The Effect of Different Curing Methods on Tack Free Curing

Amelia Davenport, Mike Idacavage, Ashten Fralick, and Neil Cramer
Colorado Photopolymer Solutions, 1880 S Flatiron Ct, Boulder, CO 80301

In almost all applications of UV Curing, the issue of oxygen inhibition must be addressed in one form or another. As such, different UV curable formulations must be optimized to contain an appropriate initiator package and UV light source to overcome oxygen inhibition which ads additional cost and development time. The advent of LED lights has enabled less expensive lights with increased operating lifetimes and improved energy efficiency. However, rather than covering a broad spectrum of wavelengths, LED lights emit in narrow bands of light. The narrow wavelength emission spectrum of LED lights will inevitably have an effect on both curing rates and oxygen inhibition. In this study, we evaluate the use of broadband mercury, both deep UV-LED and 385 nm LED lights, and Electron Beam curing across a range of different acrylic formulations. The different methods of curing are compared by examining their effect on oxygen inhibition, cure speed, and material properties.

Introduction

From coatings to biomedical implants to photolithographically controlled materials, photopolymerization has dramatic advantages. It can be utilized to *in situ* cure materials at whatever time, location and three-dimensional pattern desired. It is one of the most energy efficient processes known and can be used as a 100% solvent free process. One drawback that must be overcome in most photopolymerization applications is the severe inhibition of these polymerizations by the ubiquitous presence of oxygen.

Numerous routes to overcome oxygen inhibition have been explored including high irradiation intensity, high photoinitiator concentration, nitrogen purging, and chemical additives such as thiol monomers. Oxygen inhibition is also affected by factors such as polymerization rate, crosslink density, and resin viscosity. Generally, the routes to overcome oxygen inhibition with typical high intensity mercury broadband UV lamps are well established. With LED curing gaining prevalence throughout the UV curing industry, examining the effectiveness of these known routes to overcome oxygen inhibition and comparing to broadband UV is important to understand.

In this work, we compare methods to overcome oxygen inhibition using a typical broadband mercury irradiation source as well as numerous LED sources including 405, 385, 355, and 300 nm LEDs. We have also evaluated curing with electron beam irradiation.

Experimental Procedures

Materials

Epoxy diacrylate (PE230), polyester triacrylate (PS3220), urethane diacrylate (PU2100), and isobornyl acrylate (IBOA) were donated by Miwon North America Inc. Tripropylene glycol diacrylate (TPGDA) was purchased from Miwon North America Inc. CPS 1020 and CPS 1040 are proprietary thiol-ene based formulations. 1-hydroxycyclohexyl-phenyl ketone (Omnirad

481/I-184) and 2,4,6-Trimethylbenzoyl-diphenyl phosphine oxide (Omnirad TPO) were purchased from IGM Resins.

Procedures

Coating – substrates are coated with an ~125 μm layer of formulation using a wire wound drawdown bar.

Curing. Formulations were cured on a conveyor system using a Heraeus F300 light with 300 W/inch H bulb or a 25 W 385 nm LED (Heraeus) or a 405 nm LED that was donated by Dymax. A 300 nm LED system was donated by Lumany.

Results and Discussion

A comparison of tack free curing with a typical epoxy acrylate, polyester acrylate, and urethane acrylate was performed. Each of the acrylates was cured with 1, 3, and 4 wt. % photoinitiator. The results indicated no significant difference in curing performance across these materials. Experiments were performed with broadband UV irradiation with a typical UV photoinitiator (I-184) and with TPO. Experiments were also performed with a 25 W 385 nm LED system. Results are given in Table 1. Belt speeds for tack free curing ranged from 70 – 170 fpm with 3 and 4 wt. % photoinitiator for UV broadband irradiation. Using TPO and a 385 nm LED system, belt speeds for tack free curing ranged from 9 – 20 fpm with 3 and 4 wt. % photoinitiator. Curing was also performed with a 405 nm LED system similar in power to the 385 nm LED. Minimal differences were observed between curing performance with the 385 and 405 nm LEDs. Curing of films was also successfully performed using a 355 nm LED system. However, the 355 nm LED system was configured significantly different than the 385 and 405 nm LED systems with significantly reduced power output. As such, the results are not directly comparable.

Table 1. Generic comparison of epoxy, polyester, urethane with broadband UV irradiation and with a 25 W 385 nm LED.

	Max Belt Speed for Tack Free Curing (fpm)	
	UV Broadband	**385 nm LED**
Epoxy Diacrylate		
1 wt.% PI	10	--
3 wt.% PI	85	9 x 2
4 wt.% PI	135	20
Polyester Triacrylate		
1 wt.% PI	20	--
3 wt.% PI	90	9
4 wt.% PI	155	30
Urethane Diacrylate		
1 wt.% PI	9 x 3	--
3 wt.% PI	70	9 x 2
4 wt.% PI	140	20

The acrylate systems were compared to three different thiol-ene based formulations… As seen in Table 2, the thiol-ene based formulations all cured tack free at belt speeds of 150 – 155 fpm with 1 wt.% photoinitiator whereas the diacrylate systems (Table 1) cured at a maximum belt speed of only 20 fpm with 1 wt.% photoinitiator. At 4 wt. % photoinitiator, the thiol-ene systems achieved tack free curing at belt speeds of greater than 155 fpm (155 fpm is the maximum belt speed for the system utilized in this study) compared to belt speeds ranging from 135 – 155 for the diacrylate systems. Using TPO as the photoinitiator and the 385 nm LED the thiol-ene systems exhibited tack free curing with 5 seconds of irradiation with 1 wt. % photoinitiator and with 1 second of irradiation with 4 wt. % photoinitiator.

Table 2. Comparison of acrylate formulations to thiole-ene formulations. Varying initiator concentration. Note viscosity…

	UV Broadband (fpm)	**385 nm LED (s)**
CPS 1020		
1 wt.% PI	100	5
4 wt.% PI	155+	1
CPS 1040		
1 wt.% PI	155+	5
4 wt.% PI	155+	1

The epoxy diacrylate system was evaluated as a 50/50 mixture with two different diluents – TPGDA and IBOA (Table 3). TPGDA is a low viscosity diacrylate that results in significant drop in viscosity, but maintains high modulus and crosslink density. IBOA is a low viscosity monoacrylate that results in significant drop in viscosity, maintains high modulus, but results in significantly reduced crosslink density. The results show that tack free curing is most difficult to achieve in the system diluted with IBOA, and less difficult with TPGDA. Due to reduced viscosity the system diluted with TPGDA is more difficult to achieve tack free curing than the base system with higher viscosity. When cured with the LED light, only the epoxy diacrylate system was able to achieve tack free curing.

A study of the effect of photoinitiator concentration is shown in Table 4 for the epoxy diacrylate system mixed 50/50 with TPGDA. Here, the results show that there is a significant increase in the maximum belt speed when the photoinitiator concentration is increased from 4 to 6 wt. %. Beyond 6 wt. % photoinitiator, tack free curing is achieved with the maximum belt speed of 155 fpm. When cured with the LED light, tack free curing was not achievable in the system with 4 wt. % photoinitiator. The results show that there is a significant decrease in cure time when the photoinitiator concentration is increased from 6 to 8 wt.%.

Table 3. Comparison of acrylate formulation with three different types of diluent. All formulations contain 4 wt. % photoinitiator, I-184 for UV broadband or TPO for 385 nm LED.

	UV Broadband (fpm)	**385 nm LED (s)**
Epoxy Diacrylate	150	1
50 wt.% TPGDA	80	--
50 wt.% IBOA	55	--

Table 4. Epoxy diacrylate with 50 wt. % TPGDA. Initiator concentration

	UV Broadband (fpm)	385 nm LED (s)
4 wt.% PI	80	--
6 wt.% PI	150	60
8 wt.% PI	155	1
10 wt.% PI	155	1

EBeam curing was also evaluated for urethane diacrylate system in bulk and diluted 50/50 with TPGDA and IBOA (Table 5). Electrons are accelerated through a thin foil window impinging on a moving web at atmospheric pressure. The accelerated electrons will ionize most organic materials with this ionization leading to the formation of free radicals which initiates polymerization of the coating without the need for added photoinitiators. The EBeam parameters are typically set by selecting the total Dose of energy delivered to the sample and the belt speed. The current is adjusted as needed to deliver the total dose with the given belt speed. When curing with EBeam, the resins are typically purged with nitrogen to remove the presence of oxygen. EBeam curing has not been studied nearly as much as UV curing. Though the initiation mechanism to generate radicals is different, the fundamental polymerization kinetics should follow the same principles. For EBeam curing decreasing viscosity had no affect on curing as seen in Table 5. This is contrary to UV cured systems under ambient conditions where the affects of oxygen inhibition are more pronounced in systems with lower viscosity. Decreasing crosslinking reduces cure speed. This result is similar to UV cured systems. Polymerizations were also performed without a nitrogen blanket; here it was found that the typical diacrylate systems were not able to achieve tack free curing. However, the CPS 1040 thiol-ene system was readily able to achieve tack free curing without the aid of a nitrogen blanket.

Table 5. Electron beam curing. Diluent effects.

Formulation	Total Dose (kGy)	Belt Speed (m/min)	Current (mA)	Cure Quality
PU2100	5	30	1.36	Good
	30	30	8.16	Good
PU2100/TPGDA 50/50	5	30	1.36	Good
	30	30	8.16	Good
PU2100/IBOA 50/50	15	30	4.08	Soft
	30	30	8.16	Good

Conclusions

Several typical acrylate systems were cured with both UV broadband Mercury irradiation sources as well as LED systems. The results indicated that curing with broadband sources was more rapid than curing with LEDs. The LED systems emit significantly less energy than the broadband sources, so the reduced cure speed is not necessarily a result of reduced initiation efficiency. It was demonstrated that reducing viscosity and crosslink density both increase the effects of oxygen inhibition and increase the curing time required to achieve tack free surfaces. The use of thiol-ene based formulations was shown to significantly increase cure speed with both UV broadband and LED systems. In fact, the use of thiol-ene systems resulted in cure speeds with LED systems that were equivalent to those achieved in acrylate systems with UV

broadband. An initiator optimization study was performed and indicated that upon achieving a certain threshold initiation rate, cure times decreased dramatically. Systems cured with EBeam showed the same fundamental cure characteristics as UV cured systems.

Acknowledgements

The authors gratefully acknowledge Miwon North America Inc. for their ongoing support and discussions and for donating materials for this research.