

Strategies towards sustainable UV solutions with reduced hazard and reduced migration potential

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Abstract

With the ambition of reducing the hazards of UV systems, Sartomer showcase an innovative approach to UV curing that exploits a novel range of photoactive materials suitable for LED curing low migration applications. These novel materials show benefits of: enhanced film properties; ease of use through broad formulation latitude; reduced migration potential; reduced hazard.

Introduction

UV curing is a technology used in many application areas from inks and coatings to composites and 3D printing. UV curing systems bring many benefits to these applications, such as: zero VOCs – 100% solids systems; low energy curing; low temperature curing; instantaneous reaction and high throughput.[1]

One of the major application areas for UV curable systems is in packaging.[2] In high risk food packaging applications, it is important that appropriate measures are taken to ensure the packaging and food are safe for consumers. The process describing the transfer of components from packaging into the packed goods is known as migration. Components used in food packaging must not present a risk of migration. Ensuring that hazardous components do not find their way into foodstuffs is of paramount importance to consumer safety.

Photoinitiators and photoproducts (Figure 1 and Figure 2) are small molecules which can move freely across diffusion gradients in organic coatings. This can cause build-up of photoinitiators at the surface of the coating which leads to transfer of small molecules from packaging to packed goods during processing.[3, 4] The transfer of these components can be accelerated by foodstuffs acting as a solvent or adsorbent.

Photoinitiators are categorised into two groups based on their mechanism of initiation. Norrish Type I photoinitiators are characterised by a photolytic scission reaction generating active free radicals. The typical alkyl-aryl-ketone structure and photolytic process are shown in Figure 1. Types of Norrish Type II PIs include hydroxyacetophenones, aminoacetophenones and phosphine oxides.

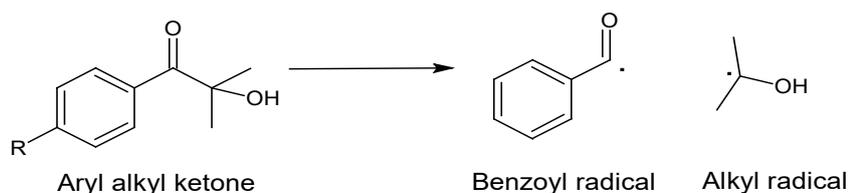


Figure 1 - A reaction scheme showing the photolysis of a Norrish Type I hydroxy acetophenone photoinitiator to form, two active radicals, the benzoyl radical and the alkyl radical.[5]

On the other hand, Norrish type II photoinitiators are characterised by a bimolecular reaction with a hydrogen donor coinitiator following photoexcitation. Figure 2 shows the Type II process with aryl-aryl-ketone and amine synergist generating active radicals on the coinitiator. Types of Norrish Type II PIs include benzophenones and thioxanthenes.

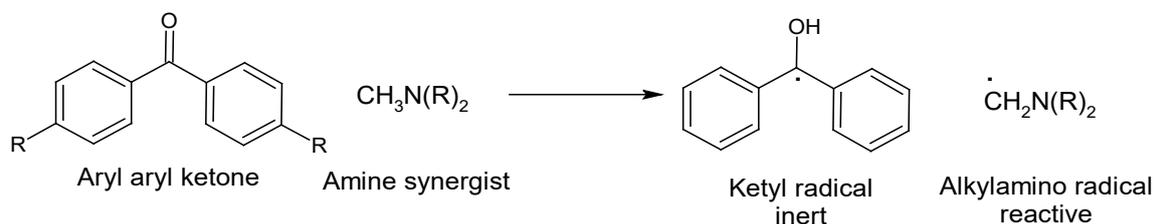


Figure 2 - A reaction scheme showing the hydrogen abstraction mechanism of a Norrish Type II, benzophenone generating two radicals, the inactive ketyl radical and the reactive alkyl amino radical.[6]

The difference in mechanisms of Type I and Type II photoinitiators can change the complexity of the migratable components. Type I PIs will create a large number of photoproducts from fragmentation, recombination and other side reactions, whereas Type II PIs generally produce only a few simple photoproducts. On the other hand, the fragments from Type I PIs are generally incorporated into the polymer backbone, whereas the chromophore in the Type II PI system does not react so can create a high concentration of migratable material.[7]

National authorities, trade associations and brand owners have implemented legislation and guidance to ensure safety for consumers. The Swiss Ordinance is the leading regulatory standard for food packaging inks and varnishes.[8] Annex 10 of this regulation defines a positive list of permitted substances that is split into two categories. Part A lists toxicologically evaluated substances with determined specific migration limit (SML). Part B lists substances which have not been toxicologically evaluated having SML default value of 10 ppb. These specific migration limits are thresholds which must not be exceeded.

Brand owners also provide their own stipulations. Nestlé's "Guidance Note on Packaging Inks" details recommendations of unsuitable products and requires inks to be formulated with Swiss Ordinance listed ingredients.[9] In addition to general exclusions, Nestlé categorizes ingredients in two lists. The first is an exclusion list consisting of items that must not be intentionally added. It features several standard photoinitiators like benzophenone (BP), isopropylthioxanthone (ITX) or 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO). The second list is a grouping of ingredients which have to be kept below their migration thresholds.

The European Printing Inks Association (EuPIA) has put in place an Exclusion Policy, based on CLP hazard representing a critical risk for health. Raw materials labeled as acute toxicity, CMR 1 or STOT 1 are to be excluded from printing inks and varnishes.[10]

In addition to these three main standards, increased regulatory testing mainly driven through ECHA has increased the severity of hazard classifications for many raw materials. Notable GHS reclassifications for photoinitiators are those of TPO, 2-Benzyl-2-dimethylamino-4-morpholinobutyrophenone and 2-methyl-1-[4-(methylthio)phenyl]2-morpholinopropan-1-one. [11-13] Historically the focus of new photoinitiator development was enhanced cure speed for higher production rates. However, modern demands for sustainable development require components of UV systems with appropriate and stable hazard classification, low migration and LED curing capability. In many UV curing formulations the photoinitiator is one of the more hazardous components and can have a high migration potential due to its low molecular weight.

Polymeric photoinitiators of high molecular weight and photoinitiator active content of 40-60%, have been developed by attaching photoinitiator functionalities to a linear or multi-armed polymer cores as shown in Figure 3. Although other polymeric photoinitiator structures are known, these specific types are the most cost effective and industrially relevant. Polymeric photoinitiators can reduce migration by limiting diffusion and can reduce toxicity and hazard through their high molecular weight.[14] Molecules with molecular weight greater than 1000 g mol^{-1} are considered not to be of toxicological concern because they cannot be absorbed through the gastro-intestinal tract. [15]

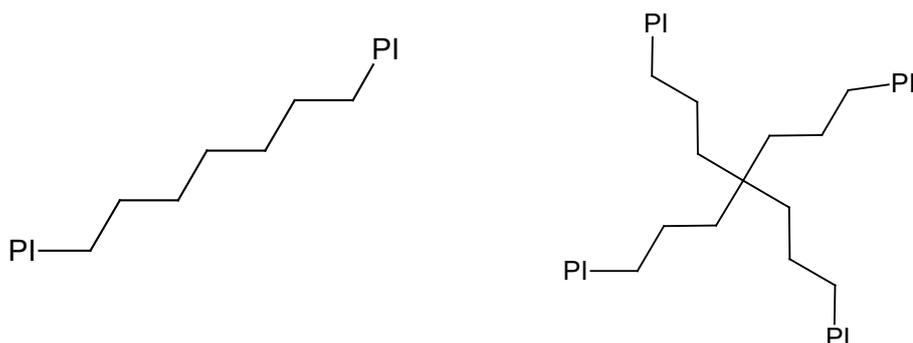


Figure 3 - Typical structure of polymeric photoinitiator showing photoinitiator (PI) end group functional inert linear or multi armed polymer.

Although high molecular weight structures can limit hazard and migration, the drawbacks are: 1. low active content which gives rise to low photoactivity; 2. the effect of the polymeric molecules on viscosity and rheology of formulations; 3. problematic physical form. All of these properties act as well-known sources of problems during processing.

While polymeric and polymerisable photoinitiators offer a route to low migration,[16] Self Curing Resins where both photoinitiator and resin functionality are included into one molecular unit, as shown in Figure 4, are an alternative approach with fewer of the aforementioned disadvantages. They represent another means of lowering migration, hazard, and improving formulation latitude and handling of UV systems and components.

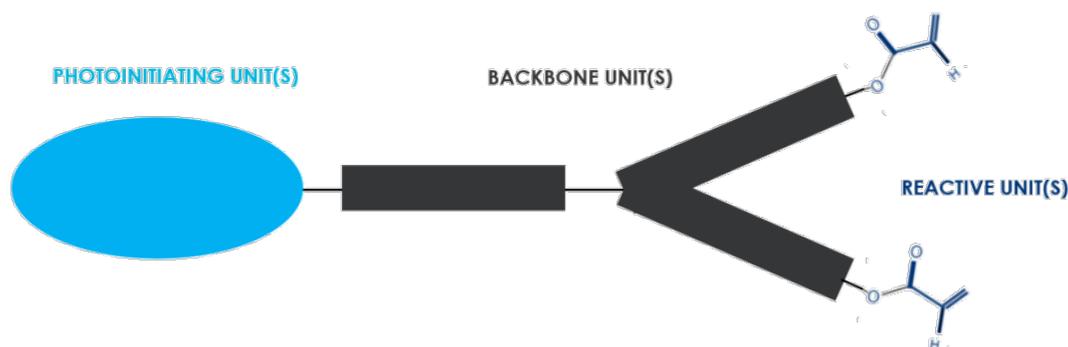


Figure 4 - General structure of Self Curing Resin with Photoinitiating units, backbone units and polymerisable (meth)acrylate functionality.

Results and Discussion

This paper focusses on the development of a new thioxanthone triacrylate (TX-TriA) with low migration, low hazard, LED curable characteristics as well as improved film properties and handling. Low migration properties are achieved by combining high molecular weight with a high number of

acrylate functional groups and a non-fragmenting Type II photoinitiator functionality. The hazard of the UV system overall can be reduced by attaching the potentially hazardous component (the photoinitiator) to a larger resin moiety with a resulting liquid high molecular weight product. Inclusion of a photoinitiating thioxanthone chromophore into the structure gives suitable long wavelength absorption appropriate for the move to LED curing. Well-selected backbone units, tailored in terms of length and chemistry, have been used to control viscosity, limit plasticizing effect and optimize the balance between flexibility and hardness of cured films.

This concept has led to the development of a new high molecular weight (960 g/mol) thioxanthone modified triacrylate exhibiting a reasonably low viscosity (< 10 Pa.s at room temperature). The UV/visible absorption spectrum (Figure 5) confirms its absorption in the LED region with an optimal response at 395 nm. Its acrylate multifunctionality, in addition to maximizing its chances of being grafted within the polymer network, allows use of the product as a reactivity booster.

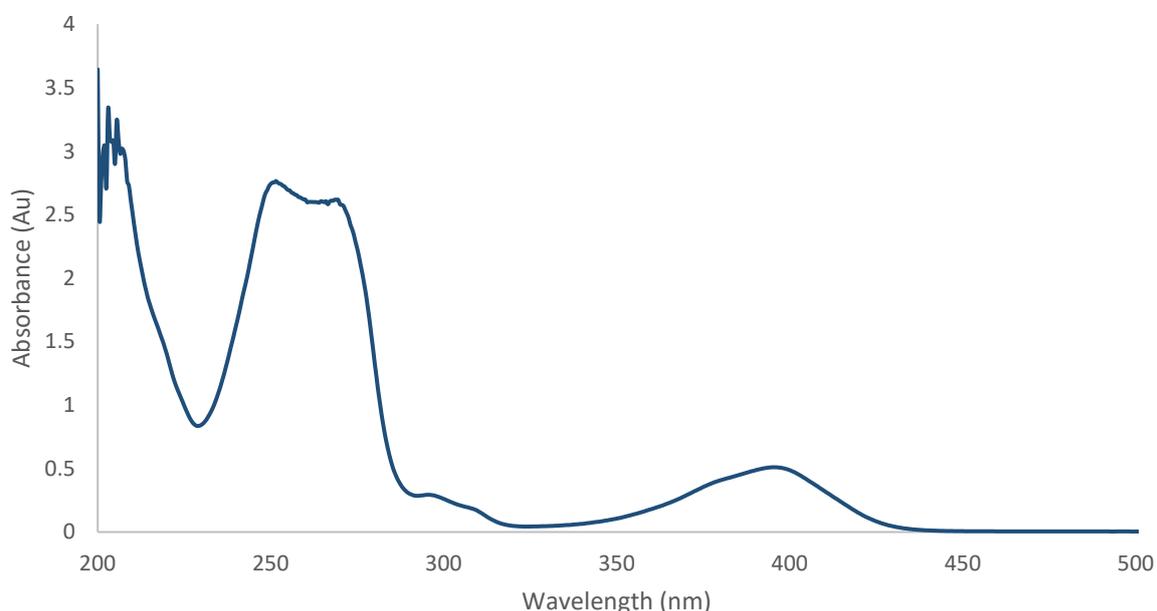


Figure 5 - UV spectrum of TX-TriA collected on a Shimadzu UV1800, using 1 cm path length and TX-TriA at 0.5 g L⁻¹ in methanol.

The thioxanthone modified triacrylate has been tested both under standard UV mercury lamp and 395 nm LED lamp in a formulation containing 15% hexafunctional polyester acrylate, 10% difunctional polyester acrylate, 10% acrylated amine synergist as hydrogen donor, 3% BAPO as type I photoinitiator, and around 60% acrylate monomers which were used to vary the thioxanthone modified triacrylate quantity. As described in Figure 6, the thioxanthone modified triacrylate is efficient at low dosage and the reactivity is continuously increased with the quantity of thioxanthone modified triacrylate. At similar thioxanthone amount, UV-Hg cured systems with the thioxanthone modified triacrylate exhibit higher surface hardness (+10%) with no significant loss on flexibility compared to systems with polymeric thioxanthone, while they are less brittle (-15%) with no loss on hardness compared to ITX. Even though the amount needed to reach similar LED reactivity was 4 times higher compared to ITX and 2 times higher compared to polymeric thioxanthone, the limited impact on viscosity of the thioxanthone modified triacrylate makes it of special interest for achieving reduced migration while handing broader formulation latitude to the user.

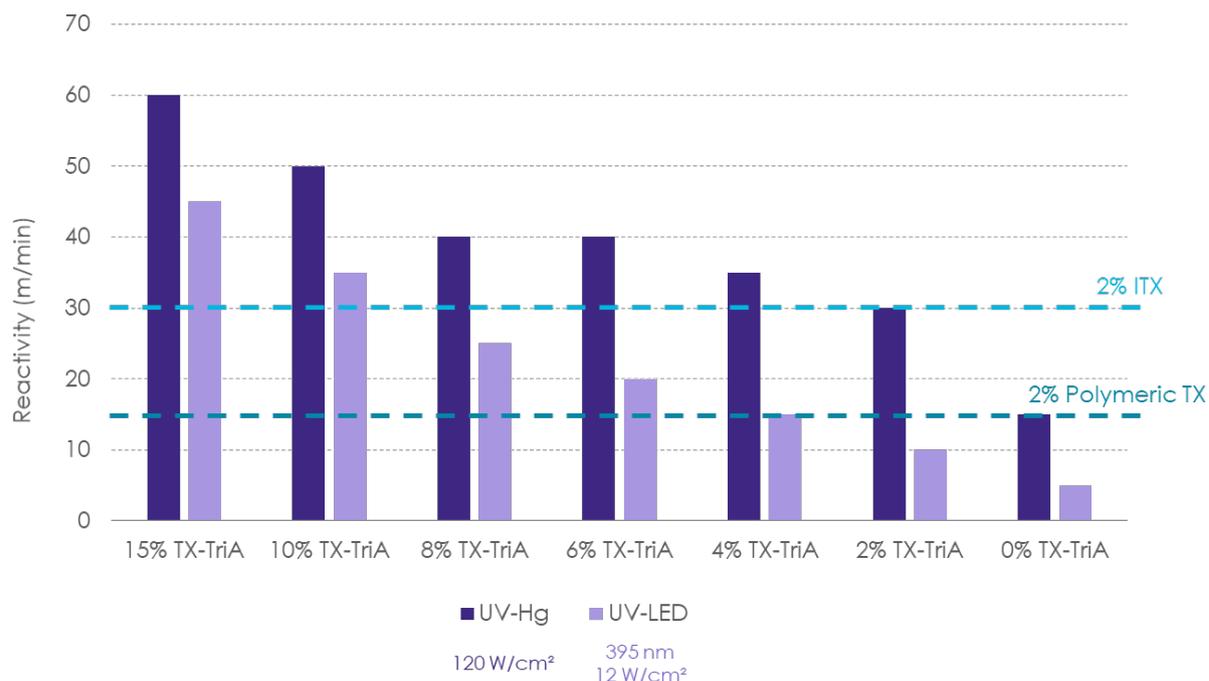


Figure 6 - Reactivity under standard UV mercury lamp (120 W cm⁻²) (dark purple) and 395 nm LED lamp 12 W cm⁻²) (light purple) of flexographic printing type formulations containing the thioxanthone modified triacrylate vs 2 % Polymeric TX and ITX.

The migration behaviour has been studied by mass spectrometry coupled with chromatography. This analysis was performed on extracts obtained by exposure of cured films (produced from formulations containing 60% difunctional acrylate monomers, 30% trifunctional acrylate monomers, and 10% active thioxanthone content) to acetonitrile for 24h at 40°C. As highlighted in Figure 7, a significant amount of extractable thioxanthone was observed in the case of the formulation containing ITX, while no thioxanthone compounds were detected in extracts from formulations containing either the polymeric thioxanthone or the thioxanthone modified triacrylate.

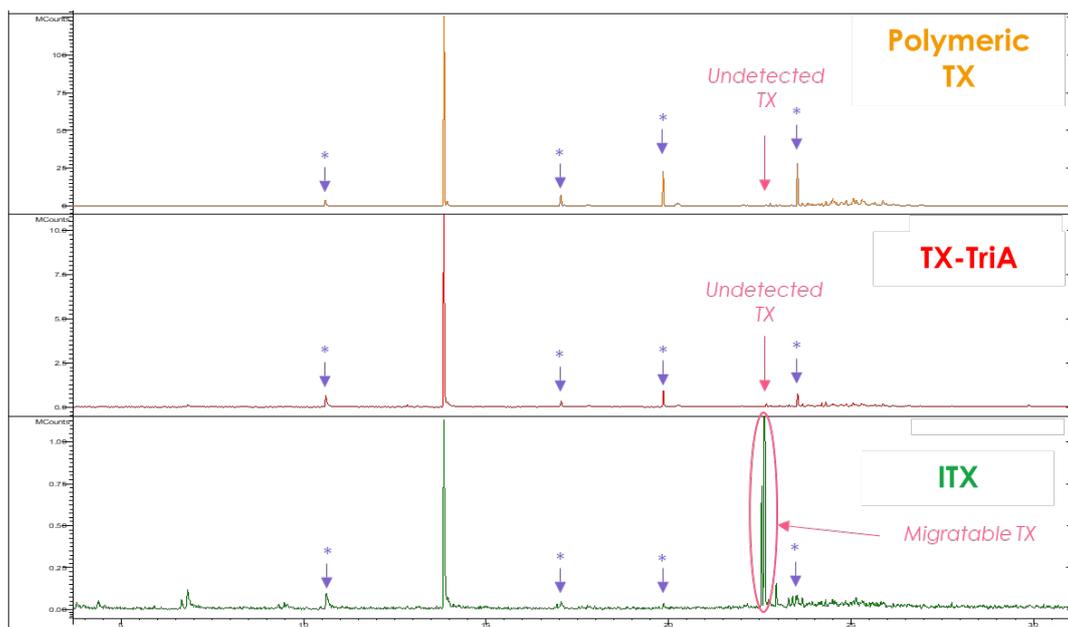


Figure 7 – Gas chromatography mass spectra of acetonitrile extracts (24h at 40°C) from cured films containing ITX, Polymeric TX and TX-TriA

Interestingly, when we compared the extraction profiles from formulations containing polymeric thioxanthone or thioxanthone modified triacrylate, a higher quantity of migratable acrylates was observed with cured films based on polymeric thioxanthone. Consequently, the thioxanthone modified triacrylate appears to be a better compromise since there was no thioxanthone migration and the level of extractible acrylates remained low.

Conclusion

Low hazard, low migration UV system development can be aided by the use of Self Curing Resins, which combine the low molecular weight photoinitiator component and the higher molecular weight resin into one molecule. Migration from these systems is not only diffusion limited but also largely prevented by formation of covalent bonds between the Self Curing Resin and monomers/oligomers during the creation of the polymer network. Inclusion of an appropriate chromophore provides an LED-active Self Curing Resin. Tailoring of the backbone chemistry and molecular weight allows control of reactivity and hardness/flexibility balance, while ensuring better ease of use than traditional solid or high viscosity solutions.

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