

UV/EB Thermoset Polymers Intended for Thermoforming Applications

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Introduction

The process of thermoforming is not a new concept as it has been used for many years with the process being refined over the years. The thermoforming process can be defined as simply heating a thermoplastic substrate to a temperature where the substrate becomes soft and flexible. The heated substrate then has a mold or dye forced into it from beneath where a vacuum was pulled to assist the forming. The vacuum pulls the thermoplastic substrate tight to the mold allowing for very detailed parts to be created. Once the vacuum is released and the mold cools the part can be trimmed or cut to the desired shape. Thermoformed parts are used in everyday applications ranging from food packaging, medical packaging, automotive applications, appliances and many others. There are many types of thermoforming methods that vary the thermoforming process and intended applications of the parts made. Some examples of thermoforming processes are vacuum forming, plug and assist forming, billow forming, pressure forming, and drape forming. The process described above is called vacuum forming. This is the method that this paper will focus on. The process of vacuum forming can be further broken down into two different categories, which are determined by the thickness of the thermoplastic substrate used. These categories are called thin gauge and thick gauge. As the names imply the difference is the thickness of the substrate to be formed. To be considered thick gauge the substrate has to be greater than 3.0 mm whereas the thin film substrate is typically less than 1.5 mm. Thin film and thick film substrates are intended for different application areas. In the thick gauge process the applications include vehicle door panels, dash panels, parts of appliances, plastic pallets, etc. Thin film applications include disposable cups, container lids, food applications, and medical applications. The thin film process is also a much more automated process and is much quicker compared to the thick gauge process which is less automated.

Substrate Selection

The various films or substrates used in thermoforming applications are thermoplastic polymers. Thermoplastic polymer substrates have the ability to form and in some cases reform when heat is applied to them because they are not crosslinked or cured like thermoset polymers are. This simply means that as a thermoplastic substrate is heated and reaches its glass transition temperature, known as its T_g (which varies for different polymers), it has very elastomeric or flexible properties and can be formed with little effort. When thermoplastic substrates cool below the T_g their properties change back to a more rigid substrate that cannot be formed. This shift of properties can be repeated simply by raising the temperature of the thermoplastic substrate above the T_g . These properties make thermoplastic substrates ideal materials for thermoforming applications. The issue with using UV/EB cured materials in thermoforming applications is that they are thermoset materials. Thermoset polymers do not have the capability to be reformed or molded simply by raising the temperature above the T_g of the material. Typical thermoset materials are liquid prior to curing with little or no properties. However once these materials are

cured whether by heat, UV irradiation, or electron beam, they become crosslinked polymer networks that can't be reversed. The crosslinking of these materials is what dictates polymer properties (**Figure 1**).

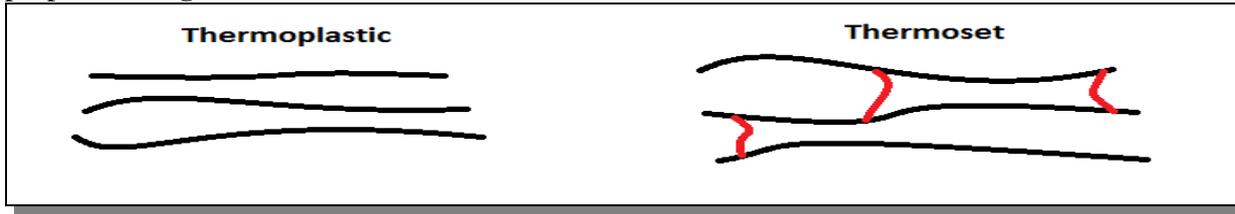


Figure 1. Crosslinks in thermosets limit the formability

A simple cooking analogy can be used to describe the difference in properties between thermoplastic polymers and thermoset polymers. Thermoplastic polymers can be thought of as a piece of chocolate that when heated to a specific temperature transforms from a hard solid material to a material that can flow into a mold and take that shape once it cools; upon reheating this material can flow into a different mold and take that shape. Thermoset polymers can be thought of as a cake mix. Prior to curing these materials are liquid and have the capability to be poured into any shape but they have no properties. Once the cake mix is heated (cured) the cake will take the shape of whatever container it is in during this process. At this point no matter how many times the cake mix is reheated it will not reflow and take on any other shape. There are many types of thermoplastic substrates used in thermoforming applications. Some examples of common substrates are polyethylene terephthalate copolymer (PETG), acrylonitrile butadiene styrene (ABS), polyvinyl chloride (PVC), polycarbonate (PC), and high density poly ethylene (HDPE).

Evaluation of UV/EB Cured Polymers

In order to better study the performance of UV/EB cured polymers in thermoforming applications a lab size unit was used. A Formech 300XQ (**Figure 2**) vacuum forming unit enabled actual parts to be made for testing different pieces of chemistry rather than solely relying on Instron® data (tensile strength, % elongation, modulus, and energy). In addition to actual forming and Instron testing (ASTM D3039), other commonly used physical property testing methods, such as Dynamic Mechanical Analysis or DMA (ASTMD7028), pencil hardness (ASTM D3363), and chemical resistance (ASTMD5402) were used to understand what types of oligomer backbones work best and the effects the monomer has on the system.

The challenge in using UV/EB cured materials in thermoforming applications comes from the fact that they are thermoset polymers that are cured and crosslinked prior to being formed. This means that the UV/EB coating must be flexible enough to survive the forming process without cracking or losing adhesion and still have sufficient surface properties. As there are various end-use applications that can vary greatly in what properties are required, developing a single formulation that fits all applications does not seem realistic at this



Figure 2. Formech vacuum forming apparatus

time. The goal of this study was to generate an understanding of what materials may be suited for thermoforming applications and to develop a coating formulation that can survive various forming molds with decent physical properties. Depending on the degree of forming desired or length of draw the coating must endure it was conceivable that through the information learned two formulations could be developed. One formulation could be designed for a mold requiring a large draw that may have lower surface properties and one formulation can be designed for a lower draw with increased surface properties such as pencil hardness, chemical resistance, scratch, and abrasion resistance.

The goal of this study was to determine what oligomer backbones have the required properties to withstand a thermoforming process and how will the molecular weight of the oligomer affect the performance. An evaluation was designed to test difunctional urethane acrylate backbones of varying molecular weight in a standard monomer package. The decision to use difunctional urethane acrylates and not epoxy acrylates or polyesters acrylates was based on the physical properties that these oligomer backbones typically have. Epoxy acrylates, commonly based off of Bisphenol A diglycidyl ether are excellent choices for coating applications that don't require a high level of flexibility, such as overprint varnish, wood flooring, and similar applications. In these applications epoxy acrylates are typically chosen as the oligomer of choice for their hardness, scratch, abrasion resistance, high refractive index, and low cost. Tensile properties of epoxy acrylates tested on an Instron using ASTM D882 show that epoxy acrylate oligomers have an elongation at break of less than 5% and a modulus of greater than 200,000. Low elongation and high modulus properties such as these would put this oligomer backbone in the category of hard/brittle and not able to withstand any degree of forming process. In addition to the lack of formability, epoxy acrylates, would also be limited in the applications they could be used for as their aromatic structure, based off of Bisphenol A, would make them yellow very quickly outdoors.

Description of Polymer	Modulus	Yield Stress	Ultimate Strength	Elongation at Break
Soft, weak	Low	Low	Low	Moderate
Soft, tough	Low	Low	Moderate	High
Hard, brittle	High	None	Moderate	Low
Hard, strong	High	High	High	Moderate
Hard, tough	High	High	High	High

Figure 3. Oligomers described as soft/tough or hard/tough are ideal, depending on application

Higher functionality polyester acrylates (typically tri- and tetra-) were ruled out for reason similar to the epoxy acrylates. Even though polyester acrylate oligomers have a higher level of flexibility (ranging from 10%-20% elongation compared to epoxy acrylates having only around 5% elongation at break), it was determined that these oligomers would not be ideal. Typical

polyester acrylates would fall somewhere between the hard/brittle category and hard/strong category. When considering the graph in (Figure 3) the ideal oligomer properties would be soft/tough or hard/tough, depending on the intended application.

The decision was made that the best chance for success would be with high molecular weight urethane acrylates that can provide good flexibility and a tough coating even at relatively low crosslink densities. The problem with this is that typically low crosslink density highly flexible oligomers are not considered for hardcoats because they may lack the necessary coating properties to protect the substrate and may also be tacky without proper formulation. Urethane acrylates are typically used when the coating requires optimal performance and long term exterior performance. Twelve difunctional urethane acrylates based off of polycarbonate, polyester, and polyether backbones and varying molecular weight were evaluated for performance (Figure 4).

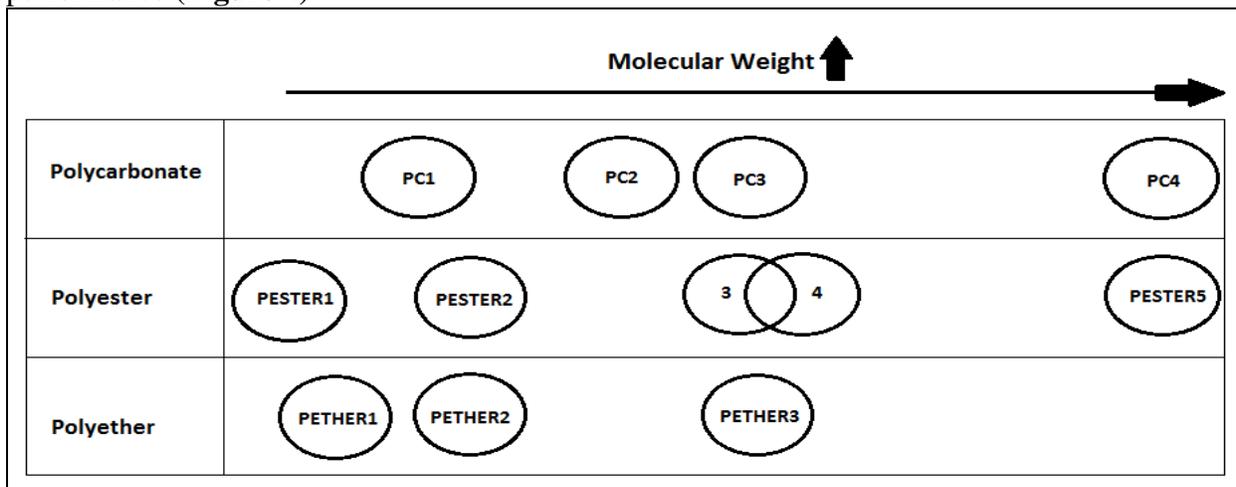


Figure 4. Oligomer candidates classified by molecular weight and backbone structure

These oligomers, referred to by their backbone structure and corresponding molecular weight, were formulated with a standardized monomer and photoinitiator package shown below.

Base Formulation

- 45% Oligomer
- 30% CTFA (cyclic trimethylolpropane formal acrylate)
- 20% IBOA (isobornyl acrylate)
- 3.0% alpha hydroxy ketone photoinitiator
- 2.0% Norrish Type II photoinitiator

As the coating thickness increases so does the stress on the coating during the forming process, so film thickness is an important factor. The oligomer formulations were tested at three different thicknesses. Formulations were drawn down with different gauge wire bars to apply the coating at thicknesses of 0.5 mils, 1.0 mils, and 1.5 mils. The substrate used for the thermoforming processes in this study was PETG and ABS. Samples were cured using a Fusion 600 w/in “H” lamp at a line speed of 50 ft/min with a total energy of 996 mJ/cm² measured using an EIT

Power Puck II. Samples were evaluated for forming capability, pencil hardness, and chemical resistance by MEK double rubs. Pencil hardness and chemical resistance test were tested before and after the forming process to monitor change. Two dyes were used for the initial evaluation to determine the effectiveness of the oligomers. First, a watch glass roughly 4 inches in diameter and ½ inch in height at the center was used to measure pencil hardness and MEK resistance after forming. A second dye was used to test various degrees of forming can be seen in (Figure 5). It was determined by evaluating the PETG and ABS substrate for substrate temperature vs. forming that the ideal temperature was 135°C.



Figure 5. Complex mold used to rate degree of forming

Performance results from pencil hardness testing can be seen in (Figure 6). An interesting result noticed in this testing was that the pencil hardness of the formulations increased after the forming process by 1-2 hardness units. The first trend that sticks out is the MW vs. pencil hardness. As the samples increase in molecular weight they decrease in pencil hardness. This is due to the decreased crosslink density. When evaluating these formulations strictly from a formability standpoint the results showed a clear trend which was not unexpected. The higher MW formulations based off of PC4 and PESTER5 were the only samples to survive the forming process without cracking when using the dye in Figure 5. Oligomer formulations PC4 and PESTER5 were able to successfully be formed without cracking at 0.5 and 1.0 mil coating thicknesses. Even though both of these oligomers formed successfully, their cured properties were considerably different. The PESTER5 oligomer was tacky post cure, indicating a lower degree of surface cure and would provide lower physical properties. Overall the polycarbonate based urethane acrylates provide the best balance of properties compared to the polyester or polyether based urethanes. Based on performance of the PC4 oligomer forming to the test dye, it was chosen as the oligomer for continued study.

Pencil Hardness of Urethane Acrylate Backbones vs. MW		
PC1: B	PESTER1: HB	PETHER1: 2B
PC2: 2B	PESTER2: 2B	PETHER2: 4B
PC3: 2B	PESTER3: 2B	PETHER3: 5B
PC4: 5B	PESTER4: 2B	
	PESTER5: 6B	

Figure 6. Pencil hardness versus backbone and MW

Effect of monomer on properties

In addition to base oligomer selection the role and effect of monomers must be examined as well. One of the major advantages to using UV/EB cured materials is the fact that they are 100% solid formulations that do not require solvent to be used to obtain a viable viscosity. This is even more crucial when using these high MW materials, as reactive diluents are required to reach a viscosity where they can be applied with standard coating methods. When formulating with 100% solid formulations monomer selection is important as they not only act as reactive diluents to control the viscosity of the formulation but they also have an effect on the properties of the formulation. To evaluate the effect of monomer functionality the PC4 oligomer was formulated with four different monomers ranging in functionality from mono to tetra. Monomer levels of 10% and 20% were chosen.

- Monofunctional: 2(2-ethoxyethoxy) ethyl acrylate
- Difunctional: tripropylene glycol diacrylate
- Trifunctional: trimethnyolpropane triacrylate
- tetrafunctional: pentaerythritol tetraacrylate

Free film samples were made to be tested on an Instron to evaluate tensile properties. Samples were drawn down on aluminum mil substrate at a film thickness of 5 mils and cured under (2) 400 w/in mercury arc lamps at a line speed of 50 ft/min with a total energy of 1496 mJ/cm² measured with an EIT Power Puck II. As the functionality of the monomer diluent increases so does the crosslink density of the coating. This increased crosslink density of the coating changes the properties from soft and flexible (adhesive-like properties) to hard and scratch resistant (hard coat properties). This effect can be seen in the **Figure 7** which compares elongation @ break and tensile strength vs. monomer functionality.

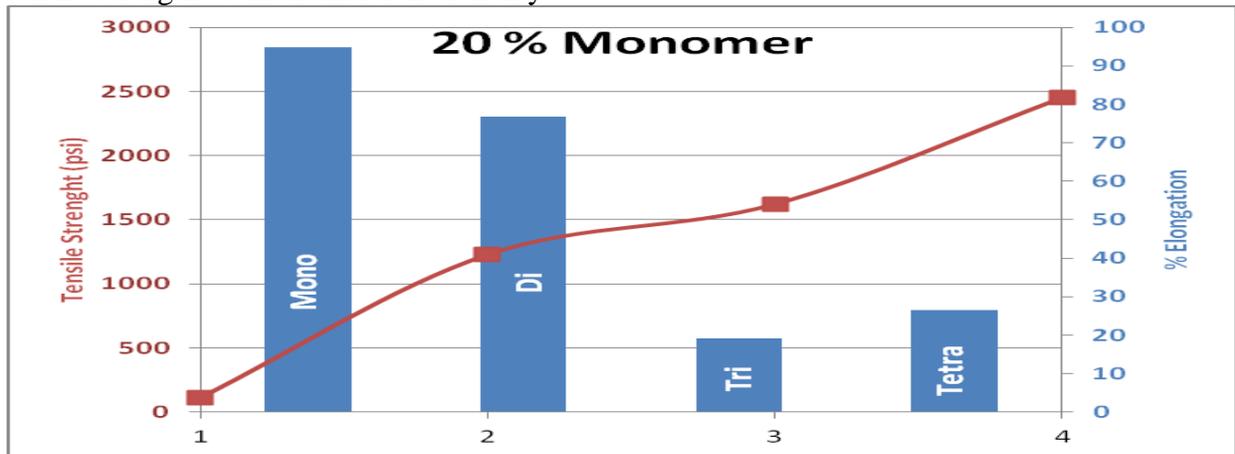


Figure 7. Effect of diluent monomer functionality on coating mechanical properties

It would be ideal if the higher functionality monomer diluent could be used in a thermoforming application as the coating properties would be better compared to the lower functionality diluents. To evaluate this possibility these samples were drawn down on PETG substrate at a 1.0 mil coating thickness and cured under (2) 400w/in mercury arc lamps at a line speed of 50 ft/min for a total energy of 1496 mJ/cm². To quantify the performance from a thermoforming

standpoint a mold was created using different height dyes. The heights of the dyes were 1/16, 1/8, 1/4, 3/8, and 1/2 inch in height.

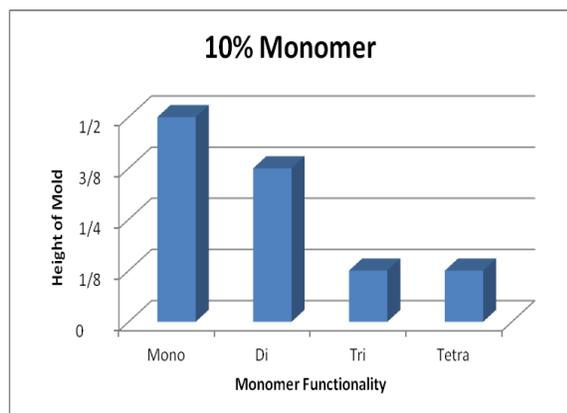


Figure 8. Thermoformability versus monomer functionality

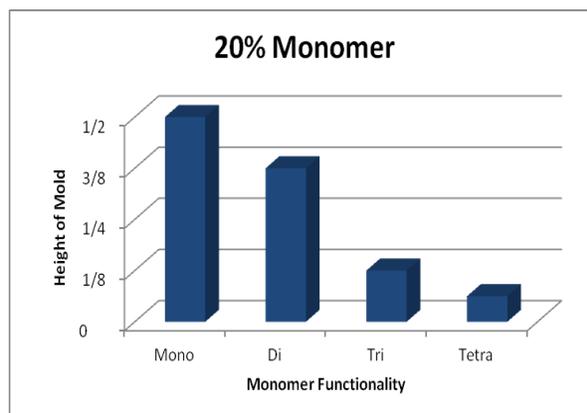


Figure 8. Thermoformability versus monomer functionality

Figure 8 and Figure 9 show that the monomer functionality plays a large part in the overall formability of the formulation even at relatively low addition levels of 10% and 20%. The above mentioned formulations based off of the PC4 oligomer with 10 and 20% levels of monomers are too high in viscosity for most application methods. Since the monofunctional monomer in this case 2(2-ethoxyethoxy) ethyl acrylate was the only monomer that was able to form the 1/2 inch dye, after cure monofunctional monomers were selected for continued study at higher addition levels. Additionally, using the 2(2-Ethoxyethoxy) Ethyl Acrylate at these levels left us with a coating that had poor properties and a tacky surface, which would not be acceptable moving forward. To increase the coating properties cyclic monofunctional monomers were evaluated at a 40% level to lower the application viscosity. These monomers were designated:

- cyclic monomer 1 (CM1)
- cyclic monomer 2 (CM2)
- cyclic monomer 3 (CM3)

Tensile properties of these monomer and oligomer blends were measured on an Instron. As expected, the formulations containing the higher level of monomer had a lower viscosity. All three monomer blends exhibited a much higher elongation at break compared to the PC4 oligomer blend with the tetrafunctional monomer formulation used in the previous test. This allowed for a much higher degree of forming as all formed the 1/2 inch dye without cracking, whereas the tetrafunctional monomer formulation could only form up to 1/8 without cracking. The more interesting results were the tensile strength and 1% modulus of the cyclic monomer 2 formulation. These tensile properties were very similar to the tetra functional monomer formulation. The formulation with the PC4 oligomer and cyclic monomer 2 had a reasonably low viscosity, decent forming, and tensile properties similar to a formulation with a higher degree of crosslinking. In order for the additional step of applying and curing a coating to a substrate to be formed the coating has to add something to the application whether that's chemical resistance, scratch and abrasion resistance, or improved weatherability of the plastic. The previously discussed coatings had the required flexibility but were lacking in hardness and chemical resistance.

Monomer	%	Viscosity @ 25C	Tensile Strength	% Elongation	1% Modulus	Energy
CM1	40	4,500 cP	826	279.6	1747	0.2366
CM 2	40	6,250 cP	1411	210.6	13500	0.3597
CM 3	40	9,125 cP	961	145.6	391	0.0806
Pentaerythritol Tetraacrylate	20	15,400 cP	942	45.4	4064	0.0683

Figure 9. Properties of 60/40 oligomer/monomer blends

How to increase the properties

Previous work showed we could formulate a coating based off of a high molecular weight polycarbonate urethane acrylate and a monofunctional cyclic monomer that can withstand a relatively high level of formability. This combination had a low enough viscosity that there was no need to cut the material in a solvent for application to a substrate. The issue was the lack of coating properties, i.e., low pencil hardness results and poor chemical resistance. In order to provide adequate coating properties that can not only withstand the rigors of the forming process but also have a decent hardness and chemical resistance, we needed to find a way to increase the crosslinking of the coating without hurting the forming properties. We learned from earlier evaluations that we can't just throw in some high functionality monomer to increase the % conversion. The issue with using high functionality monomers is that they tend to be very brittle and have a high degree of shrinkage. The use of higher functionality (6) oligomers at additive levels may provide the required crosslink density and minimize the destructive effect on the forming properties. Since oligomers are much larger molecules than monomers they tend to impart a lower degree of shrinkage and less brittleness to formulations when compared to high functionality monomers such as dipentaerythritol pentaacrylate. Not all hexafunctional oligomers will perform the same though. When comparing the tensile properties of several neat hexafunctional oligomers we can see a specific advantage to one.

	Tensile Strength	% Elongation	1% Modulus	Energy	Tg by DMA
Hex 1	Too Brittle to Test				83 C
Hex 2	Too Brittle to Test				102 C
Hex 3	4,738	3.8	98,372	0.163	131 C

Figure 10. Mechanical properties of hexafunctional oligomers

The Hex 3 oligomer was the only oligomer that had the flexibility to be tested on an Instron. Even though the elongation of this oligomer was extremely low at 3.8%, elongation at break is significant in that it could actually be tested. As shown in **Figure 11** both of the other hexafunctional oligomers were too brittle to even be tested. The Hex 3 oligomer was specifically

designed to have a higher degree of flexibility than common hexafunctional oligomers while maintaining the expected hardcoat properties of these oligomers. This can be seen in the glass transition temperature (T_g) data that was developed through DMA testing using ASTM D7028. The more flexible Hex 3 oligomer actually demonstrated a higher T_g than the others. This oligomer (Hex 3) was selected for continued study due to its inherent flexibility to increase the coating properties of the PC4 oligomer. Forming evaluations were done based on 5, 10, 15, and 20% levels of Hex 3 to determine its effect. Even though we determined that the PC4 oligomer had the capability to successfully form well at up to 1.5 mils with the standard monomer package, evaluations were conducted at 0.5 and 1.0 mils due to the added hexafunctional oligomer. Due to the lack of monomeric diluents in these formulations, they were cut in a 1:1 ratio of acrylate formulation to acetone to achieve the desired coating thickness. As seen in the graphs below (Figures 12 & 13) higher degrees of forming were tested with molds up to 1 3/8 inches in draw. As the results show when levels of the Hex 3 oligomer were used above 10% by weight the thermoforming performance dropped off quickly. Even at a low coating thickness of only 0.5 mils the 20% addition of Hex 3 could only form a mold of 1/4 inch. As stated earlier in this paper that may be acceptable for some applications so it should not be considered a failure. Looking at these results to identify the level of Hex 3 oligomer that provides the best balance of properties, the 10% formulation stands out as it was able to form the 1 3/8 mold at 0.5 mils a common film thickness for these applications. Additionally, this formulation tested well on more complex shapes with higher degree of draws.

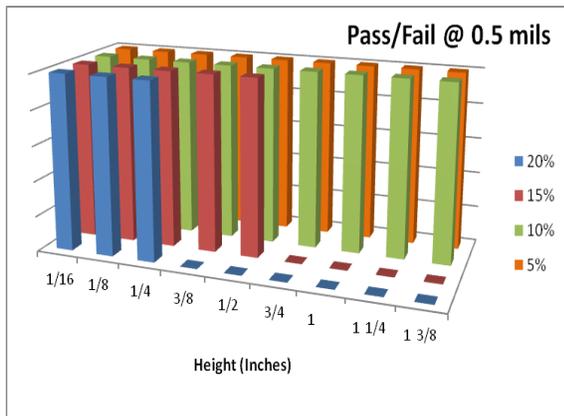


Figure 11. Forming at 0.5 mils based on Hex 3 addition

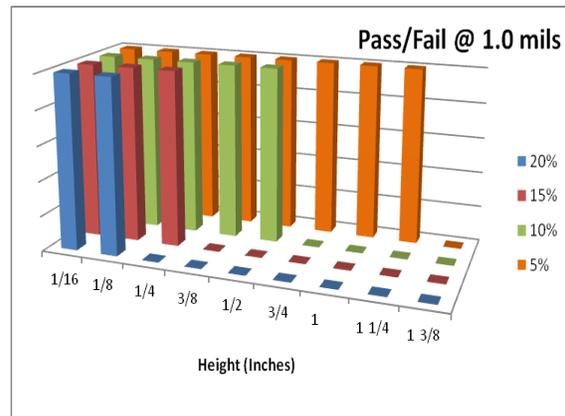


Figure 12. Forming at 1.0 mil based on Hex 3 addition

Having established an ideal ratio or maximum level of the hexafunctional oligomer identified as Hex 3 the focus shifted to lowering the viscosity of the blend. The viscosity without a monomeric diluent was 22,600 cP @ 60°C, which is too high for most application methods unless a solvent is used. Using the cyclic monomer 2 as a diluent the viscosity could be adjusted to a level suitable for various application methods without having to use a solvent. Results, seen in **Figure 14** show the viscosity achieved as a function of monomer level. At 20% monomer by weight, viscosity was reduced to a reasonable level.

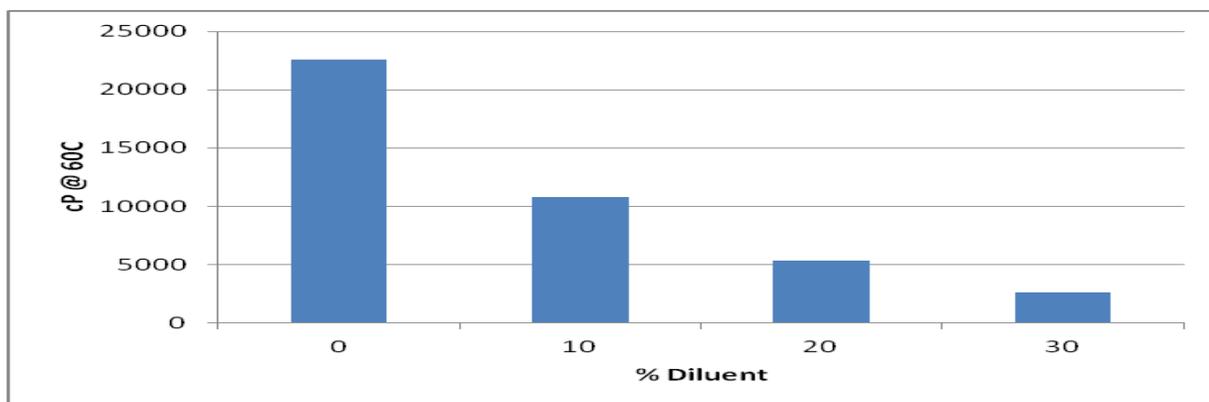


Figure 13. Effect of CM2 on viscosity

With the addition of the monofunctional monomer as a diluent the crosslink density of the coating will decrease as it would any time you use low functionality monomers in the system. So the question became: how does the addition of the monomer affect the properties of the coating that were previously achieved? The PC4 oligomer blended with 10% of the Hex 3 oligomer had a surface that was free of any tack once it was cured. A tack free surface would have to be maintained with any formulation adjustments. This is a major concern especially when dealing with high molecular weight formulations with relatively low crosslinked systems small change can have a dramatic affect on the properties.

How would the properties compare to properties of typical hardcoats? Coatings described in **Figure 15** as “hardcoats” for applications where scratch, abrasion, and chemical resistance are the most important property were compared in to these materials. Common test methods used to test hardcoats are pencil hardness, Konig, steel wool resistance, and Tabor abrasion. To compare the results for Konig hardness samples were drawn down on a piece of glass substrate at a 1.0 mil coating thickness and cured. The number represents the number of

Product #	Pencil Hardness	Konig Hardness	Steel Wool Resistance	MEK Double Rubs
Hardcoat 1	8H	103	Fail	200+
Hardcoat 2	8H	116	Pass	200+
Hardcoat 3	8H	98	Fail	200+
TF (Pre Form)	3B	35	Fail	35
TF (Post Form)	B	NA	Fail	32

Figure 14. Comparison of typical hardcoats and optimized forming coatings

pendulum swings that take place, with the higher number representing harder coating. The steel wool resistance test is a pass/fail test where a 1kg ball peen hammer is used with 0000 steel wool applied to the hammer. Ten double rubs are done on a 1.0 mil thick coating and if the coating shows any sign of scratching it is considered a failure. As seen in **Figure 15** even after a forming

process the physical properties of the thermoforming resins were not as good as a “typical hardcoat”.

Conclusion

The goal of this study was to evaluate and understand what types of monomers and oligomers will perform well in thermoforming applications. To do this different monomer and oligomer backbones along with monomer functionality were tested. This paper has demonstrated that formulation with high molecular weight urethane acrylates in combination with proper monomer selection and the right amount of high functionality oligomer can result in a robust coating that can survive a high degree of forming and still maintain decent coating properties. The coating properties achieved to date are not comparable to typical hardcoat properties. More research and testing is needed to increase the physical properties of the coatings described here. Moving forward, research will be geared towards increasing the coating performance, e.g., chemical resistance, and scratch and abrasion resistance, without affecting its formability.

References

1. http://plastics.inwiki.org/Types_of_thermoforming