

New dual function resin with initiator and acrylate functionality for low migration applications

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Abstract

A dual function UV curable resin, which contains both initiation and polymerization functional groups, was developed for applications where low migration is required. This low extractable resin was specifically designed for: 1) ease of use, 2) high compatibility, 3) photo activation under UVA excitation, and most importantly 4) negligible migration.

1. Introduction

The issue of migration (or lack thereof) is critically important for inks and coatings used for indirect food contact applications¹⁻⁴. Indeed, migration of typical resin components needs to be well below ppm levels, and some need to be on the ppb migration level to be usable⁴. This low migration limit can create a challenge, since most additives (like photoinitiators) are fairly low molecular weight and/or can photofragment into smaller entities that can readily migrate. Simple bulking up the photoinitiator's molecular weight can have negative consequences on photocure speed, solubility and cost. For example it normally slows initiation kinetics, and is a necessary dilution of the chromophore (resulting in the need to increase its usage level). In addition, most low migration type photoinitiators are solids and/or have limited solubility in the resins, which make their processability in a formulation more challenging. Thus, one of the key areas of interest for new product development is to maximize photocure speeds and processability, while at the same time minimize low molecular weight or migratory components.

In this paper we wish to describe a new low extractable (LEX) multifunctional liquid resin, which contains multiple acrylate and multiple photoinitiator moieties. The photoinitiator moieties are covalently linked to the resin. These initiating moieties are mid-UV absorbing alpha-hydroxy ketone (AHK) types, which ensures efficient Norrish Type I photocleavage^{5,6}. The polymeric resin's molecular weight is greater than 1000 Daltons. This feature combined with its reactivity ensures facile incorporation into the cured resin and negligible migration, as required for indirect food contact applications.

2. Experimental

2.1. Materials ⁷

Resins and photoinitiators

The acrylate resins and photoinitiators that were used in this study are summarized in Table 1 and Table 2.

Table 1. Resins

Resin	Description
Laromer® LR 8986	epoxy acrylate resin
Laromer LR 8869	amine modified polyether trifunctional acrylate resin
Laromer PO 77 F	amine modified polyether trifunctional acrylate resin
Laromer PO 94 F	amine modified polyether trifunctional acrylate resin
Laromer TPGDA	tripropylene glycol diacrylate monomer

Table 2. Photoinitiators

Type	Name	Code	Molecular Weight (g/mole)
alpha hydroxy ketone bound to oligomeric acrylate resin	Irgacure® LEX 201	LEX 201	> 1000
alpha hydroxy ketone	Irgacure 1173	HMPP or AHK-1	164.2
alpha hydroxy ketone	Irgacure 184	HCPK or AHK-2	204.3
alpha hydroxy ketone	Irgacure 2959	AHK-3	224.3
alpha hydroxy ketone	Irgacure 127	AHK-4	340.4
alpha amino ketone	Irgacure 369	AAK-2	366.5
alpha amino ketone	Irgacure 379	AAK-3	380.5
bis acyl phosphine oxide	Irgacure 819	BAPO	418.5

Table 3. OPV Formulations

Resin Name	Components	Amount, pph
Epoxy Acrylate OPV	Laromer ®LR 8986	26.3
	Laromer PO 77F	34.3
	Laromer TPGDA	39.4
Polyether Acrylate OPV	Laromer PO 94 F	69.7
	Laromer LR 8869	30.3
Low Viscosity Polyether Acrylate OPV	Laromer PO 94 F	21.0
	Laromer LR 8869	45.2
	Laromer LR 8863	33.8

Base resin formulations for epoxy acrylate, polyether acrylate and low viscosity polyether acrylate are summarized in Table 3.

Ink Formulation

A blue pigmented flexo ink was used for screening various photoinitiator packages. Its composition is given in Table 2.

Table 4. Blue Flexo Ink Formulation

Component*	wt%
Heliogen [®] Blue D 7110 F (old name Irgalite [®] Blue GLVO)	16
Efka [®] PX 4701	1
Laromer LR 8800	14
Laromer PO94F	24
Laromer LR8863	32.3
Ebecryl [®] 450	12
Efka [®] SL 3210	0.2
Luwax [®] AF30	0.5

2.2 Analytical and curing methods

Viscosity measurements

The viscosity of the neat resin LEX 201 was determined using an Advanced Rheology AR-2000 (18 °C to 70°C, every 2°C per point, 4°C/min, at a shear = 50 sec⁻¹ using the 40 mm 2° AL cone-and-plate geometry).

A Brookfield viscometer (Brookfield DV-II+ Pro, with a #3 spindle at 100 RPM with temperature control) was used to determine viscosities of resin formulations.

Thermo-mechanical property assessment

A DMA Q 800 (TA Instruments) was used for DMA (dynamic mechanical analysis) and stress-strain tensile curve analysis of photocured coatings. DMA was run on samples (dimensions of 12.6 x 5.53 x 0.125 mm³ and of 8.89 x 5.53 x 0.08 mm³) at a rate of 3°C/min using an amplitude of 15 µm and a frequency of 1 Hz. Tensile testing was done at a strain rate of 0.5%/min. Tensile testing was done on samples having dimension of 8.0343 x 5.5300 x 0.1100 mm³.

Test method for extraction

Irgacure LEX 201 was heated to 60°C for approximately 15 minutes to make it less viscous. Four samples were made of epoxy acrylate OPV with photoinitiator at “high” and “low” concentrations. Irgacure LEX 201 was incorporated into the OPV at 6.37% wt% and 15.02 wt%. Irgacure 184 (HCPK) was incorporated into the OPV at 4.08 wt% and 10.99 wt%. Samples were also heated to 60°C to ensure complete incorporation.

Next, a 3x5 inch cardstock template was used to cut out ten samples of aluminum foil. The samples were weighed on an analytical balance. The average weight was recorded at 0.6008 +/- 0.0115 grams. This number was used to calculate the actual coating weights later on.

Sheets of aluminum foil (Reynolds Heavy Duty Aluminum Foil) were then carefully wrapped around metal panels, and the OPVs were applied with a number 0 (white rod) drawdown bar at 4 microns. Care was taken to avoid cross-contamination. The panels were then passed through the Fusion UV 600 Watt Curing unit with a D lamp at 50 feet per minute. A “low” and “high” dose was obtained by using one pass at 30% power and then two passes at 100% power respectively. The UVA exposure for the low dose was 0.086 J/cm² and 2.208 J/cm² for the high dose.

The double bond conversion of the acrylate bonds was monitored by FTIR after the curing of the samples.

A new 3x5 inch aluminum foil template was then used (a clean one for each sample) as a template to cut each sample with a razor blade. The razor blade was cleaned with acetone in between each sample to avoid cross-contamination. The coated samples were weighed on an analytical balance and the average aluminum foil weight was subtracted to obtain a coating weight.

The cured sample cut out was placed in a sealed plastic cup with lid and transferred to the analytical group (N-EDN/T). Each sample was then cut into smaller pieces, cleaning the scissors with acetone in between each sample. The smaller pieces were then placed into scintillation vials with chloroform to extract overnight on a shaker. The chloroform was then analyzed by GC/MS.

The GC/MS experiments were performed on an Agilent 6890 GC coupled to a 5973 MS system. The injection port of the GC was at 220°C. Helium was the carrier gas with a constant flow of 2.5 cc/min. The GC oven started at 100°C, ramping at 10°C/min to 250°C and holding at 250°C for 15 minutes. The mass detector was on from 0.01 min- 0.96 min, off from 0.96-2.00 min and then on from 2.00-30.00 min. A split ratio of 10:1 was used. The temperature of the MS detector was at 250°C.

Test method for migration set-off

For set-off migration, fully cured ink samples were pressed against LDPE films sandwiched between aluminum coil coats (with uncoated Al side towards sample or LDPE contact film). The assembly (Figure 1) was placed during one week in an oven at 40°C.

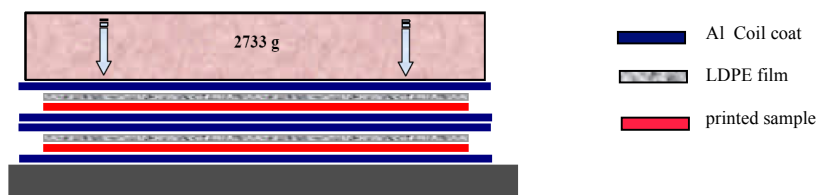


Figure 1. Set-up used for simulated migration

Discs of 30 mm diameter were cut from the set-off LDPE samples. Each disc of 30 mm diameter was immersed in 25 ml EtOH 95 % (food simulant) in a two-side migration test during 2 h at 70°C. The total surface (two sides) of the disc being 0.141 dm², the volume to surface ratio is 176.68 mL/dm².

Using the EU calculation assuming a volume to surface ratio of 1L/ 6 dm², a concentration of 100 µg/L of a migrant in the ethanol solution corresponds to 106.01 ppb into food.

The extract was carefully concentrated and analyzed by HPLC using standard solution of reference substances (photoinitiators). All tests were run in triplicate from three different samples. The detection limit is < 1 ppb into food.

Solvent & stain resistance

The stain tests involved placing various liquids on top of the cured surface for one hour exposure. A watch-glass cover was used to prevent evaporation of the liquid during the test. A passing grade was when there was no discoloration or staining or change in apparent gloss of the coating.

Photocuring and characterization

For OPV or coatings, the samples were applied using a Bird bar onto white aluminum panels. The specimens were subsequently photo-cured in air at ambient temperature with Fusion UV 600 watt gallium doped “D” lamp.

The UV inks were applied to Leneta charts at 1.7 gram/m² and photocured in air using an IST UV lamp (200 W/cm).

For set off migration experiments, the samples were photocured using an IST UV belt line, which was equipped with two medium pressure mercury lamps (electric power of 80 W.cm⁻¹). At the belt speed used, 5 m/min, the UV exposure received by the sample at each pass under the lamp was measured to be approximately 0.9 J.cm⁻².

FTIR double bond conversion evaluation

A Nicolet Avatar 370 DTGS spectrophotometer (ThermoElectron Corp.) was used to obtain the FTIR/ATR spectra. The spectrophotometer was equipped with a diamond crystal and a smart orbit accessory. Data acquisition used a resolution 4 cm⁻¹ and data spacing of 1.929 cm⁻¹, and each spectrum was an average of 32 scans, taken from 4000 cm⁻¹ to 400 cm⁻¹ and referenced against an air background.

The reported percent double bond conversion (% conv) was determined from ATR-FTIR spectra. The double bond conversion is expressed as % conv = 100*(“Initial”-“Final”)/“Initial”, where “Initial” & “Final” observables are integral ratios of (Acrylate Absorbance Integral at 815 cm⁻¹)/ (Carbonyl Absorbance Integral at 1704 cm⁻¹). ATR-FTIR spectra were done on top and bottom sides of the coating.

MEK solvent resistance of the photocured coatings

The solvent resistance is a well-known measure of cure⁸. The use of methyl ethyl ketone (MEK) as the solvent is often used in the industry. The method is to perform double rub on the coating surface with a cloth soaked with MEK solvent.

3. Results and Discussion

The dual functional polymeric resin (which is referred to as LEX 201) was designed first to eliminate the problem of photoinitiator migration and to ensure good photo speed of cure in air with medium pressure mercury lamps (either IST unit using H-bulb or Fusion unit using iron doped D-bulbs). It was also designed to impart high gloss and solvent resistance. It was further designed to be compatible with most non-aqueous acrylate based resins.

As will be shown below, LEX 201 is well suited for thin clear coatings (i.e., over-print varnishes) or for improving surface cure of inks or pigmented coatings. Because of its dual functionality, it is designed to be both resin and photoinitiator. In this way it forces us to rethink the standard formulation paradigm, as shown in Figure 2. Namely the photoinitiator and resin are covalently bound to each other.

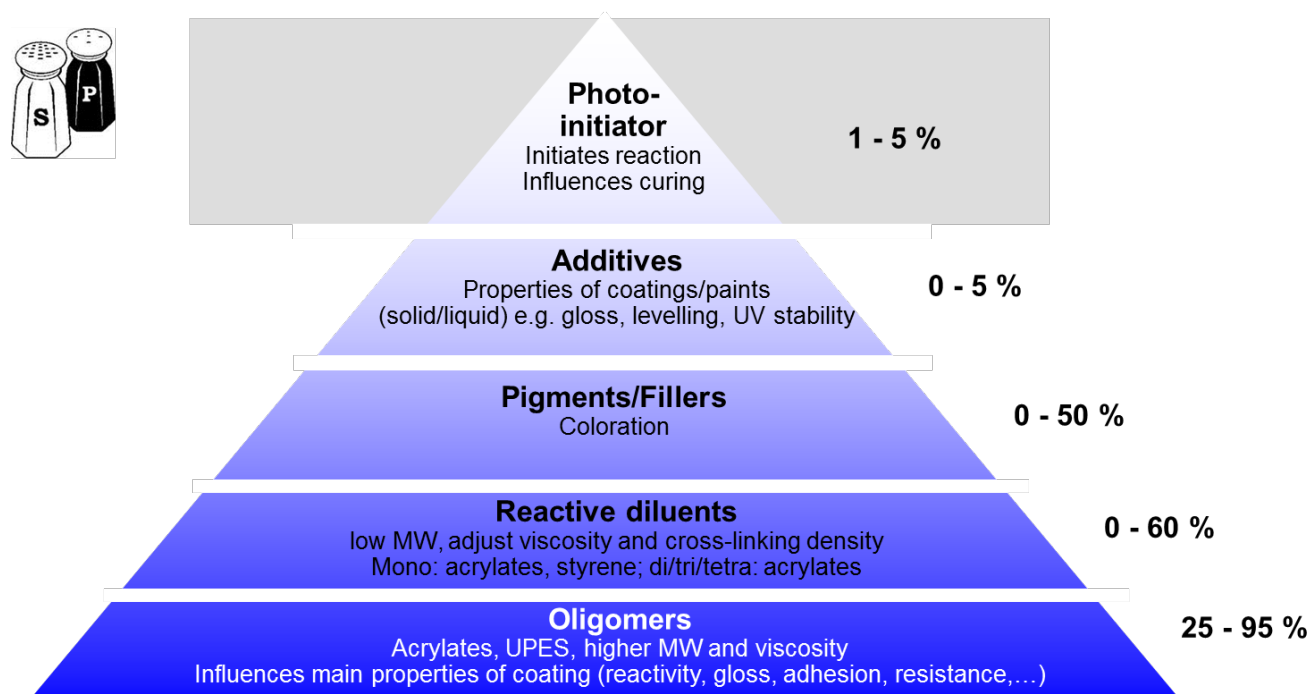


Figure 2. Traditional formulation pyramid

Thus, the formulation pyramid is modified as we replace a photoinitiator (whether it is a polymeric photoinitiator or the more common low molecular weight derivative) with the acrylate/photoinitiator functional resin.

It is noted that this approach, as exemplified by LEX 201, differs significantly from a simple polymeric photoinitiator (which lacks reactive acrylate groups). Without the extra acrylate functionality, the ability to get locked into the matrix is more challenging, since one needs to rely purely on the photoinitiator radical to serve as a bonding point to the polymer matrix.

As will be shown, there is merit in the new approach of having photoinitiator moieties chemically anchored onto a high molecular weight (reactive) polymer. With this approach one gets to the goal of high cure efficiencies, final end properties and most importantly negligible extractables.

Physical property characterization

Table 5 summarizes the physical properties of the LEX 201. It is a viscous amber colored liquid. The dual functional polymer bound photoinitiator has a molecular weight greater than 1000 g/mole. It is a viscous liquid at room temperature. A low migrating diluent, ethoxylated TMPTA at 30 wt % was used to lower its viscosity. In the uncured state the LEX 201 has a viscosity of 120,000 to 160,000 cps. It forms an amorphous glass (non-crystallizing) at low temperature, with a glass transition temperature of -27 °C.

The neat LEX 201 is photocurable “as is”. Namely, it is not necessary to add photoinitiator to it, since it has covalently linked photoinitiator moieties on it. Some of the salient photocured properties of the LEX 201 are given in Table 5. It has a Tg of 69 °C (DMA). Its room temperature modulus of 1030 MPa with an elongation-to-break value of 8%. The photocured LEX 201 also showed very high gloss and hardness.

Table 5. Physical property summary of LEX 201

Appearance	viscous amber liquid
Molecular weight	> 1,000 g/mol
Refractive index (Abbe, 20°C)	1.512 ±0.001
Viscosity at 20°C	120,000 – 165,000 cps
Viscosity at 60°C	4,000 – 4,500 cps
Tg (Uncured)	-27 °C (broad transition)
Tg (Cured), peak of tan δ	69 °C
Elongation to break (Cured)	8%
Young's Modulus (Cured)	1030 MPa
Gloss (Cured)	114.4 (60 degrees)
König Pendulum Hardness (Cured)	132
Solid content	70% in TMPEOTA

Electronic absorption spectra

Knowledge of the UV spectrum of a photoinitiator is very important. It helps us to identify which lamps are needed and what concentration of the photoinitiator should be used for a given application.

As given in Figure 3, the absorbance spectrum of LEX 201 shows that it has a strong $\pi\pi^*$ transition around 270 nm and also an $n\pi^*$ transition at 320-370 nm. The absorption spectrum is typical for an alpha-hydroxy ketone type initiator.

Based on these results we would expect to use more LEX 201 to get similar optical densities as with other standard low molecular weight AHK type photoinitiators.

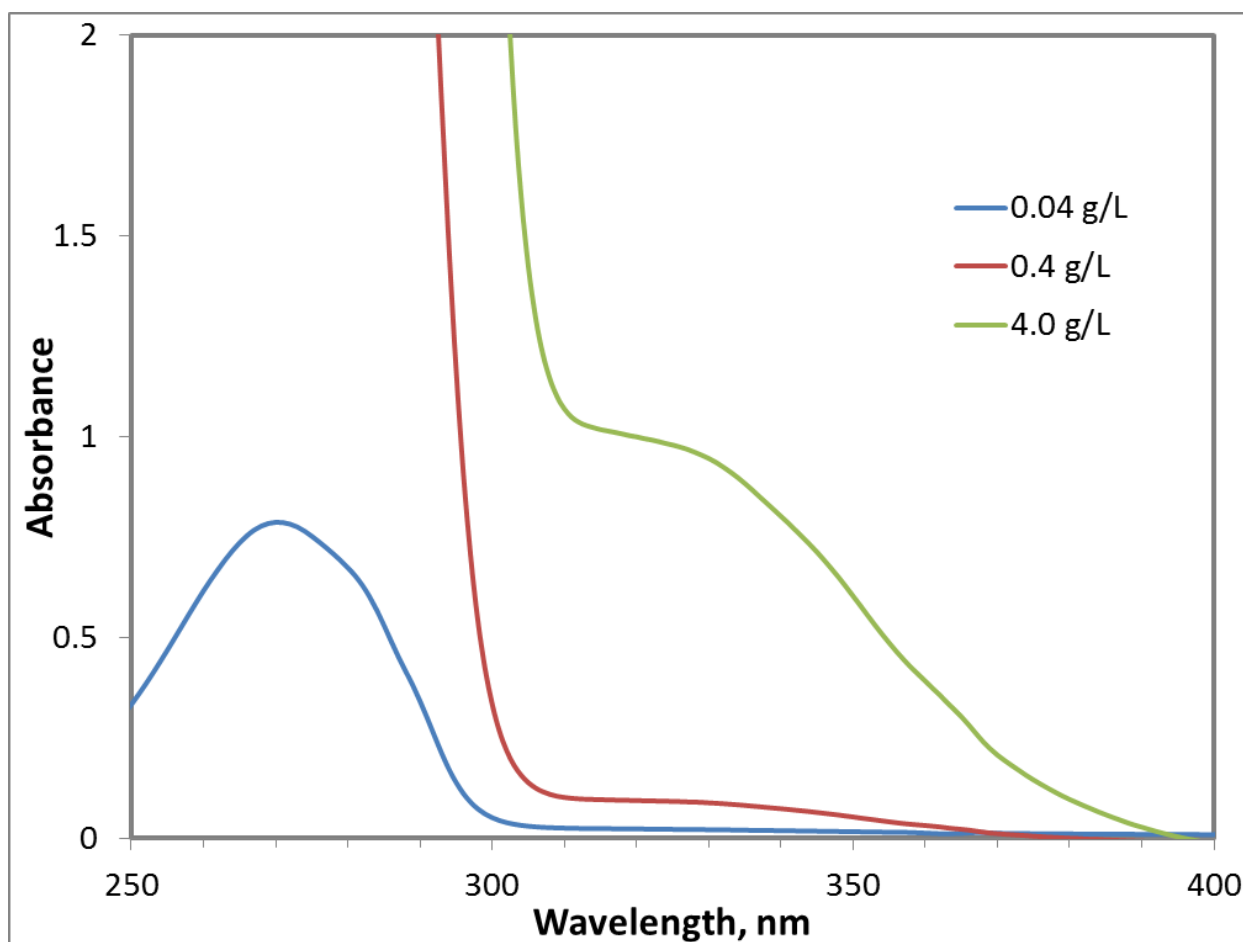


Figure 3. Electronic absorption spectra of LEX 201 at various concentrations in tetrahydrofuran.

Viscosity and effect of heat aging

The viscosity of the dual functional LEX 201 decreases exponentially with increasing temperature, as shown in Figure 4. For example, at 22°C the viscosity is 1520 poise, which decreases to 44 poise at 60°C.

Since it is a reactive resin, it is of interest to know how the viscosity changes after heat aging. The effect of heat aging (2 weeks, 70°C) is actually minor. This result is also consistent with the room temperature storage for over one year, where the viscosity increased by only 10%. It is further noted that no apparent change in color or photoactivity was seen on the room temperature stored material. Thus, the LEX 201 was found to have good storage stability.

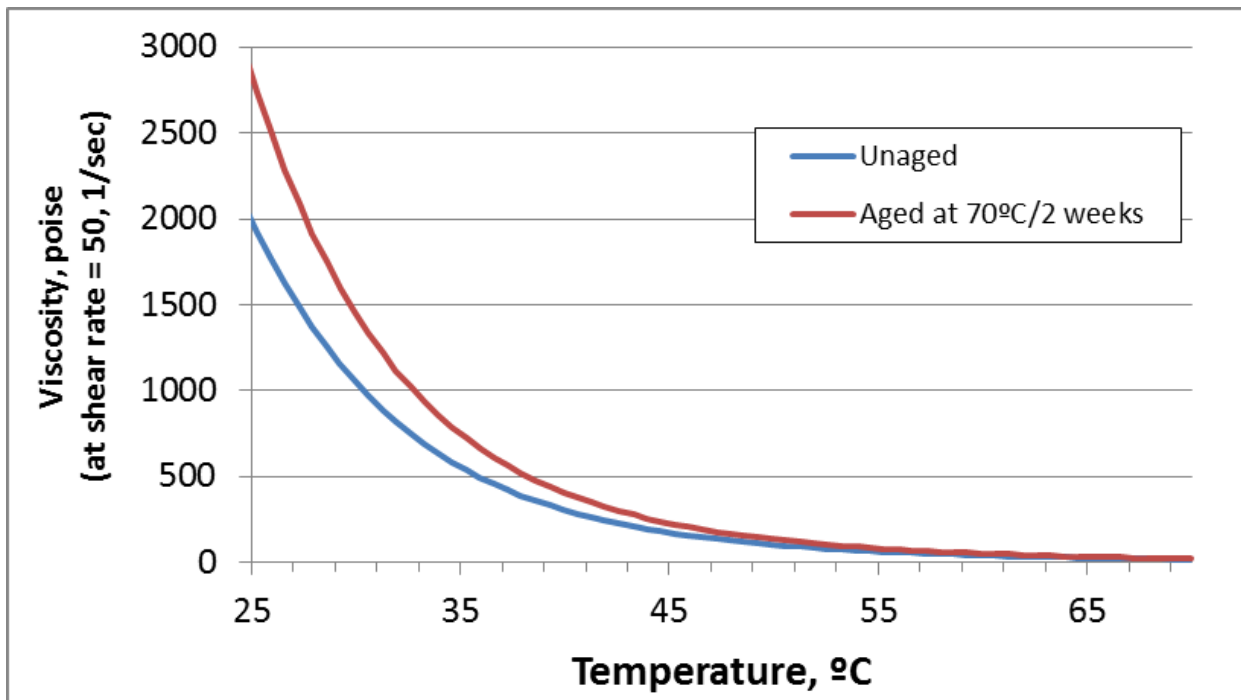


Figure 4. Viscosity of LEX 201 (before and after aging at 70°C for 14 days)

Compatibility/Miscibility in common solvents/diluents

The liquid LEX 201 is compatible with most resins, as shown in Table 6. This feature means less work in mixing the LEX 201 into the resin. Because it is a liquid, one can also avoid issues of agglomeration, which may be seen with other lower molecular weight solid photoinitiators.

Table 6. Solubility of LEX 201 in common monomer/resins

Solvent/monomer	Solubility/Miscibility at 22°C
Acetone	> 50 wt%
Ethyl acetate	> 50 wt%
TMPEOTA	> 50 wt%
Epoxy acrylate	> 50 wt%
Amino triacrylate	> 50 wt%
Water	Insoluble

Thermo-mechanical properties of photocured LEX 201

Photocured LEX 201 is ductile and strong, as shown in the stress-strain curve (Figure 5) and DMTA plots given in Figure 6.

It was found that when fully cured LEX 201 has high gloss (114, at 60 degrees) and hardness (König pendulum hardness = 132 revolutions). It also has a relatively high temperature for its “glass transition” or Tg. In this case the peak of tan delta = 69 °C., which means it can be safely used in standard hard coatings.

The fully cured neat LEX 201 also has good cross-link density⁹ without too much brittleness. This is based on its good elongation to break (8%) at room temperature and high storage modulus of 1100 MPa (below 50 °C). Even above the Tg (peak of tan δ) the fully cured LEX 201 showed a high equilibrium modulus of 12 MPa (above 130 °C), indicating good network structure.

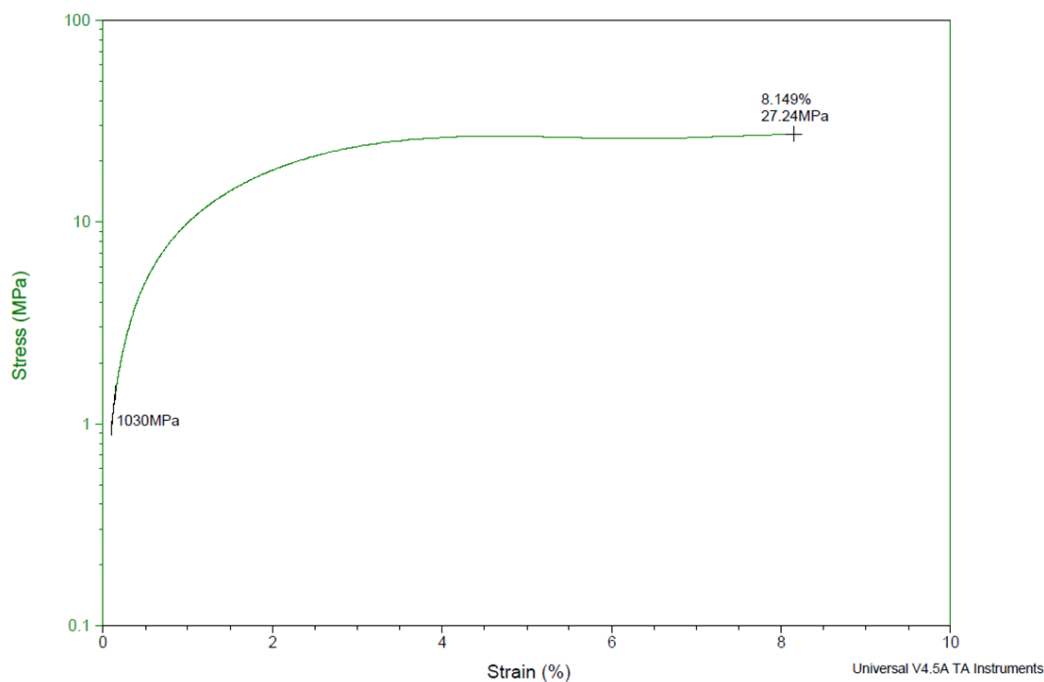


Figure 5. Stress-Strain curve of the photocured LEX 201 (room temperature)

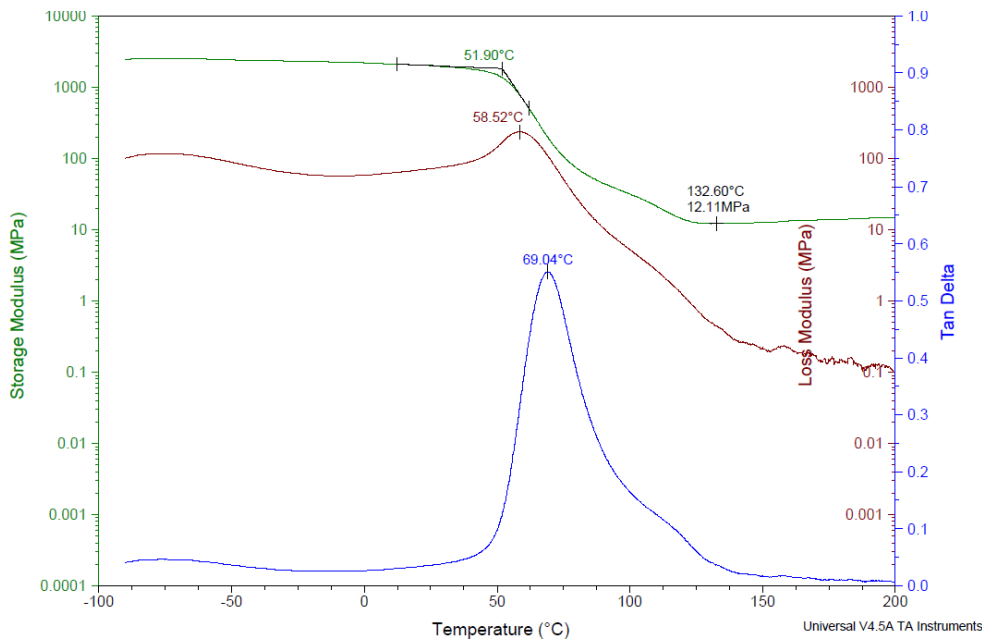


Figure 6. DMTA of photocured LEX 201.

Stain-resistance properties

In keeping with the attractive thermo-mechanical properties of the photocured LEX 201, we also found excellent solvent and stain resistance. The photocured LEX 201 coating showed high solvent resistance (> 100 MEK double rubs). This result indicates LEX 201 provides structural integrity (unlike a plasticized or nonreactive polymer), which is consistent with the DMA results.

The photocured LEX 201 also passed several key stain tests, as given in Table 7. To pass the stain tests the material needs to show no change after 1 hour of contact with the staining agent. Namely, a “pass” is when after 1-hour exposure there were 1) no discoloration or staining, and 2) no change in apparent gloss of the coating. As given in Table 7, photocured LEX 201 passed the stain tests.

Table 7. Stain resistance testing of photocured LEX 201

Staining Agent	Result
Mustard	pass - no staining or visual change in the coating
Skydrol (hydraulic fluid)	pass - no staining or visual change in the coating
Grape juice	pass - no staining or visual change in the coating
10% Hydrochloric acid	pass - no staining or visual change in the coating
5% Nitric acid	pass - no staining or visual change in the coating

From these physical property assessments we learned that the LEX 201 is an amorphous viscous liquid, which has high compatibility in the common UV curable resins. By itself, it can be photo-excited in the UVA spectral region. We also learned that it is photocurable and forms a tough high gloss film with high solvent resistance.

We are now interested in using the LEX 201 as an active component in OPV and inks. To this end we are interested in how LEX 201 behaves (as a resin component) in the formulations, and what level is needed to get a good photocure response. We are also interested in demonstrating that it does not migrate in the cured coatings.

Formulating with LEX 201 in common OPV formulations

The effects of using the LEX 201 in standard OPV type formulations are summarized in Tables 8. As expected it was found the viscosity increased due to the addition of the LEX 201. This viscosity increase can be compensated for by adding a low migrating, low viscosity acrylate, such as LR 8863 (EOTMPTA).

For the epoxy OPV we see the expected high double bond conversion and high MEK solvent resistance. This means that LEX does not change these key properties in a negative way. The faster curing polyether OPV is similar, but in this case its MEK resistance is lower than the cured epoxy OPV. This result also is consistent with the chemical nature of the final coating.

Table 8. Summary of properties using LEX 201 in an epoxy acrylate formulation

Sample	Composition	Viscosity (cP) at 22°C¹	% double bond conversion^{2,3}	MEK double rub
1	Epoxy Acrylate OPV	135		
2	Epoxy formulation (195 p) + LEX 201 (34 p)	411	80 to 90	100
3	Polyether Acrylate OPV	267		
4	Polyether Formulation (272 p) + LEX 201 (49 p)	683	80 to 90	18
5	Low Viscosity Polyether OPV	58		
6	Low Viscosity Polyether formulation (170 p)+ LEX 201 (30 p)	187	80 to 90	40

¹⁾ Brookfield, with a #3 spindle at 100 RPM

²⁾ Double bond conversion measured from FTIR spectra

³⁾ OPV's were photocured using Fusion 600 W D bulb, at 5 micron thickness over aluminum panels, at UV exposure = or < 0.9 J/cm²)

Photocure response comparison to common AHK photoinitiators

It is now of interest to compare the photocure speed of the LEX 201. It is noted that to match optical densities of the initiating chromophore a higher amount is needed for the higher molecular weight LEX compared to the lower molecular weight small molecule photoinitiator.

As given in Figure 7 (for the Epoxy OPV) and Figure 8 (for the Polyether OPV), the photoresponse in a formulation can be matched using approximately 3 to 4 times of LEX compared to low molecular weight (200 – 300 g/mole) AHK photoinitiators.

It is important also to note the photocure response increases as more LEX 201 is used. These results demonstrate that no negative quenching effect occurs when using the LEX 201 at high concentration.

It is also important to probe the double bond conversion, which reflects how well a particular photoinitiator can affect photocuring. As given in Figure 9, a good match in photocure of the resin is seen for LEX 201 as well as for the standard low molecular weight photoinitiators as the UV light exposure is varied. Noting that LEX 201 has a high molecular weight, we might have expected a lower double bond conversion, due to slowed radical pair dynamics compared to the competing effects like oxygen quenching. What is seen is that this potentially negative effect is well managed in the systems examined. It suggests that this is a result of the fact the LEX 201 resin contains acrylate moieties and not just photoinitiator moieties alone.

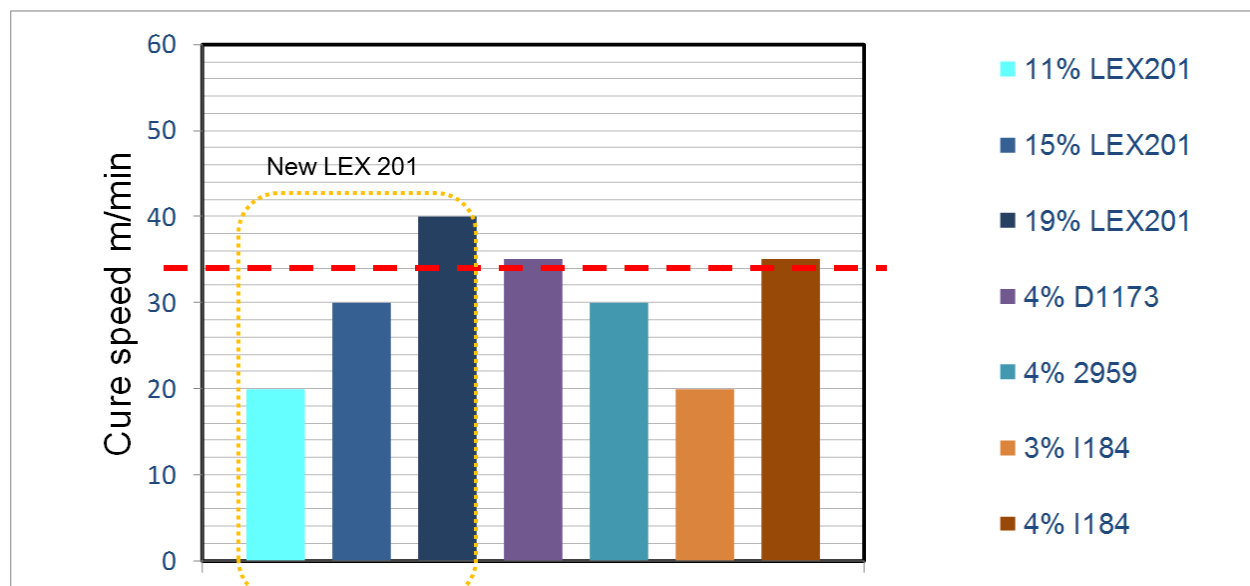


Figure 7. Effect of photoinitiator on cure speed of a standard epoxy acrylate formulation (thickness 6 μ m, Leneta cardboard, 200W/cm Alu)

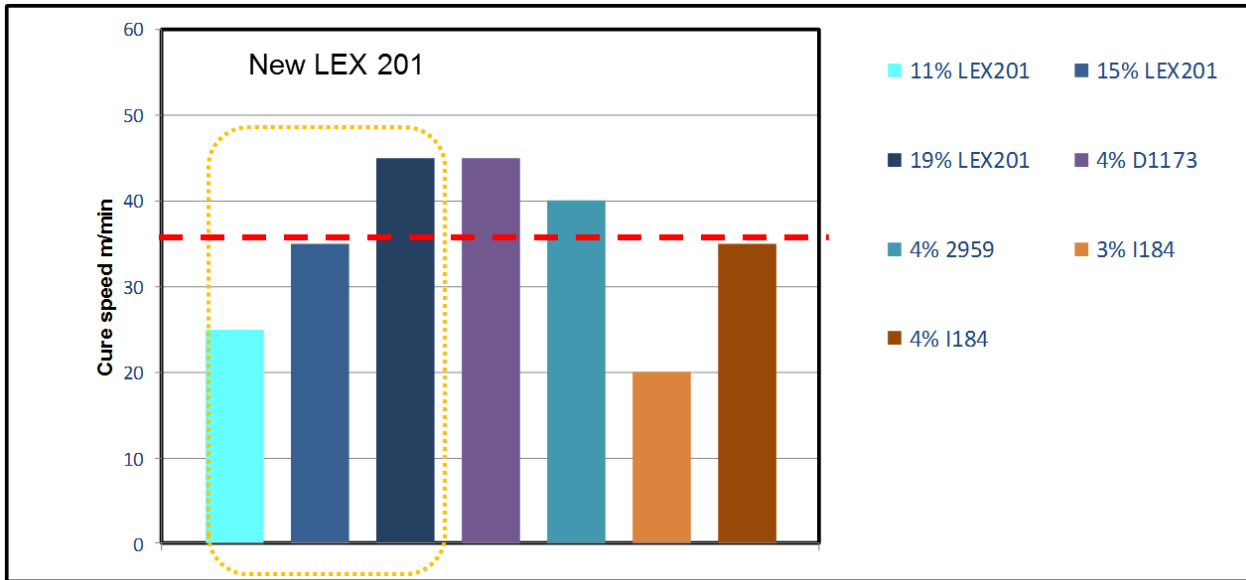


Figure 8. Effect of photoinitiator on cure speed of an amine modified Polyether OPV, thickness 6 μ m, Leneta cardboard, 200W/cm Alu

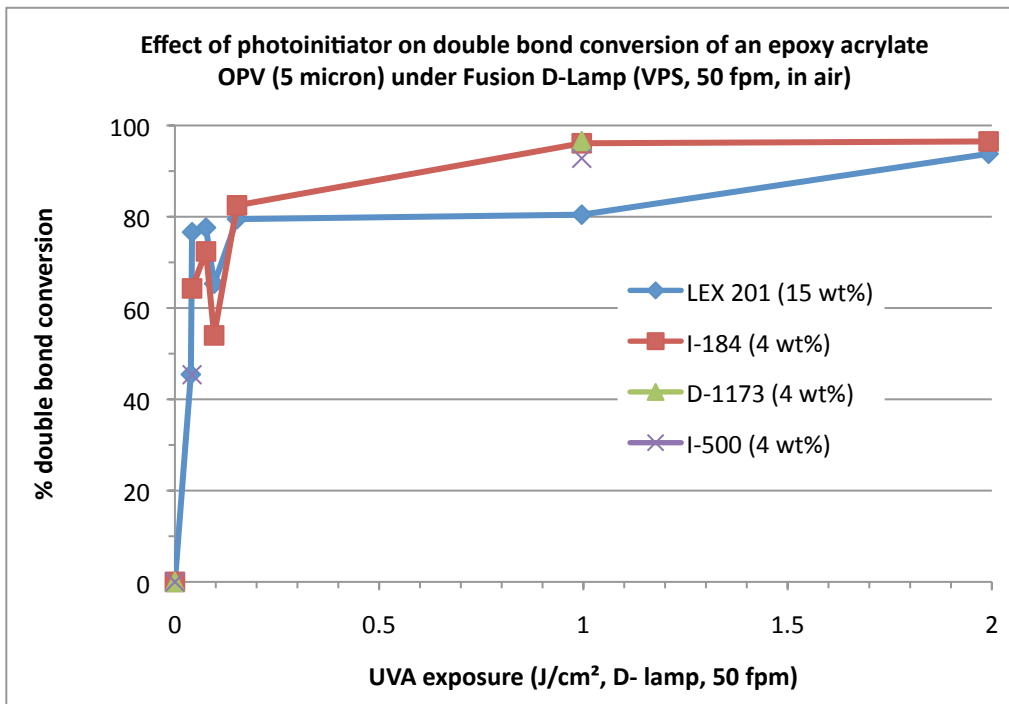


Figure 9. Effect of photoinitiator on acrylate double bond conversion for an epoxy acrylate OPV.

In summary, the photocure response studies show that at equal chromophore concentration a similar cure speed is seen with the LEX 201 as compared to low molecular weight photoinitiators. At issue now is demonstrating the low migration nature of the LEX 201.

3.4. Migration and extraction - comparison between LEX 201 and common AHK photoinitiators

To this end two experiments were devised to test migration. The first test is the so-called “set-off migration” and the second, which is arguably more severe, was chloroform solvent extraction.

3.4.1. Set-Off Migration

Set-off migration is an extremely important test, to determine whether a component in an ink or coating can transfer from one surface to another, which simulates the conditions in a printed reel, where a printed ink layer is in contact with the back side of the substrate which later might come in contact with the packed goods. The methodology we used was:

- Set of printed samples is covered with LDPE film and stored at 40°C for 10 days to simulate situation on a printed reel or stack
- Extraction of LDPE film with 95% Ethanol at 70°C/2h
- HPLC analysis

For these set-off experiments we used 15 wt% LEX 201 versus 5 wt% AHK-3. The results given in Table 9, show that LEX 201 did not migrate but the AHK-3 did. This is significant since the AHK-3 is considered a standard in the industry for low migration. The LEX 201 surpassed the performance of the AHK-3. It also suggests that the LEX 201 is efficiently bound to the network (making migration of it negligible).

Table 9. Set off migration of photoinitiator from a photocured epoxy OPV and polyether OPV

OPV type, and photocure speed	LEX 201 (ppb into food)	AHK-3 (ppb into food)
Epoxy OPV, 30 m/min	not detected	1
Polyether OPV, 60 m/min	not detected	1.4

Chloroform extraction: LEX 201 versus HCPK

To further test this idea of the efficiently bound LEX 201 we used an aggressive solvent extraction test. In this case we used chloroform (CHCl₃) as the solvent.

Table 10. Recovered photoinitiator from extraction of a fully cured (high light exposure) epoxy acrylate varnish, with thickness of 5 micron over aluminum substrate

Photoinitiator (wt% used in OPV)	D-Lamp UV exposure (J/cm ²)	benzaldehyde extracted (ppm)	Photoinitiator detected, wt% (ppm detection limit)
LEX 201 (15%)	2.208	0	0
LEX 201 (6%)	2.208	0	0
HCPK (11 wt %)	2.208	5466	30
HCPK (4 wt %)	2.208	2543	13

Table 11. Recovered photoinitiator from extraction of a partially cured (low light exposure) epoxy acrylate varnish, with thickness of 5 micron over aluminum substrate

Photoinitiator in epoxy OPV	D-Lamp UV exposure (J/cm ²)	benzaldehyde extracted (ppm)	PI detected, wt% (ppm detection limit)
LEX 201 (15%)	0.086	0	0
LEX 201 (6%)	0.086	0	0
HCPK (4 wt %)	0.086	330	87
HCPK (4 wt %)	0.086	550	85

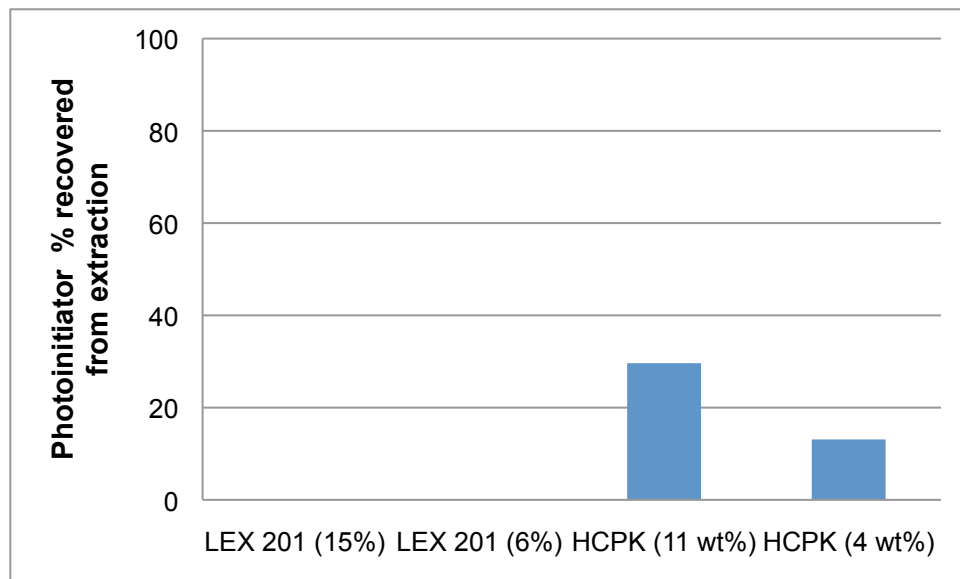


Figure 10. Photoinitiator extracted from OPV with CHCl₃, (ppm detection limit). OPV photocured at high conversion (> 80% double bond conversion) Light exposure = 2.208 J/cm² J/cm² D-Lamp (2 passes 100% Power, 50 fpm), DFT 5 micron over Al

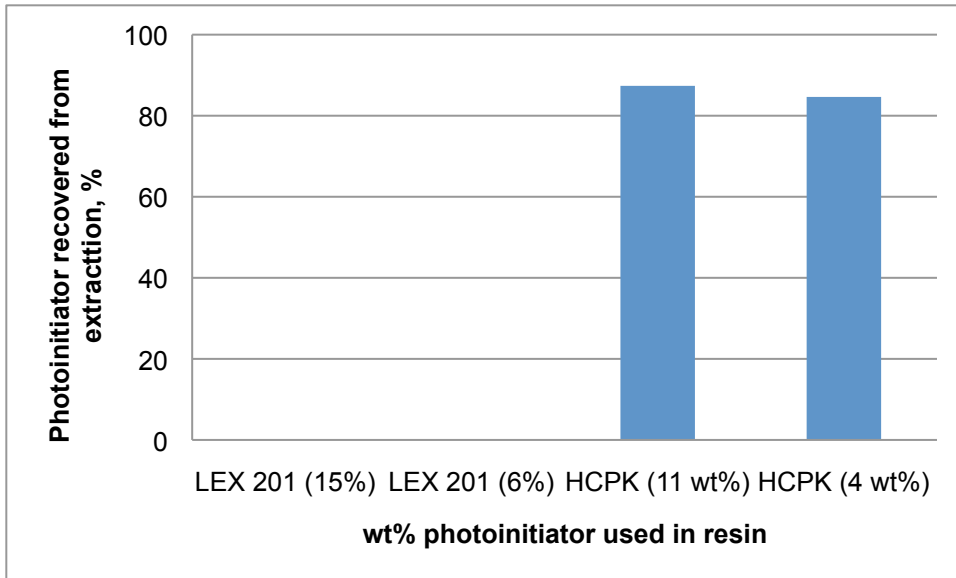


Figure 11. Chloroform extraction of photoinitiators from partially cured coatings. Photoinitiator extracted from OPV, (ppm detection limit) using low exposure to cure (maximum double bond conversion of 70%) used 0.086 J/cm² from Fusion D-Lamp (30% Power, 50 fpm), DFT 5 micron over Al

From the extraction data it was found that LEX 201 did not extract even under low UV light exposure (0.086 J/cm²). In contrast, HCPK generated benzaldehyde and easily extracted under the same conditions.

More benzaldehyde was generated at higher exposure when using HCPK, as found under high UV exposure conditions. The higher benzaldehyde seen is presumably because acrylate consumption was higher, which would leave the photogenerated acyl radicals from HCPK to either recombine or abstract a hydrogen. The benzaldehyde would be a hydrogen abstraction by-product.

No benzaldehyde was detected when using LEX 201, either under low or high light exposure conditions.

Thus, higher light exposure ensures more complete cure the acrylate resin, but for low molecular weight photoinitiators one can expect an increase in secondary photo by products. This is not the case when using LEX 201. No detectable extraction of it was seen.

In summary, Irgacure LEX 201 did not extract even for fully cured and most importantly did not extract in significantly under-cured OPV coatings. The extraction results are consistent with the lift-off migration studies (which also showed it was not migrating, below < 10 ppb)

LEX 201 for inks and other applications

For UV inks one is generally interested in good uniformity of cure. Because of the presence of pigments there is an optical gradient and less light exposure occurs at the bottom of the ink compared to the top

surface. For this reason, one generally uses a photoinitiator (like an alpha hydroxyl ketone AHK or benzophenone Type II) to target surface curing while the more red shifted photoinitiators (like the alpha aminoketone AAK or the photobleachable acylphosphine oxides (MAPO or BAPO)) provide through-cure.

For low migration or low odor sensitive ink applications the standard AHK or benzophenone types would be inappropriate for the surface cure photoinitiator, whereas the LEX 201 would be.

In this regard it is of interest to compare the photoresponse of an ink using LEX 201 as the surface cure initiator. As given in Figure 12, a good photocure response was seen using LEX 201 in combination with AAK-3 (I-379) and/or with BAPO (I-819).

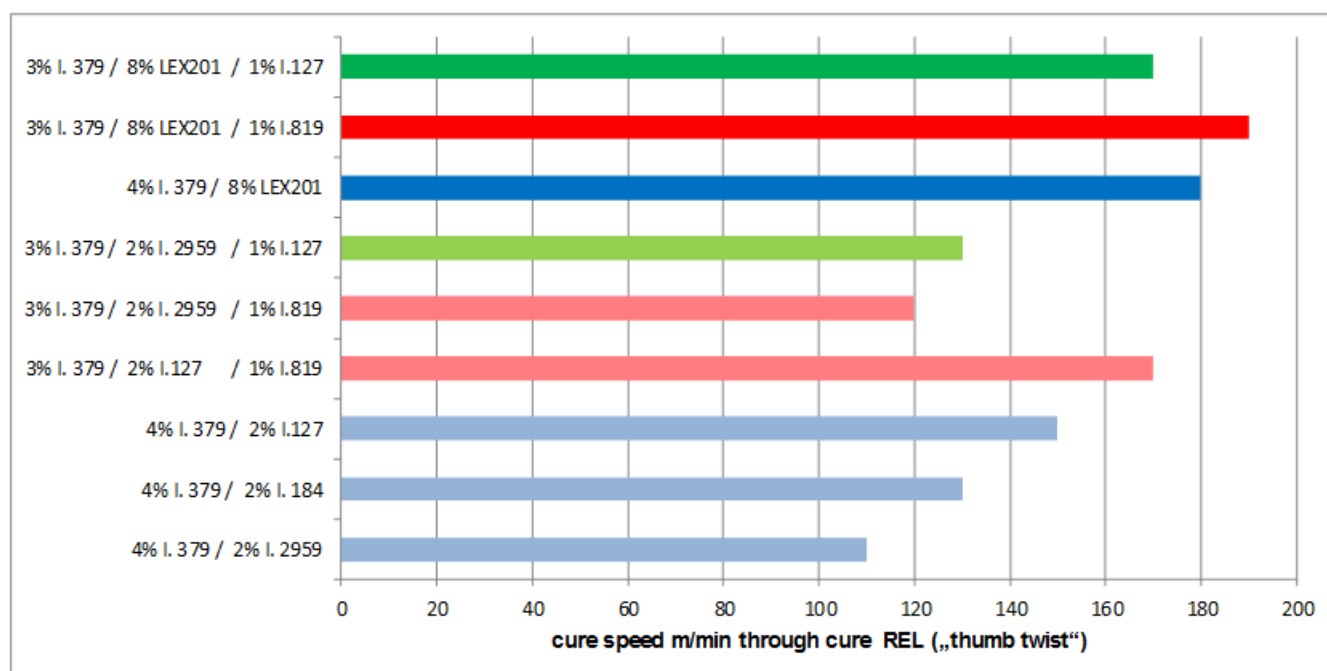


Figure 12. Ink photoresponse – comparison of photoinitiators in Cyan Flexo Ink (200W/cm printed @OD 2.5)

Because of the dual nature of LEX 201, we expect many other applications where it can be useful. For example, it could be a bridge for UV/EB applications. This could be done because LEX 201 would be curable under either direct electron beam (EB) excitation or direct UV light excitation. The potential benefit for this feature in low migration applications would be for lowering nitrogen use in EB (thus improving cost in use), since surface sealing with the LEX 201 would be possible in a combined UV+EB process.

We also expect the high toughness and solvent resistance properties of the Irgacure LEX 201 could be used in many coating applications, such as for wood or composites.

4. Conclusions

- LEX 201 is a dual functional polymer, which contains both acrylate and photoinitiator moieties
- LEX 201 showed negligible migration, excellent gloss and low odor
- LEX 201 may be used as a replacement of conventional alpha-hydroxy ketone photoinitiators for UV light curing of coatings and inks for indirect food contact applications

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