

Effects of Very Low Levels of UV Energy Density and Peak Irradiance on the Thermomechanical Properties of UV-Polymerized Films: A Poster Presentation

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ABSTRACT

An investigation was conducted in the *Center for Applied Polymer Science Research (CAPSR)* to determine the effects of very low levels of UV energy density and peak irradiance (PI) on the thermomechanical properties of UV-polymerized films. This work culminates a long-term investigation into the effects of these key UV light parameters on a variety of tensile and thermomechanical properties of UV-polymerized films. Earlier work demonstrated a lack of PI effect on a variety of polymer film properties for values above 400 mW/cm². The current study focused on PI levels from about 80 mW/cm² up to about 440 mW/cm² to determine if a postulated “saturation effect” exists below 400 mW/cm². Such an effect could well preclude the observation of PI influences on properties above that level. Results are interpreted with this issue in mind.

INTRODUCTION

Previous reports from this laboratory¹⁻⁴ indicated that using relatively high intensity (irradiance) ultraviolet (UV) light to polymerize acrylate-based formulations produced no discernable effects on the tensile or thermomechanical properties of the resulting polymer films. In those studies, peak irradiance (PI) values ranging from about 400 mW/cm² to more than 5000 mW/cm² were investigated. The lack of a peak irradiance correlation with polymer film properties in those studies was unexpected and led to a consideration of a proposal put forward by Prof. Christian Decker.

Decker and Moussa⁵ developed an experimental technique in 1988 that they referred to as “Real Time Infrared” (RTIR). This technique allows the kinetics of UV-polymerization processes to be monitored quantitatively. Based on some RTIR results, Decker⁶ postulated a “saturation effect” near 200 mW/cm². He was referring to the fact that separate RTIR scans of the same formulation above this irradiance were identical to each other, indicating a leveling-off of the increase in the percent conversion of monomer to polymer with irradiance and time. He attributed this result to the fact that when the rate of polymerization is very high, as it is in most photopolymerization processes, the diffusion of monomer becomes the rate-determining step, rather than the rate of radical generation.

The implication of this is that above about 200 mW/cm² PI, further increases in irradiance should not have a significant effect on the percent conversion and, therefore, on the properties of the polymer film. If true, this would help explain the lack of correlation between the PI values and the thermal and thermomechanical properties of UV-polymerized films observed previously in this laboratory. Since the lowest peak irradiance evaluated was about 400 mW/cm², it would also indicate the possibility that films polymerized with PI values significantly below 200 mW/cm² might exhibit a peak irradiance correlation with film properties. Thus, it

seemed useful to investigate the properties of films that were polymerized and crosslinked using levels of peak irradiance below 200 mW/cm², in order to determine if the “saturation effect” could be identified. A second concurrent purpose was to extend the previously reported work¹⁻⁴ to very low peak irradiance values (<400 mW/cm²) and UV energy density - *also known as “UV dose”* - levels (<200 mJ/cm²).

EXPERIMENTAL

Materials: The following raw materials were provided without charge by their respective suppliers and were used without further purification:

ALU-350 acrylated aliphatic urethane oligomer was provided by Echo Resins and Laboratory, Versailles, MO.

Trimethylolpropane triacrylate (TMPTA), *1,6-hexanediol diacrylate (HDODA)*, and *isobornyl acrylate (IBOA)* were all provided by Surface Specialties UCB, Smyrna, GA.

1-hydroxycyclohexylphenyl ketone (Irgacure[®] 184) photoinitiator was provided by Ciba Specialty Chemicals Corporation, Tarrytown, NY.

Equipment:

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

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

EIT's *PowerView 1.01* software was used to analyze the data collected by the radiometer.

TA Instruments' *Dynamic Mechanical Analyzer (DMA), Model 2980*, was used to determine the effect of temperature on the storage modulus, the loss modulus, and the so-called “tan δ ” of the polymer films. From the peak maximum in the alpha-transition of the loss modulus, the apparent glass transition temperature (T_g) was ascertained.

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

Procedures:

Preparation of the Formulation -

The liquid formulation used in this study consisted of 80% by mass of the ALU-350 oligomer, 20% by mass of an equal-mass mixture of each of the three monomers, and two parts per hundred (pph) of the 1-hydroxycyclohexylphenyl ketone photoinitiator. Small samples of this formulation were prepared in 4-oz brown jars, as outlined below, and then they were blended together to make a single larger “batch” of the formulation known as “80/20/2 pph”.

The monomer “master batch” used to prepare this formulation was prepared by mixing 24.0 g each of TMPTA, IBOA, and HDODA into a brown glass jar. Next, 56.0 g of the oligomer were placed into each of five 4-oz jars. Subsequently, 14.0 g of the monomer master batch were added to each of the 4-oz jars containing oligomer. The jars were then placed in an oven between 45° and 50°C in order to reduce the oligomer viscosity. This aided the mixing process.

After all the individual mixtures were uniform in appearance, 1.4 g of photoinitiator were added to each jar and the mixtures were shaken until the liquid formulations were completely homogeneous in appearance. Finally, each of these small homogeneous mixtures was poured into a 20-oz brown jar to form the finished “80/20/2 pph” formulation.

Preparation of Plates -

A square, flat glass plate was used as the base for the films. A layer of Mylar® polyester film was taped firmly to the surface of the glass. Some of the “80/20/2-pph” formulation was then poured onto the top end of the base-layer of Mylar and then a cover sheet of Mylar was placed over the formulation. A wire-wound rod was subsequently used to “draw down” the liquid formulation between the two Mylar films, forming a Mylar-coating-Mylar “sandwich”. This procedure not only provides a means for making films of a relatively uniform thickness but also serves to minimize oxygen inhibition during the polymerization process.

Experimental Design:

To the extent possible, films were made of uniform thickness by the method describe above. These polyester-coating-polyester “sandwiches” were then passed under the UV lamp at various UV energies and peak irradiance values to produce the polymer films. Care was taken to insure that the UV energy density was held constant when varying the peak irradiance values and visa-versa. Manipulating the line speed varied the energy density, with faster speeds producing lower energies. The peak irradiance was varied by changing the relative amount of electrical power being supplied to the lamp with higher power settings producing higher peak irradiance values. The distance of the lamp from the moving web was held constant during this investigation.

This study involved the use of seven peak irradiance values and five UV energy density values in two separate trials. These were the independent variables for this study. The values for these variables ranged from 80 to 442 mW/cm² for the peak irradiance and from 75 to 220 mJ/cm² for the UV energy density. The purpose of the second trial was simply to corroborate the observations from the first.

The dependent variables evaluated in this study were generated using DMA technology. This characterization technique generates curves representing the storage modulus, the loss modulus, and the so-called “tan δ ” of the polymer film as a function of temperature. **Figure 1** depicts an example of a DMA run showing these three curves. A discussion about the significance of key transitions in these curves follows in the **RESULTS AND DISCUSSION** section of this presentation. These transitions constitute the dependent variables for the current study.

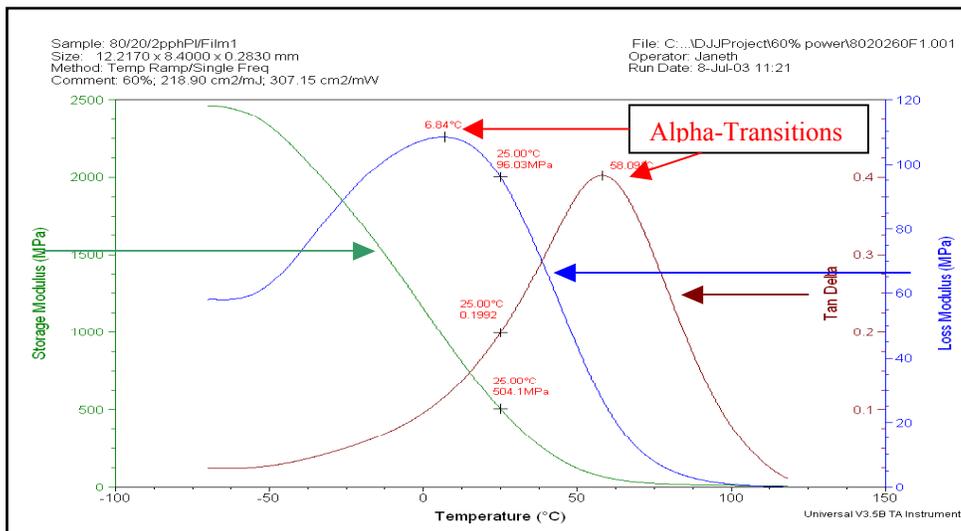


Figure 1
Dynamic Mechanical Analysis Curves

Data Analysis Methodology:

The DMA data obtained in both of the trial runs were analyzed using the same method. This method involved treating the data points representing specific UV energies as “pseudo-replicates”. That is, for each specific value of UV energy density in each trial run, there were seven different responses for a given dependent variable corresponding to the seven different PI values being used. This is depicted in **Figure 2**. The average of these responses was used to plot the UV energy effect for each dependent variable.

The rationale for doing this is that while variation was evident in the peak irradiance response data (see **Figure 3**) for a given UV energy, no clear trends appeared. This is completely consistent with previously reported results¹⁻⁴ and indicates that peak irradiance does not significantly influence the polymer film properties evaluated. Therefore, the variation observed in the dependent variable responses at a given UV energy was considered to be similar to the random scatter in results that would have been observed if seven true replicates at each UV energy had been evaluated. This is illustrated in **Figure 2** where a plot of UV energy vs. the loss modulus alpha-transition data is given. This figure shows that for each UV energy density, there are seven data points corresponding to the seven different peak irradiance values, as previously stated. Since it is known that the PI has little or no effect on the thermomechanical properties of UV-polymerized films, then each of the seven data points for a given UV energy in **Figure 2**, theoretically, should have been the same. Since they are not the same, they can be thought of as being representative of the variation in the UV energy data. This “pseudo-replicate” assumption was used in the analysis of data for this study.

RESULTS AND DISCUSSION

This study involved the generation of thermomechanical property data using dynamic mechanical analysis techniques. This technology produces curves such as those shown in

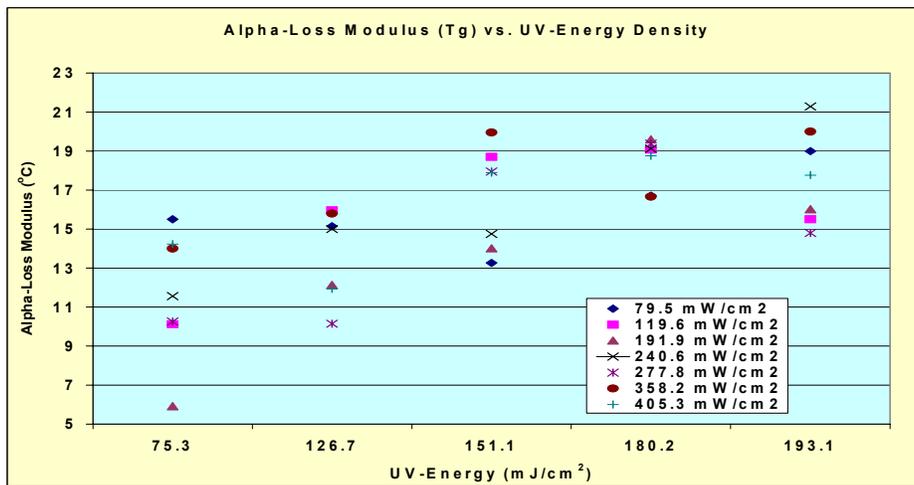


Figure 2
“Pseudo-Replicates” for UV Energy Density

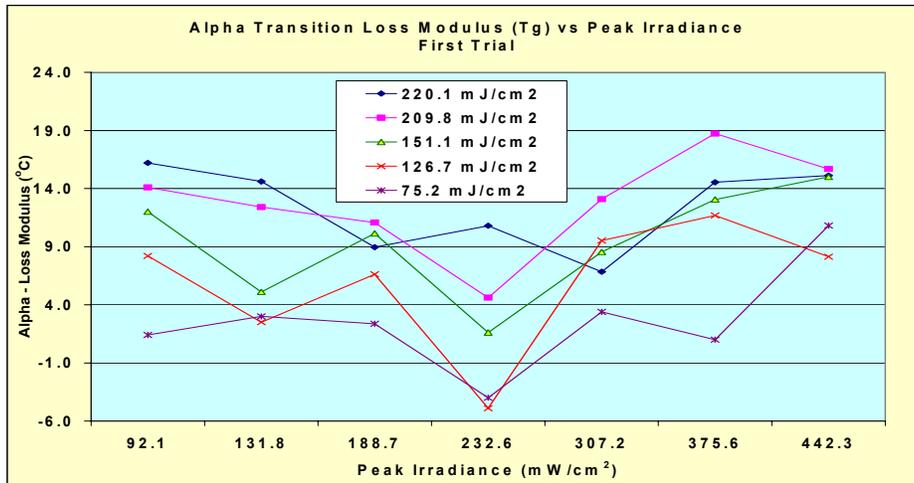


Figure 3
Loss Modulus α -Transition vs. Peak Irradiance – Trial 1

Figure 1. That figure shows the effect of temperature on the storage modulus and the loss modulus of the polymer film being characterized. It also gives the $\tan \delta$ curve. This curve is the locus of points representing the ratio of the loss modulus to the storage modulus at each temperature. It should be noted that the loss modulus and storage modulus axes are of the same units but have different scales.

Since these polymer films are “viscoelastic” materials, they have both “liquid-like” and “solid-like” characteristics. The loss modulus curve in the DMA scan represents the “viscous” or “liquid-like” properties of the polymer as a function of temperature, while the storage modulus curve represents the “elastic” or “solid-like” properties of the polymer as a function of temperature^{3, 4}.

In this investigation, the effects of UV energy density and peak irradiance on the alpha-transitions of the loss modulus and $\tan \delta$ were evaluated. These transitions are the larger

peaks on the right side of each curve. For the storage modulus, the alpha transition is the temperature where the slope of the curve begins to decrease rapidly. However, in this study, the effects of UV energy density and peak irradiance on the storage modulus were evaluated at 25°C, rather than at the alpha-transition, since that transition was more difficult to evaluate with precision.

Theoretically, all three alpha-transitions might be expected to occur at the same temperature, the T_g . However, for most systems, they do not occur at the same temperature and there is debate about which value best represents the T_g .³ While many researchers refer to the $\tan \delta$ peak as the T_g for the polymer, in this study, the peak of the alpha-transition for the loss modulus was taken to be the best representation of the T_g . This was because the films were all quite flexible at 25°C, while all the observed $\tan \delta$ peaks are significantly higher than 25°C and the loss modulus alpha-transitions are all somewhat lower than 25°C.

Figures 4 and 5 show the effect of the peak irradiance on the Storage Modulus at 25°C for the first and second trials, respectively. Once again, these data indicate that peak irradiance

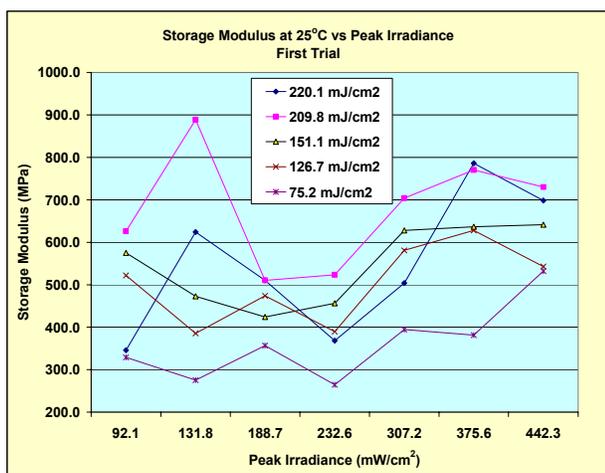


Figure 4
PI vs. Storage Modulus @ 25°C - Trial 1

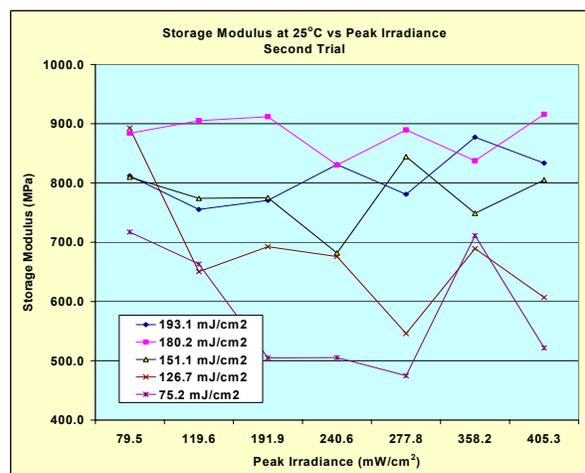


Figure 5
PI vs. Storage Modulus @ 25°C - Trial 2

exhibits little or no reproducible effect on the 25°C storage modulus. The different curves in these figures represent different constant UV energies, as indicated in the legends. A definite UV energy effect is evident. But from around 80 mW/cm² to above 400 mW/cm² PI, there is scatter in the data but no discernable trend, particularly in the second trial run. In fact, comparison of the 25°C storage modulus data with those reported by Christmas, et. al.³, where the PI values ran from 1080 to 2230 mW/cm², indicates that the 25°C storage moduli are all in the range of 300 to 900 MPa. Thus, in spite of very large changes in peak irradiance, very little, if any, changes in 25°C storage moduli have been observed.

This same lack of a PI effect is evident for the loss moduli, as shown in **Figures 3 and 6**, and for the $\tan \delta$ data shown in **Figures 7 and 8**. So, as with the studies involving peak irradiance values above 400 mW/cm², this study shows no obvious reproducible effect of very low peak irradiance on the thermomechanical properties of the polymer films. This means that if the postulated “saturation effect” exists, it does not produce a measurable effect on the thermo-

mechanical properties of the films in the peak irradiance range from 80 mW/cm² and 440 mW/cm².

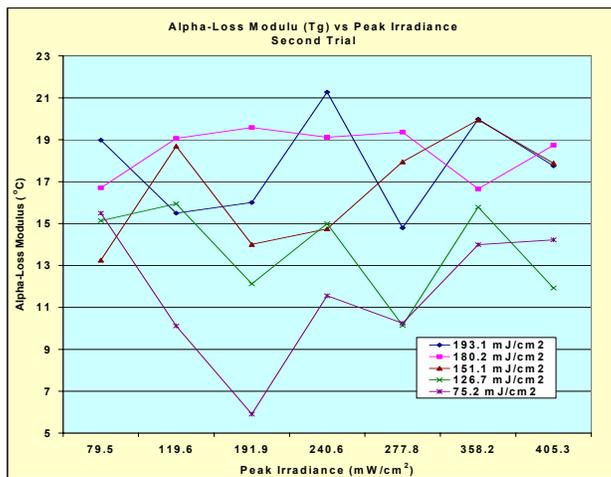


Figure 6
PI vs. Loss Modulus α -Transition – Trial 2

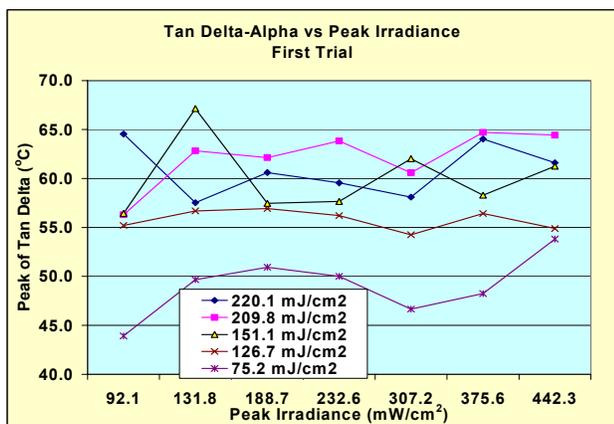


Figure 7
PI vs. Tan δ α -Transition – Trial 1

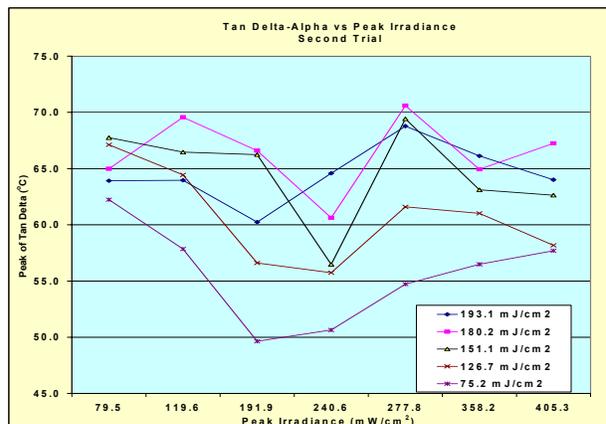


Figure 8
PI vs. Tan δ α -Transition – Trial 2

While the peak irradiance exhibits no significant effects on any of the mechanical and thermomechanical properties thus far evaluated, the results of this investigation do show measurable UV energy effects. For example, **Figures 9 and 10** show significant positive effects of UV energy on the 25°C storage modulus. In both trial runs, sharp increases in storage moduli were observed, indicating that when the UV energy density is increased, a corresponding increase in either percent conversion or crosslink density or both occurs, as expected with free radical polymerization processes. This results in a “stiffer” film, one that is able to absorb energy more effectively.

As with the storage modulus, **Figures 11 and 12** both show that an increase in UV energy also produces a significant increase in the peak of the alpha-transition of the loss modulus, or the T_g. This too is expected, since an increase in the conversion and/or crosslink density should produce an increase in the resistance of polymer chains to coordinated segmental motions that occur at the T_g.

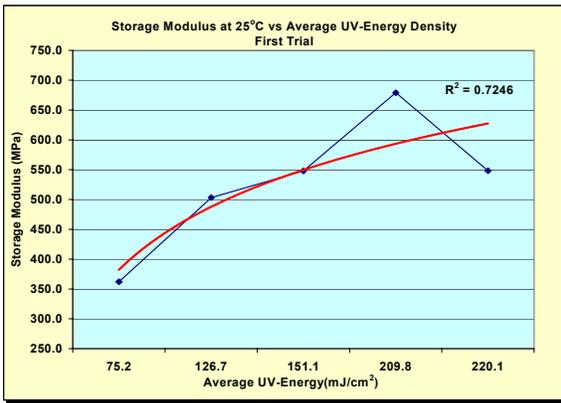


Figure 9
UV Energy vs. Avg. 25°C Storage Modulus

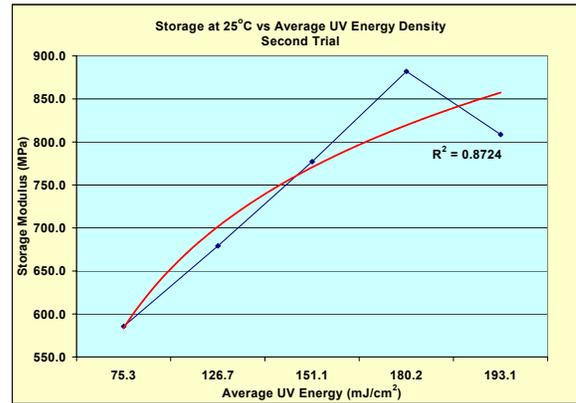


Figure 10
UV Energy vs. Avg. 25°C Storage Modulus

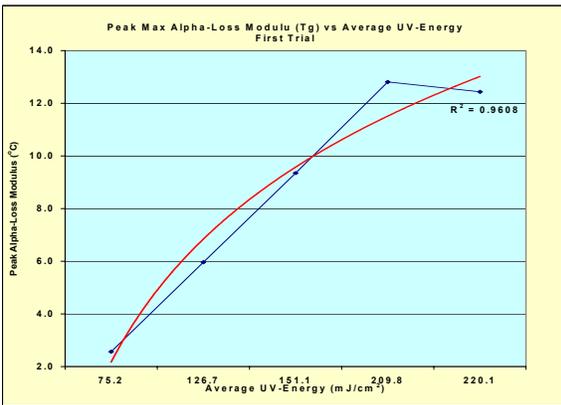


Figure 11
UV Energy vs. T_g

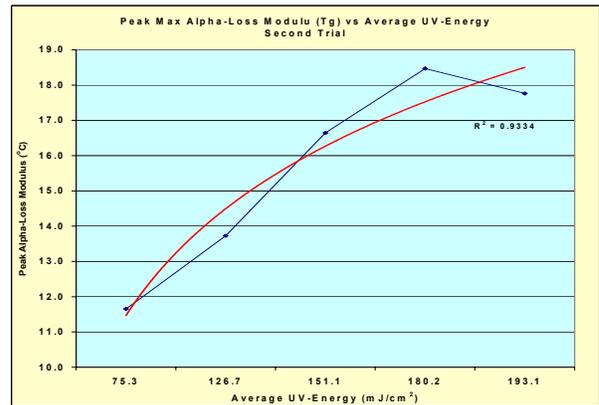


Figure 12
UV Energy vs. T_g

A comparison of the data generated from the two trials for the storage and loss moduli, using the “pseudo-replicate” approach to the analysis, did not indicate perfect reproducibility in absolute terms. For example, the T_g's ranged from about 11.5°C to about 18.5°C in the second trial run, while for the first trial, they ranged from about 2.5°C to about 13°C. But in this study, emphasis was placed on verifying the trend in the effects and those trends are clearly indicated by the data in both sets of experiments.

By contrast, the two trials for the UV energy effects on the alpha-transition in the tan δ curve were more comparable, as can be seen in **Figures 13 and 14**. What are plotted in these graphs are the temperatures at which the ratio of the loss modulus to the storage modulus is at a maximum. The ratios themselves are not plotted, so these graphs do not give direct indication of the relative amounts of “liquid-like” versus “solid-like” properties of the polymer films. Rather, once again, they indicate that as the UV energy density is increased, the percent conversion and/or the crosslink density are increasing, causing the maximum in the tan δ curve to occur at a higher temperature.

This effect is further indicated by data plotted in **Figures 15 and 16**. These figures show the effects of increasing UV energy on the value of the tan δ at 25°C. Since the tan δ is the ratio of “liquid-like” properties to “solid-like” properties, these figures give indication that as the UV

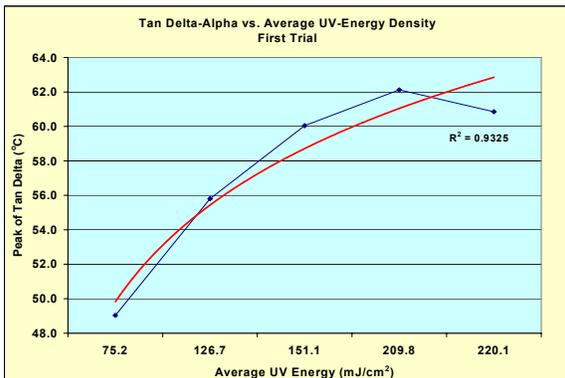


Figure 13
UV Energy vs. Peak of Tan δ

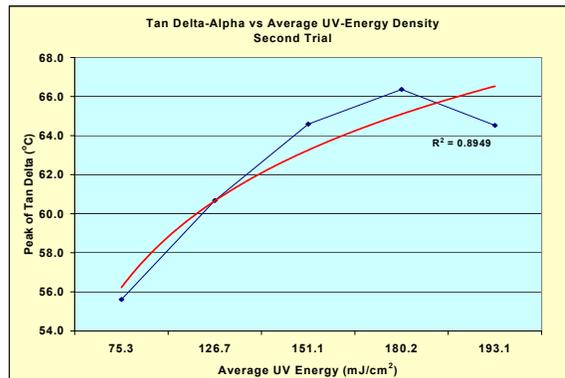


Figure 14
UV Energy vs. Peak of Tan δ

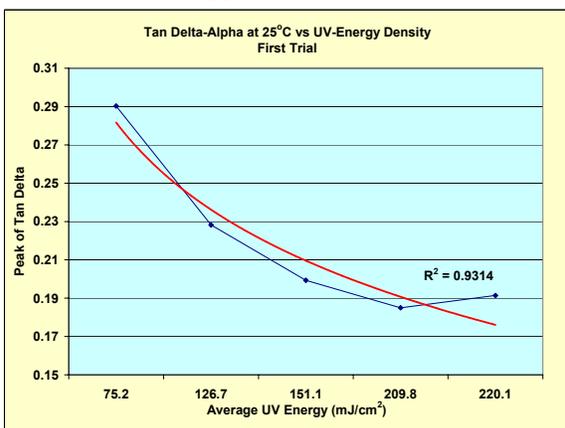


Figure 15
UV Energy vs. 25°C Tan δ

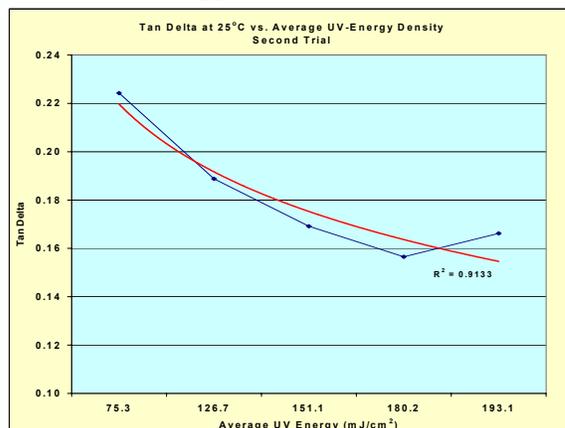


Figure 16
UV Energy vs. 25°C Tan δ

energy density increases, the “liquid-like” nature (the viscous component) decreases at 25°C. This would be expected for a system that was increasing in percent conversion of monomer to polymer and/or crosslink density. The polymer should, in fact, be more “solid-like” under conditions of higher percent conversion and/or crosslink density.

SUMMARY AND CONCLUSIONS

This set of experiments completes a long and detailed study designed to investigate the effects of UV energy density and peak irradiance on the mechanical and thermomechanical properties of UV-polymerized films. The model formulations used throughout were based on an acrylated aliphatic urethane oligomer and an equal mass mixture of three acrylate-functional monomers; one trifunctional, one difunctional, and one monofunctional. The mechanical properties investigated in previous studies included tensile strength, elastic modulus, and %-elongation and were evaluated using Instron tensile testing equipment¹⁻⁴. The thermomechanical testing was done using DMA techniques^{3,4}.

Prior to this report, the peak irradiance values ranged from 400 mW/cm² to over 5000 mW/cm². For the current study, they ranged from 78 mW/cm² to 450 mW/cm². This study is the fifth in the series and as with the other four, no correlation of PI with thermomechanical properties was observed. This finding indicates that the postulated “saturation effect” believed to possibly be responsible for the lack of observed peak irradiance effects above 200 mW/cm² is not

detectable by this method. This study spanned the range both below and above this “threshold” level of UV irradiance and yet, no effects were observed.

As in the previous four studies, the results of this investigation showed the expected effects on properties of increasing the UV energy density. The UV energy used to polymerize a sample is the total energy the film experiences per cm^2 of surface; the total number of photons each cm^2 of film experiences when passing through the “curing” chamber. Thus, if higher UV energy densities are used, more total photons strike the film. This means that more photons are absorbed effectively by the photoinitiator molecules and more radicals are thus formed. As the concentration of radicals increases, more acrylate double bonds are reacted and the percent conversion of monomer-to-polymer goes up. In the presence of multifunctional oligomers and monomers, the crosslink density would also be expected to increase. Both of these expected results would have direct effects on tensile strength, elastic modulus, storage modulus, loss modulus, $\tan \delta$, and T_g . Throughout this investigation, these effects have been observed.

The results of this and the four previously reported investigations give strong indication that the tensile and thermomechanical properties of UV-polymerized films are most significantly affected by the UV energy density. In contrast, the peak irradiance experienced by the formulations during polymerization seems to have little or no effect on the final film properties, even at values as low as 78 mW/cm^2 or as high as 5000 mW/cm^2 , as long as the total UV energy is held constant. This result demonstrates the fact that relatively high amounts of UV light irradiance can be utilized in order to enhance the rate of the photopolymerization reaction and, thus, production line productivity, without jeopardizing tensile or thermomechanical properties of the resulting polymer.

FUTURE PLANS

While this report represents a certain level of “closure” to a long-term laboratory investigation, there remain other aspects of such a study to be investigated. One can imagine that the investigation could, and possibly should, be expanded to include UV-polymerizable systems based on something other than acrylated aliphatic urethane oligomers; perhaps acrylated epoxies or acrylated polyesters should be evaluated. However, there is no theoretical basis to believe that the overall results would be different, since the acrylate functionality is common to all three systems.

One can also imagine a continuation of this study wherein other end-use properties are investigated for their response to UV energy density and peak irradiance. For example, a detailed literature review is currently underway to determine what results have been reported concerning the weathering properties of coatings polymerized with relatively high irradiance UV light versus those polymerized with lower irradiance light⁷. Depending on the results of this literature review, it is expected that a project will be developed to look more closely at these irradiance effects on weathering, abrasion resistance, and related coating properties.

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