CURABLE EPOXY RESIN ACCELERATED BY BORIC ACID AND ITS ANALOGS

The present invention relates to the art of epoxy resin formulations, and particularly to formulations that are useful for making electrical laminate structures.

Ordinary electrical laminates are made by the process of:

(a) impregnating a substrate (which is usually a woven or nonwoven cloth) with a formulation of epoxy resin, curing agent, catalyst and solvent;

(b) optionally subjecting the impregnated substrate to heat and/or reduced pressures to draw off solvent and/or partially cure the resin, in order to make a prepreg;

(c) pressing together alternating layers of prepreg and conductive material at high temperature and pressure to cure the formulation and form a laminate; and

(d) optionally subjecting the laminate to high temperature for additional time in order to post-cure it.

This process is repeated batchwise for each individual electrical laminate. It makes adequate electrical laminate, but it contains many steps and takes a long time to complete.

Continuous processes are now being developed. In a continuous process, one or more continuous webs of substrate are impregnated, laminated together with conductive material, and pressed between the moving plate at high temperature to cure. Those processes usually require a resin that cures much faster than resins which are used in conventional processes. The curing step in conventional processes usually lasts about an hour, but the curing step in continuous processes is preferably about 10 minutes. Therefore, an improved accelerator is required.

Alternative laminating processes are being developed in which the resin serves as an adhesive to bind conductive layers together, optionally with insulating layers, but without a fibrous substrate. For instance:

(a) a curable formulation is applied as a coating on at least one face of a conductor, such as copper foil or polymer-coated copper foil;

(b) the coated conductor is heated to optionally evaporate the solvent and to partially cure (B-stage) the curable formulation;

(c) two or more layers of the B-staged coated conductor are pressed together (optionally with one or more insulating layers) with sufficient heat to cure the resin and form a laminate.

This process can also benefit from accelerated curing.

Accelerated curing would also be useful in many other end uses to increase productivity and reduce production cost. What is needed is a way to accelerate curing at the

curing step by using materials that do not undesirably shorten the shelf-life of the varnish and the B-staged materials.

One aspect of the present invention is a process of curing a curable composition which contains:

(1) at least one epoxy resin;

(2) at least one catalyst or curing agent for curing of epoxy resin; and

(3) a boric acid compound

characterized in that:

(a) the composition contains more than 1 phr and less than 10 phr boric acid compound; and

(b) the composition contains 0 to less than 0.6 moles of catalyst per mole of boric acid compound.

The boric acid compounds used in the present invention give several advantages over the prior art. The boric acid compound does not substantially accelerate the self-curing of epoxy resins at about room temperature, so that the formulations have a long pot-life. However, excess boric acid over the number of equivalents of curing catalyst can greatly accelerate the reaction of epoxy resin with a curing agent at curing temperatures, so that the formulation can be cured quickly.

Formulations used in the present invention contain an epoxy resin. The epoxy resin may be any compound or mixture of compounds that contains on average more than one epoxide group per molecule. Examples include low molecular weight liquid epoxy resins or higher molecular weight advanced epoxy resins. The epoxy resin preferably has an epoxy equivalent weight (EEW) of at least about 100, and more preferably at least about 170. The EEW of the epoxy resin is preferably no more than about 2000, and more preferably no more than about 1000. (EEW and methods to measure it are described in H. Lee & K. Neville, Handbook of Epoxy Resins at 4-15 to 4-21 (McGraw-Hill Book Co. 1967).

The epoxy resin preferably contains one or more poly(glycidyl ether) or poly(glycidyl ester) compounds. Examples of preferred epoxy resins are described in numerous references such as: Walker, U.S. Patent 5,066,735 (November 19, 1991); Koenig, U.S. Patent 5,122,932 (May 12, 1992); Bertram, U.S. Patent 5,134,239 (July 28, 1992); Liao, U.S. Patent 5,188,903 (February 23, 1993); Liao et al., U.S. Patent 5,206,312 (April 27, 1993); and Schultz et al., Ser. No. 08/146,652 (filed November 2, 1993). The epoxy resin more preferably contains a poly(glycidyl ether) derived from a biphenol compound, a bisphenol compound, a trisphenol compound, a novolac, an aliphatic diol or a halogenated variation of those compounds. The epoxy resin most preferably contains a diglycidyl ether of bisphenol A, bisphenol F or a halogenated variation of those resins. Suitable epoxy resins are commercially available or can be made by techniques familiar to persons of ordinary skill in the art.

Formulations used in the present invention preferably contain a curing agent. The curing agent is any compound that reacts during curing with two or more epoxy resin molecules to link them together. Curing agents preferably contain any of the following functional groups: primary or secondary amine moieties, carboxylic acid moieties, phenol moieties, amide moieties, anhydride moieties, or diguanide moieties. The curing agent most preferably contains at least about 2 primary or secondary amine or amide moieties. Suitable curing agents are well-known in the art, and are described in numerous references, such as Bertram et al., U.S. Patent 5,079,314 (January 7, 1992); Schultz et al., Ser. No. 08/146,652 (filed November 2, 1993); and C. A. May, Epoxy Resins - Second Edition at 465 et seq. (Marcel Dekker, Inc., 1988). Examples of suitable curing agents include dicyandiamide, novolacs and other polyphenols, diaminodiphenyl sulfone, phthalic anhydride and its derivatives, methylenedianiline, and diaminocyclohexane.

The curing agent is preferably not mixed with the formulation during storage, since it may cross-link with the resin over time. However, the curing agent is preferably mixed with the formulation before it is applied to a substrate. The concentration of curing agent is preferably at least about 0.1 equivalents curing agent per equivalent epoxy resin, more preferably at least about 0.5 equivalents curing agent, and most preferably at least about 0.7 equivalents curing agent. The formulation preferably contains no more than about 1.5 equivalents curing agent per equivalent of epoxy resin, more preferably no more than about 1.3 equivalents of curing agent, and most preferably no more than about 1.1 equivalents of curing agent.

Formulations used in the present invention may optionally contain a chain extender, which builds up the molecular weight of the epoxy resin without substantially cross-linking it. Chain extenders preferably contain about 2 phenolic hydroxyl groups per molecule. Examples of suitable chain extenders include biphenols and bisphenols. Bisphenol A, bisphenol F and tetrabromobisphenol A are preferred chain extenders. When the formulation contains a chain extender, its weight is treated as part of the epoxy resin for calculating proportions of materials.

The formulations used in the present invention preferably contain a catalyst when they are used, but preferably do not contain a catalyst when they are stored. The catalyst speeds the curing reaction of the epoxy resin (either with the curing agent or with itself if there is no curing agent) without being consumed. Examples of suitable catalysts are described in Bertram, U.S. Patent 5,169,473 (December 8, 1992); and Schultz et al., Ser. No. 08/146,652 (filed November 2, 1993).

The catalyst is preferably a tertiary amine, quaternary ammonium, tertiary phosphine, quaternary phosphonium, a sulfonium compound or a heterocyclic nitrogen-containing compound. The catalyst is more preferably a tertiary amine or quaternary ammonium salt. It highly preferably contains a heterocyclic ring, such as an imidazole, oxazole,

thiazole or triethylene diamine. The catalyst is most preferably an imidazole compound, such as 2-methylimidazole.

The concentration of catalyst should be high enough to catalyze the curing reaction of epoxy resin and, optionally, curing agent at a speed reasonable for the intended use ("a catalytic amount"). The concentration of catalyst varies depending upon the catalyst selected, but is easily determined by a person of ordinary skill in the art. The concentration of most catalysts is preferably at least about 0.05 phr, more preferably at least about 0.1 phr, and most preferably at least about 0.15 phr. The concentration of most catalysts is preferably no more than about 1.5 phr, more preferably no more than about 1 phr, more highly preferably no more than about 0.5 phr, and most preferably no more than about 0.35 phr. Higher-molecular-weight catalysts may require a higher concentration.

Formulations used in the present invention also contain a boric acid compound. The boric acid compound is either boric acid itself, or derivatives such as metaboric acid, boric anhydride, boroxine or trimethoxyboroxine. It has previously been reported that boric acid compounds are curing inhibitors when they are used in about equimolar proportions with the catalyst. See, Gan et al., U.S. Patent 5,314,720 (May 24, 1994); and Gan et al., U.S. Patent 5,308,895 (May 3, 1994).

We have discovered that boric acid compounds are curing accelerators when they are used in a stoichiometric excess over the quantity of catalyst. The formulation contains less than 0.6 moles of catalyst per mole of boric acid compound, preferably contains no more than about 0.5 moles of catalyst per mole of boric acid compound, and more preferably contains no more than about 0.4 moles of catalyst per mole of boric acid compound. It preferably contains at least about 0.05 moles of catalyst per mole of boric acid compound.

The concentration of boric acid compound is at least 1 phr, and is preferably at least about 1.2 phr, more preferably at least about 1.5 phr and most preferably at least about 2 phr. The concentration of boric acid compound is preferably less than 10 phr, more preferably less than 6 phr and most preferably no more than about 4 phr.

The boric acid compound may optionally be mixed with the epoxy resin before the resin is stored and before the catalyst and curing agent are added to the formulation.

The formulation preferably further contains one or more solvents to dissolve the solid components. The solvents may be aqueous, but are preferably organic. Examples of suitable solvents include aromatic hydrocarbons, ketones, ethers and glycol ethers, alcohols, aliphatic hydrocarbons, halogenated hydrocarbons and amides. Preferred solvents include acetone, methyl ethyl ketone, methanol, ethanol, propylene glycol methyl ether, dimethylformamide and xylene. The concentration of resin, curing agent, catalyst and boric acid compound (solids) in the formulation is preferably maximized in order to reduce the use and discharge of organic solvents. The solids concentration is preferably at least about 20 weight percent, and more preferably at least about 40 weight percent. Solids concentration

may be as high as 100 weight percent (a solvent-less formulation), but it is preferably no more than about 80 weight percent and more preferably no more than about 50 weight percent, due to practical considerations, such as viscosity.

The formulation may optionally contain known additives, such as stabilizers, flame retardants, fillers, flow-modifying agents and wetting agents. Examples of suitable additives are described in: Walker, U.S. Patent 5,066,735 (November 19, 1991) and C. A. May, Epoxy Resins - Second Ed. at 506-512 (Marcel Dekker, Inc., 1988).

The formulations of the present invention can be used to make rapid-curing curable compositions for electrical laminates. The composition preferably cures in no more than about 20 minutes, more preferably no more than about 10 minutes, more highly preferably in no more than about 5 minutes, and most preferably in no more than about 3 minutes.

The formulations are preferably used to make electrical laminates. One preferred process for making the electrical laminate has the following steps:

(1) The formulation is impregnated onto a substrate. The substrate is preferably a woven or nonwoven cloth. Examples of suitable fibers include: glass, carbon, aramid, nylon or quartz. The formulation may be contacted with the substrate by ordinary means such as spraying, rolling or dipping. The temperature is not critical, as long as the formulation remains a liquid with suitable viscosity. The temperature is preferably between about room temperature and about 120°C.

(2) Optionally, the solvent is removed from the prepreg. This step is carried out by subjecting the prepreg to increased temperatures and/or reduced pressures. Preferably, the pressure is about ambient pressure, and the temperature is between 100°C and 200°C. This step may also be used to partially cure, or "B-stage" the resin.

(3) One or more layers of prepreg is laminated with one or more layers of conductive material, and the laminate is cured. Examples of conductive material include copper, gold or silver. Preferably, at least two layers of prepreg are laminated together with layers of conductive material between the layers of prepreg. This step is preferably carried out at elevated temperature and pressure. The temperature is preferably 120°C to 250°C. Continuous processing is usually performed near the top of the temperature range, and ordinary processing near the middle of the range. The pressure is preferably at least about 100 psi and more preferably at least about 300 psi.

(4) The laminate may optionally be post-cured. Post-curing is preferably carried out at a temperature between 150°C and 250°C. It is preferably carried out at about ambient pressure. The post-curing step is preferably carried out for 1 to 12 hours.

The resulting laminate contains substrate and conductive material embedded in a cured resin. The properties of the laminate may vary depending upon its intended use. In low-performance (punchable) laminates, the cured resin may have a glass transition temperature (T_g) of 40°C to 50°C; in medium-performance boards, the T_g is preferably 130°C to 140°C; and in high performance laminates, the T_g is preferably 160°C to 180°C or more. However, formulations used in the present invention frequently provide higher T_g than similar formulations without boric acid. The laminate can be used for ordinary purposes for electrical laminates, such as for making electrical components and circuits.

Another preferred method to make laminates uses the formulation as an adhesive between layers of conductive material, as described previously. The preferred methods and conditions for applying the formulation, B-staging it and curing it are the same as previously described for other laminating methods.

The process of the present invention can also be used to cure epoxy resins for other uses, such as in coatings and structural composites.

The invention is illustrated by the following working examples.

The following examples are for illustrative purposes only. They should not be taken as limiting either the specifications or claims. Unless otherwise stated, all parts and percentages are by weight.

Throughout the examples, we have used gel-time as an indirect measure relative to cure rates. A faster gel-time has been taken as indicating a faster cure rate. The test for gel-time is described hereinafter.

Example 1

A mixture was made that contained 80.75 weight percent advanced brominated epoxy resin dissolved in acetone. The brominated epoxy resin is a reaction product of tetra-bromobisphenol A and diglycidyl ether of bisphenol A, and it has an EEW of about 432.

A mixture containing 20 weight percent boric acid dissolved in methanol was added to 25 grams of the brominated epoxy resin mixture. The quantity was selected to obtain the concentration of boric acid shown in Table 1. The formulation was mixed until it was homogeneous and then stored for 12 to 16 hours.

A 40 weight percent solution of 2-methylimidazole catalyst dissolved in methanol was mixed into the formulation in a quantity selected to provide the concentration of catalyst in Table 1. A 10 weight percent solution of dicyandiamide curing agent dissolved in a mixture of dimethylformamide and glycol ether was mixed into the formulation in a quantity selected to provide the concentration of curing agent in Table 1. The mixture was allowed to stand for about 2 hours at room temperature.

The stroke-cure gel-time of the formulation was measured by the following test:

(1) The bottom side of a Model C01-T thermocouple (or equivalent) is pasted to a hot plate using a small amount of OMEGATHERM™ 201 thermally conductive paste,

or equivalent. The thermocouple is attached to a Model 450-ATT thermocouple thermometer (or equivalent). The hot plate control is adjusted until a stable temperature of 171°C ± 0.5 is obtained. The hot plate should be located in a constant temperature area away from drafts to prevent temperature variations.

(2) A 0.5 to 0.7 mL sample of formulation is applied to the hot plate, and a timer is started. The sample rests undisturbed on the hot plate for 60 seconds ± 1. Then the sample is stroked with a wooden spatula by pushing the resin puddle back and forth over an area of about 1 in^2 with the same side of the spatula in contact with the resin. The resin will thicken as it is stroked. Eventually, it becomes stringy, and then becomes a rubbery gel. That is the endpoint. The timer is stopped and the time is recorded. The resin is scraped from the plate using a razor blade being careful not to scratch the plate surface.

(3) The test is repeated three times, and the average time to form a gel is recorded.

The glass-transition temperature of the cured resin was determined by a method modified from the test published by The Institute for Interconnecting and Packaging Electronic Circuits in the IPC Test Methods Manual as test 2.4.25 (revision B, dated 12/87):

(1) A resin sample obtained from the stroke-cure gel-time test is baked in a 175°C oven for one hour.

(2) A specimen is cut from the sample and mounted in a standard aluminum sample pan. (The sample should not be higher than the edge of the pan). The sample is not a laminate, and so references to copper in the published test method can be ignored. An empty pan is used as a reference.

(3) The glass-transition temperature is measured using a DuPont Model 912 differential scanning calorimeter or equivalent, starting well below the point of interest and increasing temperature at a rate of 10°C/minute until 175°C is reached. The inflection point is taken to indicate the glass-transition temperature.

The results of those tests are shown in Table 1:

TABLE 1

Sample	Boric Acid (phr)	2-MI (phr)	Ratio - Boric Acid : 2-MI	Dicy (phr)	Gel Time (sec)	Tg (°C)
a	3	0.35	8.57	2.5	25	144
b	2	0.175	11.43	2	24	149
c	2	0.175	11.43	2.5	82	143
d	2	0.35	5.71	2	85	140
e	1.51	0	-	2	46	110
f	2	0	-	2.75	26	142
g	3	0	-	2.5	22	150
h*	0	0.35	0	2.5	79	132
i*	0	0.35	0	2	92	143
j*	0	0.175	0	2.5	142	145
k	2	0.35	5.71	2.5	98	144
l	1.51	0.35	4.31	2.5	102	158

* - Not an Example of the Invention

Example 2 - Making Adhesive on Copper Foil

A formulation was made which contained: 52.85 parts TACTIX™ 742 epoxy resin (Trademark of The Dow Chemical Company); 16.8 parts QUATREX™ 6410 epoxy resin (Trademark of The Dow Chemical Company); 16.8 parts tetrabromobisphenol A; 0.08 parts methyl-4-toluenesulfonate; 1.81 parts boric acid (which is dissolved in a 20 weight percent solution with methanol); and 13.81 parts DOWANOL™ PM solvent (Trademark of The Dow Chemical Company).

A 125 part quantity of the solution was mixed with 1 part 2-methylimidazole (dissolved in a 10 weight percent solution with DOWANOL™ PM solvent) to make a laminating formulation. The laminating formulation was applied to a roll of 17 μm copper foil and B-stage by heating at 150°C for a residence time of about 2 minutes. Two layers of the coated foil were stacked and cured under 25 kg/cm^2 pressure by heating from 30°C to 200°C and holding at 200°C for a total cure time of 190 minutes. The cured resin in the laminate had a glass transition temperature of about 226°C. After 30 minutes post-curing at 240°C, it had a glass transition temperature of 241°C. It lost only 0.035% of its weight after 1 hour in air at 260°C.

1. A process of curing a curable composition which contains:

(1) at least one epoxy resin;

(2) at least one catalyst or curing agent for the curing of the epoxy resin; and

(3) a boric acid compound

characterized in that:

(a) the composition contains more than 1 phr and less than 10 phr boric acid compound; and

(b) the composition contains 0 to less than 0.6 moles of catalyst per mole of boric acid compound.

2. A process as described in Claim 1 wherein the formulation contains at least 0.05 phr catalyst.

3. A process as described in Claim 2 wherein the catalyst contains a quaternary ammonium moiety.

4. A process as described in any of Claims 2 or 3 wherein the concentration of catalyst is 0.1 to 0.5 phr.

5. A process as described in any of the preceding claims wherein the composition contains at least 0.1 equivalents of a curing agent per equivalent of epoxy resin, and wherein the curing agent contains any one or more of primary amine moieties, secondary amine moieties, carboxylic acid moieties, phenol moieties, amide moieties, anhydride moieties or guanidine moieties.

6. A process as described in any of the preceding claims wherein the formulation further comprises a chain extender.

7. A process as described in any of the preceding claims wherein the composition contains 1.5 to 8 phr of boric acid compound.

8. A process as described in any of the previous claims wherein the composition contains 2 to 5 phr of boric acid compound.

9. A process as described in any of the previous claims wherein the composition contains 0.05 to 0.2 moles of catalyst per mole of boric acid compound.

10. A process as described in any of the previous claims wherein the cured product is an electrical laminate.

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