

DIFFERENTIAL PHOTOCALORIMETRY: ADVANCEMENTS FOR THE ANALYSIS AND CHARACTERIZATION OF FREE RADICAL, CATIONIC AND HYBRID PHOTOPOLYMERS

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ABSTRACT

Differential Photocalorimetry (DPC) studies were conducted to differentiate a variety of free radical, cationic and hybrid photopolymers. Results presented elucidate the effects of critical formulating variables on cure speed and product performance properties. An understanding of these effects provide key information for the development of new products, quality control of the manufacturing process, competitive analysis of materials and insight into the mechanism of photopolymerization. The utility of the DuPont DPC as an advanced analytical instrument for the investigation of the photopolymerization process is established.

INTRODUCTION

Differential photocalorimetry (DPC) is a new and powerful analytical tool for the characterization of ultraviolet (UV) curable materials.

Photopolymerization is based on two fundamental mechanisms: 1) free radical propagation with acrylates or methacrylates or 2) cationic initiated ring opening of epoxies and double bond addition with vinyl ethers. Product performance properties achievable from these individual photopolymer systems are limited.

Recent studies in the advancement of photopolymerization technology have explored combinations of free radical and cationic initiated materials, called hybrid photopolymers. These hybrids can provide unique product performance unattainable with the individual photopolymers.

The purpose of this investigation was to use DPC as an analytical tool to differentiate the free radical, cationic and hybrid photopolymers. The results show the effects of the photopolymer composition on parameters such as degree of cure, heat of polymerization and UV exposure dose. Thermomechanical analysis (TMA) was used to determine the glass transition temperature and coefficient of thermal expansion of the photopolymers.

INSTRUMENTATION

Differential Photocalorimeter

The DuPont 2100 Thermal Analyzer was used for all data acquisition and analysis. The differential photocalorimetry data were obtained by using the DuPont 910 Differential Scanning Calorimeter (DSC) and the 930 Differential Photocalorimeter (DPC). A schematic drawing of the DPC is shown in Figure 1. A 200 W high pressure mercury arc lamp was used in the DPC for all experiments. The UV exposure time was controlled by a computer activated two blade shutter. The UV intensity was controlled by a photofeedback circuit and quantified with a UV radiometer. The UV radiation passed through two UV windows into the temperature controlled oven of the DuPont DSC. The sample was placed in an open hermetic aluminum pan inside the DSC oven. The oven of the DSC was purged with nitrogen for all experiments. The sample temperature was obtained from a thermocouple which was calibrated for the melting point of indium. DuPont data analysis software was employed to generate the results from the DPC experiments.

Thermomechanical Analyzer

The DuPont Thermomechanical Analyzer (TMA) 2940 was used to analyze the glass transition temperature and the coefficient of expansion of the UV cured samples. The samples, approximately 1mm thick, were exhaustively cured by UV exposure in the DPC. The cured sample was removed from the aluminum sample pan. The cured sample was placed between the probe and stage of the TMA 2940. The TMA 2940 applied a small force (50 mN Newtons) to hold the probe in contact with the sample. The furnace around the sample was heated at 3°C/min. The sample length changed as the temperature increased. A displacement transducer measured the movement of the probe as the sample expanded. DuPont TMA data analysis software used to calculate the coefficients of thermal expansion (CTE) and glass transition temperatures (T_g).

EXPERIMENTAL

Photopolymer Compositions

The photopolymer compositions were prepared from commercially available monomers and photoinitiators. The formulas were examples of free radical acrylate homopolymers, cationic epoxy homopolymer, cationic vinyl ether homopolymer, and hybrid polymers of epoxy/acrylate and vinyl ether/acrylate. The monomers were supplied as follows: trimethylolpropane triacrylate and hexanediol diacrylate from Radcure Specialties, Inc.; 3, 4-epoxy cyclohexylmethyl 3, 4-epoxycyclohexyl carboxylate (UVR-6110) from Union Carbide Corporation; triethyleneglycol divinyl ether from GAF Chemical Corporation. The photoinitiators were supplied as follows: the free radical photoinitiator hydroxymethyl phenylpropanone (Darocur 1173) from EM Ind., the cationic photoinitiator triaryl sulfonium hexafluoroantimonate salt (UVI-6974) (50% active) from Union Carbide Corporation. The following is a list of the photopolymer formulas used in this study. All percentages are in weight percent. All photopolymers were prepared with equal weight percent photoinitiator.

TRIACRYLATE	
Trimethylolpropane triacrylate	98%
Hydroxymethyl phenylpropane	2%
DIACRYLATE	
Hexanediol diacrylate	98%
Hydroxymethyl phenylpropane	2%
DIEPOXY	
3, 4-Epoxy cyclohexylmethyl	96%
3, 4-Epoxy cyclohexyl carboxylate	
Triarylsulfonium salt	4%
DIVINYL	
Triethyleneglycol divinylether	96%
Triarylsulfonium salt	4%
DIEPOXY and TRIACRYLATE	
3, 4-Epoxy cyclohexylmethyl	48.5%
3, 4-Epoxy cyclohexyl carboxylate	
Trimethylolpropane triacrylate	48.5%
Hydroxymethyl phenylpropanone	1%
Triarylsulfonium salt	2%
DIVINYL and TRIACRYLATE	
Triethyleneglycol divinylether	48.5%
Trimethylolpropane triacrylate	48.5%
Hydroxymethyl phenylpropanone	1%
Triarylsulfonium salt	2%

Three microliters (about 3 mg) of sample was placed in a tared aluminum hermetic pan. The sample was spread to evenly cover the bottom of the pan. The pan was reweighed to obtain the exact sample weight.

Long Exposure Experiment

The DSC oven was isothermal at 35°C while the samples were exposed to UV light (60 mW/cm² intensity) for five minutes. This was long enough to expose all samples during the complete curing reaction. This experiment was useful in determining the enthalpy of polymerization during continuous UV exposure. This enthalpy was used to calculate the maximum degree of cure caused solely by UV exposure.

Theoretical Heat of Reaction

The heat released during the curing reaction is related to the number of reactive sites available in the formulation. The theoretical heat of reaction is calculated assuming all reactive sites are consumed in the curing reaction. The following equation was used to calculate the theoretical heat per gram of formation.

$$A = \frac{B * C * D}{MW}$$

where:

- A = Joules/gram of formulation
- B = Number of sites/mole of monomer
- C = Fraction of monomer in formula
- D = Joules/mole of reactive site
- MW = Grams/mole for monomer

The number of reactive sites per mole of monomer was taken from the functionality of the monomer. The fraction of monomer in the formula was calculated from the weight ratio of monomer to total formula weight. If more than one type of monomer was present, then the joules per gram calculated for each monomer were added to obtain the total joules per gram of formula.

The joules per mole of reactive sites were obtained for model compounds from published sources. (Ref 1) The model compounds selected were: acrylate-n-butyl acrylate; vinyl ether-vinyl butyl ether; epoxidepropylene oxide.

	Enthalpy (kJ/mol)	Ref.
Triacrylate	78	2
Diacrylate	78	2
Divinyl ether	60	3
Diepoxy	76	4

The enthalpy for the model epoxy, propylene oxide, is believed to be too high because it is less steric hindered than the diepoxy. Data for a better model cyclohexene oxide was unavailable.

Post UV Exposure Thermal Curing

In this experiment, the samples were cured with a five minute exposure of UV light. The samples were then heated at 5°C/min. Some samples had an exothermic peak when heated. This experiment identified the samples that required additional temperature to advanced the degree of cure.

Flash Photolysis Experiment

This DPC experiment was designed to differentiate photopolymers, since minimal UV exposure time should allow reactivity differences to be magnified. The sample was given only 0.7 seconds of exposure at 60 mW/cm² UV intensity. The degree of cure from this short exposure was a measure of how efficiently the monomer polymerized when the initiation of photopolymerization was limited by a short dose of UV.

Sequential Flash Photolysis

Several of the samples, primarily those containing the diepoxy monomer, did not completely cure with one short exposure. The 0.7 seconds exposure was repeated in 5 minute intervals. This experiment was designed to determine if the cure could be accelerated with sequential second and their exposures to UV light.

TMA Experiments

The DuPont Thermomechanical Analyzer (TMA) 2940 was used to analyze the glass transition temperature (T_g) and the coefficient of thermal expansion (CTE) of the UV cured sample. The sample, approximately 1mm thickness, was exhaustively cured by UV exposure in the DPC. The cured sample was removed from the aluminum sample pan. The cured sample was placed between the probe and stage of the TMA 2940. The TMA 2940 applied a small force (5mN Newtons) to hold the probe in contact with the sample. The furnace around the sample was heated at 3°C/min.

The expansion in micrometers per meter was plotted versus sample temperature. The slope of this line was the CTE. The CTE increased after the glass transition. The glass transition temperature was measured as the intersection of the CTE before and after the point where the CTE changed.

DISCUSSION OF RESULTS

Degree of Cure

The continuous exposure heat of reaction versus theoretical enthalpy results are summarized in Table 1, and are graphically displayed in Figures 2-5.

TABLE 1
DEGREE OF CURE
CONTINUOUS UV EXPOSURE

	Mol Wt	Theory J/g	Actual J/g	Percent Cure
Dinvinyl	202	570	596	100%
Dinvinyl/ Triacrylate	296 202	671	492	73%
Diepoxy/ Triacrylate	296 252	775	362	47%
Diepoxy	252	579	172	30%
Diacrylate	226	676	155	23%

The degree of cure of the homopolymers show the following order: divinyl ether > triacrylate > diepoxy > diacrylate. The higher functionality of the triacrylate gave higher degree of cure than the diacrylate.

The divinyl ether/triacrylate hybrid gave a degree of cure (73%) equal to the average (73%) of the homopolymers. This supports the independent photopolymerization of the two monomers into an interpenetrating polymer network (IPN).

The diepoxy/triacrylate hybrid gave a higher degree of cure (47%) than the average of the homopolymers (38%). The degree of cure for this hybrid was unexpected and further experiments are required to understand it.

Post UV Exposure Thermal Curing

In these experiments the sample was exposed to 5 minutes of UV light. The heat flow returned to the baseline after 5 minutes indicating that the UV initiated curing reaction had reached completion. All samples were heated in the dark after the UV exposure. The degree of cure results are summarized in Table 2 and Fig. 6.

TABLE 2
DEGREE OF CURING
 UV AND THERMAL CURING

	UV Cure	Thermal Cure	Total Cure	Visc mPa S
Divinyl	100%	0%	100%	3
Diepoxy	30%	44%	74%	400
Diepoxy/ Triacrylate	47%	27%	74%	250
Triacrylate	48%	0%	48%	100
Diacrylate	23%	0%	23%	8

The acrylate, divinyl ether homopolymer and divinyl ether/acrylate hybrid gave no thermal cure after UV exposure. Divinyl ether monomer gave complete cure with only UV exposure. All diepoxy photopolymers gave additional thermal cure when heated after UV exposure.

The effect of viscosity on the cure profiles was apparent from the data, and low viscosity contributes to the high degree of cure for the divinyl monomer. High viscosity may contribute to the low degree of cure for the diepoxy photopolymers. Further experiments are needed to support this hypothesis.

The thermal curing of the diepoxy homopolymer and diepoxy/triacrylate hybrid occurred below 160°C. The thermal curing of these hybrids was unlikely due to increased polymer chain mobility. Independent DSC experiments showed that the thermal cure occurred at temperatures significantly lower than the thermolysis temperature of the photoinitiators. This lead to the belief that most of the post UV exposure thermal curing of diepoxy photopolymers was due to increased polymer chain mobility. This was nature of evidence for the living polymer nature of the cationic epoxy photopolymerizations.

Cure Speed

The sequential flash photolysis degree of cure results are summarized in Table 3 and Figure 7.

TABLE 3
DEGREE OF CURE
 SEQUENTIAL FLASH PHOTOLYSIS EXPOSURE

	FIRST	SECOND	SUM
Divinyl	100%	-	100%
Divinyl/ Triacrylate	63%	9%	72%
Diacrylate	53%	25%	77%
Triacrylate	38%	4%	42%
Diepoxy/ Triacrylate	27%	8%	35%
Diepoxy	6%	3%	9%

The cure speed as determined by flash photolysis was a measure of the reactivity. The order of reactivity for the homopolymers was: divinyl ether >> diacrylate > triacrylate >> diepoxy. The higher diacrylate reactivity compared to the triacrylate was likely due the lower viscosity (Table 2). The lower viscosity of the divinyl ether may account for some of the high reactivity of the divinyl ether homopolymer and divinyl ether/acrylate hybrid.

The divinyl ether/triacrylate hybrid gave a degree of cure (63%) close to the average (69%) of the homopolymers. Also, the diepoxy/triacrylate hybrid gave a degree of cure (27%) close to the average (22%) of the homopolymers. In the case of flash photolysis, both hybrids polymerized as if the two monomers were acting independently.

The previous kinetic model for DPC photopolymeration (Ref. 5) was used for analysis of these DPC results. The autocatalytic kinetics model could not represent the photopolymerization mechanism for all these diverse photopolymers. The best way to analyze the kinetics of these photopolymers, as a measure of their relative cure speed, was by comparison of their conversion/time curves for both the continuous (Figure 5) and flash photolysis (Figure 7) exposures.

Thermomechanical Analysis

The DuPont TMA 2940 was used to determine the mechanical properties of the photopolymers after exhaustive UV curing. The TMA results are summarized below in Table 4 and Figures 8-10.

TABLE 4
THERMOMECHANICAL ANALYSIS
GLASS TRANSITION TEMPERATURE

	Tg °C	CTE @25 ($\mu\text{m}/\text{m}^\circ\text{C}$)	COLOR	
			UV	HEAT
Diacrylate	88	86.5	Clr	Yel
Triacrylate	76	30.6	Yel	Yel
Divinyl/ Triacrylate	56	172	Orn	Red
Diepoxy/ Triacrylate	45	63.4	Yel	Orn
Diepoxy	45	109	Yel	Brn
Divinyl	30	291	Orn	Red

Triacrylate and diacrylate homopolymers showed distinct and high glass transition temperatures and TMA curve profiles, evidence of complete cure.

Diepoxy and divinyl ether, both as homopolymers or hybrids, showed changes between the first and second TMA scans. Characteristic color changes were observed for these photopolymers after their high temperature exposure from the TMA analysis.

The CTE values at 25°C are reported in Table 4. These results were not amenable to interpretation without further experiments.

SUMMARY AND CONCLUSIONS

The utility of DPC as a diagnostic tool for the analysis and characterization of photopolymers has been further established.

The various types of free radical acrylate, cationic epoxy and vinyl ether and hybrid photopolymers were differentiated by their characteristic DPC results. Acrylate homopolymers were characterized by lack of post UV exposure thermal cure and by their distinct and highest glass transition temperatures. The diepoxy homopolymer and hybrid photopolymer were characterized by their thermal post UV exposure curing behavior. The divinyl ether homopolymer and hybrid photopolymer were characterized by fast photocure speeds and by the color change of the UV cured sample to red after heating to high temperature.

The cure speed of the diepoxy/triacrylate hybrid was faster than expected. Further experiments are needed to understand this observation.

An understanding of the DPC results provides key information for the development of new products, quality control of the manufacturing process, competitive analysis of materials and insight into the mechanism of photopolymerization.

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KEYWORDS

DIFFERENTIAL SCANNING CALORIMETRY

DIFFERENTIAL PHOTOCALORIMETRY

THERMOMECHANICAL ANALYSIS

PHOTOINITIATION

DEGREE OF CURE

PHOTOPOLYMER

FREE RADICAL

VINYLETHER

CATIONIC

ACRYLATE

EPOXY

930 DP SCHEMATIC

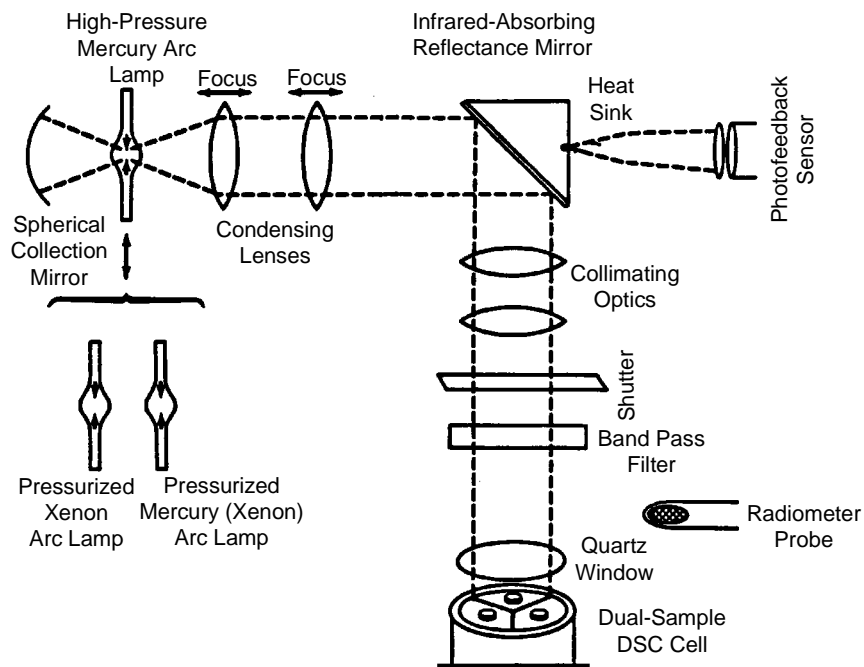


Figure 1: Schematic diagram of the DuPont DPC 930.

TRIACRYLATE AND DIACRYLATE CURING

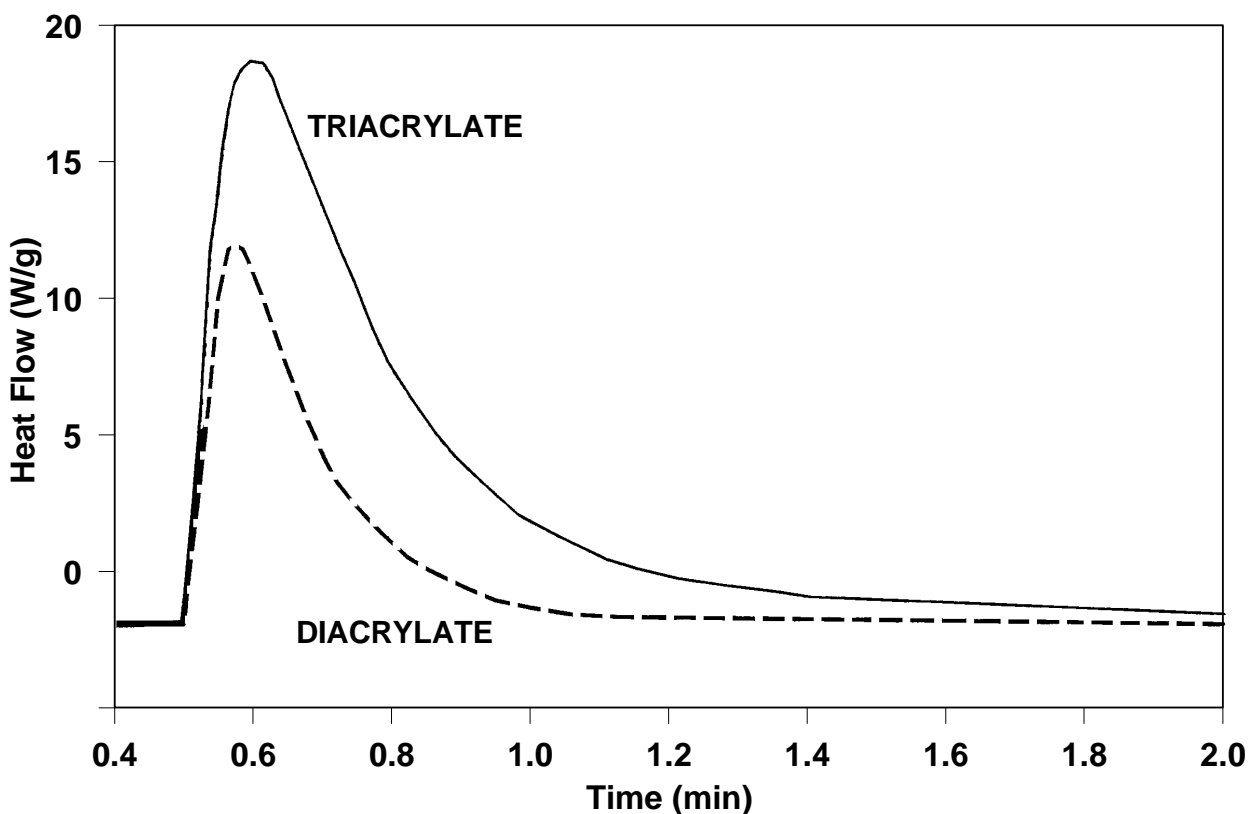


Figure 2: Comparison of the curing of triacrylate and diacrylate during continuous UV exposure.

CURE COMPARISON DIVINYL TRIACRYLATE AND HYBRID

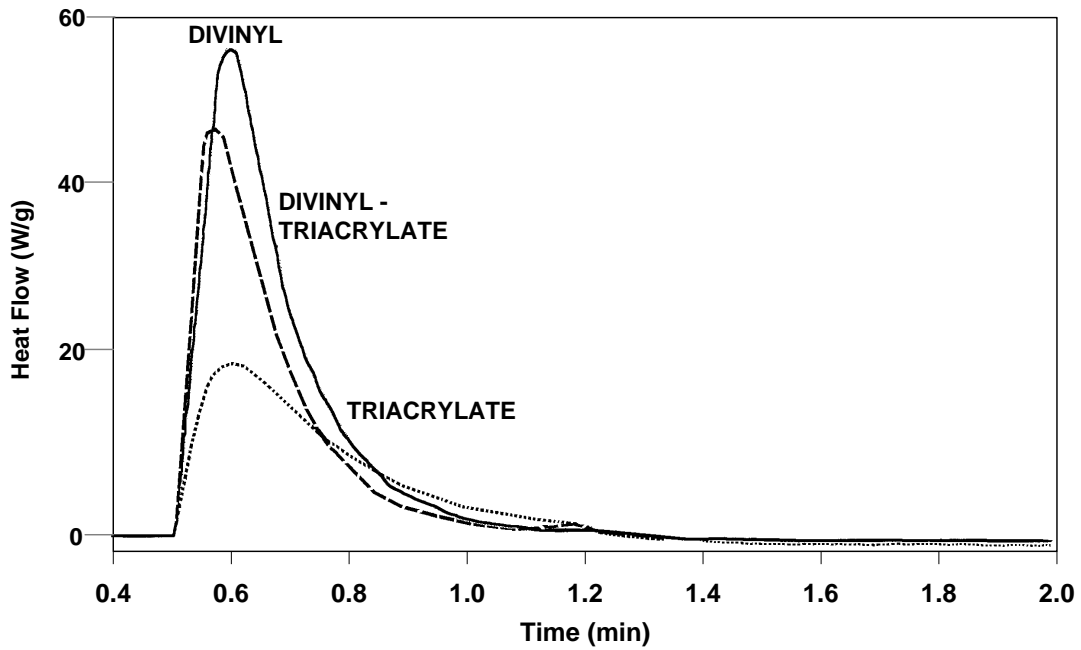


Figure 3: Comparison of the curing of divinyl, triacrylate and the hybrid during continuous UV exposure.

CURE COMPARISON DIEPOXY, TRIACRYLATE AND HYBRIDE

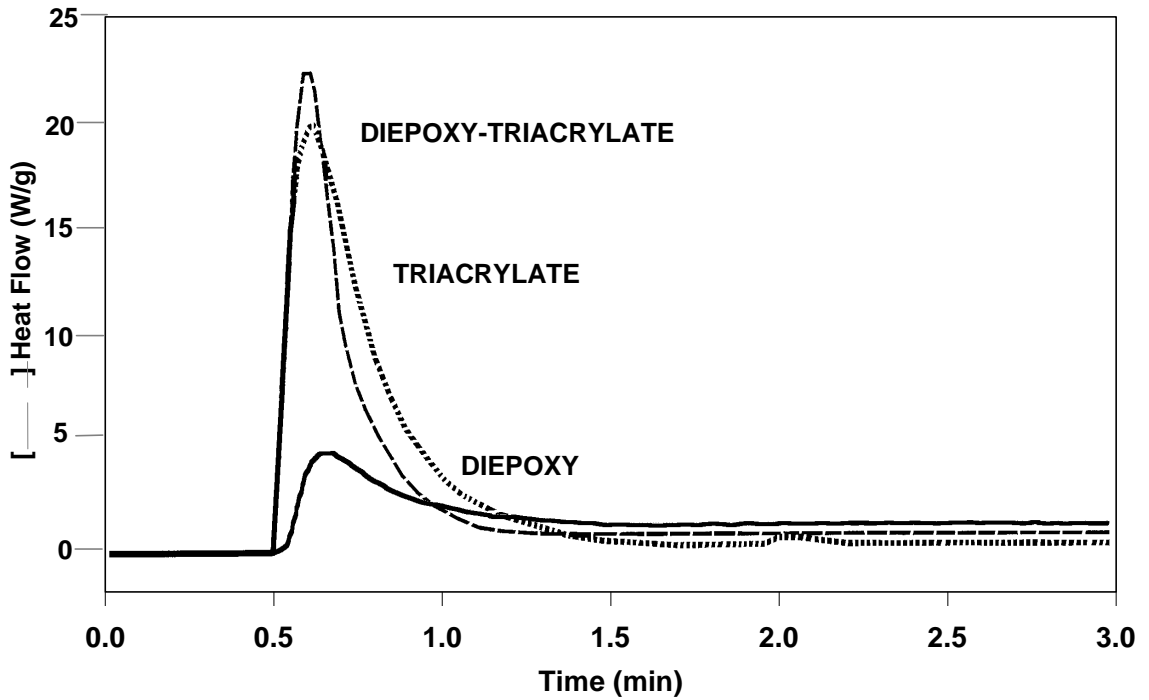


Figure 4: Comparison of the curing of diepoxy, triacrylate and the hybrid during continuous UV exposure.

%CURE HOMOPOLYMERS AND HYBRIDES

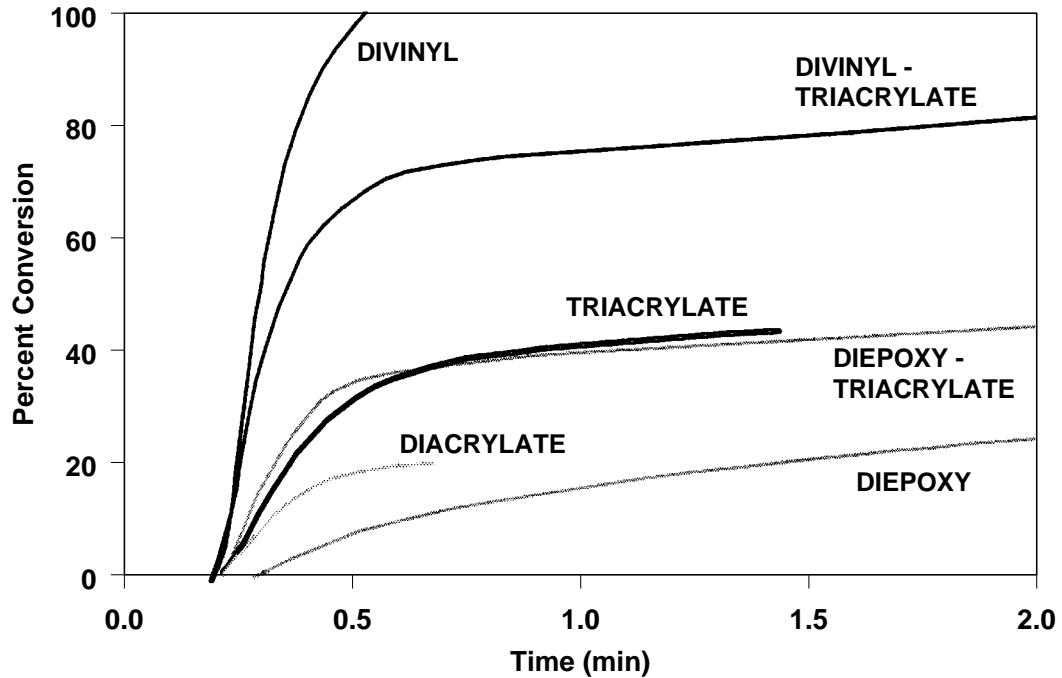


Figure 5: Percent cure versus time for continuous UV exposure. Percent cure has been corrected for the theoretical enthalpy for complete reaction.

POST UV EXPOSURE DIEPOXY & DIEPOXY TRIACRYLATE HYB

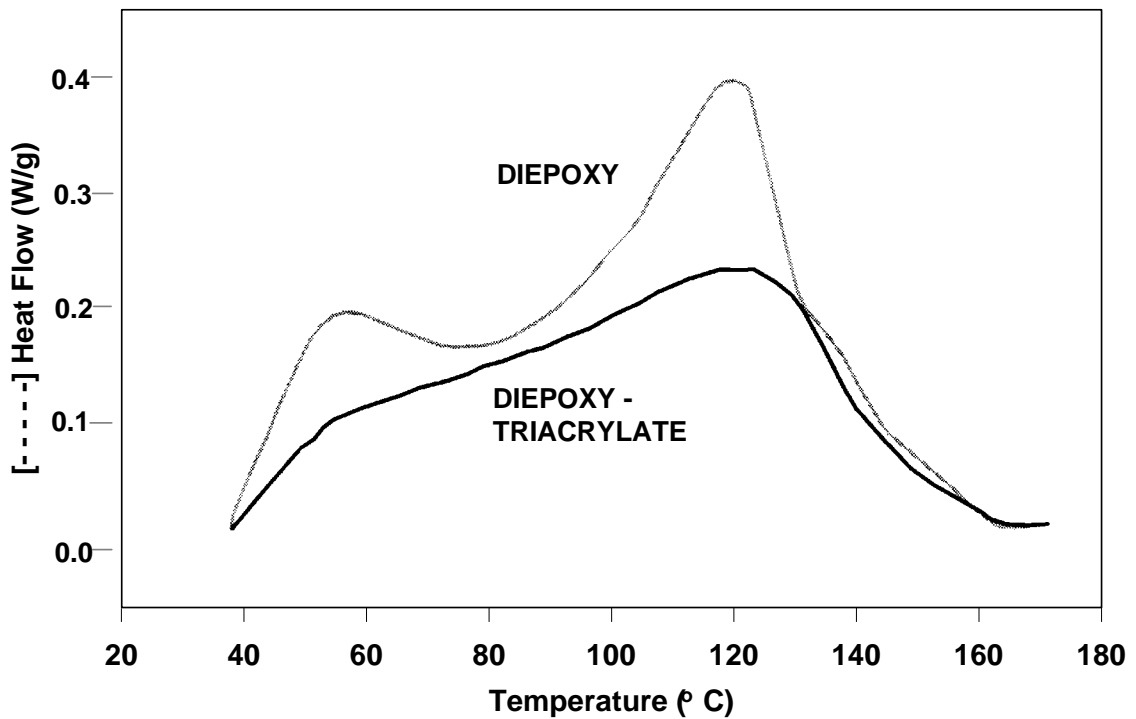


Figure 6: Post UV exposure thermal cure of the diepoxy and diepoxy-triacrylate hybrid.

%CURE AFTER 0.7 SEC HOMOPOLYMERS AND HYBRIDES

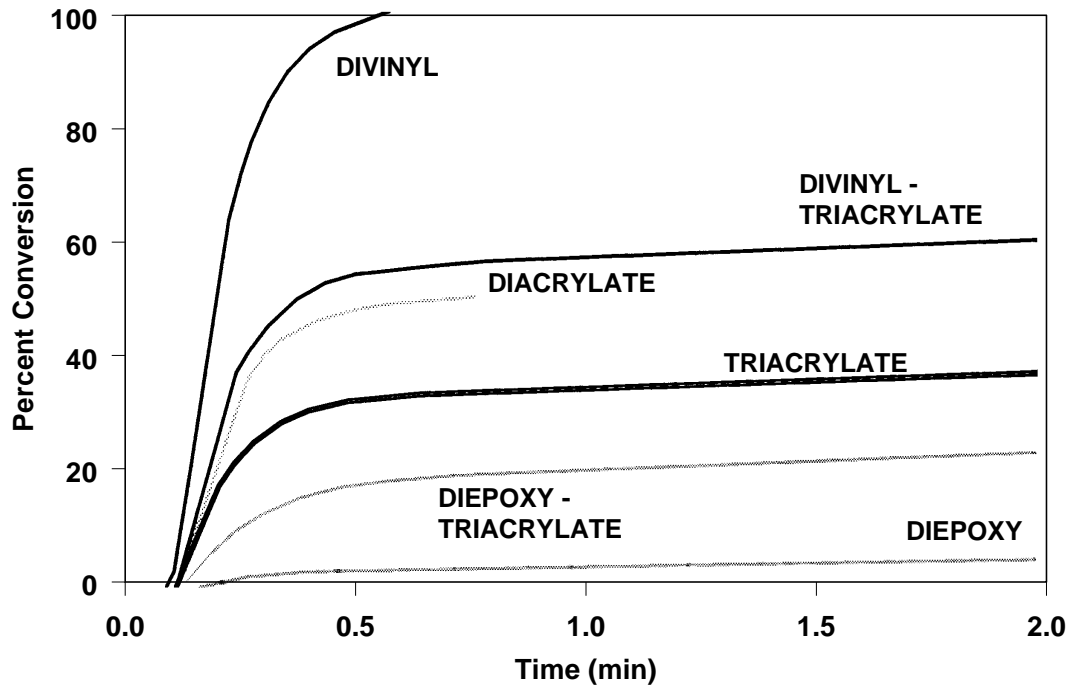


Figure 7: Percent cure versus time after 0.7 second UV exposure. Percent cure has been corrected for the theoretical enthalpy for complete reaction.

DIMENSIONAL EXPANSION OF UV CURED ACRYLATES

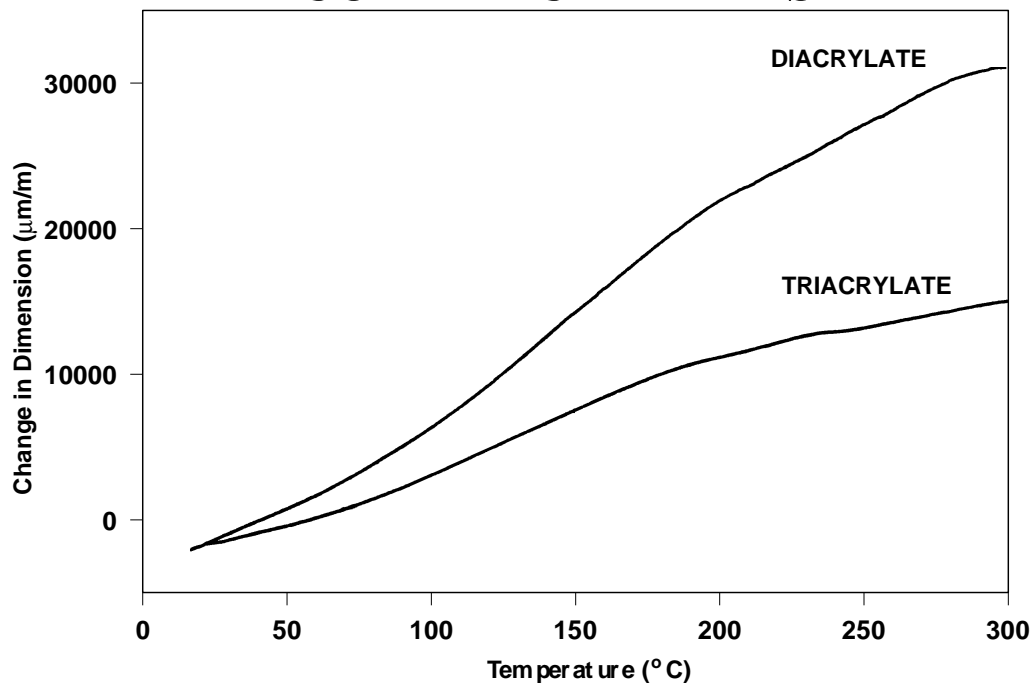


Figure 8: Dimensional expansion of exhaustively UV cured diacrylate and triacrylate versus temperature.

DIMENSIONAL EXPANSION OF UV CURED DIVINYL

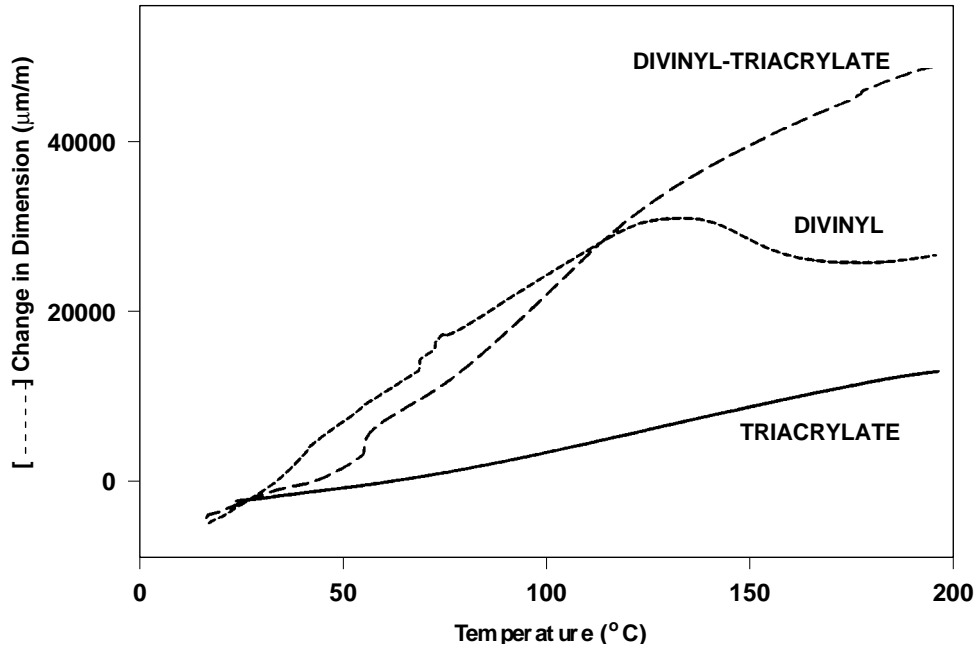


Figure 9: Dimensional expansion of exhaustively UV cured divinyl, triacrylate and divinyl-triacrylate hybrid versus temperature.

DIMENSIONAL EXPANSION OF UV CURED DIEPOXY

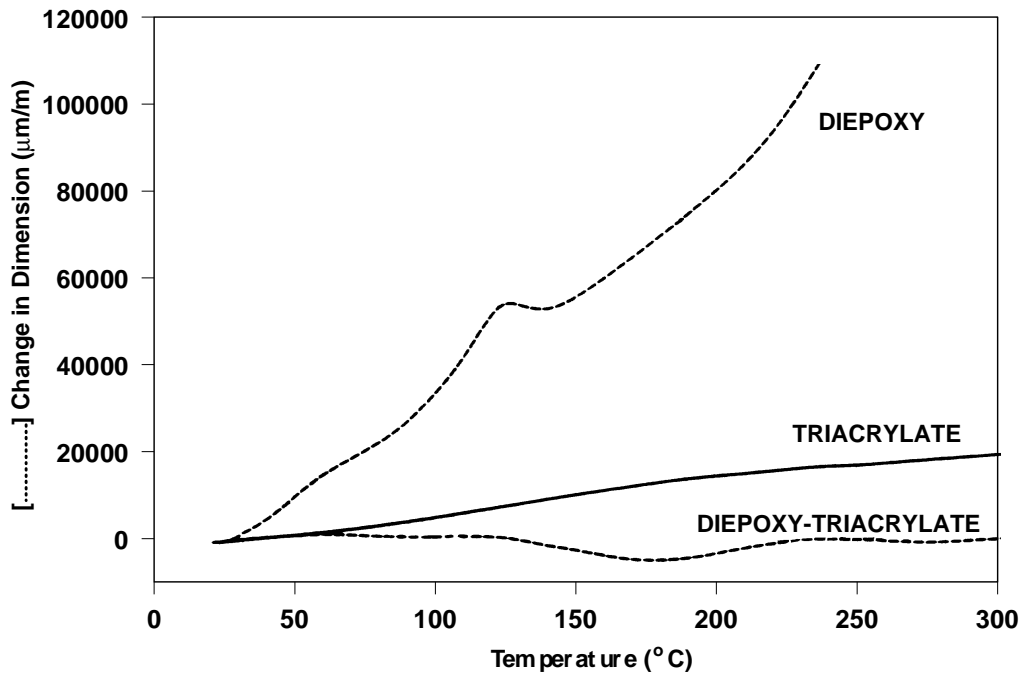


Figure 10: Dimensional expansion of exhaustively UV cured diepoxy, triacrylate and diepoxy-triacrylate hybrid versus temperature.