Performance Characteristics of UV/EB Curable Oligomers Utilizing Tin-Alternative Catalysts

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For over 50 years, tin–based metal catalysts have been the primary workhorse for urethane systems. With increasing environmental and health concerns regarding tin–catalyzed systems, certain markets have implemented constraints on these legacy products. These constraints require the development of urethane systems with alternative catalysts to eliminate concerns that tin catalysts provide. Much research has been done on tin–alternative urethane catalysts regarding their reactivity, focusing primarily on 2K systems. In this study, we will investigate alternative catalysts to tin for replacement in urethane (meth)acrylate oligomer synthesis. The primary objective of this research is to quantify any variations in oligomer performance compared to the tin–catalyzed system in both liquid and cured states. Using this knowledge, we will attempt to mitigate any differences recognized in the tin–alternative catalyzed oligomers to develop a tin–free oligomer with near indistinguishable physical properties to its tin–catalyzed counterpart.

Introduction

In recent years, tin–based catalysts have raised concerns with various health and regulatory organizations for their potential negative impact on humans and the environment. Health organizations, such as ECHA (European Chemical Agency), have placed a ban on the use of organotin catalyzed urethanes in nail coatings,[1] while other agencies and industrial markets have suggested concentration restrictions of such chemistries. As the world focuses on safer and greener chemistries, the reduction of organotin catalysts and the development of oligomers that contain bio–sourced raw materials are highly desired. Introducing a tin–free oligomer that utilizes these bio–sourced materials creates interesting opportunities for the next generation of oligomers focused on human health and reducing environmental impact. From this study, tin–free, biobased oligomers are developed which present the environmental benefits that UV/EB chemistries already offer, with the added benefit of removing tin catalysts. Ultimately, this generates a solution that is environmentally conscious without sacrificing physical performance.

Unfortunately, it can be difficult to find an alternative catalyst to tin that can reproduce certain physical properties that organotin catalyzed polymers exhibit, and this can be particularly true within the context of polyurethanes. Generally speaking, the synthesis of polyurethanes involves the reaction between isocyanates and polyether or polyester polyols.[2]

Catalyst selection plays a large role in this reaction effecting the polymer structure, molecular weight, and the incidence and intensity of these side–chain reactions during synthesis, all of which impact physical properties.[3] Much research has been done identifying tin–free catalysts that promote urethane reactions, primarily as it pertains to synthesizing isocyanate–terminated prepolymers or elastomers.[2,4] The purpose of this study is to expand on this prior work to evaluate these alternative catalysts in the synthesis of polyurethane acrylate oligomers and create tin–free, biobased oligomers.

Experimental

The screening process involved two separate steps: 1) the synthesizing of new oligomers with varying catalysts and 2) quantifying the physical properties of those new oligomers. The new oligomers were derived from the following materials:

- a 100% biobased polyether polyol,
- an aliphatic diisocyanate,
- a single catalyst,
- a methacrylate capping agent,
- and a free radical scavenger for stability

A widely used organotin catalyst was selected for use in the control oligomer. The alternative catalysts included a variety of metal complexes, metal salts, and organic catalysts. All catalysts evaluated for this study are commercially available, procured from other manufacturers, and used as received.

To yield the best possible comparative data, a controlled experiment was designed and executed. Oligomers were synthesized using identical synthetic parameters, including raw materials and their concentrations, order of addition, temperature of reaction, and mixing profile. The only intentionally manipulated variable throughout the study was the catalyst. The synthesized oligomers are designated throughout this paper by the catalyst that was used in synthesis.

In this study, there are two distinct steps in the oligomer synthesis: a pre–polymerization reaction step involving the reaction of the isocyanate and polyol, and an end–capping step involving the reaction of the isocyanate–terminated prepolymer with the methacrylate capping agent. The pre–polymerization reaction was monitored by FTIR at 15–minute intervals to determine completion. The pre–polymerization

step was completed when the absorbance of the isocyanate peak, about 2270 cm^{-1} on the IR spectrum, became constant. Prepolymer completion was further verified by the titration method described in ISO 14896. A sample of the prepolymer was obtained and titrated to determine the experimental percent isocyanate concentration, [%NCO] which was then compared to the calculated theoretical [%NCO], assuming the pre–polymerization reaction completed. If the [%NCO] from titration was within 2.0% of the theoretical [%NCO], next steps were performed in synthesis. The end–capping stage was complete when all isocyanate was reacted and there was no longer an observable absorbance peak at 2270 cm^{-1}.

Cured physical property data was collected for each synthesized oligomer. Given the relatively low viscosity of the control oligomer, the cured physical property formulations did not include a reactive diluent. Testing the properties of the neat material should yield more observable changes as the oligomer catalyst is varied. A model formulation was used to evaluate oligomer performance in the cured state, see Table 1.

Formulations were prepared identically and cured under the same conditions as described below. The oligomers cured and uncured properties were compared to the organotin catalyzed Control oligomer.

Table 1. Model formulation for physical property testing

Material	%
Oligomer	100.00
Photoinitiator	2.00

Testing

Formulations were mixed until all solid components were dissolved and the mixture was homogenous. Viscosities were measured using a Brookfield CAP 2000+ viscometer at 25°C with spindle 5 at a speed of 5RPM. For APHA color deter–mination, unformulated neat oligomer was transferred and sealed in borosilicate glass vial. The vial was then degassed in a sonicator to remove any air bubbles before color measure–ment. Color measurements were performed on a HunterLabs ColorQuest XE spectrophotometer in accordance with ASTM D1209–05 (2019).

Molecular weight determination of the oligomers was determined by gel permeation chromatography (GPC) in accordance with ASTM D5296–19. GPC analysis was done using a Shimadzu Gel permeation chromatography instrument with a refractive index detector. THF was used as the mobile phase at a flow rate of 1mL/min. Oven temperature was set to 40°C and separation occurred using an Agilent ResiPore 3µm HPLC column.

Cured test specimens of each formulation were prepared according to the relevant test methods identified below and cured with a broad spectrum Dymax 2000–EC flood curing unit for 2 minutes per side. The irradiance was measured at approximately 50 mW/cm^2. Specimens were allowed to rest for at least 16 hours at ambient temperature before testing.

Glass transition temperature (T$_g$) was assessed using dynamic mechanical analysis (DMA) methods per ASTM D648. Specimens were tested using a TA Instruments DMAQ800 with dual cantilever geometry and the data output analyzed using the TA Universal Analysis software. T$_g$ determination for this paper is described as the temperature correlating to maximum peak height of the tan delta curve.

Type IV "dogbone" specimens were cast and cured for tensile mechanical testing. Tensile properties of all specimens were obtained using an Instron tensile tester and related software according to ASTM D638. Specimens were extended at a strain rate of 25 mm/minute.

Durometer hardness testing was performed according to ASTM D2240. Approximately 4–grams of formulated oligomer was poured into a 2" ID circular aluminum dish. Contents of the dish were cured for two minutes under EC–2000 floodlamp, then removed from the dish. The hardness puck was inverted and cured for an additional two minutes. Durometer readings were done using an Asker CL–150 constant loader tester attached to a D–scale durometer.

Color of the cured coating was measured and recorded per ASTM D2244–11. Color measurements were made using a BYK Spectro–Guide with spherical geometry. A 10–mil wet drawdown was applied to a 3"x 4" x 1/8" glass slide and cured for two minutes by EC–2000 floodlamp. The specimens were exposed to UV light for two minutes on one side only. Results are given CIELAB color space units of L, a*, b*, Δb* and ΔE are calculated per ASTM D2244–11.

Initial Screening

Screening Matrix

As a starting point, a broad screening of eight tin–alternative catalysts was performed with the goal of selecting only a few for further optimization. The screening matrix below provides the criteria for choosing which catalysts were selected for optimization. Catalysts that completed a pre–polymerization reaction in under 120 min were considered a "Pass". Catalysts that completed the end–capping stage in 24 hours or less were also considered a "Pass".

Table 2. Initial screening matrix (all catalysts)

Oligomer	Pre-polymerization Stage	End-Capping Stage	Viscosity (cP)
Control	Pass	Pass	73,000
Catalyst 1	Pass	Pass	115,000
Catalyst 2	Pass	Pass	100,000
Catalyst 3	Pass	Fail	78,000
Catalyst 4	Fail	Fail	55,000
Catalyst 5	Pass	Fail	71,000
Catalyst 6	Fail	Fail	105,000
Catalyst 7	Fail	Fail	113,000
Catalyst 8	Pass	Pass	94,000

Discussion of Initial Screening

While catalyst activity is generally relevant to oligomer synthesis, this study focuses primarily on the ability to replicate the physical properties of an oligomer produced with an organotin catalyst. However, the ability to synthesize a product in a reasonable amount of time is significant and

should not be overlooked. Of all the catalysts screened, three of them, Catalyst 4, 6, and 7, failed to complete the pre–polymerization stage and therefore have been excluded for further discussion. Of the five remaining, alternative catalysts, three of them, Catalyst 1, 2, and 8, were able to successfully complete both reaction steps, however they exhibited viscosities and molecular weights much greater than that of the control oligomer.

Both viscosity and molecular weight prove important factors in the structure–property relationship of polyurethanes.[5] These two properties are typically related to each other and further examination of them can provide more insight into how a material will perform, mechanically, in its cured state. Figure 1 shows a plot of viscosity versus molecular weight for the five tin–alternative catalysts still under consideration along with the Control. Of these, only one of them, Catalyst 5, aligns closely to the Control oligomer. Catalyst 3 is also somewhat interesting because of its similar viscosity to the Control, but its molecular weight is higher than what would have been predicted given the viscosity. A closer investigation, then, is needed to determine Catalyst 3's viability.

Molecular Weight Distribution

Compared to the Control and Catalyst 5, the Catalyst 3 oligomer has observable differences in the molecular weight distribution analyzed using GPC. As seen in Figure 2, the molecular weight distribution of Catalyst 5 closely resembles the molecular weight distribution of the Control as we would expect given the viscosity versus molecular weight plot above. On the other hand, the oligomer portion of Catalyst 3 elutes off the column earlier than the Control and Catalyst 5, indicating a higher molecular weight oligomer. This would normally suggest that the oligomer synthesized with Catalyst 3 would have a higher relative viscosity in comparison to the Control and Catalyst 5, however that is not the case. The unexpected lower viscosity of Catalyst 3 can be explained by the other noticeable difference in molecular weight distribution, the increased di–adduct concentration. The di–adduct is the unintended

Figure 1. Relationship between molecular weight and viscosity of all catalysts
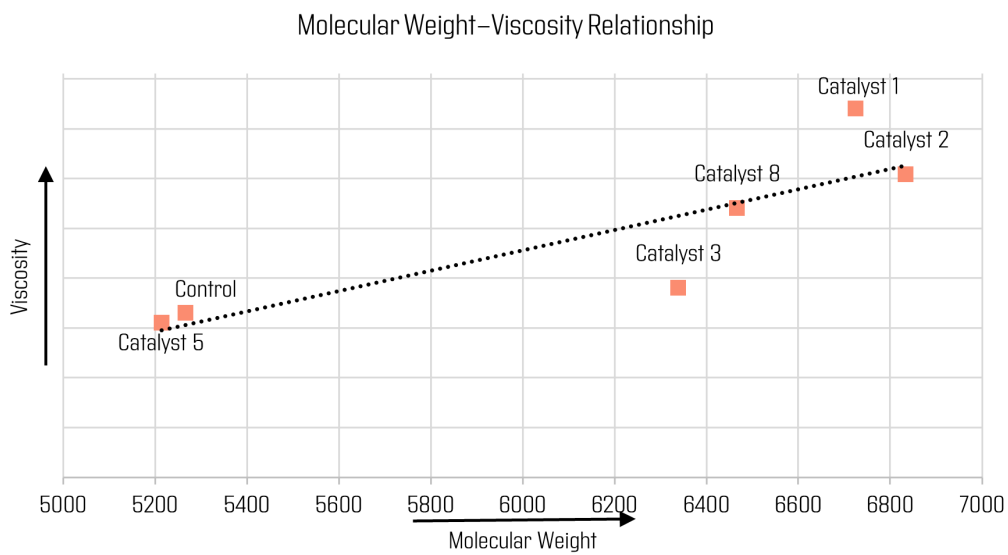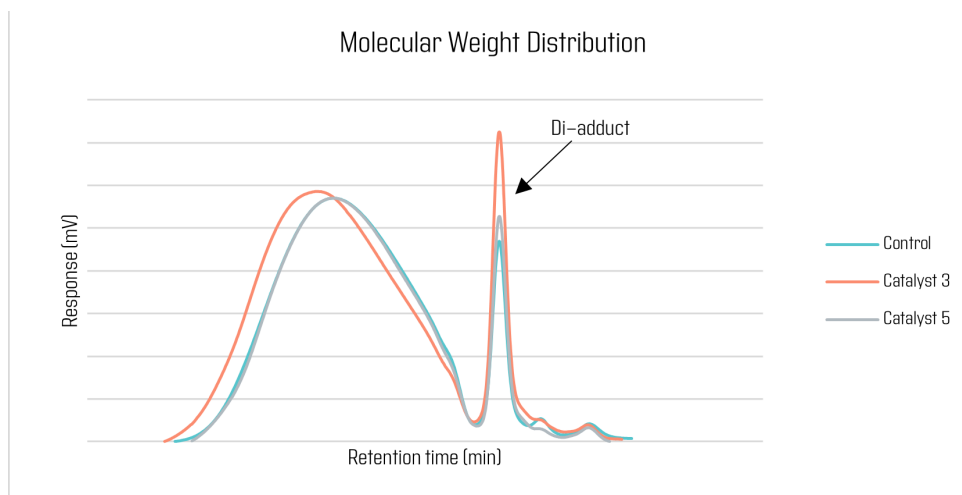
Molecular Weight–Viscosity Relationship

Figure 2. Molecular weight distribution of the Control, Catalyst 3, and Catalyst 5 oligomers.

Molecular Weight Distribution

methacrylate monomer formed during synthesis that impacts the physical properties by acting as something akin to a reactive diluent masking the effect of the higher molecular weight species. Higher levels of this di–adduct would also be expected to increase the crosslink density of the cured material, directly relating to increased T_g and tensile strength.[5]

Initial Cured Physical Property Screening

The cured physical properties of the Control, Catalyst 3 and Catalyst 5 oligomers were assessed using the parameters described in the experimental section and are displayed below.

Table 3. Physical properties of selected catalysts as they compare to the Control

Oligomer	Color (APHA)	Tg (°C)	Tensile (psi)	Elongation (%)	Modulus (psi)
Control	26	65	1,100	39	12,580
Catalyst 3	16	67	1,100	42	13,550
Catalyst 5	32	62	950	38	11,250

Based on the physical properties in table 3, Catalyst 3 nor Catalyst 5 stands out as a superior candidate for oligomer optimization. Each catalyst appears to have its advantages and disadvantages in comparison to the control oligomer. Catalyst 3 exhibits a lower color, but a higher T_g and modulus as expected from the higher di–adduct concentration. Catalyst 5 presents similar tensile properties, however, is slightly higher in color and lower in T_g. Given that Catalyst 5 matches the molecular weight and viscosity profile of the control more closely as well as matching most of the cured properties, Catalyst 5 was selected for further optimization.

Optimization

The prime candidate for optimization, based on molecular weight distribution and physical properties, is Catalyst 5. The drawback of the alternative catalyst used in this oligomer was that the end–capping reaction did not complete in the allotted timeframe.

From Table 2, Catalyst 5 passed the pre–polymerization stage but failed to complete the end–capping stage in the allotted 24–hr period. The IR spectra indicate a small amount of unreacted isocyanate around 2270 cm^{-1} at 24 hours. Given that the absorbance value of the isocyanate peak is very low, additional catalyst can be used to drive the reaction to completion.

Synthesis of the Catalyst 5 oligomer was repeated as before with the addition of a secondary catalyst to ensure 24–hr reaction completion. The concentration of secondary catalyst was added at half the amount of the initial catalyst charge for each optimization batch. Synthetic parameters were held constant with the only adjustment being the addition of a secondary catalyst. Given the data provided from the screening process, Catalyst 5 should set a prepolymer molecular weight comparable to the Control within 1 hour of catalyst addition. Based on structure–property relationships described previously, if the molecular weight of Control and Catalyst 5 oligomers are similar, the physical properties should also be comparable. The secondary catalyst charge occurs after all other raw materials are added to the reaction vessel and therefore should not disrupt the pre–polymerization reaction in any way. The only purpose of the secondary catalyst is to complete the end–capping reaction, extinguishing the residual isocyanate observed in Figure 3 within a maximum of 24 hours.

Optimization Screening of Secondary Catalysts

From the initial screening, Catalyst 1, 2, and 8 oligomers appear to be good candidates for secondary catalysts as they all led to the timely completion of the end–capping stage. That observation was true here as well when these catalysts were added during the later stage reaction step as secondary catalysts. As shown in Table 4, in all three cases these catalysts successfully completed the isocyanate reaction well within the 24–hour period. Adding additional Catalyst 5 was also attempted to determine if higher concentration of that catalyst alone may complete the isocyanate reaction. The result of that synthesis showed that it was not an effective method for completing the reaction.

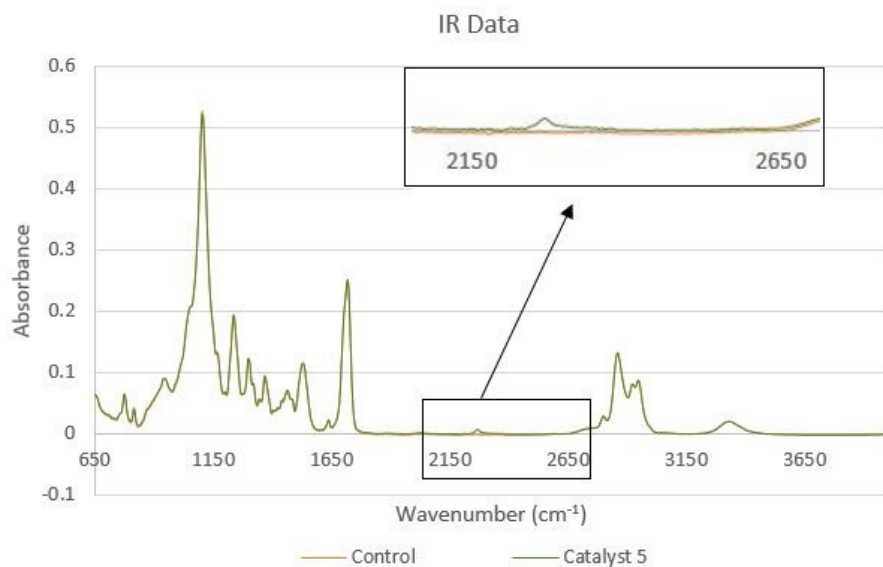**Figure 3.** IR spectra of Catalyst 5 compared to the Control

Table 4. Optimization screening of secondary catalysts

Optimization	Secondary Catalyst	Reaction Completion
Control	-	Yes
1	5	No
2	1	Yes
3	2	Yes
4	8	Yes

Reaction considered complete if no observable isocyanate peak on IR after 24 hours.

Initial Physical Property Comparison of Optimized Oligomers

The addition of the alternative catalyst used in the Catalyst 5 oligomer did not drive the Optimization 1 oligomer to completion, leaving three viable optimizations.

Table 5. Physical properties of optimized oligomers as they compare to the Control

Optimization	Viscocity at 25°C	Tg (°C)	Color (APHA)	Tensile (psi)	Elongation (%)	Modulus (psi)	Durometer hardness
Control	73,000	65	26	1,100	39	12,580	42
2	73,000	65	40	1,200	41	13,900	42
3	72,000	64	49	1,100	36	12,500	42
4	78,000	65	32	1,300	46	14,900	41

Percent difference can be utilized to determine which optimized oligomer most closely matches the Control based on physical properties. From the percent difference analysis of each property, Optimization 2, and Optimization 4 exhibit properties closest to that of the Control. Initial liquid color of each optimized oligomer shows high deviation from the Control when compared to other properties. Optimization 4 displayed the greatest overall deviation from the Control oligomer and was therefore excluded from further analysis.

Table 6. Percent difference of physical properties between Optimization 2, 3, and 4 oligomers as compared to the Control

| Optimization	Viscocity	Tg	Color	Tensile	Elongation	Modulus	Durometer hardness
2	0%	0%	42%	9%	5%	10%	0%
3	1%	2%	61%	0%	8%	1%	0%
4	7%	0%	21%	17%	16%	17%	2%

The significant difference in liquid color between Optimization 2 and 3 with the Control oligomer does not necessarily dictate the color of the oligomer in its cured state. Cured color can give more insight into how the optimized oligomers behave in color sensitive applications. The cured color data in Table 7 concludes that there is no significant difference between Optimization 2, Optimization 3, and the Control, opposing what was initially observed in the liquid state. In fact, the Δb^* value for the optimizations when compared to the control oligomer showed less yellowing in the cured state than the control. The overall color difference of the cure coating (ΔE) is less than 1 which, according to ASTM D2244–11, is considered undetectable by the human eye. Therefore, the initial cured color of Optimization 2 and 3 oligomers are essentially identical to the cured Control oligomer.

Table 7. Cured color readings for the Control, Optimization 2, and Optimization 3

Oligomer	L	a*	b*	Δb^*	ΔE
Control	91.1	-2.4	3.6	-	-
Optimization 2	91.0	-2.3	3.6	-0.02	0.11
Optimization 3	91.2	-2.4	3.6	-0.04	0.06

The radar chart of Figure 4 provides a visual overview of the similarities and differences in the physical properties of Optimization 2, Optimization 3, and the Control oligomer.

Figure 4. Radar chart comparing physical properties of Optimization 2, Optimization 3, and the Control
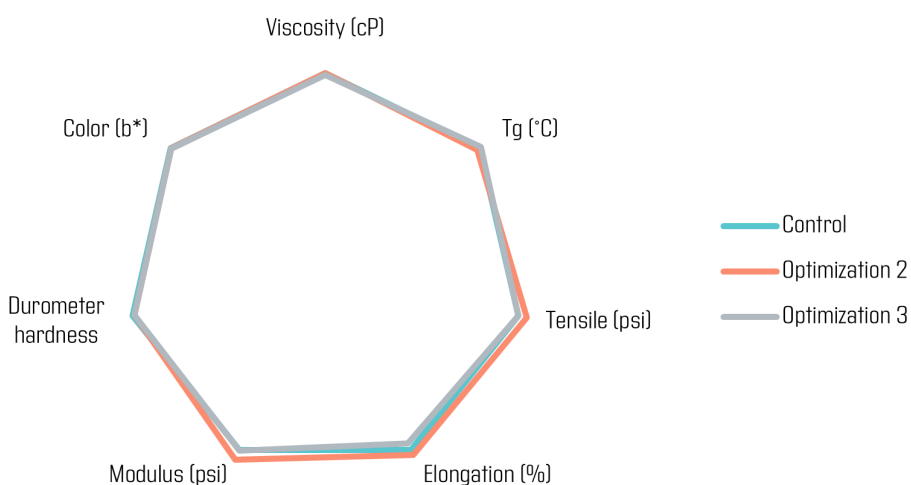
Stability

Gelation Testing

Optimization 2 and Optimization 3 oligomers succeeded in closely matching the physical properties of the organotin-based Control oligomer. To determine how both optimizations compared to the Control, in terms of thermal stability, the oligomers were exposed to extreme thermal testing for a short period of time. Approximately 21 grams of each synthesized oligomer was sealed in a borosilicate glass vial and placed in an oven at 90°C for four days. At 24-hour intervals, each oligomer was analyzed for signs of gelation by inverting the glass vial. If the oligomer inside the vial was no longer flowing, the material was considered to be "gelled". All tested oligomers passed the 4-day 90°C stability test indicating that there is no significant difference in the extreme temperature stability with the optimized catalyst packages.

Color & Viscosity Stability of Liquid Oligomer

To gauge shelf-life stability and gain insight into system performance of the optimized tin-free oligomers over time, accelerated aging was executed. In this test, oligomers were distributed into borosilicate vials and placed into a 70°C oven for four weeks. On a weekly basis, color and viscosity measurements were collected.

Over the course of four weeks, significant color growth was observed across all oligomers, as seen in Figure 5. The Control oligomer exhibited the highest color growth from its starting point (Initial) to Week 1, and continued to grow in color at a slower rate thereafter. Optimization 2 and Optimization 3 oligomers also experience similar color growth as the control over the four-week period. After the 1st week, Optimization 2 displayed a lower APHA color than the control and that trend was consistent until week 4. At week 4 the Control Oligomer and Optimization 2 were within 10 APHA of each other, mitigating the initial higher color of Optimization 2. Viscosity remained stable across all oligomers, with minor variations over the course of four weeks, as seen in Figure 6.
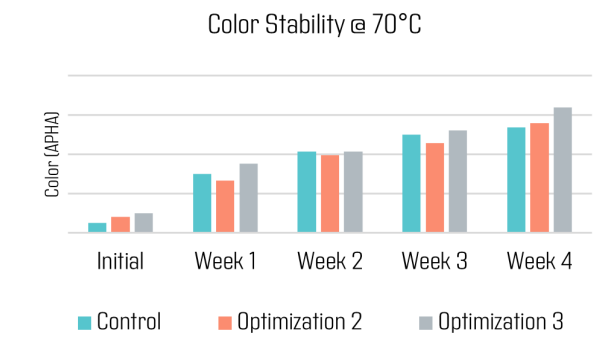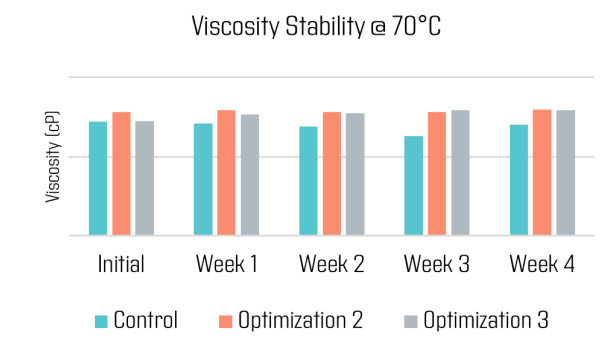
Figure 5. Color stability at 70°C

Color Stability @ 70°C

Figure 6. Viscosity stability at 70°C

Viscosity Stability @ 70°C

Stability of Cured Coating

Color growth at elevated temperatures was also evaluated in the cured state. The same glass slides used in the initial cured color study were placed in a 70°C oven for four weeks. Color was examined on weekly basis to observe color change. The cured coating was too soft to mechanically remove the tacky layer; therefore a cover was placed over the panels to prevent dust and debris from settling on the panels during heat aging. Since the liquid aging material showed considerable yellowing, the b* value of the cured coating was the focus of this experiment. Figure 7 is displaying the b* value of the heat aged panels over four weeks. There are some very minor fluctuations in the b* value of the cured coatings over the testing period. Optimization 2 showed the least amount of yellowing initially as well as over time. Overall, the color of the cured system appears to stable at 70°C for all the tested oligomers.

Figure 7. Color generation of the cured coating over time

Cure Coating Color @ 70C

Legend:
- Control
- Optimization 2
- Optimization 3
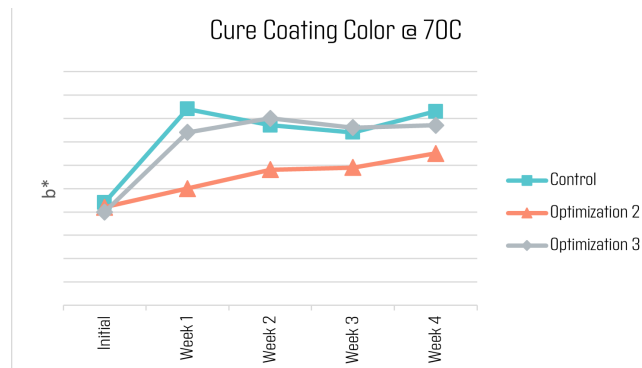
CONCLUSION

Through this work, tin-free biobased oligomers were developed to closely match the physical properties to an organotin-catalyzed control oligomer. Eight different catalysts were screened using a controlled experiment to determine what effects each alternative catalyst had on the oligomers cured and uncured properties. The Catalyst 5 oligomer was selected for further analysis based on its similarities to the Control oligomer in viscosity, molecular weight distribution, and T_g. Further optimization of Catalyst 5 was needed to complete the end-capping stage of synthesis in the allotted time frame which included the addition of a secondary tin-alternative catalyst.

Similar to the initial screening process, optimizations were also controlled to determine which secondary catalyst most resembled the properties of the Control while completing end-capping stages in a 24-hour period. Optimization 2 and Optimization 3 oligomers yielded cured and uncured characteristics nearly indistinguishable to the organotin Control oligomer without significantly effecting the stability of the system. Liquid color was the notable exception to the similarity with the optimized oligomers exhibiting roughly a 20 APHA increase as compared to the Control oligomer. However, further color analysis of the oligomers in the cured state indicated that cured color of the optimized oligomer was indistinguishable from the Control. This would tend to validate the assumption that the color change of 20 APHA in the liquid state would have minimal impact in actual application.

This work proves that it is possible to produce an organotin-free urethane methacrylate with almost indistinguishable cured and uncured properties to its organotin-catalyzed counterpart. Further research is needed to determine if these optimizations can be successfully leveraged with different raw material combinations and/or synthetic parameters to yield similar results.

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