

Adhesion Promoting Resins

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Abstract

A consistent “Achilles heel” for coatings is attaining acceptable adhesion to glass, metal and low surface energy substrates such as polyolefins and PET. A cost-effective improvement or solution for UV cured coatings has been regularly sought.

Myriant Corporation has developed a series of resins based on bio succinic acid and other naturally-derived building blocks that demonstrate a remarkable affinity for “difficult” substrates. These novel oligomers are cost competitive, especially when compared to conventional silane adhesion promoters and corona type treatments. Of equal importance, the experimental oligomers have a high bio-renewable content with no price premium.

These oligomers will respond to UV irradiation; in addition, variants bearing hydroxyl functionality can be selected for dual cure applications, as well as pendant carboxyl alternatives for enhanced adhesion to higher energy substrates.

This paper will detail the formulation and testing of these novel oligomers, with particular emphasis on adhesion to difficult substrates.

Introduction

Myriant has recently developed a variety of oligomers for coatings applications based on succinic acid that exhibit a remarkable adhesion to low energy substrates. Examples of these low energy substrates include, but are not limited to polyester, polypropylene, polyethylene, and polycarbonate films. For the demonstration of this paper, experiments were performed on polyester, polyethylene and polypropylene. One can infer their efficacy on similar substrates.

In addition, these oligomers were evaluated on high energy substrates; for the scope of the paper, high energy substrates include steel, aluminum, and glass. While the original oligomer recipes exhibited some adhesion to these, especially when coupled with a commercially available methacrylated phosphate ester, their performance was marked but not overwhelming. When reformulated to become acid functional, however, a second version did indeed perform very well on high energy substrates. In essence, the technology shows maximum efficacy if the original version is used for lower energy substrates, while an acid functional variant is applied to higher energy. Conversely, the application of our technology (either one) coupled with a methacrylated phosphate ester delivers the optimal performance to high energy substrates.

While the compositions of these oligomers can theoretically vary to infinite degrees depending on the applications and desired properties, for the scope of this paper, an optimal formulation was selected and named Myribond®.

One unique aspect of the Myribond® is a prevalence of three different reactive, carbon-carbon double bonds on the backbone: (meth)acrylate, maleate, and allylic. The three types of double bonds appear to offer a synergistic curing mechanism that reveals several ancillary curing properties.

Evaluation of these oligomers was performed on a contract basis at two independent, professional UV laboratories under direct supervision of UV coatings professionals. All tests were performed blindly by personnel at labs in Greensboro, North Carolina and in Chicago, Illinois. Results were recorded and interpreted later to ensure no bias would be present. Furthermore, the blend compositions were recommendations by the labs themselves. While we assume that these compositions are effective and representative, they are by no means a complete, exhaustive optimization of a system.



Our findings can be summarized as follows:

- The oligomers adhere to a variety of substrates
- The oligomers contribute to tough, flexible coatings with cycloaliphatic character
- The oligomers exhibit an alternate curing mechanisms that reveal a post/depth cure character
- The oligomers contain substantial bio-renewable content with no price premium

Evaluation: Greensboro

For evaluation of adhesion to low energy substrates, the following blends were mixed together using a mechanical stirrer. The oligomer and other constituents were warmed, mixed, re-warmed and re-mixed until complete homogeneity was assured. The samples were then allowed to rest at room temperature for twenty-four hours minimum in order to eliminate all entrained air bubbles. Compositions are as follows:

Figure 1: Blend Compositions, Greensboro, #1

		Oligomer	IBOA	polyether/ester tetra acrylate	PI	APR*
1	Myribond® 	35	38	22	5	
2	Epoxy Acrylate	35	38	22	5	
3	Polyester Acrylate	35	38	22	5	
4	Myribond® 	35	33	22	5	5
5	Epoxy Acrylate	35	33	22	5	5
6	Polyester Acrylate	35	33	22	5	5

* = phr



Details of table:

Myribond®:	Bio renewable adhesion promoting resin synthesized in the Myriant corporation laboratory in Woburn, MA.
Epoxy acrylate:	a standard bisphenol A di-acrylate epoxy resin
Polyester acrylate:	a general purpose polyester acrylate oligomer
IBOA:	isobornyl acrylate diluent monomer
Polyether/ester tetra acrylate:	a four functional acrylate monomer
PI:	a proprietary liquid photoinitiator blend
APR:	a methacrylated phosphate ester adhesion promoting oligomer

All constituents (other than the experimental resin) are commercially available. It must be noted that the components were blended on a percentage basis with the APR being added in phr or parts per hundred nomenclature; therefore, the total “percentage” would add to over 100 for the last three examples. This was per design in order to keep the blends consistent and uniform. This approach is consistent throughout the paper




Adhesion was then evaluated by drawing the coating down on a respective substrate with a 3 Meyer rod and curing via UV irradiation at a speed of 100 ft/min. Each sample was passed through three times to ensure complete cure. Results are as follows:

Figure 2: Adhesion Results, #1, Greensboro, NC

		Tape Adhesion				
		Polyester	Polypropylene	Polyethylene	Glass (crosshatch)	Steel (crosshatch)
1	Myribond® 	pass	pass	pass	fail	fail
2	Epoxy Acrylate	fail (50%)	fail (40%)	fail	fail	fail
3	Polyester Acrylate	fail	fail	fail	fail	fail
4	Myribond® 	pass	pass	pass	pass (95%)	pass
5	Epoxy Acrylate	fail	pass	fail	fail	fail (80%)
6	Polyester Acrylate	fail	fail (50%)	fail	fail (50%)	fail (50%)

Not surprisingly, the epoxy acrylate and polyester acrylate failed in adhesion on all tests even with IBOA, a known adhesion promoting monomer. The experimental oligomer adhered to all three low energy substrates. Initially, however, the experimental oligomer failed to adhere to glass and steel (as did the incumbent technologies). However, upon addition of the commercially available methacrylated phosphate ester adhesion promoter, the experimental resin passed on both glass and steel. While the incumbent technologies failed, the APR did indeed improve their performance also. In order to improve the oligomer performance without the need of additional additives, an acid functional variant was formulated. Results are observed in Figure 3:

Figure 3: Acid functional Myribond®



		Oligomer	IBOA	polyether/ester tetra acrylate	PI	APR*	Glass (crosshatch)	Steel (crosshatch)
1	Myribond® 	35	38	22	5		fail	fail
4	Myribond® 	35	33	22	5	5	pass (95%)	pass
7	acid functional 	35	33	22	5		fail (20%)	pass

* = phr

Samples 1 and 4 are from Figure 1, above. Acid functional versions appear to increase the adhesion to steel but not glass.

To assess the performance of the oligomer in a monomer other than IBOA, 2-ethylhexyl acrylate (2-EHA) was used as diluent monomer instead and results are shown in Figure 4. All other constituents remained the same. The objective was to determine if the oligomer adhesion effects are still realized without the use of IBOA.



Figure 4: Blends, Greensboro, #2

		Oligomer	2-EHA	polyether/ester tetra acrylate	PI	APR*
7	Myribond® 	35	38	22	5	
8	Epoxy Acrylate	35	38	22	5	
9	Polyester Acrylate	35	38	22	5	
10	Myribond® 	35	33	22	5	5
11	Epoxy Acrylate	35	33	22	5	5
12	Polyester Acrylate	35	33	22	5	5

* = phr

Curing techniques remained identical; results are seen in Figure

Figure 5: Adhesion Results, #2, Greensboro, NC



		Tape Adhesion				
		Polyester	Polypropylene	Polyethylene	Glass (crosshatch)	Steel (crosshatch)
7	Myribond® 	pass	fail (50%)	pass	fail	fail (80%)
8	Epoxy Acrylate	fail	fail	pass (95%)	fail	fail
9	Polyester Acrylate	fail	fail	pass	fail	fail
10	Myribond® 	pass	fail (25%)	pass	fail (15%)	pass
11	Epoxy Acrylate	fail	fail	pass	fail	fail
12	Polyester Acrylate	fail	fail	pass	fail	fail

As shown in Figure 5, the adhesion did suffer slightly; polypropylene failed for the experimental material as well as the incumbents. Of interesting note was the success of an epoxy acrylate on polyethylene where it had previously failed with IBOA. Furthermore, even with the addition of an APR, adhesion to glass was lost while steel remains effective for the Myribond® oligomer.

To no surprise, results from this comparison seem to indicate that the effects of our oligomer can be magnified or diminished by the choice of formulation components. For example, the replacement of IBOA with 2-EHA in the above series ruins adhesion to polypropylene for our experimental oligomer yet assists in adhesion to polyethylene for incumbent oligomers. Nonetheless those skilled in the art should be able to optimize the final formulations to their respective applications.

It was desired to compare the effects of using a methacrylate monomer versus an acrylate monomer; we predicted that perhaps these novel oligomers would perform better in a methacrylate system than acrylate. Two blends were prepared initially (Figure 6). Note that for these blends, the final two components were both added in a phr level. TBPB or tert-Butyl peroxybenzoate (CAS # 614-45-9), a commercially available peroxide which serves as a thermally decomposing free radical initiator, was added to the second blend to compare its effect in curing and performance.

Figure 6: Methacrylate Blends, Greensboro

		Oligomer	TMPTMA	PI*	TBPB*	Glass (crosshatch)	Steel (crosshatch)
1	Myribond® 	70	30	5		pass (95%)	fail (75%)
2	Myribond® 	70	30	5	2	pass (90%)	pass

* = phr


From the adhesion tests, it appears that methacrylate oligomers may give the adhesion to high energy substrates that was previously lacking. For example, adhesion to glass was observed for both and adhesion to steel was only fully achieved with the addition of peroxide. This data led to a hypothesis that the three types of double bonds present in our oligomers make the curing process slightly slower than traditional acrylate oligomers and peroxide type initiator could be more beneficial to speeding up the curing process. These ideas will be explored later in this paper.

Evaluation: Chicago

Further adhesion testing was performed on the same oligomers at an alternate facility in Chicago, IL. All substrates, monomers, curing lamps, etc. were variant. Only the oligomer remained the same.

Initial testing involved the comparison versus a urethane acrylate. It was theorized that perhaps because of the improved adhesion of a urethane acrylate when compared to an epoxy or polyester acrylate, this may be a pertinent data point.



Figure 7: Initial Chicago blends and results

						Tape Adhesion
		Oligomer	IBOA	polyether/ester tetra acrylate	PI	n/a
1	Myribond® 	35	38	22	5	100%, P
2	Aliphatic Urethane Acrylate	35	38	22	5	100%, P
3	Aliphatic Urethane Methacrylate	35	38	22	5	50%, F

For these three, the experimental oligomer passed tape adhesion to polyester, as did the urethane acrylate. The urethane methacrylate failed at 50%, revealing one data point to indicate the experimental oligomer compares to a much more expensive urethane acrylate.

In order to evaluate whether the adhesion performance was largely due to the effects of the oligomers or the monomer, the following experiments with higher concentrations of oligomers were conducted. Triethyleneglycol dimethacrylate (TEGDMA) was used as a diluent monomer. For these blends, adhesion was evaluated on polyester film only.

Figure 8: Chicago Blends and Results, #2



						Tape Adhesion	
		Oligomer	TEGDMA	PI	TBPB*	Polyester	
1	Myribond® 	60	35	5		100%, P	
2	Epoxy Acrylate	60	35	5		100%, P	
3	Polyester Acrylate	60	35	5		50%, F	
4	Myribond® 	60	35	5	2	75%, F	
5	Epoxy Acrylate	60	35	5	2	100%, P	
6	Polyester Acrylate	60	35	5	2	100%, P	

* = phr

These results are mixed; as this system seems to work decently with the incumbent. Furthermore, addition of a peroxide seems to, in effect, ruin the cure for the experimental resin and help the polyester acrylate; an unexpected result.

For the next round of testing, the monomer content was reduced further in order to exemplify the adhesion performance due to the oligomer as much as possible. A flexibility test was also performed. The Myriant bio-renewable oligomer appears to reveal resilience in the cured coatings.

Figure 9: Chicago Blends and Results, #3




						Adhesion		Flexibility	
		Oligomer	TEGDMA	PI	TBPB*	Aluminum (crosshatch)	Steel (crosshatch)	90°	180°
1	Myribond® 	85	15	5		100%, P	100%, P	pass	pass
2	Epoxy Acrylate	85	15	5		0%, F	<i>not run</i>	pass	crack
3	Polyester Acrylate	85	15	5		0%, F	<i>not run</i>	pass	pass
4	Myribond® 	85	15	5	2	100%, P	100%, P	pass	pass
5	Epoxy Acrylate	85	15	5	2	0%, F	<i>not run</i>	crack	n/a
6	Polyester Acrylate	85	15	5	2	0%, F	<i>not run</i>	pass	pass

* = phr

This round of testing revealed some very noteworthy results. Primarily, the adhesion to aluminum and steel was remarkable. In addition, the coatings showed a urethane-like flexibility even up to 180°.

As an additional point of interest, the adhesion promoting resin was blended with a bio-renewable polyester acrylate and compared to an identical formula using a commercially available polyester acrylate. Both compositions had good flow characteristics and adhesion to polyester was 100% for both the control and the highly bio-renewable content material. In other words, a cost-effective, highly bio renewable composition performed exceptionally as a coating.

Figure 10: Crossover Data, Chicago

		Oligomer	IBOA	polyether/ester tetraacrylate	PI	Tape Adhesion Polyester
1	Myribond® 	25	30	15	5	100% P
	Bio-Renewable Polyester Acrylate 	25				
2	Myribond® 	25	30	15	5	100%,P
	Polyester Acrylate	25				

Evaluation: Cure Speed

At this point, one could surmise that the effects on adhesion are difficult to argue with. We decided to investigate the curing mechanism further. Through simple observation, one can tell that the novel oligomers do not cure with the same speed as a traditional acrylate system. However, alternate curing mechanisms appear anecdotally.

Blends of the experimental oligomer in both TRPGDA (Tri-Propylene Glycol Di-Acrylate) and TRPGDMA (Tri-Propylene Glycol Di-MethAcrylate) were produced at 80% oligomer, 20% monomer. To that, 5 phr of a liquid photoinitiator blend were added. Similar blends (both acrylate and methacrylate) were also mixed for an epoxy acrylate and polyester acrylate.

It must be noted that the epoxy acrylate used in these experiments is a commercially available system supplied already pre-diluted to 80% in TRPGDA. While it was understood that further diluting this to 80% in more TRPGDA would yield an oligomer/monomer blend of 64%

oligomer and 36% TRPGDA, we decided to go through with the inconsistent blend simply because our intention was to compare the cure speed of our experimental oligomer, as supplied, against the incumbents, as supplied.

Each blend was then drawn down on steel using a 3 Meyer rod and passed through the UV unit for an indicated number of passes at 100 ft/min. The energy delivered was measured to be 264 mJ/cm² per pass.

The coating was then scanned on a Bruker ALPHA-P spectrometer with a diamond ATR crystal with:

- Two-minute sample scan time at 4 cm⁻¹ resolution
- One-minute background scan between each sample
- Sample plate cleaned with acetone between samples

Data for one and two passes versus ten passes (ultimate cure) is seen in Figures 11 – 14:

Figure 11

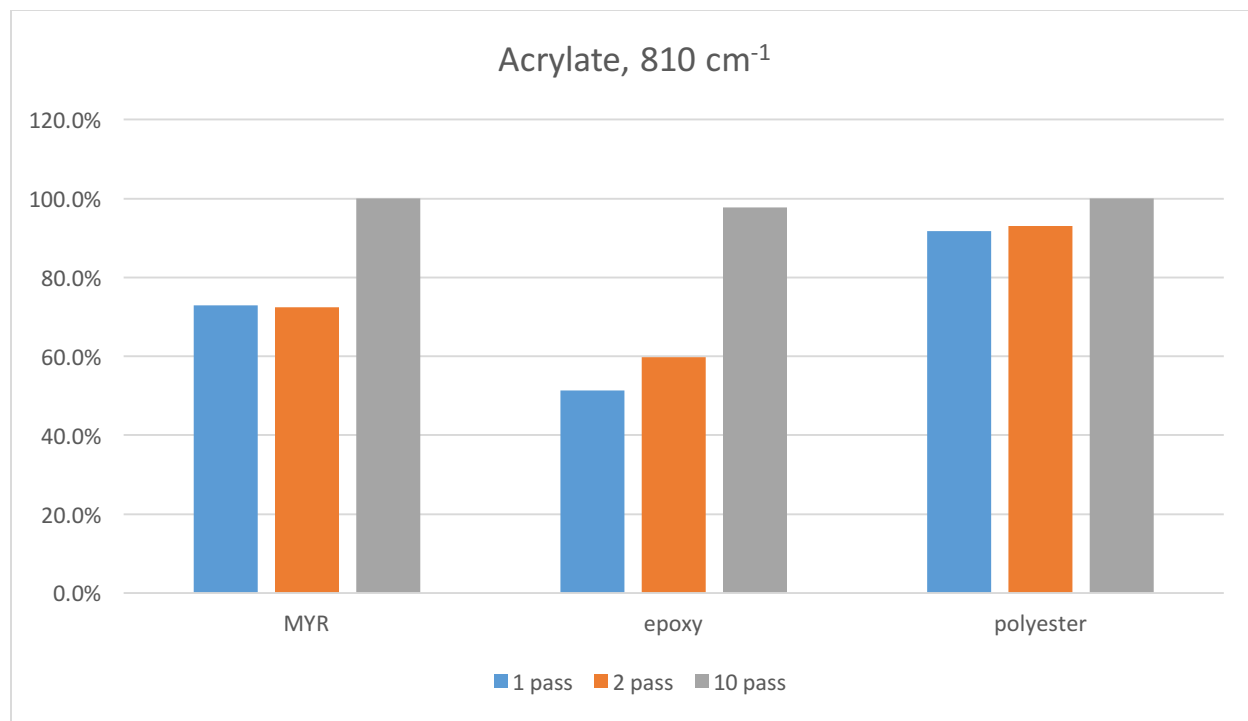


Figure 12

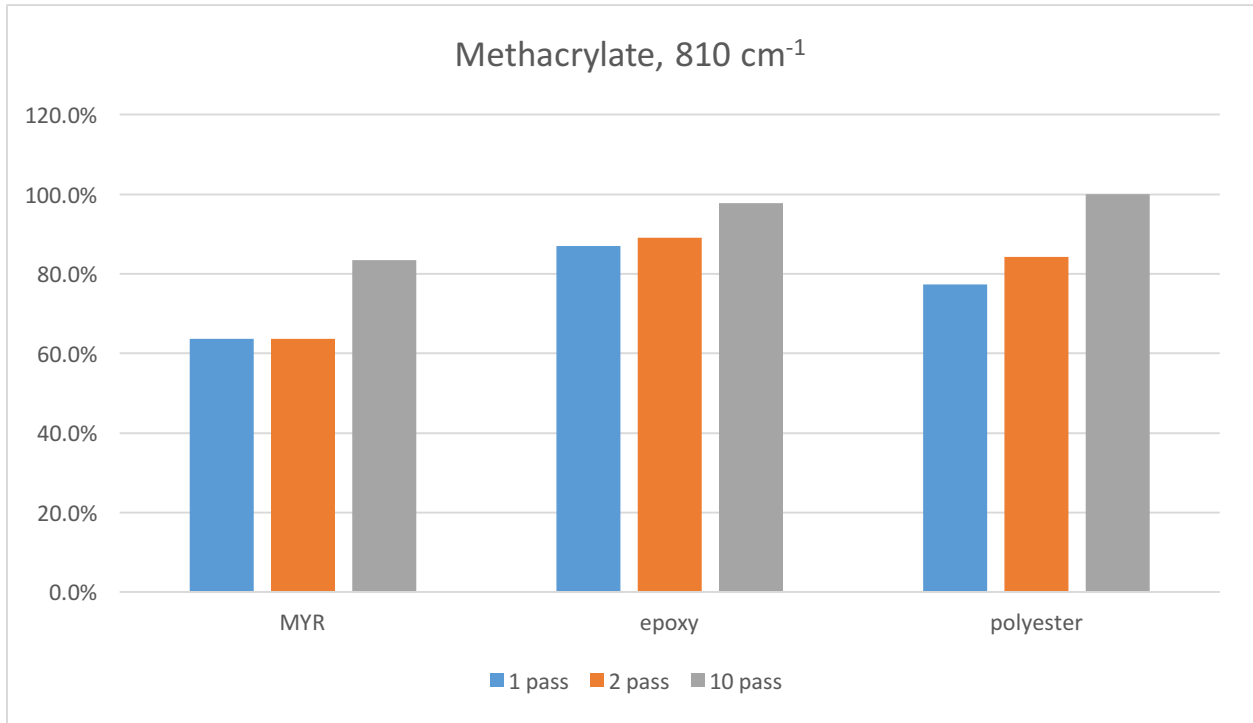


Figure 13

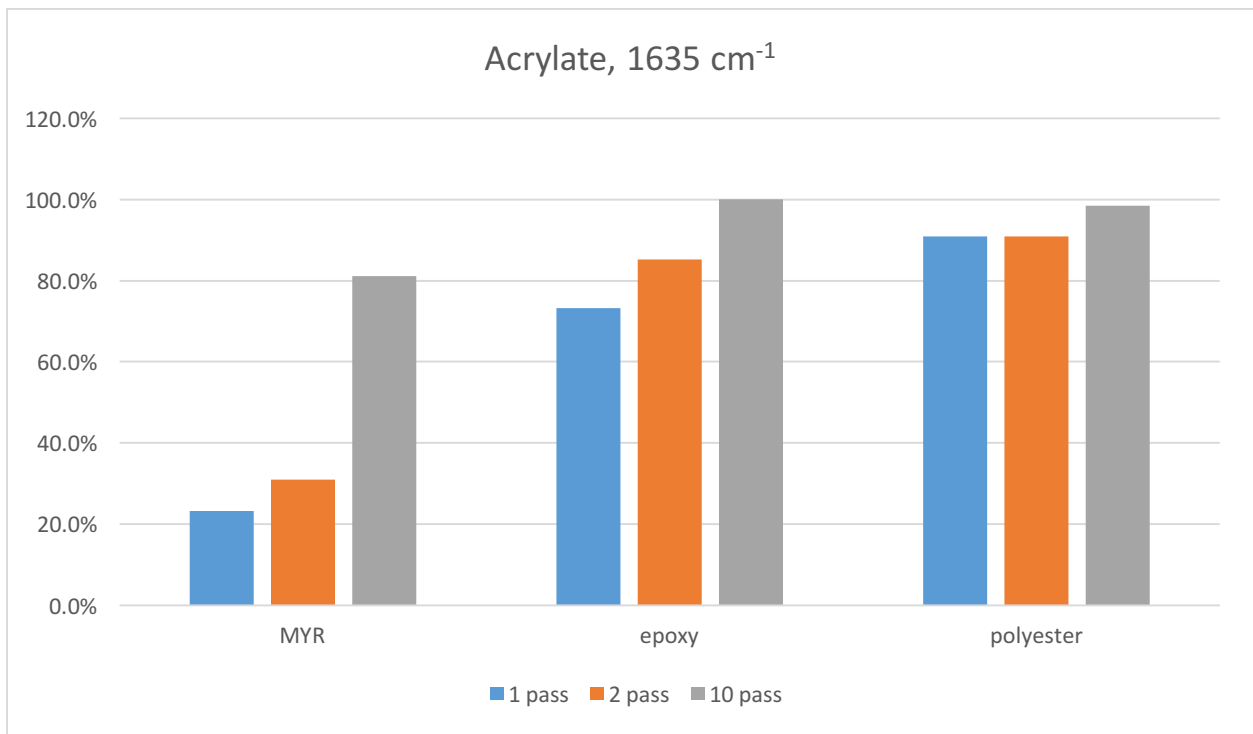
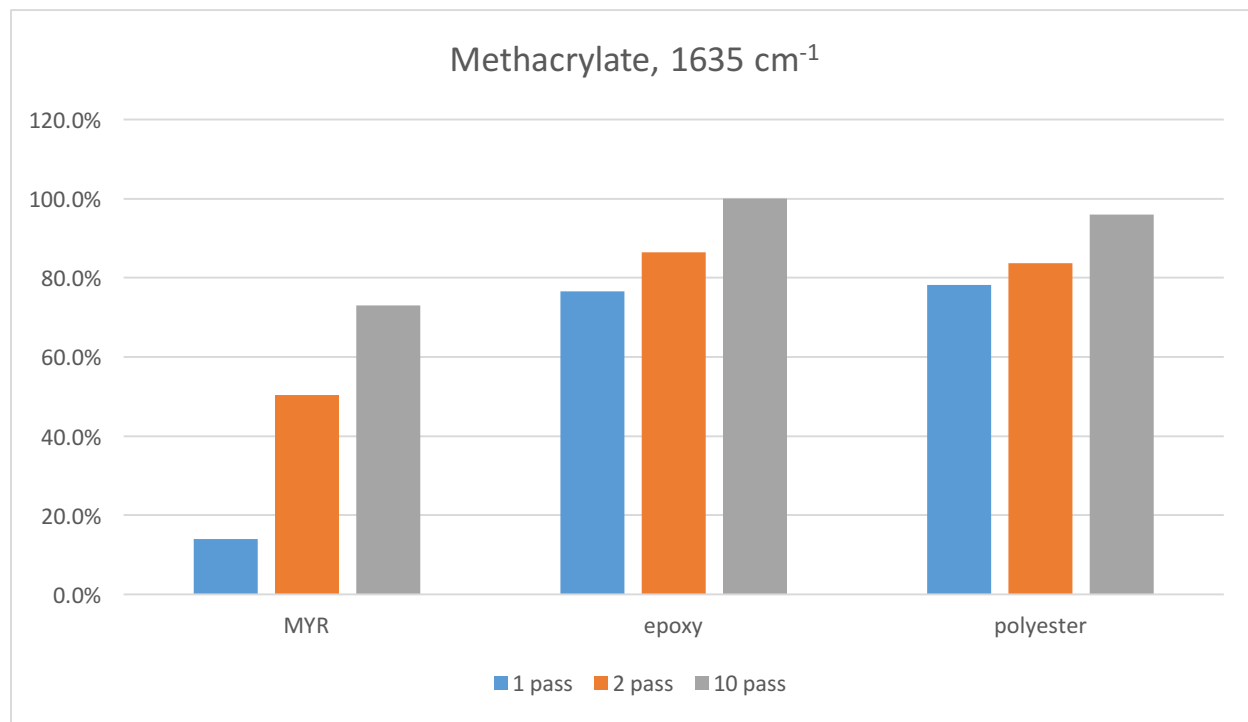


Figure 14



Data for 810 cm^{-1} is indicative of C-H out of plane bending of a vinyl group while 1635 cm^{-1} indicates a carbon-carbon double bond stretching vibration. Both peaks are common for evaluation of free radical crosslinking. It must be noted, however, that the inclusion of three different types of carbon-carbon double bonds in the test oligomer may have an unknown (to this point) effect on the IR spectra. Nonetheless, the data re-emphasized what can be seen through simple observation: the test oligomers cure slowly when compared to traditional acrylate or methacrylate systems. Further study, however, leads us to believe that the alternate curing pattern may actually bring some benefit to a coating that will more than compensate for a slower cure rate.

Ancillary benefits



First and foremost, it appears that the experimental oligomer crosslinks more effectively with methacrylate than with acrylate species. Acrylates tend to homo-polymerize around the oligomer, creating an interpenetrating polymer network (IPN)-type effect as seen in the hazy appearance of a casting (Figure 15). A methacrylate species, conversely, will crosslink into the polymer forming a more homogenous casting. While this is neither a benefit nor a penalty, it is worth noting when formulating.

Figure 15: Acrylate (right) versus Methacrylate (left and center)



In addition, these systems will cure via thermal energy, especially with the aid of a peroxide. In the following test matrix, the experimental oligomers cured after ten hours in a 70°C oven (in the dark) in both acrylate and methacrylate monomer. The traditional systems did not.

Figure 16: Thermal Curing

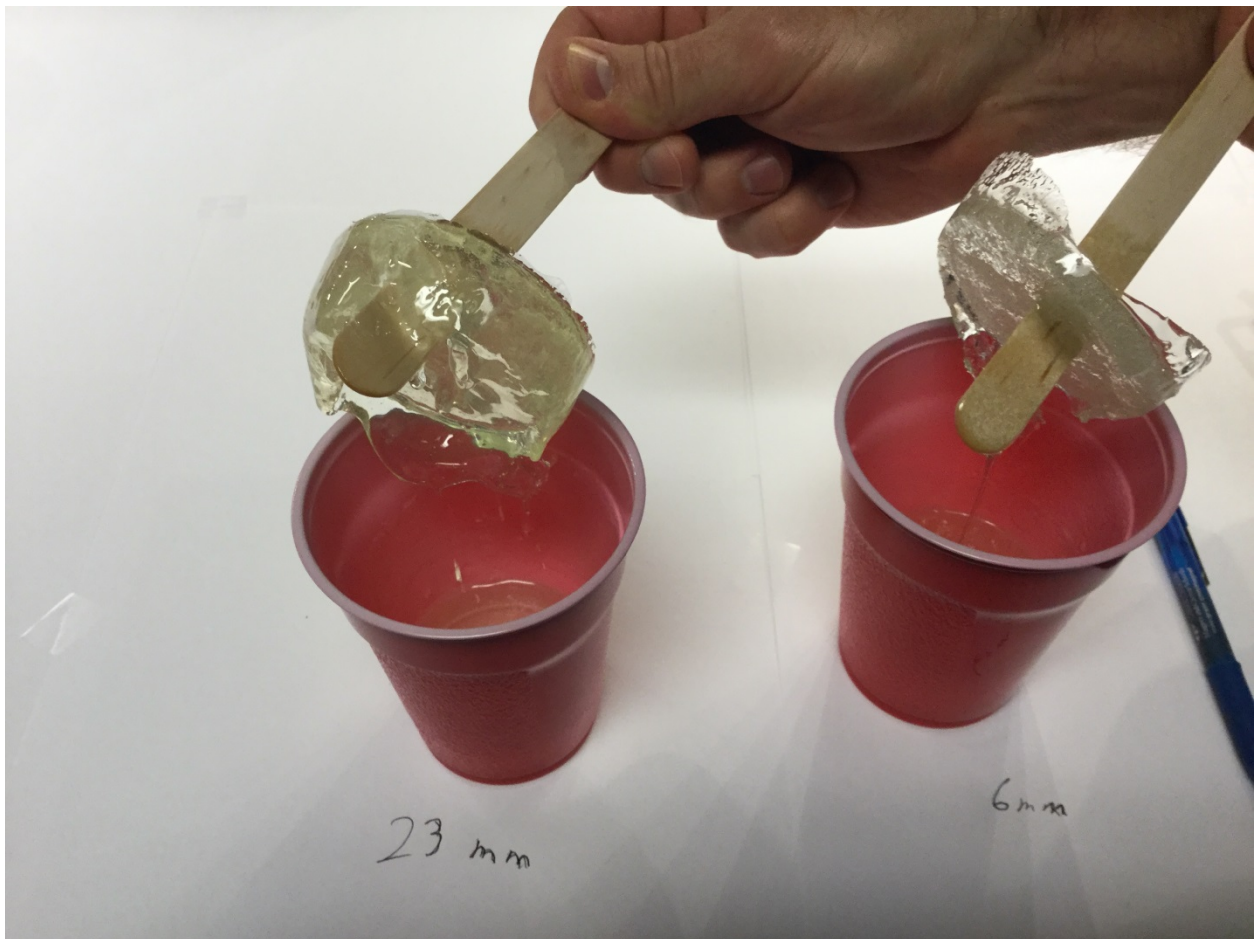
		Oligomer	IBOA	TEGDMA	polyether/ester tetra acrylate	PI	TBPB*	Heat curing 70°C, 10 hours, dark
1	Myribond® 	60		35		5	2	solid (100% cure)
2	Myribond® 	35	38		22	5	2	solid (100% cure)
3	Polyester Acrylate	60		35		5	2	liquid (0% cure)
4	Aliphatic Urethane Acrylate	35	38		22	5	2	stringy liquid

* = phr

One might initially view the addition of a peroxide to a system as a shelf-stability issue, several stability tests have been started. Even though final results are pending, shelf stability appears to be a balancing act that can indeed be resolved.

While the adhesion promoting oligomers do slow down cure, they can in effect continue to cure after the UV irradiation is eliminated via oxidative and/or thermal mechanisms. This effect can be improved through the addition of small amounts of peroxide and/or metal drier salts. Furthermore, the curing has a tendency to carry through to portions of the matrix that are not subject to direct UV light. This can be seen in Figure 17, below. Initially, a sample of Myribond® was diluted to 80% in TRPGDMA. To that, 3 phr of liquid photoinitiator blend was added, as well as 2 phr of TBPB. For a control, the same curing package was added to an epoxy acrylate in TRPGDA. Each blend was weighed to 100 grams in a cup. This cup was set in the sun for exactly ten minutes, after which the cups were brought back inside. The tongue depressors were pulled out, and the thickness of cured matrix was measured. As seen in Figure 17, the Myribond® blend (on the left) measured to 23 mm thick, while the epoxy acrylate control measured 6 mm thick.

Figure 17: Depth cure measurement



Summary

Even though the exact mechanism at present remains undefined, these oligomers enhance adhesion to low energy substrates. High energy substrates also show an improved performance over incumbent material, especially when the experimental oligomer is acid functional. Further adhesion to high energy substrates is gained via inclusion of methacrylate monomers and/or methacrylated phosphate ester adhesion promoters. Conversely, acrylate monomers appear to be the choice for low energy substrates

In addition, the new oligomers bring ancillary benefits including a thermal/oxidative curing response and depth curing, especially when combined with a metal drier and/or a peroxide.

While the ideal application for this technology remains ambiguous, we leave it to the audience of trained professionals to determine applications that best suit the oligomer's benefits. Wood coatings, polycarbonate substrates and other possibilities are immediate arenas where further investigation should merit positive results. There are many more. In addition, Myriant again defers optimal formulation recommendations to our audience.

In essence, the new oligomers:

- adhere to a variety of substrates
- contribute to tough, flexible coatings with cycloaliphatic character
- exhibit an alternate curing mechanisms that reveal a post/depth cure character
- contain substantial bio-renewable content with no price premium