which shows the dramatic effect the monomer's functionality has on the resultant cured properties. All monofunctional monomers may be used to increase the Mc and flexibility, but the tensile property would decrease. Most formulators blend mono and multifunctional monomers to achieve compromises and approach conventional urethane properties. The bottom line, though, is the acrylated systems are usually more crosslinked than their conventional counterparts.

To demonstrate this, Chart 1 shows the properties of a flexible aromatic urethane acrylate oligomer diluted 25% with a monofunctional monomer, isobornyl acrylate (IBOA) compared to those properties of the same oligomer diluted 25% with the difunctional HDDA, discussed above, to show the effect of higher crosslink density. Data for both systems are then compared to a long-time industry standard aromatic urethane, Uralane® 5753-A/B, originally developed more than 25 years ago by Furane Plastics. The IBOA system was selected because it closely matches the viscosity, tensile strength and modulus properties of the industry standard. However, the hardness, Tg and elongation differ substantially. It is the combination of all of these properties that make the urethane standard important to military/space applications.

Military and Space Application Requirements

Military and space applications demand that materials be capable of withstanding a wide range of severe conditions and environments for long periods of time. Protection, reliability and high performance are critical for these materials. A generic list of the key bulk material requirements for those materials is as follows:

- Operating temperature ranges
  –55°C to 125°C (military)
  –100°C to 200°C (space)
- Hydrolytic Stability—3,000-hour aging, 65°C/95%RH, per Mil spec.
- Minimal Stress Properties
  low modulus <1000 psi
  high elongation >150%
  low Tg < -40°C
- Adhesion to a wide range of substrates, including ceramic, gold, printed circuit board materials and a variety of metals and plastics (Note: Adhesion to itself for repair application is essential.)
- Low Outgassing:
  –Pass NASA requirements per ASTM E-595 (space)
  –No contaminants during operation life (military)
  –Complete cure, especially under components
- Repairability—This is a critical aspect due to the high costs associated with the components, circuit boards, materials, etc.

Recent Developments and Test Results

For more than 25 years, the field-proven Uralane technology was the preferred choice for military and space grade adhesives, coatings and encapsulants. Since performance and reliability were paramount, material handling and production costs were usually of little or no concern. But in the mid 1990s, as the satellite, communications and military electronics businesses started to boom, production rate and cost issues became more important and caused major contractors to look at more production-friendly materials including UV-curing adhesives and coatings. However, as discussed earlier, matching the properties of Uralane 5753-A/B adhesive/encapsulant or 5750-A/B (solvated conformal coating version) with acrylated urethanes was a very difficult task. After trying the commercially available UV-curing urethanes on the market at that time, Hughes Space and Communications Company (HSC), now Boeing Satellite Systems (BSS), approached Aptek Laboratories, Inc. to take on this challenge. In order to achieve this goal, a major development program was needed to address issues like morphology, crosslink density, backbone chemistry, functionality, molecular weight distribution, multiple curing mechanisms, structure-property relationships and outgassing.

While working closely with HSC engineering, a unique line of UV-curing, low modulus, low outgassing, acrylated urethane products were developed. Chart 2 displays how closely the same measured properties, discussed in Chart 1, for UVIKOTE™ 7504LM match the industry standard urethane.

Although the properties do not match perfectly, the discrepancy between acrylated and conventional urethane technologies has been greatly reduced. HSC was pleased with the combination of properties and proceeded with extensive testing including DMTA, Mil-46058C, NASA outgassing and hardware performance testing.

DMTA (dynamic mechanical thermal analysis) was used by HSC as a tool to simulate stress modulus over the operating temperature range and predict the temperature cycling performance on solder joints.
The following graph used with permission of HSC/BSS, shows the dynamic function, 'G', as a function of temperature.

According to S. Felstein [5,6], "the goal of the formulation effort was to duplicate 5750 performance. As shown in Graph 1, UVIKOTE™ 7504LM is somewhat higher (in modulus) than 5750 from -25-40°C. From 40-100°C, it is slightly lower. If the area between the UVIKOTE™ 7504LM line and the 5750 line is compared to the area between the

Chart 2

Comparison of measured properties for acrylated and conventional urethane technologies

Product	Viscosity Cps@ 25°C	Shore Hardness	Tg (°C)	Tensile strength	Elongation %	Young modulus @ 25°C psi
UVIKOTE 7504LM	6000	55A	-65	250	200	700
Uralane 5753-A/B	6000	55A	-60	350	250	650

97040-2 (predecessor to 7504LM) and 5750, the reduction is approximately 90%. This means the goal of matching 5750 dynamic modulus performance was 90% successful. This modulus reduction will reduce thermal induced stress on solder joints. The final determination of success will await completion of the solder joint test vehicles."

DMTA turned out to be useful in predicting stress failure in solder joints; UVIKOTE™ 7504LM passed the rigorous 1,200 cycle requirement and was approved as an adhesive/encapsulant for printed circuit boards.

The next major hurdle was to pass the NASA outgassing requirements of less than 1% total mass loss (TML) and less than 0.1% collected volatile condensable material (CVCM). The results were 0.80% TML and 0.016% CVCM. It should be noted that when the cold traps were analyzed with FTIR to identify any organic components collected, the "results showed *only* carbon dioxide and water in qualitatively measured quantities." This was amazing in that no measurable quantity of the polymer itself had outgassed. To date, no UV-cured adhesive/coating having properties similar to Uralane 5753/5750 had ever performed this well.

The final set of major testing performed by HSC/BSS related to the hydrolytic stability tests called out on well-known MIL-I-46058C specification for conformal coatings. The test results were positive, so Aptek had the full battery of tests performed by an outside, qualified laboratory and UVIKOTE™ 7504LM and 7503LM (solvated, sprayable version) passed all the requirements and are QPL listed to types UR and AR.

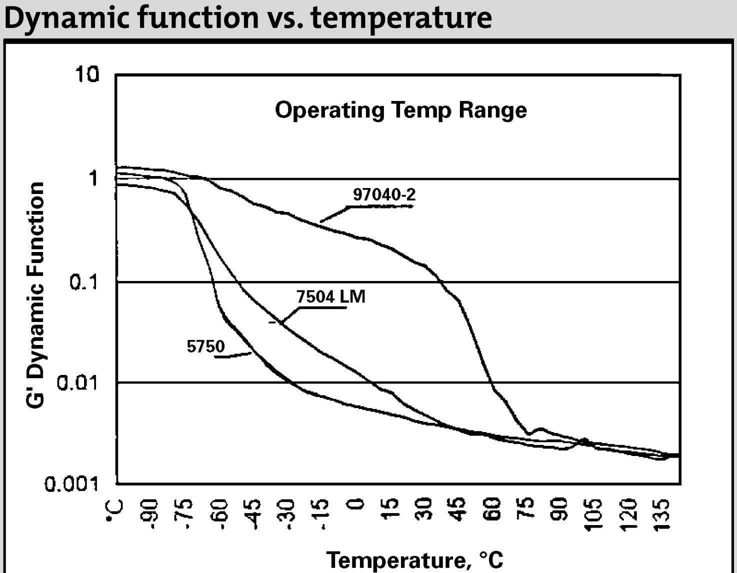
Besides the adhesive/encapsulant version and the conformal coating version, HSC/BSS wanted a thixotropic version for bonding/staking wires and components to printed circuit boards. Thus, UVISTAKE™ 7205LM was developed. All three products of this family have been approved and for the past seven years, have performed well on satellite hardware in space. The unique features and benefits of these products are:

- Multicure mechanism for complete cure in shaded areas underneath components.
- Excellent flexibility and low modulus for reduced stress in the encapsulation of sensitive components (for example, glass-bodied diodes.)
- Meets NASA requirements for high-vacuum environments.
- Highly reversion resistant for good physical stability under high heat and humidity environments.
- Low Tg (-65°C) for excellent low-temperature cycling, storage and performance.
- Excellent adhesion to plastic/metal components and substrates. Adheres well to itself for multicoat and repair applications.
- Exceed all requirements of MIL-I-46058C for military applications.

In addition to BSS, major military contractors like Litton/Northrop Grumman and Raytheon are either utilizing this new technology on existing military programs or evaluating/qualifying it for new military programs.

GRAPH 1

Dynamic function vs. temperature



Conclusions

Advancements in acrylated urethane technology continue to bring the properties of UV-cured systems closer to those of conventional urethane technology. For rigid, industrial grade adhesives and coatings, UV-cured polyurethanes in many cases are superior to conventional systems. Higher crosslink densities for scratch/mar/solvent resistance, lower viscosities for easy application and rapid cure speed for high throughput make UV-cured systems preferred. For military and space programs, where a combination of low modulus, high elongation, low Tg, low outgassing, and high reliability characteristics are required, UV technology of late has made great strides to approach conventional urethane technology. There is always, however, room for more improvement. So the development efforts continue, as the industry's needs dictate. ◗

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