*Kirk-Othmer Encyclopedia of Chemical Technology.*

# COMPOSITE MATERIALS, THERMOSET POLYMER-MATRIX

Thermosetting unsaturated polyester resins constitute the most common fiber-reinforced composite matrix today. According to the Committee on Resin Statistics of the Society of Plastics Industry (SPI), 454,000 t of unsaturated polyester were used in fiber-reinforced plastics in 1990. These materials are popular because of their low price, ease of use, and excellent mechanical and chemical resistance properties. Over 227 t of phenolic resins were used in fiber-reinforced plastics in 1990 (1–3). Phenolic resins (qv) are used when their inherent flame retardance, high temperature resistance, or low cost overcome the problems of processing difficulties and lower mechanical properties.

## 1. Polyester Resins

Unsaturated polyester resins predominate among fiber-reinforced composite matrices for several reasons. A wide variety of polyesters is available and the composites fabricator must choose the best for a particular application. The choice involves evaluation of fabrication techniques, temperatures at which the resin is to be handled, cure time and temperature desired, and required cured properties (see Polyesters, unsaturated).

### 1.1. Manufacture

Polyester resins are manufactured by the reaction of dibasic acids with glycols. Common dibasic acids used in polyester production are phthalic anhydride [85-44-9], isophthalic acid [21-91-5], maleic acid [110-16-7], and adipic acid [124-04-9]. The phthalic acids provide stiffness, hardness, and temperature resistance; maleic acid provides the vinyl unsaturation to accommodate free-radical cure; and adipic acid provides flexibility and ductility to the cured resin. Commonly used glycols are propylene glycol [57-55-6], which reduces crystallization tendencies and improves solubility in styrene [100-42-5]; ethylene glycol [107-21-1], which costs the least; and diethylene glycol [111-46-6], which reduces crystallization tendencies. The diacids and glycols are condensed, eliminating water, and then dissolved in a vinyl monomer to a suitable viscosity. Vinyl monomers used are styrene, vinyltoluene [25012-15-4], *p*-methylstyrene [622-97-9], methyl methacrylate [80-62-6], and diallyl phthalate [131-31-9]. The addition of a polymerization inhibitor, such as hydroquinone [123-31-9], *tert*-butylcatechol [98-29-3], or phenothiazine [92-84-2], extends the shelf life of polyester resins.

Resins based on phthalic anhydride are termed *orthophthalic polyesters,* and resins based on isophthalic acid are *isophthalic polyesters.* The most commonly encountered resins are the orthophthalic polyesters, because the isophthalic polyesters, although offering improved mechanical and thermal properties, are higher in cost. Resins based on terephthalic acid [100-21-0] improve upon the property set of isophthalic polyesters, but are very uncommon owing to higher cost.

Polyesters offer low and tailorable viscosities by dilution with vinyl monomers. Low viscosity is important in the fabrication of fiber-reinforced composites to insure good wetting of the fibers and fillers. Poor wetting results in large losses of mechanical properties. Too low a viscosity results in resin-starved areas from gravity

**Table 1. Resin Properties Required for Various Fabrication Methods**

| Process | Viscosity, mPa·s (=cP) | Cure temperature, °C | Thixotropy | Filler, % | Glass, % |
|---|---|---|---|---|---|
| SMC/BMC[a] | 200–2500 | 150 | no | 25–50 | 25–50 |
| hand lay-up | 400–800 | RT | yes | | 20–40 |
| filament winding | 600–2000 | RT-150 | yes and no | | 40–70 |
| pultrusion | 400–2000 | 100–150 | no | 0–20 | 60–80 |
| prepreg | 50, 000+ | 100–150 | no | | 60–80 |
| spray up | 200–1000 | RT | yes | 0–20 | 20–40 |

[a] SMC = sheet molding compound; BMC = bulk molding compound.

drainage. Typically, polyesters are manufactured with styrene concentrations producing resin viscosities of 200 to 1000 mPa·s(=cP), though specialty resins may range from 20 mPa·s(=cP) to 2000 Pa·s(20,000 P). Although styrene monomer dominates the polyester industry, other vinyl monomers are sometimes used in combination with styrene for special purposes. The addition of methyl methacrylate to polyesters improves uv resistance, and the addition of divinyl-benzene [1321-74-0] and diallyl phthalate increases thermal resistance.

### 1.2. Application

Polyesters are cured by free radicals, most commonly produced by the use of peroxides. A wide range of peroxide initiators (qv) are available for use in curing polyesters. Most peroxide initiators are thermally decomposed into free radicals, and the common initiators used at room temperature require the use of a promoter such as dimethylaniline or cobalt octoate.

Because the elevated temperature curing resin systems are thermally activated, they provide a very long time at lower temperatures for fabrication (pot life). Long pot lives make applications such as sheet molding compounds possible; it is the attribute responsible for most of the elevated temperature cure applications. An example of a room temperature curing resin system is 100 parts by weight (pbw) thermosetting polyester resin, 1 pbw methyl ethyl ketone peroxide (90%), and 0.2 pbw cobalt octoate (6%). An elevated temperature curing resin system might include 100 pbw thermosetting polyester resin and 1 pbw di-*tert*-butyl peroxide.

Some characteristics restrict the application of polyesters. Polyesters have a limited shelf life, slowly polymerizing over a period of months at room temperature. The shelf life can be extended by cold storage or the addition of polymerization inhibitors by the manufacturer. Styrene emissions occur during the handling and cure of polyesters, and these emissions have increasingly come under government scrutiny. Cured polyesters have relatively low heat resistance with typical $T_g$'s ranging from 60° to 120°C. The higher $T_g$ resins are normally brittle with tensile elongation of 1% or less at failure. Polyesters are not resistant to ultraviolet light; the matrix slowly erodes on prolonged exposure. Polyesters have limited resistance to alkaline exposure because of the hydrolyzable ester linkages. Short exposure to strong base causes the resin to soften and become sticky; long exposure dissolves it.

Ease of cure, easy removal of parts from mold surfaces, and wide availability have made polyesters the first choice for many fiber-reinforced composite molders. Sheet molding compound, filament winding, hand lay-up, spray up, and pultrusion are all well adapted to the use of polyesters. Choosing the best polyester resin and processing technique is often a challenge. The polyester must be a type that is well adapted to the processing method and must have the final mechanical properties required by the part application. Table 1 lists the desirable properties for a number of fiber-reinforced composite fabrication methods.

Most fabricators of fiber-reinforced composites concentrate on only a few of the possible fabrication processes well suited to the parts they produce. Heat cures are used when a large number of parts are made, maximum properties are needed, or the shortest molding cycle time is required. Heat cures require more rigid and expensive molds, along with presses or other equipment to handle these molds. Molding times with heat cures can be as short as 60 s. Room temperature cures can be done on wood, plaster, or plastic molds. These molds are adequate for short runs and are fairly inexpensive. Room temperature cures normally require molding times of an hour to a day, depending on the ambient temperature, thickness, and complexity of the part.

To optimize the resin system for a given process and part, consideration should be given to fillers that can greatly affect the cost and performance of the composite. Because of their low viscosity, fillers can often be added to polyesters. Fillers are often much cheaper than the resin they displace, and they can improve the heat resistance, stiffness, and hardness of the composite. Certain fillers, such as fumed silica, impart thixotropy to the resin, increasing its resistance to drainage.

### 1.3. Health, Safety, and Environment

Manufacturers of fiber-reinforced polyester composites need to be concerned with proper handling of hazardous wastes, emissions of volatile organic compounds, and a host of recent laws and regulations. Of primary concern is worker exposure to, and plant emissions of, styrene. OSHA permissible exposure limits on air contaminants for 1990 placed an 8-h time-weighted average of 50 ppm for styrene. The listing of styrene as a probable carcinogen has led to increased regulation. Styrene's flammability needs to be considered in plant design and resin handling. California has recently further restricted emissions of volatile organic compounds, resulting in additional expenditures for pollution control equipment on the part of many polyester resin users.

Organic peroxides need to be stored separately from the polyester resins and promoters. If a peroxide is contaminated with a promoter, violent decomposition can result. Promoters should always be thoroughly mixed into the resin prior to the addition of the peroxide to prevent violent peroxide decomposition. Peroxides can become unstable if stored for too long or at too high a temperature. Peroxide manufacturers advice for storage and disposal must be strictly followed.

## 2. Phenolic Resins

Most processors of fiber-reinforced composites choose a phenol formaldehyde (phenolic) resin because these resins are inherently fire retardant, are highly heat resistant, and are very low in cost. When exposed to flames they give off very little smoke and that smoke is of low immediate toxicity. Phenolic resins (qv) are often not chosen, however, because the resole types have limited shelf stability, both resole and novolac types release volatiles during their condensation cure, formaldehyde [50-00-0] emissions are possible during both handling and cure, and the polymers formed are brittle compared with other thermosetting resins.

### 2.1. Manufacture

Phenolic resins are diverse in structure and functionality. A phenol and less than a stoichiometric amount of formaldehyde are condensed with an acid catalyst resulting in a thermoplastic resin termed a *novolac.* These resins are oligomers that are terminated by phenol groups. They require the addition of a curing agent to effect curing. Novolacs are usually solid resins. Condensing phenol and a stoichiometric amount of formaldehyde with an alkaline catalyst and stopping the reaction while the resin is still a thermoplastic results in a resole. Resoles are terminated by methyl groups. They can be cured by heating or by the addition of a catalyst and are normally produced as liquids. The bulk of the phenolic resins used in fiber-reinforced composites are mixtures of novolacs and curing agents.

### 2.2. Application

Curing agents for novolacs are aldehydes or methylene donors. Paraformaldehyde [30525-89-4], hexamethylenetetramine (HEXA) [100-97-0], formaldehyde, propionaldehyde [123-38-6], glyoxal [107-22-2], and hexamethylmethoxymelamine (HMMM), may be used. HEXA is probably the most common novolac curing agent. On heating HEXA breaks down to ammonia and formaldehyde, forming cross-links between the phenol rings.

Resoles can be cured by the addition of base or by heat alone. Their shelf life is thus limited, which is a significant deterrent to their use in fiber-reinforced composites. Resoles are often used in unreinforced applications in electronics and high moisture areas.

The principal limitation on the use of phenolic resins in fiber-reinforced composites is that they are usually solvent borne and as condensation polymers give off volatile by-products during cure. These volatile by-products consist of water or alcohol that produces property-reducing voids in the cured composite. Phenolic resins are often cured under high pressure to reduce these effects. High pressure curing requires more sophisticated and expensive equipment. Considerable efforts have been expended to develop a room temperature curing phenolic resin for hand lay-up. Some recent success has occurred, making phenolic resins a viable alternative to fire-retardant unsaturated polyester resins. Heat-cured phenolic prepregs have almost completely replaced all other thermosetting resins in aircraft and other transit interiors, where flammability and toxicity of combustion products is a prime consideration.

### 2.3. Health and Safety

Free phenols may be present in phenolic novolacs and resoles. Phenol [108-95-2] is poisonous and caustic, irritating the skin and mucous membranes. Formaldehyde and ammonia [7764-41-7] are often emitted during the cure of novolacs and must be properly vented. Formaldehyde is listed as a human carcinogen; worker exposure and emissions are controlled by OSHA and the EPA.

## 3. Epoxy Resins

Currently, epoxy resins (qv) constitute over 90% of the matrix resin material used in advanced composites. The total usage of advanced composites is expected to grow to around 45,500 t by the year 2000, with the total resin usage around 18,000 t in 2000. Epoxy resins are expected to still constitute about 80% of the total matrix-resin-systems market in 2000. The largest share of the remaining market will be divided between bismaleimides and polyimide systems (12 to 15%) and what are classified as other polymers, including thermoplastics and thermoset resins other than epoxies, bismaleimides, cyanate esters, and polyimide systems (see Composites, polymer-matrix–thermoplastics).

The earliest and still the most widely used matrix resins in high performance composites are the bisphenol A based epoxy resin systems. Full-scale commercial production of epoxy resins began in 1950. Initial significant industrial applications of epoxy resins were in surface coatings and also in potting and encapsulation of electrical components. However, by 1952 epoxy resins were being used in electrical laminates and a filament-wound pressure tank for the F-84 jet fighter. Probably the most widely recognized property of cured epoxy resin systems is their excellent adhesion to a very broad range of substrates and reinforcements. A contributing factor is the low shrinkage exhibited by epoxy resin systems during cure, which results in lower stress levels in the composite than is found in other polymer systems with higher shrinkage. Another factor contributing to the excellent strength of articles produced from epoxy resins is that no by-products are formed during cure. Thus, there are no volatiles liberated that can lead to voids nor are nonvolatiles generated that can act as plasticizers.

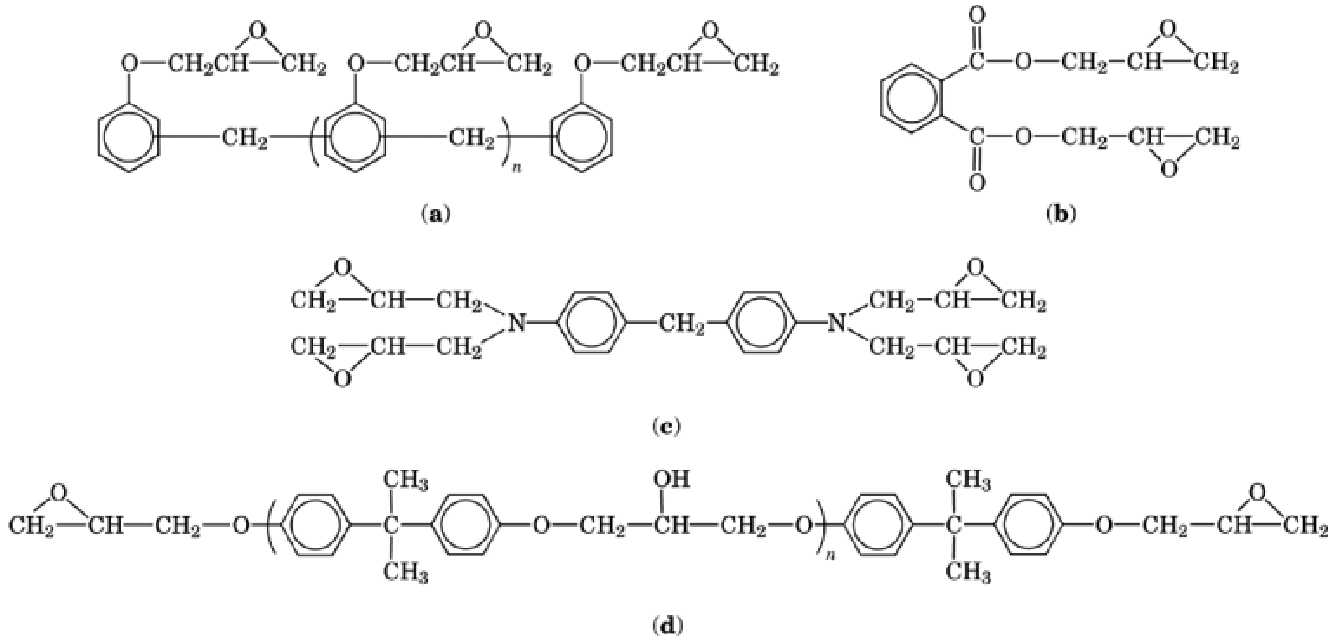


**Fig. 1.** Structures of commercial epoxy resins: (**a**) phenolic novolac epoxy resin, (**b**) glycidated polybasic acid, (**c**) glycidated polyamine (*N,N,N′,N′*-tetraglycidyl-4,4′-diaminodiphenylmethane [28768-32-3] (TGMDA)), and (**d**) glycidated bisphenol A.

Epoxy resins can be generically characterized as a group of commercially available oligomeric materials that contain one or more epoxy (oxirane) groups per molecule. The value of epoxy resins is that they can be processed into a variety of useful products, such as protective coatings, adhesives, and structural components of almost any size and shape, by reaction of the epoxy groups with an appropriate curing agent. The products obtained from epoxy resins that contain more than one epoxy group per molecule are thermosetting polymers.

Figure 1 shows the structures of commercial epoxy resins based on a phenolic novolac, an aromatic diacid, an aromatic polyamine (methylenedianiline), and bisphenol A [80-05-7]. Bisphenol A based epoxy resins make up by far the largest portion of the total epoxy resin market. Currently, about 94% of all the epoxy resin sold in the United States is of the bisphenol A or brominated bisphenol A type. This figure does not include epoxidized oils, which are not customarily cured to make thermoset polymers as are standard epoxy resins. Of the remaining 6%, about 3% is made up of specialty resins such as cycloaliphatics, glycidylamines, glycidyl esters, glycidated aliphatic polyethers, and glycidated multifunctional phenols.

Epoxidized novolacs and high molecular weight epoxy resins, sometimes called phenoxy resins, constitute 2% and 1% of the total market, respectively. In commercial products the $n$ value ranges from 0 to about 25; the thermoplastic or high molecular weight resins have values of $n$ of 200 or more. As $n$ increases, the epoxy equivalent weight, or EEW, increases, as does the number of hydroxyl groups. Thus, epoxy resins with lower $n$ values are normally used with curing agents that react with the epoxy group, whereas those resins with higher *n* values are cured through the hydroxyl functionality. Typical liquid bisphenol A epoxy resins have *n* values of 0 to 1; resins having values greater than 1 are solid.

Liquid resins such as glycidyl esters and bisphenol A epoxy resins are used mainly in ambient temperature cure coatings, electrical castings, flooring, electrical laminates, and fiber-reinforced composites. These applications require low viscosity materials for good flow and are cured through the epoxide ring. The higher *n* value resins, particularly those above 3000 molecular weight, are normally used in solution and find their greatest application in heat-cured finishes. In these resins the concentration of epoxy groups is low, so they are cured with materials that react with the hydroxyl groups along the backbone.

For more demanding uses at higher temperatures, for example, in aircraft and aerospace and certain electrical and electronic applications, multifunctional epoxy resin systems based on epoxy novolac resins and the tetraglycidyl amine of methylenedianiline are used. The tetraglycidyl amine of methylenedianiline is currently the epoxy resin most often used in advance composites. Tetraglycidyl methylenedianiline [28768-32-3] (TGMDA) cured with diaminodiphenyl sulfone [80-08-0] (DDS) was the first system to meet the performance requirements of the aerospace industry and is still used extensively.

### 3.1. Curing Agents

Epoxy resins are reactive intermediates composed of a mixture of oligomeric materials containing one or more epoxy groups per molecule. To convert epoxy resins into useful products they must be cured or cross-linked by chemical reaction into a three-dimensional network. Cross-linking agents, or curing agents, function by reacting with, or causing the reaction of, the epoxide. The two principal classes of curing agents used in epoxy matrix resins for advanced composites are aromatic diamines and anhydrides. Table 2 gives the structures and properties of several of the more commonly used aromatic diamine and anhydride curing agents.

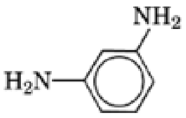
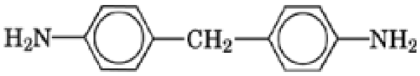
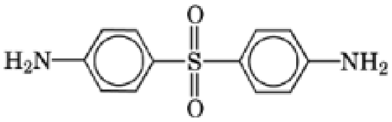
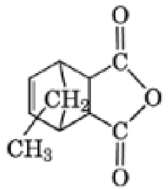
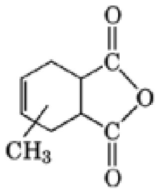
### 3.2. Manufacture

Liquid epoxy resins are generally manufactured from bisphenol A and epichlorohydrin [106-89-8]. Typically, the bisphenol A reacts with epichlorohydrin to give a bischlorohydrin, which is dehydrohalogenated with caustic to give the desired epoxy resin. In practice condensation of the bisphenol A with epichlorohydrin and dehydrohalogenation are carried out simultaneously. A consequence of reacting in this manner is that substantial resin is formed before all the phenolic hydroxyl is consumed, leading to attack by the phenol on the resin epoxide instead of on the epichlorohydrin. Glycidylamines such as tetraglycidyl methylenedianiline (TGMDA) are manufactured by a similar process. However, the glycidation of amine is carried out by a two-step procedure because (*1*) the high reactivity of the basic nitrogen compared with that of the phenolic results in free amine reacting with the epoxide as it is formed, resulting in higher molecular weight or even gelled product, and (*2*) having all the epichlorohydrin in contact with the amine could lead to a highly exothermic reaction (see Epoxy resins).

## 4. High Performance Epoxy Resins

Although bisphenol A resins are used extensively in composites, they are limited by the maximum obtainable glass-transition temperature of the bisphenol A systems, which is generally below 180°–190°C. The glass-transition temperature of cross-linked systems is in part related to the cross-link density of the system, and higher $T_g$s can be obtained through additional cross-linking by using epoxy resins of functionality greater than 2. For example, a liquid bisphenol A resin having an epoxy equivalent weight of 189 when cured by diaminodiphenyl sulfone has an ultimate glass transition temperature of 175°C. Using a tetrafunctional resin, tetraglycidyl methylenedianiline, with the same curing agent results in $T_g$s greater than 250°C.

**Table 2. Structure and Properties of Aromatic Diamines and Acid Anhydrides Used in Epoxy-Matrix Resins**

| Name | CAS Registry Number | | Molecular weight | Amine equivalent weight | Typical usage, phr | Heat-deflection temperature,[a] °C |
|---|---|---|---|---|---|---|
| | | *Diamines* | | | | |
| *m*-phenylenediamine | [108-45-2] |  | 108 | 27 | 14 | 150 |
| 4,4′-methylenedianiline | [101-77-9] |  | 198 | 50 | 27 | 155 |
| 4,4′-diaminodiphenyl sulfone | [80-08-0] |  | 248 | 62 | 18 | 176 |
| | | *Anhydrides* | | | | |
| nadic methyl anhydride | [25134-21-8] |  | 178 | | 80–90 | 128 |
| hexahydrophthalic[b] anhydride | [85-42-7] | | 154 | | 75–80 | 130 |
| methyltetrahydrophthalic anhydride | [71070-44-3] |  | 166 | | 75–80 | 130 |

[a] Deflection temperature obtained with resin having an epoxide equivalent weight (EEW) of 190.

[b] Structure as below; no methyl, no C–C double bond.

Tetraglycidyl methylenedianiline cured with diaminodiphenyl sulfone has been the principal resin system used in high performance composite applications. Although the specific details of most formulated matrix resins are proprietary, formulations of some of the more popular early systems for carbon fiber prepreg based on TGMDA–DDS are given in Table 3. The bisphenol epoxy novolac resin and glycidyl ester are believed to be

**Table 3. Typical Epoxy Resin Prepreg Formulation**

| Properties | System 1 | System 2 | System 3 |
|---|---|---|---|
| resin components, phr | | | |
| tetraglycidyl methylenedianiline[a] | 90 | 100 | 85 |
| bisphenol epoxy novalac[b] | 10 | | |
| diglycidyl phthalate[c] | | | 15 |
| diaminodiphenyl sulfone | 30 | 32.0–32.1 | 34 |
| boron trifluoride complex | | 1.5 | 0.5 |
| resin/fiber, wt % | | | |
| resin | 44.6 | 36.2 | 40.0 |
| T-300 graphite fiber | 58.4 | | |
| AS graphite fiber | | 63.8 | 60.0 |

[a] ARALDITE MY 720 (trademark of CIBA GEIGY Corp.).
[b] Epi-Rez SU-8 (trademark of Rhône Poulenc).
[c] Epi-rez A-100 (trademark of Rhône Poulenc).

formulated into the systems to modify the curing characteristics and tack and drape, respectively. The boron trifluoride complex is added as an accelerator. These matrix resin systems offer a combination of ease of melt processing into prepreg as well as tack and drape of the prepreg and out time.

Current TGMDA systems, however, do not meet all the requirements for advanced composites for future aircraft. Specifically, TGMDA systems lack the necessary hot–wet performance and they are too brittle. These shortcomings are inherent in the basic resin, which is a highly polar molecule having a high level of functionality. Since the early 1980s resin suppliers have been working on new systems to meet the requirements for commercial and military aircraft of the 1990s.

The highly polar nature of the TGMDA–DDS system results in high moisture absorption. The plasticization of epoxy matrices by absorbed water and its effect on composite properties have been well documented. As can be seen from Table 4, the TGMDA system can absorb as much as 6.5% (by weight) water (4). This absorbed water results in a dramatic drop in both the glass transition temperature and hot–wet flexural modulus (4–6).

New products designed to overcome these shortcomings are beginning to appear. The Dow Chemical Company has introduced a glycidyl ether based on a hydrocarbon epoxy novolac (7) under the trade name TACTIX 556. The structure of the resin is given in Figure 2, and the properties of neat resin castings are given in Table 5. This multifunctional epoxy resin has a glass transition temperature of over 223°C when cured with DDS and outstanding moisture resistance and thermal oxidative resistance. Moisture absorption in boiling water is reported to be about 2.4 wt % for TACTIX 556 cured with DDS. Under the same conditions the corresponding TGMDA system has about a 4.5 wt % equilibrium water uptake.

Shell Chemical Company has introduced a new tetraglycidyl amine and a new stiff backbone diglycidyl ether under the respective trade names EPON HPT Resin 1071 [103490-06-8] and EPON HPT Resin 1079 [47758-37-2] (8, 9), which have superior hot–wet performance compared with TGMDA. These two materials are chemically *N,N,N′,N′*-tetraglycidyl-$\alpha$,$\alpha'$bis(4-aminophenyl)-*p*-diisopropylbenzene and diglycidyl-9,9-bis(4-hydroxyphenyl) fluorene. The structures of these two resins are given in Figure 2. As can be seen from Table 5, the moisture gain (after 2 weeks' immersion in water at 93°C) for EPON HPT Resin 1071 and EPON HPT Resin 1079 cured with DDS is 3.7 and 2.8 wt %, compared with 5.7 wt % for the corresponding TGMDA system. This results in a much improved hot–wet performance for these two new resins over TGMDA. Specifically, under hot–wet conditions, under water at 93°C after 2 weeks' immersion at 93°C, the TGMDA system retained only 65% of its dry room temperature modulus, whereas the EPON HPT Resin 1071 and EPON HPT Resin 1079 retained 85 and 91%, respectively, of their dry room temperature modulus under hot–wet conditions.

**Table 4. Effect of Absorbed Water on the Mechanical Properties of the TGMDA–DDS System[a]**

| | Stoichiometry of DDS | |
|---|---|---|
| Properties | 54% | 100% |
| components, phr | | |
| tetraglycidyl methylenedianiline | 100 | 100 |
| bisphenol A epoxy novolac[b] | 8.2 | 8.2 |
| 4,4-diaminodiphenyl sulfone | 28.0 | 51.9 |
| glass-transition temperature, °C | | |
| dry | 242 | |
| wet | 174 | |
| flexural properties, RT/dry | | |
| strength, MPa[c] | 117 | 131 |
| modulus, GPa[d] | 4.0 | 3.0 |
| elongation, % | 3.5 | 4.7 |
| flexural properties, hot/wet[e] | | |
| strength, MPa[c] | 84 | 74 |
| modulus, GPa[d] | 3.2 | 24 |
| elongation, % | 3.4 | 3.7 |
| moisture gain, wt %[f] | 4.7 | 5.8 |

[a] Cured 2 h at 150° and 4 h at 200°.

[b] Epi-Rez SU-8 (trademark of Rhône Poulenc).

[c] To convert MPa to psi, multiply by 145.

[d] To convert GPa to psi, multiply by 145,000.

[e] Tested in water at 93°C after 2 weeks' immersion at 93°C.

[f] Conditioned 2 weeks at 93°C.

**Table 5. Mechanical Properties of High Performance Epoxy Resins[a] in Unreinforced Resin Castings**

| Properties | TGMDA | EPON HPT[b] 1071[c] | EPON HPT[b] 1079[c] | TACTIX[d,e] |
|---|---|---|---|---|
| $T_g$, °C | | 249 | 279 | 556 |
| flexural properties RT/dry | | | | |
| strength, MPa[f] | 138 | 117 | 124 | 136 |
| modulus, GPa[g] | 3.9 | 3.9 | 3.3 | 3.1 |
| elongation, % | 5.0 | 3.7 | 4.7 | |
| flexural properties hot/wet[h] | | | | |
| strength, MPa[f] | 76 | 90 | 90 | |
| modulus, GPa[g] | 2.5 | 3.4 | 3.0 | 3.0[h] |
| elongation, % | 4.7 | 3.6 | 4.1 | |
| moisture gain, wt %[i] | 5.7 | 3.6 | 2.8 | 2.4[j k] |

[a] Resin cured with 100% diaminodiphenylsufone.

[b] Trademark of Shell Chemical Co.; see Fig. 2.

[c] Cured 2 h at 150° C and 4 h at 200°C.

[d] Trademark of The Dow Chemical Company.

[e] Cured 3 h at 177°C and 2 h 232°C.

[f] To convert MPA to psi, multiply by 145.

[g] To convert GPa to psi, multiply by 145,000.

[h] Tested in water at 93°C after 2 weeks' immersion at 93°C.

[i] Specimens conditioned 200 h in boiling water.

[j] Conditioned 2 weeks in 93°C water.

[k] Conditioned 200 h in boiling water.

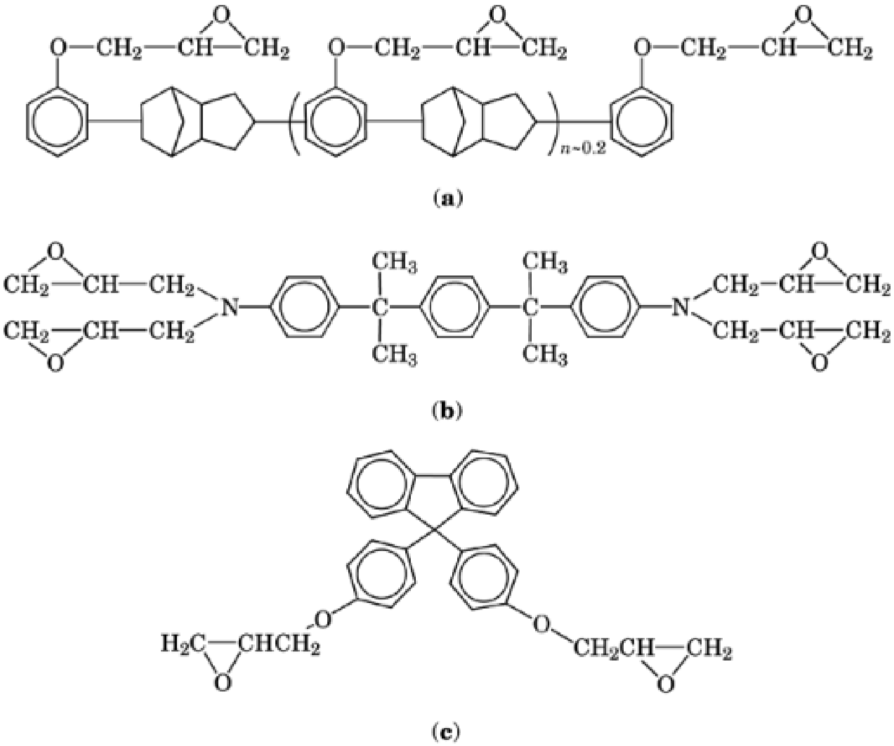


**Fig. 2.** Epoxy matrix resins for advanced composites: (**a**) TACTIX 558 (Courtesy of The Dow Chemical Company), (**b**) EPON HPT Resin 1071 (Courtesy of Shell Chemical Co.), and (**c**) EPON HPT Resin 1079.

Although changes in the structure of highly functional epoxy resins have resulted in improved hot–wet performance, brittleness is an inherent property of highly cross-linked systems. Improvements in ductility, fracture resistance, and impact strength, however, can be achieved without substantially degrading the thermal and mechanical properties of the epoxy matrix. For example, carboxyl terminated butadiene–acrylonitrile copolymer, which is initially soluble in conventional bisphenol A epoxy resins, forms a second phase of dispersed particles on cure, resulting in an epoxy resin system with improved toughness (10). The degree to which any epoxy resin system can be toughened depends on many factors, including the type of modifier, heterophase size distribution, interfacial adhesion between the heterophase and the matrix, combination of resin and curing agent, cure conditions, and molecular weight between cross-links in the matrix. A thorough and critical review of all the variables affecting the ability to toughen epoxy resin systems is beyond the scope of this discussion (see Ref. 11).

The use of elastomeric modifiers for toughening thermoset resins generally results in lowering the glass transition temperature, modulus, and strength of the modified system. More recently, ductile engineering thermoplastics and functional thermoplastic oligomers have been used as modifiers for epoxy matrix resins and other thermosets (12).

### 4.1. Applications

Epoxy resins constitute over 90% of the matrix resin material used in advanced composites. In addition, epoxy resins are used in all the various fabrication processes that convert resins and reinforcements into composite

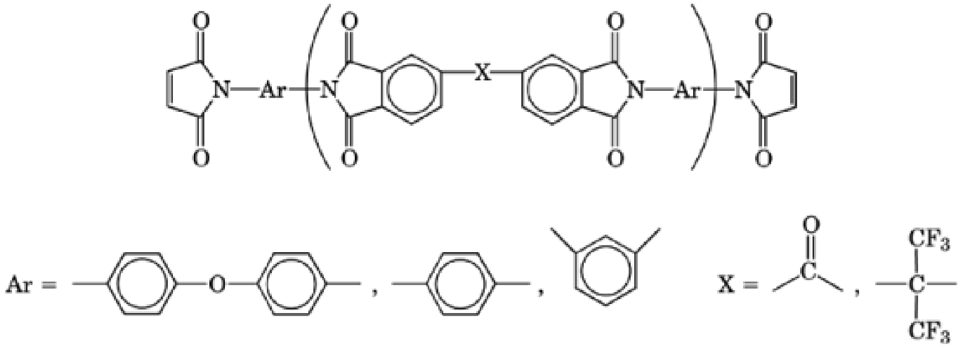


Fig. 3. Structures of bismaleimide resins.

articles. Liquid resins in combination, mainly, with amines and anhydride are used for filament winding, resin transfer molding, and pultrusion. Parts for aircraft, rocket cases, pipes, rods, tennis rackets, ski poles, golf club shafts, and fishing poles are made by one of these processes with an epoxy resin system.

## 5. Bismaleimides

Bismaleimides (BMI) are a relatively young class of thermosetting polymers that are gaining acceptance by the industry because they combine a number of unique features including excellent physical property retention at elevated temperatures and in wet environments, almost constant electrical properties over a wide range of temperatures, and nonflammability properties. Bismaleimides have become a leading class of thermosetting polyimides. Their excellent processibility and balance of thermal and mechanical properties have made them popular in advanced composites and electronics.

Bismaleimides are best defined as low molecular weight, at least difunctional monomers or prepolymers, or mixtures thereof, that carry maleimide terminations (Fig. 3). Such maleimide end groups can undergo homopolymerization and a wide range of copolymerizations to form a highly cross-linked network. These cure reactions can be effected by the application of heat and, if required, in the presence of a suitable catalyst. The first patent for cross-linked resins obtained through the homopolymerization or copolymerization of BMI was granted to Rhône Poulenc, France, in 1968 (13). Shortly after, a series of patents was issued on poly(amino bismaleimides) (14), which are synthesized from bismaleimide and aromatic diamines.

A number of BMI resins based on this chemistry became commercially available through Rhône Poulenc for application in printed circuit boards and molding compounds and Rhône Poulenc recognized the potential of bismaleimides as building blocks for temperature-resistant thermoset systems. The basic chemistry, however, was not new, because the Michael addition reaction had been employed by Du Pont to obtain elastomeric reaction products from bismaleimides and liquid polymeric organic diamines (15).

Following the initial patent disclosures, research organizations worldwide have worked in this new area as evidenced by approximately 500 patent applications in the following 20 years. Numerous chemical modifications can be carried out (16) and mixtures formulated to improve rheology and cured resin properties. Melt processible bismaleimide systems specifically designed for fiber reinforced applications are disclosed in a U.S. patent granted to Technochemie (17). The approach of blending selected bismaleimide monomers and further formulating them with reactive diluents or comonomers provided formulated bismaleimide resins that are equivalent in processing to the conventional 177°C service epoxy resins. The breakthrough with respect to application as tacky autoclavable prepreg was achieved by US-Polymeric (now British Petroleum Chemicals) with their V378A BMI system (18). This system was used to build the delta wings of the General Dynamics F16XL demonstrator combat aircraft (19) and found application for parts of the McDonnel Douglas AV8-B vertical takeoff aircraft (20).

The principal concern with BMI resins has been their inherent brittleness owing to their high cross-link density. Ciba Geigy, however, demonstrated that BMI–*o,o*′-diallylbisphenol A copolymers are tougher than TGMDA–DDS epoxy resins (21). The *o,o*′-diallylbisphenol A–BMI copolymers were patented in Switzerland in 1975, but the significance of this invention, that is, their toughness, was not recognized before toughness became an issue to the aerospace industry. Experience has taught that a useful BMI-resin system comprises both a bismaleimide part (the BMI resin) and a comonomer part (reactive diluent).

### 5.1. Building Blocks and Systems

A standard synthesis of *N,N*′-arylene bismaleimide involves the chemical dehydration of *N,N*′-arylene bismaleamic acid with acetic anhydride [108-24-7] and sodium acetate [127-09-31] as a catalyst at temperatures below 80°C (22). The yield of pure recrystallized BMI is usually 65–75%. Various by-products, such as isoimides and acetanilides, are responsible for the relatively low yield of pure BMI (23). Almost every aromatic amine (diamine) can be converted to the corresponding maleimide (bismaleimide). The most widely used building block is 4,4′-bismaleimidodiphenylmethane [13676-54-5], because the precursor diamine is readily available and cheap. Bismaleimides based on aromatic diamines are crystalline substances with high melting points. Table 6 gives the chemical structures and melting points of bismaleimides based on substituted and isomeric diphenylmethanes. Of interest to resin formulators, whose aim is to achieve unique properties in resins and adhesives, are the melting points and polymerization characteristics, which are used to tailor the flow and cure properties of their products. For reasons of processibility BMIs with low melting points are the preferred building blocks.

**Table 6. Structures and Properties of Bismaleimides**

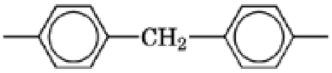
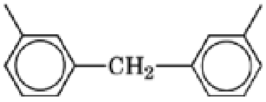
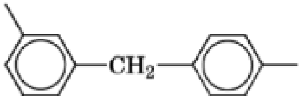
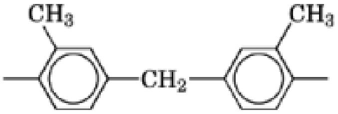
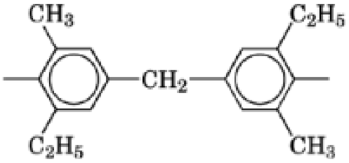
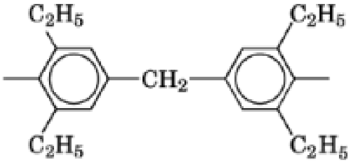
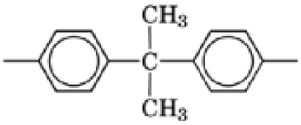
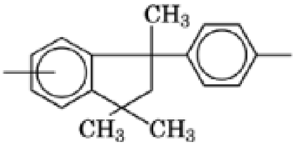
| R[a] | Mp, °C | $T_{\max}$[b], °C | $\Delta H_{\mathrm{pol}}$[c], J/g[d] |
|---|---|---|---|
|  | 155–157 | 235 | 198 |
|  | 195–196 | | |
|  | 164–165 | | |

**Table 6.** ***Continued***

| R[a] | Mp, °C | $T_{\max}$[b], °C | $\Delta H_{\mathrm{pol}}$[c], J/g[d] |
|---|---|---|---|
|  | 210–212 | | |
|  | 150–154 | 298 | 187 |
|  | 149–151 | 328 | 206 |
|  | 235 | 290 | 216 |
|  | 90–100 | 203 | 89 |

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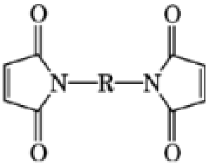
[a]



[b] From differential scanning calorimetry (dsc) data from Technochemie GmbH–Verfahrenstechnik. Heating rate = 10°C/min; $T_{\max}$ = cure exotherm peak maximum.

[c] $\Delta H_{\mathrm{pol}}$ = heat of polymerization from dsc data.

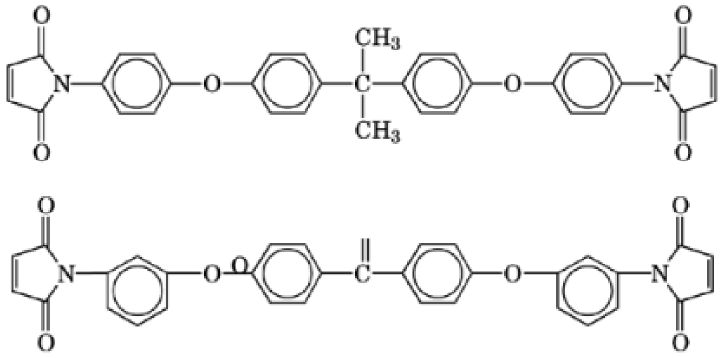


**Fig. 4.** Bismaleimides of polyaromatic diamines.

[d] To convert J to cal, divide by 4.184.

The order of melting transitions for the diphenylmethane bismaleimides is surprising (Table 6) because the 4,4′-MDA-BMI melts lower (155–157°C) than the 3,3′-MDA-BMI. The tetra alkyl-4,4-MDA-BMI also melts around 150°C. The BMI based on the isomeric diphenylindane diamine (24) is very low melting because it is a complex blend of various isomers.

The most important property of a bismaleimide is its ability to undergo a temperature-induced polymerization. The maleimide double bond is highly activated owing to the adjacent carbonyl groups of the imide ring; therefore, heating the BMI above its melting point effects polymerization. The cure exotherm peak temperature taken from a dynamic dsc scan is used to characterize the reactivity of individual BMIs. The reactivity is influenced by the chemical nature of the residue between the maleimide terminations and by the molar mass between the reactive maleimide groups. Normally, electron-donating groups, such as alkyl groups, reduce the BMI reactivity, provided that they are present in the maleimide rings that carry the maleimide groups. On the other hand, electron-attracting groups such as $SO_2$, carbonyl, and so on, have the opposite effect. Increasing the molecular weight between cross-links ($M_c$) generally provides a more latent system owing to steric effects.

The BMI-building blocks primarily used in commercial bismaleimide resins are 4,4′-bismaleimidodiphenylmethane, 2,4-bismaleimidotoluene [6422-83-9], 1,3-bismaleimidobenzene [3006-93-7], and, sometimes, aliphatic BMIs based on *n*-alkanes. However, because of toxicity problems associated with MDA (4,4′-diaminodiphenylmethane) and other diamines with only one or two aromatic rings, polyaromatic diamines and BMIs based on them are of increasing interest (Fig. 4) (see Amines, aromatic—Methylenedianiline).

In the past, it was almost impossible to introduce novel BMI building blocks with increased molecular weight because of the processing problem associated with high melting points and high melt viscosities. With new processing techniques, such as powder prepregging and blending with liquid reactive diluents such as *o,o*′-diallylbisphenol A [1745-89-7], such limitations could be partially overcome. It is questionable, however, whether such expensive building blocks will find application in commercial bismaleimide systems.

Besides low molecular weight building blocks, long-chain maleimide-terminated oligomers have been synthesized for molding, adhesive, and composite applications. The key step is the preparation of an amine-terminated intermediate needed to introduce the maleimide group. For example, long-chain thermosetting arylimides synthesized from long-chain sulfone–ether diamines and maleic anhydride have been described. The resulting bisamic acid was cyclodehydrated in the usual way with acetic anhydride–sodium acetate (25).

The cured arylimides are heat stable systems possessing high glass transition temperatures ($T_g$) and moderate to high modulus plateaus above their $T_g$, depending on the molecular weight between the (maleimide)

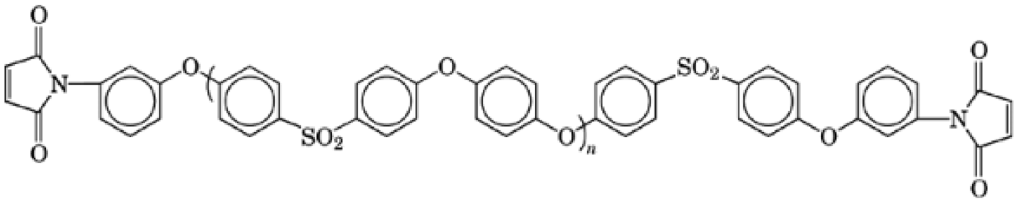
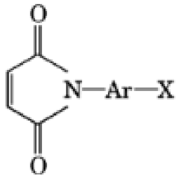


**Fig. 5.** Structure of a maleimide-terminated sulfone–ether prepolymer.

cross-links. The sulfone–ether backbone (see Fig. 5) alleviates problems associated with solubility of the uncured material. High solids solutions can be prepared in common organic solvents.

Other backbone structures that have generated a great interest are the polyether ketones. An attempt was made to synthesize amino-terminated arylene ether ketones, which were subsequently converted into the corresponding maleimide-terminated oligomers (26). The aim of this approach was to obtain tough, solvent-resistant, high temperature thermosets.

The common synthetic route to bismaleimides or maleimide functionalized oligomers is the condensation of diamines or amino-terminated oligomers with maleic anhydride. Another possibility is the use of an AB-type monomer of the following general formula to build the polymaleimide, where X represents a functional group that can be employed in condensation reactions.



The maleimide is prebuilt into the molecule in a separate step. Maleimidobenzoic acid [17075-07-7] or its acid halide was used to synthesize maleimide-terminated polyamides (16, 17) or polyesters (27) from amino- or hydroxy-terminated polyamides and polyesters, respectively. The literature on bismaleimide prepolymers and bismaleimide building blocks is quite extensive (28), but only a limited number of BMI building blocks have been used for commercial resin formulations.

### 5.2. Bismaleimide Resin Concepts

The bismaleimide building block is not the final resin product. Although building blocks usually make up 50–75% by weight of the resin, other ingredients, such as comonomers, reactive diluents, processing additives, elastomers, and catalysts, are combined with BMI so as to obtain a product suitable for the application considered. The application areas for bismaleimide resins are reinforced composites for printed circuit boards (with glass fabric), structural laminates (with glass, carbon, and aramid fibers), and moldings (with short fibers and particulate filters).

In order to fulfill the processing requirements, bismaleimide building blocks have to be formulated into products that enable their use as highly concentrated solutions, powders, or hot melts.

An early attempt in BMI modification with respect to achieving a meltable, noncrystalline resin was made by blending a complex combination of bismaleimides and crystallization inhibitors (29). The resin (COMPIMIDE 353 [51569-11-0], now Shell Chemical Company/Technochemie), although it is not a formulated product, shows a very low melting transition and is a low viscosity fluid at 110°C. (Table 7). Such noncrystalline low

**Table 7. COMPIMIDE 353 Resin Data**

| Property | Test method[a] | Value | Comment |
|---|---|---|---|
| physical form | | | resolidified melt |
| appearance | | | yellow–red brown transparent mass |
| gel time, min | DIN 16945 | 35–65 | |
| viscosity mPa·s(=cP) | DIN 16945 | 400–1400 | |
| dsc | | | |
| $T_B$, °C | TC–TM 14 | 193 ± 10 | heating rate 20°C/min |
| $T_{max}$, °C | | 275 ± 15 | |
| polymerization energy, J/g[b] | TC–TM 14 | $\Delta H$220 ± 40 | |
| composition | TC–TM 25 | comparison with standard | hplc |

[a] DIN = German industry norm; TC − TM = Technochemie test method.
[b] To convert J to cal, divide by 4.184.

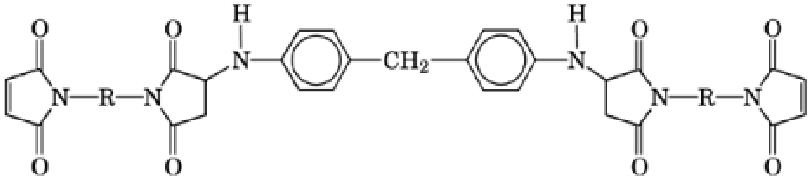


**Fig. 6.** Michael addition product of bismaleimide.

melting BMI resins can be further formulated with a wide range of vinyl (or allyl, etc), compounds to provide prepreg resins that are tacky at room temperature and suitable for low pressure autoclave molding.

The divinylbenzene approach to modify BMI into a hot-melt prepreg resin was followed by US-Polymeric (18). The resin system, known in the industry under the trade name V-378A, was the first BMI formulation used in a primary aircraft application (30). Although this resin is relatively brittle in comparison with epoxy resins, it provides outstanding high temperature mechanical properties in both dry and wet environments. V 378 A prepreg can be cured under standard low autoclave pressure of 0.7 MPa (7 bars) and temperatures similar to current 177°C curing epoxy systems. However, postcure temperatures of 245–260°C are required to maximize elevated temperature strength retention.

### *5.2.1. Michael Additions*

The reaction of a bismaleimide with a functional nucleophile (diamine, bisthiol, etc) via the Michael addition reaction converts a BMI building block into a polymer. The nonstoichiometric reaction of an aromatic diamine with a bismaleimide was used by Rhône Poulenc to synthesize polyaminobismaleimides as shown in Figure 6 (31).

The reaction product of 4,4′-bismaleimidodiphenylmethane and 4,4′-diaminophenylmethane, known as Kerimide 601 [9063-71-2], is prepolymerized to such an extent that the resulting prepolymer is soluble in aprotic solvents such as *N*-methylpyrrolidinone [872-50-4], dimethylformamide [68-12-2], and the like, and therefore can be processed via solution techniques to prepreg. Kerimide 601 is mainly used in glass fabric laminates for electrical applications and became the industry standard for polyimide-based printed circuit boards (32).

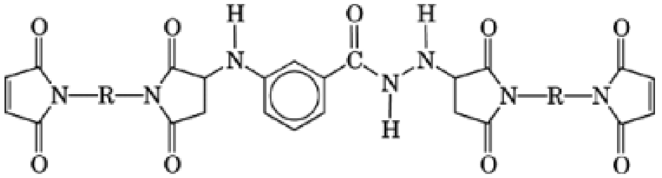
Another approach to processible bismaleimide resins via a Michael addition chain extension, is the reaction of bismaleimide, or a low melting mixture of bismaleimides, with aminobenzoic hydrazide to provide a resin that is soluble in various solvents, such as acetone [67-64-1], methylene chloride [75-09-2], and

**Table 8. Properties of BMI[a] Printed Circuit Laminates[b]**

| Properties | Value |
|---|---|
| dielectric constant (1 MHz) | 4.6–4.7 |
| dielectric loss constant (1 MHz) | 0.01 |
| dielectric strength, V/μm | 29.5 |
| volume resistivity, Ω·cm | $10^{15}$ |
| water absorption,[c] % | <1 |
| peel strength of copper foil,[d] N/mm | 1.2–1.4 |
| heat stability at 287°C, s | >60 |
| thermal expansion coefficient, $10^6$/°C | |
| *x,y* direction | 14–16 |
| *z* direction | 36–38 |
| flammability in comparison with UL 94[e] | $V^0$–$V^1$ |

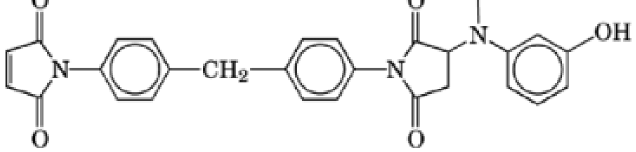
[a] COMPIMIDE 183.
[b] Properties measured using 1–1.5 mm laminates; glass fabric U.S. 2116, resin content 45% by weight.
[c] After postcuring at 210°C.
[d] Gould TC polyimide grade 35-μm thickness; to convert N/mm to ppi, divide by 0.175.
[e] $V^0$ rating for 3-mm laminates; $V^1$ rating for 1.5-mm laminates.

dimethylformamide [68-12-2] (33). The idealized chemical structure for a 2:1 BMI–aminobenzoic hydrazide resin is as follows:



Two resin systems based on this chemical concept are commercially available from Shell Chemical Company/Technochemie under the COMPIMIDE trademark: COMPIMIDE 183 (34) [98725-11-2], for use in printed circuit boards, and COMPIMIDE 796 [106856-59-1], as a resin for low pressure autoclave molding (35). Typical properties of COMPIMIDE 183 glass fabric–PCB laminates are provided in Table 8. COMPIMIDE 183 offers a combination of advantageous properties, such as a high glass transition temperature, low expansion coefficient, and flame resistance without bromine compound additives.

The Michael addition reaction has attracted many researchers as a route to convert high melting BMI building blocks into resins with improved processibility as compared with the BMI precursors. Heat-resistant resin compositions are prepared from BMI and *para*- or *meta*-aminophenol (38). The idealized structure of such a BMI–*m*-aminophenol adduct follows.



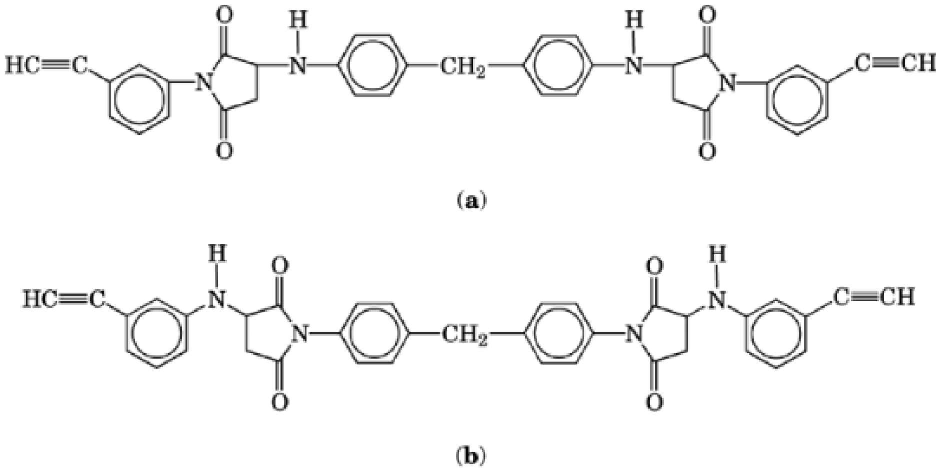
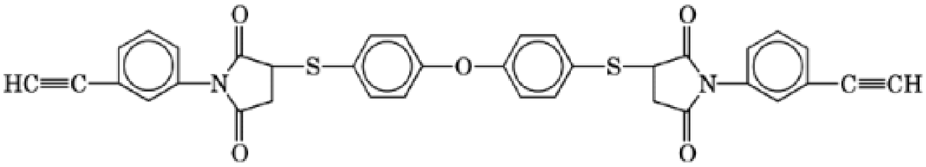


**Fig. 7.** Acetylene-terminated aspartimides. (**a**) Reaction of aromatic diamine with *N*-(3-ethynylphenyl)maleimide [105280-01-1] in a 1:2 molar ratio yields a prepolymer of this general formula. (**b**) Bismaleimide reacts with 3-ethynylaniline [54060-30-9] in a 1:2 molar ratio to yield a prepolymer of this general formula.

BMI–*m*-aminophenol adducts can further react with epoxy resin and subsequently be cured with imidazole catalyst. 1:2 BMI–aminophenol adducts have been used as curing agents for epoxy resin (37).

An interesting approach to thermosetting acetylene-terminated polyimides via the Michael addition reaction has appeared (38). Acetylene-terminated aspartimides are readily prepared in high yield via two routes, shown in Figure 7.

The Michael addition of nucleophiles to the carbon–carbon double bond of maleimide has been exploited in the synthesis of a variety of linear polymers through reaction of bismaleimide with bisthiols (39). This method has been used to synthesize ethynyl-terminated imidothioether from the reaction of 4,4′-dimercaptodiphenyl ether [17527-79-6] and *N*-(3-ethynylphenyl)maleimide (40). The chemical structure of this Michael addition imide thermoset is as follows:



The Michael addition reaction of amines and thiols with bismaleimides or functionalized monomaleimides is a versatile tool in the synthesis of chain-extended maleimide-terminated prepolymers. These prepolymers generally are soluble in organic solvents from which they can be processed to prepreg and molded to high quality, void-free laminates.

### *5.2.2. Bismaleimide Resins via ENE Reaction*

The copolymerization of a BMI with *o,o*′-diallylbisphenol A [1745-89-7] (DABA) is a resin concept that has been widely accepted by the industry because BMI–DABA blends are tacky solids at room temperature and therefore provide all the desired properties in prepregs, such as drape and tack, similar to epoxies. Crystalline BMI can easily be blended with DABA, which is a high viscosity fluid at room temperature. Upon heating BMI–DABA blends copolymerize via complex ENE and Diels-Alder reactions as outlined in Figure 8.

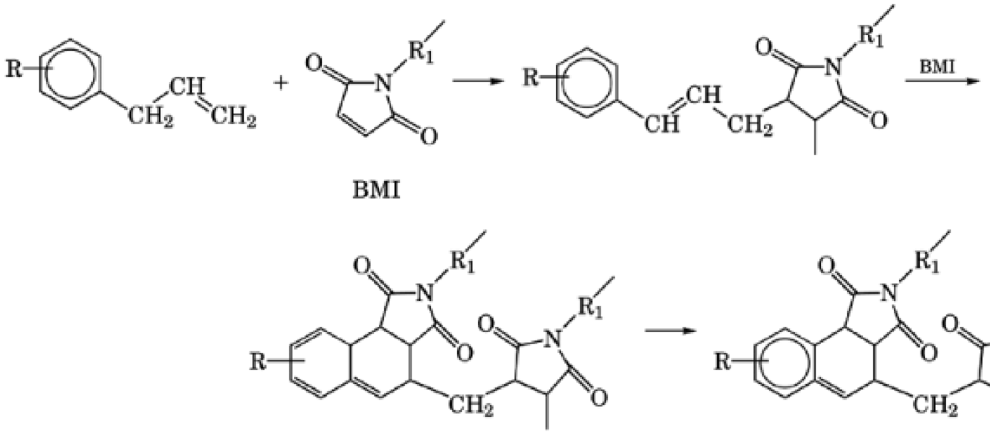
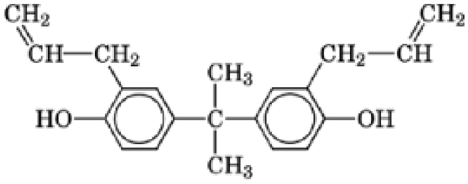


**Fig. 8.** Polymerization of bismaleimides with *o,o*′-diallylbisphenol A via complex ENE–Diels-Alder reactions.

Reportedly, *o,o*′-diallylbisphenol A is an attractive comonomer for bismaleimides because the corresponding copolymer is tough and temperature resistant (41). Toughness, however, is a function of the BMI–diallylbisphenol A ratio employed. In one study optimized toughness properties were achieved when BMI and diallylbisphenol were employed at a close to 2:1 molar ratio (42). In Table 9, the mechanical properties of BMI–bis(3-allyl-4-hydroxyphenyl)-*p*-diisopropylbenzene resins are provided, showing optimized properties for the 60/40 BMI–diallylbisphenol composition. The *o,o*′-diallylbisphenol A is commercially available under the trademark Matrimide 5292. Another bisallylphenyl compound is available from Shell Chemical Company/Technochemie under the trademark COMPIMIDE 121.



*o,o*′-diallylbisphenol A

Both materials meet the processing requirements of the industry because they are honeylike fluids at room temperature and low viscosity liquids between approximately 70° and 90°C and thus act as reactive diluents and tougheners at the same time.

The synthesis of bis[3-(2-allylphenoxy)phthalimides] and their copolymer properties with BMI have been reported (43). These allylphenoxyimide–BMI copolymers provide toughness and temperature resistance when used in carbon fiber laminates (44).

### 5.2.3. Diels-Alder Copolymers

The Diels-Alder reaction can also be employed to obtain thermosetting polyimides. If bismaleimide (the bisdienophile) and the bisdiene react nonstoichiometrically, with bismaleimide in excess, a prepolymer carrying maleimide terminations is formed as an intermediate, which can then be cross-linked to yield a temperature-resistant network.

**Table 9. Mechanical Properties of BMI–bis(3-allyl-4-hydroxyphenyl)-*p*-diisopropylbenzene Blends**[a]

| | Composition, % BHPDB | | | |
|---|---|---|---|---|
| Property[b] | 20 | 30 | 35 | 40 |
| flexural properties[c] | | | | |
| room temperature | | | | |
| strength, MPa[d] | 117 | 133 | 140 | 160 |
| modulus, GPa[e] | 4.69 | 4.48 | 4.09 | 4.46 |
| elongation, % | 2.48 | 3.00 | 3.46 | 3.78 |
| 177°C | | | | |
| strength, MPa[d] | 90 | 107 | 117 | 133 |
| modulus, GPa[e] | 3.75 | 3.59 | 3.39 | 3.47 |
| elongation, % | 2.42 | 2.76 | 3.32 | 4.56 |
| 250°C | | | | |
| strength, MPa[d] | 79 | 84 | 90 | 75 |
| modulus, GPa[e] | 2.86 | 2.91 | 2.89 | 2.79 |
| elongation, % | 2.90 | 3.22 | 4.44 | >5 |
| fracture energy, $G_{\mathrm{Ic}}$, J/m$^2$[f] | 30 | 60 | 98 | 217 |
| moisture gain[g], % | 3.33 | 3.02 | 3.04 | 3.18 |

[a] BMI is a eutectic bismaleimide blend; the other component is abbreviated BHPDB.

[b] Cure cycle: 3 h at 160°C, 4 h at 210°C, and 5 h at 240°C.

[c] Flexural properties were determined dry at various temperatures.

[d] To convert MPa to psi, multiply by 145.

[e] To convert GPa to psi, multiply by 145,000.

[f] To convert J/m$^2$ to ft lbf/in.$^2$, divide by 2100.

[g] 1000 h, 94% RH, 70°C.

Styrene can react with bismaleimide via a complex Diels-Alder-ENE route in a 1:2 stoichiometric ratio as outlined in Figure 9. Other vinylbenzene compounds, such as propenylphenoxydiphenyl sulfone [106818-12-6] (45) and bis(*o*-propenylphenoxy)benzophenone [109423-33-8] (46), react in a similar way with bismaleimide. Their synthesis involves a straightforward nucleophilic halogen displacement reaction. *o*-Allylphenol [1745-81-9] reacts with 4,4′-dichlorodiphenyl sulfone [80-07-9] or 4,4′-difluorobenzophenone [345-92-6] at 160°C in *N*-methylpyrrolidinone [872-30-4] as a solvent in the presence of potassium carbonate [584-08-7] as a catalyst. The alkaline reaction conditions are responsible for the $o{-}\text{allyl} \longrightarrow o{-}\text{propenyl isomerization}$. A wide variety of structurally similar bis(propenylphenoxy) compounds are possible by simply using *p*-substituted allylphenols (eugenol) or isomeric dihalosulfones or dihalobenzophenones in the synthesis. The bis(*o*-propenylphenoxy) compounds are low melting, low viscosity materials that can easily be melt blended with bismaleimide and then cured at temperatures of 170–230°C. Table 10 provides the mechanical properties of a series of cured resins. These copolymer resins are attractive because they show improved toughness and reduced moisture absorption in comparison with the unmodified BMI, and also have a lowered glass-transition temperature. Bis(*o*-propenylphenoxy)benzophenone resins are commercially available from Shell Chemical Company/Technochemie under the trademark COMPIMIDE 123 [109423-33-8].

Propenylphenoxy compounds have attracted much research. BMI–propenylphenoxy copolymer properties can be tailored through modification of the backbone chemistry of the propenylphenoxy comonomer. Epoxy resins may react with propenylphenol (47, 48) to provide functionalized epoxies that may be low or high molecular weight, liquid or solid, depending on the epoxy resin employed. Bis[3-(2-propenylphenoxy)phthalimides] have been synthesized from bis(3-nitrophthalimides) and *o*-propenylphenol sodium involving a nucleophilic nitro displacement reaction (49). They copolymerize with bismaleimide via Diels-Alder and provide temperature-resistant networks.

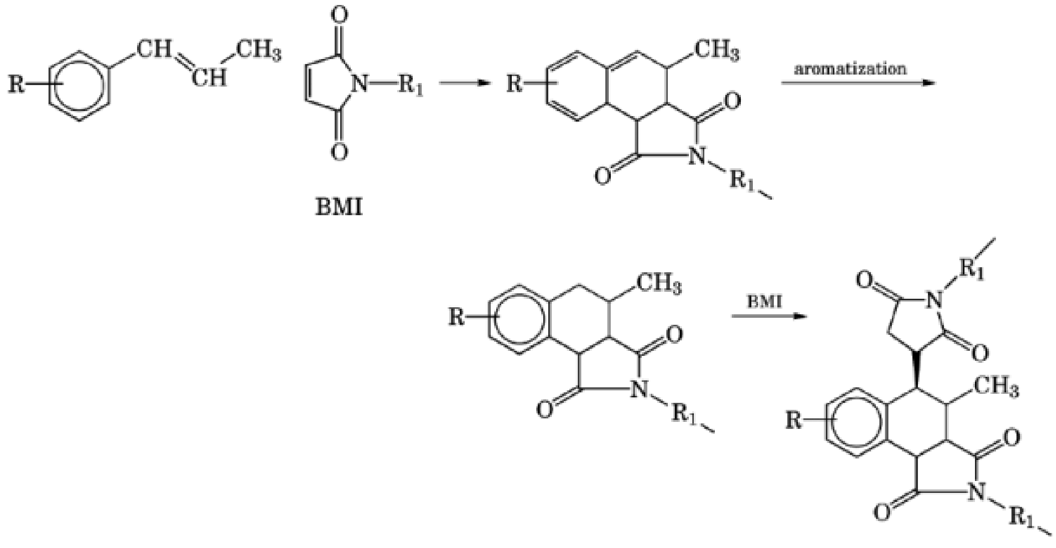


**Fig. 9.** Reaction of $\beta$-methylstyrene with a bismaleimide via a complex Diels-Alder-ENE route.

**Table 10. Mechanical Properties of Bismaleimide Diels-Alder Resins**[a]

| | | Flexural strength MPa[c] | | Flexural modulus, GPa[d] | | Flexural Elongation, % | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| BMI,[a] % | Composition toughener,[b] % | 23°C | 250°C | 23°C | 250°C | 23°C | 250°C | $G_e$, J/m$^2$[e] | $T_g$[f], °C | Water absorption, % |
| 100 | | 76 | 31 | 4.64 | 3.03 | 1.7 | 1.03 | 63 | >300 | 4.30 |
| 82 | 18[g] | 98 | 70 | 3.99 | 2.93 | 2.49 | 2.37 | 185 | 285 | 4.00 |
| 60 | 40[g] | 114 | 73 | 3.58 | 2.15 | 3.20 | 4.50 | 267 | 256 | 2.90 |
| 80 | 20[h] | 87 | 56 | 3.85 | 2.82 | 2.3 | 2.0 | 234 | 300 | 3.74 |
| 60 | 40[h] | 128 | 83 | 3.49 | 2.38 | 3.9 | >5 | 378 | 277 | 3.63 |
| 80 | 20[i] | 106 | 65 | 3.96 | 2.66 | 2.34 | 2.52 | 191 | 275(266) | 3.66 |
| 60 | 40[i] | 132 | 56 | 3.70 | 1.71 | 3.75 | 4.86 | 439 | 261(249) | 2.59 |
| 80 | 20[j] | 114 | 78 | 4.17 | 2.47 | 2.87 | 3.73 | 247 | 273(252) | 3.46 |
| 60 | 40[j] | 122 | 81 | 3.59 | 2.44 | 3.44 | 4.52 | 466 | 265(260) | 2.90 |

[a] BMI = COMPIMIDE796·
[b] Diphenyl sulfones or benzophenones as indicated.
[c] To connect MPa to psi, multiply by 145.
[d] To convert GPa to psi, multiply by 145,000.
[e] To convert J/m$^2$ to ftlbf/in.$^2$, divide by 2100.
[f] By dma analysis. Values in parens by tma analysis.
[g] 4,4′Bis(*o*-propenylphenoxy)diphenyl sulfone.
[h] 4,4′Bis(*o*-methoxy-*p*-propenylphenoxy)diphenyl sulfone.
[i] 4,4′Bis(*o*-propenylphenoxy)benzophenone.
[j] 4,4′Bis(*o*-methoxy-*p*-propenylphenoxy)benzophenone.

Under appropriate thermal conditions, the strained four-membered ring of benzocyclobutene undergoes electrocyclic ring opening to generate, *in situ, o*-chinodimethane, which, in the presence of bismaleimide, reacts via a Diels-Alder reaction (50). The chemistry of the BMI–benzocyclobutene copolymerization is provided in Figure 10. Both bismaleimide and bisbenzocyclobutene can undergo thermal homopolymerization. Therefore, blends of bismaleimide (BMI) and bisbenzocyclobutene (BCB) with either BMI or BCB in excess provide

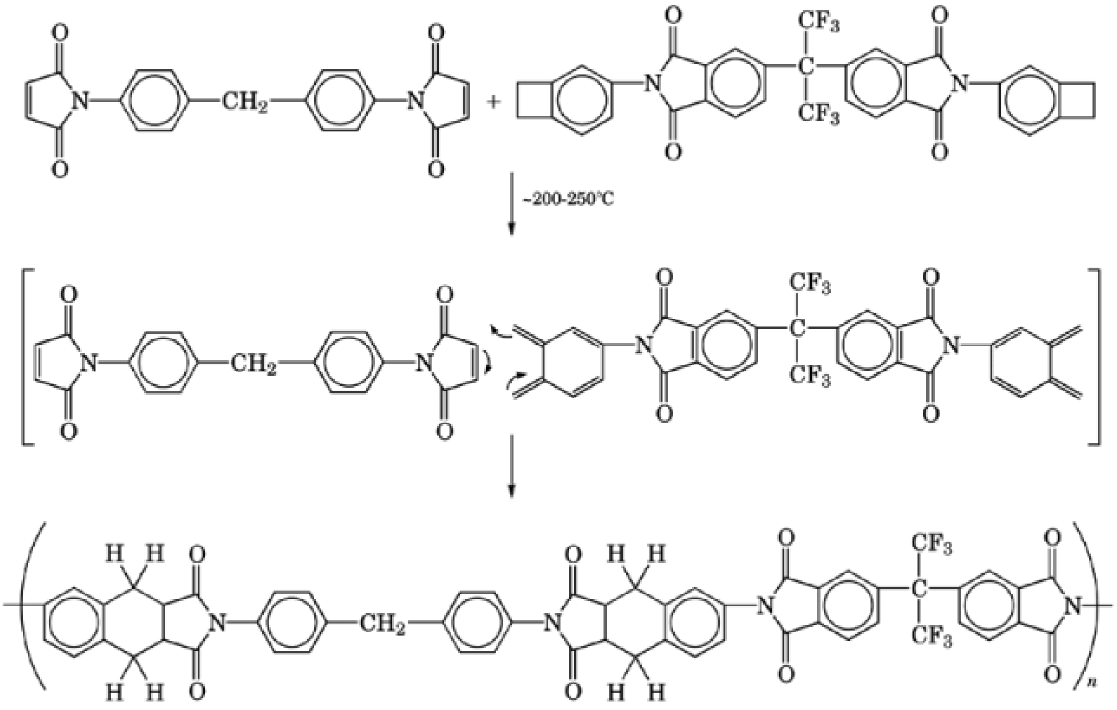


**Fig. 10.** Bismaleimide–benzocyclobutene copolymerization.

thermosetting polyimides with either maleimide or benzocyclobutene terminations. Certain bisbenzocyclobutene–BMI (COMPIMIDE 353) blends form compatible mixtures in a wide range of ratios, which after cure, show remarkable thermal oxidative stability and high glass transition temperatures (51). Interestingly, it can be demonstrated that the thermal oxidative stability of nonstoichiometric BMI–BCBs with excess BMI is far superior to the BMI homopolymer. BMI–BCB systems, however, are not yet commercial. Another not yet commercial family of dienes, the bis(3,4-dimethylene-pyrrolidines, has emerged (40).

The resin system V-378A, mentioned earlier, is a bismaleimide system that has been modified with divinylbenzene to achieve drape and tack in prepreg form. Divinylbenzene-modified BMI is appreciated because of its outstanding hot–wet environmental resistance and epoxylike cure (18). BMI–divinylbenzene systems cure via a Diels-Alder reaction.

### 5.3. Modified Bismaleimides

Bismaleimide resins may be further modified and blended with other thermoset resins or reactive diluents to achieve either specific end-use properties or processibility. Thermoset resins that can be used for modification are unsaturated polyesters, vinylesters, cyanate esters, and epoxies.

#### *5.3.1. BMI–Epoxy Modifications*

Bismaleimide–diamine prepolymers poly(amino bismaleimides) as described earlier can be used as curing agents for epoxy resins (52). Polyfunctional epoxy–novolac resin (EPIKOTE Resin 154) and tetraglycidyltetraphenylolethane (EPON Resin 1031 [7328-97-4]) have been cured with this BMI. Heat-resistant, solventless resins comprising an epoxy resin, anhydride curing agent, and BMI resin are claimed in a U.S.

**Table 11. Properties of BMI–Epoxy[a] Electrical Laminates**

| Properties | Value | |
|---|---|---|
| laminate composition, BMI–epoxy | 70/30 | 50/50 |
| flexural strength, 23°C, MPa[b] | 462 | 441 |
| flexural modulus, 23°C, GPa[c] | 22 | 21 |
| dielectric constant, 23°C | 4.32 | 4.48 |
| dissipation factor, 23°C | 0.0083 | 0.0098 |
| dielectric strength, V/$\mu$m | 30 | 31 |
| volume resistivity, $\Omega \cdot$cm | $2.1 \times 10^{16}$ | $1.9 \times 10^{16}$ |
| surface resistivity, $\Omega \cdot$cm | $3.8 \times 10^{16}$ | $>1.9 \times 10^{16}$ |
| flammability, UL-94 | V–O | V–O |
| copper peel, J/m$^2$[d] | 1208 | 1348 |
| methylene chloride, mg uptake | 1.1 | 1.7 |
| water absorption, wt % | | |
| 103 kPa[e] steam, 1 h. | 0.28 | 0.31 |
| boiling, 24 h | 1.32 | 1.24 |
| solder shock[f] | pass | pass |
| etchability[g] | 0.03 | 0.04 |
| tga, 5 wt % loss in air, °C | 360 | 335 |

[a] COMPIMIDE 1206–EPON 1151.
[b] To convert MPa to psi, multiply by 145.
[c] To convert GPa to psi, multiply by 145,000.
[d] To convert J/m$^2$ to lbf/in., divide by 175.
[e] 101.3 kPa = 1 atm.
[f] 20s at 268°C 1 h after 103 kPa[e] steam.
[g] 5 min in conc $H_2SO_4$.

patent (53). COMPIMIDE 795, a BMI–*m*-aminobenzoic hydrazide adduct, has been blended with tetraglycidylmethylenedianiline (TGMDA) and 3,3′-diaminodiphenyl sulfone [27133-91-1] for use in hot-melt carbon fiber prepreg (43).

Heat-resistant resin compositions based on bismaleimide–epoxy blends are achieved by reaction of a BMI–*m*-aminophenol [591-27-5] (1:1) adduct with epoxy. This prepolymer is fully cured with an imidazole catalyst (54). Blends of hydroxy-terminated BMI–aminophenol adducts can easily be B-staged, that is, prepolymerized, and subsequently ground to provide a powder that can be molded by the application of heat and pressure.

A modified BMI–epoxy resin system has been introduced by Shell Chemical Company. The system is a highly reactive blend of a bismaleimide, COMPIMIDE 1206 (55–60% by weight solution of BMI in DMF), and EPON Resin 1151, a polyfunctional epoxy resin (55). In contrast with many polyimide resins on the market, no free methylenedianiline (MDA) is present in the product. This is an important feature, since MDA has been identified as an animal carcinogen and possible human carcinogen. This resin system has been fully evaluated for use in multilayer PCB boards (56). 2-Methylimidazole [693-98-1] is recommended as a catalyst. However, if required, the processing window can be widened by using 2-phenylimidazole [670-96-2], which is a more latent catalyst. There is a wide window for lamination of this system, from hot start, single pressure to dual pressure, vacuum assistance. The formulation consisting of 70 parts of COMPIMIDE 1206-R60 and 30 parts of EPON Resin 1151-BH 60 has an excellent property profile for the manufacture of multilayer circuit boards. Typical properties of COMPIMIDE 1206–EPON 1151 electrical laminates are compiled in Table 11.

### *5.3.2. BMI–Biscyanate Modification*

Based on the triazine technology developed by Bayer AG in Germany in the late 1960s (57), Mitsubishi Gas Oil Chemicals created a new family of resins that are blends of bismaleimides with biscyanates or biscyanate prepolymers. Biscyanate resins are also known as triazine resins, triazine referring to the chemical structure of the

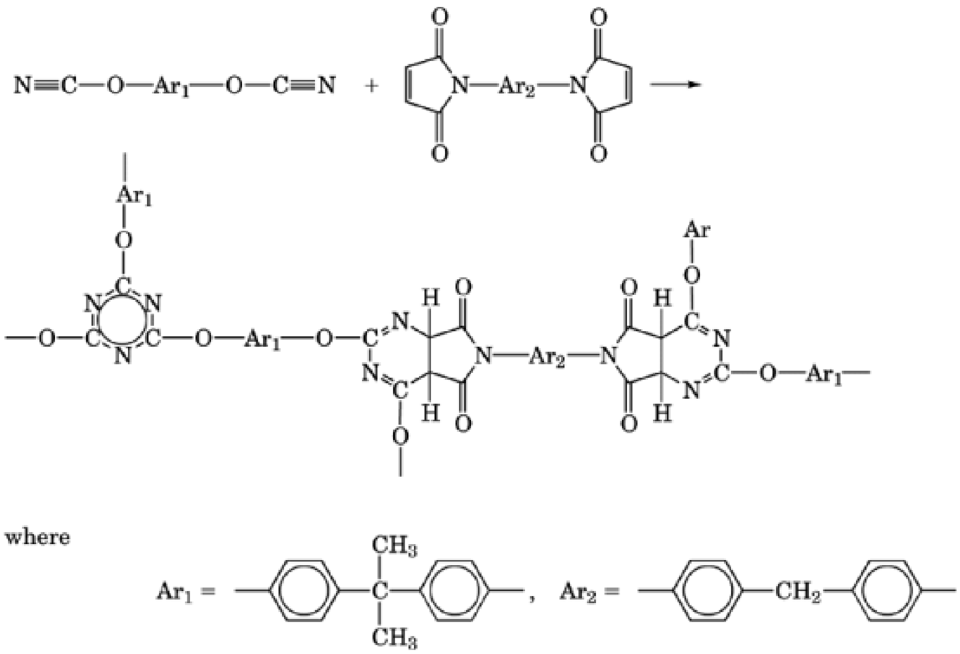


**Fig. 11.** Proposed copolymerization mechanism for bismaleimides with dicyanates.

polymerized cyanate. Blends of bismaleimides and triazines are commercialized as BT resins (B-bismaleimide, T-triazine). There is no scientific literature available that deals with the chemistry of their copolymerization. The product manual for the commercial products claims that the copolymerization results in structures such as those given in Figure 11.

A great variety of resin formulations is possible because other thermosets, such as epoxies or acrylates, and reactive diluents, such as *o*-diallyl phthalate [131-17-9], triallyl cyanurate [101-37-1], or triallyl isocyanurate [1025-15-6], can be used to further modify the BT resins. The concept is very flexible because bismaleimide and biscyanate can be blended and copolymerized in almost every ratio. If bismaleimide is used as a major constituent, then homopolymerization of the excess bismaleimide takes place in addition to the copolymerization. Catalysts such as zinc octoate or tertiary amines are recommended for cure. BT resins are mainly used in printed circuit and multilayer boards (58).

### 5.4. Toughened Bismaleimide Resins

Bismaleimide homopolymers are brittle thermosets and laminates made from them display low impact damage tolerance. The techniques used to toughen brittle bismaleimides include: the use of monomers or monomer–comonomer systems that provide inherently tough networks through reduced cross-link density; the use of elastomeric materials as modifiers to achieve second-phase toughening similar to rubber-modified polystyrene; and the use of engineering thermoplastics instead of elastomers to maintain the high elastic modulus of the thermoset in the toughened system.

BMI comonomer (allylphenols, propenylphenoxy compound) systems are significantly tougher than BMI homopolymers or BM-Michael-addition copolymer systems. BMI may also be toughened through elastomers and thermoplastics.

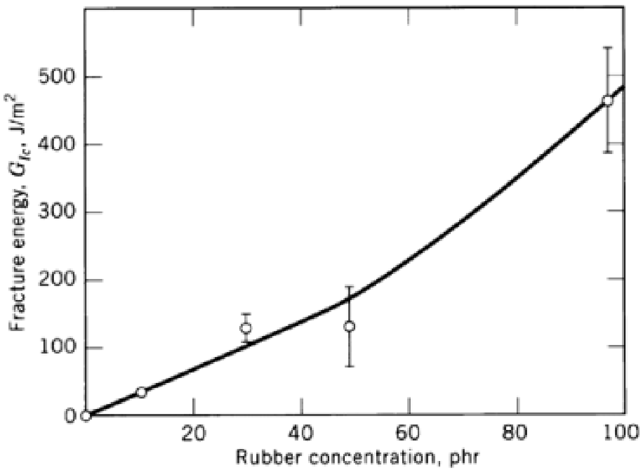


**Fig. 12.** Influence of rubber concentration on fracture energy ($G_{Ic}$). To convert J/m$^2$ to ft lbf/in.$^2$, divide by 2100.

### *5.4.1. Rubber-Toughened Bismaleimides*

Toughening of BMIs with carboxy-terminated acrylonitrile–butadiene rubbers (Hycar $1300 \times 8$ from BF Goodrich [68891-46-3]) has been reported (59). In contrast to epoxy resins, Hycar $1300 \times 8$ is not compatible with COMPIMIDE 353 bismaleimide at room temperature, and even at an elevated temperature (110°C) the rubber is not soluble in the BMI resin. However, during cure, the rubber chemically reacts with the BMI resin (via the double bonds present in the CTBN-rubber backbone) and becomes compatible to the extent that a microphase-separated morphology similar to the CTBN-rubber modified epoxy is achieved. The influence of the rubber concentration on the fracture energy $G_{\mathrm{Ic}}$ is presented in Figure 12. A significant improvement is achieved when rubber concentrations in excess of 50 phr are used.

The properties of CBTN-rubber modified BMI depend on the chemical composition of the rubber (60). The acrylonitrile content influences BMI–CTBN-rubber compatibility and therefore the morphology and the fracture energy of the modified resin. High acrylonitrile rubbers are more soluble and compatible with the BMI resin and provide a lower degree of phase separation and thus lower toughness. The principal drawback of CBTN-rubber toughened BMIs is the significant loss of high temperature properties, such as glass-transition temperature ($T_g$) and elastic modulus. As expected, the long-term aging stability at 200°C is poor.

### *5.4.2. Thermoplastic Toughening of Bismaleimides*

Thermoplastics are increasingly used for the toughening of bismaleimide resins to improve their damage tolerance without compromising other important properties, such as glass transition temperature ($T_g$) and modulus of elasticity. High $T_g$ thermoplastics such as polyhydantoins (61, 62) (Resistofol N, Resistherm PH-10, Bayer AG), polyether-sulfones (51) (P1700, UCC), polyimides (53) (Matrimide 5218, CIBA GEIGY), polyetherimides (Ultem 1000, General Electric), and a series of poly(arylene ethers) (63), have been used to toughen BMI resins. All these thermoplastics, except the polyhydantoin PH-10, provided polyphase morphologies, and, at approximately 20% by weight of thermoplastic, phase inverted systems with the thermoplastic as the continuous phase are obtained. The influence of thermoplastic content on the fracture toughness of the cured BMI–thermoplastic blend system has been investigated, and, as expected, higher thermoplastic levels provide increased toughness. However, the various thermoplastics show different degrees of toughening (Table 12).

Many factors contribute to the toughness of a polyphase BMI–thermoplastic system, such as solubility parameters, phase adhesion, phase morphology, particle size, and particle size distribution. Another

**Table 12. Properties of Thermoplastic-Modified BMI[a] Resins**

| Property | Control[a] | 20 wt % PH-10[b] | 20 wt % RN[c] | 20 wt % M 5218[d] | 20 wt % P 1700[e] | 13 wt % Ultem[f] | 20 wt % PAE-1[g] | 20 wt % PAE-3[g] | 20 wt % PAE-4[g] |
|---|---|---|---|---|---|---|---|---|---|
| $T_g$, °C | 316 | 294 | 280 | 284 | 200 | 220 | 159.7 | 180.3 | 213.4 |
| dry flexural properties | | | | | | | | | |
| room temperature | | | | | | | | | |
| strength, MPa[h] | 115 | 115 | 118 | | 0.5 | 117 | 114 | 124 | 132 |
| modulus, GPa[h] | 3.86 | 3.65 | 3.51 | 3.75 | 3.49 | 3.72 | 3.65 | 3.65 | 3.84 |
| elongation, % | 3.05 | 3.09 | 3.52 | | 2.67 | 3.35 | 3.21 | 3.40 | 3.64 |
| 120°C | | | | | | | | | |
| strength, MPa[h] | | 95 | 94 | | 37 | 97 | 84 | 108 | 95 |
| modulus, GPa[h] | | 2.88 | 2.89 | 3.13 | 1.93 | 3.02 | 2.60 | 3.04 | 3.00 |
| elongation, % | | 3.44 | 3.52 | | 2.70 | 3.38 | 4.06 | 4.50 | 3.28 |
| 177°C | | | | | | | | | |
| strength, MPa[h] | 84 | 91 | 78 | | | 45 | 26 | 30 | 100 |
| modulus, GPa[h] | 3.27 | 2.77 | 2.38 | 2.64 | | 1.71 | 0.64 | 0.66 | 3.08 |
| elongation, % | 2.73 | 4.52 | 4.74 | | | 2.99 | 6.61 | >7.20 | 4.27 |
| fracture toughness, $K_q$, kPa$\sqrt{m}$ | 573 | 822 | 1322 | 929 | 763 | 805 | 1521 | 1235 | 1025 |
| fracture energy, $G_{Ic}$, J/m$^2$[i] | 85 | 185 | 498 | 230 | 167 | 174 | 634 | 418 | 274 |
| moisture gain[j], % | 2.72 | 3.01 | | 3.23 | | | 2.88 | 2.77 | 3.05 |

[a] COMPIMIDE 796–COMPIMIDE 123.

[b] Resisttherm PH-10 polyhydantoin.

[c] Resistofol *N* polyhydantoin.

[d] Matrimide 5218 polyimide.

[e] Polyethersulfone.

[f] Polyetherimide.

[g] Poly(arylene ether)s.

[h] To convert MPa to psi, multiply by 145.

[i] To convert J/m$^2$ to ftlbf/m.$^2$, divide by 2100.

[j] Moisture gain was obtained on test specimens after 500 h at 94% rh.

important factor is the molecular weight of the thermoplastic modifier. It has been demonstrated for a particular poly(arylene ether) backbone that high molecular weights increase the toughness of the blend system more than the low molecular weight counterparts (64). The toughness of the neat thermoplastic is likely to be a key factor in the corresponding thermoplastic–BMI blend.

Thermoplastic-modified BMIs are mainly used as matrix resins for advanced composites; therefore it is important that the good BMI-TP toughness in neat resin form translates into the composite and thus improves damage tolerance as measured via compressive strength after impact (CAI). For a BMI–polyetherimide system the toughness and morphology spectrum have been investigated, showing that for certain thermoplastic concentrations (>35% TP) the resin morphology is the same for the neat resin and the resin in the presence of the reinforcement. The thermoplastic is the continuous phase with very small (>0.5 nm) BMI inclusions (65). The fibers in the composite do not influence the development of the BMI–PEI morphology and, therefore, neat resin toughness correlates with composite toughness.

The principal disadvantage of the thermoplastic approach with high molecular weight polymers is the loss of processibility and the solvent sensitivity of thermoplastic–BMI blends. Therefore, attempts have been made to use reactive thermoplastics (functionalized thermoplastics) that can react into the BMI network and provide solvent resistance without loss of toughness. For a series of functionalized poly(arylene ethers), it has been demonstrated that a $M_w$ (weight average molecular weight) of approximately 30,000 is required to maintain

**Table 13. Commercially Available BMI Resins**

| Company | Resin name | Description |
|---|---|---|
| CIBA GEIGY Corp. | Matrimide 5292 A,B | two-component resin system comprising 4,4′-bismaleimido-diphenylmethane (M5292A) and diallylbisphenol–A (M5292B) |
| | RD85–101 | BMI building block based on diaminodiphenylindane; designed for hot-melt prepregging |
| | Araldite XU5292 | bismaleimide resin solution for PCB applications |
| Du Pont Co. | MVA-2 | 1,3-bismaleimidabenzene building block |
| Mitsubishi Gas Chemicals Co. | BT resins | blends of bismaleimide(B) and triazine(T) resins; used primarily in printed circuit boards |
| Mitsui Toatsu Chemicals, Inc. | Bismaleimide-S | 4,4′-bismaleimido-diphenylmethane. (The company also offers other BMI building blocks.) |
| Rhône Poulenc Chimie | Kerimide 601 | soluble BMI powder for multilayer board application |
| | FE70000 | series of research and development products |
| | Rhodimid M3 | 4,4′-bismaleimido-diphenylmethane |
| Shell Chemical Co.[a] | COMPIMIDE MDAB | high purity 4,4′-bismaleimido-diphenylmethane |
| | COMPIMIDES 353, 353A, 796 | unformulated BMI resins |
| | COMPIMIDE 15 MRK | for injection and compression molding |
| | COMPIMIDE 65 FWR | for filament winding |
| | COMPIMIDE 121 | liquid bis(allylphenyl) compound |
| | COMPIMIDE 123 | [bis-(*o*-propenyl)phenoxy] benzophenone |
| | COMPIMIDE 1206-F55 | 55–60 wt % solution of bismaleimide for prepregging |

[a] Also, Technochemie GmbH-Verfahrenstechnik, Dossenheim, Germany is a member of the Royal Dutch/Shell Group of Companies.

the toughness provided by the high molecular weight polyarylene ether. However, solvents do not completely destroy the blend system (64). Similar results have been obtained for BMI–diallylbisphenol A resin modified with amine-terminated poly(arylene ether sulfone) (66).

Toughening of BMIs with thermoplastics is a promising approach; however, more information is required about the toughening mechanism involved in order to select the most promising polymers in terms of backbone chemistry, molecular weight, and reactive groups.

### 5.5. Commercial BMI Resins

Since the late 1960s, bismaleimide resins have been commercially available. The first company in the marketplace was Rhône Poulenc Chimie, France. Several others, Technochemie, Germany; CIBA GEIGY, Switzerland; DSM, The Netherlands, BASF, West Germany; Mitsubishi Gas Chemicals and Mitsui Toatsu, both of Japan; Reichhold and Polyorganics from the United States; and Shell Chemical Company, United States (through the acquisition of Technochemie by Deutsche Shell AG), followed. Some of them lost interest in this speciality market sector. Table 13 indicates the BMI resins available at the end of 1992. No reference is made to prepreg systems available from various sources. A complete list of available products and information on any particular material should be obtained from the suppliers.

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