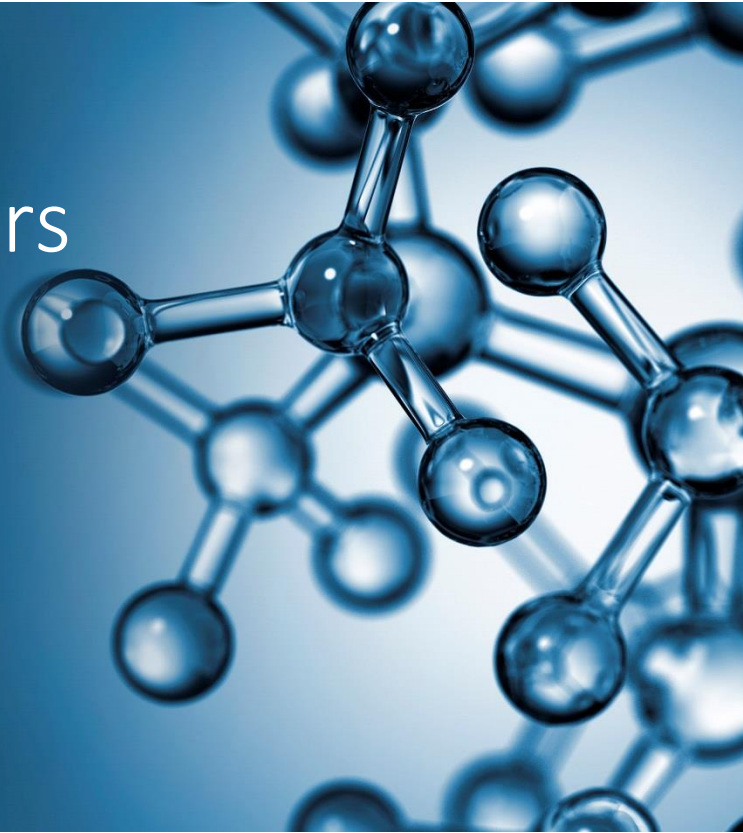


Dendritic Oligomers for LED-Curable Formulations



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The present work addresses a strong market demand for oligomers that can be used in LED-curable formulations. Dendritic acrylate oligomers, with their hyper-branched, highly functionalized structures, are known to impart excellent properties like increased cure speed, chemical resistance, and scratch resistance to traditional UV formulations. This presentation expands on this knowledge by discussing the properties of coatings formulated with these dendritic materials when cured with an LED light source. As expected, we have found that when cured with LED these oligomers offer very fast curing, possess excellent chemical and scratch resistance, and experience less oxygen inhibition. These oligomers would then be suitable for use in LED-curable pigmented ink applications.

Introduction

LED-curing systems offer several advantages over traditional UV systems. A longer usable life, a more efficient energy consumption profile, and a reduced environmental impact are just some of these benefits.¹ For these reasons, LED curing has seen significant growth in recent years and is being increasingly used in applications such as cosmetics and 3D printing.² Curing with LED does have drawbacks, however. Low cure speeds³ and oxygen inhibition⁴ are among the chief issues associated with LED curing, either of which can possibly lead to incomplete cure and inferior mechanical properties relative to traditional, broad-spectrum curing.³

In light of these problems, the present work will explore the use of dendritic acrylate oligomers in LED-curable formulations. Dendritic materials are known to impart very rapid cure speeds, exceptional chemical and scratch resistance, and high film hardness when cured with traditional methods. This is due to their hyper-branched, highly functionalized structures.⁵ Some dendritic materials have also been shown to reduce the effect of oxygen inhibition.⁵ With strengths such as these, it seems that dendritic acrylate oligomers would be good candidates for use in LED formulations. The goal of this work will be to evaluate this possibility and determine whether the enhanced properties of dendritic acrylate oligomers can be seen in LED-cured systems.

Experimental

For this work, four different dendritic acrylate oligomers (DAO) of varying molecular weights and functionalities were synthesized. All oligomers were analyzed with gel permeation chromatography (Polymer Labs PL-GPC 50 equipped with RI detector and mixed D-columns and FTIR (Perkin Elmer Spectrum 100). Viscosities were measured using a Brookfield CAP 2000+ viscometer. The oligomers were tested for potential use in LED-curing applications using a simple model formula found in Table 1. Formulations were mixed using a FlackTek DAC 150.1 FVZ SpeedMixer at 3,000 rpm for 2.5 minutes. It can be appreciated that this formula could be readily modified to a 100% solids system or to suit the needs of a particular application.

Table 1. Model Formulation

Component	Wt%
DAO	47.5
Visible Light Photoinitiator	1.0
Broad Spectrum Photoinitiator	1.5
Solvent	50.0
Total	100.0

The formulations were applied to the various substrates described below at a wet coating thickness of 2.0 mil. The coating was then dried at 90°C for 15 minutes to give a final dry coating thickness of 1.0 mil. All coatings were cured at a 405 nm wavelength using a Dymax BlueWave® LED Flood system with a VisiCure® 405 lamp for 1 second. The intensity was measured at 300 mW/cm² using a Dymax ACCU-CAL™ 50-LED radiometer.

To measure the level of oxygen inhibition, coatings were applied to a glass substrate and any tack layer present after cure was removed by wiping with acetone. The thickness of the tacky layer was calculated by comparing the coating thickness before and after the layer was removed. The pencil hardness of the coatings was measured on a glass substrate according to ASTM D3363. Flexibility was determined by applying the coatings to a 5.0 mil thick polycarbonate substrate and testing the flexibility according to ASTM D522. A Gardco Cylindrical Mandrel Test Apparatus was used for this purpose. The reported result is the diameter of the mandrel where cracking of the coating occurred.

The coatings were also evaluated for their resistance to a wide range of chemical exposures. Acid and stain resistance was measured according to ASTM D1308. For acid resistance, coatings were applied to steel substrate and exposed to 37% HCl (aq), 86% H₃PO₄ (aq), and 50% H₂SO₄ solutions for 24 hours. The coatings were then examined for any visual defects. For stain resistance, the coatings were applied on glass and exposed to an amount of yellow mustard for 48 hours. The degree of yellow staining was then measured using a Hunter ColorquestXE colorimeter, which reports yellowness as change in the b* value of the coating. The coatings' resistance to solvent was determined after application on glass and according to ASTM D4752 using MEK as the solvent and a 1 pound (454 gram) hammer as weight.

Finally, the coatings were evaluated for resistance to physical wear. To determine the scratch resistance, coatings were applied to a glass substrate and rubbed with steel wool weighted with a 1 pound (454 gram) hammer. The amount of haze that developed on the coating was then measured with a Hunter ColorquestXE colorimeter according to ASTM D1003. Resistance to abrasion was measured according to ASTM D523 using a Linear Taber Abrader with a CS-10F Weraser under a 500 gram load. A black ABS/PC substrate was used for this test and the results were reported as a change in the coatings' gloss at an angle of 60°.

Results and Discussion

Oligomer Characterization

Table 2 provides characterization data for the four synthesized DAOs. Neat viscosity is an important parameter to consider for ease of processing and for targeting final formulation viscosities. Oligomers A, D, and especially B have fairly low viscosities that should be easily pourable at room temperature. Even the higher viscosity Oligomer C flows at room temperature, but it would likely need to be heated slightly to make processing more efficient.

The four DAOs have varying molecular weights and nominal functionalities. Consistent with the general properties of dendritic materials, all of them are of high functionality reaching up to an average of 30 acrylate groups with Oligomer C. When taken together, the molecular weight and functionality of the oligomers can give an estimate of their acrylate equivalent weight. This, in turn, may be used as a rough estimate of the ultimate crosslink density of the cured material. Generally speaking, a lower acrylate equivalent weight should give a higher degree of crosslink density and, therefore, higher hardness and better resistance properties.

Table 2. Oligomer Characteristics

DAO	Viscosity (cP)	Mw	Nom. Functionality	Acr. Eq. Wt. (g/acrylate)
A	50,000 at 25°C	High	18	250
B	1,500 at 25°C	Low	6	150
C	1,500 at 60°C	Medium	30	100
D	20,000 at 25°C	Medium	15	200

Oxygen Inhibition, Hardness, and Flexibility

The thickness of the oxygen inhibited tack layer after cure is shown in Table 3. All oligomers show very little oxygen inhibition with Oligomer B being the most inhibited with only a two-hundredths of a mil thick tack layer. There does appear to be a slight inverse correlation between the level of oxygen inhibition and oligomer molecular weight. Viscosity may also play a role. Oligomer B with both the lowest molecular weight and lowest viscosity may have more dissolved oxygen present, or be more susceptible to oxygen diffusion before and during cure, which would explain its higher degree of oxygen inhibition. In any case, the relatively little amount of oxygen inhibition that is present with any of the oligomers should be readily mitigated with standard formulation techniques.

Table 3 also gives the pencil hardness and flexibility results. As expected, all the oligomers show a good degree of hardness in direct proportion to their estimated cross link densities. The flexibility results, too, are mostly consistent with the expected crosslink density of the oligomers. Oligomer A has the lowest expected crosslink density and so has the lowest pencil hardness of the group of H but the greatest flexibility. In contrast, Oligomer C has the highest expected crosslink density and therefore has the maximum pencil hardness of 9H but the worst flexibility. Surprisingly, Oligomer B has the same flexibility as Oligomer A. This could possibly be related to its higher level of oxygen inhibition and be indicative of incomplete cure.

Table 3. Thickness of Oxygen Inhibition Layer, Pencil Hardness, and Flexibility

DAO	Tack Layer (mil)	Pencil Hardness	Flexibility (mm)
A	0.008	H	3
B	0.023	3H	3
C	0.014	9H	25
D	0.011	2H	6

Chemical Resistance

The oligomers' chemical resistance is presented in Table 4. All the oligomers show excellent resistance to solvent. Even after 200 double rubs with MEK, none of the coatings showed any degradation or hazing. The oligomers also have substantial resistance to staining. The stain from the yellow mustard was barely noticeable to the naked eye on all coatings. However, when measured with a colorimeter

slight differences in yellowness could be detected which were generally consistent with the higher crosslinked oligomers showing better results.

In regard to acid resistance, none of the coatings experienced a total coating failure. The worst effect observed due the exposure to acid was staining of the coating. All of the oligomers were impervious to the 50% H₂SO₄ solution and Oligomers A and C showed very similar degrees of staining to the other acids. Oligomer C, with its high crosslink density, was only minimally affected by the 86% H₃PO₄. Oligomer B had some unexpected results in that it had the least resistance to the 37% HCl solution. This could also be related to the oxygen inhibition effect described above with the lesser cured coating of Oligomer B allowing the smaller HCl molecule to penetrate and stain its surface.

Table 4. Solvent, Stain, and Acid Resistance

DAO	Solvent Resistance (# Double Rubs)	Stain Resistance (b* Value)	Acid Resistance		
			37% HCL	86% H ₃ PO ₄	50% H ₂ SO ₄
A	>200	27.76	Moderate	Moderate	None
B	>200	17.73	High	Low	None
C	>200	20.29	None	Very Low	None
D	>200	24.56	Moderate	Moderate	None

Scratch and Abrasion Resistance

Figures 1 and 2 show the steel wool scratch and abrasion resistance of the coatings, respectively. The resistance to scratch by steel wool correlates perfectly to the expected crosslink density of the oligomers. Oligomer C was unaffected by a single steel wool rub and even at five rubs there was only a minimal amount of hazing. Oligomer A had the poorest scratch resistance with the haze after one rub being greater than the haze at five rubs for the other oligomers.

In terms of abrasion resistance, Oligomers A, C, and D showed excellent resistance to abrasion. All of them had a decrease in gloss of less than 1.5 units after 50 cycles and less than 5 units after 200 cycles. Oligomer B appears to be an outlier showing a much greater drop in gloss than any of the other oligomers. Again, this is likely due to the higher level of oxygen inhibition seen with Oligomer B. During testing, the Wearaser of the Linear Taber Abrader may have smudged the tack layer instead of abrading the coating thereby decreasing the gloss more than expected.

Figure 1. Steel Wool Scratch Resistance

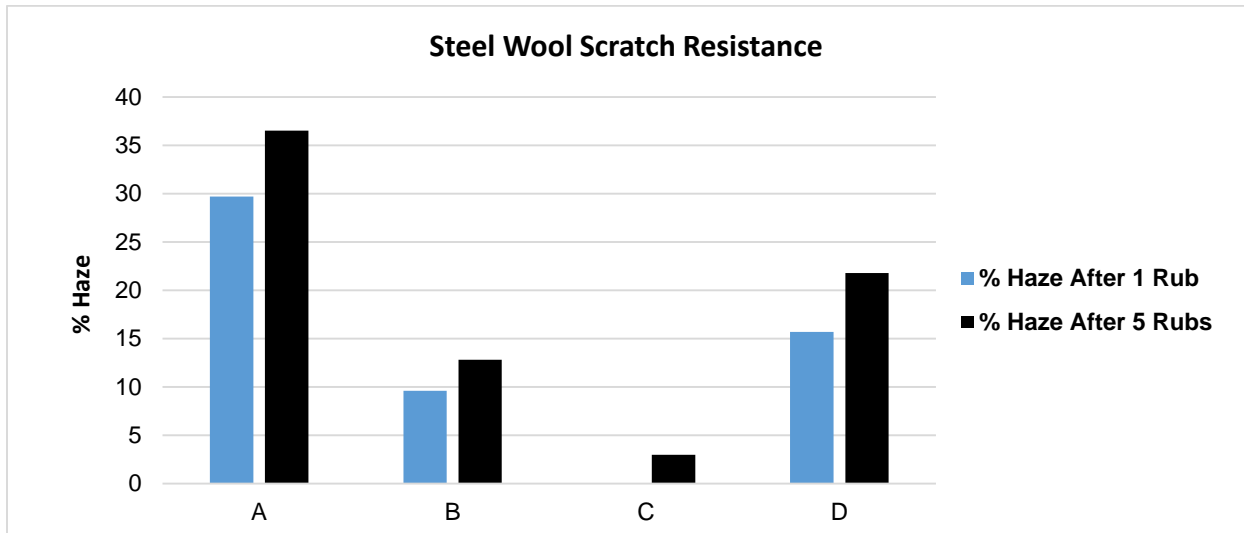
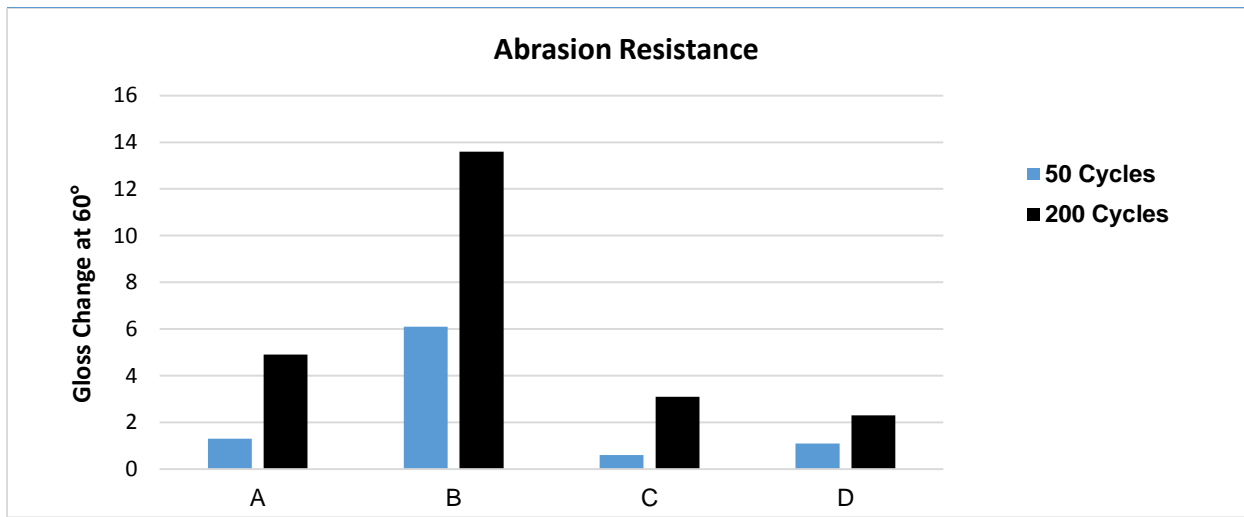


Figure 2. Abrasion Resistance



Conclusion

Dendritic materials are well known to impart rapid cure speeds, high hardness and resistance characteristics, and reduced oxygen inhibition when used in formulations cured by traditional UV systems. The purpose of this work was to evaluate these materials when cured with an LED system which are noted to have issues with both cure speed and oxygen inhibition. As we have illustrated, even when cured with a low-intensity LED lamp for durations as low as 1 second, dendritic acrylate oligomers still exhibit the exceptional properties they are known for. With proper tailoring of the dendritic material's molecular weight and functionality to balance the desired physical properties, these materials should be able to form the backbone of high-performance LED formulations.

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