BTDA® AS A THERMAL CURATIVE FOR EPOXY POWDER COATINGS: AN OVERVIEW

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ABSTRACT

Dianhydrides, specifically 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA), are an effective thermal curative for epoxy powder coatings, offering enhanced heat and chemical resistance, mechanical and dielectric properties. While interest in BTDA dates to the late 1960s, applied research on its use in powder coatings has been ongoing and steady. BTDA is ideally suited for dry processing, and the multiple tips and techniques presented herein are important to grasp in order to derive the full benefit of performance properties inherent to this technology.

INTRODUCTION

Commercialized in the 1950s, powder coatings serve an important role in a number of consumer and industrial applications including the decoration and protection of appliances, outdoor furniture and electronic componentry. They can be applied as thin-mil films of 25-75 um in solution or as 250-2500 um high body coatings via fluidized bed or electrostatic spray. Heat is used to fuse the coating particles together into a discrete film. In the case of powder coating systems based on epoxy resin binders, heat further serves to drive cure and establish a thermoset polymer network resistant to thermal and corrosive environments [1].

Epoxies are the most widely used of all thermosetting powder coatings, and are especially suited for these niche areas:

- Electronic components – Epoxies are ideal for electrical applications due to their robust dielectric properties. Examples include molding compounds to encase very small parts such as resistors and LEDs, to sensors, motor armatures, coil windings and busbars. Further benefits include heat and chemical resistance, appropriate for the expanding use of electronics in automotive and power generation systems.
- Pipe coatings – Fusion bonded epoxy (FBE) coatings are formulated for steel substrates used in infrastructure. These include exterior primers or coatings for onshore piping e.g. shale gas transmission and interior coatings for crude oil and petroleum derivatives. Benefits include improved corrosion and abrasion resistance of underground pipe coatings exposed to soil stress, bacteria, fungus, soil acids and alkalis; as well as underwater pipe coatings exposed to salt water, wastewater, petrochemicals, solvents and corrosive gases.
- Reinforcing bars – Epoxy-coated steel rebar for concrete reinforcement has been used since the 1970s. These coatings provide corrosion protection, physical durability and chloride impermeability. Ultimately, this technology extends the service life of concrete bridge decks and structures in transportation networks worldwide [2].

It is important to note that epoxies are less suited for outdoor applications due to chalking effects from UV exposure. In these instances, hybrids with acrylics or other resins are utilized.

LITERATURE AND PATENT REVIEW

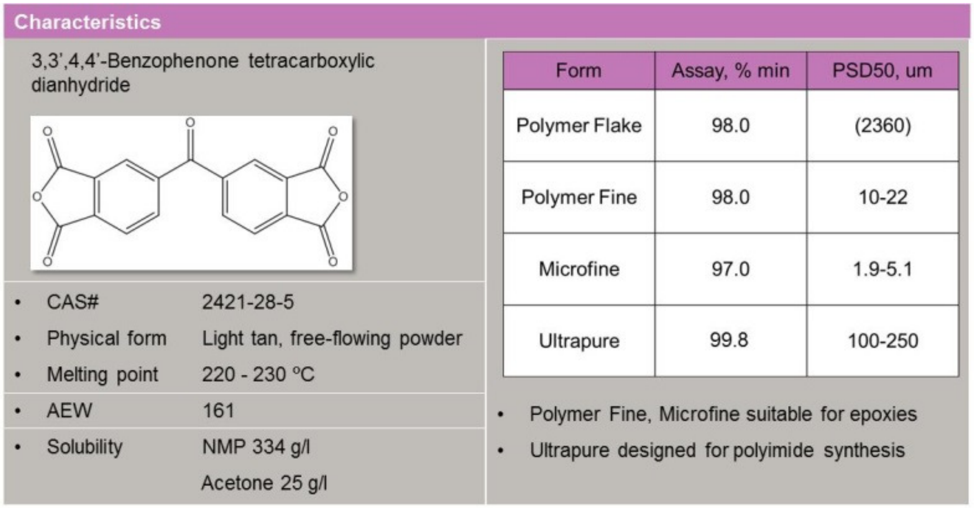
Powder coatings of all chemistries are available and continue to be developed. However, since the 1960s, the study of pure epoxy powder coatings has remained at the forefront by researchers looking to advance performance properties. In 1968, Lee studied the processing advantages of epoxy compositions cured with a variety of anhydrides including BTDA [3]. Work continued into the 1990s, where Doone et. al. [4] as well as Chiba et. al. [5] developed epoxy formulations cured with BTDA having desirable chemical and water resistance for insulation coatings. Kitagawa [6-8] and then, by the 2000s, Yamamura [9-11] were actively studying different epoxy formulations cured with BTDA to address storage stability, flow control during application and surface quality in service. Fujibuchi produced BTDA-cured epoxy powder coatings with unexpected flexural and tensile strength, as well as what he called fireproof systems [12-15]. Sumiyama found improved heat resistance, impact resistance and other mechanical properties with epoxy coatings formulated with dianhydrides, specifically BTDA [16-21]. Recent work includes that of Lee, Seok et. al., who developed epoxy powder coatings with good corrosion, abrasion and bending resistance for steel pipes [22-23]; and Hu, Gao et. al., who formulated anticorrosive epoxy powder coatings with anhydride curatives for structural steel [24].

THERMAL CURATIVE SELECTION

Epoxy thermal curatives for powder coatings include dicyandiamides, phenolic resins and dianhydrides. Dianhydrides, specifically BTDA, contribute to optimal levels of mechanical, thermal and dielectric behavior of coated parts.

BTDA is supplied as a free-flowing powder with characteristics shown in Table 1.

Table 1 – BTDA Overview [25]



Characteristics

3,3',4,4'-Benzophenone tetracarboxylic dianhydride

CAS#	2421-28-5
Physical form	Light tan, free-flowing powder
Melting point	220 - 230 °C
AEW	161
Solubility	NMP 334 g/l Acetone 25 g/l

Form	Assay, % min	PSD50, um
Polymer Flake	98.0	(2360)
Polymer Fine	98.0	10-22
Microfine	97.0	1.9-5.1
Ultrapure	99.8	100-250

- Polymer Fine, Microfine suitable for epoxies
- Ultrapure designed for polyimide synthesis

A comparison of systems is presented, utilizing a DGEBA epoxy resin (Epon 2002) [4].

Table 2 – Powder Coating Formulations

Component	1	2	3
BTDA	56		
DICY		5	
Phenolic			47
ZnAcAc	1		
2-Methylimidazole			0.5

Notes:
1) All values in phr.
2) All formulations contained 1.5 phr flow aid, 30 wt% TiO2.
3) Cured 15 minutes at 200°C

Table 3 – Property Comparison

Property	Units	1	2	3
Volume Resistivity @ 25°C	ohm-cm	5.3 x 10E15	9.1 x 10E8	7.8 x 10E14
Volume Resistivity @ 200°C	ohm-cm	4.8 x 10E10	3.8 x 10E8	Conductive
Dielectric Constant @ 1kHz, 200°C		8.1	Conductive	Conductive
Dissipation Factor @ 1kHz, 200°C		0.0089	Conductive	>1
Dielectric Strength @ 25°C	volts/mil	1000	440	960
Glass Transition Temperature (Tg)	°C	138	104	94

In all cases, the competitive advantage of the BTDA-cured system is evident. For Tg development, a 30°C differential is not unusual. While Tg is certainly a function of resin chemistry, values approaching 200°C are possible, owing to the high degree of crosslinking afforded by the tetrafunctional structure of BTDA.

TIPS FOR USING DIANHYDRIDES

Often, the full benefit of the dianhydride component is not fully realized. A measurable increase in Tg may only be a fraction of what can be achieved via optimization of blend ratio, A/E ratio and dosing level.

The following recommendations are offered to improve results:

Formulating

The Epoxy Equivalent Weight (EEW, or E) of the resin is best obtained from the manufacturer's literature. Resin blends require careful calculation of EEW.

The Anhydride Equivalent Weight (AEW, or A) must be calculated for BTDA or the selected blend. For neat BTDA, AEW = 161.

Dosing level, expressed in parts per hundredweight resin (phr), is defined as A/E x 100, where A/E works best in the 0.5 - 0.6 range for BTDA and 0.9 - 1.1 range for blends, as opposed to strict 1:1 stoichiometry.

An additional tool to determine optimal dosing is the empirical K value, defined as A/E x % BTDA Anhydride Equivalents.

Working within a K range of 40 to 50 can improve Tg by up to 30ºC.

Higher EEW epoxy resins may require further adjustment of curative phr in order to account for an excess of hydroxyl functionality.

Processing

While some processes may be challenging due to the physical form of BTDA, a dry solid, in the case of powder coatings, BTDA is in the ideal form.

Dry blending involves high intensity mixing in order to create homogeneity between resin, curative, pigment and additives.

Additional steps may include melt compounding via extruder, followed by cooling and grinding to reduce the coating powder to the desired particle size.

Wet blending requires the use of a volatile solvent to facilitate mixing of ingredients, typically in a mill configuration. A secondary spray drying step is required to remove residual solvent and prepare the coating powder for packaging.

The incorporation of liquid or paste forms of curatives may introduce viscosity variations and require additional attention to maintain homogeneity of the coating powder.

Housekeeping

Users of thermally-cured epoxy formulations may experience pot life drift or surface imperfections due to overlooked housekeeping practices in the production environment. This is mistakenly remedied by adjusting mix ratios of epoxy/dianhydride or compensating with accelerators.

All dianhydrides contain residual free acid in ppm levels as part of the manufacturing process. This seemingly insignificant amount, can serve as a welcome accelerator by enhancing monoester formation, which subsequently reacts with epoxide groups.

However, when improperly stored, free acid levels can increase to single digit weight percents, owing to the inherent sensitivity of dianhydrides to moisture. This hydrolysis reaction can occur when a package is left opened and exposed to air especially in humid environments, or during extended periods, perhaps during shift changes or overnights.

Instead of an accelerating effect, the reduced assay of the dianhydride may lead to processing variations and quality issues including pot life drift and incomplete dissolution of dianhydride particles.

To optimize product handling and storage, special packaging should be considered, as well as a review of all housekeeping practices in the manufacturing environment.

CONCLUSIONS

1. BTDA is a legacy thermal curative for epoxy powder coatings, offering enhanced heat- and chemical resistance, mechanical and dielectric properties.
2. BTDA is ideally suited for dry processing of powder coatings.
3. Multiple techniques are required in order to derive the full benefit of performance properties.

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