

The Relative Effects of AC- and DC-Powered UV Lamp Systems on the Properties of UV-Polymerized Films

Mr. Timothy Morales, Ms. Elda Rueda, and Prof. Byron Christmas
University of Houston-Downtown, Houston, TX 77002

Abstract

An investigation into the relative effects of AC-powered vs. DC-powered UV lamp systems has been conducted in this laboratory. It has been reported that DC-powered lamps may produce polymer film properties in acrylate-based UV-polymerizable systems that represent improvements over those generated by AC-powered lamps under the same polymerization conditions. The purpose of this project was to investigate this hypothesis using dynamic mechanical analysis (DMA) and other relevant techniques. DMA properties such as 25°C storage moduli, “rubbery plateau” storage moduli, $\tan \delta$ peak temperatures, and $\tan \delta$ half-height widths were evaluated. The results highlight the similarities and differences between these two types of UV lamp systems. They also give indication of the effects of relative crosslink density on the observed variation.

INTRODUCTION

A new direct current (DC)-powered electrodeless ultraviolet (UV) lamp system was recently introduced for use in UV-polymerization processes¹. Kazuo Ashikaga, on behalf of Jönsson, et al., reported in February 2007 that this lamp may be able to improve, among other properties, the homogeneity of UV-polymerized acrylate-based formulations by reducing the amount of microgel formation that occurs in the initial stages of the polymerization process². This was based on the reasonable assumption that a constant (non-fluctuating) UV power source would minimize premature termination of growing polymer chains, thus, decreasing the microgel formation. This hypothesis was tested by Jönsson, et al. primarily by comparing and contrasting photomicrographs of trimethylolpropane triacrylate (TMPTA) polymerized using either an alternating current (AC)-powered lamp or the new DC-powered UV lamp system.

It has been well established^{3,4} that acrylate-functional systems, when UV-polymerized and crosslinked, produce polymer films that are quite heterogeneous on the molecular scale. This, indeed, is believed to be the result of rapid microgel formation³ during the initial stages of the process. These microgels create domains within the polymer matrix that are very different in density and morphology from one another and from the more uniform amorphous matrix in which they are dispersed. **Figure 1** shows a schematic representation of microgels in an amorphous polymer matrix.

In these heterogeneous polymer films, there are multiple interfaces among areas of varying density. These represent sites where crack propagation may occur, reducing the impact resistance and other mechanical properties of the polymers. A uniformly amorphous polymer containing no microgels should have a very high impact resistance as it would represent a nearly perfect absorber of energy. This has, in fact, been demonstrated by Hoyle, et al. using selected thiol-ene systems⁵.

The non-uniform microdomains within a polymer also produce a broad glass transition temperature (T_g) range as the morphologies within these microdomains are quite different from each other and from that of the polymer matrix. The range of T_g s for a given polymer film can be as large as 150 to 200°C as can be observed in $\tan \delta$ curves obtained during dynamic mechanical analyses (DMA). **Figure 2** depicts the $\tan \delta$ curves of a relatively heterogeneous

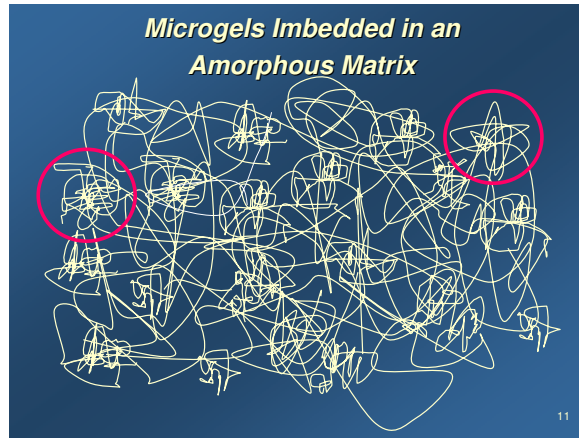


Figure 1

Schematic Representation of Microgels
 Courtesy of Prof. Charles E. Hoyle, University of Southern Mississippi
 Used by Permission

polymer film and one that is relatively homogeneous. The $\tan \delta$ width at the half-height of the more heterogeneous film (left) covers a temperature range of about 80°C or more while the more homogeneous polymer (right) exhibits a much narrower $\tan \delta$ range of about 15°C. DMA technology allows one to easily determine the width of the $\tan \delta$ at its half-height. From these data, the relative degree of polymer heterogeneity can be determined.

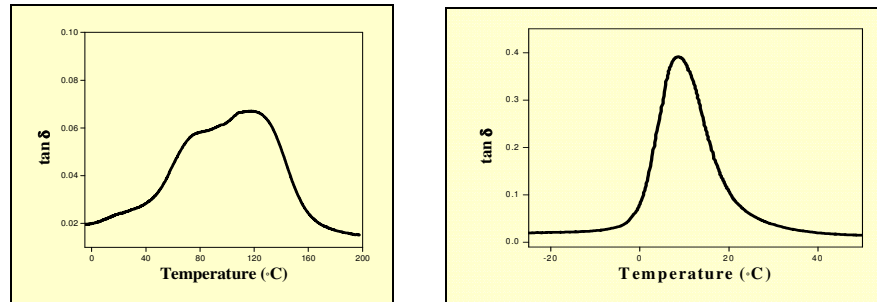


Figure 2

Heterogeneous (left) vs. Homogeneous (right) Polymers
 Courtesy of Prof. Charles E. Hoyle, University of Southern Mississippi
 Used by Permission

It has also been demonstrated, both in this laboratory⁶ and in others⁷, that the relative average acrylate functionality of the formulation is directly related to microgel formation and the degree of heterogeneity. The higher the overall average functionality of the formulation, the more microgel formation is expected. This effect is demonstrated very convincingly in **Figure 3** where the $\tan \delta$ curves for a series of formulations are displayed. These formulations differ in the level of monofunctional monomer present. The formulation with the highest level of monofunctional monomer should produce the lowest crosslink density. It also should produce the least amount of microgel formation and have the narrowest $\tan \delta$ curve. In contrast, the formulation with no monofunctional monomer should have the highest level of microgel formation. This is precisely

what is seen in **Figure 3**. The top $\tan \delta$ curve is the narrowest and each succeeding curve in the series has increased half-height width over the one preceding it. From top to bottom they represent uniformly decreasing levels of monofunctional monomer.

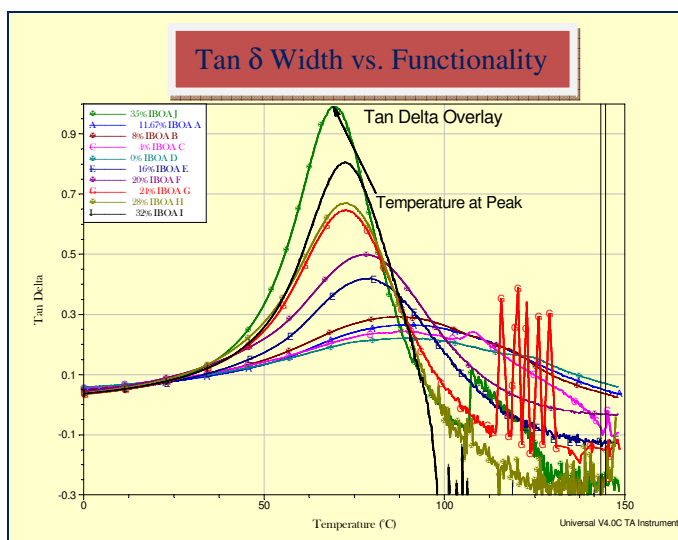


FIGURE 3
Tan δ Curve Width vs. Average Functionality⁶

With DMA and other polymer characterization techniques available, it seemed reasonable to use some of them to determine what, if any, polymer property differences could be observed between identical formulations polymerized using an AC-powered lamp and those polymerized using a DC-powered UV lamp. The initial objective was to use the $\tan \delta$ peak half-height widths to determine the relative heterogeneity of identical UV-polymerizable systems prepared using the two different lamp systems. Further, this investigation sought to determine what other thermal and thermo-mechanical property differences might be observed, whether or not the polymers were determined to have different levels of heterogeneity. The final objective of this project was to assess the effects of relative oligomer/monomer functionality and, thus, crosslink density, on the overall heterogeneity of acrylate-based UV-polymerizable systems.

EXPERIMENTAL

Materials:

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

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

1,6-Hexanediol diacrylate (HDODA), *Propoxylated Glycerol Triacrylate (OTA-480)*, and *trimethylolpropane triacrylate (TMPTA)* were provided by Cytec Surface Specialties, Smyrna, GA.

Irgacure®184, a Norrish I cleavage-type photoinitiator, 1-hydroxycyclohexylphenyl ketone, was provided by Ciba Specialty Chemicals Corporation, Hawthorne, NY.

Equipment:

An *I600M* AC-powered UV lamp system with *VPS 6* power supply and a *Light Hammer 10* DC-powered UV lamp, both with 600 W/in H-Bulbs, were mounted on a *DRS 120* movable web system and were provided by Fusion UV Systems, Inc., Gaithersburg, MD.

A Fischer Scientific *Solid State/Ultrasonic FS-14 Sonicator* was used to aid the mixing of the formulation components.

An Electronic Instrumentation and Technology (EIT) *UV PowerMap™* was used to determine the UV-A total energy density and peak irradiance values utilized in the polymerization process.

A *Model 2980* Dynamic Mechanical Analyzer (DMA) from TA Instruments was used to determine the thermomechanical properties of the polymer films.

Experimental Design:

Phase 1 - The first part of the project involved a 2^3 -factorial designed experiment⁸. This involved selecting three independent variables to determine their effects on four dependent variables. To effectively do this, eight experiments were planned and executed. **Table 1** indicates the independent and dependent variables.

TABLE 1
Selected Variables for 2^3 -Factorial

Independent Variables	Dependent Variables
Oligomer Concentration	25°C Storage Modulus
UV Total Energy Density (UV Dose)	“Rubbery Plateau” Storage Modulus
AC vs. DC Lamp System	Peak of Tan δ (Tg)

Two-level factorial designed experiments involve the selection of appropriate high and low levels of the independent variables. All of these independent variables can then be compared for their relative effects on the selected dependent variables in a minimum of experiments equivalent to 2^n . So this study involved doing eight separate experiments. Each was replicated at least three times to determine reproducibility and improve the accuracy of the results. The median values that resulted from each set of replicates were then used to calculate the relative quantitative effects of each of the independent variables using a Yates Algorithm⁸.

Phase 2 - Following the factorial designed experiment, attempts were made to make more highly crosslinked polymer films in order to more closely match the material prepared and evaluated by Jönsson, et al. These experiments involved relatively high concentrations of trifunctional monomers including TMPTA and propoxylated glycerol triacrylate (PGTA). The bulk of the

experimental effort involved attempts to prepare films that were flexible enough to be cut into the appropriate size for DMA testing.

Formulations:

Table 2 gives the composition of the formulations used in the first part of this project:

TABLE 2
Composition of Formulations (% by mass)

Components	65/35/2 pph	45/55/2 pph
ALU 350™ Oligomer	65.0	45
1,6-Hexanediol Diacrylate	17.5	27.5
Trimethylolpropane Triacrylate	17.5	27.5
Irgacure®184 Photoinitiator	2 pph	2 pph

Specific compositions evaluated during the second part of the project were 100 % TMPTA and PGTA with either 1 pph or 0.1 pph photoinitiator.

RESULTS AND DISCUSSION

As previously stated, the research reported in this paper was conducted in two phases. **Phase 1** involved the factorial designed experiment previously mentioned. **Phase 2** involved attempts to prepare films with significantly higher crosslink density than that obtained for the **Phase 1** formulations.

Phase 1: 2³-Factorial Designed Experiment

Factorial designed experiments allow a maximum amount of information about the effects of independent variables to be obtained with a minimum number of experiments. These variables can be either quantitative or qualitative. The qualitative variable in this study was the lamp system. The DC-powered lamp was taken to be the “high” value of this variable and the AC-powered lamp was assigned the “low” value. **Table 3** shows the high and low levels of each of the three independent variables while the eight experiments conducted are represented in **Table 4** where high levels are marked with a “+” and low levels are marked with a “-”.

Dynamic Mechanical Analyses - As previously stated, each of the experiments itemized in **Table 4** were run at least three times to insure adequate reproducibility. Examples that demonstrate the reproducibility are given in **Figures 4** and **5**. These DMA scans include storage moduli, loss moduli, and the “damping factor” or $\tan \delta$. They indicate that reproducibility is quite good, particularly for the storage moduli and the $\tan \delta$. **Figure 4** shows the best replication of the series and **Figure 5** shows the least reproducible experiment. But even in this latter case, the

TABLE 3
Independent Variables

Variables	High	Low
UV Lamp System	DC	AC
Oligomer Concentration	65 % by mass	45 % by mass
UV Total Energy Density	1200 mJ/cm ²	600 mJ/cm ²

TABLE 4
Experiments Conducted

Experiments	UV Lamp System	Oligomer Concentration	UV Total Energy Density (UV “Dose”)
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

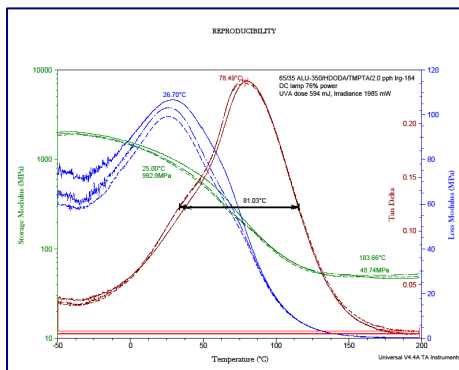


Figure 4

Best Reproducibility

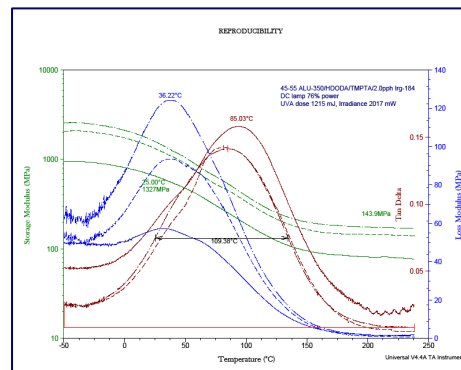


Figure 5

Least Reproducibility

reproducibility seems acceptable. The median curves were used in making comparisons among the three independent variables. The remainder of the DMA data presented will exclude the loss modulus curves (blue).

Total UV Energy Density Effects: Figures 6 and 7 demonstrate the relative effects of the total UV energy density (UV dose) on the thermo-mechanical properties of the films polymerized with the DC- and AC-powered lamps, respectively. The oligomer concentration was the same in both

formulations at 45% by mass. This formulation will produce a higher crosslink density than the 65% oligomer formulation under the same conditions of polymerization.

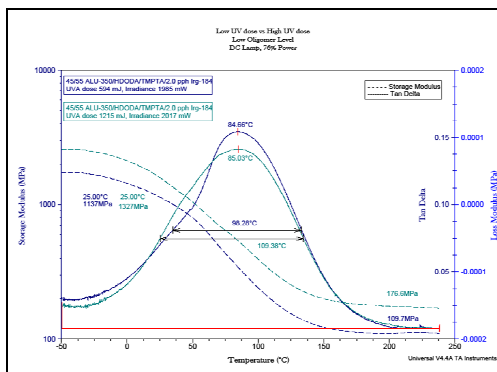


Figure 6

Low vs. High UV Total Energy Density
45/55/2 pph w/DC-Powered Lamp

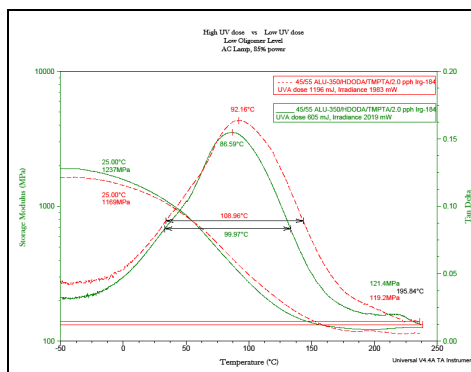


Figure 7

Low vs. High UV Total Energy Density
45/55/2 pph w/AC-Powered Lamp

The storage modulus data for the films prepared using the DC lamp show some differences at the two different UV dose values. The 25°C modulus for the higher dose sample was 16.7% higher than the other sample and in the rubbery plateau region above the T_g, it was 61.0% higher! This latter value indicates a higher crosslink density, as would be expected when using twice as much UV dose to make the polymer. Similar storage modulus differences were *not* observed with the AC-powered lamp.

The tan δ data give information about how the T_g and the relative heterogeneity are affected by increasing the UV dose. Unlike the storage modulus data, there is very little difference apparent in most of the tan δ data. For the DC lamp, the T_gs are essentially identical at the two different dose levels but the half-height widths do show some difference with the higher UV dose resulting in about 11% increase in half-height width. For the films cured with the AC lamp, the T_g of the film polymerized with the higher UV dose, was about 6.4% higher, but this is probably within the sensitivity of the instrument and, therefore, may not be significant. Like-wise, the apparent heterogeneities do not appear to be significantly different for the AC-cured films.

Oligomer Concentration Effects: The oligomer contains two terminal acrylate groups per molecule and has a higher molecular mass than either of the two monomers. Therefore, on either a molar or a mass basis, the oligomer contributes significantly less to the crosslink density of the resulting polymer than do the two multifunctional monomers. Thus, when the oligomer level is increased from 45% to 65% (at the expense of the monomers), it is expected that the crosslink density will be reduced and all indications in this study are that this is the case. **Figures 8 and 9** show comparative DMA data for 45%- and 65%-oligomer films cured using the DC- and AC-powered lamps, respectively. All four polymer samples represented in these two figures were cured at the higher level of UV dose.

For all films represented in these four DMA scans, the data show significant increases in apparent crosslink density and heterogeneity for the films containing the lower amount of oligomer. **Figure 8** shows that with the DC-powered lamp, the storage modulus at 25°C for the 45%-oligomer formulation was 24.3% higher than for the 65%-oligomer formulation. Also, the storage modulus in the rubber plateau was 292 % higher, giving very strong indication of

significantly higher crosslink density in the polymer made with less oligomer. Very similar but lower differences were also seen for the films polymerized with the AC-powered lamp.

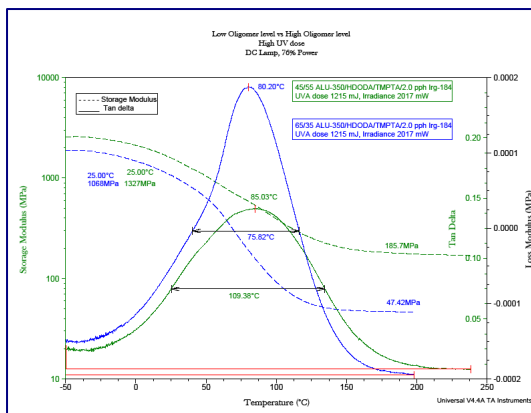


Figure 8

45% Oligomer vs. 65% Oligomer
1215 mJ/cm² UV Dose w/DC-Powered Lamp

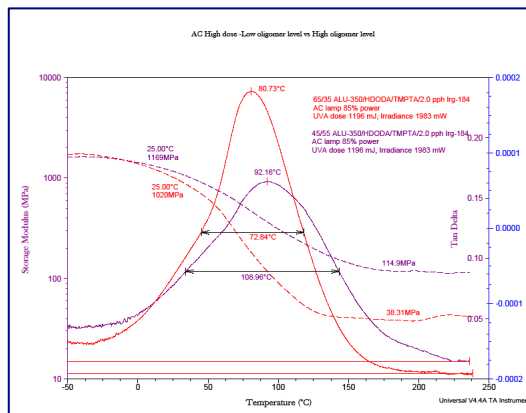


Figure 9

45% Oligomer vs. 65% Oligomer
1196 mJ/cm² UV Dose w/AC-Powered Lamp

Since the formulations with the lower concentration of the oligomer have a higher overall functionality and produce a higher crosslink density polymer, they would be expected to exhibit a higher T_g and more heterogeneity than the formulations with the higher concentration of oligomer. These expectations were also met in this study. **Figure 8** indicates that the higher functionality formulation had a slightly higher T_g and a 44.3% wider tan δ half-height when polymerized with the DC-powered lamp. The films polymerized with the AC-powered lamp showed an even higher difference in these two tan δ parameters. Clearly the higher average functionality of the 45%-oligomer-based formulation produced a polymer that was significantly different from that of the 65%-oligomer-based formulation. In fact, of the three independent variables investigated in this factorial experiment, the oligomer level made the largest difference in the dependent variable properties of the polymers.

AC Power vs. DC Power Effects: The initial objective for this study was to determine whether or not the DC-powered lamp would produce a more homogeneous polymer film. **Figures 10** and **11** show DMA comparisons of films polymerized using DC- and AC-powered lamps, respectively. The films in **Figure 10** contained 45% oligomer while those in **Figure 11** contained 65% oligomer. In both cases, the highest UV dose level was used. For the 45% oligomer-based formulation, the DC-powered lamp produced higher 25°C and rubbery plateau storage moduli. At 25°C, the storage modulus of this formulation was 35.9% higher when polymerized with the DC-powered lamp. Also, in the rubbery plateau, the storage modulus was 53.3% higher for the DC-polymerized film. However, these significant differences were not observed for the 65% oligomer-based formulation. Neither were there any significant differences for this latter formulation in the tan δ properties. Both polymers had the same T_g and the same apparent heterogeneity based on the tan δ half-height width. For the 45% oligomer-based formulation, the T_g of the DC-polymerized film was marginally higher (about 7°C or about 8.4%) but the tan δ half-height widths were essentially the same. For the formulations polymerized at the lower total UV energy density (not shown), the differences between AC and DC were even smaller. Thus, for the two formulations used in this part of the study, although the DC-powered lamp gave somewhat higher crosslink density, especially for the formulation with the lower concentration of oligomer, no real difference in heterogeneity could be observed using the tan δ data from DMA analyses.

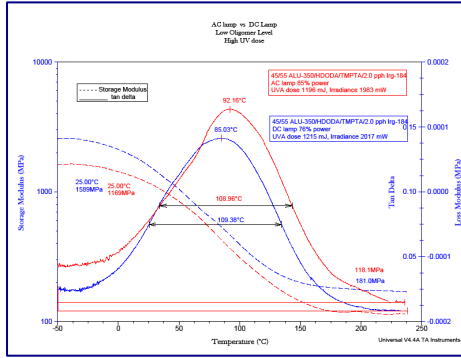


Figure 10

DC- vs. AC-Powered Lamp
45% Oligomer-Based Formulation

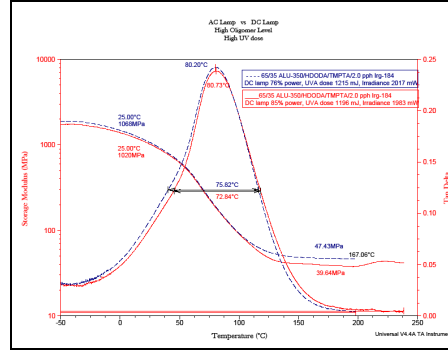


Figure 11

DC- vs. AC-Powered Lamp
65% Oligomer-Based Formulation

Yates Algorithm - The DMA data presented above gives a semi-quantitative “picture” of the relative effects on DMA properties of the three chosen independent variables in this two-level factorial designed experiment. However, by using the Yates algorithm described in **Reference 8** to assess the significance of the data, a more robust quantitative analysis can be made. This algorithm allows the calculation of primary, secondary, and tertiary relative effects of the independent variables on the dependent variables. The larger the values calculate, the more significant the effects are for a given independent variable. **Table 5** shows the results of the Yates Algorithm calculations for the storage moduli at 25°C. These results can be interpreted by comparing the dependent variable effects for their relationship to each other and to the overall

TABLE 5

Yates Algorithm Results - 25°C Storage Moduli

1	2	3	4	5	6	7
P	O	D	y-Values	y-Effects		
UV		UV	Storage Moduli	Dependent	Independent	Type
Lamp	Oligomer	Dose	@ 25°C	Variable Effect	Variable	Effect
AC-	45%	600	1227.0	1130.41	Average	
DC+	45%	600	1266.0	58.03	P	Main
AC-	65%	600	982.6	-224.18	O	Main
DC+	65%	600	992.7	-49.98	PO	2- Factor
AC-	45%	1200	1150.0	26.68	D	Main
DC+	45%	1200	1327.0	33.48	PD	2- Factor
AC-	65%	1200	1046.0	34.68	OD	2- Factor
DC+	65%	1200	1052.0	-35.53	POD	3- Factor

average effect. These data, for example, indicate that of the three independent variables, the oligomer concentration has the largest effect on the 25°C storage modulus. This effect is negative because the higher the oligomer concentration, the lower the crosslink density of the film and, thus, the lower the storage modulus. This effect is considered significant since it is about 25% of the average storage modulus value for this set of experiments. The second most significant independent variable on the storage modulus is the UV lamp used during polymerization and crosslinking. The positive 58.03 calculated effect is not large compared to the oligomer effect,

but its positive sign (+) indicates that using a DC-powered lamp does increase the modulus of the polymer at room temperature. The least important effect of the three independent variables on the storage modulus was the UV dose. The main effect of this variable was less than 2.5% of the average 25°C storage modulus.

Calculations using the Yates Algorithm also allow for the calculation of binary and ternary effects; these are based on statistical interactions among the independent variables. So for the 25°C storage modulus, the third largest effect was the secondary or “2-factor” effect of the type of lamp power used and the oligomer concentration. This secondary effect was nearly twice as large as the main effect of the UV dose.

Table 6 gives the results of the Yates Algorithm calculations for the storage moduli in the rubbery plateau. These storage modulus values reflect the relative crosslink density of a polymer. The table shows clearly that the oligomer concentration had the most significant effect on the relative crosslink density as reflected in the rubbery plateau. As expected, this effect was negative and was nearly 100% of the average storage modulus values obtained in this experiment. The lamp effect, while an order of magnitude lower than the oligomer concentration effect, was the second strongest effect observed. The calculated effect indicated that the DC-polymerized films had marginally higher crosslink density than the AC-polymerized films.

The T_g and the relative apparent heterogeneity data are given in **Tables 7** and **8**, respectively. Once again, the oligomer concentration had the largest effect on these two properties of the polymers, albeit, its effect on the T_g was minimal (7.8 % of average T_g). For the apparent heterogeneity, the oligomer concentration effect was calculated to be 32.6% of the average tan δ

TABLE 6
Yates Algorithm Results - Rubbery Plateau Storage Moduli

1	2	3	4	5	6	7
P	O	D	y-Values	y-Effects		
UV				Dependent		
Lamp		UV	Storage Mod. in	Variable	Independent	Type
Power	Oligomer	Dose	Rubbery Plateau	Effect	Variable	Effect
AC-	45%	600	129.4	88.81	Average	
DC+	45%	600	130.2	7.91	P	Main
AC-	65%	600	46.3	-83.44	O	Main
DC+	65%	600	48.5	-5.65	PO	2- Factor
AC-	45%	1200	118.1	0.39	D	Main
DC+	45%	1200	144.4	6.42	PD	2- Factor
AC-	65%	1200	45.6	-1.06	OD	2- Factor
DC+	65%	1200	47.9	-6.33	POD	3- Factor

peak half-height width indicating a significant effect. However, the effect of changing the lamp from AC- to DC-power was negligible.

Phase 2: Systems with Very High Crosslink Density

The 2³-factorial designed experiment indicated that for the formulations investigated and the polymerization conditions used, the hypothesis that a DC-powered UV lamp would produce a

TABLE 7**Yates Algorithm Results - Glass Transition Temperature**

1	2	3	4	5	6	7
P	O	D	y-Values	y-Effects		
UV			Glass Transition	Dependent	Independent	Type
Lamp		UV	Temperature	Variable	Variable	Effect
Power	Oligomer	Dose	(Tg)	Effect	Average	
AC-	45%	600	81.5	82.64		
DC+	45%	600	84.7	-1.09	P	Main
AC-	65%	600	78.3	-6.41	O	Main
DC+	65%	600	78.5	0.91	PO	2- Factor
AC-	45%	1200	92.2	3.78	D	Main
DC+	45%	1200	85.0	-2.74	PD	2- Factor
AC-	65%	1200	80.7	-1.72	OD	2- Factor
DC+	65%	1200	80.2	2.39	POD	3- Factor

TABLE 8**Yates Algorithm Results - Tan δ Half-Height Width**

1	2	3	4	5	6	7
P	O	D	y-Values	y-Effects		
UV			Apparent	Dependent	Independent	Type
Lamp		UV	Heterogeneity	Variable	Variable	Effect
Power	Oligomer	Dose		Effect	Average	
AC-	45%	600	106.7	92.22		
DC+	45%	600	103.9	0.94	P	Main
AC-	65%	600	78.5	-30.06	O	Main
DC+	65%	600	81.0	2.14	PO	2- Factor
AC-	45%	1200	109.0	-0.63	D	Main
DC+	45%	1200	109.4	1.07	PD	2- Factor
AC-	65%	1200	72.8	-4.48	OD	2- Factor
DC+	65%	1200	76.4	-0.56	POD	3- Factor

more homogeneous polymer film was not supported. In trying to develop an explanation for this, the functionality and crosslink density of the systems actually investigated must be considered. The systems investigated in this study had significantly less crosslink density than the formulations studied by Jönsson, et al.² That group evaluated a simple homopolymer of TMPTA, a very highly crosslinked material. Perhaps a relatively high functionality and resultant crosslink density is necessary for one to actually observe the differences hypothesized for the DC-powered lamp. Thus, the second phase of this investigation involved evaluating homopolymers of high functionality monomers using DMA techniques.

Preparing a usable sample of homopolymer TMPTA proved to be a very difficult task. Both 1 % photoinitiator (as used by Jönsson, et al.) and 0.1% photoinitiator were utilized in an attempt to minimize the brittleness of the resulting polymer films. However, when a tack free state was obtained, the films were too brittle to actually cut into appropriate dimensions for DMA. In some cases, the films were so brittle that they shattered during removal from the glass substrate.

To overcome this problem, a variety of different materials were tested. These included using homopolymer HDODA. Being lower in functionality than TMPTA, it was assumed that it would not be as brittle. This basically was the case. However, no significant differences could be observed between the AC-powered lamp and the DC-powered lamp used to make these homopolymers. A 95/5 % blend of TMPTA with the urethane-based oligomer was also prepared in an attempt to make the film less brittle. This failed to produce a film that was sufficiently flexible.

Finally, a sample of PGTA was successfully prepared with adequate flexibility for a film to be prepared without breaking. This monomer is inherently more complicated and has a higher molecular mass than TMPTA. Thus its actual molecular structure has more potential variability as a result. This, in itself, would be expected to produce a more heterogeneous film, apart from microgel formation considerations. **Figure 12** shows an overlay of three DMA scans for AC-polymerized PGTA films and two scans for DC-polymerized films. As with the two-level factorial experiment, no significant differences can be distinguished between films cured with the

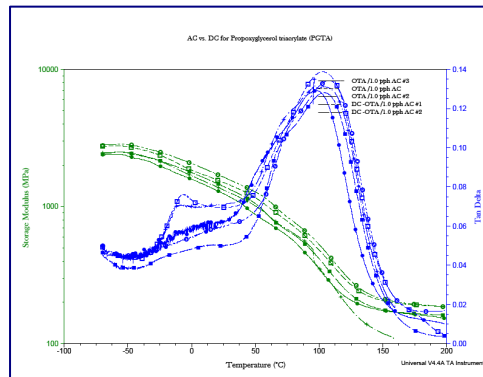


Figure 12
AC- vs DC-Polymerized PGTA

two different lamps. It appears that the storage moduli of the DC-polymerized films are marginally higher, as was observed in the factorial experiment. But the relative heterogeneity is not discernibly different.

The ability to make non-brittle films of PGTA was partly related to a technique developed in this laboratory. Prior to removal of the polymer from the glass substrate, the glass plate with polymer attached was heated briefly on a hot plate. This technique allowed the polymer to be easily removed from the glass and for it to be cut into suitable sizes for DMA characterization without shattering. With this new technique available, samples of homopolymer TMPTA were, once again, prepared and subjected to this same small heat treatment. This time, acceptable films were obtained and samples were prepared for evaluation using DMA. **Figure 13** shows the DMA results of two films that were polymerized with the AC-powered lamp and two polymerized with the DC-powered lamp. The results were consistent with the other experiments reported in this paper. The apparent heterogeneity of all four films was very large, as was expected with homopolymer TMPTA. But significant scatter is indicated in these data. The largest tan δ curve is for a film polymerized with the DC-powered lamp, while the second and third largest ones were cured with the AC-powered lamp. Finally, the narrowest curve is for a DC-polymerized film. Thus, no real difference in the apparent heterogeneity was observed with homopolymer TMPTA.

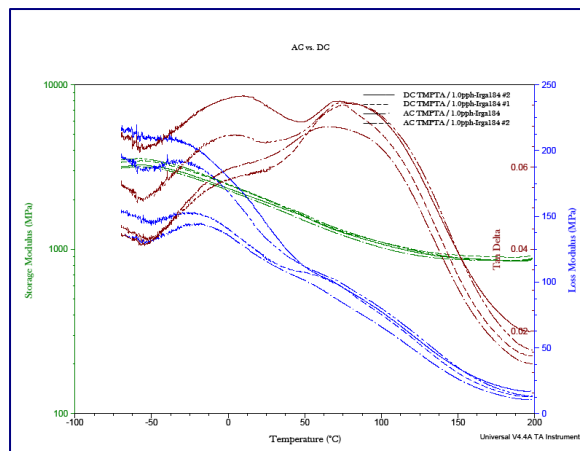


Figure 13

AC- vs DC-Polymerized TMPTA

SUMMARY AND CONCLUSIONS

This investigation was initiated to examine the hypothesis that a DC-powered UV lamp would provide improved properties over those of an AC-powered UV lamp, including greater homogeneity in the polymer morphology. It was expected that the continuous output of the DC-powered system would preclude or minimize rapid termination and microgel formation in the polymer matrix. Since the width of the $\tan \delta$ curve in a DMA scan had been previously demonstrated to be a useful measure of heterogeneity, this parameter was used in this study to test the hypothesis. A 2^3 -factorial designed experiment was conducted to determine the relative importance of the particular type of UV lamp on the apparent heterogeneity vis-à-vis two other independent variables, the oligomer concentration and the total UV energy density or “UV dose”. In this two-level factorial investigation, it was found that the concentration of the oligomer had the most significant impact of the three independent variables while the type of UV lamp used had little to no impact on the relative heterogeneity. However, this study also indicated that the DC-powered lamp did improve the storage moduli of the polymer films over those films prepared using the AC-powered lamp.

A further investigation was conducted to determine if the relative amount of functionality in the polymer system was precluding the observation of any difference in heterogeneity. Thus, homopolymer PGTA and TMPTA were prepared and subjected to DMA analyses. These experiments also indicated some improvement in the storage moduli when using the DC-powered lamp, but no improvement in the apparent heterogeneity of the polymers.

The DC-powered lamp does appear to give higher storage moduli than an AC-powered lamp, probably due to higher %-conversion of functional groups at a given UV dose and peak irradiance. If this is true, the DC lamp may be demonstrating higher efficiency for the polymerization process. Further work is needed to determine the complete range of possible advantages the DC technology may offer to those interested in UV-polymerization chemistry and technology.

ACKNOWLEDGEMENTS

1. Fusion UV Systems, Inc. for providing equipment and scholarships for this investigation.

2. Dr. Rong Bao of Fusion UV Systems, Inc. and Dr. Kazuo Ashikaga of Fusion UV Systems Japan KK, respectively, for consultation on this project.
3. Echo Resins and Laboratory for supplying the ALU-350 aliphatic urethane oligomer.
4. Cytec Surface Specialties for supplying all of the monomers used in this study.
5. Ciba Specialty Chemicals for supplying the photoinitiator used in this investigation.
6. The Robert A. Welch Foundation for their continuing support of research conducted in the *Center for Applied Polymer Science Research* through the ***Chemistry Departmental Grant, No. BJ-0027.***
7. The Scholars Academy of the College of Sciences and Technology at the University of Houston-*Downtown* for additional scholarship support.
8. Electronic Instrumentation and Technology (EIT) for radiometer calibration services.

REFERENCES

- ¹ U.S. Patent 6,908,586 B2, Assigned to Fusion UV Systems, Inc., Gaithersburg, MD (USA).
- ² S. Jönsson, R. Bao, J. Okamitsu, D. Harbourne, T.Y. Lee, and C.E. Hoyle “Film Properties as a Function of Alternating Versus Direct Current”, presented by Dr. Kazuo Ashikaga of Fusion UV Systems Japan KK at the Fusion UV Systems Japan 2007 UV Curing Seminar, Tokyo and Osaka, Japan, February 2007.
- ³ Kloosterboer, J. G., *Adv. Polym. Sci.* 84, 1, **1988**.
- ⁴ Elliott, J. E. and Bowman, C. N., *Macromolecules*, 32, 8621-8628, **1999**.
- ⁵ Huanyu, W., Senyurt, A., Jönsson, S., and Hoyle, C., *J. Polym. Sci., Part A, Polym. Chem.*, 45, No. 5, 822-829, **2007**.
- ⁶ Martinez, T., Carandang, C., Pirani, Z., Rodriguez, B., and Lopez, C., “The Effects of Decreasing Average Acrylate functionality on Thermo-mechanical Properties and Relative Reactivity, Part 2”, a poster presented at the 5th Annual Graduate School and Internship Fair, UH-*Downtown*, November 5, 2004.
- ⁷ Lu, H., Lovell, L., and Bowman, C., *Macromolecules*, 34, 8024, **2001**.
- ⁸ Box, Hunter & Hunter, *Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building*, Wiley Publishing, New York, NY, 1978.