

# **Effect of polymer composition on performance properties of maleate-vinyl ether donor-acceptor UV-curable systems**

*Neena Ravindran, Ankit Vora, and Dean C. Webster, North Dakota State University, Fargo, ND 58105*

## **Introduction**

UV curable polymers continue to find new applications as environmental regulations continue to propel coatings research into finding zero or low VOC alternatives. Non-acrylate UV curable coating is an area of research interest especially in view of the health concerns associated with acrylate systems. The major categories in non-acrylate technology include cationic polymerization, thiol-ene systems and free-radical induced alternating copolymerization. Some of the benefits to be derived from alternate technologies are those of comparative cure times as acrylates, low toxicity and more importantly that of design flexibility. Free-radical induced alternating photocopolymerization takes place when an electron-rich vinyl group is mixed with an electron deficient vinyl group.<sup>1,2</sup> General features of this type of polymerization such as stoichiometric dependence, formation of charge-transfer complexes etc. have been described in several publications.<sup>2,3,4</sup> Studies on systems containing a stoichiometric balance of maleate and vinyl ether functional groups have been previously reported.<sup>5,6,7</sup> In these studies the effect of unsaturated polyester and polyether on charge-transfer complex formation, UV-curing and film properties were investigated. The effect of variation in the oligomeric backbone on film properties has also been studied.

We are interested in using UV curable polymer systems as laminating layers for use in multilayered flexible electronic devices. The performance requirements for this application are complex. The process comprises steps like metallization, chemical etching, and laser ablation and so on. This translates into a demand for a polymer with a complex mix of properties such as films that cure fast, are hard, flexible, transparent, thermally stable, exhibit good solvent and acid etch resistance and are dimensionally stable. In order to evaluate donor-acceptor technology for this application, a series of polymers were synthesized using a wide range of compositions to potentially yield a range of polymer film properties and then use this data to assess this technology for flexible electronic device manufacture.

## **Experimental**

### **Materials**

All monomers used for polyester synthesis, except 1, 4 CHDA and 2-Ethyl hexanol, were purchased from Sigma Aldrich. 2-Ethyl hexanol was purchased from Alfa Aesar and 1, 4 CHDA was obtained from Eastman Chemical Company. Triethyleneglycol divinyl ether (TEGDVE) was provided by BASF. Photoinitiator, 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173), was supplied by CIBA. All chemicals were used as received without further purification.

## Polyester Design

All polyesters were formulated to be hydroxyl functional with a molecular weight of approximately 800. Compositions were designed so that the average number of double bonds per polymer chain was greater than 2.5 and the desired acid value was less than 30 mg of KOH per gram of sample. Maleic anhydride was the source of unsaturation in all formulations and the monomers used were varied in order to obtain polyesters with a wide variety of backbone structures. Chemical composition of various polyesters and the symbols used to represent the same are as per Table 1.

**Table 1. Polyester composition**

Polyester	Composition
1	NPG/IPA/DEG/MA
2	CHDM/DEG/AA/IPA/MA
3	DEG/PG/IPA/MA
4	HD/TEG/IPA/MA
5	HD/NPG/TEG/IPA/MA
6	HD/NPG/TEG/CHDA/MA
7	DEG/HD/CHDA/MA
8	TMP/HD/CHDA/MA
9	DEG/NPG/IPA/MA
10	HD/EH/CHDA/MA

The abbreviations used in Table 1 read as follows: NPG- Neopentyl glycol, IPA- Isophthalic acid, DEG- Diethylene glycol, MA- Maleic anhydride, CHDM-1,4-cyclohexane dimethanol, AA- adipic acid, PG- propylene glycol, HD- 1,6-Hexane diol, TEG- triethylene glycol, CHDA – 1,4-cyclohexane dicarboxylic acid, TMP- trimethylol propane, EH – 2 ethyl hexanol.

The number of moles of monomer used in each formulation, the final acid value and the theoretical molecular weight based on the same are listed in Table 2.

**Table 2. Moles of monomer used, final acid value and theoretical molecular weight**

Poly-ester	NPG	DEG	TEG	CHDM	1,6 HD	TMP	IPA	AA	1,4 CHDA	EHA	MA	Acid Value	Mol. Wt. (Theo.)
1	0.878	0.627					0.206				1.00	21	672
2		0.953		0.713			0.198	0.146			1.00	17	780
3		1.421					0.160				1.00	15	776
4			0.491		1.015		0.218				1.00	6	953
5	0.512		0.236		0.767		0.210				1.00	13	776
6	0.512		0.236		0.768				0.235		1.00	29	679
7		0.824			0.625				0.172		1.00	14	772
8					1.161	0.387			0.333		1.00	16	1034
9	0.950	0.570					0.166				1.00	2	727
10			1.334						0.200	0.111	1.00	30	776

## **Polyester Synthesis**

The series of unsaturated polyesters were prepared using standard melt esterification techniques. Monomers were weighed into a 250 ml, three-necked flask, equipped with a mechanical stirrer, temperature controller and a nitrogen inlet. A nitrogen blanket was maintained inside the reaction flask during the course of the reaction in order to preclude side reactions such as oxidation of double bonds. The reaction mixture was heated in a ramped manner and temperatures were set at 60°C, 120°C and 180°C. Reaction was continued until the desired acid value was reached. Acid value was determined by titration with alcoholic KOH.

## **Polyester Characterization**

Viscosity, molecular weight and glass transition temperature were used to characterize the polyesters. Viscosity measurements were made at 100°C using an ICI cone and plate viscometer. Molecular weight was determined using Waters 2410, Gel Permeation Chromatograph equipped with a refractive index detector. A 1% sample solution in tetrahydrofuran using a flow rate of 1ml/min was used. Calibration was performed using polystyrene standards. Differential scanning calorimetric (DSC) measurements were conducted using a TA Instruments Q1000 series DSC. The testing method used was a heat-cool-heat cycle. The samples were first equilibrated at -70°C and then subjected to a heat cycle at the rate of 5°C/min to 200°C, followed by a cooling cycle to -70°C at a rate of 10°C/min and a final heating cycle at a rate of 5°C/min to 200°C.

## **Formulations**

Coating formulations were prepared by combining the unsaturated polyester and triethyleneglycol divinyl ether as the reactive diluent, in a ratio of 1:1 of the reactive functional groups, viz. maleate to vinyl ether functionality. The mixture was homogenized using heat. Four percent of the photoinitiator, based on the combined weight of resin and reactive diluent, was added to the formulation and this was followed by mixing to obtain a uniform coating. The final coating formulations are as shown in Table 3 and coatings based on polyesters 1 to 10 are represented as A to J respectively.

**Table 3. Coating compositions**

Sample	Polyester	Polyester weight (g)	TEGDVE (g)	Darocur (g)
A	1	5.63	2.12	0.464
B	2	5.90	1.82	0.464
C	3	5.54	2.22	0.466
D	4	5.98	2.00	0.479
E	5	5.90	2.07	0.478
F	6	5.92	2.02	0.476
G	7	5.32	2.02	0.440
H	8	5.51	1.76	0.436
I	9	5.91	2.27	0.491
J	10	5.90	1.81	0.463

### Coating Characterization

Coatings prepared as described previously were used to prepare films. Films were deposited onto a substrate using a bar-coater with a 4 mil clearance. Substrates used were aluminum for hardness measurement and glass to obtain free films for DMTA and other tests. Application was followed by curing of samples under ultraviolet (UV) light until films that were non-tacky to touch were obtained. Dymax 200 EC silver lamp (UV-A, 365 nm) with an intensity of 35 mW/cm<sup>2</sup>, measured with an International Light digital radiometer (Model IL1400A) was used as the source for UV radiation. Testing on film samples were performed after allowing the samples to equilibrate at room temperature for at least 24 hours.

Real time FTIR measurements were made using a Nicolet magna FTIR spectrometer. A LESCO Super Spot MK II UV curing lamp equipped with a fiber optic light guide was the source for UV irradiation of samples. Uncured sample was spin-coated at an rpm of 3000 onto a KBr disk and was simultaneously exposed to IR and UV irradiation. The sample was placed at a distance of 20 mm from the end of the fiber optic cable.

Photo-DSC measurements were acquired using the Q1000 DSC outfitted with a photocalorimetric accessory (PCA). The samples were subjected to UV irradiation for 120 seconds at an intensity of 40mW/cm<sup>2</sup> using fiber optic light guides.

Dynamic mechanical properties of cured films were evaluated using a dynamic mechanical thermal analyzer (DMTA 3E, Rheometric Scientific). Free films of 3 mm length, 5 mm width and 0.05-0.08 mm thickness were characterized using settings of a frequency of 10 rad/sec, heating rate of 5°C/min over a temperature range of -50°C to 250°C. The geometry employed was that of rectangular tension/compression.

Thermogravimetric analysis was run on samples using a Perkin Elmer thermogravimetric analyzer and samples were heated between temperatures of 25°C to 650°C, at a rate of 10°C/min.

Film hardness was measured using a BYK-Gardner pendulum hardness tester on aluminum panels and König hardness value was reported in seconds.

## Results and Discussion

### Polyester synthesis

The results of polymer characterization are outlined in Table 4.

**Table 4. Viscosity, molecular weight, polydispersity and glass transition temperature of polyesters.**

Sample	Viscosity (Poise) at 100°C	$\bar{M}_n$	$\bar{M}_w$	PD	T <sub>g</sub> °C
1	5.4	1352	1888	1.40	-12.47
2	7.1	1157	1927	1.67	-15.50
3	4.2	1193	2112	1.77	-18.73
4	4.6	1803	3254	1.80	-35.61
5	5.0	2341	3193	1.36	-28.04
6	2.2	1337	1965	1.47	-31.97
7	3.4	1492	2489	1.67	-41.07
8	9.5	1829	3933	2.15	-36.62
9	5.8	1256	2323	1.85	-9.57
10	2.4	1394	2263	1.62	-39.36

The number average and weight average molecular weights obtained are in reasonable agreement with design values. Polydispersity (PD) of the synthesized polyesters was found to range between 1.40 and 2.15, typical of polymers synthesized by step growth polymerization.

Analysis of glass transition temperatures showed that compositions containing HD yielded comparatively lower glass transition temperatures than compositions without it. It was further seen that combinations of HD in combination with TEG further lowered the glass transition temperature. Compositions consisting of only flexible monomers HD/DEG/CHDA showed the lowest glass transition temperatures.

It was seen that the viscosity of the polyester resins varied as a function of composition. With a few exceptions, the viscosity trend was similar to the glass transition trend. Compositions that contained HD generally showed lower viscosities as compared to those without it. HD/TEG combinations lowered the viscosities further. HD/TEG/CHDA combination yielded the lowest viscosity. As expected a combination of HD/CHDM/EH also yielded a very low viscosity. The composition TMP/HD/CHDA/MA showed a higher viscosity and this may be attributed to the presence of a trifunctional monomer.

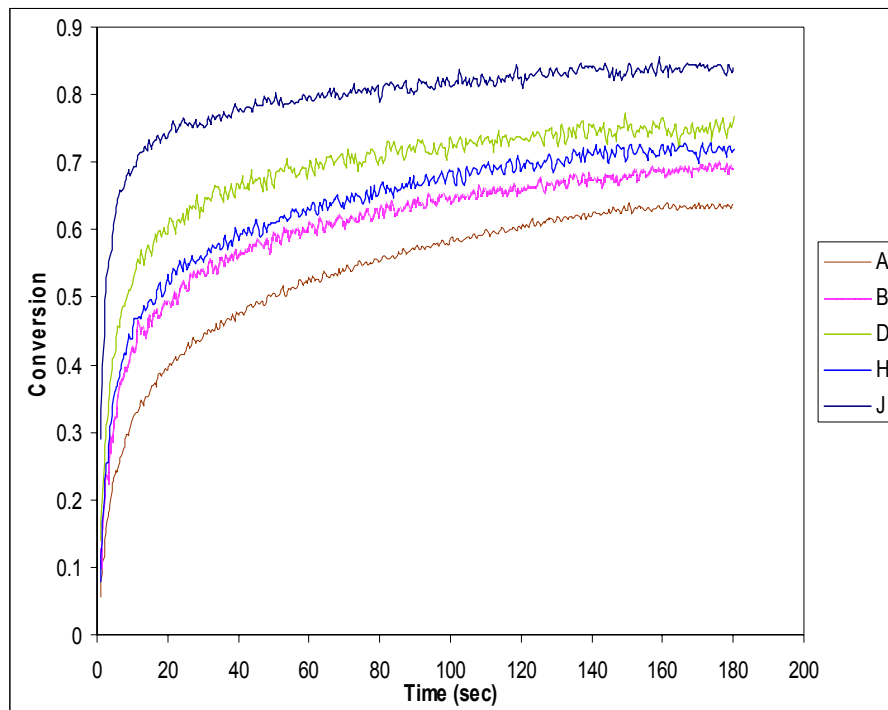
It was also observed that polyesters that contained IPA yielded higher viscosity and glass transition temperatures than those polyesters containing CHDA.

## Coatings

The coatings were evaluated for mechanical and thermal properties and cure characteristics.

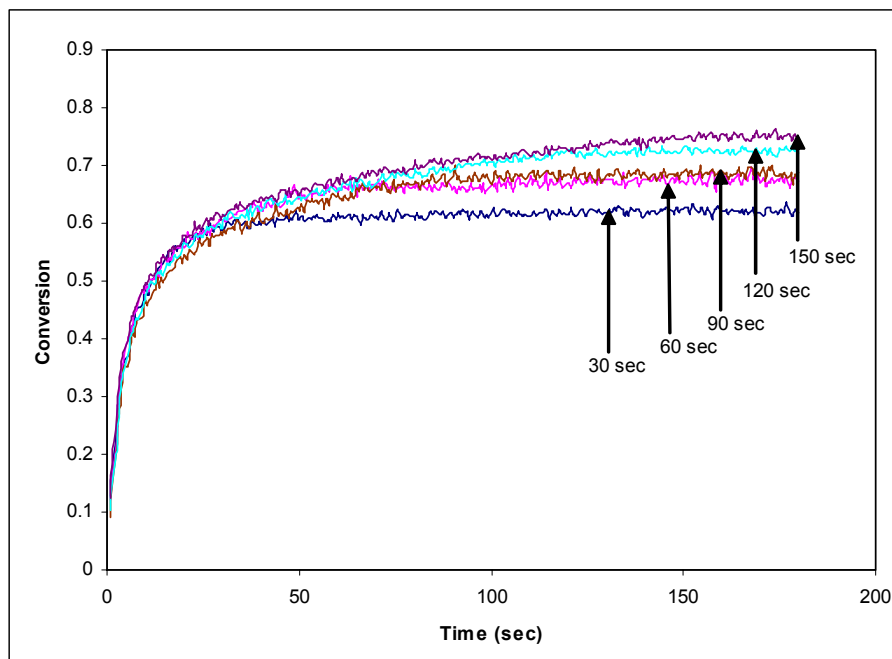
### *Real time Infra Red Spectroscopy*

Real-time IR was used to study the disappearance of the vinyl ether peak at  $1639\text{ cm}^{-1}$  and utilizing the same to monitor the extent of reaction. In order to study the effect of composition on the extent of cure, samples were subjected to a 150 sec UV light exposure and typical results obtained are in Figure 1.



**Figure 1. Conversions of vinyl-ether double bonds at  $1639\text{ cm}^{-1}$  for different formulations after UV exposure of 150 seconds**

It was also observed that that the conversions were a function of both the polymer composition and the exposure time. The change in vinyl ether conversions as a function of different UV exposure times is illustrated in Figure 2.



**Figure 2. Conversion in coating E changes as a function of exposure time**

In light of this, RTIR experiments were done for all samples at several exposure times. Percent conversions were calculated at 30 and 150 seconds and compiled in Table 5.

**Table 5. Percent conversion of vinyl ether groups at  $1639\text{ cm}^{-1}$  after UV exposure times of 30 and 60 seconds**

Coating	A	B	C	D	E	F	G	H	I	J
% Conversion after 30 sec	39	55	59	65	61	60	50	53	45	63
% Conversion after 150 sec	61	69	73	77	75	84	63	57	62	84
Polyester $T_g$	-12.47	-15.5	-18.73	-35.61	-28.04	-31.97	-41.07	-36.62	-	-39.36

The data shows that complete conversion was not obtained and this may be attributed to an increase in viscosity as cure proceeds and the subsequent inability of the reacting moieties to find each other due to sluggish segmental mobility. A general trend observed was that when the constituent polyester had a higher  $T_g$ , lower conversions were observed and vice versa. Another factor that influenced conversion was the viscosity of the coating. Coating H, despite having a low  $T_g$ , showed very low conversion and may have been due to high viscosity of the constituent polyester which in turn could be attributable to the presence of a tri-functional monomer. Thus, the initial viscosity of the polyester has an impact on the ultimate conversion achieved.

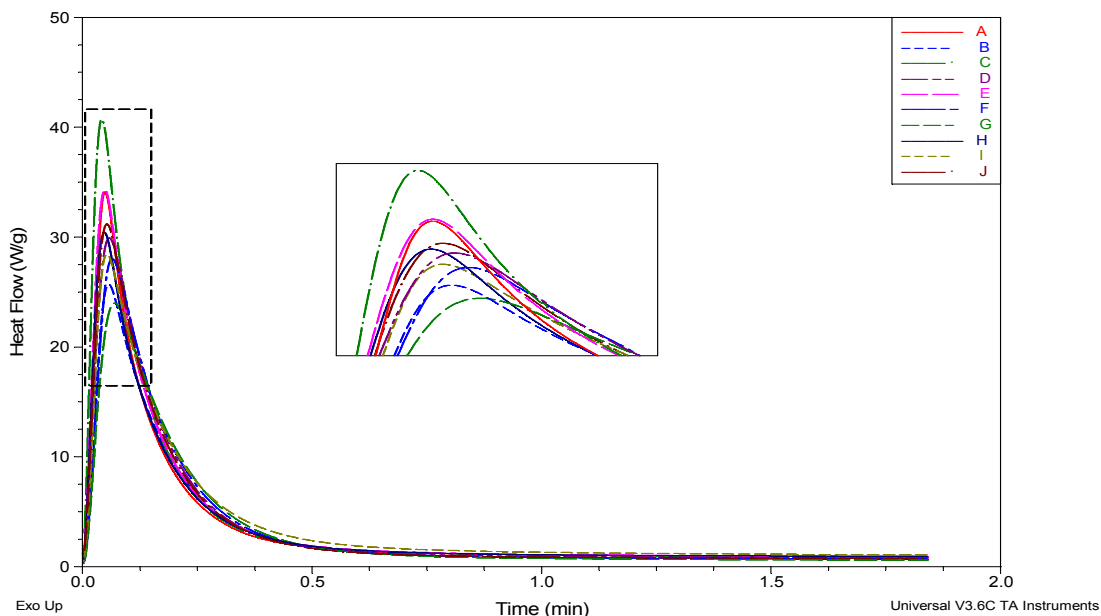
### Photo Differential Scanning Calorimetry (PDSC)

Heat flow for cure reaction was determined for coatings using a PDSC and the values obtained are as outlined in Table 6. The values were obtained by calculating the area under the curve. The peak maximum time is a time at which maximum cure is achieved and data in Table 6 shows that maximum cure was achieved at extremely short exposure times.

**Table 6. Onset times and heat flow for cure**

Coating	A	B	C	D	E	F	G	H	I	J
Peak max (min)	0.05	0.06	0.04	0.06	0.05	0.06	0.07	0.05	0.05	0.05
Heat flow (J/g)	277.7	259.7	290.6	285.8	288.2	285.6	275.1	255.2	287.6	283.3

PDSC plots of cure as illustrated in Figure 3 show that there are variations in the heat evolved during the photopolymerization. However, due to the variation in polymer composition detailed analysis of the molar concentration of reactive groups is required in order to obtain normalized heats of reaction. This work is currently ongoing.



**Figure 3. Plot of heat flow during cure for different formulations after UV exposure of 2 minutes**



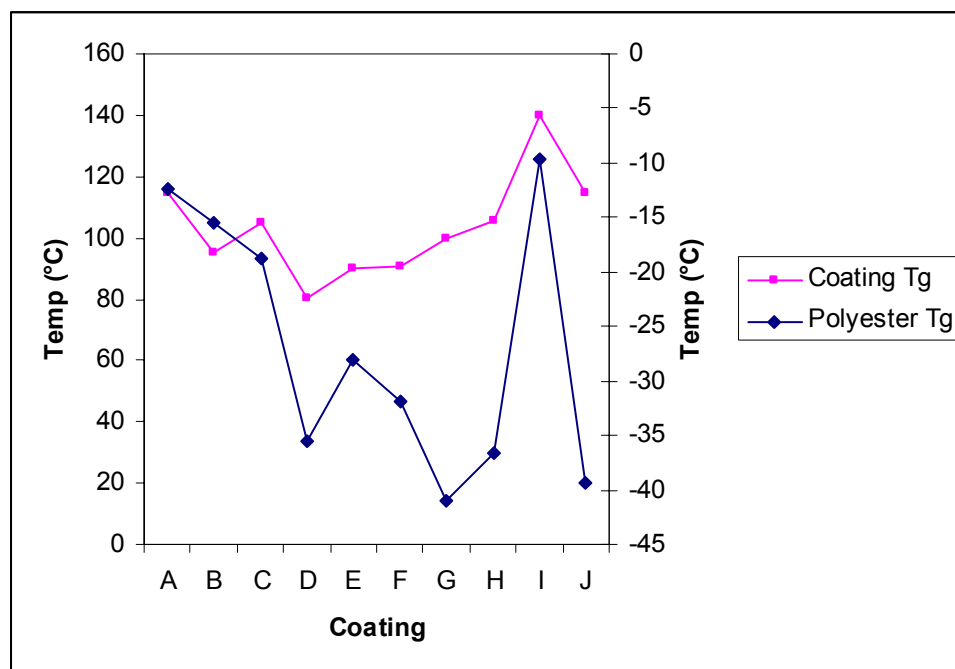
### Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was used to determine the glass transition temperature and crosslink density of the coatings and values obtained are in Table 7. As expected, the crosslink densities and glass transition temperatures were found to vary as a function of composition.

**Table 7. Glass transition temperature and crosslink density of coatings**

Sample	T <sub>g</sub>	Crosslink density (mol/cm <sup>3</sup> )
A	114.96	5.27x10 <sup>-3</sup>
B	94.929	3.66x10 <sup>-3</sup>
C	104.93	7.07x10 <sup>-3</sup>
D	80.478	3.65x10 <sup>-3</sup>
E	90.08	4.96x10 <sup>-3</sup>
F	90.417	0.13x10 <sup>-3</sup>
G	99.983	5.44x10 <sup>-3</sup>
H	105.43	5.54x10 <sup>-3</sup>
I	139.78	2.53x10 <sup>-3</sup>
J	114.91	0.14x10 <sup>-3</sup>

Backbone structure influences the T<sub>g</sub> of coatings. The presence of aromatic and/or cyclic monomers resulted in coatings with high T<sub>g</sub> values. It was seen that coatings that comprised flexible monomers like HD or EH showed relatively low T<sub>g</sub>. The final T<sub>g</sub> of coatings followed a trend similar to that of constituent polyesters as shown in Figure 4.

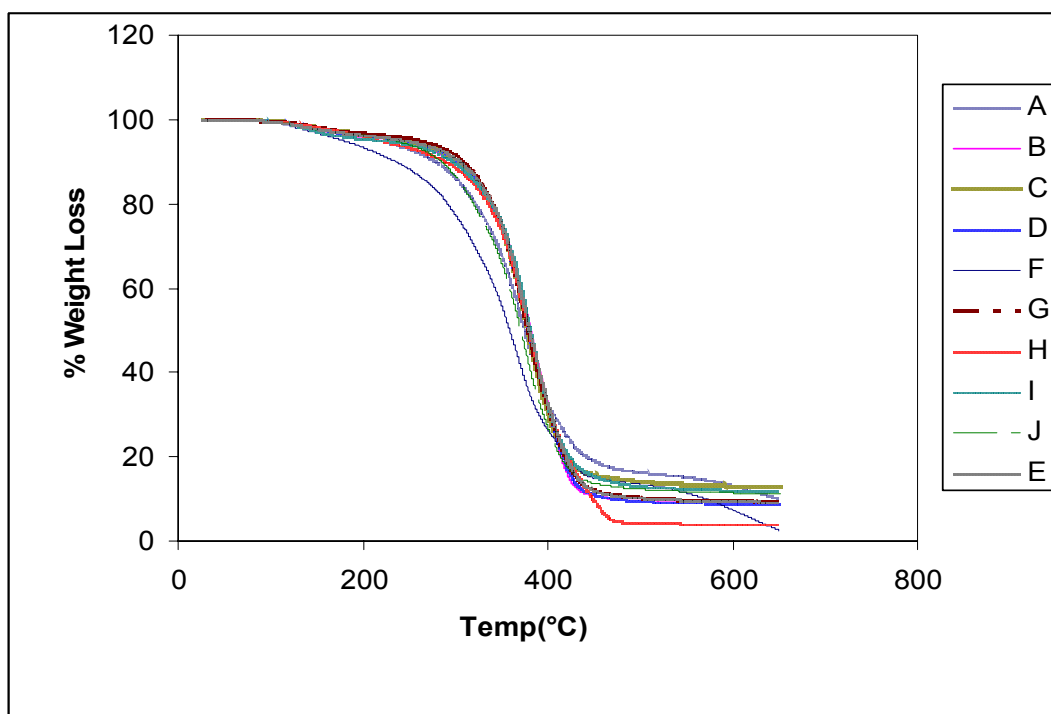


**Figure 4. A comparison of polyester and final coating T<sub>g</sub>**

The crosslink density fell into a rather narrow range, with the exception of samples F and J. Since we attempted to maintain the same vinyl (maleic) functionality for all of the polyesters and also since the polymerization reaction is stoichiometric, this is not unexpected. Samples F and J which have much lower crosslink density are made from polyesters 6 and 10. These polyesters have the highest acid values which suggests that the degree of polymerization is not as high for these two polymers as the others.

### Thermogravimetric analysis

Thermal stability of the cured coatings were compared for weight loss at a temperature of 150°C and the values were found to be less than 4% which may be attributed to moisture loss or a volatilization of low molecular weight, unreacted components in the crosslinked film. A temperature of 150°C was chosen based on the temperature that the coating would be subjected to during the manufacturing process. The thermal stability curves are in Figure 5.



**Figure 5. Thermal stability curves for different formulations**

It was seen that coatings with an aromatic backbone showed better thermal stability at a temperature of 600°C. It was also seen that coatings containing CHDA showed lower thermal stability at a temperature of approximately 200°C in case of E and at 600° in case of coatings H and F.

## Pendulum Hardness

König pendulum hardness was determined for different formulations and was found to vary as a function of composition. Figure 6 illustrates the trend observed for hardness values. A general trend observed was that formulations with aromatic backbones like A, B, C, D, E and I showed generally higher hardness values. The hardness values could also be correlated with degree of crosslinking. Coatings F and J had a low crosslink density resulting in a low pendulum hardness value.

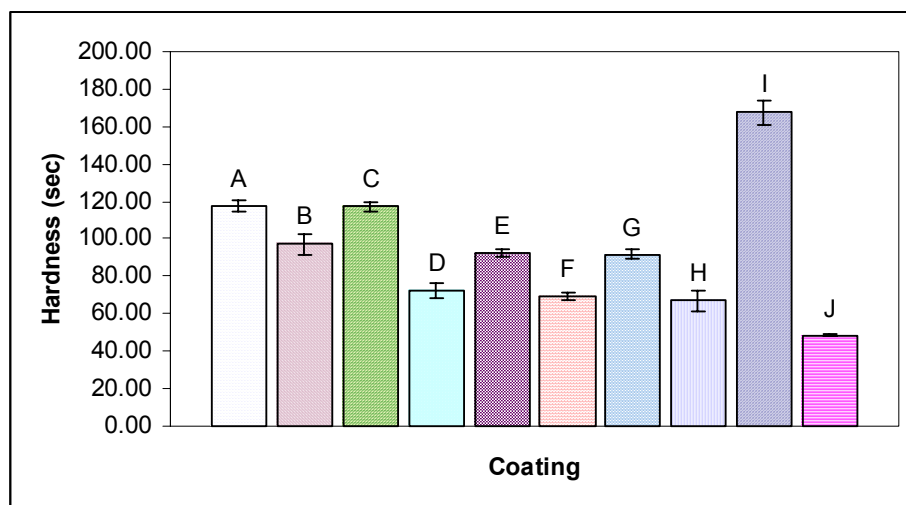


Figure 6. Hardness value results for different formulations

## Conclusions

Donor-acceptor radiation curable coatings can be designed in order to meet specific application requirements. This is achieved by varying the composition of the unsaturated polyester backbone. Polyester properties such as viscosity and glass transition temperatures were found to change as the proportion of flexible monomers used were changed. Cure times and conversions were found to vary as a function of both composition and UV exposure times. Further trends in property changes were observed when the coatings were prepared from these polyesters were tested. The glass transition temperature and crosslink densities were found to be different when the composition changed. The coatings prepared exhibited good hardness values and higher hardness values were observed in compositions containing aromatic or aromatic like monomers. All coatings exhibited good thermal stability.

## References

1. Hall, HK, Jr; Padias, AB, *Aldrichimica acta*, 28(2), 37 (1995)
2. Jonsson, S., Sundell, P., Hultgren, J., Sheng, D., Hoyle, CE., *Prog. Org. Coatings*, 27, 107 (1996)
3. Zhang, L., Liu, L., Chen, Y., *J. Appl. Polym. Sci.*, 74, 3541 (1999)

4. Decker,C., Decker,D., *Polymer*, 38(9), 2229 (1997)
5. Noren,GK., *ACS Symposium series* 673,121 (1997)
6. Lapin,SC., Noren,GK, Schouten,JJ., *Radtech Asia*, 149 (1993)
7. Lapin, SC., Noren, GK, Julian, JM., *Polym. Mater. Sci. Eng.,Proceedings of ACS Division*, 72,589 (1995)

### **Acknowledgements**

We would like to thank the Defense Microelectronics Activity (contract #DMEA90-02-C-0224) for funding this project.