

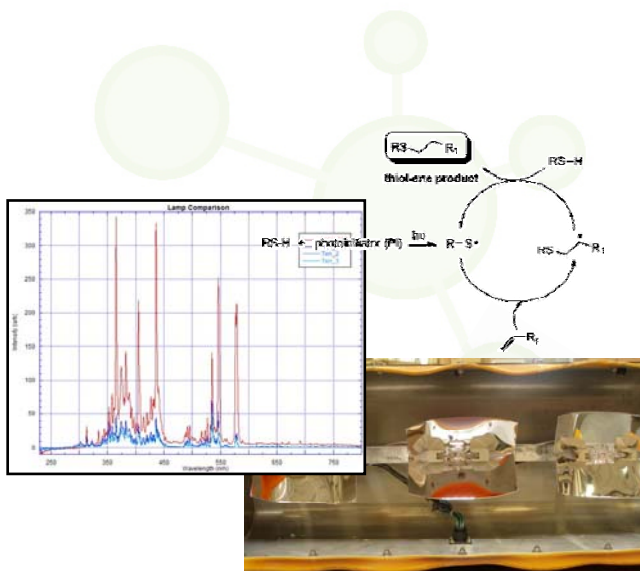
sometimes answers need to be discovered
sometimes they need to be invented



Significant Acceleration of a UV-Cured Coating

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Abstract

Except for rare cases, increased cure speed of a UV-cured coating is greatly desirable. Our client approached us with a thiol-ene floor coating plagued with an excessively slow curing rate (9 cm/sec) and desired a 10x improvement. A wide range of process and reactant changes were explored but to little avail. Success was ultimately achieved when an alternate ene monomer was chosen despite literature references that indicated the monomer would instead *decrease* the reaction rate.

Introduction

The history of thiol-ene chemistry can be traced back for over 70 years [1], and is the subject of hundreds of research reports published since then. Despite this large body of knowledge, UV-cured thiol-ene chemistries are seldom discussed in commercial applications, with acrylate systems being far more common. Consistent with all other UV-curing systems, thiol-ene chemistry offers the advantages of being 100% solids, making it a solvent-free "green" chemistry. However, thiol-ene systems have one significant advantage over acrylate systems: they do not show any oxygen inhibition as commonly occurs in acrylates.

In the broadest example, the reaction is between monomer with a thiol group,



Figure #1: A Thiol

and a monomer with an ene group.



Figure #2: An Ene

The ene shown above is terminal, but that topology is certainly not required.

The polymerization reaction of thiol-enes is quite unique in that this is an addition (radical chain) polymerization but the resulting polymer is a copolymer, something more common to a step (condensation) polymerization. The author is not aware of any other polymerization process that

encompasses these exclusive reaction mechanisms.

The reaction steps for polymerization are few in number and are shown in Figure #3. Starting on the left side, the photoinitiator (PI) is activated with light and then reacts with a thiol to form a thiyl:

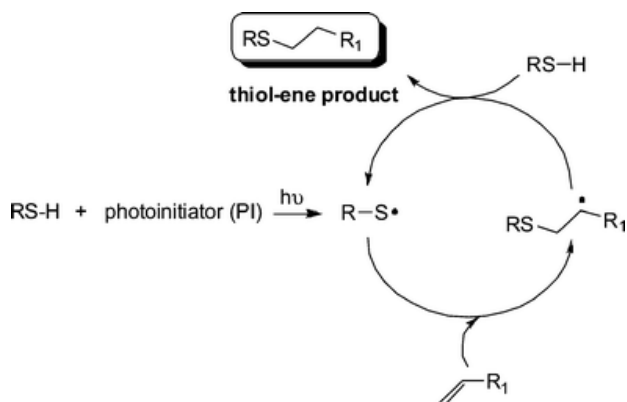


Figure #3: Photopolymerization Process (from [5])

Note that both Norrish Type I (photocleavage) as well as Type II (hydrogen abstraction) initiators can be successfully used for photoinitiation, although a photoinitiator is not even required because the S-H bond is photo-labile [2] and capable of initiating polymerization. Photoinitiators are commonly used however, as the curing reactions do proceed more quickly when they are used.

Following the creation of the thiyl, two propagation steps occur which allow the chain to grow. The activated thiol first reacts with an unsaturated functional group adding itself to the molecule across the double bond in an anti-Markonikov orientation, creating a carbon-centered radical in the process. This radical then abstracts a hydrogen atom from another thiol monomer so that the polymerization can continue.

Not shown in Figure #3 are the termination steps. Termination results from the usual steps of combination (radical-radical coupling). (Only the thiyl combination is illustrated here.)



Figure #4: A Representative Termination Step

The reactions have been diagramed here with monofunctional monomers. It is possible and in fact quite likely that at least some of the monomers would have more than one functional group on each monomer. Di-, tri-, and higher functional monomers (of the thiol, the ene, or both) will create a crosslinked network.



One of the largest advantages of photocured thiol-ene chemistry over photocured acrylate systems is the lack of oxygen inhibition. When the carbon-centered radical shown above in propagation step 2 encounters oxygen, a peroxy group forms which is then able to abstract a hydrogen atom from a thiol group akin to the second initiation step above. This incorporation allows for the reaction to continue unhindered.

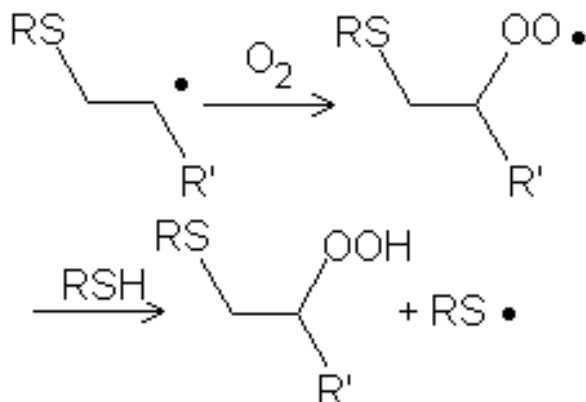


Figure #5: Oxygen Incorporation

As was already stated, the chemistry here has been extensively studied and consequently review papers exist as well [3, 4, 5]. In these papers, relationships have been empirically developed to correlate and thereby predict the impact that the molecular structure of the monomer will have on the reactivity. In particular, it has been found [6] that enes that are electron rich react more quickly. Some references [4, 6] provide the following list of reactivities which meet this criterion:

Vinyl ether > allyl ether > allyltriazine > allylisocyanurate > acrylate > unsaturated ester

A similar list has been developed for thiol monomers. It is considerably shorter (due to the smaller number of thiol monomers available and studied) and also is strictly empirical with no rationalizations available for the ordering.

Alkyl 3-mercaptopropionates > alkythioglycolates > alkyl thiols.

The purpose of this study was to increase the cure speed of an existing formulation using any and all available technologies. In order to have a commercially viable product, it was necessary to increase the cure speed by a minimum factor of 10.

Experimental

In this particular case, our client had developed a UV-cured thiol-ene coating for refinishing floors. The coating was applied to the floor with a paint roller, and then a small lamp cart containing a bank of 3 UV lamps was rolled over the floor to cure it. The area under the cart exposed to the UV light was approximately 70 cm wide (27 in) and 18 cm (7 in) deep. The client desired to maximize the base of potentials customer and so the combined electrical duty of the lamps was limited to 120 VAC and 15 amps.

The thiol-ene coating that the client had originally developed met all their performance requirements (low color, 4H pencil hardness and excellent adhesion to the substrate) except one: the cure time was too slow. Even though the coating cured in just under 2 seconds, the shortness of the UV exposure area limited the speed at which the lamp cart could be pushed to no faster than 9 cm/sec. This is the equivalent to 0.2 mph, an unbearably slow speed for the operator pushing the cart, and one that resulted in excessively long times to cure the floor coatings in large rooms. Increasing the cure speed by a factor of 10 would allow the operator to walk at 2 mph, a comfortable speed. Higher speeds than this were not necessary as they would make it more difficult for the operator to still keep the lamp cart moving in a straight line while walking so quickly.

A number of different approaches were identified to attempt increasing the cure speed. These are listed below in order of increasing difficulty to complete.

- 1) Optimize the output from the UV lamps
- 2) Use thermal initiators to increase the cure speed
- 3) Reformulate using different monomers.

Each of these options will be discussed in detail.

Optimization of the UV Lamp Output

Two obvious options to increase the UV lamp output were not available for implementation. The first was to use higher wattage bulbs. As was indicated earlier, the existing lamp cart was already running at the maximum output, thereby preventing the use of either higher wattage bulbs or more bulbs.

Another option that was not available to improve the lamp output was to reduce the distance of the lamps above the floor. Doing so would have not only reduced airflow in to and around the lamps but also would have



resulted in an unacceptably high heat build up just above the floor. The heat could then reach high enough levels that damage to some flooring surfaces was possible. (Early prototypes of the equipment had melted vinyl tiles.)

Several approaches were explored to optimize the lamp output. The first was to ensure that the spectral output of the lamps was appropriate for the photoinitiator being used. The spectral output of the lamp was measured and found to overlap well with the measured UV absorption peak of the photoinitiator, so no further effort was put into this option.

Through a separate series of experiments, it was found that the reflectors behind the lamps were not ideal, not only in their reflectivity but also in their geometry. Additionally the total output of the bulbs was inexplicably low. Replacing the reflectors with more effective designs and also the use of higher output bulbs helped to double the cure speed, a significant improvement but still not enough.

Use of Thermal Initiators

As mentioned in the previous section, UV lamps typically create high levels of IR radiation and thereby heat. An attempt was therefore made to harness some of the heat by using azo-based thermal initiators, in particular azoisobutyronitrile and azobis(2,4-dimethylvaleronitrile), both chosen because of their relatively low decomposition temperatures. The results of this effort were of limited success because their implementation required a very careful balancing of multiple contradictory requirements.

First, solubility of the initiators in the uncured coating at room temperature was poor. This was improved by heating the uncured coating fluid, but since the initiators used were ***thermal*** initiators, too much thermal input (a combination of both the time and temperature profile of the thermal history) resulted in the initiator prematurely decomposing and thereby initiating the curing reaction so that the liquid coating would gel while it was still in the bottle.

There was an additional paradox that needed to be confronted with the use of thermal initiators. The thermal initiator required heat from the lamp to activate it, but since the purpose of the initiator

was to reduce the time the coating spent under the lamp, using a thermal initiator would mean less heat was available from the lamp to activate the thermal initiator, thereby lessening the ability of the thermal initiator to function as needed.

Despite these challenges, the use of thermal initiators did show some successes, albeit inconsistently. In the end, this approach was discontinued. The inconsistency of the results and the challenges in controlling the formulation, particularly during scale up and production, led to the decision to end the effort of this potential solution.

Reformulation with Different Monomers

The formulation as initially developed by the client used an alkyl 3-mercaptopropionate monomer for the thiol source, a functional group that was noted above for its high reactivity. No changes were made to this monomer. However, the ene monomer was based an allylisocyanurate. As noted above, there are a number of functional groups that are reported to have higher curing speeds, so all effort was focused on finding one or more replacement monomers that would duplicate the properties of the existing formulation but would cure faster.

A wide range of monomers incorporating the various ene functional groups were tried. Most of these were tri- or tetra functional in an effort to achieve a higher gelation point at a lower degree of conversion.

The table below shows many of the monomers that were examined and a measure of the pencil hardness when cured at the indicated speed. Pencil hardness ranges from 9B (softest) down through 1B, crossing over to 1H and increasing in hardness to 9H [7]. Each of the monomers will be discussed below.



Monomers that were used, and the hardness of the cured coating when cured at 90 cm/s (2 mph).

Monomer	Pencil Hardness
TAIC	4H (cured 2x)
DEGDVE	B
TEGDVE	6B
BDDVE	6B
PETAE	Uncured
TAIC	2H
TVBTM	5H
EPTA	< 6B
ETPTA	<6B
PETA	6H
TMPTA	3H

Abbreviations and Suppliers:

BASF supplied DEGDVE – diethylene glycol divinyl ether

Aldrich supplied TEGDVE – triethyleneglycol divinyl ether, BDDVE – butanediol divinyl ether, PETAE – pentaerythritol allyl ether, TAIC – triallyl isocyanurate, TVBTM – Tris[4-(vinylxy)butyl]trimellitate.

Sartomer supplied EPTA – ethoxylated pentaerythritol tetraacrylate, ETPTA – ethoxylated trimethylolpropane triacrylate, PETA – pentaerythritol tetraacrylate and TMPTA – trimethylolpropane triacrylate. All monomers were used as received.

As was suggested by the technical literature, many of the vinyl ethers (DEGDVE, TEGDVE and BDDVE) were able to cure much faster (5x to 10x faster) than the allylisocyanurate. Two particularly fast monomers were diethylene glycol divinyl ether (DEGDVE) and triethylene glycol divinyl ether (TEGDVE).

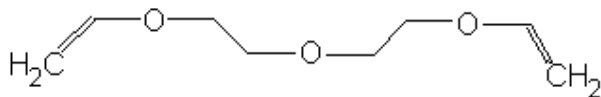


Figure #6: Diethylene glycol divinyl ether

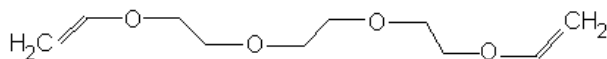


Figure #7: Triethylene glycol divinyl ether

Unfortunately, the resulting films were softer than the existing formulation, with the TEGDVE being softer than the DEGDVE. This was believed to be due to the increased number of ethylene glycol

linkages located between the vinyl groups. Because there are only two bonds on the oxygen atoms and because they are located 180° opposite of each other, these bonds are able to freely rotate under applied stress, thereby leading to a softer material.

The allyl ether (PETAE) was also expected to cure faster, but no cure was achieved at all. It is not known why this occurred and was not explored further. The allylisocyanurate (TAIC) provided an interesting result, in that it was from a different supplier than for the existing formulation, but actually cured both faster and harder. However, the hardness of the cure was still too low to be acceptable, so no further work was undertaken with that monomer.

The TVBTM monomer provided great success, but upon further investigation it was found that the supplier was unsure of future production plans. It was decided to continue the investigation.

The first two listed acrylate monomers, (EPTA and ETPTA) began to raise suspicions about what had been previously cited from the literature – that acrylates cure slower than allylisocyanurates. Coatings made using this monomer cured faster than expected although lacked in hardness. As a result, additional acrylate monomers were considered that had been previously ruled out.

Complete success was ultimately achieved in this unexpected manner. The use of a tri- or tetrafunctional acrylate ((PETA and TMPTA, Figures #8 and #9 respectively) produced coatings that cured 10x faster than the existing formulation and matched (or nearly matched) its hardness, color and adhesion as well.

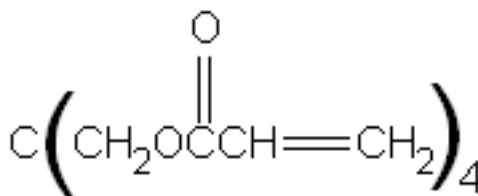


Figure #8: Pentaerythritol tetraacrylate

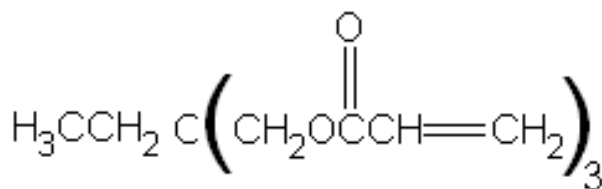


Figure #9: Trimethylolpropane triacrylate



The success of both these monomers was surprising since, as was noted previously, the literature had guided the effort away from acrylates. While the faster cure could possibly be rationalized for the tetraacrylate because of its higher functionality (the existing ene monomer was only trifunctional) such an argument could not be made with the triacrylate monomer.

Since the original list of relative cure speeds culled from research reports was only empirical and lacked a theoretical basis, the surprising results of this work do not require that a new theory be developed as none exists. Nonetheless, they results serve as a reminder as to the reliability of generalizations made from research results. This also raises the question of whether the thiol monomer should have been looked at more closely. The same body of literature also suggested that it was the fastest reacting monomer, a suggestion that should have been questioned. Such work was not completed at this time.

Lastly, as was noted above, use of ethylene glycol spacers in the ene monomers led to softer coatings with vinyl ethers. This was true also for the acrylates as well. Figure #10 shows the EPTA monomer, a tetrafunctional acrylate identical to the PETA acrylate in Figure # 8 except for the glycol spacer in each arm of the monomer. This monomer also cured quite quickly but the resulting coating was also softer than the non-ethoxylated acrylate.

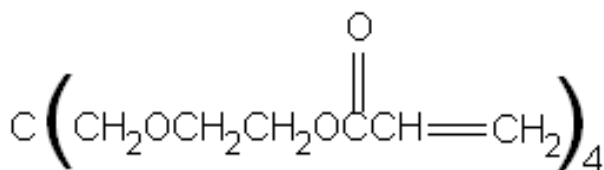


Figure #10: *Ethoxylated pentaerythritol tetraacrylate*

In the end, the improvements to the lamps and reflectors led to a 2x speed improvement, while the change in monomer led to an additional 10x improvement. Combined, these improvements resulted in a 20x cure speed increase, far more than the 10x improvement originally sought.

Conclusions

While the initially developed formulation had a relatively quick cure time (approximately 1 second), lamp geometry constraints resulted in the coating curing too slowly for its intended application, refinishing of floors. This was achieved through two separate changes. First, the UV lamps and their reflectors were improved. Second, changes were made to one of the monomers – the ene. The monomer change was one that was specifically opposite of suggestions made in the technical literature. The result of this effort was that a 20x increase in cure speed was achieved, twice the 10x increase that was desired.

References and Notes

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- [7] Two additional hardness values, HB and F exist between the xH and the xB scale, but were left out of the discussion for clarity and simplicity. No coatings were found to have those particular hardness values either.

Key Words: UV Cure, Thiol, Ene, Thiol-Ene, Acrylate, 100% solids, Green chemistry