

Formulation and Performance Advances In (Meth)acrylate Based Sealants : A UV/Peroxide Dual Cure Feasibility Study

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Abstract :

UV curable sealants offer both processing and performance advantages in a variety of applications. Sealants based on (meth)acrylate functional monomers and oligomers can be formulated for zero VOC, fast cure and rapid property development but have limitations in use for optically dense formulations and substrate geometries that have shadows or dark spots. This paper will explore the effectiveness of organic peroxide addition as a co-initiator to overcome these limitations and enhance critical sealant performance properties such as heat stability and creep resistance.

Introduction

Industrial sealant and potting/encapsulant formulators continually face new challenges in terms of performance requirements for longer service life and processability improvements for increased production and cost savings. Conventional single component solventborne and waterborne sealants such as polybutyl rubber, polyvinyl acetate, silicone, polyurethane, and polyacrylic latex materials used in construction applications provide good gap filling, joint sealing, and barrier properties but they require time and/or heat to dry and harden. Two-component “chemically curing” sealant technologies such as methyl methacrylates, epoxies, polyurethanes, and modified silicones provide the higher strength and higher temperature and chemical resistance required for more demanding applications such as automotive, aerospace, and electronics assembly.¹ The two-component systems, while providing good performance, require plural component application equipment and may not always provide adequate speed of cure.

UV cure technology has found growing interest in these higher end chemically curing sealant and encapsulant applications due to the potential for a single component package, zero VOC, and the very fast cure speeds that have been demonstrated in traditional UV cure markets such as coatings for flooring, adhesives for optical media assembly, and printing inks for graphic arts. However, there are unique sealant and potting/encapsulant application process and performance challenges that are not shared with traditional UV cure markets. For example, in UV cure applications such as coatings and adhesives the UV-curable material is applied as a thin layer on a flat substrate to either protect the

substrate or bond two substrates together. These types of applications lend themselves well to UV energy curing because the limitations of UV technology, namely curing through shadows or dark spots and through thick or non-transparent layers, do not come in to play. On the other hand, sealants and encapsulants are applied in thicker cross-sections to fill voids and act as impermeable barriers so rheology and resistance to a variety of environmental and mechanical stresses are critical to their performance. Sealants can be formulated to be viscous for minimal flow, in order to seal substrates at the glue line or in expansion joints, or they can be low-viscosity to penetrate narrow gaps by capillary action, as in anaerobic acrylic sealants for automotive applications. Sealants and encapsulants are typically formulated to have lower strength and higher elongation than typical UV cured systems so that they are effective at holding together substrates of different coefficient of thermal expansion (COTE). They are often designed to provide thermal, acoustical, and electrical insulating properties as well as extended service life under exposure to a variety of liquids such as water, lubricating oils, cooling fluids and cleaning solutions.¹ Therefore, development of UV curable sealant and encapsulant systems requires the proper selection of materials to meet the demanding performance requirements. Additionally, a tailored combination of photoinitiator and lamp technology is required to cure the complex, three-dimensional, optically dense assemblies where sealants and encapsulants are being used. Formulators must have a good understanding of UV curing process advantages and limitations and a good understanding of UV curable monomer and oligomer functionality and backbone chemistries.

In a previous UV cure sealant study by Goodrich², experiments were conducted to compare the effect of monomer type and functionality, and urethane acrylate oligomer backbone chemistry on hardness and tensile modulus under ambient conditions and high temperature and humidity conditions. The study demonstrated that it was feasible to formulate UV curable systems for use in sealants and encapsulants and that their performance could be adjusted by varying the functionality, molecular weight, and backbone structure of the acrylate monomers and oligomers in the composition. Specifically, monomers and oligomers containing polyether groups exhibited good performance in both dry and humid environments.

The intent of our paper is to validate and advance the findings of the Goodrich study in terms of the effect of material selection on UV cured sealant and encapsulant properties such as hardness, flexibility, and thermal resistance in air and after water immersion. A second goal of the current study is to evaluate the effect of a secondary or co-initiator, such as peroxide, both with and without a post thermal curing process, on the same sealant and encapsulant performance properties.

Experimental

A multivariable design of experiments was developed to study monomer and oligomer backbone structure and equivalent weight effects on cure performance and physical properties with a limited number of single component UV cure sealant formulations. A series of three experiments were conducted that allowed comparison of three independent variables, namely, monomer type (monofunctional vs. difunctional, polyether vs. alkane), oligomer type (epoxy acrylate vs. urethane acrylate, aromatic vs. aliphatic) and polyether oligomer equivalent weight. The performance factors studied were cured sealant hardness, flexural modulus, and heat distortion temperature (HDT). Additionally, hardness was measured after UV curing only and after water immersion at elevated temperature. Subsequently, a secondary experimental study was done to evaluate peroxides as co-initiators and test their effect on physical properties for sealant formulations exposed to UV energy only

and UV cure plus thermal post cure. In this study, the effect of peroxide type (diacyl, peroxyester, dialkyl) and peroxide half life temperature on cured sealant properties were evaluated.

The monomers and oligomers selected for this study are listed in Table 1. The preliminary research discussed in the Goodrich paper suggested that monofunctional polyether-based monomer blended with polyether-based urethane acrylate oligomer provided a good combination of hardness and modulus under varying temperature and humidity conditions. It also suggested that diacrylate or triacrylate monomers caused the sealant formulations to be too hard and brittle to withstand more extreme environmental and mechanical stresses. In this study, a high molecular weight diacrylate monomer, propoxylated neopentylglycol diacrylate (PO NPGDA) was evaluated with aliphatic urethane acrylates having varying polyol backbone chemistries (polyester-based urethane acrylate (PEsUA), polyether-based urethane acrylate (PEtUA), and polycarbonate-based urethane acrylate PCUA) to maintain hardness and flexibility. Additionally, a high hardness aromatic epoxy acrylate oligomer bisphenol A epoxy acrylate (BPAAE), was evaluated with alkane monoacrylate monomers (octyldecyl acrylate (ODA), trimethyl cyclohexyl acrylate TMCHA), and isobornyl acrylate (IBOA) as an alternative to aliphatic urethane acrylate oligomer to achieve higher hardness while maintaining good flexibility.

Table 1. Monomers and oligomers tested with generic designation and description

| Material Designation | Monomer or Oligomer Description | Viscosity (cps) | Functionality | Equivalent Weight |
|-----------------------------|--|--------------------------|----------------------|--|
| PO NPGDA | Polyether Acrylate Monomer | 15 (@ 25 °C) | 2 | 164 |
| EO BPA1 | Aromatic Polyether Acrylate Oligomer | 1080 (@ 25 °C) | 2 | 256 |
| EO BPA2 | Aromatic Polyether Acrylate Oligomer | 610 (@ 25 °C) | 2 | 388 |
| EO BPA3 | Aromatic Polyether Acrylate Oligomer | 680 (@ 25 °C) | 2 | 828 |
| ODA | Alkane Acrylate Monomer | 4 (@ 25 °C) | 1 | 203 |
| TMCHA | Alkane Acrylate Monomer | 6 (@ 25 °C) | 1 | 210 |
| IBOA | Alkane Acrylate Monomer | 8 (@ 25 °C) | 1 | 208 |
| BPAAE | Aromatic Epoxy Acrylate Oligomer | 18.9K (@ 60 °C) | 1 | 259 |
| PEsUA | Aliphatic Polyester Urethane Acrylate Oligomer | 17.6K (@ 60 °C) | 2 | 838 |
| PEtUA | Aliphatic Polyether Urethane Acrylate Oligomer | 5.5K (@ 25 °C) | 2 | 838 |
| PCUA | Aliphatic Polycarbonate Urethane Acrylate Oligomer | 46.5K (@ 60 °C) | 2 | 838 |
| Material Designation | Peroxide Description | % Active Peroxide | SADT (°C) | 1 Hr Half-Life Temperature (°C) |
| PEROX1 | Diacyl Peroxide | 40 – 42 | 55 (45# package) | 92 |
| PEROX2 | Diperoxyketal | ≥ 92 | 60 (HAST) | 115 |
| PEROX3 | Dialkyl Peroxide | 93 - 95 | 86 (30# package) | 140 |

The base formulation used for all of the experiments which used only UV curing is described as Base Form 1 in Table 2. Goodrich demonstrated that a photoinitiator package consisting of a benzophenone derivative blend and a longer wavelength deep curing BAPO initiator in combination with a Fusion UV Systems D lamp achieved optimum UV cure response for sealant formulations cast up to 7 mm thick. In the current study, the same photoinitiator combination and defoaming agent were chosen to allow direct comparison to the prior results. The formulations were prepared by dissolving photoinitiators into the monomer and defoaming agent and placing the mixture in an oven at 60 °C. The oligomers were preheated to 60 °C and then added to the monomer/photoinitiator blend using a low shear blade mixer. Brookfield viscosity was measured at 25 °C for each formulation following ASTM D2196.

The curing conditions were established by conducting a short screening study displayed in Figure 1. A Base Form 1 test formulation was cured by using two passes through a Fusion UV Systems 600 W/in² D lamp at variable line speeds to determine acceptable conditions for complete cure. Degree of cure was assessed by measuring cured material hardness. A line speed of 50 feet per minute was selected for the study due to the high hardness observed. These cure conditions yield a total UV energy of 3.2 J/cm².

The base formulation used for the UV/peroxide dual cure study is described as Base Form 2 in Table 2. The peroxide initiators tested are listed in Table 1. The peroxide initiators were added to Base Form 1 sealant formulations and stirred in by hand mixing until homogeneous. The three peroxide initiators included in the study were a diacyl peroxide (PEROX1), a peroxyketal (PEROX2), and a dialkyl peroxide (PEROX3).

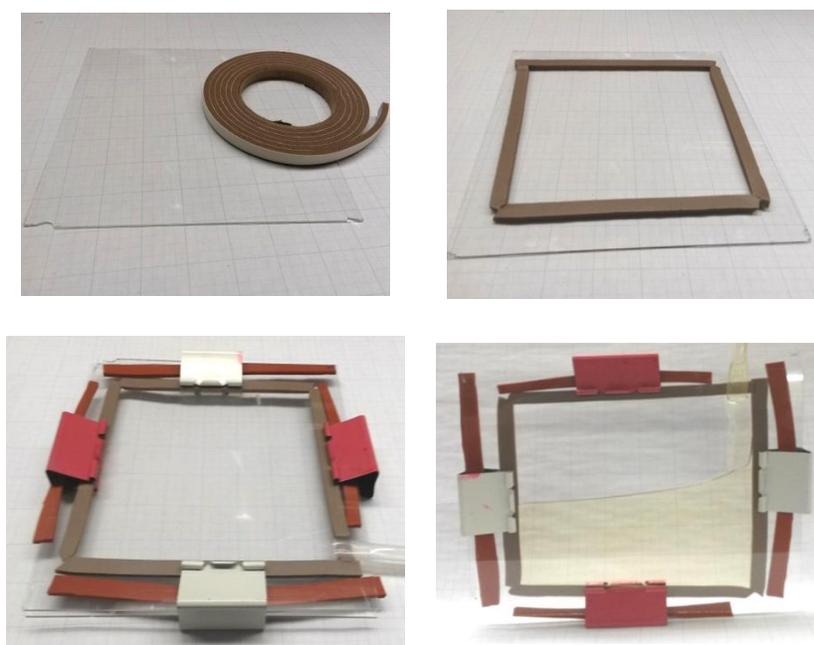
Table 2. Base formulations for UV cure and UV/peroxide dual cure sealant evaluation

| Component | Wt. % | | Comment |
|---|-------------|-------------|--|
| | Base Form 1 | Base Form 2 | |
| Acrylate Monomer | 50.00 | 50.00 | Variation in functionality and equivalent weight |
| Acrylate Oligomer | 50.00 | 50.00 | Comparison of backbone types |
| Benzophenone, 2-methyl benzophenone, 4-methylbenzophenone | 2.00 | 2.00 | BPO photoinitiator blend (220-320nm cure range) |
| Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide | 0.50 | 0.50 | BAPO initiator (340-440nm cure range) |
| Byk® 088 | 0.50 | 0.50 | Silicone defoaming agent |
| Peroxide Co-initiator | ---- | 0.25 | Variation in type and half-life temperature |

Sealant samples for curing and testing were prepared by pouring each formulation into a 5" x 5" mold consisting of two glass plates (sprayed with mold release) clamped together with a 1/8" thick silicon rubber gasket spacer as shown in Figure 2. The filled mold samples were placed on the curing unit conveyor belt and cured through the glass plate using the cure conditions described above. Cured samples were aged for 72 hours at ambient lab temperature (~23 °C) to allow post cure completion. The cured sealant properties tested were Shore durometer hardness (both A & D) following ASTM D2240 and flexural properties following ASTM D790. Cured samples were then immersed in water at 60 °C inside a LabLine Imperial V forced air oven and Shore durometer hardness measurements were recorded

at regular time intervals. The goal of this test protocol is to provide a good representation of bulk stiffness and flexibility and the effect of water exposure on these properties. Additionally, a qualitative determination of degree of shrinkage during cure was noted. This property is a good gauge for how durable the sealant will be under the internal stresses found in certain end use application environments. Finally, the Deflection Temperature Under Load (DTUL) or Heat Distortion Temperature (HDT) was measured for each sample using a TA Instruments Q800 Dynamic Mechanical Analyzer following ASTM D648. This measurement provides an assessment of the service life temperatures that the formulations can withstand without detrimental effects on performance properties.

Figure 2 Glass mold for sample preparation and curing and performance property testing



Results

To understand how equivalent weight (molecular weight/functionality) affects cured sealant hardness and flexural strength, we prepared Base Form 1 in Table 2 with both the monomer and the oligomer being polyether based structures. The oligomers tested varied from low to high equivalent weight (BPAEA < EOBPA1 < EOBPA2 < EOBPA3) and the monomer was the diacrylate PO NPGDA. Table 3 lists viscosities, degree of shrinkage, and heat distortion temperatures for these formulations. In general, formulation viscosity decreases with increasing equivalent weight due to higher polarity and solubility in the polar diacrylate monomer. Sealant formulations with higher equivalent weight exhibit less shrinkage due to lower crosslink densities but they also exhibit lower heat distortion temperatures, which would limit end use service temperature. In Figure 3 the Shore D hardness of these formulations is plotted as a function of time during 60 °C water immersion testing. Sealant formulations containing higher equivalent polyether oligomers such as EO BPA3 exhibit lower hardness and poor hardness retention after water immersion due to lower crosslink density and higher ether content. Figure 4 shows the flexural modulus for these formulations. The data indicate that the BPAEA epoxy acrylate and the EO BPA1 polyether oligomer offer the best performance in terms of flexural properties because of the combined flexibility from the PO NPGDA monomer and high crosslink density from the oligomer.

Table 3. Summary of oligomer equivalent weight effect on sealant properties

| Property | BPAEA | EO BPA1 | EO BPA2 | EO BPA3 |
|---|-------|---------|---------|---------|
| Viscosity 25 °C (cps) | 950 | 120 | 110 | 170 |
| Degree of Shrinkage | high | high | high | low |
| Heat Distortion Temperature by DMA (°C) | 64 | 40 | -1.2 | -34 |

Figure 3. Plot of oligomer equivalent weight effect on Shore Hardness after water immersion

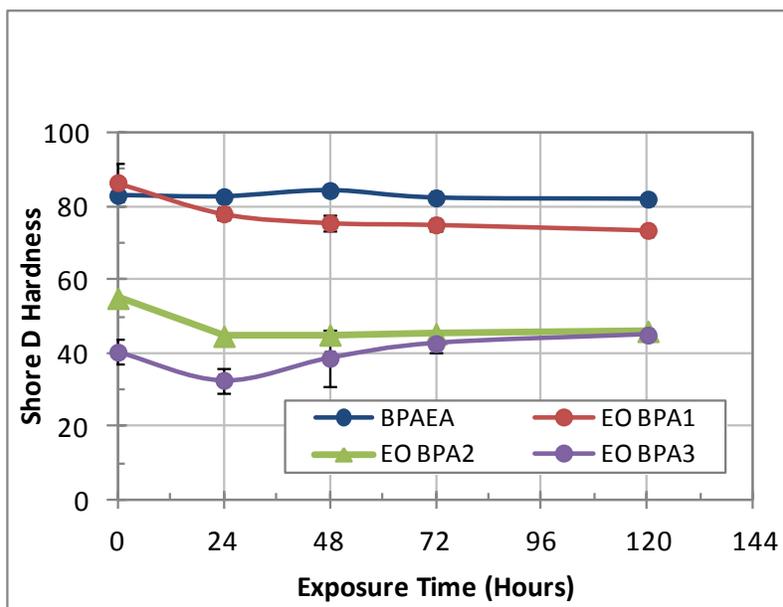
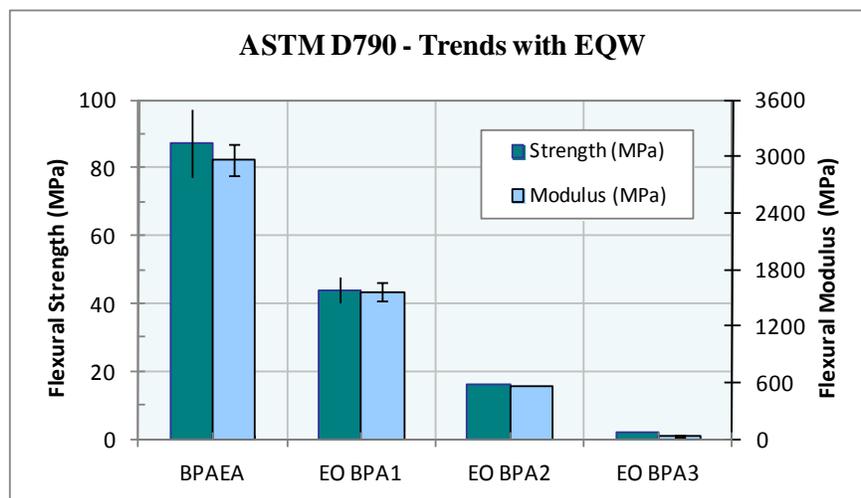


Figure 4. Summary of oligomer equivalent weight effect on Flexural Properties



After observing that oligomers with a high equivalent weight and high ether content yield high flexibility but low hardness and low water resistance, we focused the next series of experiments on reducing the polyether content by replacing the diacrylate polyether monomer with various hydrophobic monoacrylates. In this case, the monomer in Base Form 1 in Table 2 was chosen from a series with alkane backbones that cover a range of glass transition temperatures, T_g (ODA < TMCHA < IBOA) and the oligomer was the BPAEA epoxy acrylate oligomer.

Table 4 lists viscosities, degree of shrinkage, and heat distortion temperatures for these formulations. In general, formulation viscosity increases with increasing monomer T_g due to the cyclic structures of TMCHA and IBOA versus the slightly branched structure of ODA. Sealant formulations with monoacrylate monomers in place of the diacrylate monomer all exhibit low shrinkage due to their lower crosslink density. However, in this case the high T_g IBOA monoacrylate also exhibits a moderate heat distortion temperature, which would allow it to be used at moderate end use service temperatures. In Figure 5 the Shore D hardness of these formulations is plotted as a function of time for 60 °C water immersion testing. Sealant formulations containing alkane monoacrylate monomers TMCHA and IBOA exhibit higher hardness than and equal hardness retention after water immersion to the polyether diacrylate monomer PO NPGDA. Figure 6 shows the Flexural Modulus for these formulations. The data indicate that sealant formulations containing the cyclic alkane monoacrylates TMCHA and IBOA exhibit improved flexural properties over the polyether diacrylate monomer PO NPGDA. Overall, the combination of BPAEA epoxy acrylate oligomer and IBOA monoacrylate exhibited the best combination of properties including low shrinkage, good flexural properties and a high HDT, which would allow use at higher service temperatures.

Table 4. Summary of alkane monomer type effect on sealant properties

| Property | ODA | TMCHA | IBOA |
|---|-----|-------|------|
| Viscosity 25 °C (cps) | 115 | 340 | 680 |
| Degree of Shrinkage | Low | Low | Low |
| Heat Distortion Temperature by DMA (°C) | 2 | 67 | 79 |

Figure 5. Plot of alkane monomer type effect on Shore Hardness after water immersion

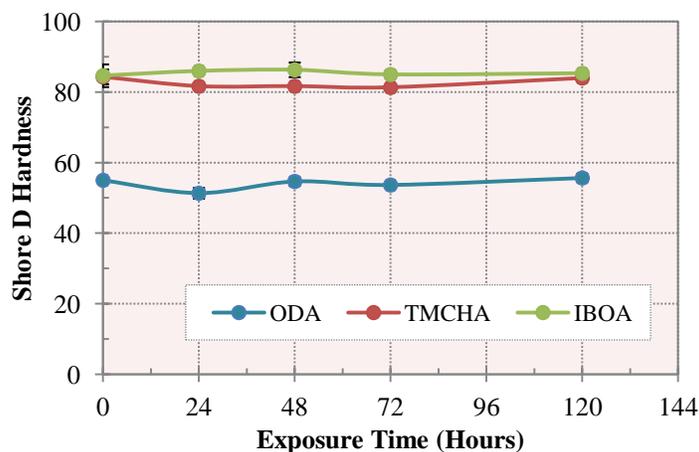
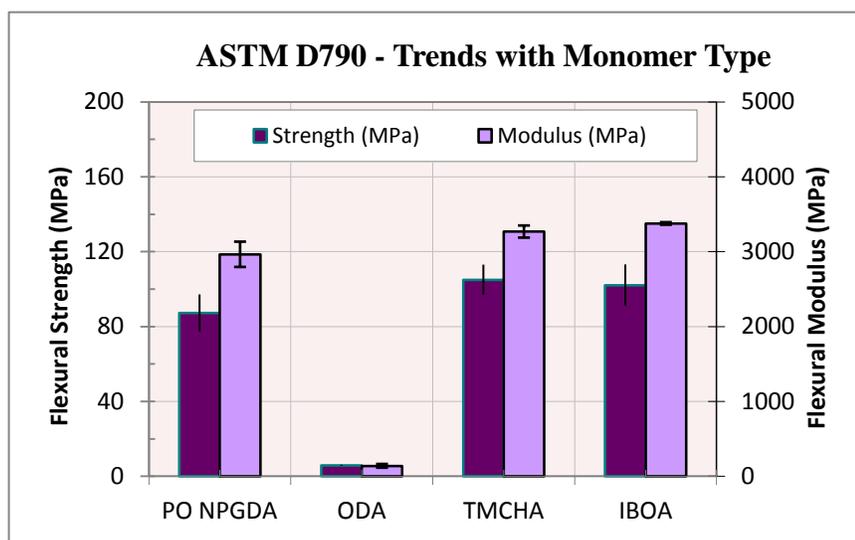


Figure 6. Plot of alkane monomer type effect on Flexural Properties



The combination of high strength aromatic BPAEA epoxy acrylate oligomer with high T_g IBOA monomer may be too rigid for some sealant applications that involve holding substrates with different coefficients of thermal expansion together. Therefore, in the third set of experiments of this study, the BPAEA epoxy acrylate oligomer was replaced with a series of aliphatic urethane acrylate oligomers in the Base Form 1 listed in Table 2. The urethane acrylates tested have similar equivalent weights but vary in polyol backbone type ((polyester (PEsUA1), polyether (PEtUA2) and polycarbonate (PCUA3)). The monomer used in these formulations was the diacrylate PO NPGDA.

Table 5 lists viscosities, degree of shrinkage, and heat distortion temperatures for these formulations. In general, formulation viscosity is lowest for the polyester UA. Unexpectedly, the polyether UA formulation exhibits the highest viscosity. All of the sealant formulations containing aliphatic urethane acrylate oligomers in place of the aromatic epoxy acrylate exhibit lower shrinkage due to the higher molecular weight from the polyol in the backbone. All three urethane acrylate formulations exhibit low heat distortion temperatures, which would limit their end use service temperature. Figure 7 shows the Shore D hardness of these formulations as a function of time during 60 °C water immersion testing. The sealant formulation containing polyether based urethane acrylate exhibit slightly lower hardness and hardness retention after immersion. The formulation with polycarbonate based urethane acrylate exhibits moderate hardness and retains hardness after water immersion. Figure 8 shows the Flexural Modulus for these formulations. These results indicate that the polyester based urethane acrylate offers the best performance in terms of flexural properties because of a good combination of flexibility and crosslink density.

Table 5. Summary of oligomer backbone chemistry effect on sealant properties

| Property | PEsUA | PEtUA | PCUA |
|---|-------|-------|-------|
| Viscosity 25 °C (cps) | 1,480 | 4,120 | 1,600 |
| Degree of Shrinkage | low | low | Low |
| Heat Distortion Temperature by DMA (°C) | 21 | -3 | 8 |

Figure 7. Plot of oligomer backbone structure effect on Shore Hardness after water immersion

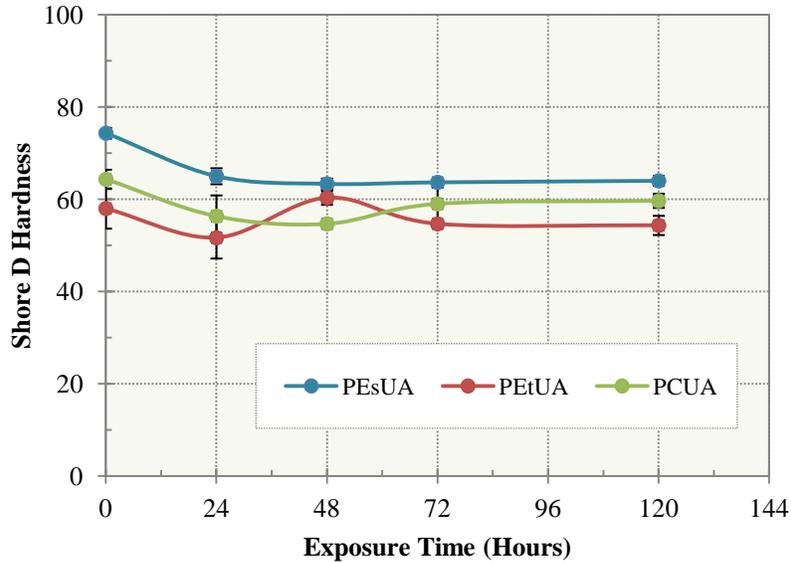
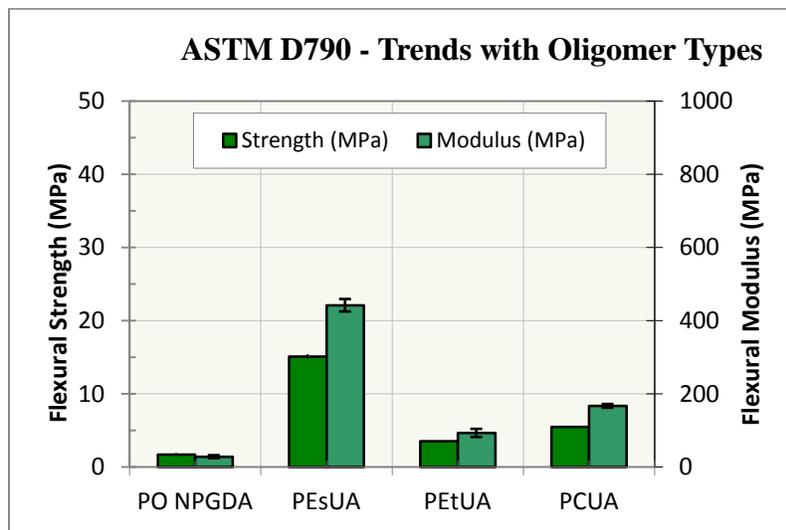


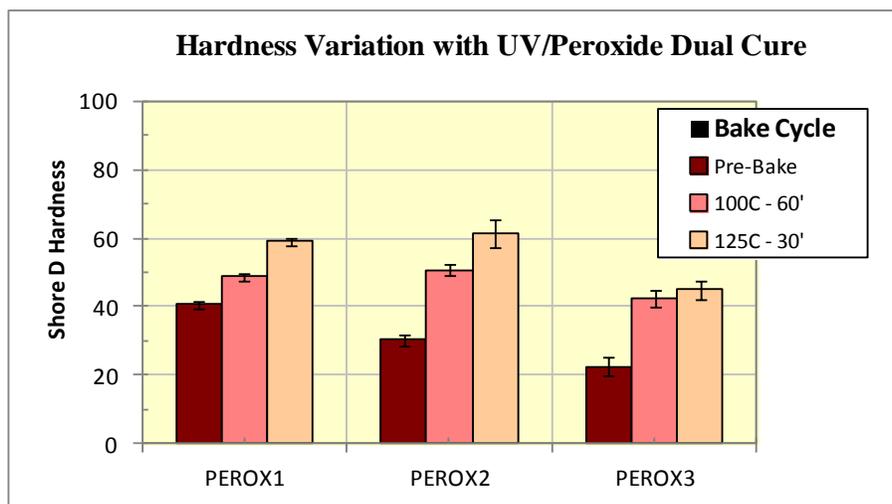
Figure 8. Plot of oligomer backbone structure effect on Flexural Properties



Formulating UV curable sealants and encapsulants using aliphatic urethane acrylates and a polyether based diacrylate monomer was shown to produce a system with good flexibility but only moderate hardness and heat distortion temperature. Therefore, a second study was conducted to determine the degree of cure after UV energy exposure only, as compared to UV cure followed by thermal peroxide post-cure using three different peroxides as co-initiators, to determine if the resulting hardness and HDT can be enhanced by increasing the degree of cure.

The peroxides tested are described in Table 1 along with their respective characteristics (percent active peroxide, Self-Acceleration Decomposition Temperature (SADT) and one hour half-life temperature). The SADT is important for safety and handling considerations. The half-life temperature is also important because it is a measure of the rate of decomposition of the peroxide and the percentage of peroxide conversion to peroxy radical to achieve optimal cure. The base formulation for these samples is referred to as Base Form 2 in Table 2. For this study PEtUA2 was selected as the oligomer and the polyether diacrylate PO NPGDA was chosen as the monomer. The peroxide initiators varied by type (Diacyl peroxide (PEROX1), Diperoxyketal (PEROX2) and Dialkyl peroxide (PEROX3)). The three peroxides selected also varied from low to high one hour half-life temperature (PEROX1<PEROX2<PEROX3). These formulations were exposed to one pass under a 600 watt/inch Fusion UV Systems D lamp at 100 feet/minute. The reason for the reduced UV cure in this study is that the goal was to cure the samples enough to be handled and to minimize shrinkage during thermal post cure. Thermal post cure was done at 100°C for 60 minutes and an equivalent cure at 125°C for 30 minutes.

In general, formulation viscosity was unaffected by the peroxide addition because it is added at a low level. Sealant formulations with peroxide added exhibited only a slight increase in shrinkage versus UV cure only at both thermal post cure conditions. In Figure 8 the Shore D hardness of these formulations is plotted after pre-bake and after thermal post cure at 100°C for 60 minutes and 125°C for 30 minutes, respectively. Sealant formulations with added peroxide exhibit significantly higher hardness than formulations cured by UV energy only. **Figure 8. Plot of UV/peroxide dual cure effect on Shore Hardness**



Conclusion

The results of this work suggest that the selection of UV curable acrylate chemistry, photoinitiators and lamp technology can have a significant influence on properties such as hardness, flexural strength, and resistance to hot, damp environments that are important to high end sealant and encapsulant/potting formulators. UV cure technology has been shown to be a feasible solution for sealant formulators to provide a single component, low VOC formulation exhibiting fast cure and low shrinkage. This paper also demonstrates that formulations can be tailored for performance by varying the backbone structures

and molecular weight of the acrylate monomer and oligomer components. Alkane backboned monomers in combination with BPA based epoxy acrylate oligomer provide high hardness and good hardness retention for sealant applications exposed to hot and damp environments. For sealant applications requiring moderate hardness and enhanced flexibility, the combination of a high molecular weight ether-based diacrylate monomer with a polyester or polycarbonate-based urethane acrylate oligomer can provide a solution for formulators' consideration.

Finally, this study has shown that the addition of peroxide to a UV curable system, as a co-initiator, in combination with a secondary thermal cure can result in enhanced performance by overcoming the UV curing limitations presented in high end sealant applications. Most notably, these limitations include the inability to achieve optimal cure for complex assembly geometries having shadow areas and depth of cure in thick, optically dense applications. The work presented here suggests that a sealant formulation based on a polycarbonate urethane acrylate oligomer, polyether diacrylate monomer, photoinitiator and a peroxide that is cured by UV energy to a hardness sufficient for handling and physical stresses encountered during the assembly process and then thermally cured during finishing is a possible solution for a high demand/high performance system. Future work will involve additional study of photoinitiator and peroxide combinations and further testing in fully formulated sealant and encapsulant/potting systems.

References

¹ Petrie, Edward M., 2000, Handbook of Adhesives and Sealants, McGraw Hill, pp 31-34, 475-499

² Goodrich, James E., "Suitability of (Meth)acrylates for Use in Sealant Applications", RadTech 2012 Technical Proceedings