

Design of new 3-ketocoumarins for UV LED curing

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Abstract

Light emitting diodes (LED) are becoming a valid alternative to Hg lamps in most radiation curable applications. Matching photoinitiator absorbance with the operation wavelength of the LED source is crucial.

In this paper, we will describe how is possible to modify the physical-chemical properties of the 3-ketocoumarins and how such modifications influence the reactivity. We will be able to design new 3-ketocoumarines with good solubility, high reactivity and low yellowing for clear and pigmented coatings. These new molecules were always compared to thioxanthenes and acylphosphine oxides, which are the only two classes of photoinitiators that show good performances at 365 and 395 nm¹ (most powerful operation wavelength for LED).

Introduction

Among the light radiation sources used in UV curing, light emitting diodes (LED) have been the subject of significant development over the past few years because of the advantages of low temperature operation, extremely long life, instant start and low energy consumption in comparison with conventional medium pressure mercury lamps. Unfortunately, while these lamps provide a series of line outputs which cover all the UV spectrum, commercial LED lamps output is a single peak centered at 365 nm or 395 nm (most powerful) with a very narrow bandwidth. Therefore, formulating for LED lamps requires photoinitiators that absorb most efficiently in the range of 365 nm and 395 nm, since these are the only outputs of most of LED lamps.

Up to now the most commonly photoinitiators used in this field, belong to the classes of thioxanthenes (ITX) and acyl phosphine oxides (TPO, BAPO).

Unfortunately, the thioxanthone derivatives, commonly used as sensitizers and photoinitiators, are prone to yellowing upon exposure and this strongly limit the use of such derivatives in all the applications in which color stability is mandatory, e.g. graphic arts.

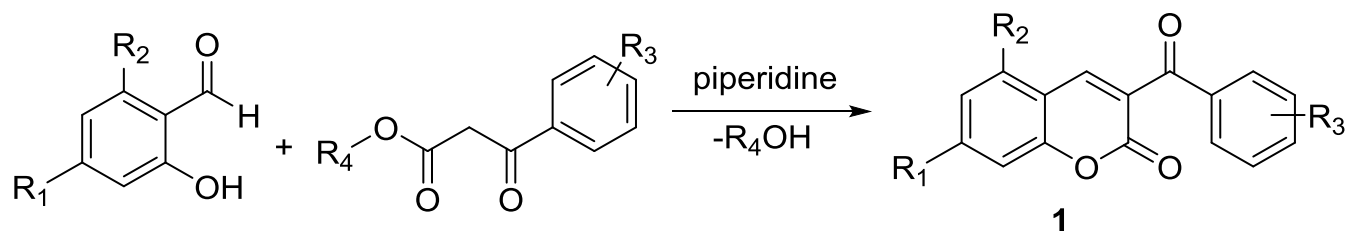
Acyl phosphine oxides photoinitiators, on the other hands, when cured under air, are very sensitive to oxygen inhibition and do not give surface cure, leaving a tacky surface.

Therefore, there is an increasing demand for the development of different photoinitiators absorbing in the region between 360-400 nm, having a good photochemical activity, low oxygen sensitivity and yellowing. In this paper, we describe how to modify the photophysical properties of 3-ketocoumarins to create a new class of photoinitiators for LED lamps.

Results and Discussion

Synthesis

The 3-ketocoumarin derivatives are easily prepared by the condensation of salicylaldehyde derivatives with β -ketoesters²



The substituents R₁, R₂ and R₃ in **1** can be widely varied. Several derivatives have been prepared as reported in Table 1.

	R ₁	R ₂	R ₃	ε value (395nm)
LFC3220	OCH ₃	H	t-but	835
LFC2887	OCH ₃	H	H	925
LFC3224	OCH ₃	H	SR ₆	1470
LFC3260	OCH ₃	OCH ₃	t-but	3894
LFC3228	OCH ₃	OCH ₃	H	4332
LFC3221	H	naphthalene	t-but	5774
LFC3218	H	naphthalene	H	6484
LFC3195	Julolidine	H	H	8530
LFC3226	SR ₅	H	H	9411
LFC3191	NEt ₂	H	H	24641

Table 1. Molecular structures and ε values at 395 nm of the new 3-ketocoumarins

Absorption Spectra

As shown in Figure 1, the ketocoumarins have absorption maxima ranging from 340 nm and 450 nm in acetonitrile and the ε value at 395 nm is enhanced when an electron-donating group is on the phenyl ring or coumarin ring. The highest values are reached with the amine substitution on the coumarin nucleus (Table 1).

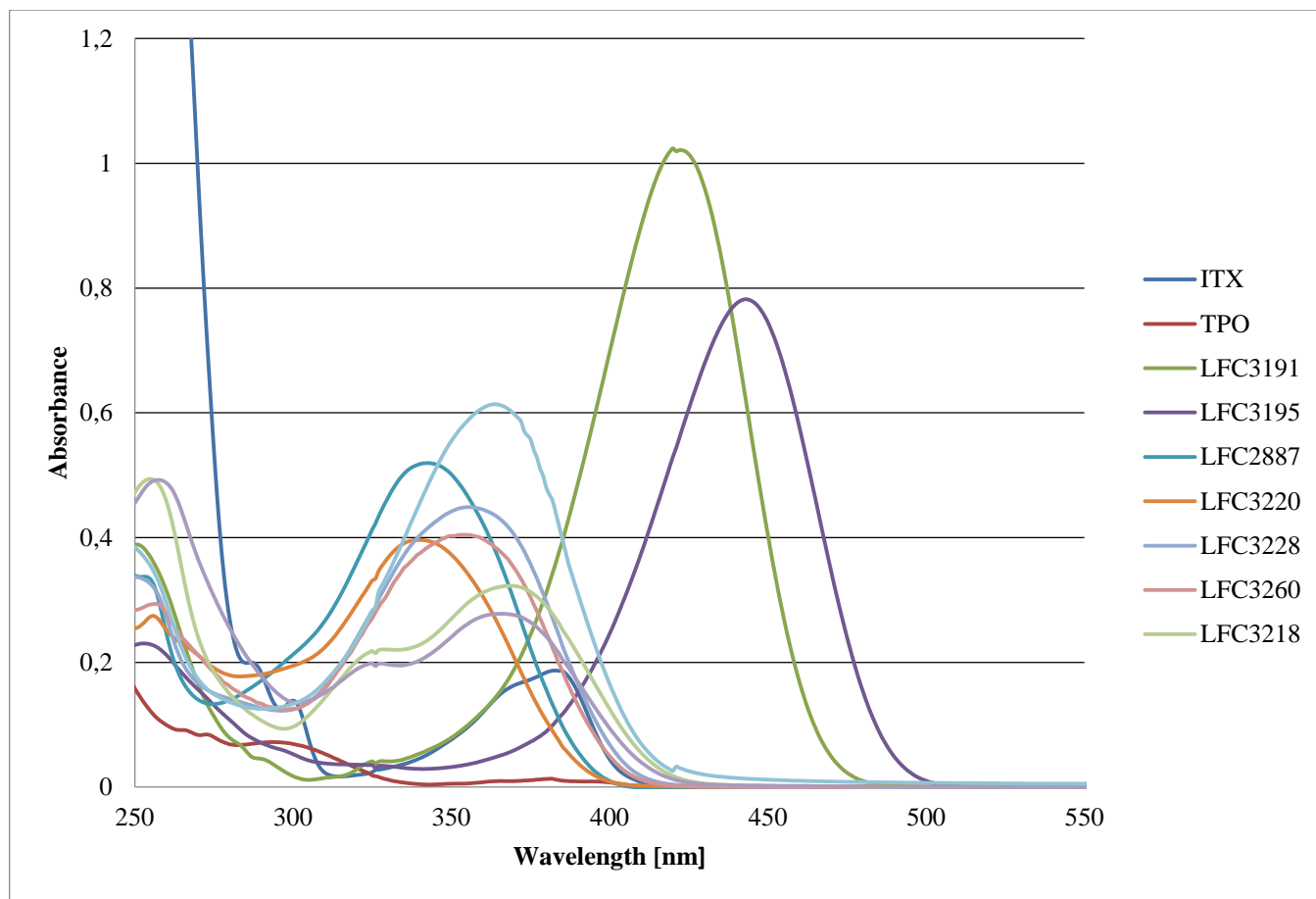


Figure 1. UV-Vis Spectra in Acetonitrile 0.001% w/w.

UV-LED Curing Tests

The first test for the evaluation of the new 3-ketocoumarins reactivity was performed by the measure of the double bonds conversion (1407 and 810 cm^{-1}) by FT-IR in a clear coating.

The photopolymerizable compositions for the test were prepared dissolving the photoinitiator and the coinitiator (Ethyl-4-dimethylamino benzoate, EDB) at a concentration of 3 % by weight each in a mixture 99.5:0.5 wt of bisphenol A epoxy diacrylate and silicone diacrylate. The LED source used was an LX400+ system equipped with a UVLED spot centered at 400nm (Excelitas).

Isopropyl Thioxanthone (ITX) and Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) were used as reference.

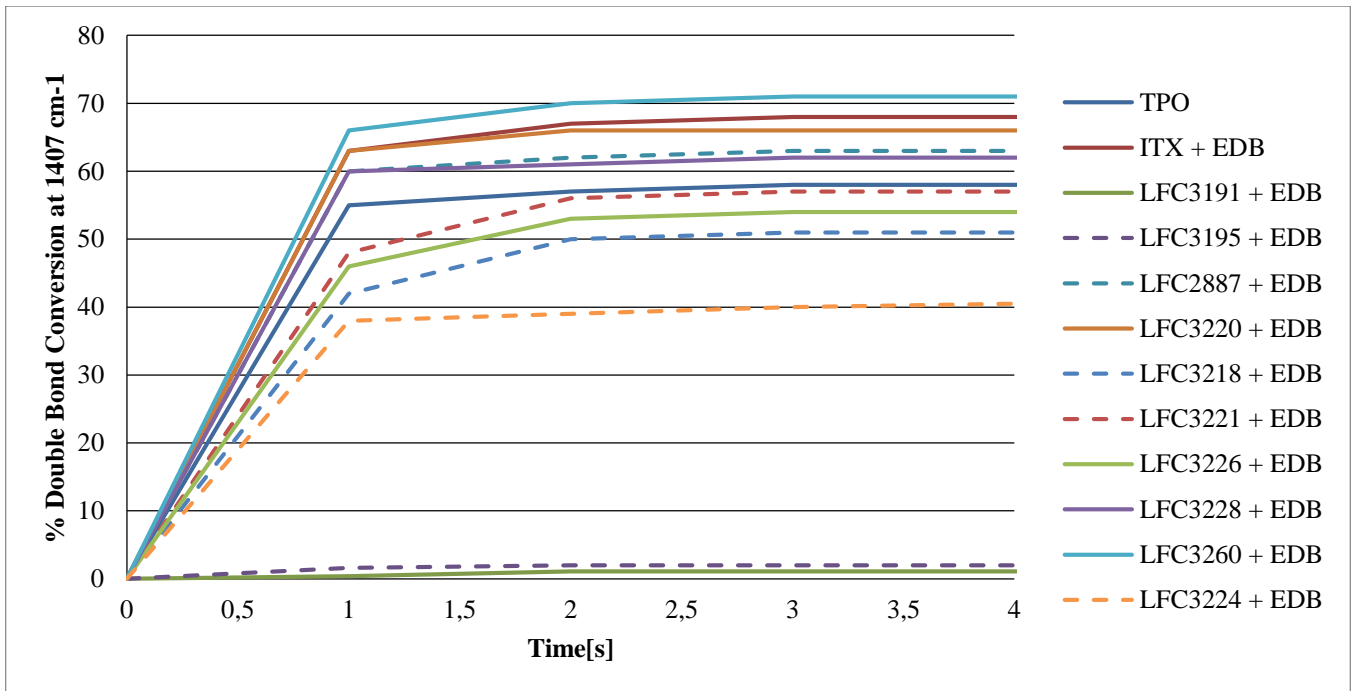


Figure 2. FT-IR at 400nm in clear coating. Conditions: PE substrate, 6 μm thickness, under air.

From Figure 2 we can observe that the most reactive molecule is LFC3260 (66% at 1'), then we have ITX and LFC3220 (63% at 1') and TPO (55% at 1'). The worst instead are the amine substituted ketocoumarins which are both under 5% of conversion.

We measure also the activity of these molecules in a cyan ink for inkjet printing, the concentration of the photoinitiator and the cointiator was 5% by weight each. The best performances are shown in Figure 3.

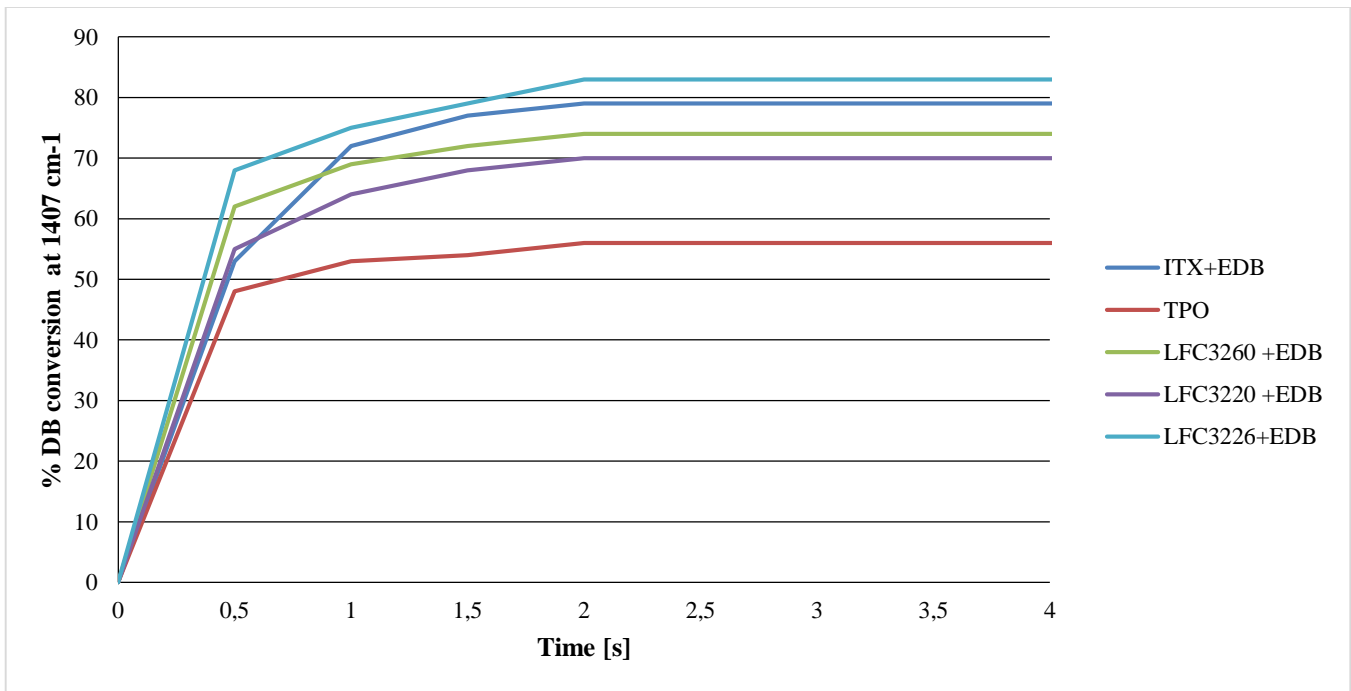


Figure 3. FT-IR at 400nm in cyan inkjet ink. Conditions: PE substrate, 12 μm thickness, under air.

The highest value of conversion is reached from the sulfur substituted ketocoumarin (LFC3226), while the worst is reached from TPO.

From Figure 2 and 3 it seems to be clear that ketocoumarins containing medium-strength (such as O, S) electron-donating groups are good candidate for working with LED at 395nm. The same result are also reached using an LED 365 nm lamp.

Therefore, the 3-ketocoumarins LFC3220, LFC3260 and LFC3226 were further evaluated. Through cure measures were performed at 395nm (4W) and 365 nm (12 W) in a cyan inkjet ink (Figure 4 and 5).

The solutions of photoinitiator and coinitiator were prepared at a concentration of 3 and 6% by weight each.

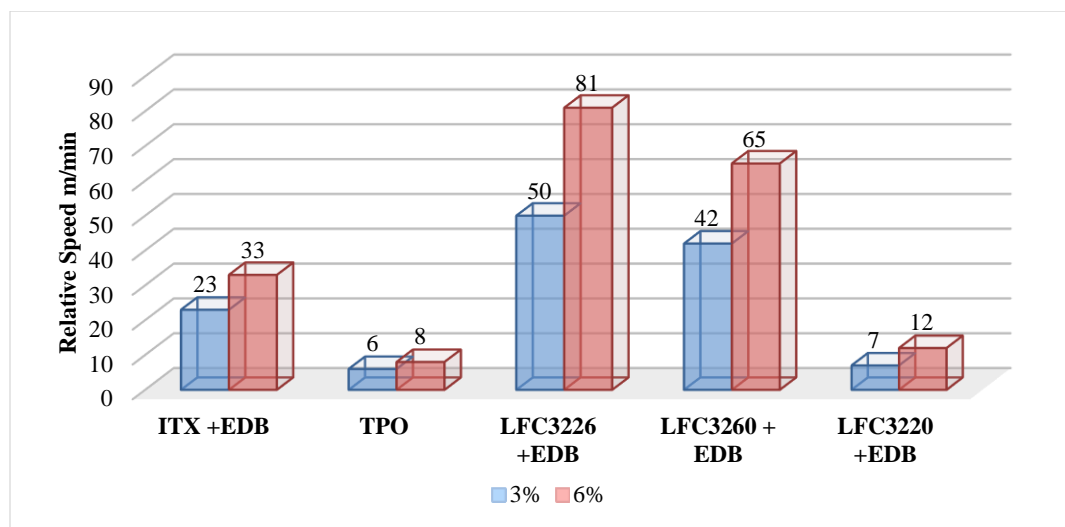


Figure 4. Through cure measurement at 395 nm in cyan inkjet ink. Conditions: cartonboard, 6 μ m thickness.

At 395 nm LFC3226 and LFC3260 show a reactivity much higher than ITX at both concentrations, while LFC3220 shows a reactivity similar to TPO (Figure 4). Despite the good reactivity, LFC3226, the alkylthio derivative, was rejected because of the yellowing (Figure 6 and 7).

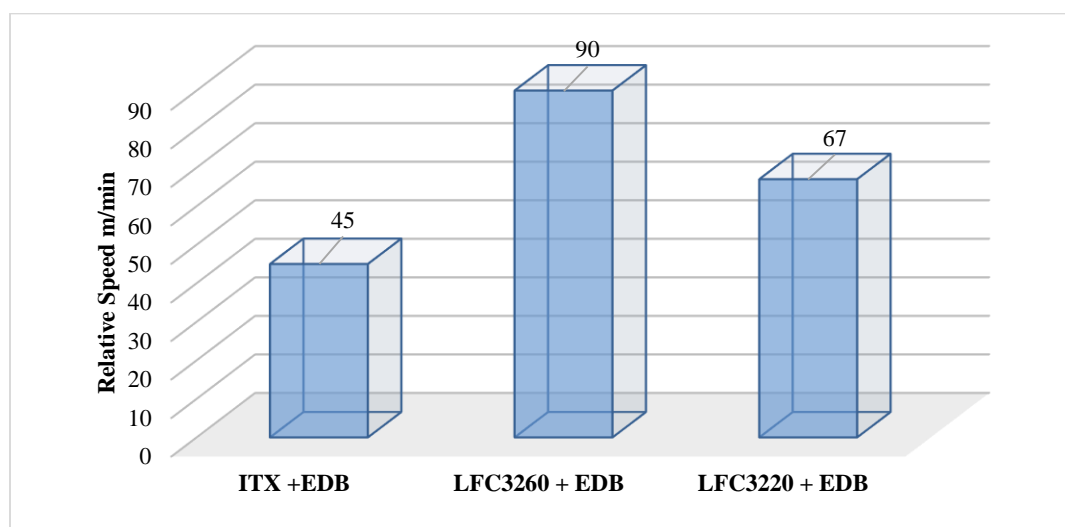


Figure 5. Through cure measurement at 365 nm in cyan inkjet ink. Conditions: cartonboard, 6 μ m thickness; PI and coinitiator concentration: 6% w/w.

At 365 nm LFC3260 is the best performer (Figure 5), it shows a reactivity twice than ITX, also LFC3220 shows a good reactivity, but significantly lower than LFC3260.

Yellowing

The color stability of LFC3260 and LFC3226 was also evaluated in clear ink for inkjet printing by a color guide BYK 45/0. The results are summarized in Figure 6.

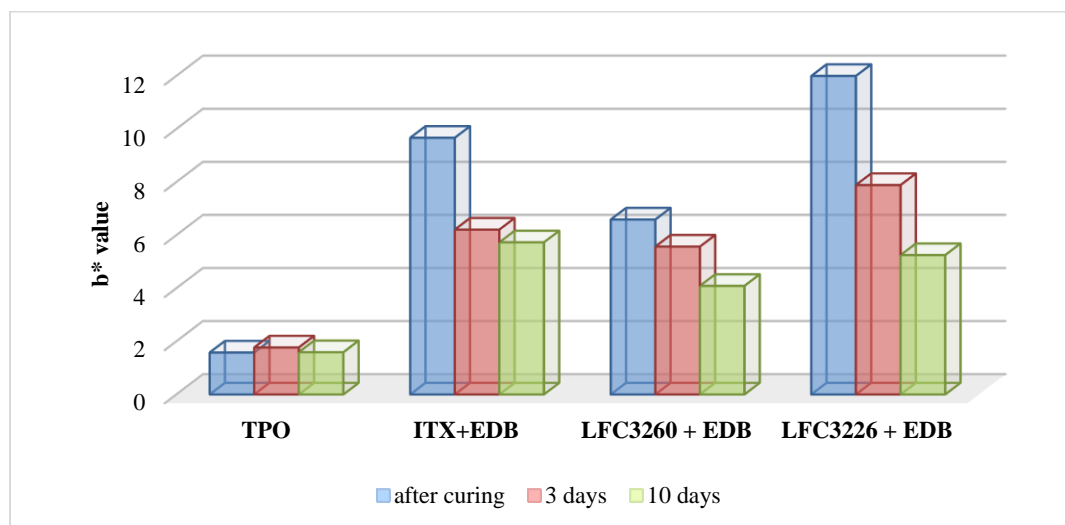


Figure 6. b^* value overtime. Conditions: 2 pass at 30 m/min, 16 W LED at 395 nm; cartonboard 6 μ m thickness; concentration: PI and coinitiator 3% w/w.

Both ketocoumarins show a yellowing higher than TPO, but while LFC3226 is also more yellow than ITX, LFC3260 shows values lower in all measurements.

An acrylated amine as coinitiator was also evaluated (Figure 7), the b^* value of LFC3260 was significantly reduced in comparison to that of LFC3226 and ITX.

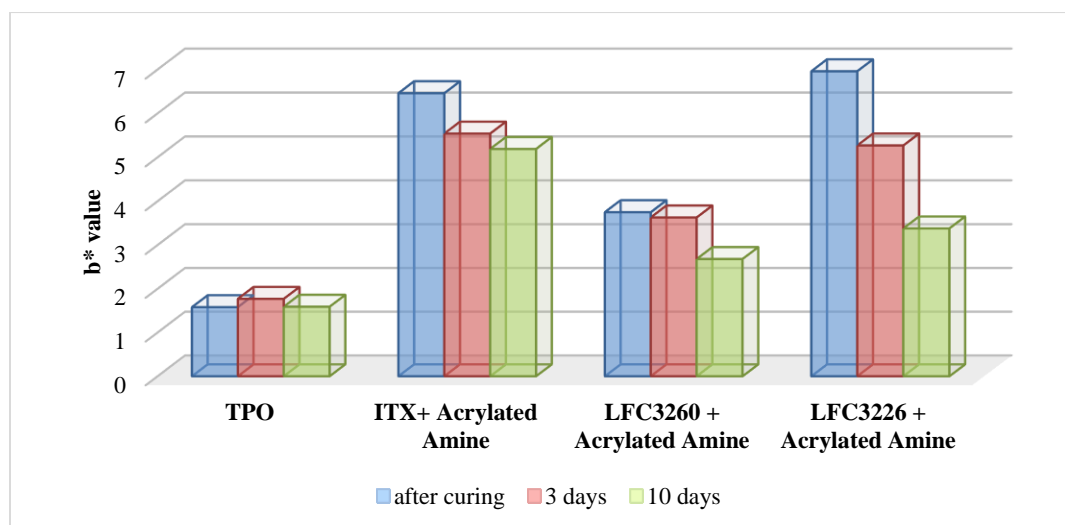


Figure 7. b^* value overtime. Conditions: 2 pass at 30 m/min, 16W LED at 395 nm; cartonboard 6 μ m thickness; Concentration: PI and coinitiator 3% w/w

Sensitization

To complete the characterization of the new ketocoumarins the ability of LFC3260 and LFC3220 as sensitizer for an aminoketone (2-Methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, Omnirad 4817) was evaluated.

The test was performed by FT-IR in a clear formulation (bisphenol A epoxy diacrylate/silicone diacrylate 99,5:0,5 by weight), with a concentration of PI at 4% and sensitizer at 0,5 by weight; an LX400+ system equipped with an UVLED spot centered at 400nm (Excelitas) was used as light source. (Figure 8)

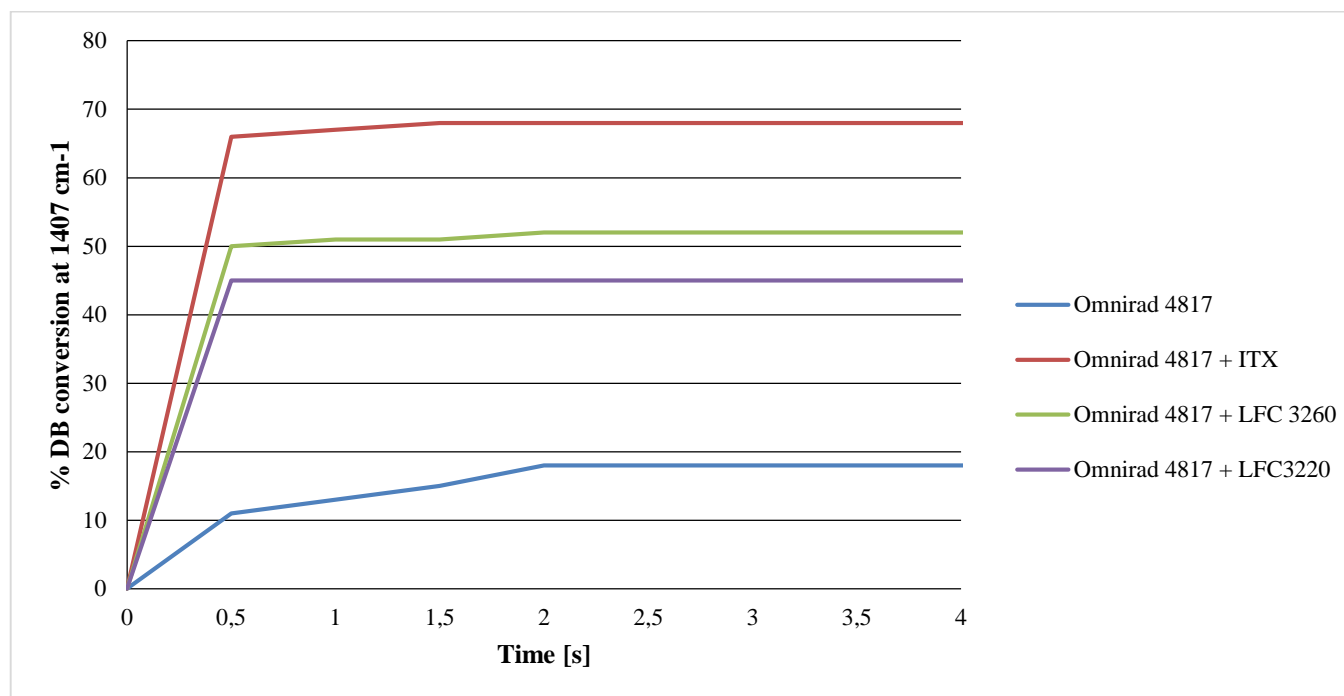


Figure 8. Sensitization effect measurement by FT-IR at 400nm.

These data, even if in clear coating seem to indicate a quite good activity of LFC3260 as sensitizer.

In conclusion, we were able to tune the absorption wavelength of the 3-ketocoumarins to balance absorption, reactivity and yellowing. The best 3-ketocoumarin is LFC3260, this molecule is strongly reactive in all tests. In fact, it shows a reactivity twice than ITX in through cure measurements at 395 nm and 365 nm and a significantly lower yellowing.

¹ Photoinitiators for UV LED, Lab Report Rahn AG, No. 2.02 June 2013.

² E. Knoevenagel, *Ber Dtsch. Chem. Ges* **31**, 2596 (1898); *Ibid.* **37**, 4461 (1904); E. Knoevenagel and S Mottek, *Ibid.* **37**, 4464 (1904); E. Knoevenagel and E. Langensiepen *Ibid.* **37**, 4492 (1904); E. Knoevenagel and R. Arnot *Ibid.* **37**, 4496 (1904); S. M. Sethna and N.M. Shah, *Chem. Rev.* **36**, 1 (1945); L. L. Woods and M. Fooladi, *J. Chem. Engng Data* **12**, 624 (1967); D. P. Specht, P. A. Martic and S. Farid *Tetrahedron* **38**, 1203 (1982).