Reactivity and Polymer Film Properties of Stabilized UV-Polymerizable Thiol/Acrylate Systems

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ABSTRACT

An investigation was conducted to determine the effects of varying levels of effective UV energy density (UV-A) on the thermal and thermomechanical properties of UV-polymerizable, thiol/acrylate-functional systems stabilized with N-PAL[®]. UV-A energy density levels from 392 mJ/cm^2 to 1233 mJ/cm^2 were utilized and the thermal and thermomechanical properties of the polymer films were determined using differential scanning calorimetry (DSC) and dynamic mechanical analyses (DMA) techniques, respectively. The relative reactivity of these stabilized systems was also investigated using differential photocalorimetry (DPC) techniques.

INTRODUCTION

Students of the *Center for Applied Polymer Science Research* (CAPSR) at UH-*Downtown* have been investigating the chemistry and technology of thiol/acrylate functional systems over the past five years. In two previous papers presented at RadTech conferences in 2002 and 2004, respectively[1, 2], data were presented that indicated a shelf-life stability problem with systems containing typical acrylate-functional compositions. Attempts to ascertain the exact causes for the instability in those studies were not successful. The instability of these systems seemed ironic since additional investigations of their relative reactivity using differential photocalorimetry (DPC) indicated that they had lower reactivity than similar non-thiol-containing acrylate-functional systems; systems that had very good shelf-life stability in the absence of thiol-functional materials.

One of the several attempts used to stabilize the thiol/acrylate formulations in those previous studies involved removing the acrylated aliphatic urethane oligomer from the systems. This action was taken to determine if by some unknown mechanism the oligomer was causing the instability. However, this did not eliminate the stability problem.

Thiol/acrylate systems polymerize through a free-radically initiated step-growth polymerization process.[3] For these systems to polymerize rapidly into a crosslinked polymer network, the thiol-functional monomers must be at least tri-functional and the acrylate-functional monomers must be at least difunctional. This process involves a rapid abstraction of the R–S-H hydrogen atom to form a thiyl

radical (**R-S·**). This thiyl radical then attacks an acrylate double bond, **CH₂=CH-C(=O)-O-R**, forming a β-thioether carbon radical.[3] This resulting radical subsequently abstracts another hydrogen atom from a different thiol and the process continues "step-wise" alternating from hydrogen abstraction to double bond attack to hydrogen abstraction, etc. Since the reactive species have an average functionality greater than 2, these systems quickly "gel" into a vitrified matrix with exposure to UV irradiation, in accordance with step-growth polymerization kinetics.

It is known that the rate constant for chain transfer to thiol is greater than that for the radical addition polymerization for the acrylates.[3] Thus, it would appear that in the previously studied systems, any event that would have generated a free radical in the system would quickly result in the formation of thiyl radicals which would then initiate polymerization and gelation. Furthermore, the thiyl radicals are very effective oxygen scavengers.[3] Since oxygen is a free radical polymerization inhibitor, this oxygen-scavenging capability could also produce instability in the system. It, therefore, became necessary to incorporate a stabilizer into these thiol/acrylate systems to give them shelf-life stability. Prof. Charles Hoyle of the University of Southern Mississippi suggested N-PAL®, an aluminum salt of *tris*-N-Nitroso-N-phenylhydroxylamine.[4] This material proved effective at relatively low concentrations. The purpose of this paper is to report the effects of this stabilizer on the shelf-life stability and relative reactivity of thiol/acrylate systems. A further purpose is to report the effects of thiol-functional monomers on the thermal and thermomechanical properties of stabilized thiol/acrylate systems containing this stabilizer.

EXPERIMENTAL

Materials

The following raw materials were used without further purification:

1, 6-Hexanediol Diacrylate (HDODA) – Cytec Surface Specialties

Trimethylolpropane Triacrylate (TMPTA) – Cytec Surface Specialties

ALU-350 acrylated aliphatic urethane oligomer – Echo Resins and Laboratory

Irgacure® 184 Photoinitiator (1-hydroxycyclohexylphenyl ketone) – Ciba Specialty Chemicals

Trimethylolpropane *tris*-(3-mercaptopropionate) – Chemische Fabrik GmbH & Company

Aluminum(III) salt of *tris*-Nitroso-N-phenylhydroxylamine (N-PAL®) – ChemFirst Chemicals

Equipment

Fusion UV Systems Model VPS-6 Power supply with an EPIQ 6000, 600 W/in H-bulb lamp system was used to polymerize the films.

Electronic Instrumentation Technology (EIT) UV PowerMap radiometer was used to measure the effective UV-A energy density and the peak power density (peak irradiance) experienced by the films during photopolymerization.

TA Instruments Dynamic Mechanical Analyzer (DMA), Model 2980, was used to determine the effect of temperature on the storage and loss moduli of the polymer films. From the peak maximum in the alpha-transition of the loss modulus, the apparent glass transition temperature (Tg) was ascertained.

TA Instruments Universal Analysis 2000 software was used to analyze the data produced by the DMA.

TA Instruments Q100 Differential Scanning Calorimeter (DSC) was utilized to determine Tgs of the polymer films as a function of the effective UV energy density (UV-A).

TA Instruments Q100 DSC w/photocalorimetry accessory (PCA) was used to evaluate the relative reactivity of formulations as a function of stabilizer concentration. The maximum rate of reaction (peak max height), the time required to reach the peak maximum (peak max time), and the induction time, were each measured. The total amount of energy evolved during the polymerization (total exotherm) was also determined for each formulation.

Procedures

Preparation of the Formulation

The liquid formulation used in this study consisted of 65.0% by mass of the ALU-350 oligomer, 15.0% by mass of an equal-mass mixture of HDODA and TMPTA, 19.5% of thiol-functional monomer, 2.0 parts per hundred (pph) of the 1-hydroxycyclohexylphenyl ketone photoinitiator and varying amounts of the ***tris*-N-Nitroso-N-phenylhydroxylamine stabilizer**. Samples were prepared by blending the oligomer, monomers, photoinitiator, and stabilizer together in 4-oz brown jars. The tri-thiol was then added so that the thiol functionality exactly matched the acrylate functionality contributed by the monomers. Oligomer functionality was NOT used in this calculation because its molecular mass is unknown. Thus, the acrylate functionality contributed by the oligomer was in "excess", allowing for a dual polymerization mechanism.

Preparation of Polymer Films

A square, flat glass plate was used as the base for the films. A sample of a chosen formulation was poured onto the top of the glass and then cover with a sheet of polypropylene film. A wire-wound rod was subsequently used to "draw down" the liquid formulation between the glass and the polypropylene. This procedure not only provides a means for making films of a relatively uniform thickness but it can also serve to minimize oxygen inhibition during the polymerization process. However, the thiol/acrylate systems are expected to be less sensitive to oxygen inhibition than conventional free radical chain-growth polymerizing systems.

Experimental Design

To the extent possible, films were made of uniform thickness by the method describe above. These glass-coating-polypropylene "sandwiches" were then passed under the UV lamp at various UV-A energy densities at a constant peak irradiance value to produce the polymer films. Care was taken to insure that the peak irradiance was held constant when varying the effective UV energy density. The

effective UV energy density was controlled by varying the web speed with faster speeds producing lower UV exposures.

This study involved the use of five UV-A energy density values and a constant peak irradiance. The values for these variables ranged from 390 to 1230 mJ/cm^2 for the effective UV-A energies and 1638.8 mW/cm^2 for the peak irradiance.

RESULTS AND DISCUSSION

Stability Studies

Previous studies in this laboratory revealed that shelf-life stability problems were generated by addition of the thiol-functional monomers to otherwise stable acrylates.[1,2] Subsequently, a recommended[4] free radical scavenger was investigated to determine if stability could be achieved for these systems without adversely affecting photoreactivity. This aluminum salt of *tris*-N-nitroso-N-phenylhydroxyl amine (stabilizer) was incorporated into thiol/acrylate formulations at various concentrations. **Table 1** gives data indicating that for systems containing only monomers (no oligomer) the shelf-life stability was increased, as expected, by increased levels of the stabilizer. The control formulation in that study contained no thiol-functional monomer and no inhibitor (**Formulation E**).

Table 1
Stability Studies for "Monomer-Only" Systems using
*Aluminum **tris-**N-nitroso-N-phenylhydroxyl amine*

Formulation	Concentration of N-PAL (ppm)	As of 11/02/04
A	0	Gelled in < 3 days
I	5	> 14 days
H	10	> 14 days
F	12.5	stable > 111 days
G	25	stable > 111 days
B	50	stable > 128 days
C	100	stable > 128 days
D	200	stable > 128 days
E	control	stable > 128 days

Formulation	A	B	C	D	E	G	F	H	I
IBOA	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g
HDODA	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g
TMPTA	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g	11.67g
Irg. 184	0.72g	0.72g	0.72g	0.72g	0.72g	0.72g	0.72g	0.72g	0.72g
Tri-Thiol	34.80g	34.80g	34.80g	34.80g	0.00g	34.80g	34.80g	34.80g	34.80g
N-PAL	0.00g	0.0035g	0.0070g	0.0138g	0.00g	0.0018g	0.0009g	0.0007g	0.00034g
	0 ppm	50 ppm	100 ppm	200 ppm	0 ppm	25 ppm	12.5 ppm	10 ppm	5 ppm

It is evident in **Table 1** that "monomer-only" thiol/acrylate systems can be stabilized with as little as 12.5 ppm of the stabilizer. A concentration of 25 ppm stabilizer was utilized in the oligomer-containing formulation evaluated in the current investigation.

The formulations shown in **Table 1** included isobornyl acrylate (IBOA), a monofunctional monomer. Since thiol/acrylate reactions follow step-growth polymerization kinetics, IBOA will act as a "chain stopper" in these systems, resulting in a reduction in crosslink density. Therefore, IBOA was removed from the formulation in the current study. The composition of this formulation is given in **Table 2**. Thus far, this formulation has remained on the shelf without gelling for more than five months.

Table 2
Formulation Composition

Components	Concentration
Oligomer	65.00 %
HDODA	7.5 %
TMPTA	7.5 %
Tri-Thiol	19.5 %
Initiator	2 pph
Stabilizer	25 ppm

Relative Reactivity – *DPC Studies*

It was expected that as the amount of stabilizer was increased in the thiol/acrylate formulations, the reactivity would be negatively impacted. DPC methodology was used to see if this was a correct prediction. A typical DPC curve is given in **Figure 1**. The times shown in this figure are based on the
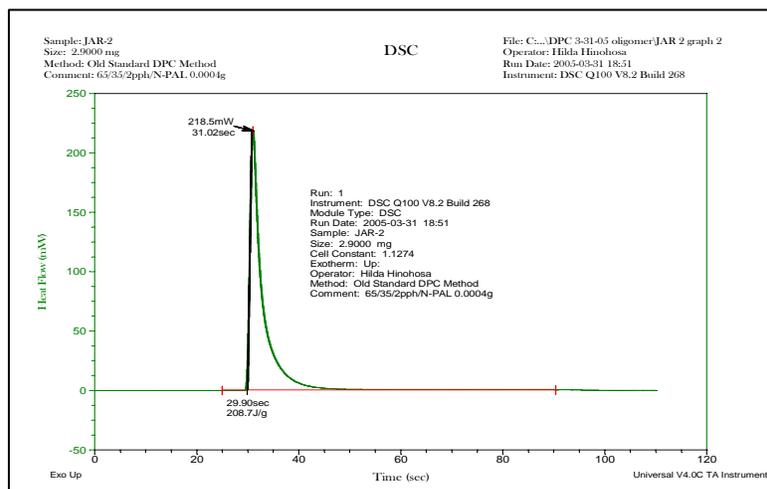
Figure 1
Typical DPC Exotherm Curve

fact that the shutter to the UV lamp was opened at the 30 second mark in the experiment. Thus, the peak max time for this sample was 1.02 s. The peak height for this sample was about 219 mW = 219 mJ/s. This is the fastest rate achieved during the photopolymerization. Finally, the total exotherm occurring during the 60 seconds that the lamp shutter was open was about 209 J/g of sample. The particular sample shown in **Figure 1** contained about 5 ppm stabilizer and no IBOA.

Figures 2, **3**, and **4** show the effects of the stabilizer level on the induction time, peak max time, and peak height, respectively, for monomer-only samples shown in **Table 1**. These figures also provide "aging" data for these samples. **Figure 2** shows that as the stabilizer concentration was increased from
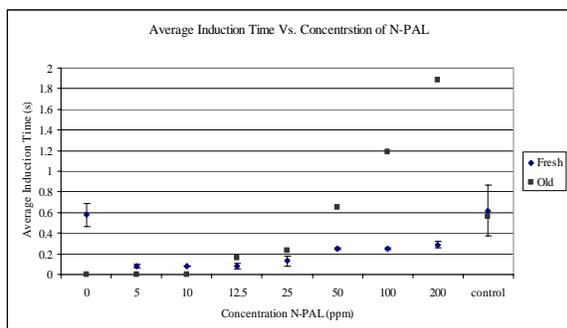

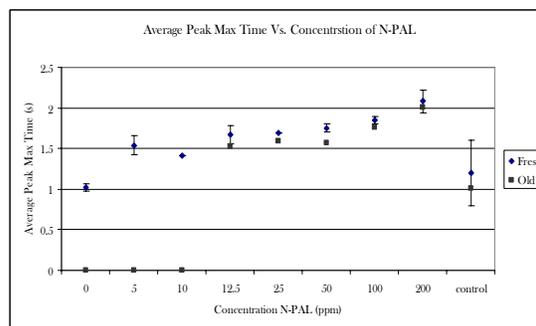**Figure 2**
Induction Time vs. ppm Stabilizer

Figure 3
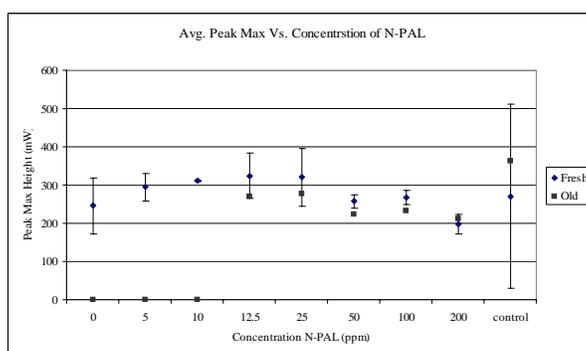*Peak Max Time vs. ppm Stabilizer*

Figure 4
Peak Height vs. ppm Stabilizer

5 ppm to 200 ppm, the induction time increased significantly, as expected. However, the induction time of all of samples containing any amount of stabilizer was significantly lower than that of the sample with no stabilizer. That particular sample had about the same induction time as the control sample that contained neither thiol nor stabilizer. Thus, it appears that there may be an interaction between the thiol and the stabilizer that reduces the induction time significantly. **Figure 2** also shows a rather profound aging effect. The data points marked "old" represent induction times of the same samples when they are three months old. Below about 30 ppm level, the induction times are essentially the same as for the fresh samples. But at 50 ppm, the induction times of the aged samples increased exponentially with stabilizer concentration. No clear explanation of this effect can be given at this time.

Figure 3 indicates that the overall reaction rate, as reflected in the peak max time is reduced by increasing levels of stabilizer. Again, this is not a surprise. Unlike the induction time data shown in **Figure 2** however, the data in **Figure 3** indicate a clear trend upward in time from 0.00 ppm to 200 ppm of stabilizer. Also, these data show little aging effect for samples with stabilizer levels higher than 10 ppm. Below 10 ppm, samples were not reevaluated after three months because they had gelled. Finally, **Figure 3** indicates that the peak max time for the control formulation was lower than for any of the formulations containing stabilizer. Thus, it may be important to minimize the amount of stabilizer to insure adequate photoreactivity in commercial operations.

Figure 4 gives data indicating that neither the stabilizer nor aging has any significant effect on the maximum rate of the reaction for these monomer-only formulations.

For the current study, the formulation shown in **Table 2** was evaluated. Since this formulation has a fixed amount of stabilizer, it was not possible to evaluate its photoreactivity as a function of stabilizer concentration. However, the reactivity of this formulation was compared with that of the 25 ppm stabilized monomer-only sample from **Table 1**. **Table 3** shows a comparison of these properties. The two systems seem to be similar in reactivity except for the maximum rate of reaction which is larger

Table 3
Relative Reactivity of
Oligomer-Containing Systems
(25 ppm Stabilizer)

Properties	Oligomer System	Monomer-Only System
Induction Time	0.2 s	0.08 s
Peak Maximum Time	1.3 s	1.38
Peak Height	177 mJ/s	410 mJ/s

in the case of the monomer-only system. This difference may be due to the fact that the concentration of total reactive groups is higher in the monomer-only system.

Thermomechanical Properties – *DMA Studies*

Figure 5 gives an example of a DMA scan showing the storage and loss moduli as a function of temperature. The so-called "alpha-transition" in the loss modulus curve at 5.45^o C is taken to be the Tg of the polymer. The relatively flat region of the storage modulus curve above the Tg indicates that elastic or "solid-like" properties of the polymer film are essentially independent of the temperature.
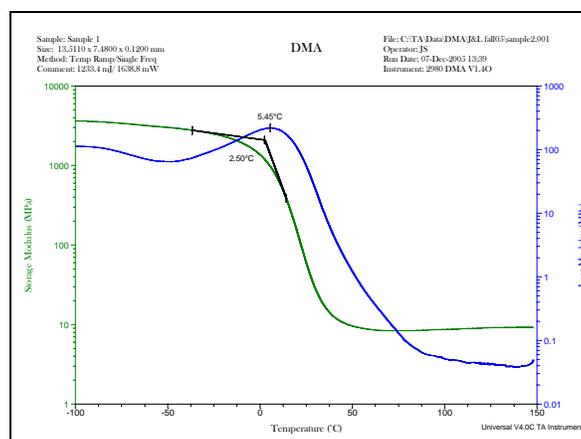

Figure 5
Dynamic Mechanical Analysis Curves

This region is known at the "rubbery plateau" and is useful for determining the relative crosslink densities of similar polymers. The higher the storage modulus in this region, the higher the relative crosslink density is expected to be.

Figure 6 shows a plot of the α-transition in the loss modulus for polymer films as a function of the effective UV-A energy density, while **Figure 7** shows a plot of the storage modulus α-transition as a
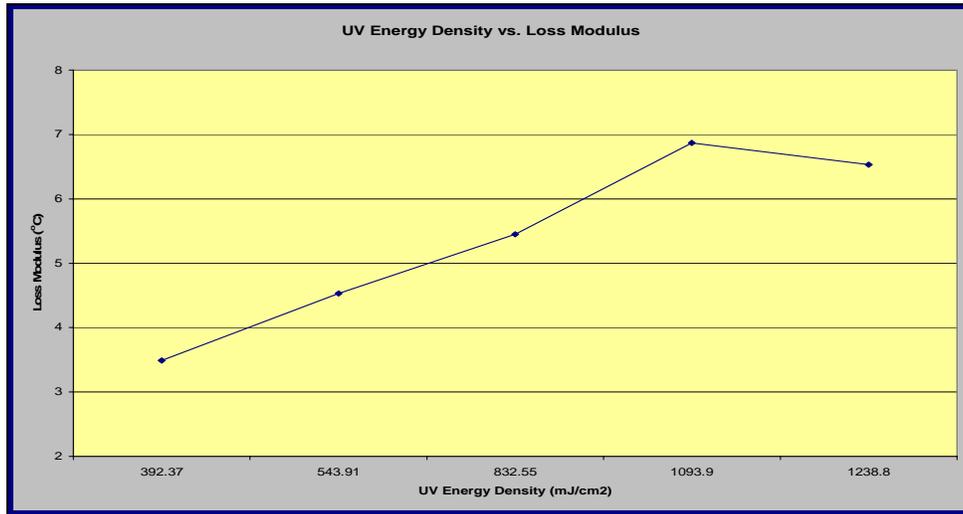

Figure 6
Loss Modulus α-Transition (Tg) vs. UV-A Energy Density

function of UV energy density. The trends in these two figures parallel each other and indicate that as the total UV energy absorbed during polymerization increases, the Tg for these systems also increases, albeit to a relatively small extent. This is expected when one considers that as the number of photons absorbed by each cm^2 of the film increases, the percent conversion of monomer to polymer should also
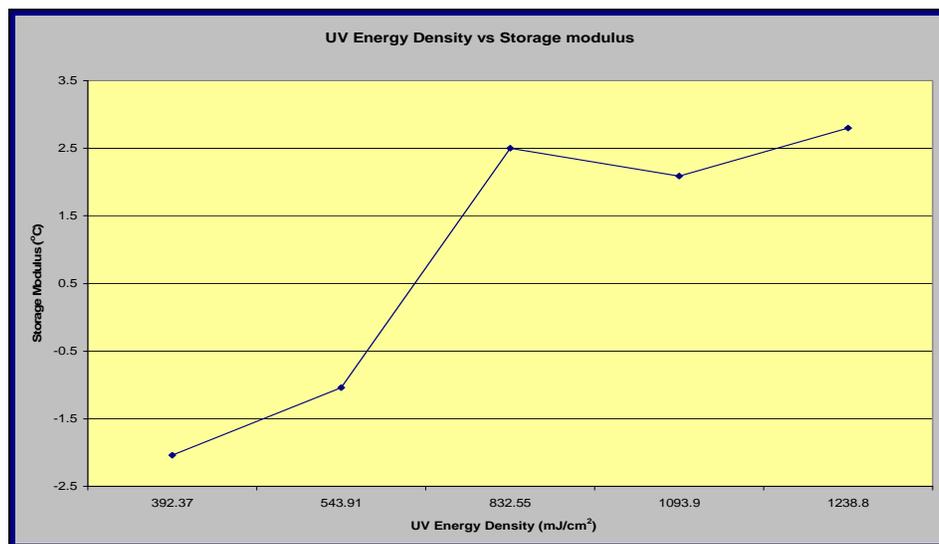
Figure 7
Storage Modulus α-Transition vs. UV-A Energy Density

increase. This should increase the crosslink density of the films, causing more restriction to segmental molecular motions, thus raising the Tg of the polymer. Further, a higher conversion would reduce the amount of free monomer present in the polymer films, thus reducing the plasticizing effect of the

unreacted monomer. It should be noted that no clear trend was observed for films polymerized with increasing levels of UV-A energy density in the rubbery plateau region of the DMA curves. Storage moduli in this region seemed to be slightly increasing up to 150°C rather than leveling out as expected. This may indicate that some thermal post-curing is occurring with most samples. The DSC results to be discussed later in this paper corroborate this hypothesis, though further DMA testing is needed wherein individual samples are run twice through the temperature cooling/heating cycle of the DMA. If thermal post-curing is occurring, the storage moduli in the rubbery plateau region should change, as should the apparent Tgs.

Thermal Properties – *DSC Studies*

DSC techniques allow the determination of a variety of thermal transitions as well as changes in heat capacity and other thermodynamic properties. For polymers, perhaps the most important thermal property is the Tg. An example of a DSC scan conducted during this study is given in **Figure 8**. Each of these experiments involved heating the sample, cooling the sample, and heating it once more. The purpose for this was to determine whether or not irreversible changes were being made in the sample during the first heating; changes such as would occur if post-curing were happening. The lower curve in **Figure 8** represents the first heating while the upper curve represents the second heating for the sample.
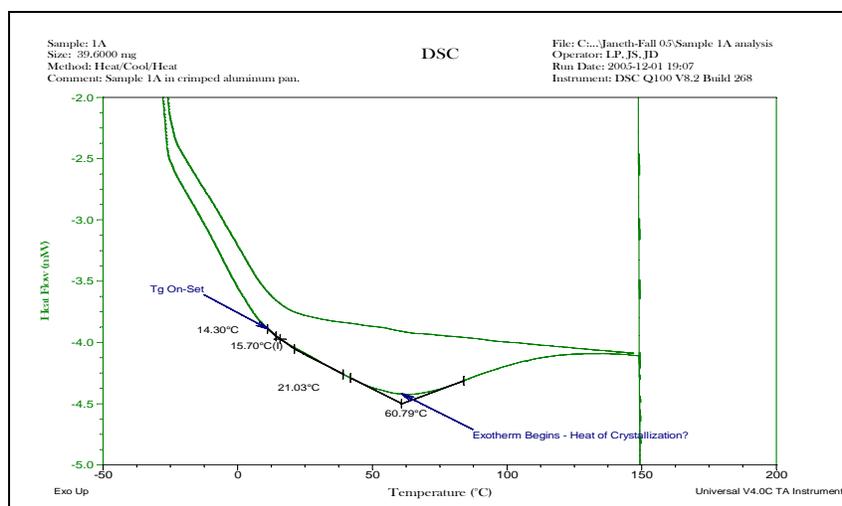

Figure 8
Typical DSC Scan of Thiol/Acrylate System

The relatively large endothermic change that occurred during the initial heating seems to have disappeared during the second heating. This, combined with the exothermic change observed in the first heating after the apparent Tg, indicates a thermal post-curing phenomenon, as previously postulated. By integrating the area under the exotherm curve, it may be possible to get a relative measure of the amount of thermal polymerization that is happening. **Figure 9** gives a plot of the post-Tg exotherm vs. the effective UV-A energy density used to polymerize and crosslink the film. It is apparent from these data that when the UV energy density used to polymerize the films is increased, the amount of unreacted material remaining in the polymer film is reduced, resulting in a smaller thermal post-cure phenomenon in DSC experiments. This is an expected result, *if* post-curing is occurring.
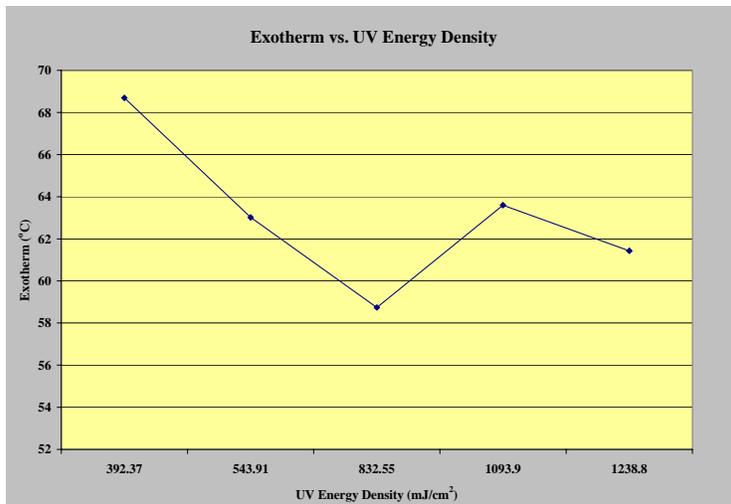
Figure 9
Post-Tg Thermal Exotherm vs.
UV-A Energy Density

The apparent post-cure phenomenon makes it difficult to interpret the DSC data for these materials. Compared with DMA, DSC is a much less sensitive technique for determining the glass transition, even under ideal conditions. If post-curing is occurring during the initial heating process, then one would assume that the Tg would be continually changing. Hopefully, these changes would result in an "ultimate" Tg that could then be identified in the second heating curve. Such transitions were identified in the second heating curves. However, they were significantly smaller than during the initial heating, resulting in a greatly reduced sensitivity. Further, these data no longer represent the thermal properties of the polymer films produced by UV energy alone, making their value questionable.

Figure 10 shows a plot of apparent Tg data for the initial heating curve along with "ultimate" Tg data for the second heating curve. There is, as expected, a significant increase in the apparent Tgs in the
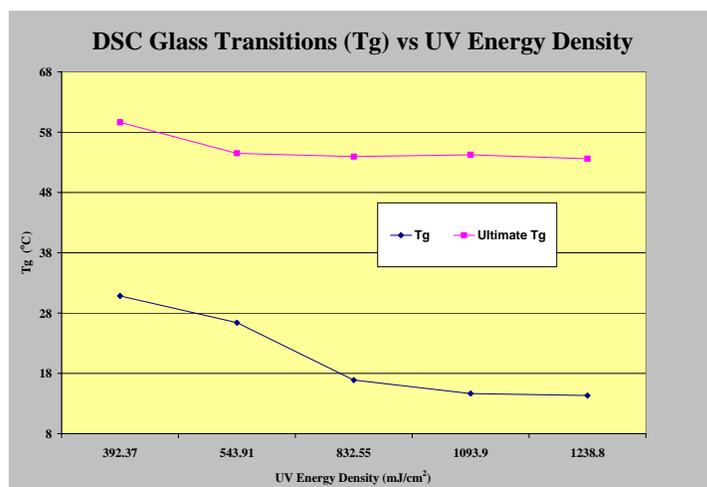

Figure 10
Apparent Tgs vs.
UV-A Energy Density

second heating curve. But strangely, both curves show the Tg to be decreasing with increasing UV-A energy density. This phenomenon is more pronounced in the initial heating curve. The "ultimate" Tgs seem to be independent of the UV-A energy density above about 540 mJ/cm^2 as might be expected with more complete conversion of monomer to polymer.

SUMMARY AND CONCLUSIONS

Aluminum *tris*-N-nitroso-N-phenylhydroxyl amine has been shown to provide good shelf-life stability for thiol/acrylate-functional systems at concentrations low enough to not adversely affect the reactivity of the formulations. It was found that as little as 25 ppm of this stabilizer was adequate to give greater than 5 months shelf-life stability to a formulation containing an acrylated aliphatic urethane oligomer, two multifunctional acrylate monomers, a trifunctional thiol monomer, and a photoinitiator. Crosslinked polymer films of this formulation were prepared using various effective UV-A energy densities and were subjected to DMA and DSC methodologies. The DMA results indicated that the Tgs of the films increased slightly with increased UV energy density, as would be expected with increased percent conversion of monomer to polymer. Increased percent conversion should reduce the amount of free monomer available to cause plasticization of the polymer and should also increase the relative crosslink density. The DSC results were complicated by apparent thermal post-curing processes during the experiment. A notable exotherm occurred for each sample following the apparent Tg in their respective thermal scans. Subsequent heating of the same samples indicated an absence of this exotherm and gave apparent Tgs at significantly higher temperatures than in the initial heating. Thus, interpretation of the UV-A energy density effects on Tg is complicated for the DSC data.

ACKNOWLEDGEMENTS

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