

BTDA™ FOR EPOXY SYSTEMS: A FRESH PERSPECTIVE

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ABSTRACT

BTDA™ (3,3',4,4'-Benzophenonetetracarboxylic dianhydride), introduced in the 1960s as a novel thermal curative for epoxy resins, has been recognized for advancing the performance and extending the service life of products operating under demanding conditions. Contributions provided by BTDA include an increase in (a) high-temperature mechanical and dielectric stability and (b) chemical- and wear-resistance for a wide array of epoxy systems. For example, glass transition temperature (T_g) improvements of up to 30°C have been observed. Due to BTDA's physical form as a dry powder, more popular liquid monoanhydrides have found favor with formulators, due to ease of mixing and metering. This paper will serve to reintroduce BTDA and its role in adding value to epoxy systems for electrical/electronic applications. Specific examples based on BTDA and anhydride blends will be discussed.

INTRODUCTION

Dianhydrides can be classified as organic or inorganic in nature. An organic anhydride is created via the elimination of water from an organic acid. The simplest structure, depicting two acyl groups bound by a common oxygen molecule, is shown in Figure 1.

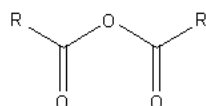


Figure 1 – Organic anhydride

Cyclic dianhydrides have proven to be popular intermediates for epoxies, polyimides, polyamides and polyesters. Common dianhydrides include:

- Pyromellitic dianhydride (PMDA)
- 4,4'-Oxydiphthalic anhydride (ODPA)
- Hexafluoroisopropylidene-bis-phthalic dianhydride (6-FDA)
- 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA)

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

Table 1 – BTDA Overview [1]

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															
	<table border="1"><thead><tr><th>Form</th><th>Assay, % min</th><th>PSD50, um</th></tr></thead><tbody><tr><td>Polymer Flake</td><td>98.0</td><td>(2360)</td></tr><tr><td>Polymer Fine</td><td>98.0</td><td>10-22</td></tr><tr><td>Microfine</td><td>97.0</td><td>1.9-5.1</td></tr><tr><td>Ultrapure</td><td>99.8</td><td>100-250</td></tr></tbody></table>	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
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	<ul style="list-style-type: none">• Polymer Fine, Microfine suitable for epoxies• Ultrapure designed for polyimide synthesis															

The advantages of BTDA as a thermal curative for epoxies include:

- Variable pot life for optimal processing (with/without catalysis)
- High melting point = lower tendency to volatilize from a hot surface before curing resins
- Lower exotherm than amines
- Variable cure schedules to accommodate existing heating equipment
- Extensive crosslinking, leading to higher T_g for enhanced thermal and dielectric behavior of fabricated parts
- Lower water absorption than amines

BTDA-epoxy systems enjoy widespread use in the electrical/electronics sector due to their excellent retention of properties at elevated temperatures for extended periods of time. This is the primary value proposition for BTDA and its 40 year young technology.

Epoxy – Anhydride Chemistry

The reaction of an epoxy resin with an anhydride is complex and consists of three primary steps [2]. Figure 2 depicts the first reaction between anhydride and hydroxyl groups present as (a) constituents on the epoxy backbone; (b) low molecular weight alcohols, e.g. ethylene glycol, added to the reaction mixture at 1-5 wt%; or (c) added water.

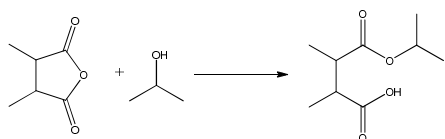


Figure 2 – Reaction 1

The reaction can be catalyzed via tertiary amines as well as influenced by other factors including (a) the free acid content of the anhydride and (b) moisture or other contamination. Reaction 1 is fast and favors the formation of monoester as shown.

In Reaction 2, monoester and epoxide are combined, as shown in Figure 3.

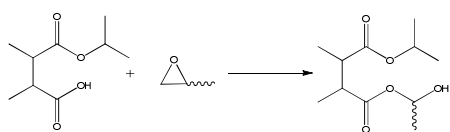


Figure 3 – Reaction 2

The carboxylic free acid group within the monoester reacts with the epoxide to form an ester linkage as shown. The resultant diester with newly-formed hydroxyl group serves to propagate the reaction and subsequent formation of the polymer network.

Higher temperatures and the use of amine catalysts drive ester formation and suppress Reaction 3, the hydroxyl group – epoxide reaction that forms an ether linkage as shown in Figure 4.



Figure 4 – Reaction 3

The epoxide ring opening may be accelerated via the use of Lewis acid catalysts or achieved via the uncatalyzed reaction with free acid within the system. Reaction 3 is the least favored, and in some cases, contested outright by researchers [3].

So the key points of epoxy – anhydride chemistry can be summarized as follows:

1. Contrary to opinion, BTDA does not react directly with epoxide. Diester formation becomes the critical step for polymerization and network formation
2. Exact stoichiometry is not a requirement. Since Reaction 3 is independent, the anhydride-to-epoxy (A/E) ratio does not need to be precise. Rather, an empirical A/E ratio of 0.5 - 0.9 is favored over 1:1 stoichiometry, but can be blend-dependent, as will be described later on.

BTDA VALUE PROPOSITION

BTDA's value over competing curing agents can be best demonstrated by reviewing a series of applications, combined with formulating advice, as challenges exist for the processing of these systems [4,5].

Applications

Adhesives – Epoxy adhesives are common for bonding integrated circuits to electronic components. The challenge is to introduce BTDA, catalyst and accelerator into a liquid epoxy resin (LER), usually as a two-pack formulation. A blend of BTDA with liquid monoanhydride facilitates mixing under high shear conditions and improves the performance properties of the adhesive. Typical curing occurs within 2 hours at 200°C, with cure time reduced to minutes via the addition of accelerators e.g. imidizoles.

Powder Coatings – Fusion bonded epoxy (FBE) coating applications may include conventional electronic components as well as pipe linings, where improved high temperature properties, chemical- and corrosion- resistance are specified. These coatings are formulated as dry systems. Optimal mixing and incorporation of BTDA is achieved via milling with subsequent grinding to the desired particle size for fluidized bed or electrostatic spray application. Typically, 10 - 15 mil coatings are cured within minutes at 250°C.

Molding Resins – Epoxy molding compounds (EMC), e.g. encapsulants for LEDs and optical sensors, as well as traditional potting compounds for electrical components, are all examples where improved thermal properties and dielectric behavior are favored. BTDA as the sole curative is typically added to heated resins until dissolved. Dissolution is confirmed by a change of appearance from solid to opaque to clear. Processing occurs within minutes, with immediate transfer into heated molds for curing.

Other processes involve dry systems, with charging of powders into heated matched metal die molds for preforming or compression molding. Reactive injection molding is yet another production method to fabricate encapsulated components. In all cases, cycle times under 2 minutes at temperatures less than 200°C are typical.

Varnishes – An all-encompassing coating application, varnishes may include insulation coatings for magnet wires; windings for electrical motors/generators used in appliances and automotive; and submersible oil-well pump motors. Requirements include abrasion, temperature and chemical resistance at service temperatures of 180 - 200°C. Dry mixing and grinding of ingredients once again allows for full incorporation of BTDA, with application via fluidized bed and curing within 2 - 3 minutes at 200°C due to the thin layer of the films.

Formulating Summary [2,4]

1. BTDA or blends with monoanhydrides are to be carefully selected depending on the processing conditions for the formulation. In all cases, BTDA is best utilized in dry form to take advantage of optimal loading. Limited solubility in epoxy resins may require shear mixing at 150 - 170°C, the addition of solvent where tolerated, or dry milling/blending.
2. Moisture must be avoided to control hydrolysis. This has been repeatedly observed when product packages are left opened and exposed to air, especially in humid environments, or during extended periods e.g. during shift changes or overnights. The reduced assay of the dianhydride may lead to processing variations and compromised quality including pot life drift and incomplete dissolution of BTDA particles.
3. The Epoxy Equivalent Weight (EEW, or E) is best obtained from the manufacturer's literature.
4. The Anhydride Equivalent Weight (AEW, or A) is to be calculated for BTDA or the selected blend. For neat BTDA, AEW = 161.
5. Dosing level, expressed in parts per hundredweight resin (phr), is defined as

$$\text{phr} = (A/E) \times 100 \quad (\text{Equation 1})$$

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.

6. The empirical K value is to be calculated, defined as

$$K = A/E \times (\% \text{BTDA Anhydride Equivalents}) \quad (\text{Equation 2})$$

7. Working within a K range of 40 to 50, and utilizing BTDA as the sole curative, can improve Tg by 20 - 30°C.

Performance Data

Over the years, epoxy formulators developed an assortment of curative systems exclusive of BTDA, as many were discouraged by an inability to understand and utilize this dianhydride to its full potential. While it is recognized that formulating comprises both chemistry and artistry gained by practical experience, we submit that the same applies to BTDA, where an acquired skill level is rewarded with intriguing performance properties. Examples are presented herein.

The influence of BTDA dosing on heat distortion temperature (HDT) is illustrated in Figure 5.

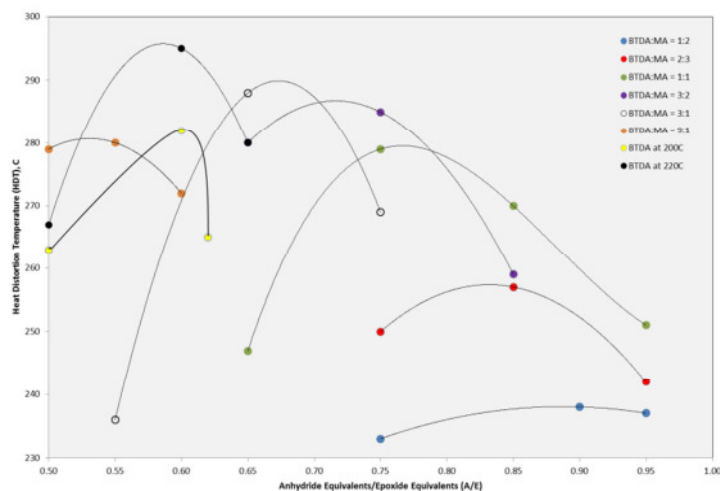


Figure 5 – HDT as a function of A/E ratio for BTDA and BTDA/maleic anhydride (MA) blends. Based on Epon 828 cured 24 hours at 200°C [4]

This classic data set, first presented by Gulf in the 1960s, demonstrates that for each given curative blend, a peak value exists for HDT, which in turn correlates with the K= 40-50 range previously cited. In short, in reading the graph from right to left, as the level of BTDA increases, HDT increases to its ultimate value. The correct dosage of curative, therefore, is determined from a host of variables beyond stoichiometry. Anhydride blend ratio, A/E, and K become equally important in dosing optimization.

Figure 6 provides an example of property retention for a laminate under high service temperatures.

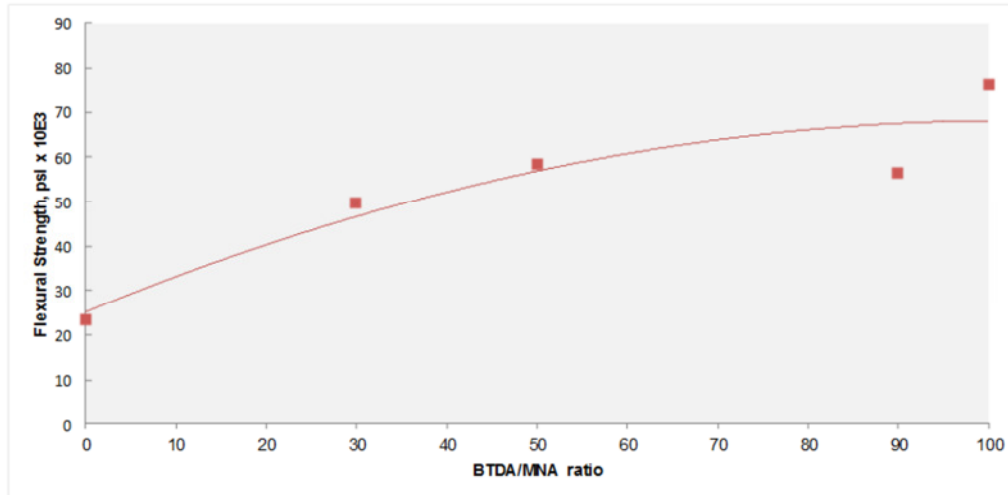


Figure 6 – Flexural strength as a function of anhydride blend ratio. Epon 828 glass laminate, 27 wt% resin, A/E = 0.85, heat aging at 260°C for 500 hours, tested at 23°C [4]

While flexural strength is shown to improve with higher BTDA content, ultimate performance is achieved with an all-BTDA curative.

Further evidence of property retention with BTDA is shown in Figure 7, summarizing the results of a thermal aging study of an adhesive formulation.

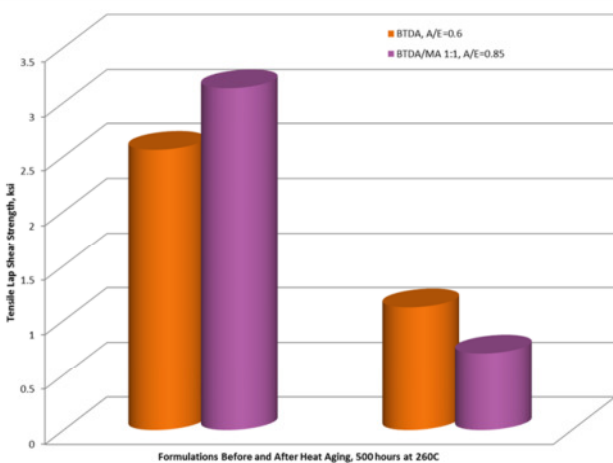


Figure 7 – Tensile lap shear strength as a function of curative blend. Epon 828 100 phr, atomized alumina 100 phr, CTBN 10 phr, fumed silica 3 phr, 2 hour cure at 200°C [4]

The epoxy cured with neat BTDA, as compared to a BTDA/MA blend, experienced significantly less degradation upon aging, owing to the integrity of the polymer network.

Future Needs

Advances in dispersion technology have created opportunities to supply BTDA as a liquid dispersion for ease of use in broader applications. Work continues in this area.

Higher levels of property retention may be provided by asymmetric dianhydrides including a-BTDA, where disruptive polymer network formation may lead to newfound levels of T_g .

BTDA-cured epoxies may be too rigid for certain applications. Current work is focused on additives to retain T_g while addressing toughness.

SUMMARY

1. BTDA remains an attractive choice for sustainable, high-temperature performance of epoxy components in electrical and electronic applications.
2. Blends with monoanhydrides must be formulated correctly to achieve the optimal contribution from BTDA.
3. Formulating flexibility allows for tailoring of product properties.
4. Both veteran epoxy formulators and young professionals new to industry can benefit by taking a fresh look at BTDA as a proven technology.

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REFERENCES

1. "Another Look at BTDA," Evonik Corporation, GlobalSpec Webinar (2014).
2. Private conversations, J. Dimmit, B. Schafran, others (2014).
3. Kolar, Frantisek, Svitilova, Jaroslava, "Kinetics and Mechanism of Curing Epoxy/Anhydride Systems," Acta Geodyn. Germater., Vol. 4, No. 3 (147), 85-92 (2007).
4. "Formulating Epoxy Resins with Gulf BTDA," Gulf Oil Chemicals, Specialty Chemicals (1968).
5. "Short Glass and Mineral Filled Epoxy Molding Compounds: Processing Guide, Sumitomo Bakelite North America, Inc. (2011).

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