Hycat™ AO-4: A Latent Catalyst for Fast, Colorless Epoxy Cures

A common problem with epoxy formulations is the tendency for the cured polymer to discolor when subjected to elevated temperatures or UV exposure. Color corruption will impair the application where light transmission is critical such as in Light-Emitting Diode (LED) or Fiber Optic Devices. It is no wonder that significant research has been spent in developing epoxy formulations where maximum light transmission and color stability are the desired goals. As a part of this research, considerable effort has also been dedicated to improve the efficiency of the catalysts used in these epoxy formulations. Because amines, quaternary ammonium salts, and imidazoles have the tendency to form color, other catalysts systems are preferred. Ideally, a catalyst that can be used in low concentration, does not contribute to color formation, gives a fast gel or cure time at low temperatures and shows latency would be desirable for this application. ***Hycat™ AO-4***, produced by Dimension Technology Chemical Systems, Inc., achieves these goals of clear and colorless and fast cures when reacting anhydrides with diglycidyl ether of bisphenol A, diglycidyl ether bisphenol F and cycloaliphatic diepoxides. Other epoxides are expected to behave favorably in similar formulations.

A Comparison of Hycat™ AO-4 to Other Common Catalysts

A clear, colorless cure resulted when Hycat™ AO-4 (2%, phr) was mixed with equal parts of diglycidyl ether bisphenol A (DER 331, Dow) and methylhexahydrophthalic anhydride (Lindride 52D, Lindau) and cured at 120^{o}C. This is a stark contrast to cures of the same resin formulation and same reaction conditions with tetrabutylammonium bromide (TBABr), 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU), benzyldimethylamine (BDMA) or 2-ethyl-4-methylimidazole (2,4-EMI). With these catalysts the cured products were highly colored, cured poorly (i.e., voids) or had significantly longer cure time when compared to the cures using Hycat™ AO-4. This comparison is shown in Figure 1. Although a colorless cure, similar to that with Hycat™ AO-4, could be achieved using a low concentration (0.2 %) of 2,4-EMI the time to cure was significantly longer when compared to Hycat™ AO-4. By increasing the concentration of the 2,4-EMI to 2% the cure time was significantly decreased but the cure polymer was highly colored. It should be noted that in this technical presentation “cure time” denotes the time required to obtain a firm-hard polymer and may not represent a total cure. The color comparison of these tests is shown in **Figure 1**. Also, the hardness of the cures showed Hycat™ AO-4 gave favorable results. These data are given in **Table 1**.

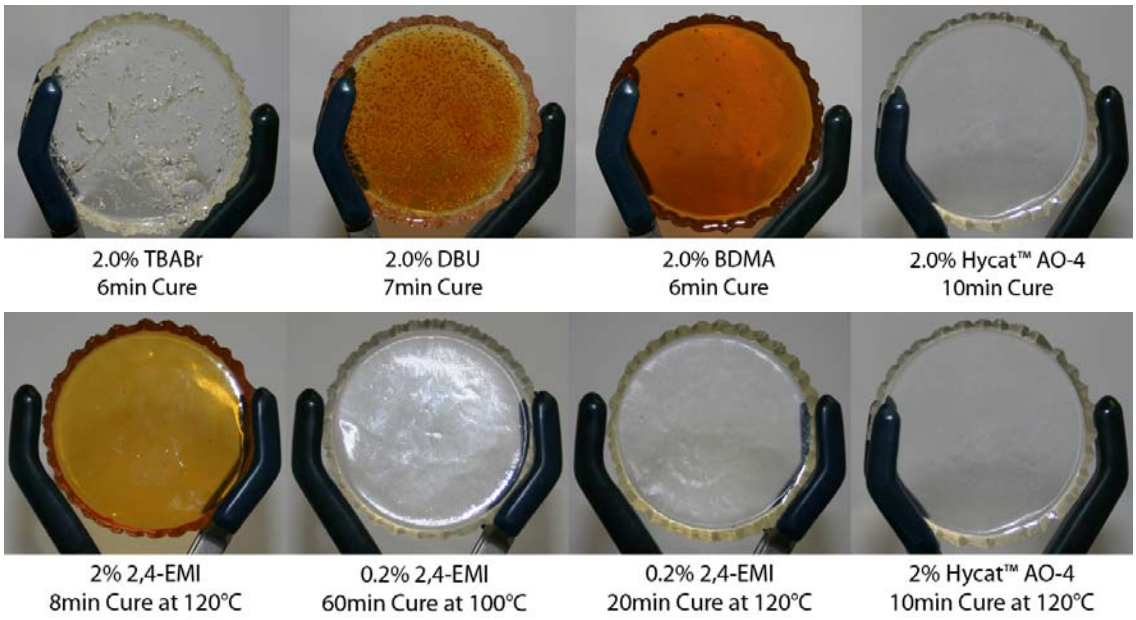

Figure 1. Photos and cure times of DER 331 and Lindride 52D with different catalysts at 2.0% loading at 120°C

	TBABr	**DBU**	**BDMA**	**0.2% 2,4-EMI**	**2% 2,4-EMI**	**Hycat™ AO-4**
Cure Time (min.)	6	7	6	20	8	10
Hardness (Durometer Type D) (0.5 hrs after cure)	87	87	86	-	-	87
Hardness (Durometer Type D) (24 hrs after cure)	-	-	-	-	-	88
Hardness (Durometer Type D) (48 hrs after cure)	-	-	-	-	-	88
Hardness (Durometer Type D) (72 hrs after cure)	89	88	-	89	90	-

Table 1. Cure times and hardness for DER 331 and Lindride 52D catalyst comparison at 2.0% loading at 120°C

The cured polymers using Hycat™ AO-4 and 2,4-EMI were exposed to heat (125 °C) for 100 hours. The two cures that were tested included the Hycat™ AO-4 at 2.0% loading and 120°C; and the 2,4-EMI at 0.2% loading and cured at 100°C. Both of these samples were placed in an oven at 125°C for 100 hours. By visual inspection, the discoloration of both samples appeared to be the same. This comparison is shown in **Figure 2**. However, when thermal exposure tests were done on just the pure catalysts, Hycat™ AO-4 showed hardly any discoloration whereas the pure 2,4-EMI showed significant color build up to a dark orange-brown color (see **Figure 3a**).

There can be no doubt that the imidazole catalyst is heat sensitive and will add to the discoloration of the cured polymer.

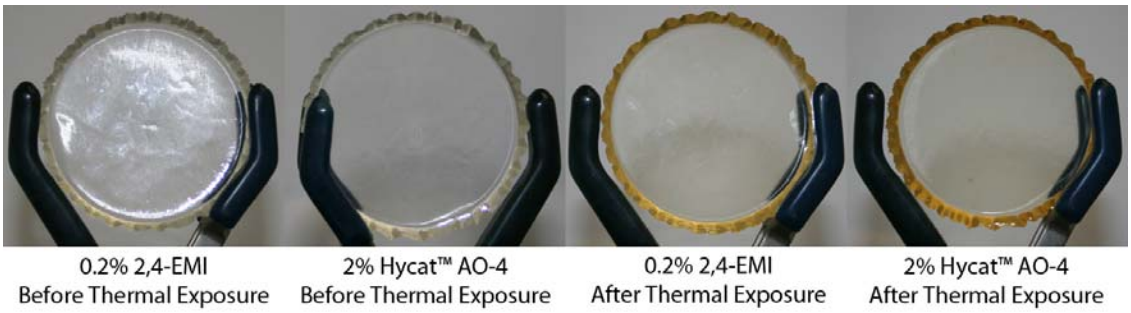

Figure 2. Photos of DER 331 and Lindride 52D with Hycat™ AO-4 and 2,4-EMI (Before and after thermal exposure at 125°C for 100 hrs)

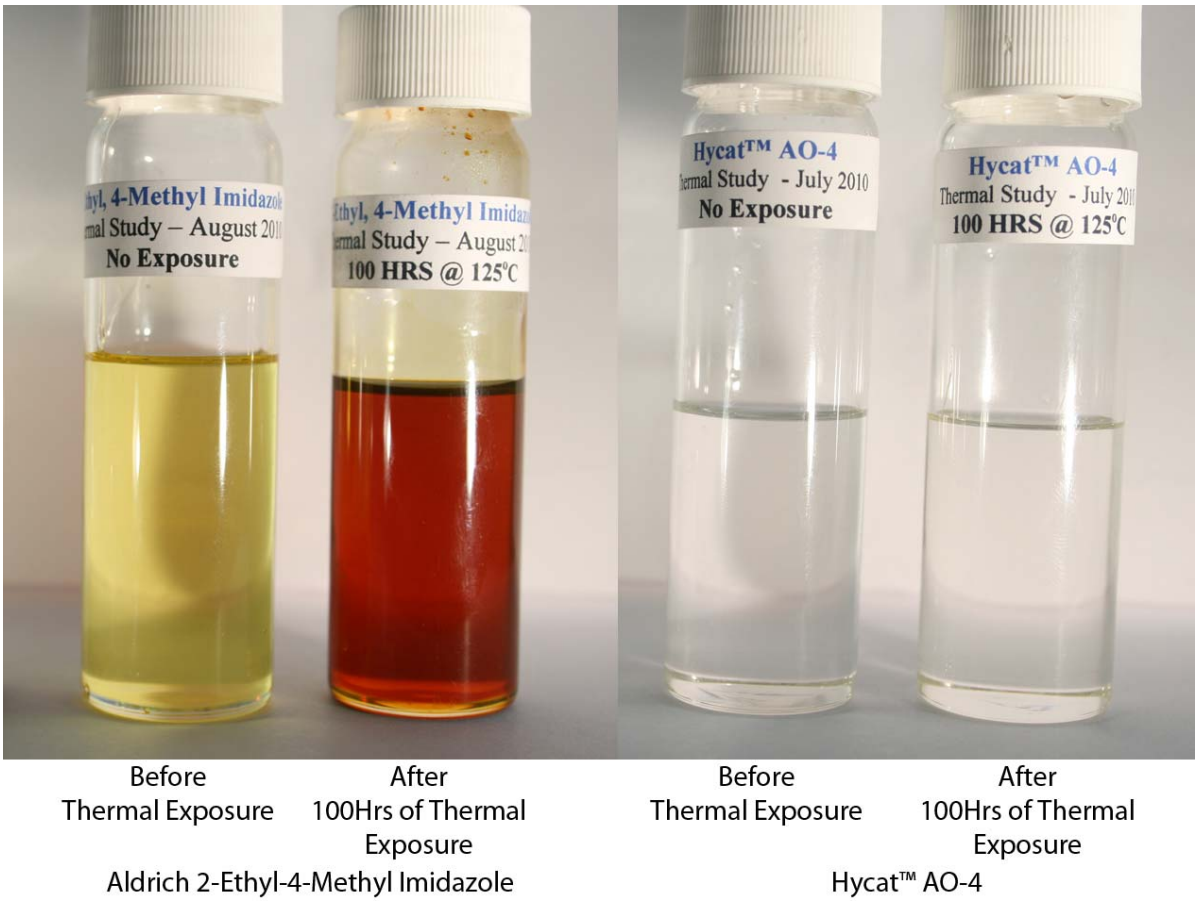

Figure 3a. Photos of Hycat™ AO-4 and 2,4-EMI before and after thermal exposure at 125°C for 100hrs

Hycat™ AO-4 was found to be significantly more stable than 2,4-EMI when exposed to UV (Dymax-5000EC/100-200mW/cm^2). Over a period of 8 hours the 2,4-EMI experienced

immediate and complete discoloration where the Hycat™ AO-4 was only slightly discolored. This is shown in **Figure 3b**.

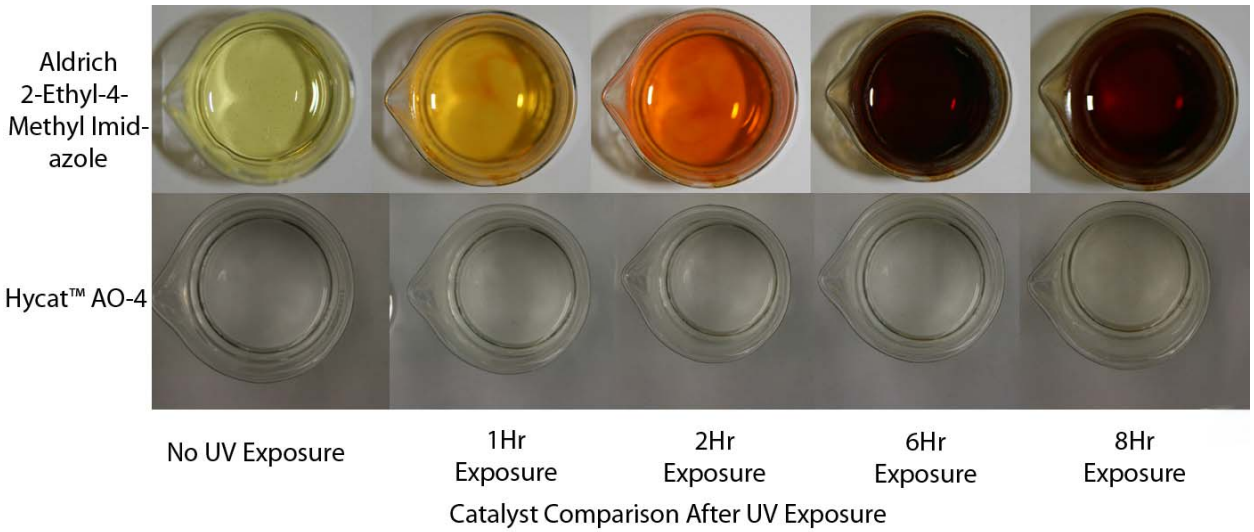

Figure 3b. Photos of Hycat™ AO-4 and 2,4-EMI before and after UV exposure for 8 hrs

Similar studies were also done with the diglycidyl ether bisphenol F (DER 354, Dow) and MHHPA (Lindride 52D) mixed at a 1:1 weight ratio. In these tests the catalysts studied included TBABr, DBU, BDMA, and compared to Hycat™ AO-4. The results show that the cure made with Hycat™ AO-4 at 2.0% catalyst loading at 120°C was clear and colorless while the cures with TBABr, DBU or BDMA were highly colored or contained a considerable amount of bubbles or voids under the same conditions. Hycat™ AO-4's cure time and hardness was favorable as well. These data are shown in **Figure 4** and **Table 2**.

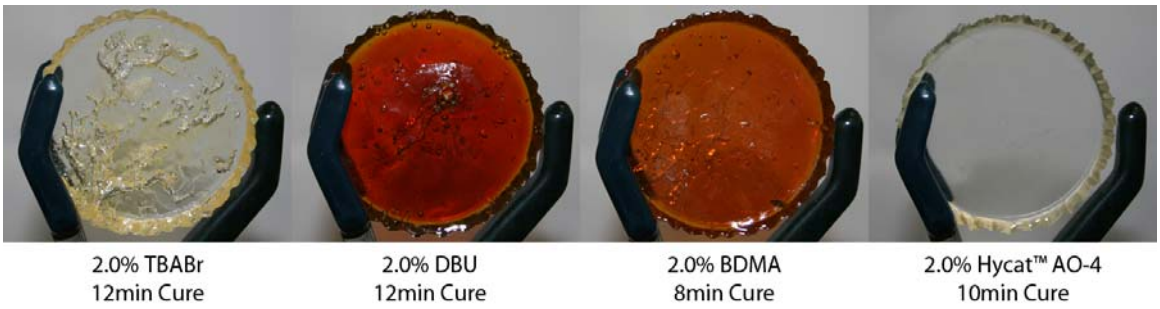

Figure 4. Photos and cure times of DER 354 and Lindride 52D with different catalysts at 2.0% loading at 120°C

	TBABr	**DBU**	**BDMA**	**Hycat™ AO-4**
Cure Time (min.)	12	12	8	10
Hardness (Durometer Type D) (0.5 hrs after cure)	86	88	86	88

Table 2. Cure times and hardness values for DER 354 and Lindride 52D catalyst comparison at 2.0% loading at 120°C

Hycat™ AO-4 also showed favorable results with a cycloaliphatic diepoxide (Lindoxy 190, Lindau) and MHHPA (Lindride 52D) which were mixed at a 1:1 weight ratio. The cure made with Hycat™ AO-4 at 2.0% catalyst loading at 120°C showed discoloration and voids which were completely eliminated by lowering the catalyst concentration to 1.0%. The BDMA cure at 2.0% looked the best in terms of color and void content but took 55 minutes to cure. These comparisons are shown in see **Figure 5**. Hycat™ AO-4's cure time and hardness was favorable as shown in **Table 3**.

Figure 5. Photos and cure times of Lindoxy 190 and Lindride 52D with different catalysts at 2.0% loading at 120°C. Photo on the far right is the same resin mixture with AO-4 at 1.0% loading for visual and cure time comparison.

	TBABr	**DBU**	**BDMA**	**1%Hycat™ AO-4**	**2%Hycat™ AO-4**
Cure Time (min.)	7	8	55	19	10
Hardness (Durometer Type D) (0.5 hrs after cure)	84	87	86	-	89
Hardness (Durometer Type D) (24 hrs after cure)	-	-	-	-	89
Hardness (Durometer Type D) (48 hrs after cure)	-	-	-	-	89
Hardness (Durometer Type D) (72 hrs after cure)	85	88	-	89	-

Table 3. Cure times and hardness for Lindoxy 190 and Lindride 52D catalyst comparison at 2.0% loading at 120°C

Effect of Catalyst Loading on Cure Time

Cure studies done with 1:1 weight ratio mixtures of diglycidyl ether of bisphenol A (DER 331) and MHHPA (Lindride 52D) at 120°C showed a slight, if any, increase in color as well as a decrease in cure time with increasing concentration of Hycat™ AO-4 from 0.5% to 3.0%. A visual comparison is shown in **Figure 6** and the effect of catalyst concentration on cure time is graphed in **Figure 7**. There were excellent hardness values at all catalyst concentrations as shown in **Table 4**.

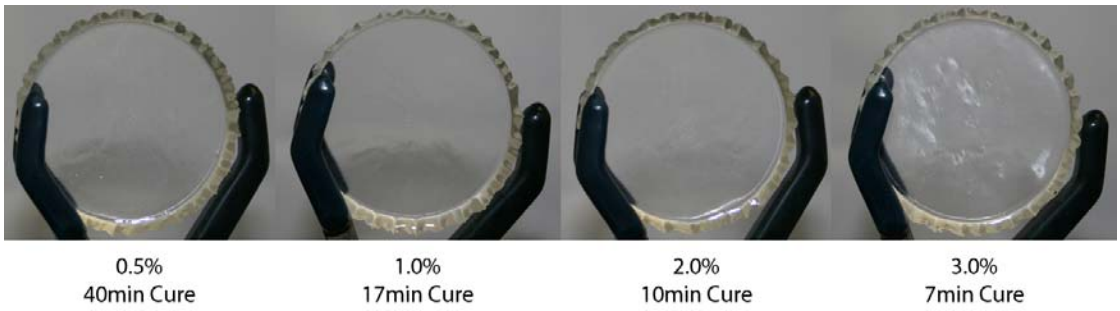

Figure 6. Photos and cure times of DER 331 and Lindride 52D with Hycat™ AO-4 at varying loading percentages at 120°C

Catalyst Loading (phr)	**0.5**	**1.0**	**2.0**	**3.0**
Cure Time (min.)	40	17	10	7
Hardness (Durometer Type D) (0.5 hrs after cure)	87	87	87	87
Hardness (Durometer Type D) (24 hrs after cure)	88	88	88	88
Hardness (Durometer Type D) (48 hrs after cure)	88	88	88	88

Table 4. Cure times and hardness values for DER 331 and Lindride 52D with AO-4 at different loading at 120°C

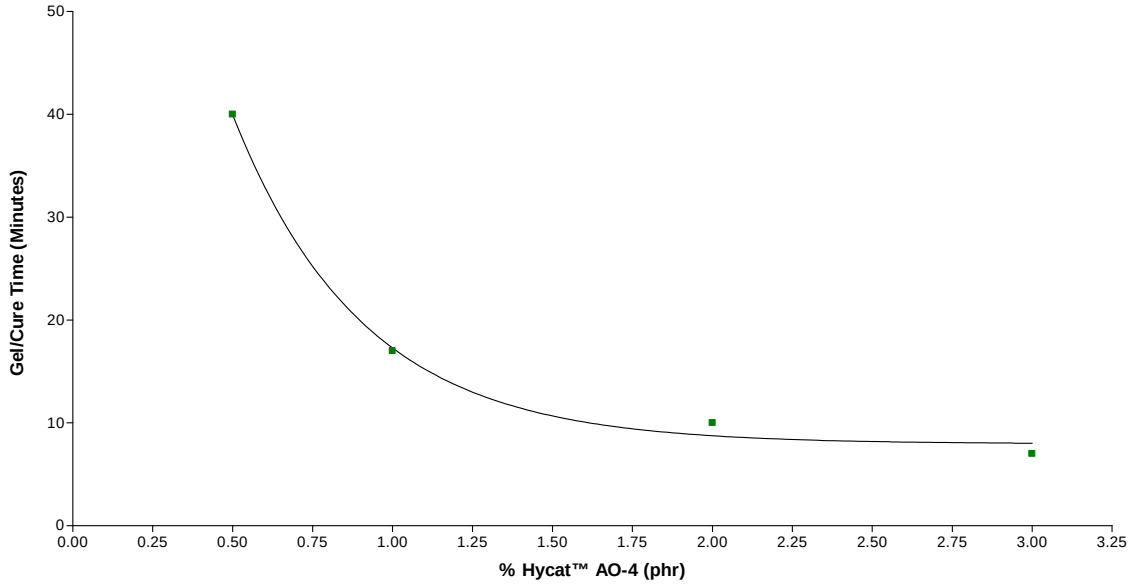

Figure 7. Effect of catalyst loading on cure times for DER 331 and Lindride 52D with Hycat™ AO-4 at 120°C

Similar results were seen when the Hycat™ AO-4 concentration was varied from 0.5% to 3.0% in a formulation of diglycidyl ether of bisphenol F (DER 354) and MHHPA (Lindride 52D) at a 1:1 weight ratio at 120°C. Cure times were favorable and decreased with increasing catalyst concentration as expected. These tests are shown in **Figures 8** and **9**. There were excellent hardness values at all catalyst concentrations as shown in **Table 5**.

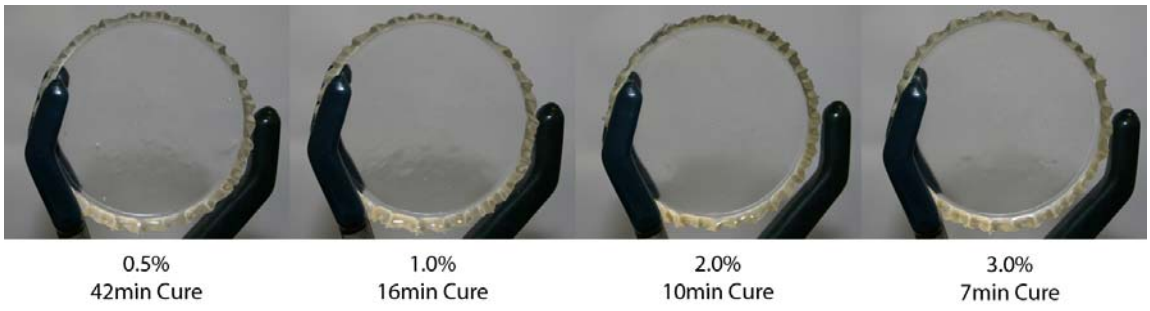

Figure 8. Photos and cure times of DER 354 and Lindride 52D with Hycat™ AO-4 at varying loading percentages at 120°C

Catalyst Loading (phr)	0.5	1.0	2.0	3.0
Cure Time (min.)	42	16	10	7
Hardness (Durometer Type D) (0.5 hrs after cure)	85	86	88	88
Hardness (Durometer Type D) (24 hrs after cure)	88	89	87	88
Hardness (Durometer Type D) (48 hrs after cure)	87	88	89	88

Table 5. Cure times and hardness for DER 354 and Lindride 52D with AO-4 at different loading at 120°C

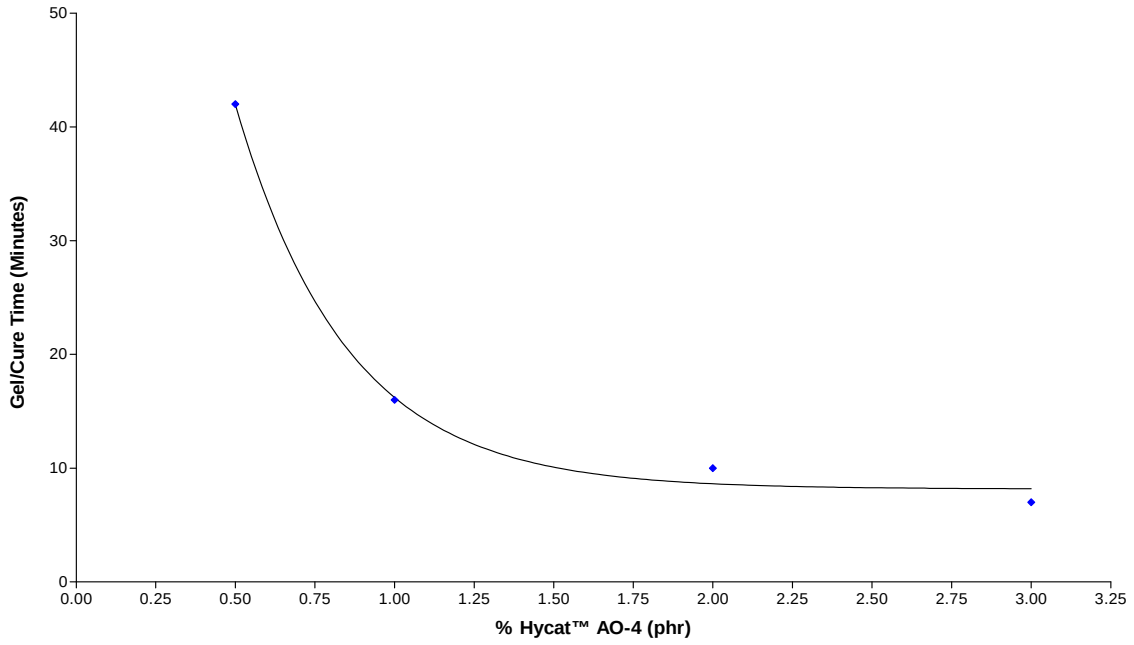

Figure 9. Effect of catalyst loading on cure times for DER 354 and Lindride 52D with Hycat™ AO-4 at 120°C

When Hycat™ AO-4 was used to cure cycloaliphatic epoxides, like Lindride 190, with MHHPA (Lindride 52D) at a 1:1 resin to hardener weight ratio and 120 ^{O}C cure temperature it was observed that discoloration and some voids were formed at higher catalyst concentrations. However, the discoloration and void problems only occurred at catalyst concentrations at 2.0% or higher. At 1% catalyst loading or lower these problems were avoided. These comparisons are shown in **Figures 10 and 11** and in **Table 6**.

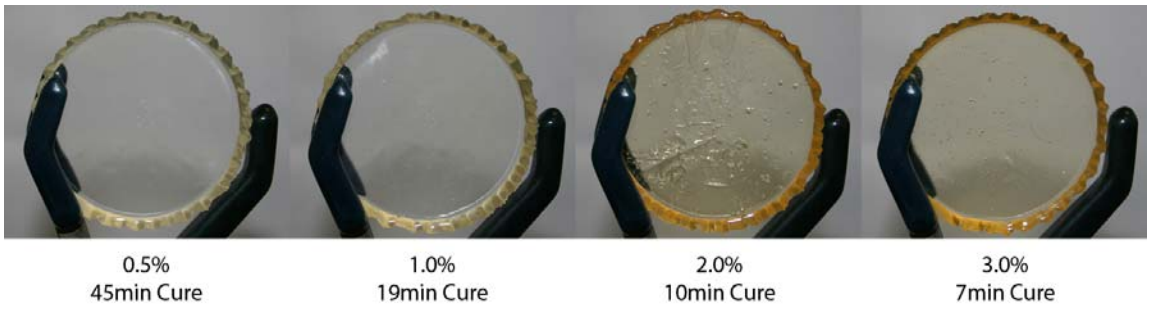

Figure 10. Photos and cure times of Lindoxy 190 and Lindride 52D with Hycat™ AO-4 at varying loading percentages at 120°C

Catalyst Loading (phr)	**0.5%**	**1.0%**	**2.0%**	**3.0%**
Cure Time (min.)	45	19	10	7
Hardness (Durometer Type D) (0.5 hrs after cure)	88.7	87	89	87.7
Hardness (Durometer Type D) (24 hrs after cure)	88.7	89	89	88
Hardness (Durometer Type D) (48 hrs after cure)	88.3	88	89	-

Table 6. Cure times and Hardness values for Lindoxy 190 and Lindride 52D with AO-4 at varying loading percentages at 120°C

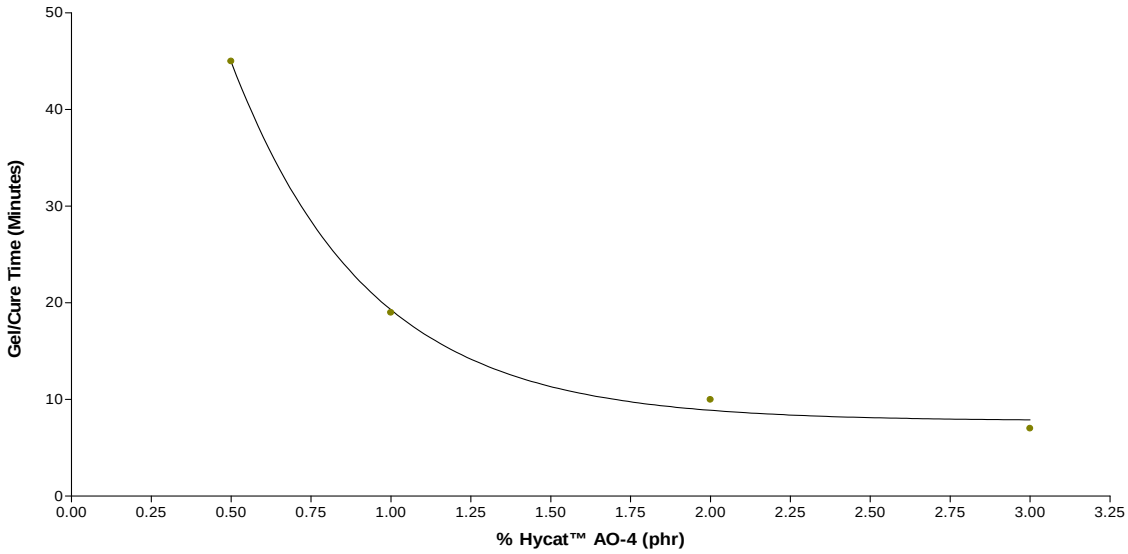

Figure 11. Effect of catalyst loading on cure times for Lindoxy 190 and Lindride 52D with Hycat™ AO-4 at 120°C

Effect of Cure Temperature

The effect of temperature on cure time and color was determined for a formulation of diglycidyl ether of bisphenol A (DER 331) and MHHPA (Lindride 52D) at a 1:1 weight ratio and a 2.0% Hycat™ AO-4 loading. Only a very slight increase in color with increasing temperature was observed as shown in **Figure 12**. As expected, cure time decreased with increasing temperature (**Figure 13**) and hardness values were consistent with previous data (**Table 7**).

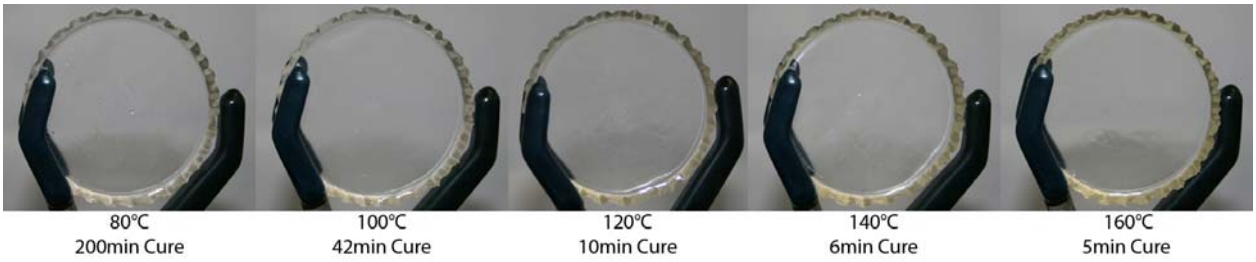

Figure 12. Photos and cure times of DER 331 and Lindride 52D with Hycat™ AO-4 at 2.0% loading at varying cure temperatures

Temperature (^{o}C)	**80**	**100**	**120**	**140**	**160**
Cure Time (min.)	200	42	10	6	5
Hardness (Durometer Type D) (0.5 hrs after cure)	87	87	87	87	89
Hardness (Durometer Type D) (24 hrs after cure)	-	-	88	86	88
Hardness (Durometer Type D) (48 hrs after cure)	-	-	88	-	-
Hardness (Durometer Type D) (72 hrs after cure)	-	88	-	-	-

Table 7. Cure times and Hardness values for DER 331 and Lindride 52D with AO-4 at 2.0% loading at varying cure temperatures

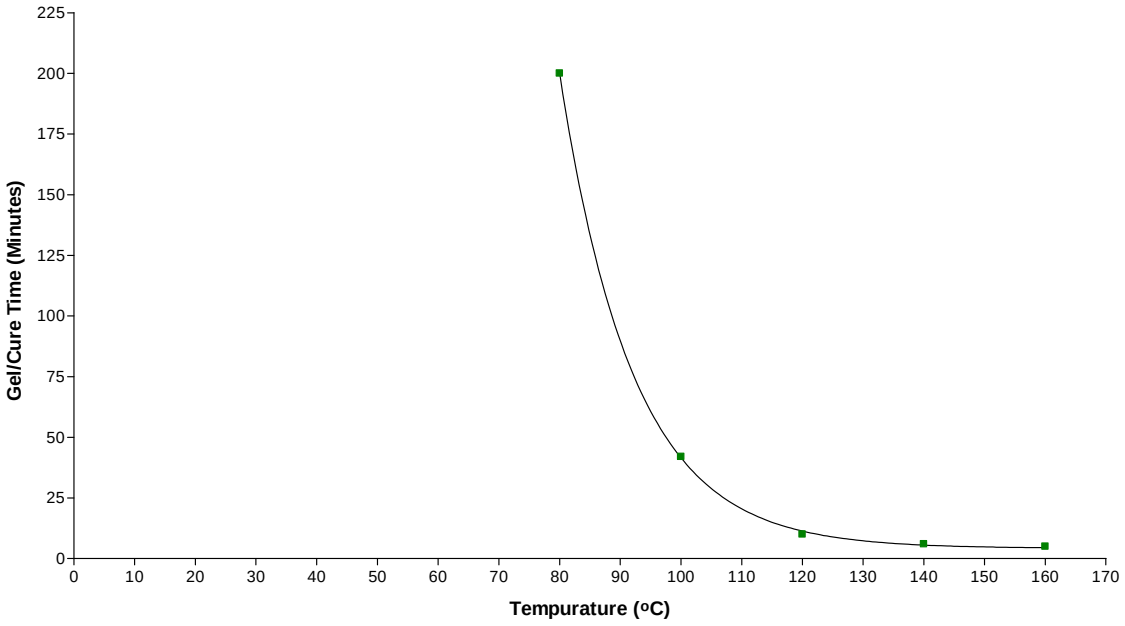

Figure 13. Effect of cure temperature on cure times for DER 354 and Lindride 52D with Hycat™ AO-4 at 2.0% loading

Similar results were observed with a 1:1 weight ratio formulation of diglycidyl ether of bisphenol F (DER 354) and MHHPA (Lindride 52D) at 2.0% Hycat™ AO-4 loading. Color slightly increased at higher cure temperature and as expected the cure time decreased with increasing temperature and hardness values were consistent with previous values. These data are shown in **Figures 14** and **15** and **Table 8**.

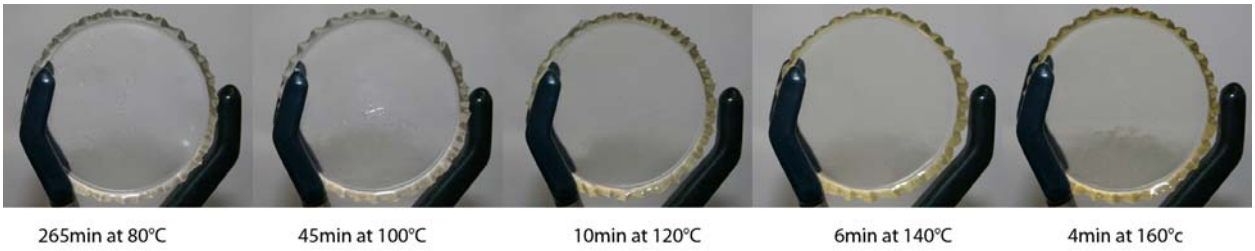

Figure 14. Photos and cure times of DER 354 and Lindride 52D with Hycat™ AO-4 at 2.0% loading at varying cure temperatures

Temperature (°C)	80	100	120	140	160
Cure Time (min.)	265	45	10	6	4
Hardness (Durometer Type D) (0.5 hrs after cure)	87.7	87.3	88	87.7	87.7
Hardness (Durometer Type D) (24 hrs after cure)	-	-	87	86	87.7
Hardness (Durometer Type D) (48 hrs after cure)	-	-	89	-	-
Hardness (Durometer Type D) (72 hrs after cure)	-	88	-	-	-

Table 8. Cure times and Hardness values for DER 354 and Lindride 52D with AO-4 at 2.0% loading at varying cure temperatures

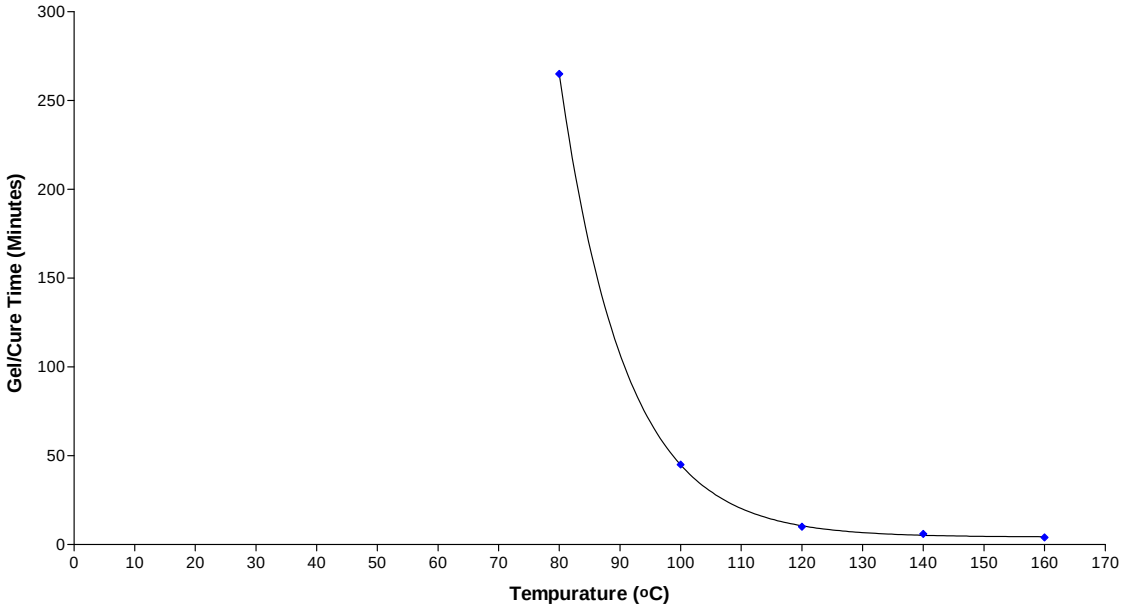

Figure 15. Effect of cure temperature on cure times for DER 354 and Lindride 52D with Hycat™ AO-4 at 2.0% loading

The 1:1 weight ratio formulation of the cycloaliphatic diepoxide (Lindoxy 190) and MHHPA (Lindride 52D) with 2.0% Hycat™ AO-4 loading was also studied. At cure temperatures above 120 ^{O}C poor cures and discoloration was observed. This was not observed at temperatures of 100^{o}C or lower. These data are shown in **Figures 16** and **17** and **Table 9**. It is possible that better cures would be obtained at higher temperatures if the catalyst loading was lowered to about 1%.

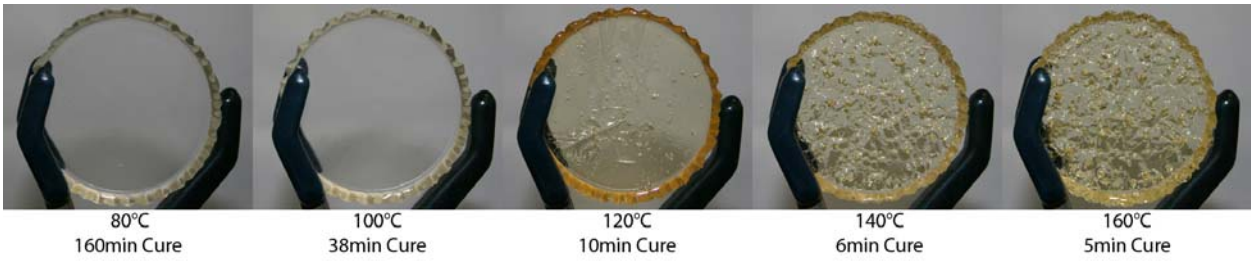

Figure 16. Photos and cure times of Lindoxy 190 and Lindride 52D with Hycat™ AO-4 at 2.0% loading at varying cure temperatures

Temperature (^{o}C)	**80**	**100**	**120**	**140**	**160**
Cure Time (min.)	165	38	10	6	5
Hardness (Durometer Type D) (0.5 hrs after cure)	84	84	89	-	-
Hardness (Durometer Type D) (24 hrs after cure)	-	-	89	-	-
Hardness (Durometer Type D) (48 hrs after cure)	-	-	89	-	-
Hardness (Durometer Type D) (72 hrs after cure)	-	88	-	-	-

Table 9. Cure times and Hardness values for Lindoxy 190 and Lindride 52D with AO-4 at 2.0% loading at varying cure temperatures

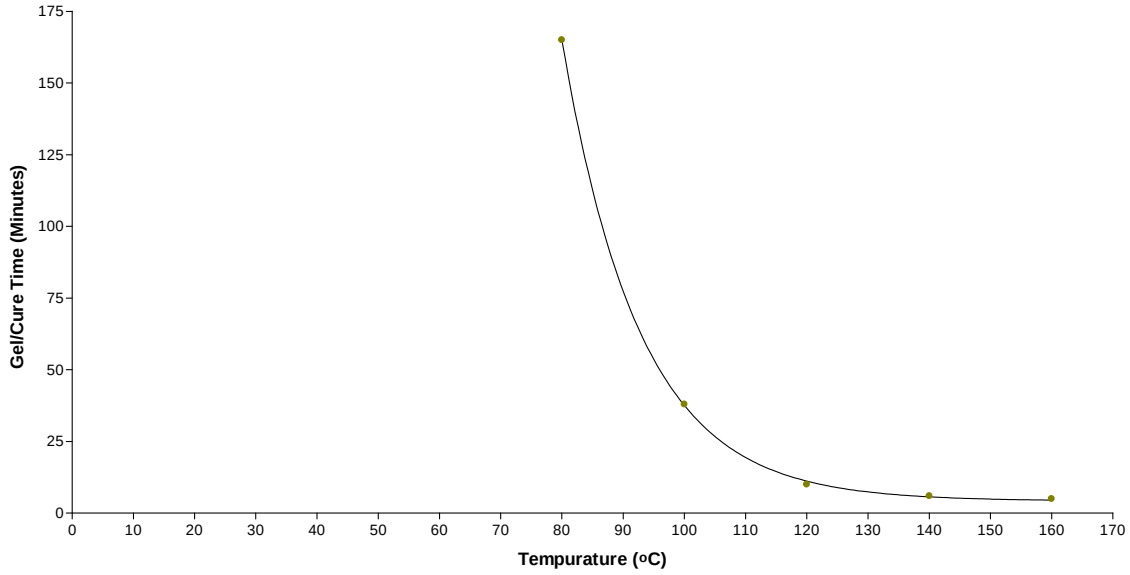

Figure 17. Effect of cure temperature on cure times for Lindoxy 190 and Lindride 52D with Hycat™ AO-4 at 2.0% loading

Properties

Typically, Hycat™ AO-4 will show the following properties:

- Appearance — Clear, Colorless Liquid Essentially Free of Foreign Matter
- Viscosity at 25°C — 60 cps
- Freezing Point — < -15°C
- Shelf Life — ~4 years

Pot Life

The formulations containing Hycat™ AO-4 show exceptional pot life. Formulations of diglycidyl ether of bisphenol A and MHHPA, diglycidyl ether of bisphenol F and MHHPA, and a cycloaliphatic diepoxide and MHHPA, all mixed at a 1:1 weight ratio, remained fluid up to approximately 50 hours at 26°C with rapidly increasing viscosity after that point. See **Figures 18**, **19**, and **20** for plots of these data.

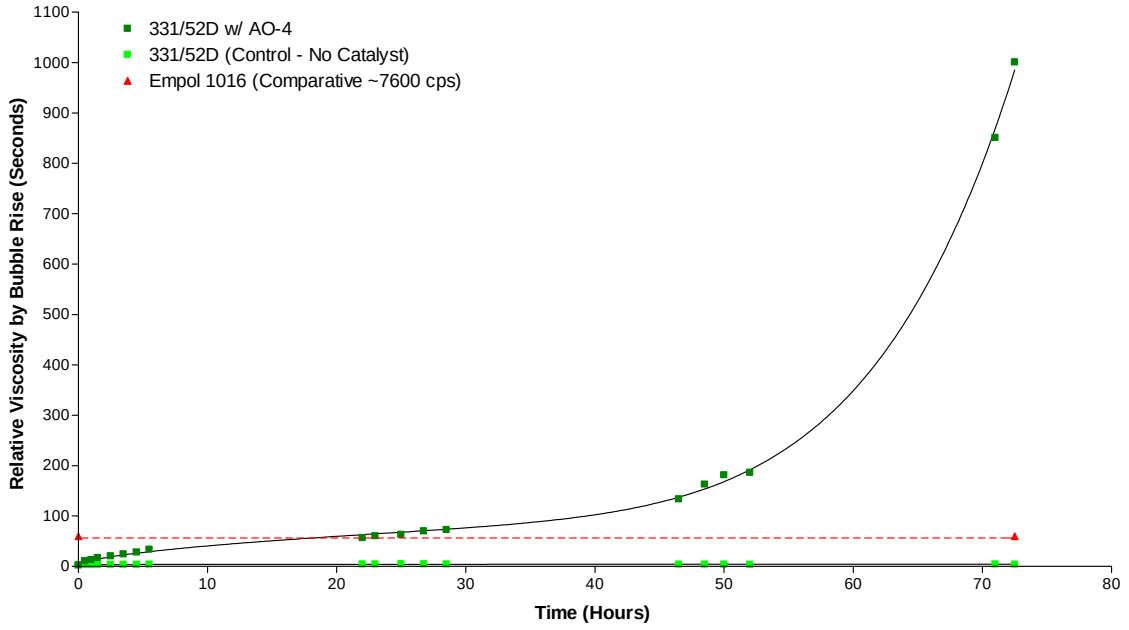

Figure 18. Pot life of DER 331 and Lindride 52D with Hycat™ AO-4 at 2.0% loading at 26°C

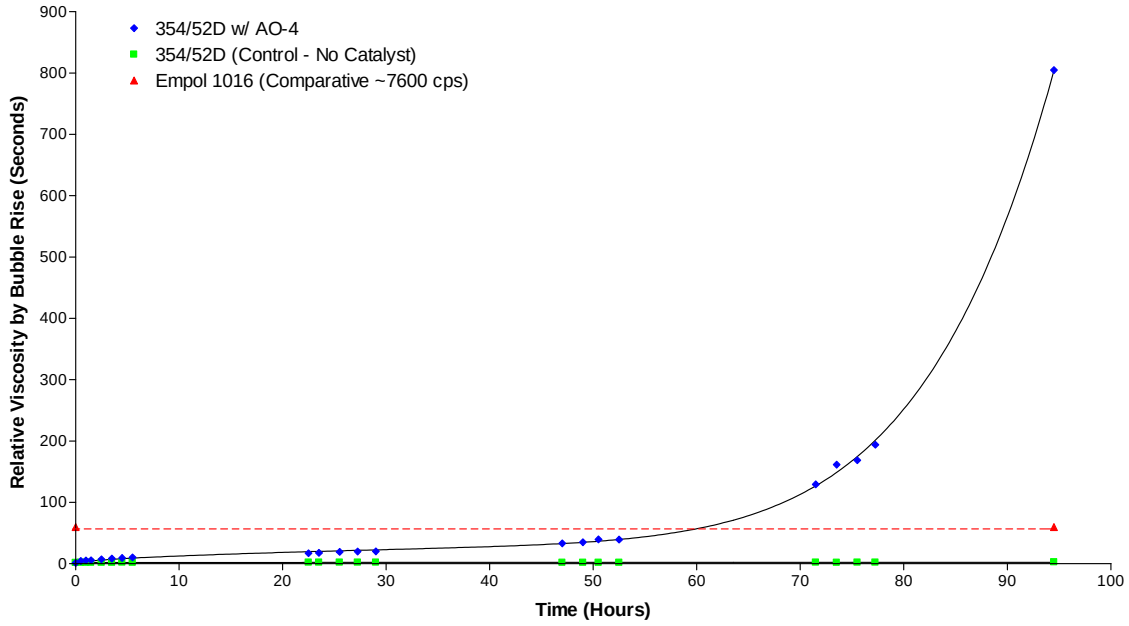

Figure 19. Pot life of DER 354 and Lindride 52D with Hycat™ AO-4 at 2.0% loading at 26°C

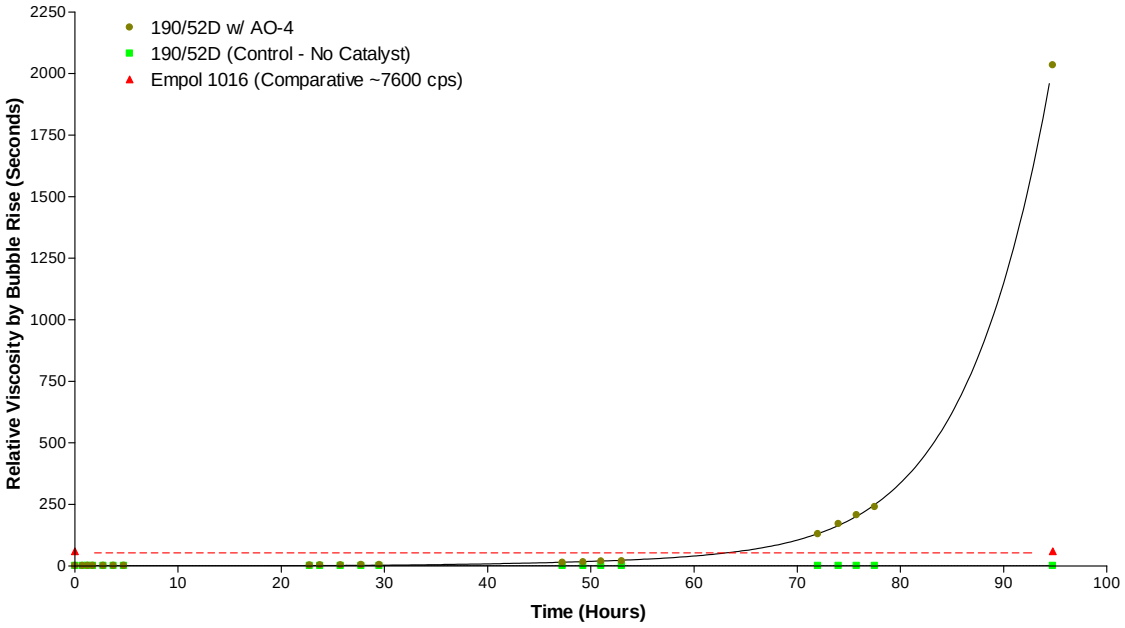

Figure 20. Pot life of Lindoxy 190 and Lindride 52D with Hycat™ AO-4 at 2.0% loading at 26°C

Homopolymerization

Hycat™ AO-4 does not promote homopolymerization of epoxy resins. Hycat™ AO-4 was dissolved in DER 354, DER 331, and Lindoxy 190 in absence of the anhydride at 2.0% loading with respect to a combined 1:1 epoxide/anhydride system. After 100 hours, all three epoxides did not show any evidence of increased viscosity that would be associated with the occurrence of homo polymerization. These data are plotted in **Figures 21**, **22**, and **23** below. It should be noted that these tests were conducted at room temperature and the apparent drop in viscosity shown in the three graphs was due to an overall increase in room temperature which would account for the lower viscosity reading with time. Since the drop in viscosity of the control samples was equal to the drop in viscosity to the test samples it is safe to claim that homopolymerization did not occur.

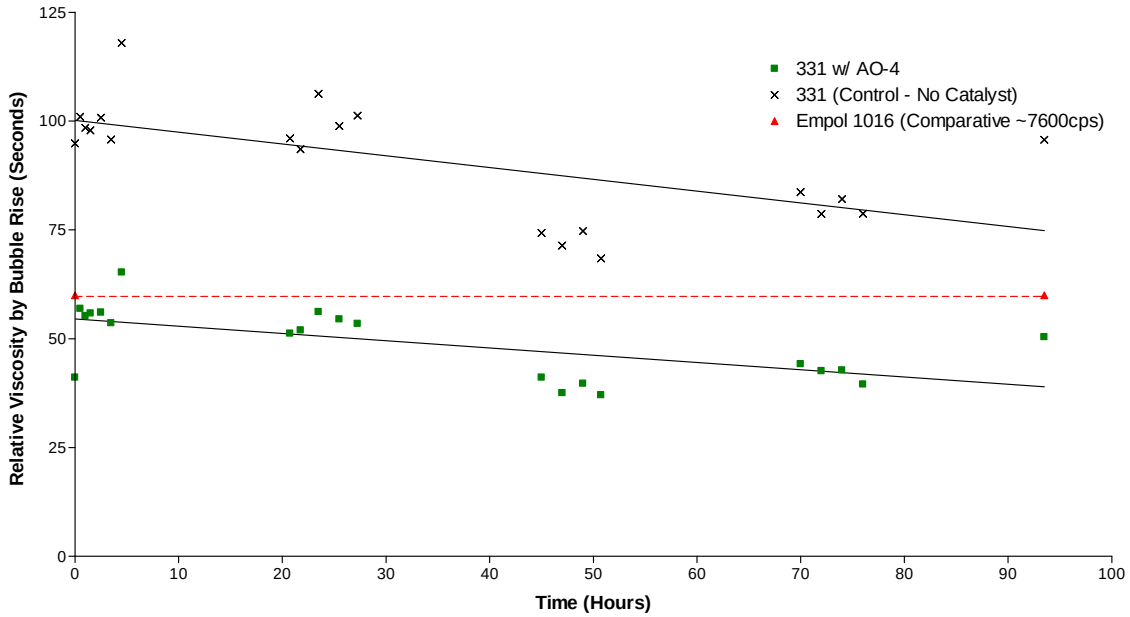

Figure 21. Pot life of DER 331 with Hycat™ AO-4 at 2.0% loading with respect to a combined epoxide/anhydride system at 26°C

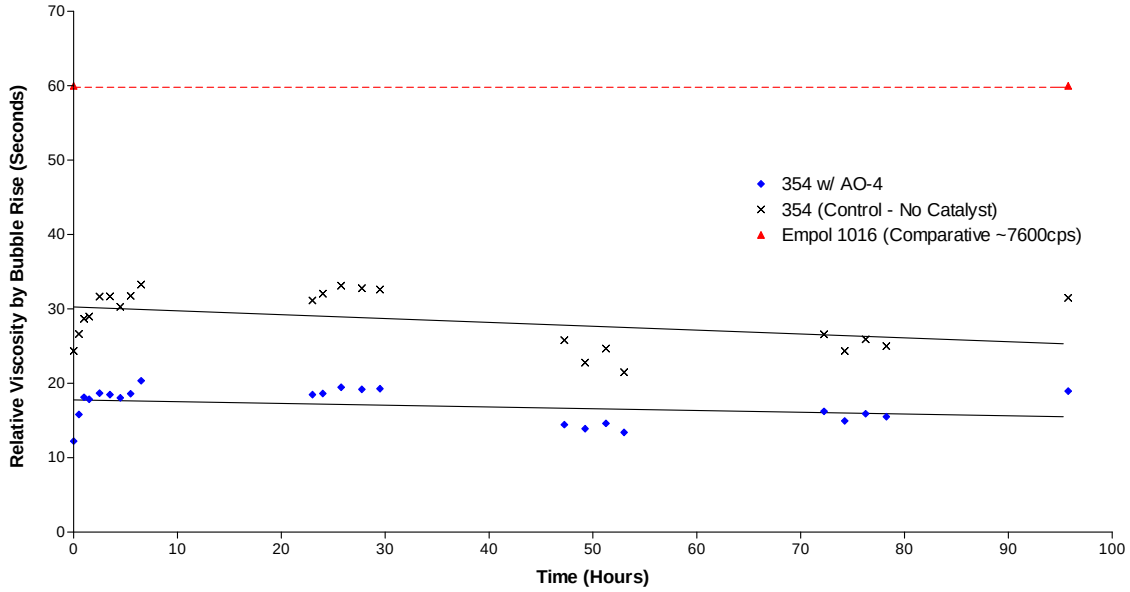

Figure 22. Pot life of DER 354 with Hycat™ AO-4 at 2.0% loading with respect to a combined epoxide/anhydride system at 26°C

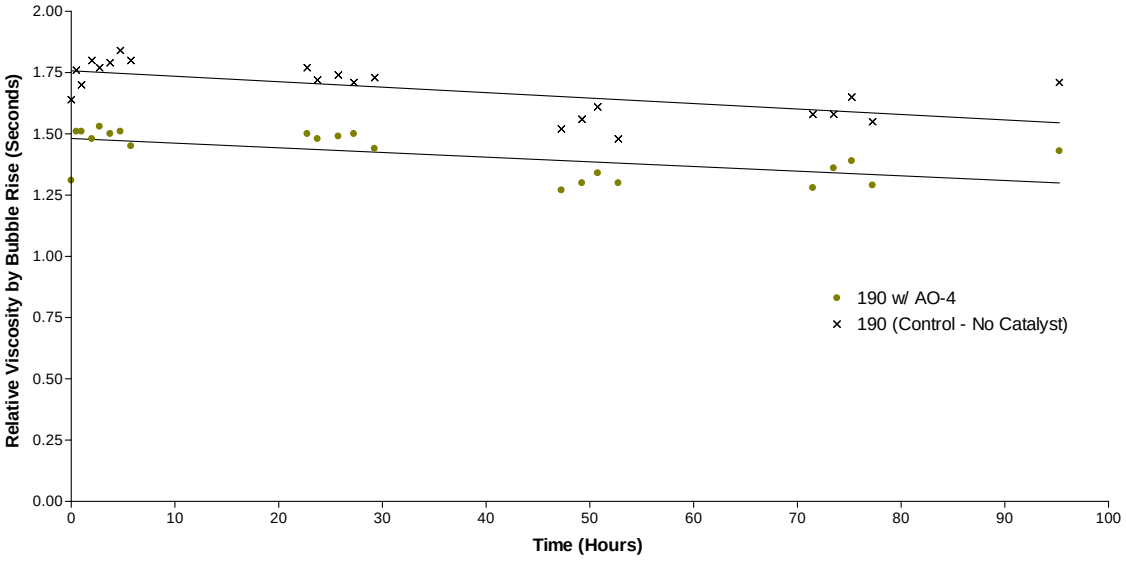

Figure 23. Pot life of Lindoxy 190 with Hycat™ AO-4 at 2.0% loading with respect to a combined epoxide/anhydride system at 26°C