

Bio-Renewable Oligomers

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Abstract

UV/EB curing technology currently enjoys a “green” or “eco-friendly” label based on 100% reactive, solvent-free formulations and low curing energy. Greater utilization of bio-renewable materials will only help to bolster that image.

The objective of this paper will be to demonstrate the efficacy of novel oligomers based on Myriant® Bio Succinic Acid as well as other bio-renewable building blocks. These oligomers can be used to create thermosets on par with incumbent petroleum-based technologies at a competitive price. The materials discussed have neither a “green premium”, nor a performance penalty.

Introduction

The details of this paper will attempt to illustrate theoretical benefits of using bio-succinic acid as a monomer in UV curable resin formulae. In addition to suggesting the theoretical, it will also demonstrate actual performance benefits through evaluation of both polyester acrylate and urethane acrylate oligomers made from bio-succinic acid. These bio-based oligomers will be compared versus industry standard, petroleum based products. The paper will then present data of evaluations of the polyester polyols themselves in urethane systems for deduction into UV systems. Finally, the paper will combine the bio-renewable polyester acrylate oligomers with bio-renewable adhesion promoting resins (Myribond®) and evaluate these coating compositions. All data will be used to support the theoretical benefits of succinic acid, dispel some common misconceptions of bio-based products as well as introduce benefits perhaps unknown to this point.

It must be noted that the acrylate oligomers used in the body of this paper offer little in the realm of intellectual property; there are no patents present. While the exact details of the compositions are withheld, they are available if need be. It is simply our desire to call attention to the use of bio based monomers such as succinic acid in the world of UV cure.

This presumption is not to be confused with bio based adhesion promoting resins (Myribond®); which, while incorporated into this paper, are discussed in more detail in an alternate paper. The aforementioned Myribond® is only available for purchase through a licensed manufacturing facility. Its composition is considered to be a patent protected secret.

For the purpose of this paper, a traditional polyester acrylate oligomer is synthesized by the condensation reaction of diacids and diols resulting in a polyol of known molecular weight

and functionality. These polyols are then reacted with acrylic acid in the presence of a strong mineral acid such as para-toluene sulfonic acid until conversion is as complete as possible. Finally, the mineral acid is then neutralized with a base and the entire polymer is washed, dried and filtered. The authors, as well as the readers, should understand that there are many alternate ways of attaining polyester acrylate oligomers including trans-esterification and epoxy neutralization.

In addition, for the purpose of this paper, a traditional urethane acrylate oligomer is synthesized by the condensation reaction of diacids and diols resulting in a polyol of known molecular weight and functionality. These polyols are then reacted with isophorone di-isocyanate (IPDI) and hydroxy ethyl acrylate (HEA) to form the urethane acrylate. The authors, as well as the readers should understand that there are many other ways of attaining urethane acrylate oligomers including alternate isocyanates and alternate hydroxyl functional acrylate monomers. In addition, the polyols themselves can be made into unsaturated polyesters and many other resins. Myriant is not suggesting the techniques presented herein are optimal or exhaustive; only representative.

The paper will also demonstrate some properties of polyesters polyols based on succinic acid as is, as opposed to incorporated into a UV curable acrylate oligomer. The purpose of this endeavor is to present some data in an unadulterated form; this ensures that results, either positive or negative, are not a result of synthetic techniques or formulation. The results are inherent in the polyols themselves. The reader can then decide the best way to incorporate these polyols into a UV curable system.

For coatings in general (UV cure or otherwise), the use of succinic acid typically improves resin flexibility without a significant loss of Tg, improve scratch resistance, and yield better gloss retention. Extrapolating this into a polyester acrylate oligomer for UV cure, one might also expect marginally better adhesion.

Without question, bio-based succinic acid will bring stable pricing. Despite unusually low oil prices which translate into low petrochemical costs for monomers such as adipic acid, few disagree that this pricing will not fluctuate in the future. One cannot deny the pricing instability in the past.

Finally, with the advent of new technologies in bio-based synthesis, the presumption of poor color will be dispelled. One can expect identical color in polyesters synthesized from bio based succinic acid when compared to petroleum based diacids.

Comparison versus industry standards

In order to evaluate bio-based oligomers versus petroleum based materials, a standard workhorse polyester acrylate oligomer, urethane acrylate oligomer and a bisphenol A-type epoxy acrylate oligomer was obtained from commercial sources. The experimental oligomers were synthesized by first creating a polyester polyol based on bio succinic acid, Susterra® propanediol, isosorbide, and smaller amounts of petroleum based diacids and glycols. The polyols were reacted to a nominal hydroxyl number in the lower 200 range; this number was not

entirely arbitrary. One would expect the PMN for such an oligomer to face less molecular weight scrutiny; in addition, it is classified as a theoretical polymer by REACH definitions. Several variants of mole ratios and functionality were synthesized; ultimately the three best were selected for further evaluation. The polyols were then either reacted with acrylic acid to form the polyester acrylates or with IPDI and HEA to form the urethane acrylates. They are coded as Bio Acrylate #1, Bio Acrylate #2 and Bio Urethane Acrylate.

Initial visual inspection revealed an unexpected surprise: not only were the colors of the bio-renewable materials no worse than the incumbents, some were, in fact, marginally better. This is demonstrated in Figures 1 & 2.

Figure 1: Bio based urethane acrylate

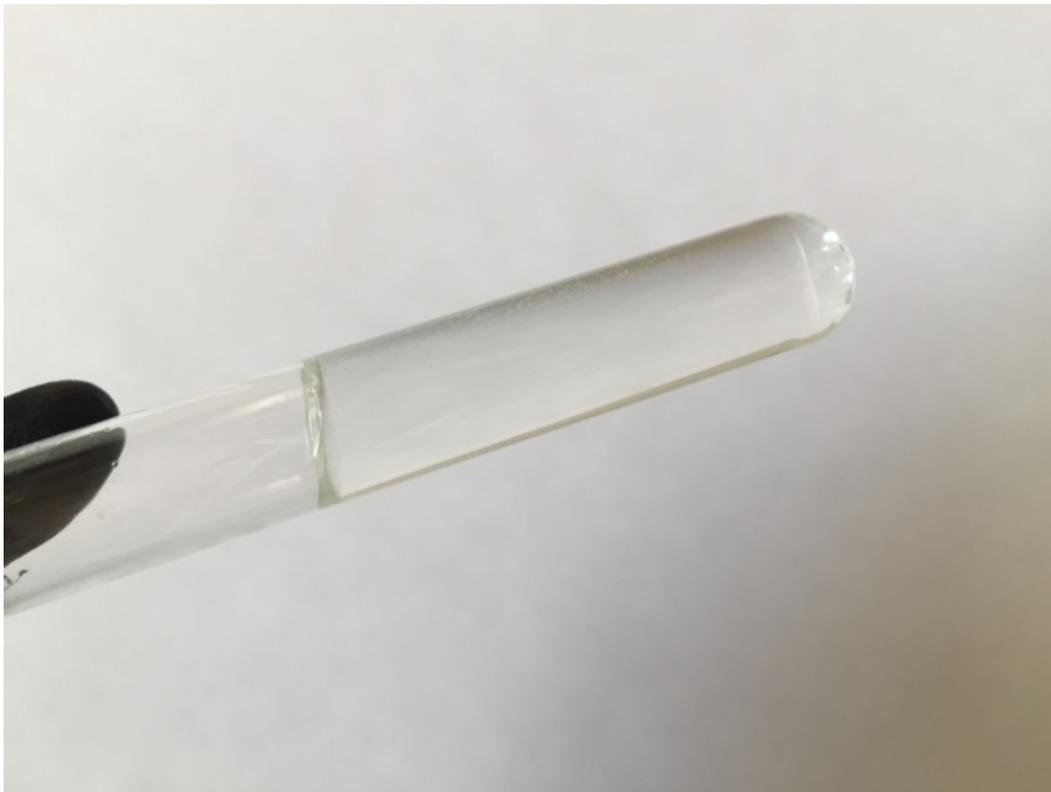
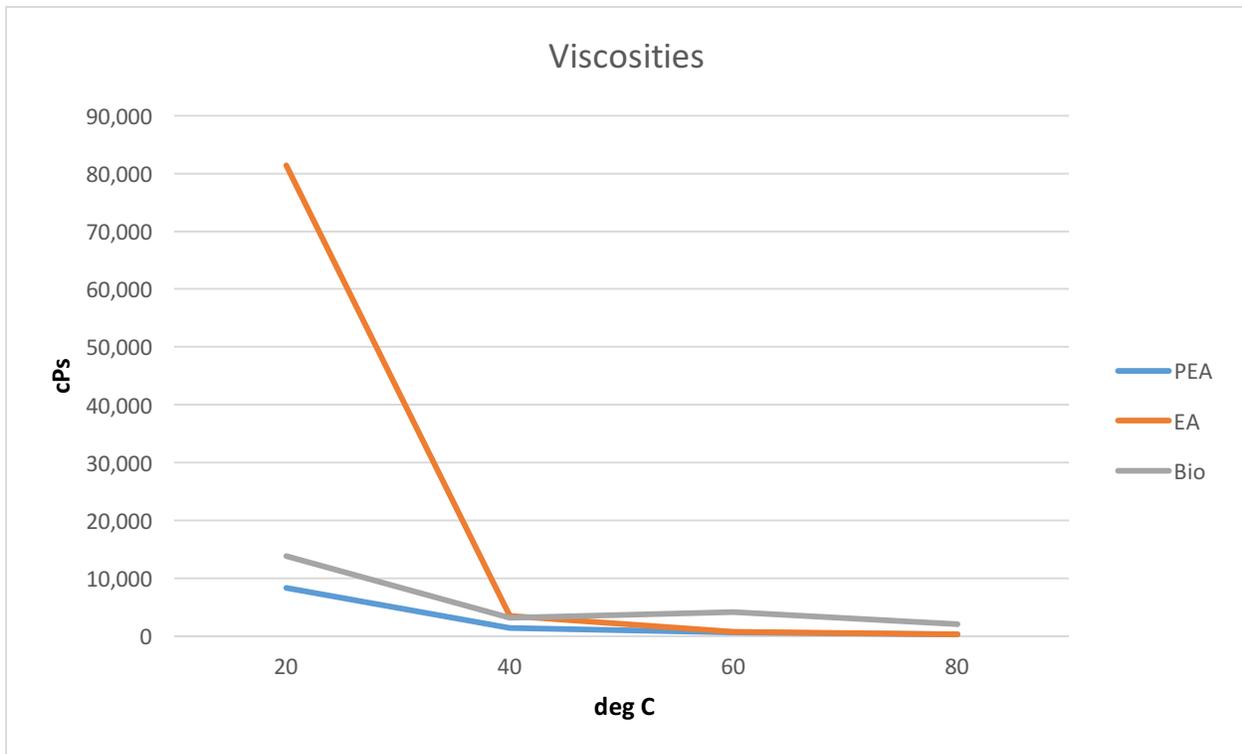


Figure 2: Bio-renewable polyester acrylate (left) versus petroleum polyester acrylate (right)



Next, the viscosities of the neat polyester acrylate oligomers were evaluated. For this data, no GPC analysis was performed to ensure similar molecular weights were representative. Rather, the assumption of polymeric materials was enough; as long as the viscosities for a workable oligomer were in line, the succinic acid was not indicted as a problem. It was not. A typical viscosity curve can be seen in Figure 3; Bio represents the experimental polyester acrylate oligomer (Bio Acrylate #1), PEA is the commercially available polyester acrylate and EA is the epoxy acrylate.

Figure 3: Viscosity curve of bio-renewable polyester acrylate oligomer and petroleum offsets



At this point, there appears to be no penalty for using bio-renewable monomers in the liquid resins. The next logical step is to evaluate a cured coating composition.

All cured property data was obtained under practiced supervision two independent, professional UV labs; one located in Greensboro, North Carolina and another in Chicago, Illinois.

The first test was a basic one; used as a screen to eliminate the poorer performing oligomers from those which held more promise. An oligomer (control and experimental) was blended with hexanediol di-acrylate (HDDA) and a liquid photoinitiator according to Figure 4. The coatings were then drawn down using a doctor blade and cured via two passes at 100 ft./min. The observed similar films exhibited no discernible defects. All substrates (experimental and control) withstood 100 MEK double rubs and none of them adhered to aluminum.

Figure 4: Initial blends

Test Oligomer	Oligomer	HDDA	PI	MEK rub	Adhesion to aluminum
Bio-Acrylate #1	80%	15%	5%	100+	failed
Polyester Acrylate (petroleum)	80%	15%	5%	100+	failed

At this point, a more detailed matrix was designed to evaluate the successful bio renewable oligomers. Details are presented in Figure 5.

Figure 5: Blend Constituents

		blend constituents			
		Oligomer	IBOA	Aliphatic Urethane Acrylate	Photoinitiator Blend
1	Bio Acrylate #1 	40%	45%	10%	5%
2	Bio Acrylate #2 	40%	45%	10%	5%
3	Epoxy Acrylate	40%	45%	10%	5%
4	Polyester Acrylate	40%	45%	10%	5%
5	Bio Acrylate #1 	50%	35%	10%	5%
6	Bio Acrylate #2 	50%	35%	10%	5%
7	Epoxy Acrylate	50%	35%	10%	5%
8	Polyester Acrylate	50%	35%	10%	5%

Key

IBOA: Isobornyl Acrylate

Each sample was then drawn down on aluminum test panels with a 3 Meyer rod and cured with three passes at 100 ft/min and subjected to the following tests:

Figure 6: Cured panel results

		Tape Adhesion	MEK	Flexibility	
		Aluminum (crosshatch)	double rubs	90°	180°
1	Bio Acrylate #1 	0%, fail	35	P	P
2	Bio Acrylate #2 	97%, pass	20	P	P
3	Epoxy Acrylate	0%, fail	45	P	P
4	Polyester Acrylate	0%, fail	30	P	P
5	Bio Acrylate #1 	50%, fail	50	P	P
6	Bio Acrylate #2 	0%, fail	40	P	P
7	Epoxy Acrylate	0%, fail	50	F	n/a
8	Polyester Acrylate	0%, fail	50	F	n/a

Again, no monumental improvements were observed, but more importantly, no penalties were apparent. One could argue that slight improvements in adhesion and/or flexibility could be attributed to the bio-based oligomer. Conversely, this may also be a monomer or urethane acrylate effect. Nonetheless, the bio based materials show no signs of weakness.

At this point, it was theorized that raw physical data would perhaps be pertinent. To that end, test oligomers, as well as as an epoxy acrylate and a polyester acrylate control were blended to 80% with HDDA. To that, 1% TPO photoinitiator was added. The resin compositions were then inserted into a Tygon tube and cured under a UV lamp. Finally, the cast “rods” were retrieved by cutting away the tubing and then cross-sectioning the cured resin into smaller rods. These specimens underwent tensile analysis using an Instron. Initial tests run with 5% of the liquid photoinitiator blend revealed an over-cure; evidently the absence of oxygen in the tube created such an aggressive cure that the rods cracked. Results are in Figure 7.

Figure 7: Tensile strength data

sample	tensile	elong
	psi	%
Bio Urethane Acrylate 	> 5000*	n/a
Bio Polyester Acrylate 	3,772	4.40%
Epoxy Acrylate	10,120	4.40%
Polyester Acrylate	4,063	4.20%

As expected, the epoxy acrylate exhibits superior physical strength. More importantly, however, the bio based oligomer performance is commensurate with the petroleum based incumbent. It must be noted that for this test, the deformation of the urethane acrylate resulted in slippage in the grip, causing grip failure well before the break of the sample.

Another basic evaluation is cure speed. Because these oligomers are acrylate functional, it was not expected to observe any cure speed issues. Each oligomer was diluted to 80% in tripropylene glycol diacrylate (TRPGDA) and 5 phr liquid photoinitiator was added. The coatings were drawn down using a 3 Meyer rod onto aluminum panels and cured via one pass at a time at 100 ft/min. Further analysis details:

- Cure speed analysis performed on a Broker ALPHA-P spectrometer with a diamond ATR crystal
 - ☞ 2-minute sample scan time at 4 cm^{-1} resolution
 - ☞ 1-minute background scan between each sample
 - ☞ Sample plate cleaned with acetone between samples
 - ☞ One pass = 264 mJ/cm^2
- Peaks:
 - ☞ 810 cm^{-1} (C-H out of plane bending; typical acrylate)
 - ☞ 1635 cm^{-1} (C=C stretch)

As seen in Figures 8 and 9, cure speed is not an issue:

Figure 8: IR data, 1635 cm⁻¹

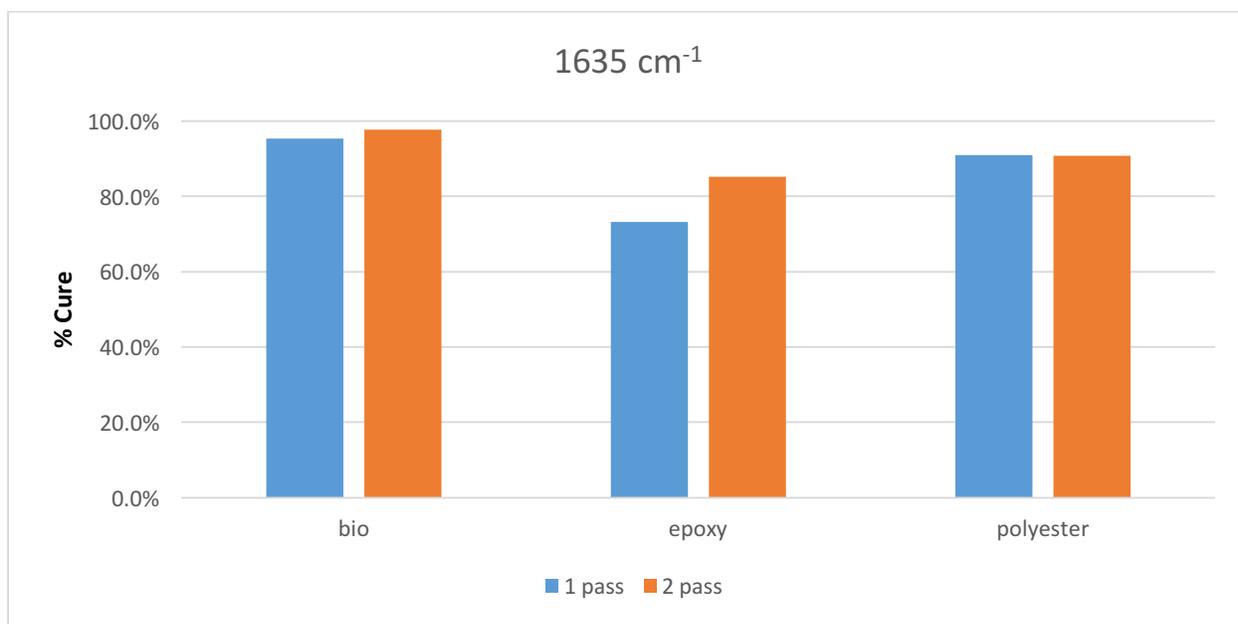
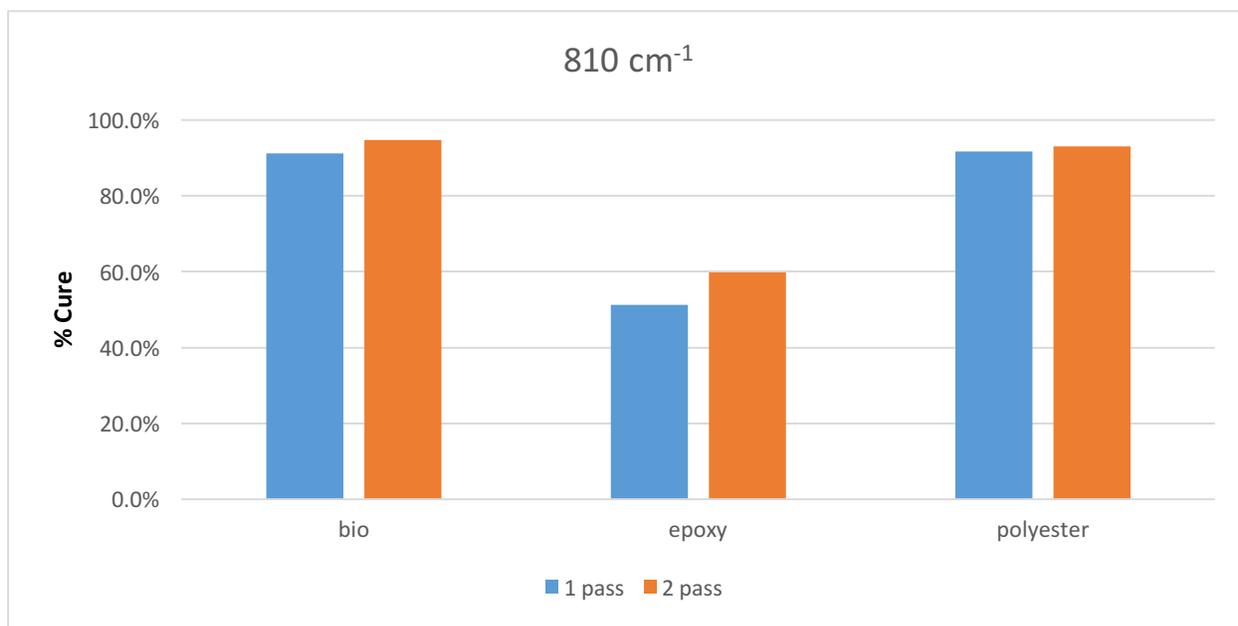


Figure 9: IR data, 810 cm⁻¹



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. The unexpected slower cure of the epoxy acrylate is presumed to be due to vitrification of the curing, acrylate-laden matrix.

At this point, basic data seems to indicate a bio-renewable polyester can be effectively implemented in an application where a traditional, petroleum based material is being used. One could possibly argue that the succinate-based acrylates offer better adhesion, but the evidence is not overwhelming. While the bio-renewable versions offer no penalties, to this point they also offer little in the way of advantages. Demonstration of a lack of defects is valuable; the main objective of this paper, however, is to find a value.

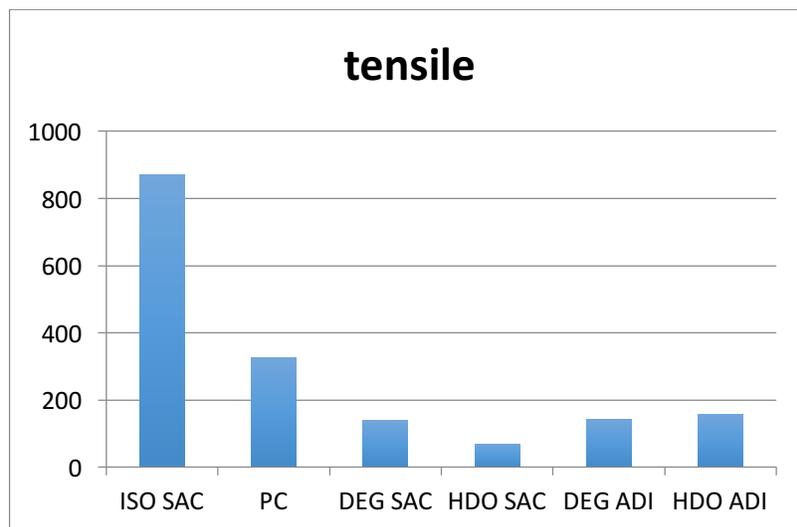
We continued with our work...

Evaluation of polyols in non-UV applications

At this point, data was gathered on the polyols alone. The previous work concentrated on a few basic polyester acrylate oligomers. Perhaps the oligomer synthesis was not optimal. Perhaps if the polyols were evaluated in an alternate system, one could observe the data and make a UV curable oligomer through other means. Perhaps companies with more experience in oligomer synthesis could take these polyols and transform into UV curable oligomers using techniques not yet investigated.

To that end, cast urethane samples were synthesized at a third independent, contract lab. These urethanes were made from Bayer's N 3200 (HDI trimer) at a 1.05 isocyanate index with each respective polyester polyol. Two adipate polyesters were included, as well as a polycarbonate for control purposes. Results for tensile strength (performed via ASTM standard protocols) are observed in Figure 10. These castings and tests were performed under a contractual basis at an independent testing laboratory.

Figure 10: Tensile strength, cast urethanes



Key:

ISO SAC: isosorbide succinate polyol
PC: polycarbonate polyol
DEG SAC: diethylene glycol succinate polyol
HDO SAC: 1,6 hexanediol succinate polyol
DEG ADI: diethylene glycol adipate polyol
HDO ADI: 1,6 hexanediol adipate polyol

All polyols had a nominal molecular weight of 500. Each was synthesized in the lab with the exception of the polycarbonate, which is commercially available.

The tensile strength for the isosorbide succinate (98% bio-renewable) is remarkable when compared versus a polycarbonate and standard polyesters. The best utilization in a UV cure oligomer is left to the audience.

Evaluate through a combination of bio renewable acrylate oligomers coupled with bio renewable adhesion promoting resins

Finally, it was decided to evaluate these oligomers when coupled with adhesion promoting resins also based on succinic acid. The bio-renewable adhesion promoting resins, labeled Myribond®, are evaluated exhaustively in another Myriant paper. Bringing the two bio-renewable technologies together would presumably bring some noteworthy results.

First, the tensile strength of a blend of the two was evaluated. In a fashion similar to Figure 7, above, a 50/50 blend of a bi-renewable acrylate and a bio-renewable adhesion promoting resin was further blended to 80% in HDDA and cured with 1% TPO in a Tygon tube. The new data point is added on in Figure 11:

Figure 11: Tensile strength, blended composition included

sample	tensile		elong
	psi	%	
Bio Acrylate 	3,772	4.4%	
Epoxy Acrylate	10,120	4.4%	
Polyester Acrylate	4,063	4.2%	
Bio Acrylate / Myribond® 	4,001	5.7%	

As one can see, the tensile strength, coupled with elongation (toughness) actually increased with a combination of renewable oligomers.

Further formulation and testing was performed as seen in Figure 12:

Figure 12: Testing of bio renewable acrylate/bio renewable adhesion promoting resins

		Oligomer	IBOA	polyether/ester tetraacrylate	PI	MEK double rubs	Impact 4 ft, 250g
1	Myribond® 	27.5	15	25	5	> 100	pass
	Bio Acrylate 	27.5					
2	Myribond® 	27.5	15	25	5	> 100	pass
	Polyester Acrylate	27.5					

A polyester acrylate control was also included. These coatings formulations bring together a nice combination of bio-renewability, adhesion, affordability, solvent resistance and impact resistance.

At this point, one could conclude that the bio-renewable products in effect offer more benefit than simple price stability. Succinate polyesters also impart adhesion, toughness, and solvent resistance.

Conclusion:

Based on the work performed, one can conclude that UV curable oligomers based on bio-based succinic acid exhibit:

- Comparable liquid color and viscosities
- Comparable cure speed
- Stable, competitive pricing
- Marginally better adhesion

A combination of bio based acrylate oligomers with Myribond® adhesion promoting resin reveals:

- Excellent adhesion
- Affordability
- Tough, resilient coatings
- Aliphatic backbone

While the exact incorporation of a bio-renewable polyol into a UV curable coating is left to the reader, one can rest assured the properties and price will not suffer