The Evaluation of Various Substituted Ureas as Latent Accelerators for Dicyandiamide Cured Epoxy Resin Formulations

By

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Introduction

It is commonly known that dicyandiamide (dicy), as a curing agent for epoxy resins, will provide one part formulations with extended room temperature shelf lives. The cured properties of these formulations are usually quite acceptable for many applications. However, a significant drawback to a dicy cure is that it must be accomplished above 170°C. Below 170°C, the reaction is sluggish at best. Therefore, to achieve cures at lower temperatures or in shorter times, accelerators have been added to epoxy/dicy formulations. Common accelerators are BF_3 amine complexes, tertiary amines, imidazoles, some proprietary compounds and substituted ureas. All of these accelerators offer some benefits and drawbacks to shelf life, cure profile and cured properties.

Applications for storage stable, one part epoxy formulations continue to grow. The use of epoxies can be streamlined by the introduction of one part formulations to production operations. These formulations can provide rapid and or low temperature cure capability coupled with excellent cured properties.

The use of one part epoxy formulations, as replacements for two part products, can result in cost savings. Production cost reductions result from the elimination of the meter-mix equipment required for two part formulations. Problems of rejects caused by incorrect mix ratios and incomplete mixing associated with the equipment are, therefore, eliminated. Equipment maintenance costs are reduced. Delivery equipment purging, which wastes material, is no longer required.

As we all know, many epoxy formulations require heat to cure and develop optimum properties. The users of heat curing formulations are continually searching for products that will cure at lower temperatures or in shorter times. Lower cure temperature produces cost savings by reducing energy usage. Shorter cure times allow increases in production line speed which also results in cost savings. As an example, the Automotive OEM utilizes one part epoxy formulations in steel reinforcement and structural adhesive applications. As paint bake oven temperatures are reduced and line speeds increased these formulations require modification, usually with accelerators, for continued utilization. In another example the manufacturers of multi-component composites realize benefits by reducing cure temperatures. Lower cure temperatures reduce internal stresses caused by differences in coefficient of thermal expansion between dissimilar materials. Distortions, delaminations and internal fractures are reduced. Using substituted ureas to accelerate a dicy cure allows the composite manufacturer to cure at lower temperatures.

One part epoxies are finding growing use in the Aerospace, Automotive, and Sporting Equipment markets. The formulations are also used in laminating, electrical and prepreg applications.

Objective

This study deals with the evaluation of some common substituted ureas as DGEBA/dicy accelerators. United States patents covering the use of substituted ureas as accelerators began to appear in the late 60's. [1,2,3] This work will help the epoxy formulator to decide which substituted urea, and what concentration amount will work best to meet their particular application needs. In this study we have identified the effect of each substituted urea on:

1. Degree of acceleration
2. Room temperature shelf life
3. Tg

Experimental

1.0 Materials

1.0 DGEBA: Liquid diglycidyl ether of Bisphenol A (LER)
EEW 182-192, viscosity at 25°C, 11,000-14,000 cps

1.2 DICYANDIAMIDE: OMICURE® DDA-10, 100% finer than 20 microns

1.3 THIXOTROPE: Aerosil R-972, hydrophobic fumed silica – Degussa

1.4 SUBSTITUTED UREAS: See Table I

Table 1 – Substituted Ureas Used in Study

Trade Name	Chemical Name	CAS #
Omicure® U-405	Phenyl Dimethyl Urea	101-42-8
Omicure U-24	2,4' Toluene bis Dimethyl Urea (Isomer Grade)	17526-94-2
Omicure U-410	2,4' Toluene bis Dimethyl Urea (Technical Grade)	17526-94-2
Omicure U-52	4,4' Methylene bis (Phenyl Dimethyl Urea) (Isomer Grade)	10097-09-3
Omicure U-415	4,4' Methylene bis (Phenyl Dimethyl Urea) (Technical Grade)	10097-09-3
Omicure U-35	Proprietary Cycloaliphatic Dimethyl Urea	39992-90-0
Diuron	3,4 Dichlorophenyl Dimethyl Urea	330-54-1
Monuron	4 Chlorophenyl Dimethyl Urea	150-68-5

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2.0 Equipment

2.1 High speed laboratory stirrer with high shear blade

2.2 Brookfield HAT viscometer with Helipath attachment and spindles

2.3 Perkin Elmer DSC-7

Procedure

We chose a blend of 100 pbw DGEBA, 8 pbw dicy and 3 pbw fumed silica as the basic (or control) formulation. The purpose of the fumed silica was to retard or eliminate settling tendencies of the solid ingredients. To this formulation were added 1, 3 and 5 pbw of each substituted urea. The ingredients were combined at slow speed in a pint can. After complete wet-out, mixing continued at high speed for only 5 minutes to retard heat build-up. The formulations were held under vacuum until bubbling ceased. Samples were stored at ambient room temperature in sealed half pint cans. A control was similarly prepared without any accelerator.

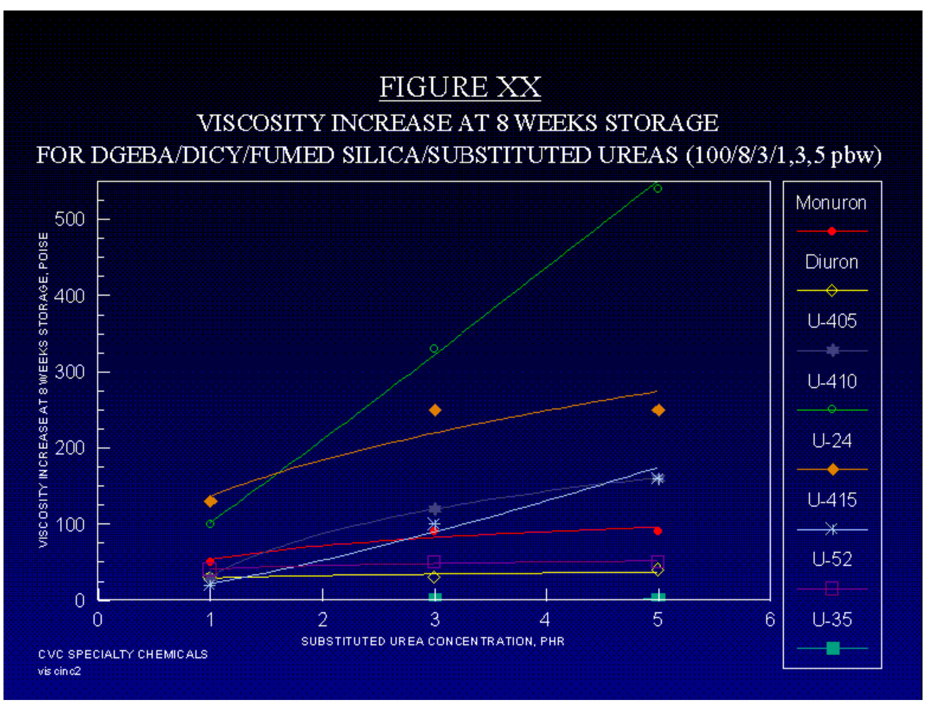
Viscosities at 25°C were determined using a Brookfield HAT viscometer with Helipath attachment. A rotation speed of 5 rpm was used. Determinations were made after one day and 1, 4, 8 and 12 weeks storage, continuing at 4 week intervals until a viscosity of two times the original was reached. Cure kinetics profiles and Tg (second scan) were determined on the DSC at a scan rate of 20°C per minute from 0° to 275°C. Isothermal curing was conducted on the DSC at appropriate temperatures between 80° and 160°C. These results provided time/temperature cure profiles, the time required to reach 95% cure, and the glass transition temperature (Tg) for all accelerated formulations.

Background

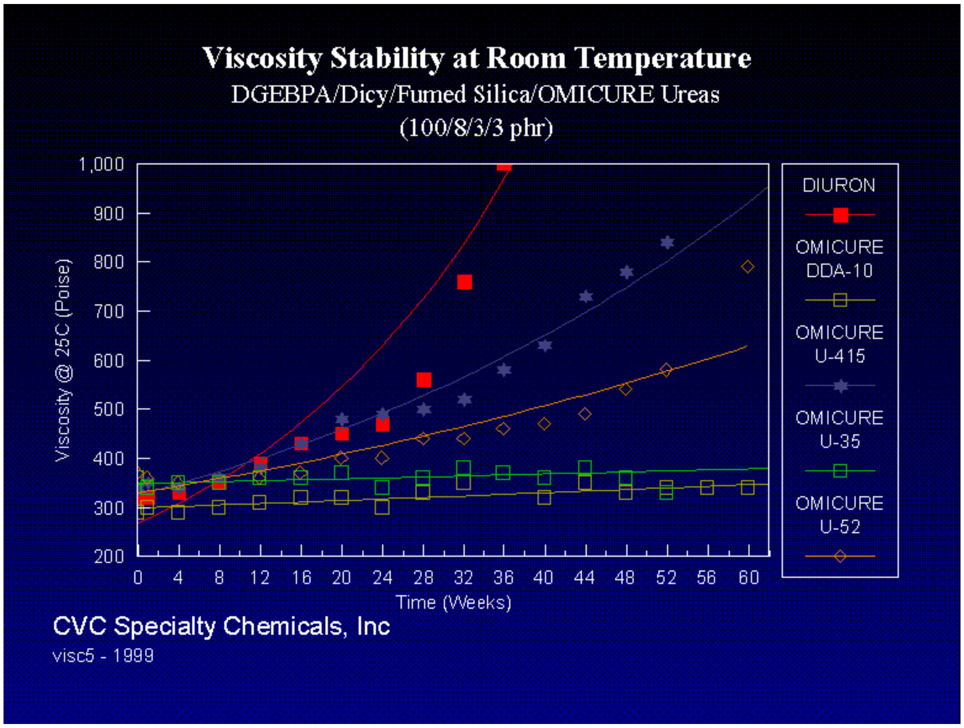
It is generally believed that dicy functions as both a catalytic (promoting homopolymerization) and as a reactive curing agent (promoting heteropolymerization) for epoxy resins. Complex mechanisms for the dicy-epoxy reaction have been proposed by Guthner and Hammer[4], and by Barwich, Guse and Brockmann.[5] While it is beyond the scope of this paper to examine these mechanisms in detail, it is apparent that the reactivity and shelf life of these systems are related to the solubility of the substituted urea in the resin.

Data and Results

As mentioned previously, the change in viscosity of each mixture was measured over time to determine shelf life, which for our purposes is defined as the time it takes a formulation to double in viscosity. **Table 2** (See Appendix) summarizes the viscosity increases vs. time and time to double in viscosity for each of the 25 formulations tested.
Figure 1 plots the results for viscosity increase through 8 weeks for urea levels of 1, 3, & 5 phr.



<u>Figure 2</u> plots the results for viscosity increase through 60 weeks for urea levels of 3phr.



The control formula for this experiment was a mixture of 100 pbw LER with 8 pbw Dicy (Omicure DDA10) and 3 pbw of Aerosil R972. The results of this system were not graphed but as seen in **Table 2**, this system was tracked for 136 weeks, and showed less than a 50% increase in viscosity. The results (shown in **Table 2**) indicate that formulations containing lower levels of substituted urea increase in viscosity at a slower rate while those with greater levels of substituted urea increase in viscosity at a faster rate.

Figures 1, and 2 present data on viscosity increases between all the substituted ureas tested. These data indicate wide variation in viscosity increases between the ureas studied. At all levels tested, the longest shelf life (taken as the time to double in viscosity) is seen with the use of Omicure U-35, followed by Omicure U-52. The shortest shelf lives were seen with Omicure U-24 and U-410. Shelf lives for Omicure U-405, Omicure U-415, Monuron and Diuron showed intermediate rates of viscosity increases at each level. Based on these data we can rank the shelf life of the substituted ureas as shown in **<u>Table 3.</u>** It is interesting to note that the technical grades of 2,4’ Toluene bis Dimethyl Urea (U-410) and 4,4’ Methylene bis Phenyl Dimethyl Urea (U-415), exhibit a greater rate of increase than those formulations containing the pure isomer grade substituted urea.

<u>Table 3</u> – Rank of Substituted Ureas for Shelf Life	
1	Omicure U-35
2	Omicure U-52
3	Diuron
4	Omicure U-415
5	Monuron
6	Omicure U-24
7	Omicure U-405
8	Omicure U-410

Isothermal cures between 80°C-160°C were measured for each of the formulations. The results for time to reach 95% cure with formulations containing 1, 3, and 5 phr urea are shown as follows in **Figures 3 through 9.**

Figure 3 – Time to 95% Full Cure @ Various Temperatures with Omicure U-35

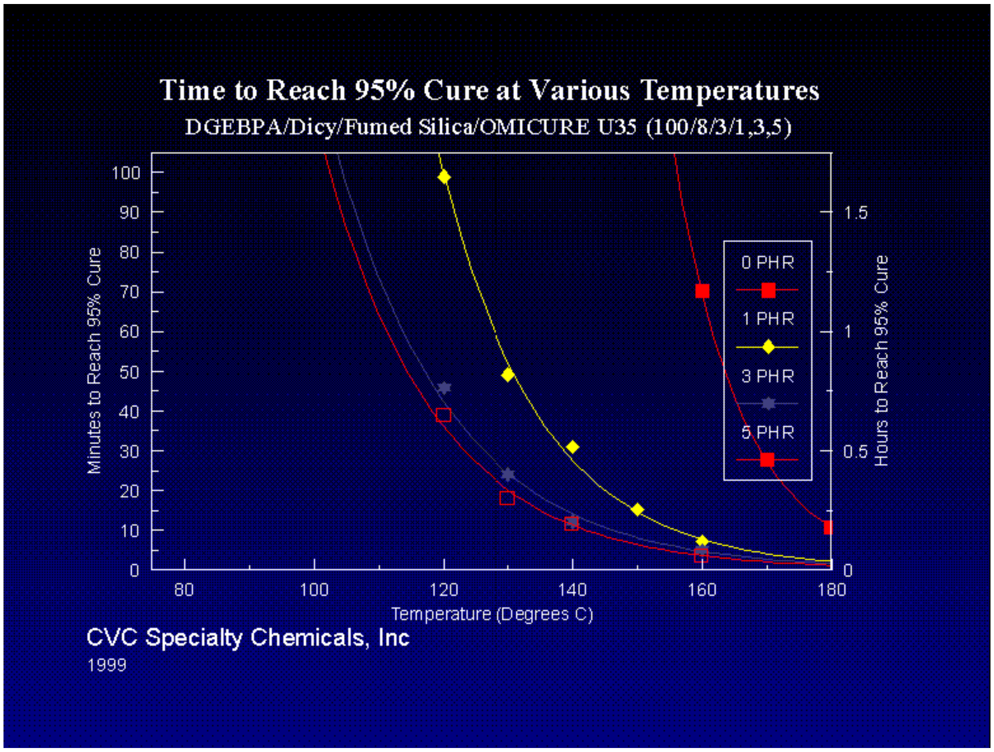


Figure 4 – Time to 95% Full Cure @ Various Temperatures with Omicure U-52

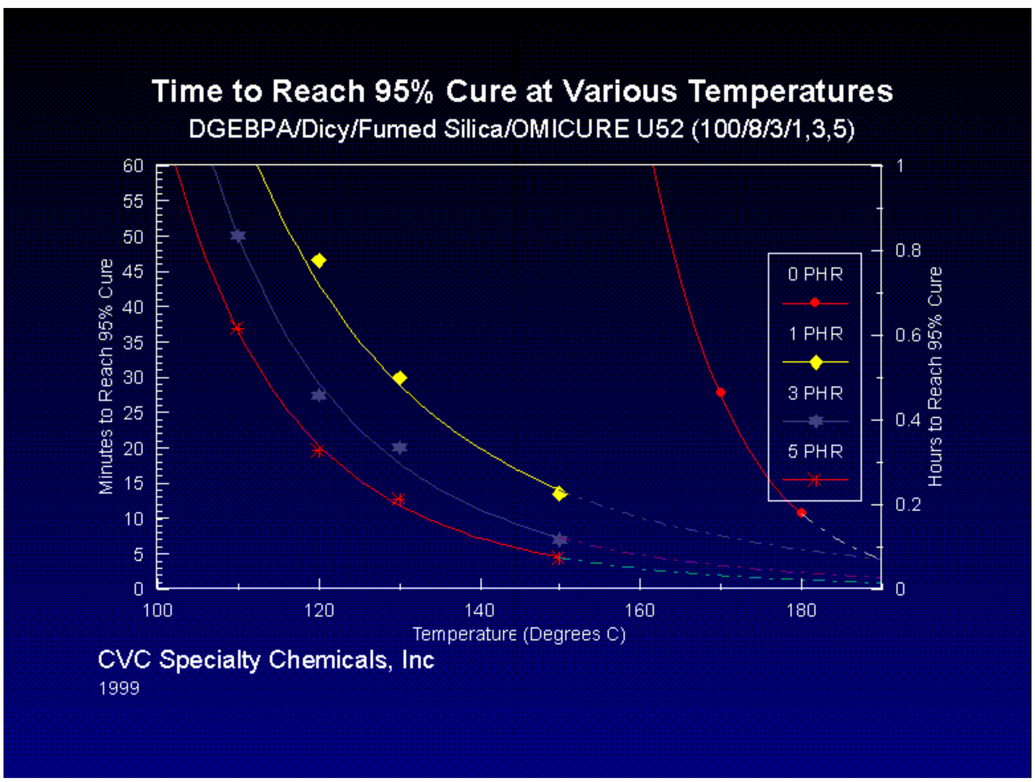


Figure 5 – Time to 95% Full Cure @ Various Temperatures with Omicure U-415

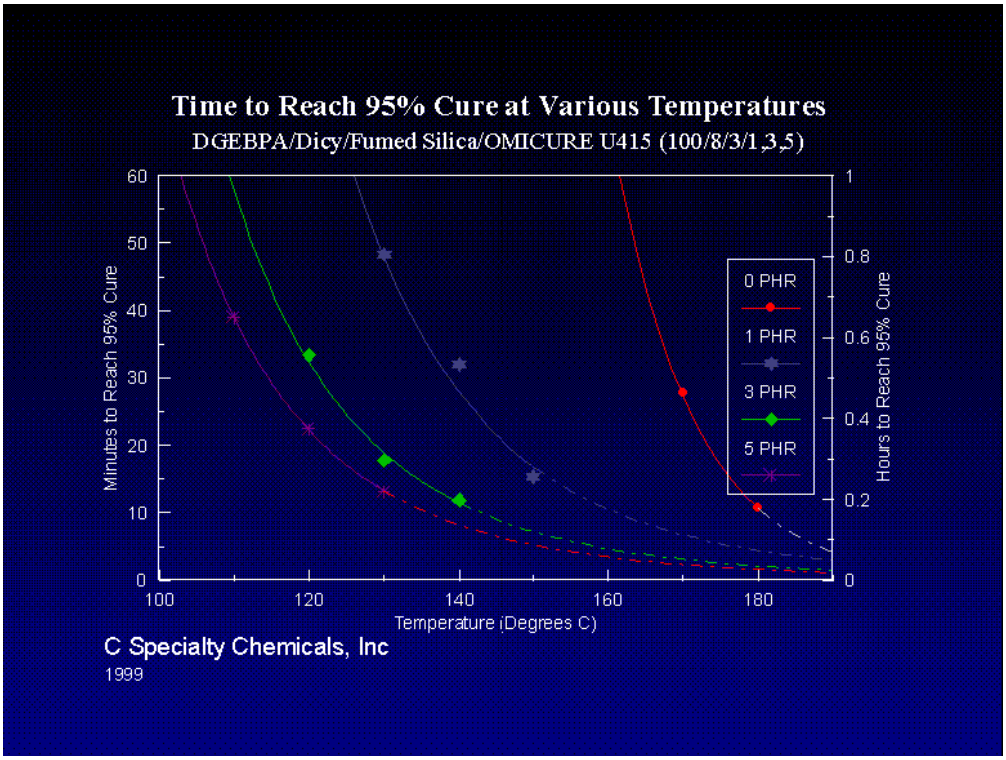


Figure 6 – Time to 95% Full Cure @ Various Temperatures with Omicure U-405

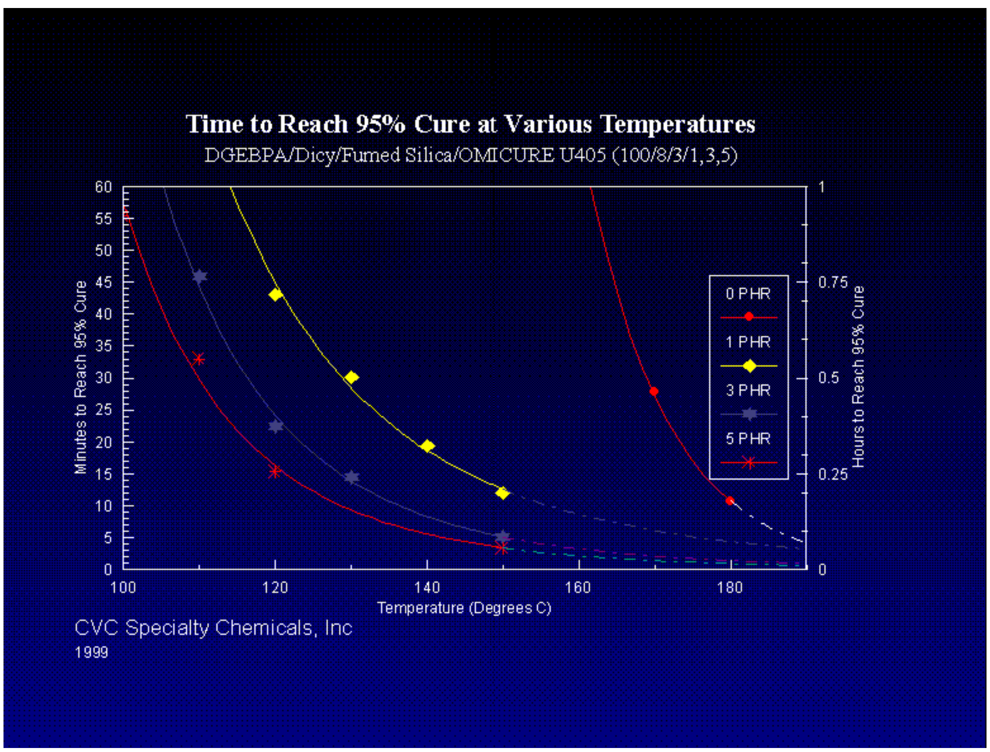


Figure 7 – Time to 95% Full Cure @ Various Temperatures with Omicure U-24

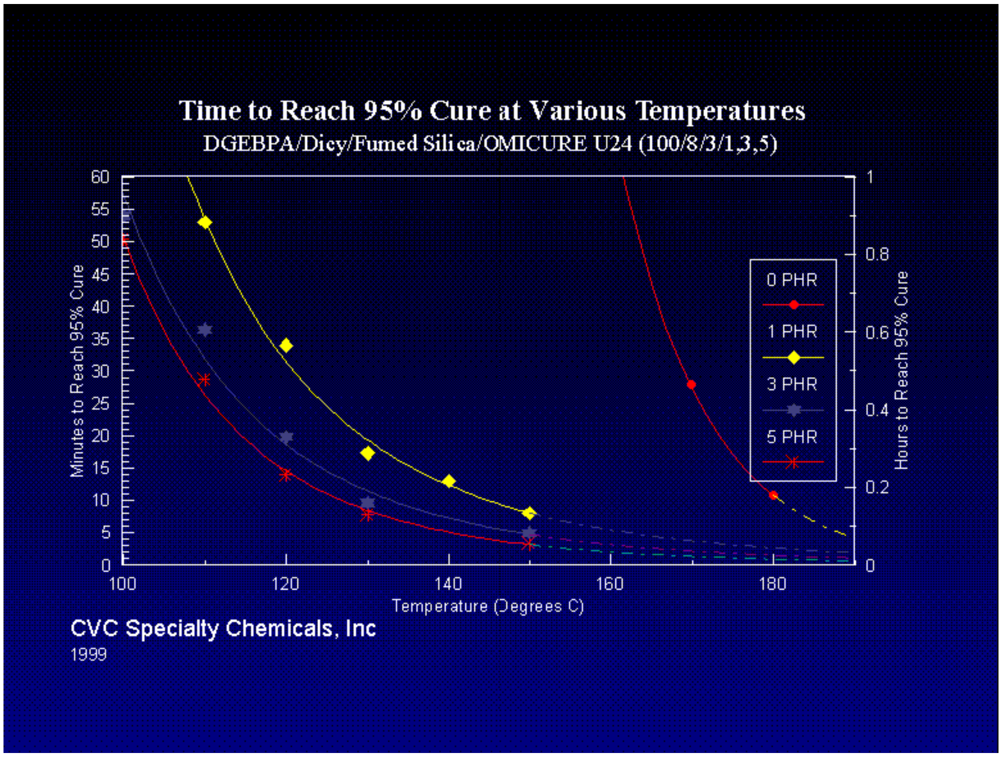


Figure 8 – Time to 95% Full Cure @ Various Temperatures with Omicure U-410

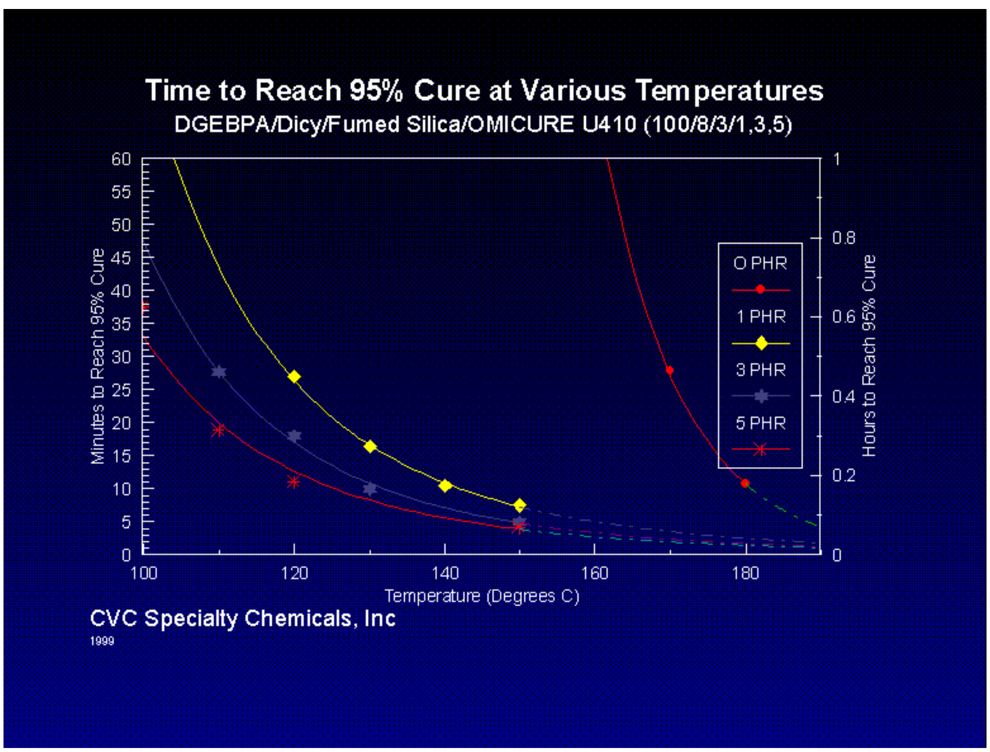
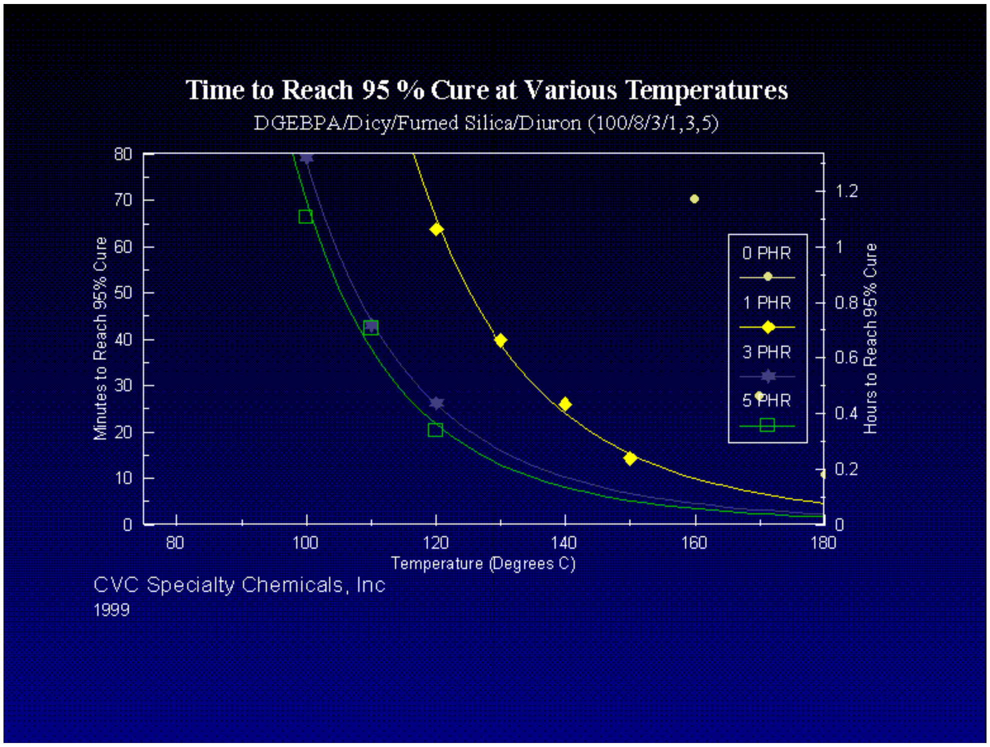


Figure 9 – Time to 95% Full Cure @ Various Temperatures with Omicure Diuron



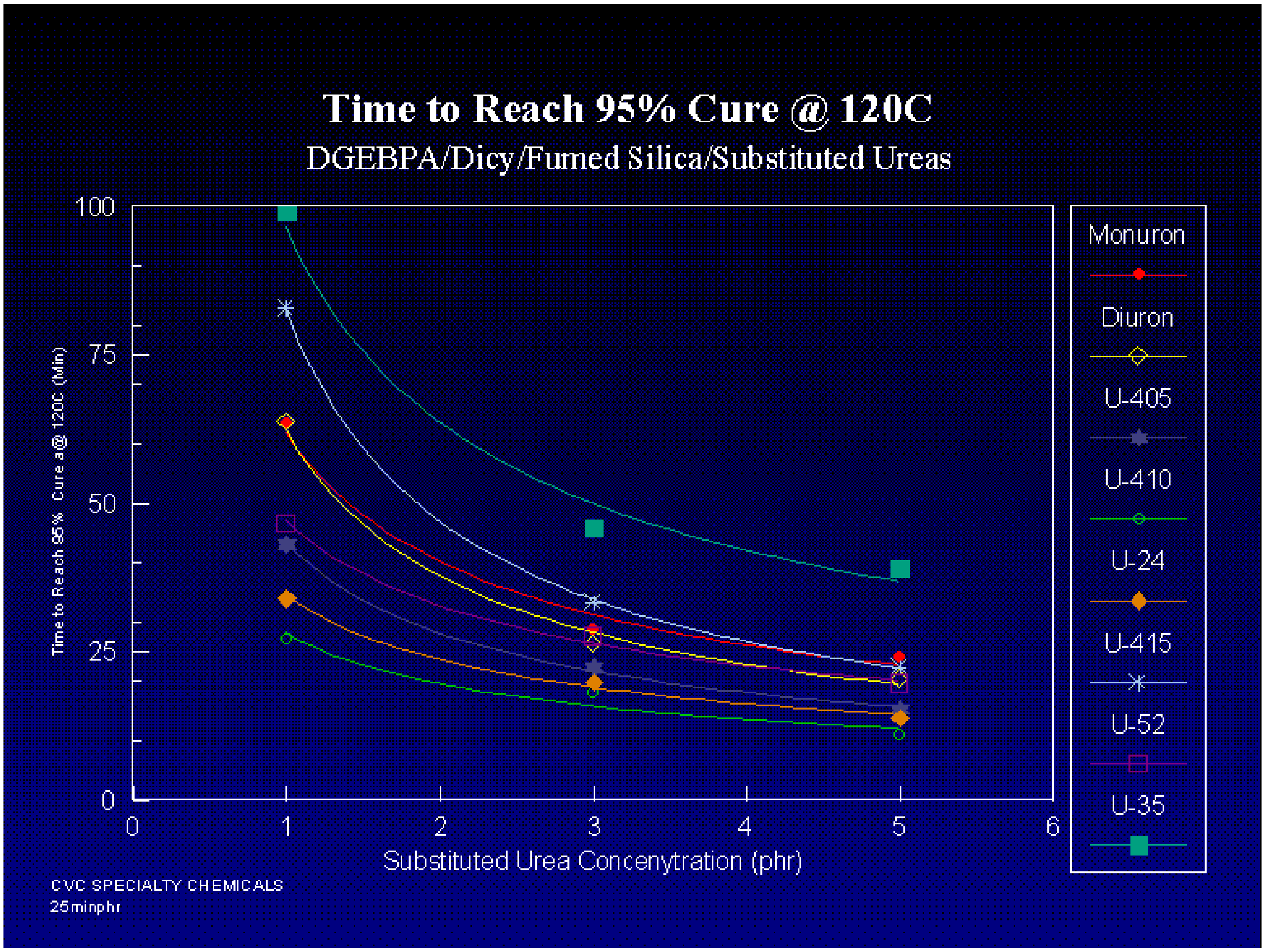
By comparing the time to reach full cure at 120°C of formulations containing 1, 3, and 5 phr urea, the degree of acceleration achieved with each urea can be ranked. **Table 4** shows the time to 95% full cure for each system in minutes at each urea level tested, and ranks the reactivity based on the sum of the times.

Table 4 – Rank of Substituted Ureas for Time to 95% Full Cure @ 120°C (minutes)

Rank	Product	@ 1phr	3 phr	5 phr
1	Omicure U-410	27	18	11
2	Omicure U-24	34	20	14
3	Omicure U-405	43	22	15
4	Omicure U-52	47	27	20
5	Diuron	64	26	20
6	Monuron	63	29	24
7	Omicure U-415	83	33	22
8	Omicure U-35	99	46	39

This data can also be shown graphically as seen in **Figure 10** below;

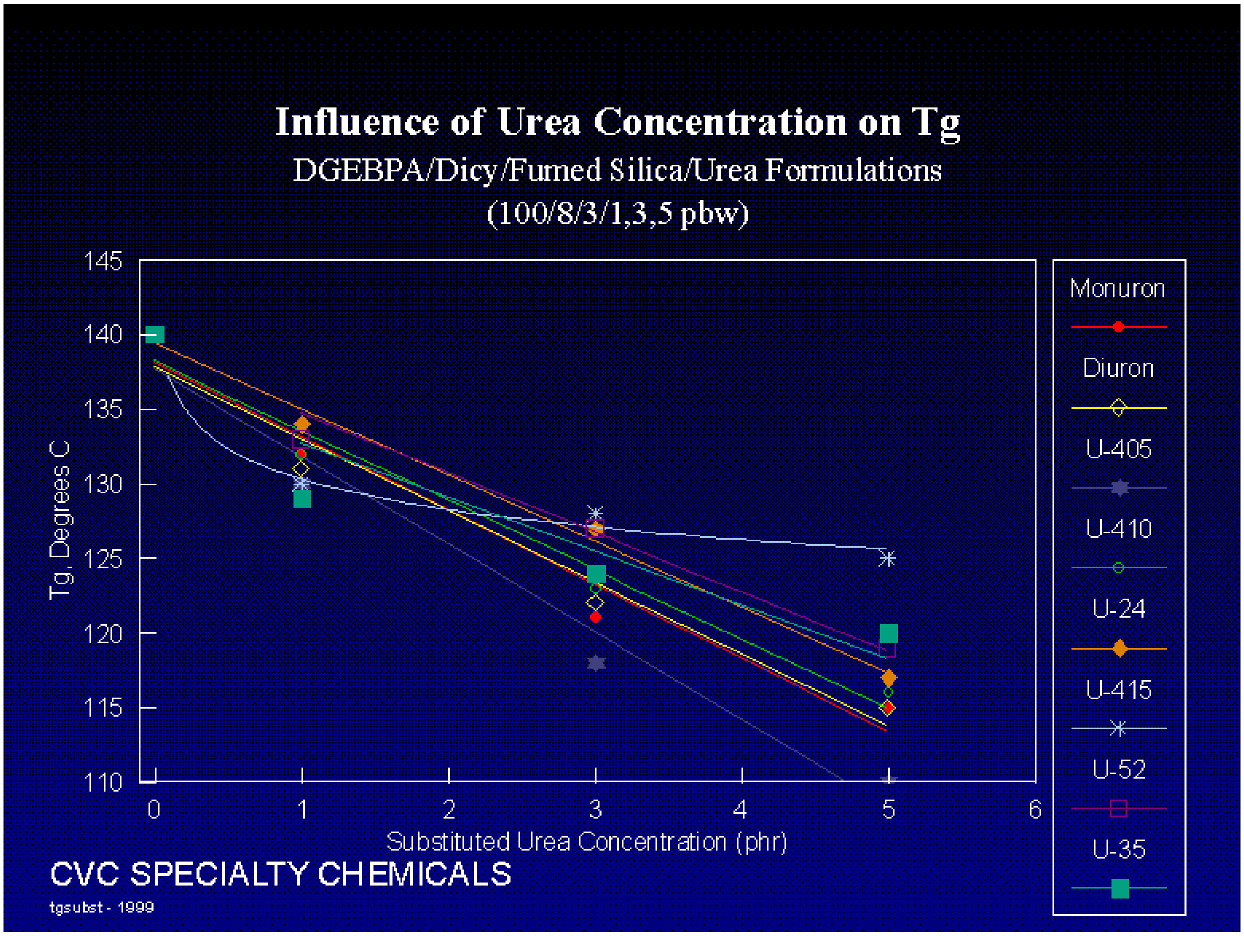
Figure 10 – Time to reach 95% Cure @ 120°C for all Ureas @ 1, 3, & 5 phr



In general, urea formulas with longer shelf lives take a longer time to cure. These data, in general, support that observation with the Omicure U-410 and U-24, which had the shortest shelf lives, showing the greatest degree of acceleration, and Omicure U-35 which had the longest shelf life, having the smallest degree of acceleration. However, Omicure U-52 is a notable exception, having the second longest shelf life, but ranking 4th out of eight products tested for speed of cure.

It is known that substituted ureas can act as chain terminators in reactions with Dicyandiamide and epoxy. Because of this, a reduction in Tg would be expected when substituted urea is used to accelerate dicy. Our data does indicate that all of the evaluated substituted ureas decrease Tg, and greater amounts create greater declines. However, some ureas produce more of a decline than others. As compared to a non-accelerated DGEBA/DICY cure, substituted ureas at 1 phr decreases the average Tg by 9°C; 3 phr, 16°C; and 5 phr 23°C. Omicure U-405 appears to reduce Tg at the greatest rate while Omicure U-415 shows the least effect on Tg (**Figure 11)**

Figure 11 – Influence of Urea Concentration on Tg



Conclusions

In the DGEBA/DICY formulations containing equal accelerator concentrations:

- Omicure U-35 provides the longest room temperature shelf life coupled with the lowest degree of acceleration.
- Omicure U-410 provides the shortest room temperature shelf life and greatest degree of acceleration.
- Omicure U-52 provides the most favorable balance of properties with respect to shelf life, acceleration and Tg, and also appears to be the most favorable candidate for replacement of Diuron and Monuron.

The formulator of one part epoxy systems wishes to produce a product with the longest possible shelf life and fastest possible reaction rate, with the least reduction in cured properties. The data presented here shows a wide range of options available. Choosing the substituted urea with the lowest concentration to achieve the required shelf life and acceleration will produce a formulation with the least decrease in Tg, lowest possible viscosity, and least effect on cost.

References

1. US 3,386,956
2. US 3,562,215
3. US 4,283,520
4. T. Guthner, and B. Hammer, J. of Applied Polymer Science, Vol. 50, 1453-1459 (1993).
5. J. Barwich, D. Guse, and H. Brockmann, Adhasion 33, 27(1989).

APPENDIX

Table 2 -- Viscosity vs. Time for Substitutued Ureas with Dicy

Formulations (pbw)

		Control																							
	U-52	0	1	3	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	U-405	0	0	0	0	1	3	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	U-410	0	0	0	0	0	0	0	1	3	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	U-415	0	0	0	0	0	0	0	0	0	0	1	3	5	0	0	0	0	0	0	0	0	0	0	0	0
	U-24	0	0	0	0	0	0	0	0	0	0	0	0	0	1	3	5	0	0	0	0	0	0	0	0	0
	U-35	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	3	5	0	0	0	0	0	0
	Diuron	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	3	5	0	0	0
	Monuron	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	3	5

Viscosity @ 25C (poise) v. Time at Amibient Temperature

	Initial	290	370	390	420	310	320	320	370	480	600	340	370	420	390	430	470	360	410	470	320	350	360	340	360	400
	1 week	300	360	390	420	320	320	320	370	480	580	350	400	460	360	400	430	340	400	450	320	330	350	330	350	400
	4 week	290	350	380	410	330	340	350	360	520	650	340	400	480	400	480	520	350	400	460	330	360	370	350	380	410
	8 week	300	410	440	470	340	440	480	470	810	1140	360	470	580	510	680	720	350	410	470	350	380	400	390	450	490
	12 week	310	360	400	430	370	1900	2140	670	1170	-	380	490	600	670	1480	1900	360	410	470	390	430	460	440	520	570
	16 week	320	370	410	450	480	-	-	1840	-	-	430	630	790	1950	-	-	360	420	480	430	480	520	540	720	740
	20 week	320	400	450	490	630	-	-	-	-	-	480	740	930	-	-	-	370	420	470	450	560	590	630	1260	1460
	24 week	300	400	450	470	970	-	-	-	-	-	430	750	1160	-	-	-	340	400	440	470	660	730	820		
	28 week	330	440	490	530	3000	-	-	-	-	-	500	960	-	-	-	-	360	420	470	560	1000	1400	1900		
	32 week	350	440	500	540	-	-	-	-	-	-	520	1330	-	-	-	-	380	440	500	760	-	-	-	-	-
	36 week		460	530	590	-	-	-	-	-	-	580	-	-	-	-	-	370	440	500	1000	-	-	-	-	-
	40 week	320	470	550	620	-	-	-	-	-	-	630	-	-	-	-	-	360	430	490	-	-	-	-	-	-
Viscosity @ 25C (poise)	44 week	350	490	580	660	-	-	-	-	-	-	730	-	-	-	-	-	380	440	510	-	-	-	-	-	-
	48 week		540	650	740	-	-	-	-	-	-	780	-	-	-	-	-	360	440	500	-	-	-	-	-	-
	52 week	330	580	710	770	-	-	-	-	-	-	840	-	-	-	-	-	330	400	470	-	-	-	-	-	-
	60 week	340	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	380	460	540	-	-	-	-	-	-
	64 week		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	380	480	560	-	-	-	-	-	-
	70 week	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	420	510	620	-	-	-	-	-	-
	74 week	364	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	430	530	630	-	-	-	-	-	-
	78 week	367	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	410	520	610	-	-	-	-	-	-
	86 week	360	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	440	560	680	-	-	-	-	-	-
	91 week	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	490	610	730	-	-	-	-	-	-
	94 week	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	460	580	700	-	-	-	-	-	-
	104 week	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	470	600	750	-	-	-	-	-	-
	114 week	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	470	600	760	-	-	-	-	-	-
	126 week	424	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	600	660	800	-	-	-	-	-	-
	136 week	432																								
Time to double viscosity (weeks)		>136	60	55	57	20	10	9	13	10	8	42	20	17	13	10	9	>126	>126	>126	30	25	24	21	16	16