Benefits of Formulating with Self-Curing Acrylic Resin In a World Filled with Photoinitiator Challenges

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Abstract

Photoinitiators are integral to most UV cured coatings and adhesives, but supply shortages, increasing prices, and regulatory constraints have challenged formulators to provide products meeting all their customer's needs. These industry struggles have created the opportunity to evaluate self-curing resin benefits not only for the formulator, but the end user. This paper describes the formulation of self-curing acrylic resin into a protective hard coat, improving the final product performance while reducing photoinitiator more than 80%.

Introduction

The use of UV curable products continues to grow but formulators have faced many challenges in recent years with a key group of raw materials in their toolbox- photoinitiators. Previous work with self-curing resins[1, 2] has shown that significant photoinitiator (PI) reduction can be achieved helping mitigate some of the current PI formulation obstacles. Unfortunately, in this early work the energy densities required for UV cure were much higher than what is expected of modern UV formulations for high production applications such as flexible packaging and labels.

Formulation

The formulation selected for this work is a UV cured hard coat (HC) designed to provide extremely high abrasion resistance to plastic films and resist yellowing in outdoor applications. A well-known self-curing resin (SCR) from the previously mentioned work was prepared at lab scale. The SCR was used to replace the aliphatic urethane acrylates in the hard coat formulation. Additional optimization was made after testing cure. All formulations were tested for the minimum energy density required to provide scratch free cure with a wooden tongue depressor using a 300 Watt/in American Ultraviolet H bulb. The lamp was set at medium power for energy densities above 50 mJ/cm^2 and low power for energy densities below 50 mJ/cm^2. Energy densities were measured with an EIT Power Puck® II (UV A+B+C).

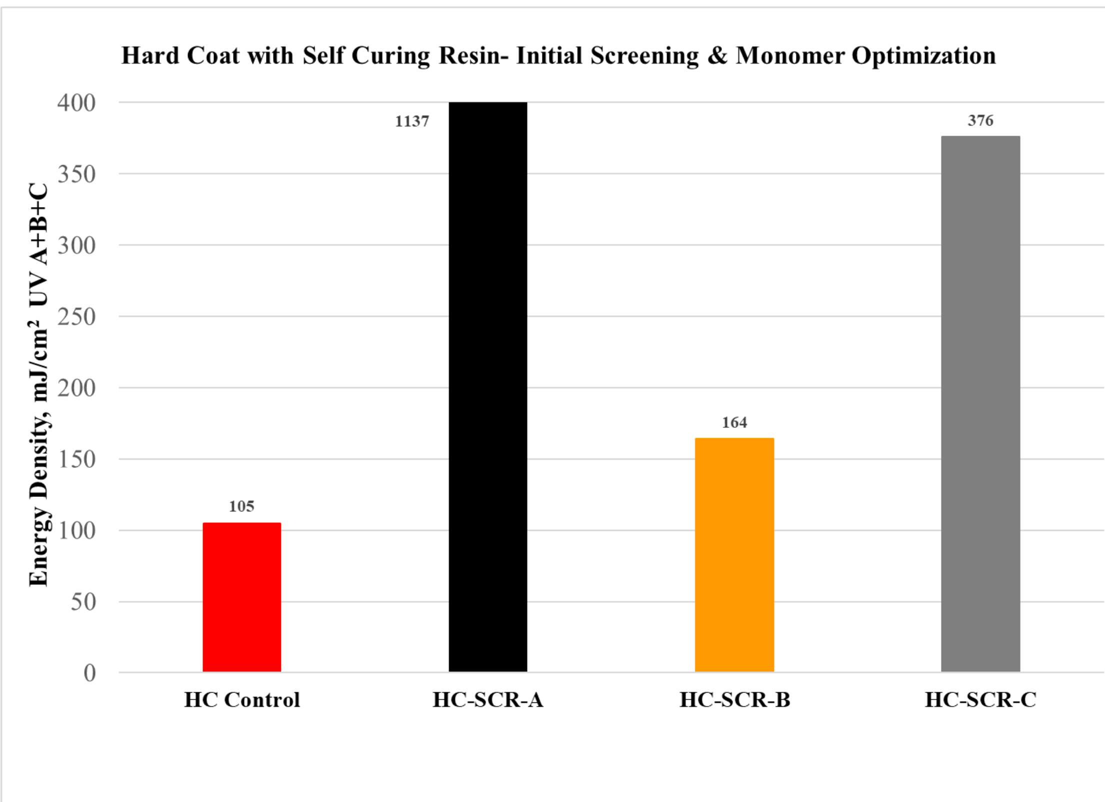
Initial Screening

Initial screening of the SCR resin in the hard coat formulation involved simple replacement of the oligomers and formulating with and without a typical non-yellowing PI. Viscosity reduction using the SCR was significant, but the cure response was poor even with the use of the typical non-yellowing PI. The SCR formulations showed signs of strong oxygen inhibition. By using only trifunctional monomer in the HC-SCR formulation with 0% PI, the energy density was reduced by 66% compared to the formulation with difunctional monomer. See formulations and viscosity in **Table 1** and cure in **Figure 1**.

Table 1

	HC Control	HC-SCR-A	HC-SCR-B	HC-SCR-C
Component	Weight %	Weight %	Weight %	Weight %
Difunctional Acrylate	10.00	10.00	10.00	
Trifunctional Acrylate	20.00	20.00	20.00	30.00
Multifunctional Aliphatic Urethane Acrylates	62.20			
Self Curing Resin (SCR)		68.20	62.20	68.20
Standatd Non-Yellowing UV PI	6.00		6.00	
UV Stabilizer Package	1.80	1.80	1.80	1.80
	100.00	100.00	100.00	100.00
Brookfield Viscosity @ 25°C, cps	6464	855		

Figure 1



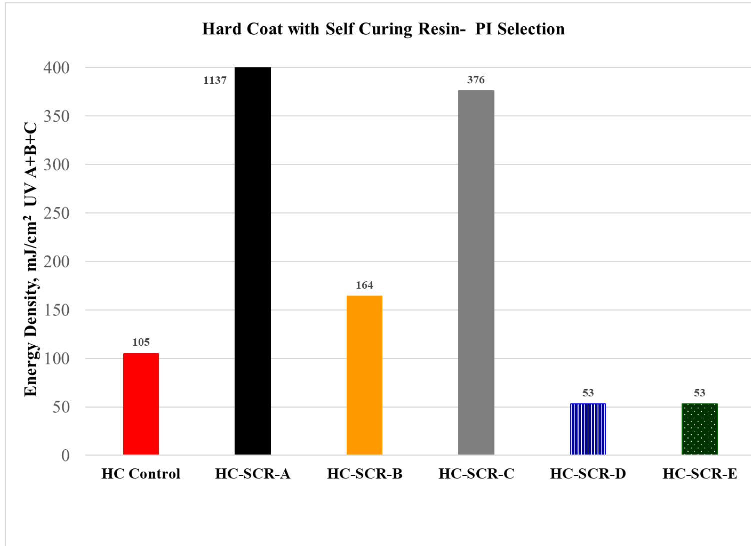
Photoinitiator Selection

Like many early LED formulations, the initial screening of the HC-SCR formulations showed significant oxygen inhibition. To overcome this, 2 LED PI packages were chosen for PI optimization. In addition to long UV wavelength PI's, an amine synergist was also used. Both these HC-SCR formulations showed greatly improved surface cure but poor depth of cure, suggesting that the PI levels could be reduced. See formulations in **Table 2** and cure in **Figure 2**.

Table 2

	HC-SCR-D	HC-SCR-E
Component	Weight %	Weight %
Trifunctional Acrylate	20.50	19.30
SCR- Self Curing Resin	62.20	62.20
Amine Synergist	9.00	11.10
LED PI Package 1	6.50	
LED PI Package 2		5.60
UV Stabilizer Package	1.80	1.80
	100.00	100.00

Figure 2



Photoinitiator Optimization

Blends of HC-SCR-C with HC-SCR-D and HC-SCR-C with HC-SCR-E were made to produce formulations with ½, ¼ and ⅛ LED PI package 1 & 2. This also resulted in corresponding reductions in amine synergist. See **Tables 3, 4, 5 & 6**.

Table 3

	HC-SCR-D½	HC-SCR-D¼	HC-SCR-D⅛
Component	Weight %	Weight %	Weight %
HC-SCR-C	50.00	75.00	87.50
HC-SCR-D	50.00	25.00	12.50
	100.00	100.00	100.00

Table 4

	HC-SCR-D	HC-SCR-D½	HC-SCR-D¼	HC-SCR-D⅛
Component	Weight %	Weight %	Weight %	Weight %
Trifunctional Acrylate	20.50	25.25	27.63	28.81
SCR- Self Curing Resin	62.20	65.20	66.70	67.45
Amine Synergist	9.00	4.50	2.25	1.13
LED PI Package 1	6.50	3.25	1.63	0.81
UV Stabilizer Package	1.80	1.80	1.80	1.80
	100.00	100.00	100.00	100.00

Table 5

	HC-SCR-E½	HC-SCR-E¼	HC-SCR-E⅛
Component	Weight %	Weight %	Weight %
HC-SCR-C	50.00	75.00	87.50
HC-SCR-E	50.00	25.00	12.50
	100.00	100.00	100.00

Table 6

	HC-SCR-E	HC-SCR-E½	HC-SCR-E¼	HC-SCR-E⅛
Component	Weight %	Weight %	Weight %	Weight %
Trifunctional Acrylate	19.30	24.65	27.33	28.66
SCR- Self Curing Resin	62.20	65.20	66.70	67.45
Amine Synergist	11.10	5.55	2.78	1.39
LED PI Package 2	5.60	2.80	1.40	0.70
UV Stabilizer Package	1.80	1.80	1.80	1.80
	100.00	100.00	100.00	100.00

The ½, ¼ and ⅛ LED PI HC-SCR formulations were tested for cure (Figure 3). Additional testing included Taber Haze abrasion resistance (Figure 4) and UV stability (Figure 5) after 100 hours of

UV exposure in a Q-Sun XE-3 Xenon test chamber with Daylight Q filter. ΔE was calculated from L*a*b values measured with BYK 6830 before and after UV exposure.

Figure 3

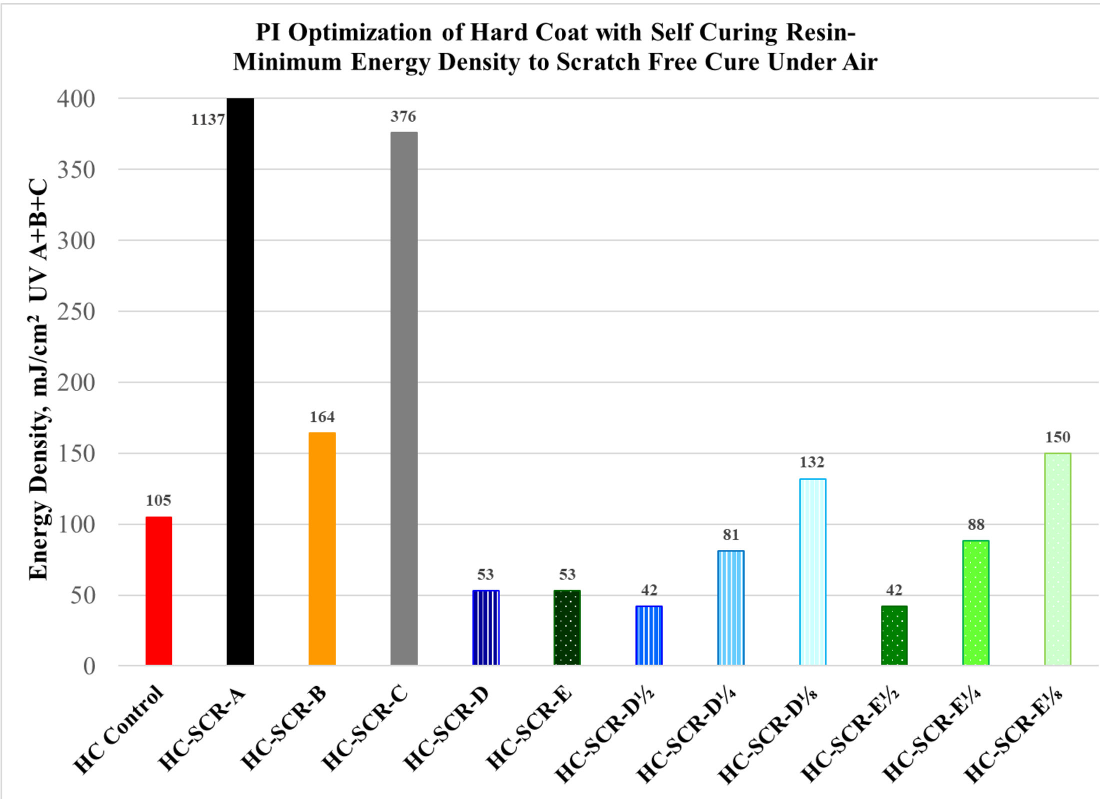


Figure 4

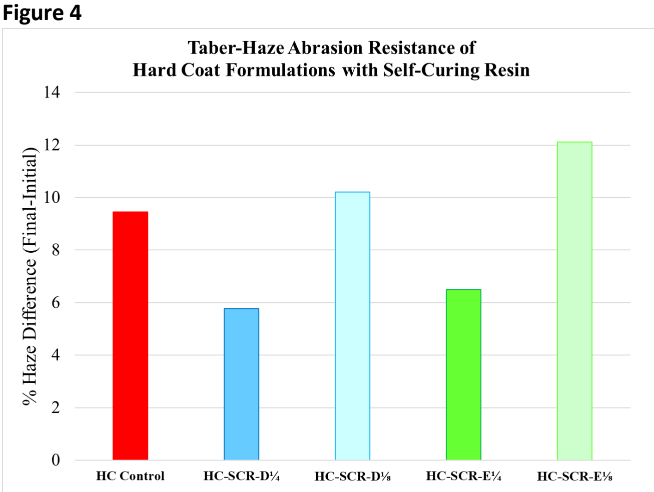
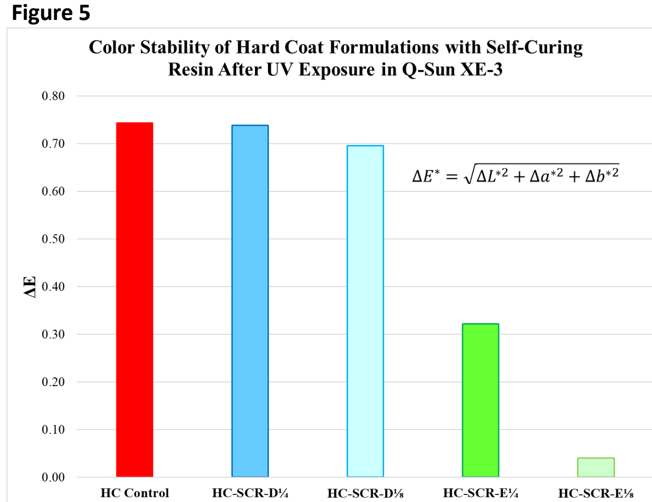


Figure 5



Interestingly, ½ LED PI packages D and E require less energy density for scratch free cure than the full level of these PI packages and all ½, ¼ and ⅛ LED PI HC-SCR formulations showed complete depth of cure. Since the ¼ and ⅛ LED PI formulations showed comparable cure to the hard coat control, the ½ LED PI formulations were not tested for abrasion resistance or UV stability. Abrasion resistance was shown to improve with increasing PI levels and UV color stability improved with decreasing PI levels. LED PI package 2 (E) shows superior color stability over D formulations. Looking at the three performance drivers- cure, abrasion resistance and UV color stability, one can easily see that HC-SCR-E¼ has the best balance of all three properties, surpassing that even of the hard coat control. Since the goal is to minimize the amount of PI used, extrapolation indicates that performance matches for cure and abrasion resistance can be met with only ⅙th of PI package E while improving UV color stability over the hard coat control. This is equivalent to an 84% reduction in PI compared to the hard coat control while improving performance.

Conclusion

Initial screening of a self-curing resin (SCR) used to replace the oligomers in a hard coat formulation indicates that there is little benefit to using a SCR. However, careful monomer and photoinitiator selection prove that improved performance in cure, abrasion resistance and UV color stability are possible while significantly reducing the amount of photoinitiator needed. The reduction of photoinitiator while maintaining or improving performance can only benefit the formulator and end user when facing the challenges of cost, supply and migration potential.

References

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2. Ananthachar, A. "UV Lithographic Inks from self-photoinitiating resins for food packaging applications" Proceedings of RadTech 2008