Suitability of (Meth)acrylates for Use in Sealant Applications

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Abstract

The use of (meth)acrylates in peroxide or amine cured sealant and potting compounds is a known and practiced art.   By extension, using UV curing in these same applications is gaining interest versus current processes. A benchmarking of various monomer and oligomer structures was performed, with a focus on their performance in the areas of heat stability, moisture resistance, dielectric strength, and dimensional stability.

Introduction

Producers and converters of goods are constantly looking for process improvements that allow them to increase productivity. To this end, UV/EB curing is an enabling technology that can increase the speed of production while decreasing the overall environmental impact. The UV/EB story is a well known one to the producers and converters of essentially 2D surfaces like flooring, optical media, and printed surfaces. There are, however, less obvious applications where UV/EB can enable process improvements. The area of sealants and potting compounds is one such area. In the past conformal coatings on circuit boards have widely used UV cured (meth)acrylate systems. Industrial sealants and potting compounds, such as those used in equipment, automotive, and electric grid construction have so far been niche areas.

These applications have a different set of requirements than other UV/EB areas. In traditional UV/EB applications the coating, adhesive, or ink is typically applied at a very thin coat weight and is there to provide some sort of surface modification or protection. In the case of sealants, the applied chemistry is expected to bridge the gap between solid surfaces and possibly tie them together. It is desirable for the sealant to have a certain surface hardness that will allow compression during assembly and the ability to withstand mechanical stresses that are applied. Potting compounds fill in pre-determined areas to protect the contents or users of the goods. Sealants and potting compounds are expected to perform in more adverse environments than standard UV cured systems. These systems could be exposed to high temperature and high humidity for extended periods of time. There is also potential exposure from liquids, such as water, cooling fluids, or lubricating oils. It is therefore necessary to understand the resistance of the UV cured system to all of these potential exposures. As with any system, changes in mechanical or adhesion properties over the service life are undesirable.

Understanding how certain monomers and oligomers can hold up under these adverse conditions becomes critical in assembling the best solution possible.

Experimental

A study was undertaken to understand the key differences in monomer and oligomer backbone structure as heat aging is applied to the UV cured sealant. The focus of the oligomer evaluations was on aliphatic urethane acrylates as these backbones allow for differentiation of the molecular weight, backbone chemistry, and functionality. By varying these elements of oligomer design a wide range of tensile, viscoelastic, solvent resistance, and liquid properties can be achieved. Within Sartomer's product line there are a plethora of monomer structures that could potentially be used in these applications. Much background work was performed to narrow the prospective products down to the ones discussed in this paper.

Paper Designation	Oligomer Description	Viscosity 25 °C	Functionality
BOEOEA	Acrylate Monomer	5 cP at 25 °C	1
EO PEA	Acrylate Monomer	24 cP at 25 °C	1
PEsUA1	Aliphatic Urethane Acrylate	18000 cP at 60 °C	2
PEsUA2	Aliphatic Urethane Acrylate	10000 cP at 60 °C	2
PEsUA3	Aliphatic Urethane Acrylate	11000 cP at 60 °C	2
PEtUA1	Aliphatic Urethane Acrylate	5500 cP at 60 °C	2
PEsUA4	Aliphatic Urethane Acrylate	20800 cP at 60 °C	2
PEtUA2	Aliphatic Urethane Acrylate	3400 cP at 60 °C	2
PCUA	Aliphatic Urethane Acrylate	83000 cP at 60 °C	2
PEA	Acrylate Monomer	12 cP at 25 °C	1
ODA	Acrylate Monomer	4 cP at 25 °C	1
CTFA	Acrylate Monomer	15 cP at 25 °C	1

Table 1. Monomers and oligomers evaluated in this study and their descriptions. [1] indicates that the oligomers were not on the TSCA inventory at the time of this paper's writing.

All of the monomers selected for the final parts of this study were monoacrylates. Through earlier research it was discovered that any higher functional monomer, such as diacrylates and triacrylates, introduced too much hardness to the systems. The higher functional acrylates could be useful at additive levels to tweak in properties but they will not be the main diluents.

Component	%	Purpose or Structure
Sartomer Monomer	50.0	Change in ratio within this amount
Sartomer Oligomer	47.0	Constant amount of oligomer for comparison
Lambson Speedcure® BEM	2.0	Blend of benzophenone, 2-methylbenzophenone, and 4-methylbenzophenone
BASF Irgacure® 819	0.5	Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide
Byk® Byk-088	0.5	Silicone defoaming agent

Table 2. Formulation used for evaluation of the different chemistries.

Examination of the different monomer and oligomer chemistries was performed by adopting a standardized formulation and changing compositions. The main evaluation techniques used for this study were Shore A hardness and tensile testing. These two methods allow for an evaluation of the surface and bulk stiffness of the UV cured systems. Taken individually they tell some, but not the entire story of what is happening to the properties. Together a clear picture can be painted of how the system is changing over exposure time.

All of the samples were cured with a Fusion UV Systems 600 W/in D lamp at 25 feet per minute for a total UV irradiation of 3.2 J/cm^2. Samples for tensile testing were prepared by drawing down the samples on Q-Panel A-612 6 x 12" mill finished aluminum panels. Tensile testing was performed according to ASTM D882 on an Instron 5543 tensile tester equipped with Bluehill analysis software. Samples for Shore A hardness were prepared by creating a 7mm thick well on an aluminum panel using Frost King vinyl foam weatherseal. Shore A hardness was performed using a tester from The Shore Instrument & Manufacturing Co., Inc and ascribing to ASTM D2240. All of the samples were exposed at 85 °C, with either 25% humidity (room) or 85% humidity. The 85 °C / 85 RH exposures were performed in a Hotpack constant temperature / constant humidity chamber, model 434304. The 85 °C / 25 RH exposures were performed using a LabLine Imperial V oven.

A good place to start in the understanding of what chemistries can withstand the exposure testing with only minor changes is to look at different monomers that have shown some utility. All of the evaluations were based on the formulation from Table 2, with PETUA1 used as the oligomer. The type and ratio of the monomers used at 50% in the formulation was changed. The two monomers used in the formulation were BOEAEA and CTFA. The formulations were all applied and UV cured at room temperature using the prescribe lamp and energy. The samples were then tested for hardness and tensile properties. Separate samples were put in the Hotpack and LabLine ovens to expose them to the different conditions for 168 hours.
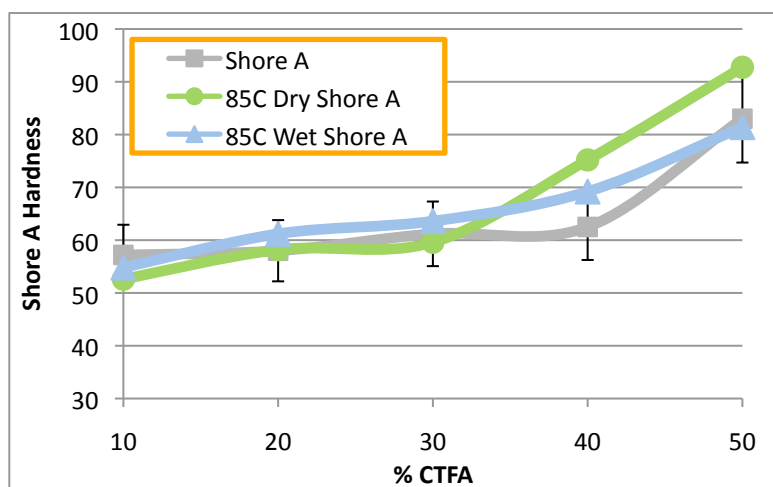

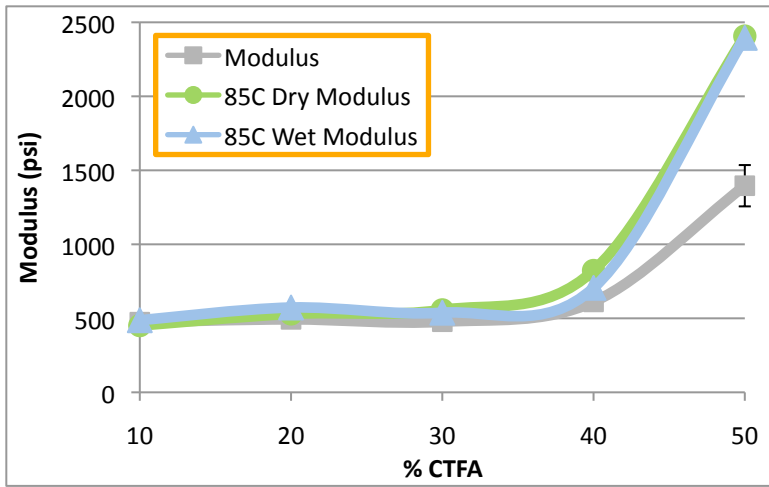**Figure 1.** Shore A hardness as a function of CTFA amount.

Figure 2. Modulus as a function of CTFA amount.

There are several pieces of information that can be gleaned from these figures. First, as the amount of CTFA is increased in the formulation the Shore A hardness of the formulation increases. This was mainly due to the T_g of CTFA versus that of BOEAEA. When UV cured, BOEAEA yields a photopolymer with a very low Tg of -73 °C (by DSC) whereas CTFA yields a T_g of 32 °C (by DSC). Simply changing the T_g of the monomer affects the overall T_g of the cured system. In this case, increasing the T_g moves the cured sealant formulation into a more glassy state with higher modulus. As seen in the formulation that only contains CTFA as the monomer, the modulus and Shore A increased dramatically.

Second, increasing the amount of CTFA in the formulation actually decreases the heat stability of the formulation. When CTFA was used at up to 30% in the formulation, the Shore A hardness and modulus of the dry and moist exposed polymers did not vary by more than 10% from the unexposed sample. Formulations with greater than 40% of CTFA increased dramatically in hardness and modulus when exposed to either dry or moist heat. From a formulation point of view, CTFA would therefore be limited in its usage level to avoid stiffening of the UV sealant during exposure.

To further confirm that CTFA causes stability issues, PEA was substituted in for the monomer and evaluated.
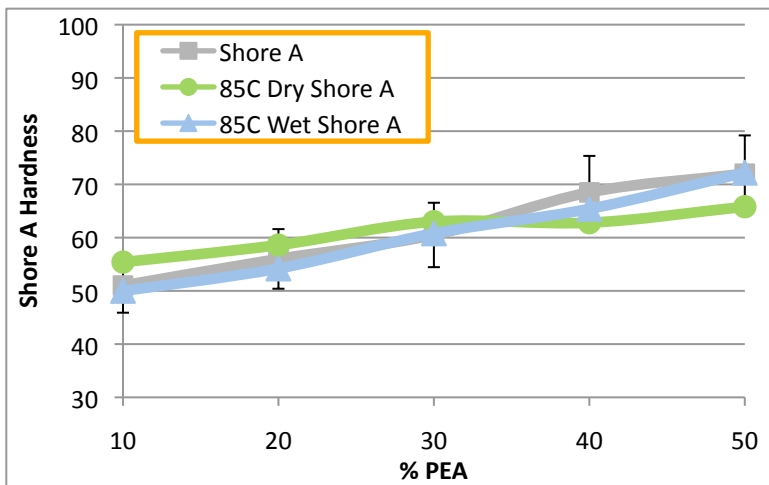

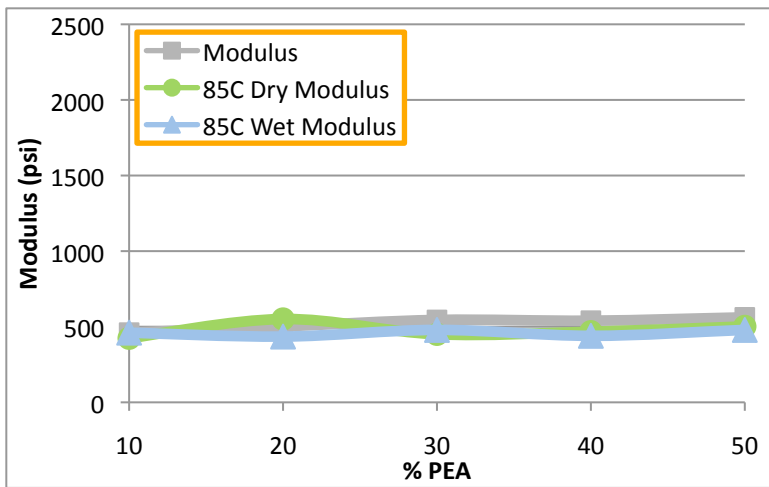**Figure 3.** Shore A hardness as a function of PEA amount.

Figure 4. Modulus as a function of PEA content.

Comparing Figure 3 to Figure 1 and Figure 4 to Figure 2 tells the entire story of performance of PEA versus CTFA. Substituting PEA for BOEAEA in the formulation gave a very even, stepwise increase in the Shore A hardness of the UV cured formulations. After dry and moist heat exposure the hardness is still within 10% of the unexposed sample. Interestingly enough, increasing the amount of PEA in the formulation does not dramatically increase the modulus of the system. After aging, the modulus of the samples is still within 10% of the unexposed samples. Quite simply, formulations based on PEA offer superior dry and moist heat aging versus those based on CTFA.

As those who have experience with UV or EB cured formulations know, the oligomer is the major contributor to the overall properties of the system. The monomer utilization and properties described above can be used to modify the base properties of the oligomers themselves. In this work, urethane diacrylate oligomers showed the best utility for sealant and potting compound applications. Use of these oligomers allows for changes in backbone structure and molecular weight and good analysis of what properties are key. The initial evaluation was to look at the properties of a polyether, polyester, or polycarbonate backbone aliphatic urethane diacrylate of very similar molecular weights. In this we were able to isolate the contribution of the specific backbones to the overall properties of the system.
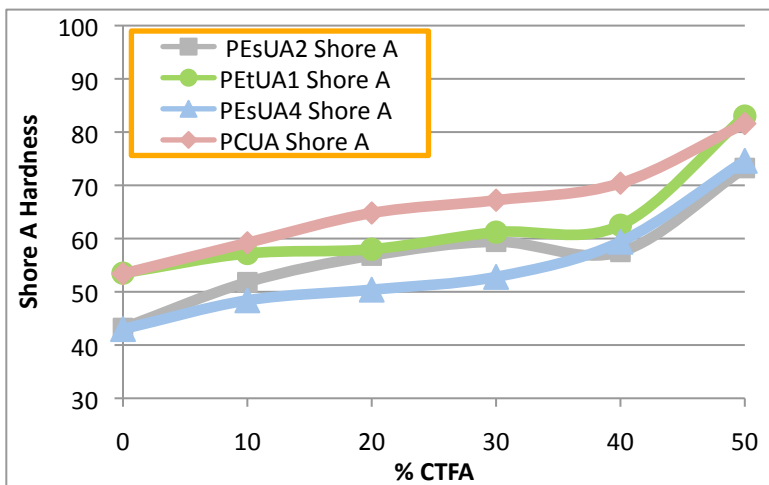

Figure 5. Shore A hardness comparison of different ALUA backbones
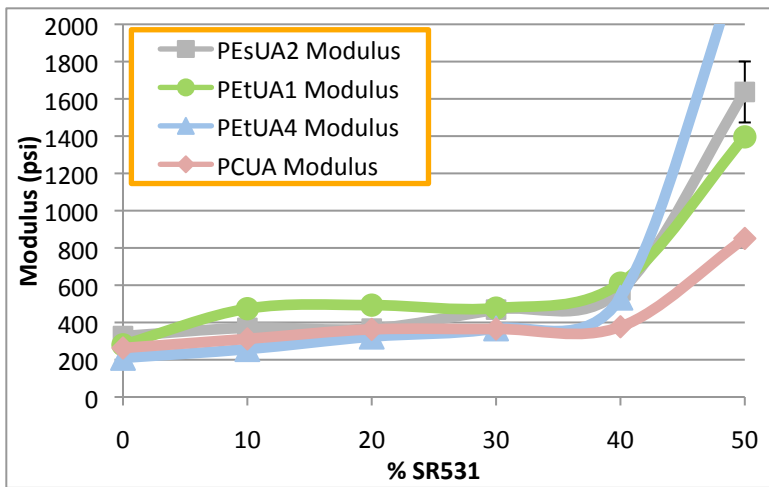
Figure 6. Modulus comparison of different ALUA backbones

Figure 6 shows that at CTFA levels of less than 40%, all of the formulations showed very similar modulus. In figure 5, however, you can see some differentiation in the oligomer backbones. The polycarbonate based oligomer has a significantly higher Shore A hardness than the polyester or polyether based ones. Surprisingly enough, the polyether based oligomer, PETUA1, showed higher Shore A and modulus than the standard polyester and hydrophobic polyester backboned PESUA1and PESUA4.
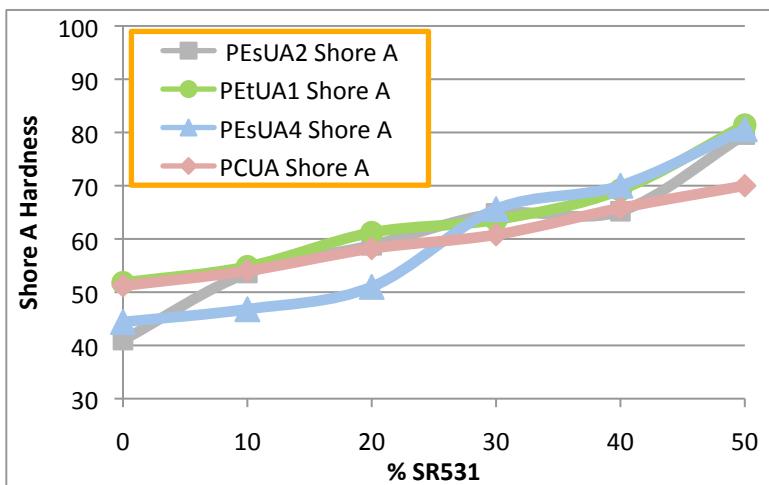

Figure 7. Shore A hardness after 168 hours at 85C and 85RH

After exposure to the 85 °C / 85RH conditions for 168 hours all of the sealants showed changes in their Shore A hardness. PETUA1 showed the best stability as the Shore A for the formulations with <40% CTFA maintained their hardness within 10% of the unexposed sealant. The good stability is probably due to its balance of hydrophobicity and hydrophilicity that allow water vapor to pass through the UV cured film with minimal effect. Also, the lack of ester linkages within the oligomer backbone eliminates one possible area of failure under these conditions. For the polycarbonate backbone a slight decrease in the hardness was seen. The standard and hydrophobic polyesters both showed a dramatic increase in the hardness after the exposure. For these two products it should be noted that the formulation does not contain organic or inorganic acids. If the formulation did contain those compounds you would expect to see hydrolysis of the polyesters under the high heat and humidity

conditions. Therefore, when exposing the cured sealants to high temperature and humidity the polyether backbone maintained its properties better than the other backbone chemistries.
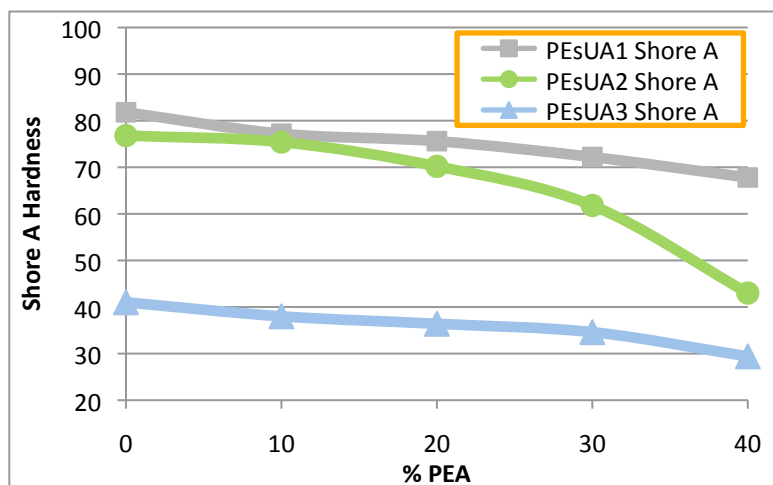

Figure 8. Shore A hardness of different molecular weight oligomers

As with any study of urethane acrylate oligomers, it is interesting to examine the effect of molecular weight on the properties of the system. The core of the urethane acrylate oligomer itself is changing in molecular weight and is effectively increasing the length between crosslinks. Of the PESUA1and PESUA2 products, the PESUA2 has a significantly higher molecular weight yet only shows a large decrease in Shore A hardness once high levels of PEA are used in the formulation. At lower levels the molecular weight differences hold little effect. The CN966 is dramatically higher in molecular weight and that effect can clearly be seen by how much softer the sealant is when based on that oligomer. Another effect, not shown here, is that the CN966-based formulation has twice the viscosity of the other two. Basically put, increasing molecular weight of your oligomer is an effective tool to manipulate the overall hardness of the system.

Component	%	Purpose or Structure
Sartomer Oligomer	47.0	Constant amount of oligomer for comparison
BOEAEA	30.0	
PEA	20.0	
Lambson Speedcure® BEM	2.0	Blend of benzophenone, 2-methylbenzophenone, and 4-methylbenzophenone
BASF Irgacure® 819	0.5	Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide
Byk® Byk-088	0.5	Silicone defoaming agent

Table 3. Formulation used for chemical soak testing

It is one thing to be able to withstand temperature and humidity conditions for a period of time, but many of the targeted applications could expose the photopolymer to liquid chemicals. Therefore, understanding how well the UV cured system can withstand long term chemical exposure is of interest. The formulation was changed based upon earlier work discussed within this paper.
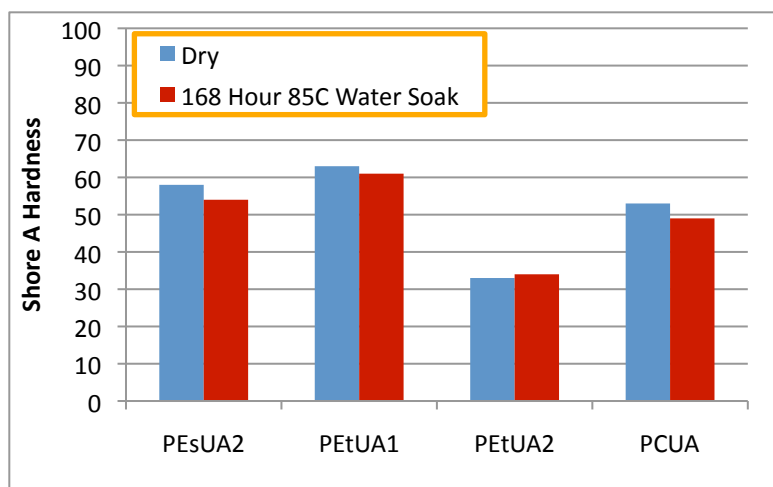
Figure 9. Comparison of Shore A hardness before and after water soak

Of all of the testing so far in the project, this was the most surprising. Typically, acrylate coatings soaked in hot water for extended periods of time will exhibit some changes in their physical properties. In the case of these samples, there is a high film thickness and it would be expected to see a much more pronounced effect. The samples were tested immediately after removing from the water so any trapped in the photopolymer would be seen could be seen through changes in its properties. In fact, after 168 hours (1 week) in 85 °C water, a negligible effect was seen on the hardness of the photopolymer. All of the Shore A hardness' were within 10% of their original values. The cured formulations have a good amount of polarity built into them and would be expected to draw in a significant amount of water during the test. That clearly did not happen and lends to the good utility of UV or EB cured chemistries in applications where chemical resistance is needed.

Conclusion

Through this study it was shown that UV or EB cured acrylate chemistries have the necessary performance to be used in sealant and potting compound applications. Requirements such as hardness, elongation, resistance to dry and humid heat, and chemical resistance can be met when the correct monomers and oligomers are used. Cured photopolymer properties can be predictably manipulated by changing backbone structures and molecular weight of the various components. Polyether backboned monomers and oligomers showed the best overall performance and maintained that performance when exposed to the dry and humid conditions. Continued investigation and development in these areas will continued focus on developing systems with enhanced adhesion properties to various substrates.