Catalysis of Thermally Curable High Solids Cycloaliphatic Epoxy Formulations

R. P. Subrayan, Daniel J. Miller, Michael M. Emmet and Werner J. Blank*

King Industries, Inc., Science Road, Norwalk, CT 06852
E-mail: werner@wernerblank.com

INTRODUCTION

This paper describes a new latent cationic super acid catalyst that thermally cures formulations containing cycloaliphatic epoxide resins. This catalyst promotes homopolymerization of the epoxide via a cationic mechanism. Copolymerization of epoxides with reactive diluents, such as polyols, cyclic ethers, vinyl ethers or amino resins is also demonstrated.

There are different types of epoxy resins (glycidyl ether, glycidyl ester, epoxidized oils, cycloaliphatic and epoxidized polybutadiene), each of which can be catalyzed by this new technology. Epoxy resins are used for various applications such as encapsulants, castings, laminates, adhesives, graphic arts, industrial coatings, etc.[1] Typically, the polymerization of epoxide resins is initiated by the addition of crosslinkers, hardeners or curing agents. These curing agents include amines, polyamines, polyamidoamines, phenol- and amino-formaldehyde resins, carboxylic acid functional polyesters, anhydrides, polysulphides and polymercaptans.[2] Formulations with the nitrogen-containing curing agents, which are typically two-component, cure under ambient conditions and have limited pot life. However, reactions of epoxy groups with alcohols, acids or anhydrides require higher temperatures, have good pot life and may require a catalyst. These catalysts include amines, Lewis acids or super acids, depending on the type of the epoxide used. For example, an imidazole can be used to catalyze aromatic glycidyl ethers but are relatively inefficient for the catalysis of cycloaliphatic epoxides. In such cases, use of a super acid is required.

Due to the low viscosity and formulating flexibility, cycloaliphatics have been the primary focus of this study. Cycloaliphatic epoxides have been used in metal, paper, plastic and wood coatings, inks, packaging, electrical insulators and bushings, insulation tapes, high-voltage coils and transformers.[3] Stable, latent super acids include triarylsulfonium or diaryliodonium salts of hexafluoroantimonate or hexafluorophosphate.[4] These catalysts are generally activated by photolysis, wherein the acid is liberated.[5] The iodonium salts may also be thermally activated at 140 ºC. Recently, Hult *et al*.[6] reported another thermally active cationic catalyst, benzyl tetrahydrothiophenium hexafluoroantimonate. This catalyst is active between 100-140 °C.

Recently, King Industries introduced several thermally active, cationic, latent, super acid catalysts for various epoxy systems.[7] These catalysts can be thermally activated at temperatures as low as 80°C depending on the epoxy system. Among these catalysts, a quaternary ammonium salt[8] (hereafter, referred as Qsalt) has demonstrated exceptional performance with cycloaliphatic epoxide resins, allowing 100% solids, low viscosity formulations with application to a variety of substrates. The film properties of formulations containing cycloaliphatic epoxides using this catalyst are discussed below.

EXPERIMENTAL SECTION

Reagents: The following reagents were used in the formulations: ERL-4221 – cycloaliphatic epoxide (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate), EW=137 (Union Carbide), AC-220E, methyl tetrahydrophthalic anhydride (MTHPA, Lonza), Cymel 1123, methylated, ethylated benzoguanamine (Cytec), Decane carbonate (Texaco), 1,4-Butanediol divinyl ether (BASF), Vikoflex 7170, epoxidized soybean oil, molecular weight 1000 (Elf Atochem), Cymel 303, Hexamethoxymethylmelamine (HMMM, Cytec), UVR-6000, 3-ethyl-3-hydroxymethyl oxetane (Union Carbide), Tone 201, 100% carprolactone polyol, OH# 313, MW 358, EW = 179 (Union Carbide), Tone 301, 100% caprolactone polyol, OH # 560, MW 300, EW=100 (Union Carbide), K-FLEX 188, 100% polyester polyol, OH# 230, MW 487, EW=243 (King Industries, Inc.), Propylene Carbonate (Texaco) and Beetle 65, Urea-Formaldehyde, 100% solids (Cytec).

Test Methods: Formulations were coated on iron phosphated steel panels using draw down bar to obtain a 25-micron film thickness. Adhesion was measured according to the ASTM D 3359 method using crosshatch tape, wherein the % coating retained on substrate is reported. König Pendulum Hardness is reported in cycles and run according to the ASTM D 4366 method. Mandrel Flexibility is run according to ASTM D 522 method the result is reported as the % elongation. Pencil Hardness is run according to ASTM D 3363 method. Tukon Hardness (Knoop or Indentation Test or Pfund Test) is run according to ASTM D 1474. Impact flexibility is reported in inch pounds. MEK Double rubs were run using a two-pound hammer.

Melting point was measured using a Thomas Hoover capillary melting point apparatus and is uncorrected. Differential Scanning Calorimetry (DSC) experiments were run under nitrogen using the Differential Scanning Calorimeter from TA Instruments (model number DSC 2010). Thermogravimetric analysis (TGA) experiments were also run under nitrogen using the thermogravimetric analyzer from TA instruments (model number TGA 2050).

RESULTS AND DISCUSSION

CATALYST PROPERTIES

Qsalt is a white crystalline solid (M.p. 108-110 °C) and is composed of a quaternary ammonium hexafluoroantimonate salt. It is soluble in polar organic solvents but is insoluble in water or non-polar organic solvents. This catalyst is also TSCA listed. The salient features of this catalyst are listed in Table 1.

Table 1. Features of the Qsalt Catalyst

Advantages	Drawbacks	Possible Applications
• Low Temperature Cure 80-100 °C • 3-6 Month Room Temperature Pot Life • Good Water	• Thermal Stability is limited by the formulation • Color shift is noticed in concentrated	• Low Temperature Cure • High Speed Applications, e.g. Graphic Arts & Coil • Formaldehyde

Resistance • Less Color Formation Than Triflates	solutions	Free Coatings • Any OEM Processes

Qsalt is a latent super acid catalyst and therefore, its catalytic activity may be inhibited in formulations containing free amines or amine containing pigments. Also, substrates with amino functionality or primers or base coats containing amines could inhibit the cure.

Before any formulations were analyzed, the DSC and TGA tests were run on the Qsalt catalyst alone. These curves are shown in Figure 1.

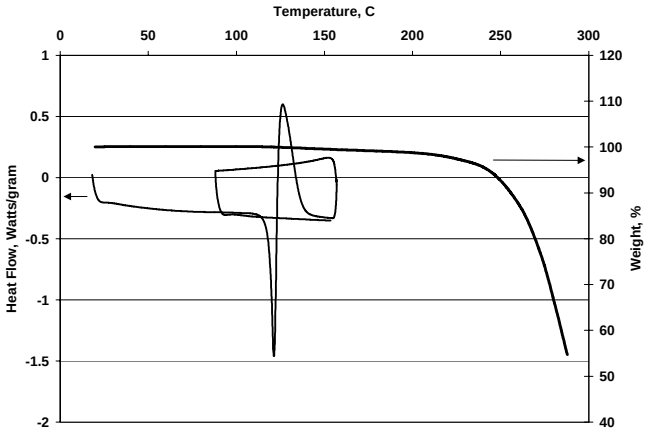

Figure 1. DSC & TGA Data of the Qsalt Catalyst; Heating rate: 5 °C/min (Exotherm up)

The DSC data showed an endothermic melting transition with the peak maximum at 120 °C, followed by an exotherm with the maximum at 126 °C. This exotherm was not observed in the repeat cycle suggesting that a chemical reaction took place. No weight loss was observed by the TGA studies during this transition. Based on the NMR, IR and GPC data, this reaction was found to be a thermal rearrangement of the quaternary ammonium moiety to a protonated tertiary ammonium group, thereby generating a weaker amine - super acid salt. The latter catalyzes the curing of the epoxy resin. The properties of the epoxy formulations containing the catalyst are described below.

HOMOPOLYMERIZATION OF THE EPOXY RESIN

The epoxy resin used in this study was 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexylcarbxylate (ERL 4221, eq. wt. 137). This was formulated with the Qsalt catalyst, at 1-wt.% level. The homopolymerization of the epoxide was initially tested by DSC and then by the film properties.

DSC Experiments

The DSC experiment showed an exotherm due to the crosslinking reaction. Three important data can be measured from this exotherm: a) onset point, which states at what temperature the reaction starts, b) slope of the exotherm, which indicates how fast the reaction proceeds and, c) enthalpy of the exotherm, which indicates how far the reaction has progressed. The onset of the crosslinking reaction was 110 ºC with a slope of 1.60 W/g/ºC with a total enthalpy of 520 J/g. Enhanced reactivity can be demonstrated by changing the DSC procedure to isothermal. In this case, the onset point is referenced as time in minutes to start the reaction. The isothermal DSC experiments were run at 70, 80 and 90 °C and the results are shown in Figure 2.

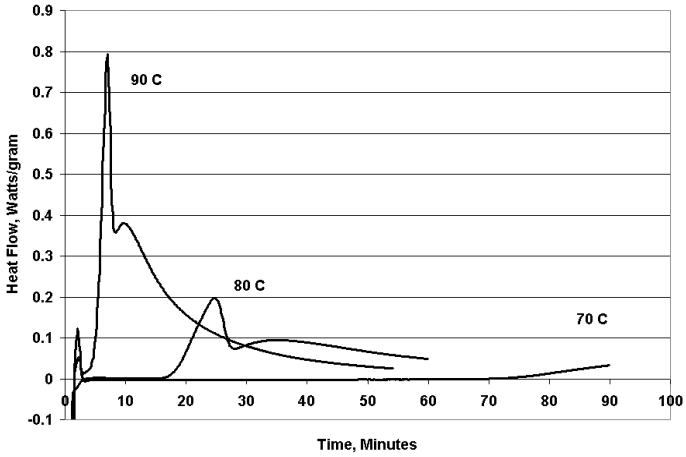

Figure 2. Isothermal DSC Plots (Catalyst: 1-wt.% Qsalt TRS, Exotherm up)

The isothermal DSC data show faster cure at 90 °C (onset < 10 min) and a slower cure at 80 °C (onset 18 min). For the experiment run at 70 °C, there is an onset at 80 minutes but the reaction will proceed at a much slower rate. This data suggest a lower cure temperature of 80 °C for the homopolymerization of the cycloaliphatic epoxide.

Cure Rate Comparison

Films were cast on iron phosphated steel panels and baked at different temperatures, to obtain a 25-micron dry film thickness. The time required (in minutes) to obtain 100+ MEK double rubs is recorded in Table 2.

Table 2. MEK Rub Data vs. Cure Temperature for Cycloaliphatic Epoxide System

Cure Temperature, °C	80	90	100	120	140	160
Time to obtain 100 + MEK double rub (min)	20	8	6	2	2	1

The data clearly show that Qsalt catalyzes the homopolymerization of cycloaliphatic epoxide based formulations at 80 °C. The MEK data also suggest that the rate of cure increases with the cure temperature.

COPOLYMERIZATION WITH REACTIVE DILUENTS

The reactive diluents used include an oxetane, vinyl ether, an anhydride, amino functional resins and polyols. These diluents were incorporated into the epoxy formulations at 25-wt.% level (with respect to the epoxy resin) along with the Qsalt catalyst (1-wt.% TRS). As before, DSC experiments were run before the properties of the cured films were studied.

DSC Studies

The DSCs of the epoxy formulations containing different reactive diluents and the catalyst, were run at a heating rate of 20 °C per minute. The results are summarized in Table 3.

Table 3. Reactivity Data of Cycloaliphatic Epoxides Containing Reactive Diluents

Resin System	DSC Data (Heating rate: 20 °C/min)			TGA Data*
	Onset Point ºC	Enthalpy J/g	Slope W/g/ºC	Residue wt.%
ERL-4221	110	520	1.60	98.5
+oxetane	102	502	1.36	96.7
+divinyl ether	106	586	2.69	86.7
+epoxidized oil	113	454	1.25	-
+anhydride, MTHPA	109	391	0.60	-
+HMMM	122	225	0.05	95.6
+benzoguanamine	117	267	0.17	-
+urea-formaldehyde	250	-	0.03	-
+Polyol OH EW=100, 2.2 epoxy/OH	110	520	1.60	-
+Polyol OH EW=179, 3.9 epoxy/OH	107	376	1.09	-
+Polyol OH EW=243, 5.4 epoxy/OH	134	378	1.40	-

* TGA = 100 ºC for 15 minutes

The DSC data showed steeper slope (i.e., higher reaction rate) with the divinyl ether. The onsets of most of these reactions are in the range, 100-110 °C and the enthalpy data show a thorough reaction. The TGA data show very little residual volatiles in these formulations. Further analysis by isothermal DSC runs using oxetane and divinyl ether, summarized in Table 4, confirm the enhanced reactivity of these formulations.

Table 4. Isothermal DSC Studies for Cycloaliphatic Formulations Containing Reactive Diluents*

	DSC Isothermal at 80 ºC for 30 minutes		
	Onset Point Minutes	Enthalpy J/g	Slope W/g/ºC
ERL-4221	18	134	0.307
+oxetane	8	422	0.232
+divinyl ether	11	465	0.212

*Co-reactant concentration = 25-wt.%;
Qsalt concentration = 1-wt.% TRS

Properties of the Cured Films Containing Reactive Diluents

The formulations were cast on iron phosphated steel panels and were cured at 100 °C for 15 minutes to give 25-micron dry film thickness. All of these films gave 200+ MEK double rub resistance suggesting that the films are completely cured. Other properties of these films are listed in Table 5.

Table 5. Film Properties (Cure Schedule: 100 ºC, 15 minutes)*

Resin System	Hardness			Flexibility		
	König	Tukon	Pencil	Mandrel	Impact (lb-in)	
	Cycles	KHN		Elonga-tion %	Direct	Rev-erse
ERL-4221	144	27	H	5	30	<5
+oxetane	153	31	H	5	40	<5
+divinyl ether	151	29	F	4	30	<5
+decane carbonate	107	18	HB	>32.5	160	90
+epoxidized oil	85	7.7	B	>32.5	160	160
+anhydride, MTHPA	146	27	H	5	40	<5
+Polyol OH EW=243, 5.4 epoxy/OH	152	22	HB	>32.5	80	20

*Co-reactant Concentration = 25-wt.%;
Qsalt concentration = 1-wt.% TRS

The film properties of the control (i.e., the homopolymerization) and the copolymerization reactions are comparable in most cases except when the reactive diluent has long chain flexibilizers as in decane carbonate, epoxidized oil or a polyol. These flexibilizers decrease the hardness and increase the flexibillity of these films.

SUMMARY AND CONCLUSIONS

In summary, the Qsalt catalyst is particularly suitable for 1K formulations containing cycloaliphatic epoxides that can be cured at temperatures as low as 80 °C. This catalyst is also suitable for the lower temperature cure of the cycloaliphatic epoxy resins with reactive diluents such as oxetane, vinyl ether or polyols. Specific applications of this catalyst in formaldehyde free coatings will be discussed.

References

1. May, C. A. In *Epoxy Resins Chemistry and Technology* May, C. A., Ed.; Marcel Dekker: New York, 1988; Chapter 1.
2. Ellis, B., *Chemistry and Technology of EPOXY RESINS*, Blackie Academic and Professional: London, 1993; Chapter 2.
3. a) *Anon.* Product Bulletin: SarCat® K126, SARTOMER, Exton, PA. b) *Anon*. Product Bulletin: Cycloaliphatic Epoxide Systems, Union Carbide, Danbury, CT.
4. a) *Anon*. Product Bulletin: SarCat® CATIONIC PRODUCTS, SARTOMER, Exton, PA. b) *Anon*. Product Bulletin, CYRACURE® Cycloaliphatic Epoxides, Union Carbide, Danbury, CT
5. a) Wicks, Jr., Z. W.; Jones, F. N.; Pappas, S. P. *Organic Coatings Science and Technology*, Wiley-Interscience: New York, Second Edition, 1999; Chapter 28. b) Fouassier, J.-P. *Photoinitiation, Photopolymerization, and Photocuring*, Hanser Verlag: Munich, 1995; Chapter 4. c) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci.: Part A: Polym. Chem*. **1996**, *34*, 3231.

6. Malmström, E.; Vestberg, R.; Carlmark, A.; Magnusson, H.; Hult, A. *Polym. Mater.: Sci. & Eng*. **2001**, *84*, 295.
7. *Anon*. Trade Literature, King Industries, Inc., Norwalk, CT.
8. NACURE® Super XC-7231 Catalyst, King Industries, Inc., Norwalk, CT.