Inherently Reactive Urethane Acrylate Resins

Don Herr, Linda Franceschini, Elaine Ruiz, Yuhong He, Brendan McGrail, & Jeff Klang
Arkema-Sartomer BU, 502 Thomas Jones Way, Exton, PA, 19341, USA

Introduction

The uses for solvent-free, 100% solids liquid UV curable materials continue to expand as the global pursuit of low carbon footprint, greener technology grows. UV curable materials can be used for a wide array of applications including industrial coatings, electronics adhesives and coatings, medical adhesives and coatings, and graphic arts to name just a few. Solvent-free UV materials provide the benefits of potentially zero-VOC processes utilizing high throughput, low energy input UV curing production lines and equipment. One common challenge in utilizing UV curable adhesives and coatings in high end and consumer-facing applications is the production of small amounts of low molecular weight by-products derived from the photoinitiators used to initiate the light curing process. It is well known that for Norrish Type I (cleavage) photoinitiators some photofragments are better initiators than others, and often by-products derived from less reactive fragments (e.g. benzaldehyde, mesitylene) result in tangible volatiles/odor or extractables in the cured products. Norrish Type II initiating systems present similar challenges, typically derived from the aromatic ketone portion of the absorber/H-donor system.[1] Such extractables and volatiles can present a safety concern (e.g. extractables components of food packaging adhesives and inks) or performance degradation (e.g. adhesion and elevated temperature outgassing issues in electronics encapsulants or adhesives). Polymeric photoinitiators, in particular polymeric Type II systems, can address some of these issues.[2] Traditional challenges with the use of polymeric photoinitiators include potentially limited compatibility with the main resin matrix and, due to relatively high required usage levels by weight, adverse impact to the mechanical properties of the cured material.

Sartomer has approached this challenge by synthetically combining the base oligomer resin with the photoinitiator package to create so-called inherently reactive urethane acrylate resins (IRUA). Such IRUA oligomers can then be formulated without the need for additional photoinitiator, because it is built in to the primary oligomer backbone. This approach is fundamentally different from traditional polymeric photoinitiators, in which the higher molecular weight portion of the photoinitiator does not play a designed functional role in the mechanical properties of the cured system. In the case of the IRUA approach, the oligomeric resin that contains the photoinitiator is specifically designed to contribute those mechanical properties to the cured material, just like a typical oligomer portion of a UV curable system. Thus, there is no degradation of mechanical properties or issues with compatibility in the main resin system oligomer, *because the IRUA is the main resin system oligomer*. In an ideal option, the formulator can use their favorite urethane acrylate resin for a given application, but make it inherently reactive using this chemical approach.

The basic process for making inherently reactive urethane acrylates is synthetically straightforward. It simply entails the incorporation of a chromophore-functional polyol into the diol portion of the standard urethane acrylate synthesis. Typically, no significant changes are required of the manufacturing process although each system is of course slightly unique. A generalized reaction scheme is illustrated in Figure 1.
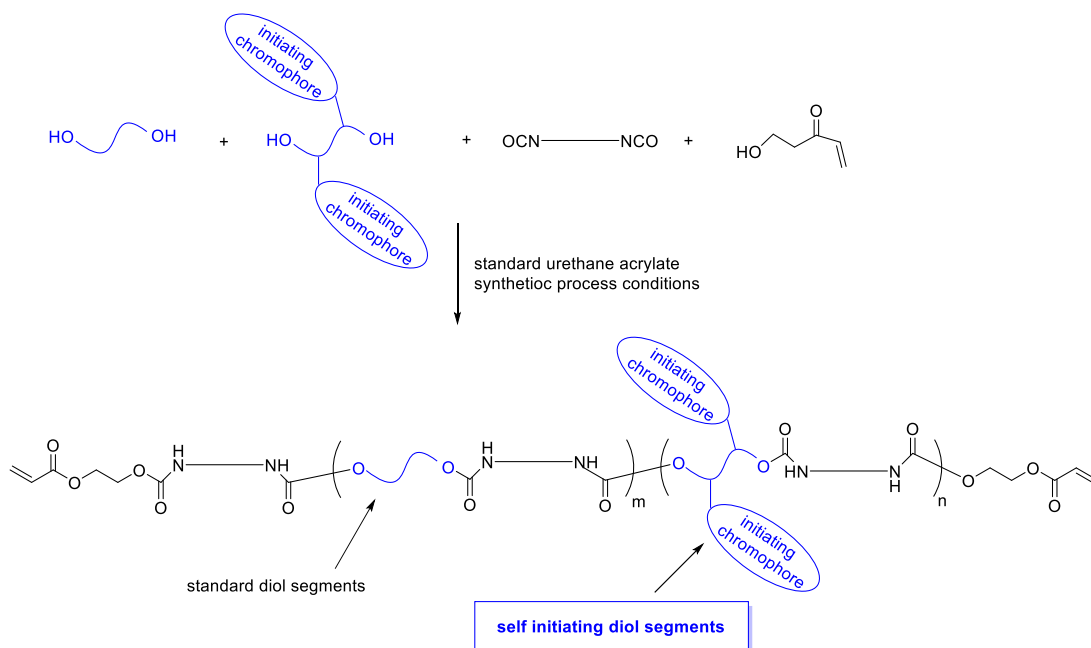
Figure 1. General Synthetic Scheme for Inherently Reactive Urethane Acrylate Oligomers

     A variety of chromophore-functional polyols have been studied and are illustrated generically in Figure 2. Polyols can be built into the oligomer backbone in either an "in-chain" or "pendant" architecture. Much of our initial work focussed on demonstrating principles using a benzophenone-functional diol hereafter denoted "BP1", but various alcohol-functional chromophores are under study. Ongoing studies utilizing thioxanthone-functional diols are also briefly described toward the end of this communication. Most systems which were synthesized also contained copolymerized amine synergist, in the form of methyldiethanol amine (MDEA), and this distinction is noted as needed in the results and discussion section. As will be seen, the efficacy of both copolymerized and added small molecule amine has been investigated. The incorporation of both the Type II chromophore and the H-donor for that Type II photoinitiating system into the polymer backbone enables the possibility of designing a self-reactive oligomer which hypothetically produces zero fragments/extractables related to the initiator portion of the total resin system. All systems studied fall into the category of aliphatic urethane acrylates. Structure-property effects within that class of materials has been studied along with overall photoactivity.
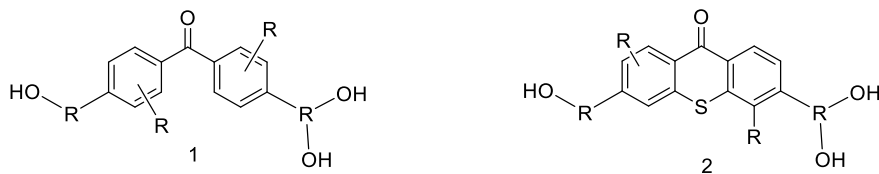
Figure 2. Generic Structures of Benzophenone- and Thioxanthone-functional Diols

Experimental Methods

Photo differential calorimetry (photoDSC) experiments were performed using a TA Q2000 DSC equipped with an EFOS A4000 Acticure light source emitting a Hg-vapor wavelength distribution guided into the DSC instrument with a quartz light guide. Typical light intensity at the sample was approximated to be ca. 190 mW/cm^2 of both UVA and UVB wavelengths based on measurements with an EIT Power Puck 2. Experiments were run with a reference cell temperature of 25 ºC. Sample size ranged between 4-6 mg, and samples were irradiated in the open lid of a DSC pan in air unless otherwise noted. For each experiment, the onset to peak time (indicative of initial reaction kinetics) and the total photopolymerization enthalpy (related directly to chemical conversion) were recorded. The onset to peak time is the time in minutes between when the lamp is initially switched on and the peak reaction exotherm rate, which is generally taken to indicate the reaction kinetics up to the gel point of the test resin system. Total Enthalpy and Onset to Peak time are illustrated on a typical photoDSC plot in Figure 3.
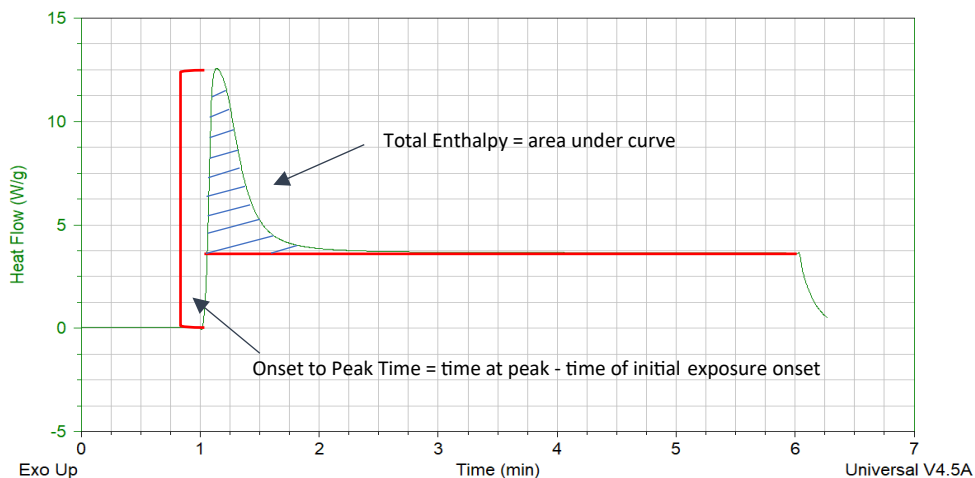

Figure 3. Total Enthalpy and Onset-to-Peak by PhotoDSC

Chemical conversions were calculated using the acrylate FT-IR C-H bending vibrational band at 812 cm^{-1}. Peak heights of this absorbance band were measured as an approximation of the concentration acrylate present in the film. Conversion was calculated from the height of this using the equation:

$$\text{Conversion} = 100 \, (H_0 - H_t)/H_0$$

Equation 1. Calculation of Chemical Conversion by FT-IR

In this equation H_0 represents the initial height of the peak centered at 812 cm^{-1}, and H_t represents the area of that band after UV irradiation for time t. Samples were run in the attenuated total reflectance (ATR) mode unless otherwise noted. Cured samples were placed in direct contact with the CdSe ATR window for analysis. The sample was cured in air on a metal substrate and could be removed freely from the substrate to allow for FT-IR analysis of both the surface and underside of the film relative to the light source. For FT-IR analysis and other bulk cured films, samples were cured in air using a Fusion/Heraeus LC-6 microwave Hg lamp equipped with a 300W/inch H-bulb at a linespeed of ca. 17 feet/minute. Unless otherwise noted, two passes under the lamp were utilized to cure film samples, which resulted in a typical UVA dose of ca. 1000 mJ/cm^2 and a typical UVB dose of 1200 mJ/cm^2. The front side of the film is defined here as the side closest to the lamp, and the back side is defined as the side against the substrate and farthest from the lamp. For FT-IR studies, a cured film thickness of 50 microns was targeted.

Mechanical properties were studied using dynamic mechanical analysis (DMA) in the thin film tensile geometry using a TA Q-800 DMA instrument. A frequency of 1Hz was used with a thermal ramp rate of 5 ºC/minute unless otherwise noted.

Reagents such as 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Speedcure TPO, Arkema), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Speedcure BPO/"BAPO" Arkema) Ethylhexylaminobenzoate (Speedcure EHA, Arkema), benzophenone (Speedcure BP, Arkema), ditrimethylolpropane tetraacrylate (SR355, Arkema-Sartomer), isopropylthioxanthone (Speedcure ITX, Arkema) and all proprietary reagents used to make the various urethane acrylate oligomers were commercial grade and used as purchased.

Results and Discussion:
Initial studies focussed on establishing that the inherently reactive oligomers did, indeed, show photoactivity and comparing that activity to cure rates and conversions obtained from common small molecule photoinitiator options. For many of these studies, aliphatic urethane acrylates (UA) of the general structure shown in Figure 4 were utilized:
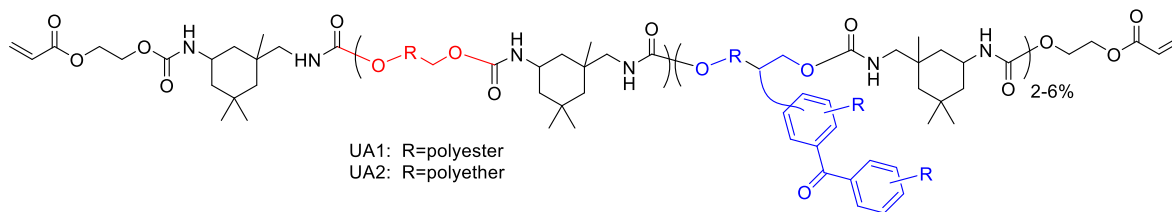
UA1: R=polyester
UA2: R=polyether

Figure 4. General Structures of Aliphatic Inherently Reactive Urethane Acrylate
Oligomers UA1 (polyester diol) and UA2 (polyether diol)

UA1 and UA2 represent a subset of a large family of resins synthesized to study the effect of chromophore structure, isocyanate, and polyol selection on structure property relationships within this new class of materials. Although not drawn for the sake of simplicity, UA1 and UA2 also both contain 0.5 wt. % methyldiethanol amine (MDEA) as a diol component in the oligomer backbone structure. This copolymerized tertiary amine provides a known source of abstractable H required for a Type II photoinitiator system. It is notable that other functionality on the oligomer backbone can also function to provide abstractable H, as will be discussed briefly hereafter.

Basic Photoactivity and Backbone Structure/Property Screening: The first screening study performed to study inherent photoreactivity was photoDSC. The basic properties measured by photoDSC were onset to peak time (a measure of initial reaction kinetics) and reaction exotherm (indicative of extent of cure during the total irradiation time) as discussed in the Experimental Methods section. For these experiments, a benzophenone diol ("BP1") was copolymerized into the two base UAs at a level of 2 wt. % to produce "UA1-BP1" (polyester diol based) and "UA2-BP1" (polyether diol based). As noted above, both of these new resins also contained 0.5 wt.% MDEA. Table 1 summarizes these compositions as well as some referenced later in this paper.

oligomer name	polyol type and isocyanate	chromophore description
Standard UA	polyester diol #1, IPDI	No polymer-bound chromophore, a typical UA benchmark
UA1-BP1	polyester diol #1, IPDI	Inherently Reactive analog of "Standard UA" with bound benzophenone + bound MDEA synergist
UA2-BP1	polyether diol #2, IPDI	Inherently Reactive UA with polyether segments & bound benzophenone + bound MDEA synergist
UA3-BP1	polyester diol #1, alternate isocyanate	Inherently Reactive UA with alternate isocyanate option & bound benzophenone + bound MDEA synergist
UA1-BP-TX	polyester diol #1, IPDI	Inherently Reactive analog of "Standard UA" with bound benzophenone + bound thioxanthone

Table 1. Basic Description of Inherently Reactive Urethane Acrylates in this Study

UA1-BP1, UA2-BP1, and the "Standard UA" resin analog with no copolymerized chromophore or MDEA were each blended individually in a 1:1 weight ratio with the SR355 monomer (ditrimethylolpropane tetraacrylate) diluent to simulate a simple oligomer/monomer formulated adhesive or coatings. For the two inherently reactive oligomers, this dilution with SR355 brought the overall

polymer-bound chromophore content of the prototype formulations to ca. 1 wt. %.   The Standard UA formulation (Standard UA + SR355) was combined with a small molecule photoinitiator package of either 1 wt.% Speedcure TPO or 1 wt.% benzophenone + 0.25 wt.% Speedcure EHA. These two formulations represent the analogous prototype formulations initiated with standard Type I and Type II small molecule photoinitiator packages for comparison to the new inherently reactive UA oligomer-bound initiator systems. All formulations contained ca. 1 wt. % photoinitiator package.
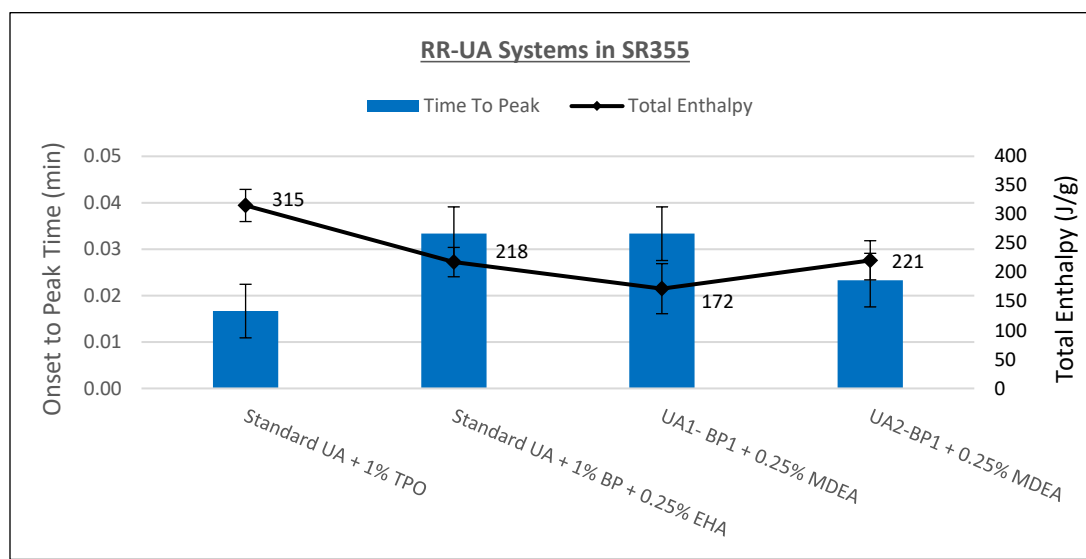

Figure 4. PhotoDSC Cure Comparisons of Inherently Reactive UA1 and UA2 with
TPO and BP/EHA Photoinitated Analogs

Comparing the Onset-to-Peak times for each system, one can see that the "Standard UA + 1 wt.% TPO" has the fastest cure rate, with an Onset-to-Peak time of just less than 0.02 minutes. As is often the case, a typical 2-component Type II photoinitiator system represented by "Standard UA + 1%BP + 0.25% EHA" exhibits slightly slower cure kinetics, with an Onset-to-Peak time of just over 0.03 minutes. One can see that the polyester diol-based UA1-BP1inherently reactive system has nearly identical cure kinetics as the standard Type II small molecule photoinitiator package, also showing an Onset-to-Peak time of about 0.03 minutes as well. The UA2-BP1 polyether diol based inherently reactive system shows improved cure kinetics vs. both the small molecule initiator systems and the UA1-BP1 inherently reactive option. The UA2-BP1 systems exhibited an average Onset-to-Peak time of just over 0.02 minutes, and its curing rate approached that of the Standard UA + 1% TPO Type I system.

Comparing the Total Enthalpy of the photoDSC photopolymerization, it can again be seen that the Standard UA + 1% TPO shows the highest conversion and a enthalpy of polymerization of 315 J/g. All of the Type II systems, be they small molecule or inherently reactive, exhibit polymerization enthalpies between 172 J/g to 221 J/g. Although this is perhaps not entirely unexpected give the high reactivity of the TPO small molecule photoinitiator, it is also notable that the Q2000 DSC instrument is a

heat flux type DSC, and as such the sample chamber can rise due to polymerization exotherm (i.e. the analysis is not truly isothermal). This rise in temperature during the photoDSC experiment would also typically produce higher conversion (and indeed also better cure kinetics). Given this instrumental source of error, the photoDSC data was not further/over analyzed.

It can be concluded that the inherently reactive oligomers UA1-BP1 and UA2-BP1 exhibit photoDSC polymerization activity similar to or better than small molecule Type II options, but are not quite as efficient as classic highly active Type I options such as TPO.

Cure efficiency was also studied by curing bulk films. As described in the Experimental section, films were cast and cured on a metal substrate to produce a cured thickness of ca. 50 microns. Such films could be carefully removed from the metal substrate and analyzed on both the front and back side by FT-IR (ATR). The various oligomers were again studied in formulations with SR355 at a 1:1 oligomer:monomer ratio. The "Standard UA" formulation (no copolymerized photoinitiator) was further formulated with 1 wt. % benzophenone and 0.25 wt.% EHA amine synergist as a representation of a typical small molecule Type II photoinitiator system. UA1-BP1 and UA2-BP1 are described above. UA3-BP1 is a second polyester diol-based urethane acrylate with a different aliphatic isocyanate option vs. UA2-BP1. Films were curd in air at three different linespeeds as notated in Figure 5, and conversion at the front/top and back/bottom side of the films were measured. For surface cure, one can see that the inherently reactive systems are cured to the same or higher conversions relative to the benchmark Standard UA small molecule photoinitiator option. As seen in the photoDSC data presented above, the UA2-BP1 polyether diol-based inherently reactive system shows slightly better surface conversions across all linespeeds studied. This is consistent with the theory that the polyether functionality in this system provides more readily available abstractable H atoms, allowing the film to better overcome oxygen inhibition and chemically convert at the film/air interface. The same trend is observed at the bottom of the film for through cure, where the UA2-BP1 system shows the highest conversion at all speeds. As with surface cure, the inherently reactive systems all exhibited through cure equal to, or exceeding, that of the Standard UA analog containing a small molecule Type II photoinitiator.
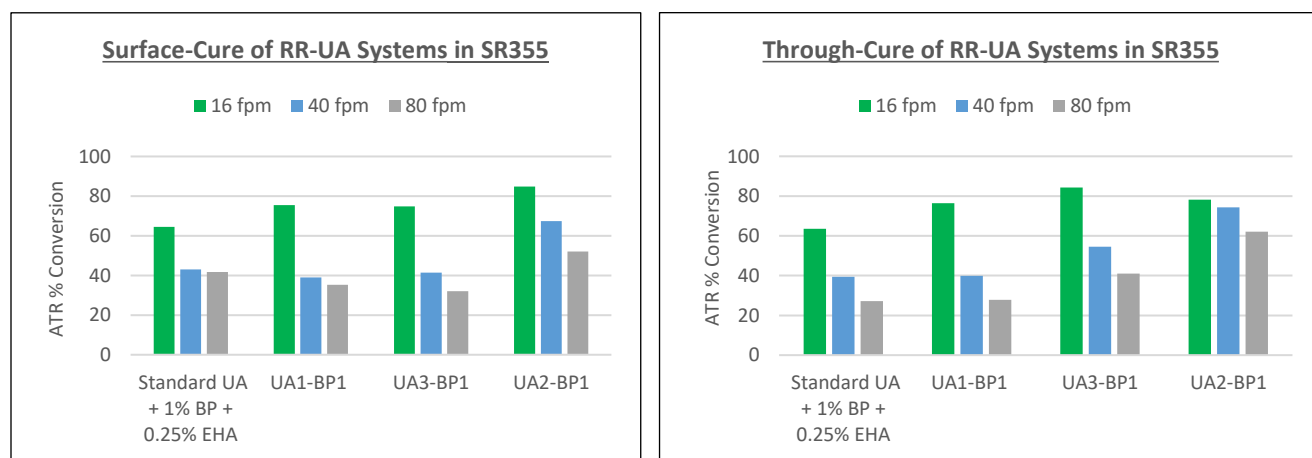

Figure 5. Surface and Through-cure of Inherently Reactive UA using FT-IR

Another basic premise of this inherently reactive oligomer approach is that the incorporation of the chromophore into the oligomer backbone at typical use levels will not have a major impact on mechanical properties of the cured formulated oligomer. Ideally, one could then take most any "standard" urethane acrylate and, *via* simple synthetic modifications, make it "inherently reactive" without having a large impact on overall performance properties. Dynamic mechanical analysis (DMA) was utilized to make some basic comparisons of the "Standard UA" and the UA1-BP1 inherently reactive system. As noted above in Table 1, these two oligomers compositionally differ only in that the UA1-BP1 oligomer contains polymer-bound benzophenone chromophore and the "Standard UA" does not. Both resins were cast and cured as free-standing films for DMA analysis as detailed in the Experimental section. The UA1-BP1 resin was coated and cured as-is with no added small molecule photoinitiator, whereas TPO was added to the Standard UA in order for it to UV cured. Thin film tensile DMA plots are shown in Figure 6.
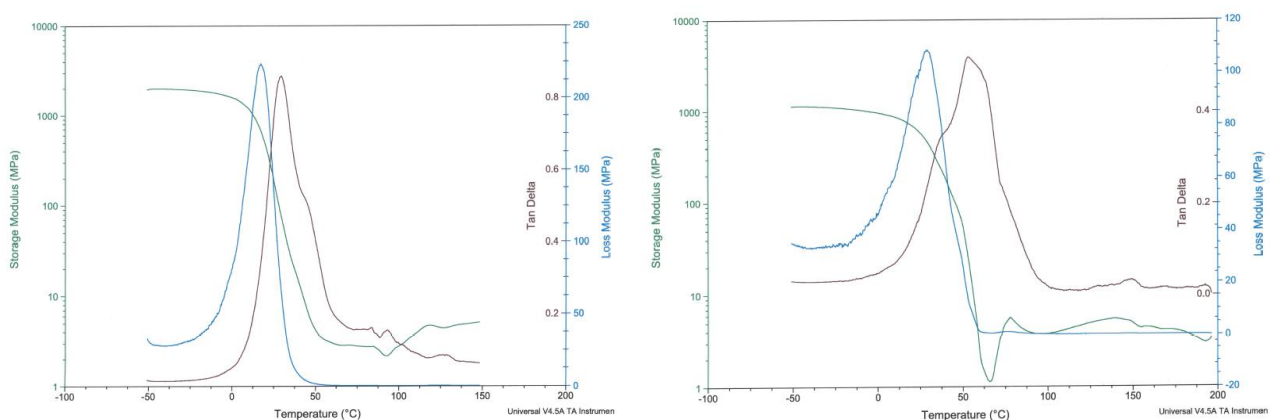

Figure 6. DMA Plots of "Standard UA" (left) and Inherently Reactive UA1-BP1 (right)

While there are some differences in the cured film DMA details which are beyond the scope of this paper, one can see that basically the mechanical properties of the Standard and Inherently Reactive UA1-BP1 are quite similar. Both have a glassy storage modulus (E') of 1500-2000 MPa and a rubbery modulus of 3-4 MPa. The Standard UA exhibits a main glass transition (T_g, as determined by the peak in the Tan Delta curve) of about 30 ºC, with a shoulder around 50 ºC, while the UA1-BP1 Inherently Reactive analog has its primary Tg at 54 ºC, with a shoulder around 40 ºC. The analysis shows that although the incorporation of the benzophenone chromophore onto the oligomer backbone of UA1-BP1 does induce some physical differences in cured films as would be expected to some degree, the general mechanical properties are quite similar. In a practical sense, the inherently reactive version of a urethane acrylate is seen to produce similar mechanical and physical properties of its base standard analog. Further comparisons of this aspect of the resin platform are underway, but initial data shows that with minor formulation modifications the inherently reactive version of a urethane acrylate resin can be used to obtain the same properties as its standard version, while offering the potential for significantly reduced odor and extractables related to the photoinitiator component/function of the formulation.

For any photoinitiator, cure rate and thick film cure are dependent on the absorbance and activity of the photoinitiator relative to the resin matrix and of course the light source emission bands. Our group has begun to study the use of thioxanthone-based polymer-bound chromophores in order to facilitate LED curable inherently reactive materials and to improve through cure by combining both benzophenone and thioxanthone chromophores onto the same oligomer. The latter is analogous to the common approach of using both a short wavelength and long wavelength photoinitiator to maximize light absorbtion and through cure for thick or pigmented films.[3] As before, all oligomers were blended in a 1:1 ratio with SR355 and UV cured using the LC-6 conveyor line equipped with an H bulb as detailed in the Experimental Methods section to produce ca. 2 mil thick films. The films were removed from the casting substrate and analyzed for conversion on the front and back side using ATR. The "Standard UA"/SR355 blend was also blended with photoinitiator packages of 4 wt.% TPO (typical Type I photoinitiator) or 2 wt.% benzophenone + 2 wt.% isopropylthioxanthone + 0.5 wt.% EHA synergist (typical Type II photoinitiator package). As detailed in Table 1, UA1-BP-TX contains both bound benzophenone and bound thioxanthone chromophore (but not bound MDEA). As a synergist for this blend with SR355, 0.5 wt.% EHA was also added. Lastly, the UA1-BP1 system with only bound benzophenone was further mixed with TPO (o.25 wt.%) to observe if a small amount of long wavelength small molecule photoinitiator improves through cure in the otherwise short wavelength UA1-BP1 inherently reactive oligomer. Surface cure and through cure FT-IR data is shown in Figure 7.
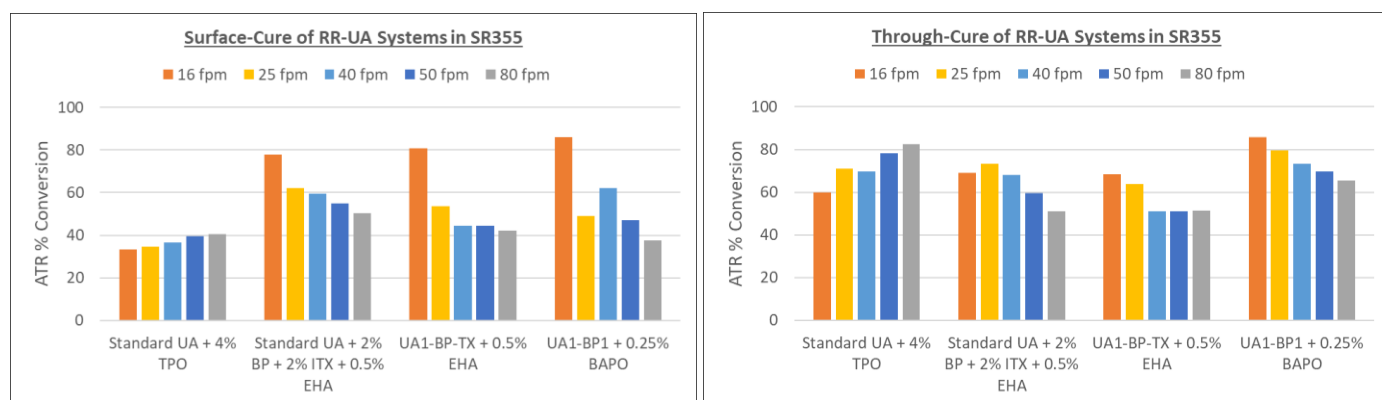

Figure 7. Oligomer-bound Benzophenone + Thioxanthone for Through Cure

As expected, it was observed for all systems that a long wavelength photoinitiator component improves through cure by facilitating light absorbtion deeper in the film. This can be seen by comparison of the through cure conversion of the various options containing a long wavelength component in Figure 7 to the through cure conversions shown in Figure 5 for photoinitiator systems based on only benzophenone. As a specific example, in Figure 5 the through cure conversion of "UA1-BP1" at a linespeed of 40 fpm was about 40%, whereas the analogous UA1-BP-TX oligomer containing both bound benzophenone and bound thioxanthone exhibited a conversion of over 50% at 40 fpm. Of course, there are other small inevitable small differences between the systems shown, and much more work is required to quantify the effectiveness of oligomer-bound thioxanthone as a through cure and LED cure option. Details related to more extensive studies of bound thioxanthone systems will be presented in the future. As another simple option, the addition of a *small amount* (0.25 wt.%) of BAPO

long wavelength small molecule photoinitiator to an oligomer-bound benzophenone system has also been shown to boost through cure. This is exemplified by the "UA1-BP1 + 0.25% BAPO" through cure conversions which are in the 70-80% conversion range for linespeeds up to 50 fpm. For such a system, the large majority of the photoinitiation can be induced by the oligomer-bound benzophenone, and if thick film cure is an objective the formulator has the option to use very small amounts of a small molecule absorber to improve through cure while still significantly reducing extractable photoinitiator by-products for the overall composition.

Conclusions:

We have demonstrated a practical and scaleable synthetic route to a platform of inherently reactive urethane acrylate resins which contain all oligomer-bound photoinitiating chromophore. These Type II systems present to possibility of low or even zero extractable components derived from the photoinitiating functionality. This further manifests itself in low odor and low toxicity UV curable material options. The new inherently reactive resins differ from traditional "polymeric photoinitiators" in that the oligomers contribute the principle mechanical properties to the cured material. No additional polymeric material, which may impact mechanical performance and add cost, needs to be added to initiate cure. Although they are generally not as active as the best Type I small molecule photoinitiation options, the inherently reactive materials have exhibited photoinitiating efficiency similar to, or better than, benchmark small molecule Type II systems.

The overall the synthetic approach is general, and in principle most common urethane acrylate resins can be made inherently reactive using this approach. Structure/property correlations involving the resin backbone functionality, spacer group effects, and bound photoinitiator structure/absorbance are underway. Work continues to expand the scope of oligomers and types of chromophores available within this novel resin platform.

References:
1. (a) Cowan, D.O., Drisko, R., *Elements of Organic Photochemistry*, **1976**, Plenum Press, 92-107. (b) Pappas, S. P., *J. Radiation Curing*, **1987**, 6-16. (c) Vesley, G., *J. Radiation Curing*, **1986**, 4-10. (d) Arendt,W., *RadTech Report*, Nov/Dec **1991**, 14-17.
2. Fouassier, J-P, *Photoinitiation, Photopolymerization and Photocuring*, **1995**, Hanser Publishers, 71-72.
3. Fouassier, J-P, *Photoinitiation, Photopolymerization and Photocuring*, **1995**, Hanser Publishers, 185-189.