

TOWARD HIGH GLASS-TRANSITION TEMPERATURES in Epoxy Powder Coatings

By Vinay Mishra, Kevin Biller,
Jeff Dimmit, and Nikola Bilic

Introduction

Epoxy-based products are used in many applications that face aggressive operating environments. Some examples (Figure 1) are electrically insulative encapsulants or powder coatings (e.g., inside electrical motors), chemical-resistant pipe linings, adhesives, and composite parts. Under extreme service conditions (e.g., regarding heat, chemical exposure, and mechanical stresses, often in combination), many traditional epoxy formulations fail because they suffer from a loss of integrity over time. Traditional solutions require switching from epoxy to alternate chemistries such as cyanate ester, bismaleimide, and polyimides, which, while suitable, can add complexity to the process and increase cost.

Aromatic dianhydrides such as BTDA® (3,3',4,4'-benzophenone tetracarboxylic dianhydride) have been known to impart high crosslinking densities to epoxy formulations.^{1,2} See details on this molecule in Table 1 and its chemical structure in Figure 2. The resulting dense crosslinking, in combination with the structure of

FIGURE 1
Among other applications, dianhydride curatives are used in long-lasting epoxy powder coatings for pipes and as electrical insulation coatings in motors (see blue coating in the rotor, pictured at right).



Based on BTDA[®]

(benzophenone tetracarboxylic dianhydride)

the BTDA linkages, leads to epoxy powder coatings with high glass-transition temperatures (T_g) and heat resistance. These formulations also offer superior dielectric properties, mechanical properties, and chemical resistance. As a result, BTDA-based powder coatings find uses in aggressive environments such as those that are high temperature, involve chemical exposure, or are for long-term electrical applications. It is noteworthy that such successes are achieved using simple, bisphenol-A based solid epoxy resins (**Figure 2**). Specialized resins such as epoxy novolacs and other multifunctional resins can certainly raise the performance but are not necessary when using a dianhydride curing agent.

A Note on Proper Stoichiometric Treatment of Dianhydride-Epoxy Formulations

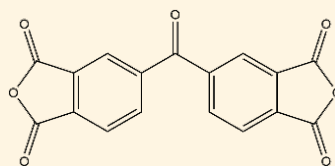
To properly design dianhydride-epoxy formulations, a few points require consideration. Dianhydrides cure epoxy formulations

TABLE 1
Chemical and Physical Characteristics of Jayhawk BTDA[®]

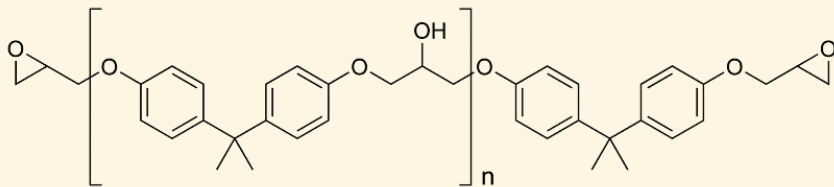
Chemical Name	3,3',4,4'-benzophenone tetracarboxylic dianhydride
Molecular Wt. (MW)	322 g/mole
Anhydride Equiv. Wt. (AEW)	161 g/eq.
Physical Form	Off-white fine powder
Specific Gravity	1.6
Melt Point in Pure State	220-230 °C (will dissolve in and react with epoxy resin at lower temperatures)

FIGURE 2
Chemical structures of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and simple solid epoxy resins based on bisphenol A.

BTDA:



Bis-A SERs:



to extremely high levels of crosslinking through esterification reactions. A proper review of the complex reaction mechanism³⁻⁶ is outside the scope of this paper. **Figure 3** describes a simplified two-step esterification reaction model that has been adopted by the epoxy industry. In the overall esterification reaction, one epoxide group reacts with one anhydride group. At first glance, this reaction implies a stoichiometric ratio of *anhydride* to *epoxide* groups (A/E ratio) to be 1.0. However, optimum A/E ratios for most dianhydride-epoxy formulations are far less than 1.0, typically between 0.65 and 0.80 for powder coatings. There are two main reasons for this.

First, an A/E ratio less than 1.0 helps address the side-reaction of epoxy etherification (also known as homopolymerization), a process which can consume epoxides without participation from anhydride groups⁷ (**Figure 4**). This is a well-established fact, and epoxy formulations using mono-anhydrides such as methyl tetrahydrophthalic anhydride (MTHPA) routinely use A/E ratios in the range of 0.90–0.96 for this reason. This approach minimizes residual anhydride groups after cure while optimizing the T_g and other properties.

However, dianhydrides require a second, crucial consideration due to the extremely high levels of crosslinking that they produce. At near-stoichiometry, formulations will readily vitrify before full cure, thus locking in unreacted functional groups, which are undesirable for long-term performance. Although it is true that post-curing at elevated temperature can lead to full cure, in many cases, the final crosslink density may be too high for the application, thus leading to suboptimal performance.

Therefore, in most epoxy powder coatings, the dianhydride usage must be well below stoichiometric—typically at A/E ratios in the range of 0.65–0.80. Any excess epoxide groups in the formulation will be consumed via etherification side reactions (epoxy homopolymerization). This approach helps avoid over-crosslinking while optimizing performance. The optimum A/E ratio for a specific application is best determined experimentally, but the recommendations in **Table 2** are a good starting point.

FIGURE 3

A simplified two-step cure mechanism for the esterification reaction between anhydride and epoxide groups that leads to crosslinking.

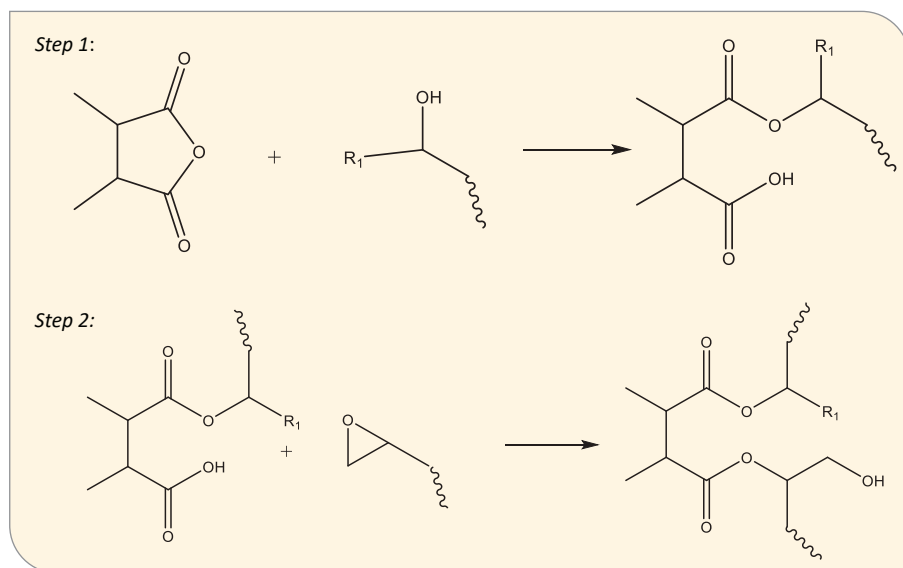


FIGURE 4

Epoxy etherification (homopolymerization), a side reaction that can consume epoxide functional groups without using up anhydrides.

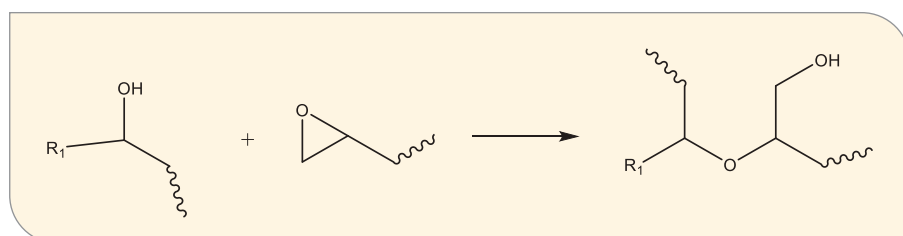


TABLE 2

Suggested Ranges for Anhydride/Epoxide Equivalent Ratio (A/E Ratio) for BTDA-Cured Epoxy Formulations, Based on Resin Epoxy Equivalent Weight (EEW)

Epoxy Resin EEW g/(equiv. of epoxide)	Suggested Equivalent Ratio of BTDA: [anhydride/epoxide] Ratio (A/E)
200–500	0.5–0.7
500–800	0.6–0.8
> 800	0.7–1.0

Example Applications

Dianhydride-cured epoxy powder coatings have long served demanding industrial applications. For example, BTDA-based epoxy powder coatings enjoy significant use within electrical applications. They effectively insulate the stator and rotor surfaces inside electric motors for uninterrupted service for the lifetime of the motor itself while operating semi-continuously, typically in high heat conditions. The heat

exposure can come from either the steady flow of electric current through the motor, or the motor's service environment itself, e.g., the under-hood of an automobile. Other applications are in high-performing pipe coatings where the high degree of crosslinking from BTDA-epoxy powder coatings provide a combination of heat and chemical resistance. A closely related application of epoxy molding powders is the encapsulation of sensitive electrical

components, again frequently under the semi-continuous high-temperature environment under the hood of an automobile. Although this last example is not a coating, these products use the same formulation technology as powder coatings use.

A Technical Exploration of BTDA-Based Epoxy Powder Coatings

A study was designed to develop a better understanding of the factors behind the unique performance of BTDA-epoxy formulations. The aim was to identify correlations between key factors (for example, formulation variables, cure parameters) and T_g obtained within model BTDA-epoxy powder coatings. It was assumed that, within a similar set of formulations, the degree of crosslinking achieved and the resulting properties are directly related to the glass-transition temperatures obtained.

Materials and Processing

Bisphenol-A-based solid epoxy resins (SERs) were provided by Olin Epoxy. Three grades were used in the work: D.E.R.TM 6224 (EEW 675–725, a 2.5-type resin),

A formulation matrix was designed for the study by using four stoichiometric ratios of BTDA for each of the three epoxy resins.

D.E.R. 664UE (EEW 860–930, a 4-type resin), and D.E.R. 667E (EEW 1600–1950, a 7-type resin). The aim was to cover a range of EEWs in this study. CABB Jayhawk Fine Chemicals supplied BTDA® Polymer Fine. Evonik Corporation provided a commercial sample of the catalyst Imicure® AMI-2 (2-methylimidazole). Other materials (pigments and additives) were procured from their respective producers or distributors (Table 3).

A formulation matrix was designed for the study by using four stoichiometric

ratios of BTDA for each of the three epoxy resins (Table 3). These model formulations were kept simple to focus primarily on T_g development. A twin-screw extruder was used for compounding, with a residence time estimated as less than 15 seconds. The barrel temperatures required for proper compounding were approximately 5 °C higher than the softening temperature of the epoxy resin. The extrudate was chilled and ground to powder form and sieved through a 140-mesh screen. Powder formulations were spray-applied on Q-panels at a thickness of 50-60µm and cured in an oven for 20 minutes at 200 °C.

Characterization

Thermal analysis was performed on cured film specimens using a differential scanning calorimeter (DSC Q100, TA Instruments) to measure their glass-transition temperatures and to look for any residual cure. Uncured powder formulations were also cured via thermal ramps or isothermal-cures and then analyzed in the DSC to measure resulting glass-transition temperatures.

TABLE 3
Formulation Matrix and Raw Materials

Formulation No.:	1	2	3	4	5	6	7	8	9	10	11	12
Formulation A/E Ratio →	0.5	0.6	0.7	0.8	0.5	0.6	0.7	0.8	0.5	0.6	0.7	0.8
Weights:												
D.E.R. 6224 (2.5-Type), EEW ~700, softening pt ~95°C	62.5	61.2	60.0	58.8								
D.E.R. 664UE (4-Type), EEW ~900, softening pt.~105°C					63.9	62.9	61.9	60.9				
D.E.R. 667E (7-Type), EEW ~1800, softening pt.~130°C									66.6	66.1	65.5	64.9
BTDA PF (AEW 161)	7.2	8.4	9.7	10.8	5.7	6.8	7.8	8.7	3.0	3.6	4.2	4.7
Cat. AMI-2 (0.5% of resin system)	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Resiflow P-67 (Flow agent)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Benzooin (Degassing agent)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Ti-Pure R960 (White pigment)	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5	28.5
Total Batch, g =	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

A/E ratio: Ratio of anhydride/epoxide functional groups in the formulation
BTDA PF: BTDA Polymer Fine, CABB Jayhawk Fine Chemicals
D.E.R.: Solid epoxy resins, Olin Epoxy
Cat. AMI-2: Imicure AMI-2 (2-methylimidazole), cure catalyst/accelerator, Evonik Crosslinkers
Ti-Pure R960: Titanium dioxide, The Chemours Company
Resiflow P-67: Flow agent, Estron Chemical

FIGURE 5

DSC thermograms showing glass-transition temperatures (as marked) for the same formulation when cured under different conditions. Formulation 3 from Table 3 used DER 6224 resin and BTDA at A/E = 0.7.

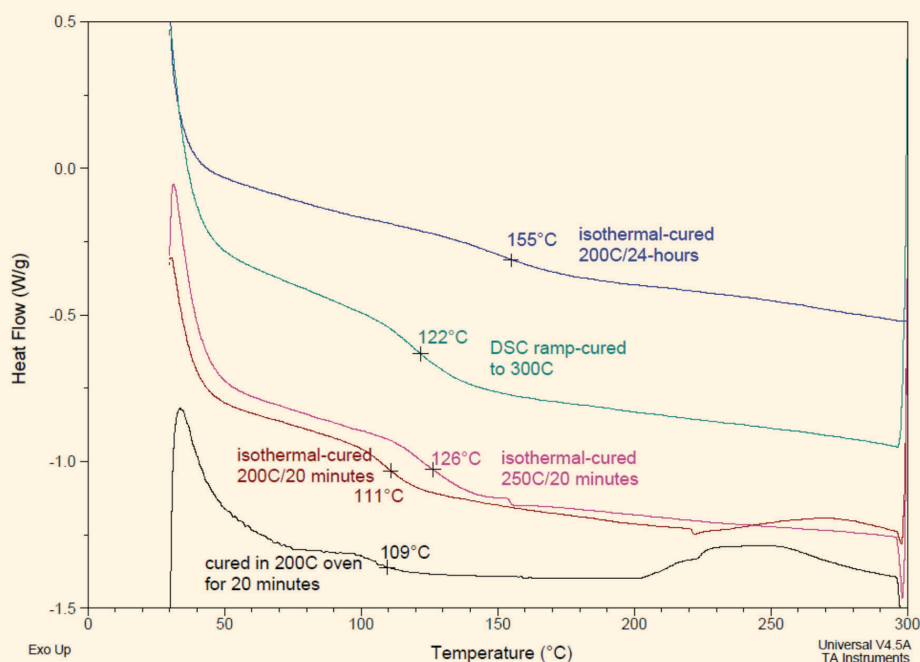
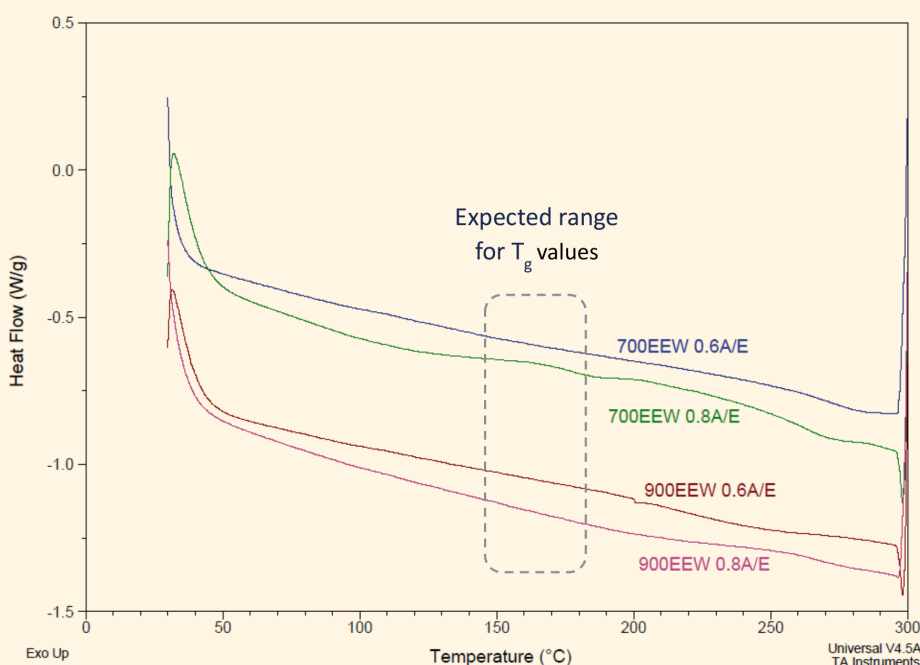


FIGURE 6

DSC thermograms showing glass-transition temperatures (as marked) for other formulations cured 24h/200 °C. Formulation details noted as resin EEW and BTDA usage A/E ratio. Most scans do not show a T_g where anticipated.



A selection of powder formulations was also evaluated using dynamic mechanical analysis (DMA Q800, TA Instruments) to understand shear modulus behavior as a function of temperature and to determine T_g .

Results and Discussion

DSC thermograms of formulations cured simply for 20 minutes at 200 °C showed glass-transition temperatures of ~ 105 °C ± 15 °C, depending upon the resin used and the A/E ratio employed. However, these specimens also displayed a substantial exotherm above the glass-transition temperatures, indicating incomplete cures. To better understand the full development of crosslinking and T_g , several cure experiments were conducted on uncured powders, followed by DSC scans for T_g determination. **Figure 5** shows a composite of several thermograms on a specific formulation (**Table 3**, column 3) cured under different conditions.

Starting with the lowest curve in the image, the specimen cured isothermally at 200 °C (oven) for 20 minutes showed at T_g of 109 °C. A similarly cured specimen, but isothermally within the DSC cell, showed a similar T_g of 111 °C. Both these thermograms show the residual exotherm pointing to some incomplete cure in the specimens.

When isothermally cured at 250 °C instead, but still for 20 minutes, the resulting T_g increased to 126 °C. A similar result was obtained (T_g of 122 °C) with a thermal ramp-cured specimen (heating from 30 °C to 300 °C at 10 °C/minute). These two thermograms do not show any residual exotherms and show similar, higher glass-transition temperatures. These observations point to the state of full cure in these two specimens, as expected from the use of higher temperatures in their cure processes.

The blue curve (**Figure 5**), however, shows an even higher T_g of 155 °C, generated after a longer (24-hour) 200 °C isothermal cure. This specimen also shows a faint T_g , indicating that its specific heat does not change as drastically through the transition as is normally expected for polymers. This points to a very high level of crosslinking, which exerts a greater influence on the specific

heat and other properties at temperatures above the T_g . These observations are consistent with literature reports that at high levels of crosslinking the T_g increases while the intensity of the transition is suppressed.⁸ Indeed, the glass-transition temperatures via DSC went undetected for a few formulations cured under the same conditions (24h/200 °C; **Figure 6**).

To better determine these missing glass-transition temperatures, DMA analysis (shear mode) was conducted on three formulations produced from the D.E.R. 6224 resin (700 EEW).

Figure 7 shows the complex shear modulus behavior versus temperature for these specimens. Note the relatively low drops in modulus through the transitions—only about one order of magnitude versus the minimum two orders that are expected from normally cross-linked epoxy networks. The relatively higher position of the rubber plateau in these curves again indicates a very high degree of crosslinking.⁹

Figure 8 shows the loss tangent ($\tan\delta$) peaks indicating glass-transition temperatures for these specimens. As expected, higher A/E ratios (BTDA usage) yield higher glass-transition temperatures. For optimal performance, the data suggest that an A/E ratio of 0.7 is a good candidate, as further increase to A/E 0.8 leads to a relatively small gain in T_g (from 164 °C to 170 °C).

Although specimens cured for 24 hours in 200 °C gave the highest glass-transition temperatures in this study, not all formulations were tested after this cure profile. Still, the other cure profiles were helpful in broad comparisons of T_g data as a function of epoxy EEWs and A/E ratios (**Figure 9**). As expected, increasing the A/E ratio (BTDA usage) consistently raises T_g . It is also evident that using a higher, 900 EEW resin lowers the T_g as compared with the 700 EEW resin. This makes sense, as the longer backbone of the higher EEW resin will act to slightly lower the average crosslink density and thus soften the cured network. Note that data from the lowest A/E ratio (0.5) and from the third resin (1800 EEW) are omitted in this chart for simplicity, but the same trends were observed.

FIGURE 7

DMA data showing complex shear modulus versus temperature for formulations made from solid epoxy resin (700 EEW). BTDA usage indicated as A/E ratios.

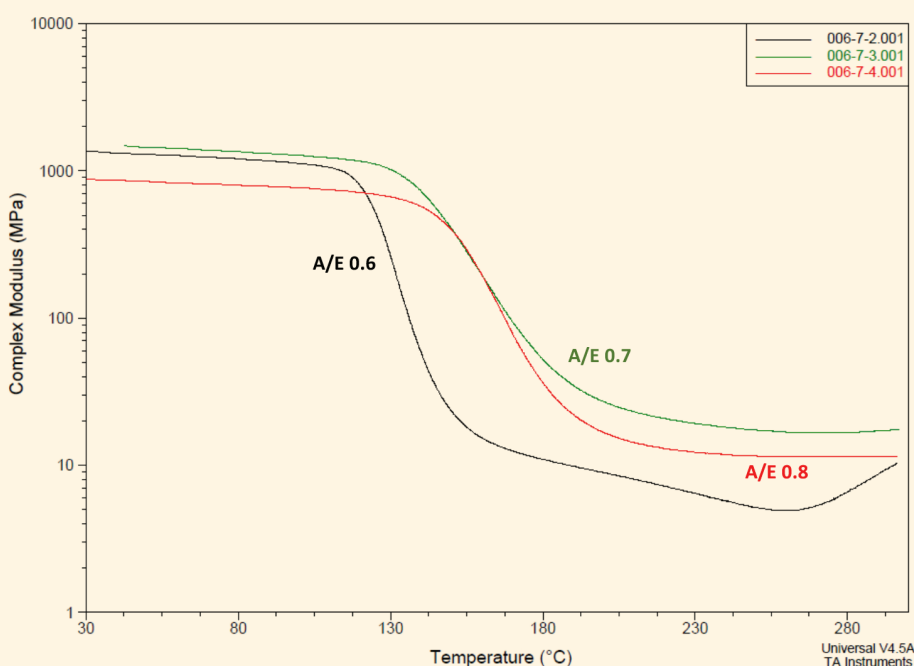


FIGURE 8

DMA data from shear modulus measurements showing $\tan\delta$ peaks as glass-transition temperatures for formulations made from solid epoxy resin (700 EEW). BTDA usage indicated as A/E ratios.

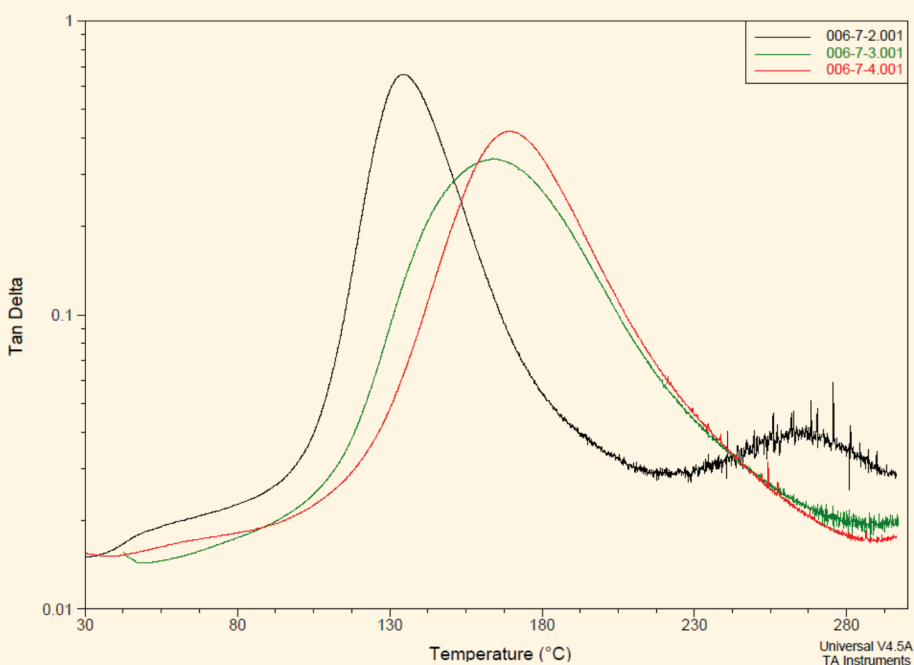
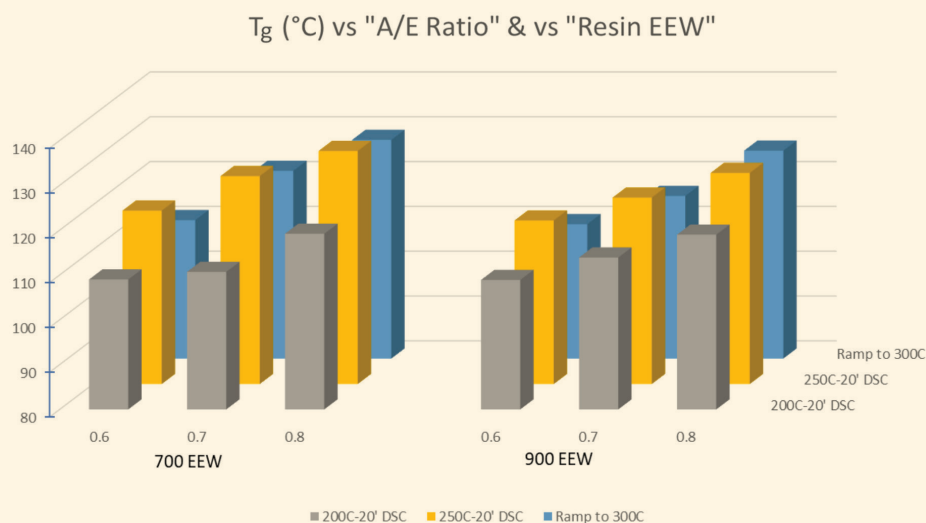


FIGURE 9

DSC T_g data for the 700- and 900-EEW resins at different A/E ratios noted on the x-axis. Cure profiles used are indicated on the z-axis.



A DSC experiment was conducted to simulate the cure of a thinly coated panel placed in an oven at 200 °C for 24 hours. The aim was to understand the extent of cure as a function of time. As shown in **Figure 10**, the cure exotherm is completely overshadowed by the strong endotherm from the rapid heating ramp of 100 °C/min. The cure exotherm is visible only at around the 5-minute marker, at the end of the heating ramp. The remainder of the thermogram shows a flat line for the heat flow, indicating that thermally measurable cure is completed within a minute of reaching the 200 °C target temperature. The above observations of the T_g rising when cured for long times at 200 °C points to ongoing, albeit slow, crosslinking reactions that continue over time.

The next phase will focus on reducing the cure times and temperatures needed to maximize crosslinking and T_g .

FIGURE 10

DSC thermograms on a sample, cured in the DSC cell via a heating ramp of 100 °C/min. from 30 °C to 200 °C followed by a 200 °C hold for 24h.

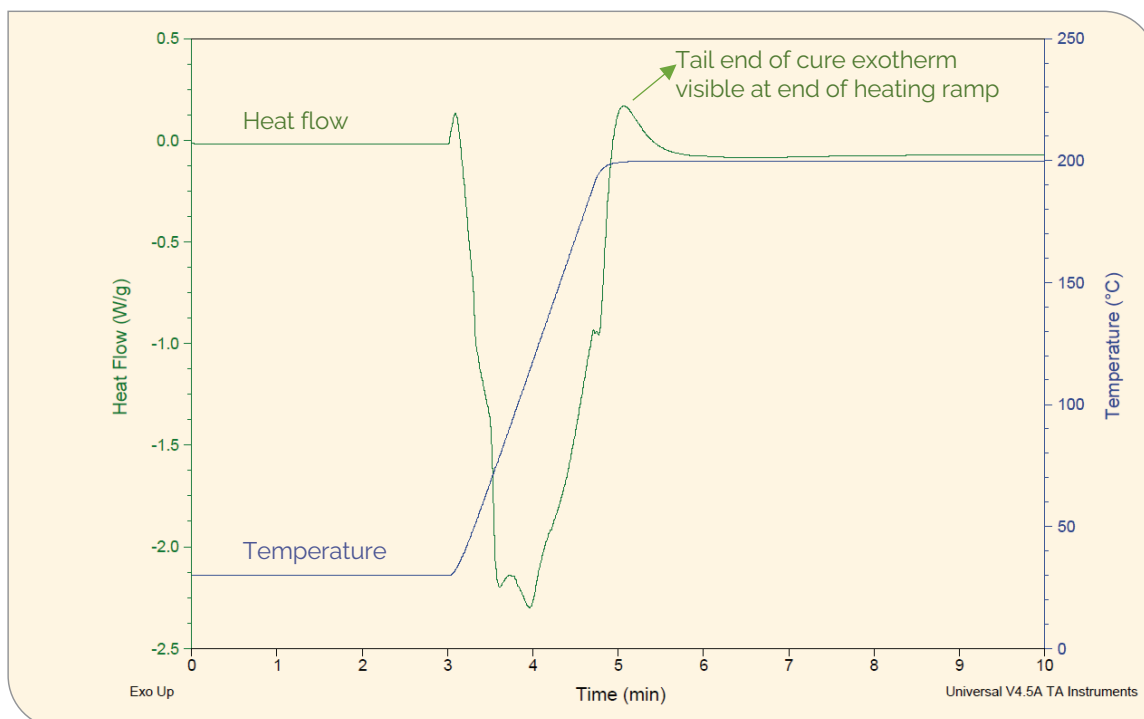


TABLE 4
Qualitative Summary of Performance vs Formulation and Process Variables

Performance \ Variables	Epoxy resin EEW	Formulation A/E (BTDA qty)	Cure Temp	Cure Time
Glass-transition temperature (T_g)	↓	↑	↑	↑ ↑
High T_g => high crosslink density => heat-resistance, electrical resistance, corrosion-resistance, chemical-resistance				
Gel time (ASTM D 4217-02)	↑	↓	-	-
Pellet Flow	↑	↓	-	-

The cure exotherm (to be pointed upwards) is overshadowed by the strong endotherm (pointed downwards) from rapid heating, with only the tail end of the exotherm visible at the end of the heating ramp. Formulation 3 from **Table 3** (page 31) used 700 EEW resin and BTDA usage at A/E = 0.7.

Based on overall results, combined with certain coating application characteristics that were measured, an overall summary of performance versus formulation or process variables is presented in **Table 4**. Additional work is underway to continue to build out this table further, as this table can guide formulators in using BTDA as a curative in epoxy coatings.

Conclusions and Summary

Dianhydrides, as exemplified by BTDA, impart very high levels of crosslinking in epoxy powder coatings. This feature leads to exceptionally high glass-transition temperatures when using simple bisphenol-A based solid epoxy resins (SERs) and without the need for higher functionality epoxy resins such as Novolacs. T_g values as high as 170 °C were observed when using a simple SER of 700 EEW (2.5-Type) and BTDA. Optimum performance is derived by lowering the usage of BTDA to stoichiometries such as A/E ratios from 0.6 to 0.8. Although T_g and other properties tied to crosslink density can be maximized by using higher A/E ratios, this work suggests

that an A/E ratio of 0.7 is a good starting point for standard SERs. With isothermal cures, slower reactions continue to build crosslink densities over a 24-hour period, raising T_g in the process. Overall data indicate that while high temperature can be employed to reach these high crosslink densities, longer cure times may play a more significant role.

Future work

Further efforts are underway to better understand model formulations based on BTDA and standard solid epoxy resins. The next phase will focus on reducing the cure times and temperatures needed to maximize crosslinking and T_g . The work will also aim to optimize formulations for performance as well as handling properties, such as gel time, pellet flow, and film appearance. The use of a finer particle size of BTDA will also be explored to understand and contrast with the grade used in this study.

Acknowledgments

The authors gratefully acknowledge the meticulous efforts by Nick Page and Nathan Biller in the compounding and spraying of powder formulations. Dr. Lingyun He and Dr. Rajesh Turakhia of Olin Corporation provided valuable technical guidance and generous samples of epoxy resins. Imidazole catalyst was provided by Dr. Pritesh Patel of Evonik Corporation. ❖

Vinay Mishra, Ph.D., is technical director for thermoset additives at CABB Jayhawk Fine Chemicals. Email: vinay.mishra@jayhawkchem.com.

Kevin Biller is president of ChemQuest Powder Coating Research, a division of the ChemQuest Group. Email: kbiller@chemquest.com.

Jeff Dimmit, Ph.D., is vice president of technology at CABB Jayhawk Fine Chemicals.

Nikola Bilic is a product compliance specialist at Chevron Phillips Chemicals. He previously worked as a scientist at National Institute for Materials Advancement, formerly the Kansas Polymer Research Center.

References

- Bott, Lawrence Lester; Helvey, Max Eugene. Thermosetting Powder Coating Compositions. EP0587757B1. March 11, 1998.
- Barie Jr., W.P.; Franke, N.W. *Ind. Eng. Chem.* 1969, Vol. 8, No. 3, 72-76.
- Barabanova, Anna, et al., *Polymer* 2019, Vol. 178, 1215902019.
- Kolar, F.; Svitilova, J. *Acta Geodyn. Geomater.* 2007, Vol. 4, No. 3, Issue 147, 85-92.
- Corcuera, M., et al., *J. Appl. Polym. Sci.* 1997, 64, 157-166.
- Bouillon, N.; Pascault, J-P; et al., *J. of Appl. Polym. Sci.* 1989, Vol. 38, 2103-2113.
- Mishra and Campanella, "Anhydride-cured epoxy composites: overview and recent advances," presented at the 2019 meeting of Thermoset Resin Formulators Association in Charleston, SC.
- Greenberg and Kusy, *Journal of Applied Polymer Science* 1980, Vol. 25, 1785-1788.
- Ferry, John D. *Viscoelastic Properties of Polymers* 3rd ed.; John Wiley & Sons: New York, 1980.

Notes

- BTDA® is a trademark of CABB Jayhawk Fine Chemicals.
- D.E.R.™ is a trademark of Olin Corporation.
- Imicure® is a trademark of Evonik Corporation.