

Description

The present invention relates to the preparation of isocyanate modified epoxy resins (epoxy-terminated polyoxazolidones) having 5 to 30 weight percent of the isocyanate content wherein from 0 to 50 percent of the isocyanate groups are converted to isocyanurate rings and from 50 to 100 percent of the isocyanate groups are converted to oxazolidone (commonly referred to in the past as "2-oxazolidinone") rings. The present invention also relates to the preparation of epoxy resin varnish compositions containing these isocyanate modified epoxy resins and to the preparation of electrical laminates.

The synthesis and properties of isocyanate modified epoxy compounds which are copolymers of polyisocyanates and polyepoxides have attracted a great deal of interest in recent years. Various isocyanate modified epoxy compounds are described as promising engineering materials for the manufacture of a wide variety of useful products including rigid foams, thermoplastics, coatings, adhesives and elastomers.

During the reaction of a polyepoxide with a polyisocyanate there is competition between formation of 2-oxazolidone rings and isocyanurate rings. The crosslinking density and branching of the formed polymer compound increases with increased content of isocyanurate rings and thereby the glass transition temperature (T_g) of the polymer is raised. Many studies have shown that many factors such as reaction temperature, nature of the catalyst, relative amounts of the reactants and solvents employed, influence the reaction and formation of 2-oxazolidone rings and isocyanurate rings. See, for example, Kinjo et al, Polymer Journal Vol 14, No 6, 505-507 (1982); Sandler, S.R., Journal of Polymer Science, A 1-5, 1481 (1967); Sayigh and Ulrich, J. Chem. Soc., 1961, 3148-51; Uribe and Hodd, Polym. Sci. Technical, 31, 251-73 (1985); Kordomenos et al, Macromolecules, 14, 1434-37 (1981); Kitayana et al, Rubber Chemistry and Technology, Vol 53, 1-6 (1980); Herweh et al, Tetrahedron Letters, No 12, 809-812 (1971); Dileone, J. Polymer Sci., A 1-8, 609-615 (1970); Herweh et al, J. Org. Chem., Vol. 33, 1409-23 (1968) and Sandler, J. Polym. Sci., A1-5, 1481 (1967). For convenience most of this fundamental studies were conducted with model compounds in dilute solutions particularly in dimethylformamide (DMF).

In general it has been found that epoxides promote formation of isocyanurate rings at low temperature. It has been shown that isocyanurate rings are formed from the isocyanate groups by the catalytic effects of nucleophilic compounds at temperatures below 100°C and are converted into oxazolidone rings at temperature above 110°C in the presence of DMF solvent. It has been disclosed that the usual reaction temperature to form oxazolidone rings is 150°C to 160°C (boiling temperature of DMF solvent).

There are three end products which can be obtained in the condensation reaction of polyisocyanates with polyfunctional epoxides. The reactants' stoichiometry (ratio of epoxide groups to isocyanate groups) determines the various end products, their remaining end groups and their possible uses. These condensation products are conventionally referred to as polyoxazolidones.

Isocyanate-terminated polyoxazolidones, are prepared using a stoichiometric excess of the polyisocyanate (isocyanate/epoxide ratio greater than 1) in the presence of a suitable catalyst. The following catalysts have been reported to promote the formation of isocyanate-terminated polyoxazolidones: quaternary ammonium salts, diethylzinc, zinc chloride/trimethylamine complex and organoantimony iodide. See, for example, Sander, J. Polym. Sci, A 1-5, 1481 (1967); Kordomenos et al, Journal of Coating Technology, 55, No. 700, pp. 49 and 59 (1983); U.S. Patent No. 4,022,721 to Mitsubishi; and PCT Patent Application WO/US 86/06734 to Dow. Isocyanate-terminated polyoxazolidones are reported to be suitable for use as resins, elastomers, paints and adhesives. The isocyanate-terminated polyoxazolidones can be further cross-linked via the catalytic trimerization of the terminal isocyanate groups to isocyanurate rings.

Linear high molecular weight polyoxazolidones are prepared using stoichiometric amounts (isocyanate/epoxide ratio = 1) of a diepoxy compound and diisocyanate compound.

Another class of resins (often referred to as "ISOX" resin) contain both isocyanurate and oxazolidone rings but the isocyanurate rings are predominant. The mechanical properties of ISOX resins can be varied from hard to flexible by changing equivalent ratio of isocyanate and epoxide groups. See, for example, Kinjo et al, Polymer Journal, Vol. 14, No 6, 505-507 (1982). This reference describes preparation of a series of thermosetting ISOX resins in which diphenylmethane-4,4'-diisocyanate (MDI) was reacted with different diepoxides in the presence of ethyl-methyl imidazole as a catalyst and as a curing agent. ISOX resin is low viscosity liquid at room temperature before curing. Compared with other conventional heat resistant solventless varnishes, ISOX resin are reported to have greater mechanical strength at elevated temperatures, and goods heat, electrical, chemical and moisture resistance properties.

U.S. Patent No. 4,070,416 (Hitachi Ltd.) describes a process for producing thermosetting resins by mixing one equivalent or more of polyfunctional isocyanate per one equivalent of a polyfunctional epoxide in the presence of a tertiary amine, morpholine derivatives or imidazole as catalysts. The catalyst is used within a range of 0.1 to 2 weight percent, based on the combined weight of the reactants. The reaction

temperature of 130°C or lower is said to result in the formation of mainly isocyanurate rings, whereas it is assumed that oxazolidone rings should be mainly formed at temperature above 130°C. The produced resins are said to exhibit excellent electrical and mechanical properties and high thermal stability. The produced resins are said to have various applications as heat resistance insulation varnishes, casting resins, impregnation resins, molding resins for electrical parts, adhesives, resins for laminating boards, resins for printed circuits etc.

Epoxy-terminated polyoxazolidones are prepared by reacting an epoxy resin with a polyisocyanate compound using stoichiometric excess of epoxy resin (isocyanate/epoxide ratio lower than 1). The following catalysts have been described in the literature to promote formation of epoxy-terminated polyoxazolidones: quaternary ammonium salts, HEXA (hexamethylenetetramine), diazabicyclooctane (sold by Air Product under the trademark DABCO), diethylzinc and organo-antimony iodide. See, for example Sander et al, *J. Appl. Polymer Sci.*, 9, 1984-1996 (1965); Uribe et al, *Polym. Sci. Technical*, 31, 251-73 (1985); Kordomenos et al, *Journal of Coating Technology*, 55, No. 700, pp. 49 and 59 (1983); and PCT Patent Application WO/US 8606734. The epoxy-terminated polyoxazolidones can be cured with conventional epoxy hardeners. The cured epoxy resin exhibit very good thermal properties and solvent stability and have generally good impact properties. The epoxy-terminated polyoxazolidones are reported to be useful for the preparation of coatings resins and adhesives.

European Patent Application No. 0113575A discloses powder coating compositions comprising epoxy-terminated polyoxazolidone resins prepared by reacting a diepoxide and a diisocyanate in amounts which provide a ratio of epoxide equivalents to isocyanate equivalents of from 1.1:1 to 10:1 and curing agents. The polyoxazolidone resins are said to have comparatively high glass transition temperatures and provide coatings of improved resistance to cathodic disbandment. The coating composition are applied by fluidized bed sintering or electrostatic spray methods.

Self thermosetting compositions of polyisocyanates and polyepoxides are described in U.S. Patent Nos. 4,564,651 and 4,631,306 (both to Markert et al) which discloses a method for the preparation of reaction resin molded materials and molded materials for insulating components, respectively containing oxazolidone and isocyanurate rings by mixing a polyepoxide and a polyisocyanate to form a resin mixture having a viscosity up to 7000 mPa·s at 25°C and the mole ratio of epoxy to isocyanate groups of 1:1 to 5:1; reacting the resin mixture in the presence of an imidazole or tertiary amine catalyst at elevated gelling temperature of from 80°C to 130°C to form a cross-linked polymer; and heating the cross-linked polymer to 130°C to 200°C to cause post-hardening and produce a molded material. The molded materials are reported to exhibit improved mechanical properties.

U.S. Patent No. 3,334,110 (Schramm) discloses a method for preparing epoxy-terminated polyoxazolidones by reacting a polyisocyanate with a polyepoxide in the presence of a catalyst mixture comprising an alcohol and tertiary amine or a quaternary ammonium salt. The epoxy-terminated polyoxazolidones can be cured with epoxy curing catalysts or reacted with epoxy hardeners to give a variety of products useful in the fields of coatings, laminating, bonding, molding, foams etc.

U.S. Patent No. 4,066,628 (Ashida et al) discloses a process for preparing polyoxazolidones by reacting an organic isocyanate with an epoxide in the presence of dialkyl zinc, zinc carboxylate, organozinc chelate compound or trialkyl aluminum as the catalyst. Polyoxazolidones prepared by this process are useful starting materials for the manufacture of a wide variety of products including foams, coatings, adhesives, elastomers and the like.

Although numerous processes for the preparation of polyoxazolidones are described in the literature and various catalysts are used in these processes, only polyoxazolidones having fixed product specifications are produced. None of the known processes allows for the preparation of epoxy-terminated polyoxazolidones in controlled manner by manipulating various process parameters. None of the known processes provides for producing epoxy-terminated polyoxazolidones which will have particularly desired physical and mechanical properties by controlling the content of the oxazolidone and isocyanurate rings incorporated in the epoxy-terminated polyoxazolidone in order to accommodate desired end use of the polyoxazolidone. Furthermore, none of the known art discloses nor suggests that imidazole compounds would be useful as catalysts in a process for the preparation of epoxy-terminated polyoxazolidones.

Heretofore electrical laminates have been conventionally prepared from bisphenol A based epoxy resins advanced with either bisphenol A or tetrabromobisphenol A and cured with a biguanide such as dicyanodiamide. However, for many applications, such as multilayered printed circuit boards, the glass transition temperature (T_g) of the cured epoxy resins is undesirably low, for example, less than 135°C and the chemical resistance of the cured epoxy resins is also undesirably low, for example, N-methylpyrrolidone pick-up is greater than 0.5 weight percent. Although in many applications these physical properties are acceptable, for many applications it is desirable to have cured epoxy resins which have glass transition

temperature above 135°C and chemical resistance such as N-methyl-pyrrolidone pick-up of less than 0.1 weight percent. There are available specialty epoxy resins and other resinous products which meet the desired higher standards but their use is limited due to the economics. In particular, the cost associated with these resins precludes them from being used in the most of the applications associated with electrical circuit boards.

There is a need in industry for a process which will allow for the preparation of epoxy-terminated polyoxazolidones in a targeted manner by controlling various process parameters to obtain materials having physical and mechanical properties targeted to specific, desired end uses of such materials.

There is also a great need for engineering materials which will have the desired physical and mechanical properties (particularly, sufficiently high Tg's and chemical resistance properties) and still be inexpensive enough to be used in the most of the electrical laminate applications, particularly in electrical circuit board applications.

The present invention provides such engineering materials which materials have physical and mechanical properties targeted to specific end uses. Moreover, the present invention provides a process for the preparation of these engineering materials which process can be controlled in a targeted manner by manipulating various process parameters.

EP-A-296450 discloses a process for the preparation of epoxy-terminated polyoxazolidones, in which a polyisocyanate is added to a polyepoxide and a phosphonium salt catalyst.

US-A-3979365 also discloses (in its reference examples) a process for the preparation of epoxy-terminated polyoxazolidones. In the said examples, the reaction is carried out in the presence of a solvent.

The present invention provides a process for the preparation of an epoxy-terminated polyoxazolidone having, when cured, a glass transition temperature greater than 135°C and N-methylpyrrolidone pick-up of less than 0.5 percent, which process comprises reacting a polyepoxide compound with a polyisocyanate compound in the presence of a catalyst for the reaction of the epoxy and isocyanate groups at an elevated temperature, said process being characterized in that

A) the catalyst is an imidazole compound;

B) (1) from 5 to 30, preferably from 5 to 20, most preferably from 10 to 20 weight percent of the polyisocyanate compound is added within a period of time of from 3 to 90, preferably from 15 to 60, most preferably from 20 to 45 minutes to (2) a mixture comprising (a) from 70 to 95, preferably from 80 to 95, most preferably from 80 to 90 weight percent of the polyepoxide compound and (b) from 0.01 to 2, preferably 0.02 to 1, most preferably 0.02 to 0.1 weight percent of the catalyst, said weight percentages being based on the combined weight of the polyepoxide compound and polyisocyanate compound;

C) the reaction mixture obtained in step B is heated to a temperature of from 110°C to 200°C, preferably from 120°C to 180°C, most preferably from 140°C to 160°C for a period of time of from 5 to 180 minutes, preferably from 30 to 120, most preferably from 60 to 90 minutes; so as to obtain an epoxy-terminated polyoxazolidone having from 50 to 100 percent of the original isocyanate groups converted to oxazolidone rings and from 0 to 50 percent of the original isocyanate groups converted to isocyanurate rings; and

D) the reaction is carried out in the absence of a solvent or other reaction diluent.

The conversion of isocyanate groups to the oxazolidone and isocyanurate rings is controlled in any of the following manner:

(i) by increasing the reaction temperature at a given amount of the catalyst and a given amount of the polyisocyanate compound used when higher conversion to oxazolidone rings is desired; or

(ii) by increasing the amount of the catalyst at a given reaction temperature and a given amount of the polyisocyanate compound used when higher conversion to oxazolidone rings is desired; or

(iii) by increasing the amount of polyisocyanate used at a given amount of the catalyst and a given reaction temperature when higher conversion to isocyanurate rings is desired; or

(iv) by increasing the rate of addition of the polyisocyanate compound at a given reaction temperature, given amount of the catalyst and given amounts of the polyepoxide and polyisocyanate compounds when higher conversion to isocyanurate rings is desired; whereby the epoxy-terminated polyoxazolidone having from 50 to 100 percent of the original isocyanate groups converted to oxazolidone rings and from 0 to 50 percent of the original isocyanate groups converted to isocyanurate rings is obtained.

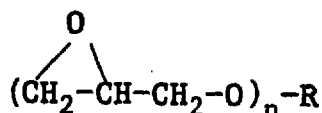
Yet in another aspect, the present invention concerns a process for preparing an epoxy resin varnish composition comprising preparing an epoxy-terminated polyoxazolidone epoxy resin by the process described hereinbefore, and mixing the epoxy resin with a hardener for the epoxy resin, an organic solvent, an accelerator, and, optionally, other conventional adjuncts.

Still in another aspect, the present invention concerns a process for preparing electrical laminates comprising the steps of:

- (a) forming a prepreg by impregnating a reinforcing web with an epoxy resin varnish composition, a hardener for the epoxy resin, an organic solvent, and optionally an accelerator;
- (b) heating the prepreg to a temperature sufficient to partially react the epoxy component of the varnish with the hardener component; and
- (c) laminating one or more layers of the prepreg with an electrically conductive material and heating the so formed laminate preferably at an elevated pressure to cur the epoxy resin, wherein the epoxy resin varnish is prepared by a process as described above.

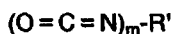
The polyepoxide compound useful in the practice of the present invention is suitably a compound which possesses more than one 1,2-epoxy group. In general, the polyepoxide compound is a saturated or unsaturated aliphatic, cycloaliphatic, aromatic or heterocyclic compound which possesses more than one 1,2-epoxy group. The polyepoxide compound can be substituted with one or more substituents which are non-reactive with the isocyanate groups such as lower alkyls and halogens. Such polyepoxide compounds useful in the practice of the present invention are described in the Handbook of Epoxy Resins by H.E. Lee and K. Neville published in 1967 by McGraw-Hill, New York and U.S. Patent No. 4,066,628.

Particularly useful polyepoxide compounds which can be used in the practice of the present invention are polyepoxides having the following general formula



wherein R is substituted or unsubstituted aromatic, aliphatic, cycloaliphatic or heterocyclic polyvalent group and n has an average value of from greater than 1 to less than 5. The preferred diepoxides include diglycidyl ether of 2,2-bis(4-hydroxyphenyl) propane (generally referred to as bisphenol A) and diglycidyl ether of 2,2-bis(3,5-dibromo-4-hydroxyphenyl) propane (generally referred to as tetrabromobisphenol A). Mixtures of any two or more polyepoxides can also be used in the practice of the present invention.

The polyisocyanate compound useful in the practice of the present invention is represented by the following general formula:



wherein R' is substituted or unsubstituted aliphatic, aromatic or heterocyclic polyvalent group and m has an average value of greater than 1 to less than 5, preferably from 1.5 to 4, most preferably from 2 to 3. Examples of suitable polyisocyanates include 4,4'-methylene bis(phenylisocyanate) (MDI) and isomers thereof, higher functional homologs of MDI (commonly designated as "polymeric MDI"), toluene diisocyanate (TDI) such as 2,4-toluene diisocyanate and 2,6-toluene diisocyanate, m-xylylene diisocyanate, hexamethylene diisocyanate (HMDI) and isophoronediiisocyanate. Mixtures of any two or more polyisocyanates can also be used in the practice of the present invention. Other suitable polyisocyanate compounds are described in U.S. Patent No. 3,313,747; 4,066,628 and 4,742,146.

Preferred polyisocyanate compounds are 4,4'-methylene bis(phenylisocyanate) (MDI) and isomers thereof, polymeric MDI and toluene diisocyanate (TDI). The most preferred polyisocyanate compounds are 4,4'-methylene bis(phenylisocyanate), isomers thereof and polymeric MDI.

A suitable catalyst is employed in the practice of the present invention to facilitate reaction of the polyepoxide compound with the polyisocyanate compound. The catalysts are imidazole compounds. Particularly, preferred catalysts are 2-phenylimidazole 2-methylimidazole, 1-methylimidazole, 2-ethyl-4-methylimidazole and 4,4'-methylene-bis(2-ethyl-5-methylimidazole).

The catalyst is generally employed in an amount of from 0.01 to 2; preferably 0.02 to 1, most preferably 0.02 to 0.1, weight percent based on the combined weight of the polyepoxide compound and polyisocyanate compound used.

In the practice of the present invention, an epoxy-terminated polyoxazolidone containing from 50 to 100 percent of the isocyanate groups converted to oxazolidone rings and from 0 to 50 percent of the isocyanate groups converted to isocyanurate rings is produced by reaction of the polyisocyanate compound with the polyepoxide compound in the presence of a suitable catalyst at elevated temperatures.

The polyisocyanate compound is employed in an amount of from 5 to 30, preferably 5 to 20, most preferably 10 to 20, weight percent, the weight percent being based on the combined weight of the polyepoxide and polyisocyanate reactants.

The polyepoxide compound is employed in an amount of from 70 to 95, preferably 80 to 95, most preferably 80 to 90, weight percent, the weight percent being based on the combined weight of the polyepoxide and polyisocyanate reactants.

The reaction of the polyepoxide with the polyisocyanate is conducted at a temperature of from 110°C to 200°C. Preferably, the reaction is conducted at a temperature of from 120°C to 180°C. Most preferably, the reaction is conducted at a temperature of from 140°C to 160°C.

In the practice of the present invention the catalyst is added to the reaction vessel containing the polyepoxide prior to the start of the addition of polyisocyanate compound. The temperature at which the catalyst is added is not critical. In general the catalyst is added at a temperature lower than the reaction temperature. The temperature is then raised and the reaction temperature maintained while the controlled addition of the polyisocyanate to the mixture of the catalyst and the polyepoxide is started. The polyisocyanate is added to the reaction vessel within a period of time of from 3 to 90, preferably 15 to 60, most preferably 20 to 45, minutes while maintaining the reaction temperature. The reaction temperature is maintained after the complete addition of the polyisocyanate for a period of time of from 5 to 180, preferably 15 to 120, most preferably 30 to 90 minutes.

The reaction of the polyepoxide compound and the polyisocyanate compound according to the process of the present invention is conducted neat, that is, in the absence of a solvent or other liquid reaction diluent.

In the practice of the present invention it has been surprisingly found that the conversion of the isocyanate groups can be controlled in a targeted manner to obtain the epoxy-terminated polyoxazolidone having from 5 to 30, preferably 5 to 20, most preferably 10 to 20, weight percent of the isocyanate content and having from 50 to 100 percent of the original isocyanate groups converted to oxazolidone rings and from 0 to 50 percent of the original isocyanate groups converted to isocyanurate rings in any of the following manner:

(i) at a given amount of the catalyst and a given amount of the polyisocyanate, higher conversion of the isocyanate groups to oxazolidone rings (up to 100 percent conversion) is achieved by increasing the reaction temperature; or

(ii) at a given amount of the polyisocyanate and a given reaction temperature, higher conversion of the isocyanate groups to oxazolidone rings (up to 100 percent conversion) is achieved by increasing the amount of the catalyst; or

(iii) at a given amount of the catalyst and a given reaction temperature, higher conversion of the isocyanate groups to isocyanurate rings (up to 50 percent conversion) is achieved by increasing the amount of the polyisocyanate; or

(iv) at a given reaction temperature and given amounts of the polyepoxide compound, polyisocyanate compound and catalyst, higher conversion of the isocyanate groups to isocyanurate rings (up to 50 percent conversion) is achieved by increasing the rate of addition of the polyisocyanate compound.

The relation between the various reaction parameters influencing conversion of isocyanate groups into oxazolidone rings can be expressed as follows:

$$\% \text{ Oxazolidone} = -3.17i + 0.135c - 2.126t + 8.685r + 0.0142t^2 - 0.184r^2$$

wherein *i* is weight percent of polyisocyanate, *c* is amount of catalyst (in ppm), *t* is reaction temperature (°C) and *r* is addition time of polyisocyanate (in min.).

Using the above equation, reaction parameters can be selected and the reaction conducted so as to obtain an epoxy-terminated polyoxazolidone having the desired content of oxazolidone rings (a margin of error: ±15 percent).

It should be understood that if the number obtained in the above equation is 100 or greater it represents 100 percent conversion of isocyanate groups into oxazolidone rings.

The process of the present invention provides for the preparation of the epoxy-terminated polyoxazolidone which have specific properties linked to the particular ratio of oxazolidone and isocyanurate rings.

The epoxy-terminated polyoxazolidones prepared according to the process of the present invention, when cured, are found to have unexpectedly high glass transition temperatures (up to 175°C and higher) and surprisingly high solvent resistance properties (for example N-methylpyrrolidone pick-up of less than 0.05 percent). The epoxy-terminated polyoxazolidones of the present invention, when cured, consistently have glass transition temperatures greater than 135°C and N-methylpyrrolidone pick-up of less than 0.5

percent. These properties make the epoxy-terminated polyoxazolidones of the present invention particularly advantageous for use in the electrical laminate applications, especially printed circuit board uses, in which high glass transition temperatures and high solvent resistance properties are highly sought after properties in the materials.

5 Laminates used in the preparation of electrical circuit boards, have been conventionally produced by impregnating a supporting or reinforcing web with a resin composition, by passing the impregnated mat through a heated chamber where the resin composition is partially cured and laminating one or more layers of the resin mat with a layer such as copper foil under the application of heat and pressure. The resin composition employed for impregnating, in general, is referred to as "varnish", and the impregnated resin
10 mat, conventionally, is referred to as "prepreg". The electrical laminate, is processed into circuit boards in known manner.

A typical epoxy resin composition for the electrical laminating applications comprises a brominated epoxy resin prepared from a diglycidyl ethers of bisphenol A and a tetrabromobisphenol A, dicyandiamide as a hardener, an organic solvent such as acetone, and an accelerator. Unfortunately, the glass transition
15 temperature of a cured epoxy resin prepared from this varnish composition is undesirably low, for example from 110°C to 135°C which causes problems in the subsequent processing steps used to prepare the printed circuit boards.

An alternative varnish composition for application to a reinforcing web used in the production of electrical laminates, comprises a blend of a diglycidyl ether of bisphenol A and either bisphenol or
20 tetrabromobisphenol A and a dicyandiamide as a hardener. The diglycidyl ether of bisphenol A is reacted in situ with bisphenol A and/or tetrabromobisphenol A and dicyandiamide during impregnation of the reinforcing web and the partial cure of the resin (see for example U.S. Patent No. 3,738,862). Unfortunately, this varnish composition also exhibit undesirably low glass transition temperatures (less than 135°C).

The present invention solves the problem experienced in the art by providing a process for the
25 preparation of an epoxy resin varnish composition comprising an epoxy resin, a hardener, an organic solvent, an accelerator and, optionally, another standard adjuncts characterized in that the epoxy resin is the epoxy-terminated polyoxazolidone having the isocyanate content of from 5 to 30 weight percent and having from 50 to 100 percent of the isocyanate groups converted to oxazolidone rings and from 0 to 50 percent of the isocyanate groups converted to isocyanurate rings.

30 The epoxy-terminated oxazolidones are prepared according to the process described hereinbefore.

When cured, the epoxy resin varnish compositions of the present invention exhibit surprisingly excellent physical and mechanical properties. In particular the cured epoxy-terminated polyoxazolidones exhibit substantially higher glass transition temperatures, for example, 175°C and higher, than the conventional epoxy resins cured with dicyandiamide. In addition, the cured epoxy-terminated polyoxazolidone exhibit
35 surprisingly high resistance to attack by various chemicals as demonstrated by the N-methylpyrrolidone pick-up of less than 0.1 percent.

The organic solvents suitably employed for the epoxy resin varnish compositions of the present invention are those organic liquids in which the epoxy-terminated polyoxazolidone and the hardener are soluble and which are sufficiently volatile such that they escape from the varnish composition before and/or
40 during the partial cure and/or before the final cure. Illustrative examples of such organic liquids are various glycol ethers such as ethylene or propylene glycol monomethylether and the esters thereof such as ethylene glycol monomethylether acetate; ketones such as methylisobutyl ketone, methylethyl ketone, acetone and methylisopropyl ketone; and aromatic hydrocarbons such as toluene and xylene or mixtures thereof. Of such organic liquids, those preferably used as the solvent in the epoxy resin composition of the
45 present invention are the ketones, particularly acetone, methyl ethyl ketone and methyl isobutyl ketone, or mixtures of these ketones with each other or with one or more of the other solvents. Other solvents that can be used are dimethyl sulfoxide (DMSO), N-methylpyrrolidone and dimethylformamide.

The amount of solvent most advantageously employed in the varnish composition of the present invention will vary depending on a variety of factors including the particular solvent, hardener and epoxy
50 resin employed, desired properties of the epoxy resin composition (for example, desired viscosity of the varnish composition and the desired resin "pick-up" of this composition by the reinforcing web). Advantageously, the composition exhibits a viscosity from 50 to 1000 millipascal seconds (mPa·s) measured using a Brookfield viscometer, Type RVT, 20 rpm and the appropriate spindle at 25°C. In general, the amount of solvent will range from 20 to 60, preferably from 25 to 50 weight percent, based on the total weight of the
55 varnish composition, the remainder comprising non-volatiles components (amount of the total solids other than the solvents). More preferably, the epoxy composition will contain from 20 to 45 weight percent of the solvent and from 55 to 80 weight percent non-volatiles.

The hardener useful in the present invention is capable of curing the epoxy-terminated polyoxazolidone and is soluble in the solvent employed. The hardener useful in the epoxy resin varnish composition of the present invention is suitably dicyandiamide system, bisphenols such as bisphenol A and tetrabromobisphenol A, and multifunctional novolacs.

The amount of the hardener in the epoxy resin varnish composition of the present invention is dependent on a variety of factors including the specific hardener and the epoxy resin employed and the desired properties of the varnish composition. In general, the amount of the hardener is selected to give the cured epoxy-terminated polyoxazolidone composition the maximum glass transition temperature. Conveniently, from 1 to 8, preferably 2 to 6, most preferably 3 to 5, phr of the dicyandiamide system are employed in the present invention. In general, the polyhydric phenolic hardener is employed in amounts such that the epoxy resin varnish composition comprises from 0.5 to 1.5 preferably 0.75 to 1.2, most preferably 0.9 to 1.1, phenolic hydroxyl groups per epoxy group.

The epoxy resin varnish compositions of the present invention will also contain an accelerator. Illustrative examples of accelerators include the stannous salts of monocarboxylic acids, such as stannous octoate and stannous laurate, various alkali metal salts such as lithium benzoate, certain heterocyclic compounds such as the imidazole and benzimidazole compounds and salts thereof, tertiary amine borates and tertiary amines. Preferred accelerators are the benzyldimethylamine and imidazoles, particularly the alkyl-substituted imidazole and phenyl-substituted imidazoles. The most preferred accelerators are 2-methyl imidazole and 2-phenyl imidazole. Additional accelerators that can be used in the present invention are described in U.S. Patent 3,738,862 (Klarquist et al).

In general, if employed, the accelerator is used in an amount sufficient to catalyze the reaction. The accelerator is generally used in amounts of from 0.01 to 2 weight percent based on the combined weight of the epoxy resin and hardener. Preferably, the accelerator is employed in an amount of from 0.02 to 1 weight percent based on the combined weight of the epoxy resin and hardener.

The epoxy resin varnish compositions can optionally contain adjuncts such as pigments, fillers, dyes. The adjuncts employed in the practice of the present invention are well-known in the art and reference is made thereto for the purposes of this invention.

The epoxy resin varnish compositions of the present invention are particularly useful in impregnating weaves, webs, fabric and cloth of variety of different materials including glass, quartz and synthetic fibers such as aramid. In the preparation of electrical laminates, a glass web is conventionally employed.

In the process of the present invention for preparing electrical laminates, the varnish composition is applied to the reinforcing web in a desired amount and the web subsequently heated to advance and/or cure the epoxy-terminated polyoxazolidone. Although the amounts of the epoxy resin varnish composition which are applied to the reinforcing web will vary depending on the specific web and epoxy resin varnish composition employed and the desired properties of the impregnated cloth and electrical laminates prepared therefrom, the epoxy resin varnish composition of the present invention is generally applied to the reinforcing web in conventional amounts; which amounts vary from 30 to 70 weight percent, based on the total weight of the impregnated web.

The impregnated web or prepreg is subsequently processed using conventional techniques. Such techniques involve advancing and/or curing the epoxy resin by heating the impregnated web to an elevated temperature such as from 100°C to 200°C. Subsequently, the prepreg is fabricated into laminates by laminating one or more prepreps, commonly cut to a predetermined size, with thin layers of an electrical conductive material such as copper foil using elevated temperatures and pressures. Conventionally, the laminating temperature vary from 130°C to 230°C, with pressures varying from 34 kPa to 6.9 MPa.

The present invention is further illustrated by the following examples in which the formation of oxazolidone and isocyanurate rings is confirmed by infrared (IR) spectrum. The percent conversions of isocyanate groups to oxazolidone and isocyanurate rings is calculated from the relative intensities of oxazolidone and isocyanurate IR bands.

Various terms and designations used in the examples are explained hereinbelow.

Epoxy Resin A stands for a diglycidyl ether of bisphenol A having an epoxy equivalent weight between 177 and 189 sold by The Dow Chemical Company under the trademark D.E.R. 330.

Epoxy resin B stands for an epoxidized phenolformaldehyde novolac resin having an EEW between 176 and 181 with functionality of 3.6 sold by The Dow Chemical Company under the trademark D.E.N. 438.

Epoxy resin C stands for a diglycidyl ether of tetrabromobisphenol A having an EEW between 325 and 375 sold by The Dow Chemical Company under the trademark D.E.R. 542.

Epoxy resin D stands for triglycidyl ether of tris (hydroxyphenyl)methane having an EEW between 145 and 175 sold by The Dow Chemical Company under the trademark TACTIX 742.

Epoxy resin E stands for diglycidyl ether of bisphenol A having an EEW of 400-475 sold by The Dow Chemical Company under the trademark D.E.R. 652 A75.

Epoxy resin F stands for brominated bisphenolic epoxy resin having an EEW of 480 to 560 and bromine content of 20.5 to 22.5 weight percent, sold by The Dow Chemical Company under the trademark D.E.R. 512 A75.

TBBA stands for tetrabromobisphenol A.

TDI stands for toluenediisocyanate

Isocyanate A stands for MDI sold by The Dow Chemical Company under the trademark ISONATE M 143.

Isocyanate B stands for polymeric MDI sold by The Dow Chemical Company under the trademark VORANATE M 220.

Isocyanate C stands for 20/80 isomer mixture of TDI.

DICY stands for dicyandiamide.

NMP stands for N-methylpyrrolidone.

The following analytical methods are used for various measurements in the examples.

The standard wet titration method was used to determine Epoxy Equivalent Weight.

The solids content was calculated from the difference of weight of a sample (approximately 1 g) before and after heating in an aluminium dish on a hot plate at 150 °C for an hour and then for a further hour in a vacuum oven at 150 °C.

The viscosity of the resin was measured according to ASTM D445 method using a Cannon Fenske Viscometer at 25 °C. Reactivity of the resins was measured according to the following method: The resin solution was blended with 0.1 phr 2-methylimidazole based on solid. 2-methylimidazole was first dissolved in acetone to form a 10 percent solution. The mixture was then reacted on the surface of a hot plate held at 175 °C. The reactivity was reported as elapsed time required for gelation.

The glass transition temperature was measured on film prepared from the varnish formulation used for reactivity measurement. The film were cured on a hot plate at 175 °C for 90 min. Samples were run at 10C°/min. from 38 °C using a METTLER TA™ 2000 DTA.

The glass transition temperature of the laminate was measured directly on the cured laminate according to the method for measuring glass transition temperature on film.

The melt viscosity was measured according to the ASTM D445 method using an ICI cone and plate viscosimeter.

To measure the chemical resistance, three pieces of etched laminates 6 cm x 1.5 cm were cut, weighed and dipped for 30 minutes in N-methylpyrrolidone solvent at 23 °C. The pieces were dried and then weighed; the solvent pick up was taken as the gain in weight.

To measure the moisture resistance, twelve pieces of etched laminates 6 cm x 1.5 cm were placed in a pressure cooker in water for 30, 60 or 90 minutes at 120 °C. Then, after being dried were dipped (20 seconds) in a tin solder bath (260 °C), to determine resistance to blistering due to moisture absorption.

The binding strength between the copper and the epoxy resin was determined through the strength needed to peel off the copper from a laminate.

The volatile determination of the prepreg was done as follows:

A sample of prepreg approximately 10 cm x 10 cm was weighed to the nearest 0.001 gram (W_1). The sample is placed in a circulating air oven at 163 °C for 15 minutes and on removal it was placed immediately in a desiccator to cool. When cooled, the sample was reweighed and the weight recorded as W_2 . The volatile content is calculated from:

$$\% \text{ volatiles} = \frac{(W_1 - W_2) \times 100}{W_1}$$

In the following examples, all parts and percentages are by weight unless otherwise expressly indicated.

Preparation of the Epoxy-Terminated PolyoxazolidonesExample 1 (10% Polyisocyanate/90% Epoxy Resin)

To a 1000 ml 3-neck flask equipped with pneumatic stirrer water cooled condenser, inlet for nitrogen padding, a thermocouple, temperature controller, heating mantle and an attached addition funnel, was added Epoxy Resin A (450 g; EEW=180). The flask was heated up to about 145 °C to 150 °C while stirring and was padded with nitrogen. 2-Methyl-imidazole (0.15 g; 0.03 percent) was then added to the flask and the resultant mixture was heated to 160 °C. At that time, of Isocyanate A (50 g) was placed in the addition funnel. Isocyanate was added dropwise to the mixture of Epoxy Resin A and 2-methylimidazole at 160 °C within a period of 30 minutes. The reaction mixture was maintained at a temperature of 160 °C for additional 15 minutes after completion of the addition of Isocyanate A.

The IR spectrum of the sample of the product showed the presence of the characteristic absorption band of oxazolidone J (C=O) at 1755 cm⁻¹. The characteristic absorption bands of isocyanate J (C=O) at 2250 to 2270cm⁻¹ and isocyanurate J (C=O) at 1700 cm⁻¹ were not present. This indicates 100 percent conversion of isocyanate groups into oxazolidone rings.

The obtained epoxy-terminated polyoxazolidone has an EEW of 222 and viscosity of 600 mPa·s at 80 °C. This product is referred to as Resin 1 hereinafter.

Example 2 (20% Polyisocyanate/80% Epoxy Resin)

To a 100 ml 3-neck flask equipped as in Example 1, was added Epoxy Resin A (400 g; EEW=180). The flask was heated to about 135 °C to 140 °C while stirring and was padded with nitrogen. 2-Phenylimidazole (0.11 g; 0.022 percent) was added to the flask and the resultant mixture heated to 150 °C. Then, Isocyanate A (100 g) was placed in the addition funnel and added dropwise to the flask within a period of time of 30 minutes while maintaining the reaction temperature at 150 °C. Samples were taken periodically after the end of addition of Isocyanate A and analyzed by titrating for residual epoxide and by infrared analysis.

The IR spectrum of the sample of the product taken at 60 minutes after the end of the addition of Isocyanate A showed the presence of characteristic absorption bands of oxazolidone J(C=O) at 1753 cm⁻¹ and of isocyanurate J(C=O) at 1709 cm⁻¹ with approximately the same absorption intensities. The isocyanate band was not present, which indicates that about 50 percent of isocyanate groups was converted to oxazolidone rings and 50 percent was converted to isocyanurate rings.

The obtained epoxy-terminated polyoxazolidone is a solid at 25 °C, has an EEW of 253 and viscosity of 460 mPa·s at 150 °C. This product is referred to as Resin 2 hereinafter.

Example 3 (9.4% Polyisocyanate/90.6% Epoxy Resin Advanced with Bisphenol A)

A. To a flask equipped as in Example 1 was added 532 g of Epoxy Resin A (EEW=180). While stirring, the flask was heated to about 85 °C to 90 °C and padded with nitrogen. At about 90 °C, 1.89 g of tetraphenylphosphonium bromide was added to the flask and the resultant mixture heated to about 150 °C. Then, 64.7 g of Isocyanate A was placed in the addition funnel and added dropwise to the flask within a period of 3 minutes. The temperature of the reaction mixture was raised by exothermic reaction to about 195 °C. Approximately 10 minutes after the end of addition of Isocyanate A, a sample was taken and analyzed by titrating for residual epoxide, and by infrared analysis. The product obtained is a semi-solid at room temperature. This product has an EEW of 234 and melt viscosity of 9280 mPa·s at 60 °C.

B. The above semi-solid product (254.8 g) was added to another flask and heated to about 85 °C to 90 °C and the flask padded with nitrogen. At about 90 °C, bisphenol A (40.5 g) was added to the flask while stirring and the temperature of the reaction mixture raised by the exothermic reaction to about 187 °C. A sample was taken 45 minutes after the addition of bisphenol A and titrated. The reaction was complete and the EEW of the product advanced in molecular weight is 416. This product is referred to as Resin 3 hereinafter.

Example 4 (30% Polyisocyanate/70% Epoxy Resin)

To a flask equipped as in Example 1 was added 350 g of Epoxy Resin A (EEW=180). While stirring, the flask was heated to about 165 °C to 170 °C and padded with nitrogen. At about 170 °C, 0.25 g (0.05 percent) of 2-phenylimidazole was added to the flask and the resultant mixture heated to 180 °C. Then, 150

g of Isocyanate A was added dropwise to the mixture during a period of 45 minutes while the reaction temperature increased from 180 °C to 190 °C. Samples were taken periodically and analyzed by titration and infrared spectroscopy. The reaction mixture was maintained at 180 °C for additional 60 minutes.

The IR spectrum of the sample taken 60 minutes after the end of addition of Isocyanate A showed the presence of the characteristic absorption band of oxazolidone J(C=O) at 1752 cm⁻¹. The characteristic band of isocyanate and isocyanurate were not present.

This product is a solid material at room temperature and has an EEW of 588. The product is referred to as Resin 4 hereinafter.

10 Example 5 (20% Polyisocyanate/80% Epoxy Resin)

To a flask equipped as in Example 1 was added 400g of Epoxy Resin A (EEW = 180). While stirring the content, the flask was heated to about 145 °C to 150 °C and padded with nitrogen. 2-Phenylimidazole (0.175 g; 0.035 percent) was added to the flask and the resultant mixture heated to 160 °C. Then, Isocyanate A (100 g) was added dropwise to the mixture within a period of 45 minutes. The temperature was raised by the exothermic reaction to about 180 °C to 185 °C. Sample of the product was taken 15 minutes after the end of addition of Isocyanate A and analyzed by titrating for residual epoxide and infrared spectroscopy. The characteristic absorption band of oxazolidone J(C=O) at 1750 cm⁻¹ was present. The isocyanate and isocyanurate absorption bands were not present. This indicates 100 percent conversion of isocyanate groups to oxazolidone rings. The product obtained is a solid at room temperature and has an EEW of 330 and viscosity of 580 mPa·s at 150 °C. This product is referred to as Resin 5 hereinafter.

Example 6 (14% Polyisocyanate/86% Epoxy Resin)

To a flask equipped as in Example 1 were added Epoxy Resin A (245 g) and Epoxy Resin C (185 g). While stirring the content, the flask was heated to about 145 °C to 150 °C and padded with nitrogen. 2-phenyl-imidazole (0.2 g dissolved in 0.2 g methanol) was added to the flask and the resultant mixture heated to about 155 °C. Then, Isocyanate B (70 g) was added dropwise to the mixture within a period of 30 minutes. The temperature of the reaction mixture was raised by the exothermic reaction to about 175 °C to 180 °C. A sample of the product was taken 30 minutes after the end of the addition of Isocyanate B and analyzed by titrating for residual epoxide and infrared spectroscopy. The infrared spectroscopy showed the presence of oxazolidone band J(C=O) at 1752 cm⁻¹. No isocyanate and isocyanurate bands were present. This indicates 100 percent conversion of isocyanate groups to oxazolidone rings.

The product obtained is a solid at room temperature and has an EEW of 356 and viscosity of 900 mPa·s at 150 °C. This product is referred to as Resin 6 hereinafter.

Example 7 (7.5% Polyisocyanate/92.5% Epoxy Resin Advanced with TBBA)

(A) To a flask equipped as in Example 1 was added Epoxy Resin A (307.6 g; EEW = 177) and the flask was heated to about 135 °C to 140 °C and padded with nitrogen while the content was stirred. 2-Ethyl-4-methylimidazole (0.276 g; 0.08 percent) was added to the flask and the resultant mixture heated to about 145 °C. Then, Isocyanate A (37.4 g) was added dropwise to the mixture within a period of 25 minutes. The temperature of the reaction mixture was kept at 160 °C. The reaction temperature was kept at 160 °C and 20 minutes after the end of the Isocyanate A addition a sample of the product was taken and analyzed by titrating for residual epoxide and by infrared spectroscopy. This product is a semi-solid at room temperature and has an EEW of 224.

(B) While the reaction temperature was kept at 160 °C, tetrabromobisphenol A (155 g) was added to the flask containing the product of above paragraph for the advancement in molecular weight of the product. The reaction temperature was then lowered to 150 °C and the advancement reaction continued at that temperature for about 30 minutes. The advanced product has an EEW of 567. This product is referred to as Resin 7 hereinafter.

Example 8 (19% Polyisocyanate/81% Epoxy Resin)

To a flask equipped as in Example 1 was added Epoxy Resin A (405 g; EEW = 177). While stirring the content the flask was heated to about 145 °C and padded with nitrogen. 2-Phenylimidazole (0.175 g; 0.035 percent) was then added to the flask and the resultant mixture heated to about 155 °C. Isocyanate B (95 g) was added dropwise to the mixture within a period of 30 minutes. A sample of the product was taken 60

minutes after the end of the Isocyanate B addition and analyzed by titration for residual epoxide and by infrared spectroscopy. The characteristic absorption band of oxazolidone $J(C=O)$ at 1752 cm^{-1} was present. The isocyanate and isocyanurate absorption bands were not present. This indicates 100 percent conversion of isocyanate groups to oxazolidone groups. The product obtained has an EEW of 320 and melt viscosity of $840\text{ mPa}\cdot\text{s}$ at 150°C .

Example 9 (7.5% Polyisocyanate/92.5% Epoxy Resin)

To a flask equipped as in Example 1 was added Epoxy Resin C (4625 g; EEW = 330). While stirring the content, the flask was heated to about 150°C and padded with nitrogen. 2-Phenylimidazole (0.25 g/ 0.05 percent) was then added to the flask and the resultant mixture heated to about 160°C . Then, Isocyanate B (37.5 g) was added dropwise to the mixture within a period of 30 minutes. A sample of the product was taken 60 minutes after the end of Isocyanate B addition and analyzed by titrating for residual epoxide and by infrared spectroscopy. The characteristic absorption band of oxazolidone $J(C=O)$ at 1752 cm^{-1} was present. The isocyanate and isocyanurate bands were not present. This indicates 100 percent conversion of isocyanate groups to oxazolidone rings. The product obtained has an EEW of 440 and melt viscosity of $920\text{ mPa}\cdot\text{s}$ at 150°C .

Example 10 (10% Polyisocyanate/90% Epoxy Resin)

To a flask equipped as in Example 1 was added Epoxy Resin D (450 g; EEW = 160). While stirring the content, the flask was heated to about 150°C and padded with nitrogen. 2-Phenylimidazole (0.175 g/ 0.035 percent) was then added to the flask and the resultant mixture heated to about 160°C . Then, Isocyanate A (50 g) was added dropwise to the mixture within a period of 30 minutes and the reaction temperature maintained at 160°C after the end of the Isocyanate addition for 60 minutes. At that time a sample of the product was taken and analyzed by titrating for residual epoxide and by infrared spectroscopy. The characterized absorption band of oxazolidone $J(C=O)$ at 1752 cm^{-1} was present. The absence of isocyanate and isocyanurate bands indicates 100 percent conversion of isocyanate groups to oxazolidone rings.

Example 11 (15% TDI/ 85% Epoxy Resin)

To a 1000 ml 3-neck flask equipped with pneumatic stirrer water cooled condenser, inlet for nitrogen padding, a thermocouple, temperature controller, heating mantle and an attached addition funnel, was added Epoxy Resin A (425 g; EEW = 180). The flask was heated up to about 150°C while stirring and was padded with nitrogen. 2-Phenylimidazole (0.15 g; 0.03 percent) was then added to the flask and the resultant mixture was heated to 160°C . At that time, of Isocyanate C (75 g) was placed in the addition funnel. Isocyanate was added dropwise to the mixture of Epoxy Resin A and 2-phenylimidazole at 160°C within a period of 30 minutes. The reaction mixture was maintained at a temperature of 160°C for additional 60 minutes after completion of the addition of Isocyanate C.

The IR spectrum of the sample of the product taken at 60 minutes after the end of the addition of Isocyanate C showed the presence of characteristic absorption bands of oxazolidone $J(C=O)$ at 1753 cm^{-1} and of isocyanurate $J(C=O)$ at 1709 cm^{-1} with approximately a ratio 85/15 absorption intensity. The isocyanate band was not present, which indicates that about 85 percent of isocyanate groups was converted to oxazolidone rings and 15 percent was converted to isocyanurate rings.

The obtained epoxy-terminated polyoxazolidone is a solid at 25°C , has an EEW of 315 and viscosity of $440\text{ mPa}\cdot\text{s}$ at 150°C . This product is referred to as Resin 11 hereinafter.

Example 12 (10% Polyisocyanate/90% Epoxy Resin)

To a 1000 ml 3-neck flask equipped with pneumatic stirrer water cooled condenser, inlet for nitrogen padding, a thermocouple, temperature controller, heating mantle and an attached addition funnel, was added Epoxy Resin A (450 g; EEW = 177). The flask was heated up to about 130°C while stirring and was padded with nitrogen. 2-Phenylimidazole (0.15 g; 0.03 percent) was then added to the flask and the resultant mixture was heated to 140°C . At that time, of Isocyanate A (50 g) was placed in the addition funnel. Isocyanate was added dropwise to the mixture of Epoxy Resin A and 2-phenylimidazole at 140°C within a period of 30 minutes. The reaction mixture was maintained at a temperature of 140°C for additional 15 minutes after completion of the addition of Isocyanate A.

The IR spectrum of the sample of the product showed the presence of the characteristic absorption band of oxazolidone J ($C=O$) at 1755 cm^{-1} . The characteristic absorption bands of isocyanate J ($C=O$) at 2250 to 2270 cm^{-1} and isocyanurate J ($C=O$) at 1700 cm^{-1} were not present. This indicates 100 percent conversion of isocyanate groups into oxazolidone rings.

The obtained epoxy-terminated polyoxazolidone has an EEW of 288 and viscosity of $600\text{ mPa}\cdot\text{s}$ at 80°C . This product is referred to as Resin 12 hereinafter.

Example 13 (10% Polyisocyanate/90% Epoxy Resin)

The reaction conditions were the same as Example 12, except the amounts of 2-phenylimidazole used was (0.075 g; 0.015 percent). The reaction mixture was maintained at a temperature of 140°C for additional 120 minutes after completion of the addition of Isocyanate A.

The IR spectrum of the sample of the product taken at 120 minutes after the end of the addition of Isocyanate A showed the presence of characteristic absorption bands of oxazolidone J($C=O$) at 1753 cm^{-1} and of isocyanurate J($C=O$) at 1709 cm^{-1} with approximately the same absorption intensities. The isocyanate band was not present, which indicates that about 50 percent of isocyanate groups was converted to oxazolidone rings and 50 percent was converted to isocyanurate rings.

The obtained epoxy-terminated polyoxazolidone is a semi-solid at 25°C , has an EEW of 204 and viscosity of $610\text{ mPa}\cdot\text{s}$ at 80°C . This product is referred to as Resin 13 hereinafter.

Example 14 (10% Polyisocyanate/90% Epoxy Resin)

The reaction conditions were the same as Example 12, except the Isocyanate A was added dropwise to the mixture of Epoxy Resin A and 2-phenylimidazole at 140°C within a period of 10 minutes (instead of 30 minutes). The reaction mixture was maintained at a temperature of 140°C for additional 60 minutes after completion of the addition of Isocyanate A.

The IR spectrum of the sample of the product taken at 60 minutes after the end of the addition of Isocyanate A showed the presence of characteristic absorption bands of oxazolidone J($C=O$) at 1754 cm^{-1} and of isocyanurate J($C=O$) at 1708 cm^{-1} with approximately the same absorption intensities. The isocyanate band was not present, which indicates that about 50 percent of isocyanate groups was converted to oxazolidone rings and 50 percent was converted to isocyanurate rings.

The obtained epoxy-terminated polyoxazolidone is a semi-solid at 25°C , has an EEW of 212 and viscosity of $1960\text{ mPa}\cdot\text{s}$ at 80°C . This product is referred to as Resin 14 hereinafter.

Example 15 (15% Polyisocyanate/85% Epoxy Resin)

To a 1000 ml 3-neck flask equipped with pneumatic stirrer water cooled condenser, inlet for nitrogen padding, a thermocouple, temperature controller, heating mantle and an attached addition funnel, was added Epoxy Resin A (425 g; EEW = 180). The flask was heated up to about 150°C while stirring and was padded with nitrogen. 2-Phenylimidazole (0.15 g; 0.03 percent) was then added to the flask and the resultant mixture was heated to 160°C . At that time, of Isocyanate A (75 g) was placed in the addition funnel. Isocyanate was added dropwise to the mixture of Epoxy Resin A and 2-phenylimidazole at 160°C within a period of 30 minutes. The reaction mixture was maintained at a temperature of 160°C for additional 15 minutes after completion of the addition of Isocyanate A.

The IR spectrum of the sample of the product showed the presence of the characteristic absorption band of oxazolidone J ($C=O$) at 1755 cm^{-1} . The characteristic absorption bands of isocyanate J ($C=O$) at 2250 to 2270 cm^{-1} and isocyanurate J ($C=O$) at 1700 cm^{-1} were not present. This indicates 100 percent conversion of isocyanate groups into oxazolidone rings.

The obtained epoxy-terminated polyoxazolidone has an EEW of 258 and viscosity of $260\text{ mPa}\cdot\text{s}$ at 120°C . This product is referred to as Resin 15 hereinafter.

Example 16 (15% Polyisocyanate/85% Epoxy Resin)

To a 1000 ml 3-neck flask equipped with pneumatic stirrer water cooled condenser, inlet for nitrogen padding, a thermocouple, temperature controller, heating mantle and an attached addition funnel, was added Epoxy Resin A (425 g; EEW = 180). The flask was heated up to about 130°C while stirring and was padded with nitrogen. 2-Phenylimidazole (0.15 g; 0.03 percent) was then added to the flask and the resultant mixture was heated to 160°C . At that time, of Isocyanate A (75 g) was placed in the addition

funnel. Isocyanate was added dropwise to the mixture of Epoxy Resin A and 2-phenylimidazole at 140 °C within a period of 30 minutes. The reaction mixture was maintained at a temperature of 140 °C for additional 60 minutes after completion of the addition of Isocyanate A.

The IR spectrum of the sample of the product taken at 60 minutes after the end of the addition of Isocyanate A showed the presence of characteristic absorption bands of oxazolidone J(C=O) at 1754 cm⁻¹ and of isocyanurate J(C=O) at 1707 cm⁻¹ with approximately the same absorption intensities. The isocyanate band was not present, which indicates that about 55 percent of isocyanate groups was converted to oxazolidone rings and 45 percent was converted to isocyanurate rings.

The obtained epoxy-terminated polyoxazolidone has an EEW of 234 and viscosity of 330 mPa·s at 120 °C. This product is referred to as Resin 16 hereinafter.

Example 17 (20% Polyisocyanate/80% Epoxy Resin)

To a 100 ml 3-neck flask equipped as in Example 1, was added Epoxy Resin A (400 g; EEW = 180). The flask was heated to about 150 °C while stirring and was padded with nitrogen. 2-Phenylimidazole (0.15 g; 0.03 percent) was added to the flask and the resultant mixture heated to 160 °C. Then, Isocyanate A (100 g) was placed in the addition funnel and added dropwise to the flask within a period of time of 30 minutes while maintaining the reaction temperature at 160 °C. Samples were taken periodically after the end of addition of Isocyanate A and analyzed by titrating for residual epoxide and by infrared analysis.

The IR spectrum of the sample of the product taken at 60 minutes after the end of the addition of Isocyanate A showed the presence of characteristic absorption bands of oxazolidone J(C=O) at 1753 cm⁻¹ and of isocyanurate J(C=O) at 1709 cm⁻¹ with approximately a ratio of 70/30 absorption intensity. The isocyanate band was not present, which indicates that about 70 percent of isocyanate groups was converted to oxazolidone rings and 30 percent was converted to isocyanurate rings.

The obtained epoxy-terminated polyoxazolidone 15 a solid at 25 °C, has an EEW of 284 and viscosity of 280 mPa·s at 150 °C. This product is referred to as Resin 17 hereinafter.

Example 18 (15% Polyisocyanate/85% Epoxy Resin)

To a 100 ml 3-neck flask equipped as in Example 1, was added Epoxy Resin A (400 g; EEW = 180) and Epoxy Resin B (25 g; EEW 185). The flask was heated to about 150 °C while stirring and was padded with nitrogen. 2-Phenylimidazole (0.1 g; 0.02 percent) was added to the flask and the resultant mixture heated to 160 °C. Then, Isocyanate A (75 g) was placed in the addition funnel and added dropwise to the flask within a period of time of 30 minutes while maintaining the reaction temperature at 160 °C. Sample was taken 60 minutes after the end of addition of Isocyanate A and analyzed by titrating for residual epoxide and by infrared analysis.

The IR spectrum of the sample of the product showed the presence of the characteristic absorption band of oxazolidone J (C=O) at 1755 cm⁻¹. The characteristic absorption bands of isocyanate J (C=O) at 2250-2270 cm⁻¹ and isocyanurate J (C=O) at 1700 cm⁻¹ were not present. This indicates 100 percent conversion of isocyanate groups into oxazolidone rings.

The obtained epoxy-terminated polyoxazolidone has an EEW of 263 and viscosity of 50 mPa·s at 150 °C. This product is referred to as Resin 18 hereinafter.

Preparation of Varnishes and Laminates

Using procedures described in the Examples hereinbefore, Resins 1 to 7 and 9 were prepared in larger quantities in a 10 liter stainless steel reaction. After the completion of the reactions which was indicated by the absence of the isocyanate band in the IR spectra of the samples taken, each reaction mixture was cooled to about 130 °C and diluted with methylethylketone to give a solution of from 70 to 80 percent solids content.

Epoxy Resin varnishes are prepared by mixing solution of an epoxy-terminated polyoxazolidone of this invention, a hardener, a solvent and an accelerator at room temperature in a container equipped with a stirrer according to the proportions (based on solid resins) indicated in Table 1 below. Approximately 15kg of each Epoxy Resin Varnish were prepared.

The resulting varnishes were used to impregnate a glass cloth (Marglass 7628 finish 782). This cloth is an industrial glass silk fabric having equal warp and weft (plain weave) of electrical grade glass treated with finish 782. The glass silk fabric was impregnated with the varnish on the horizontal pilot plant size Caratsch treater.

The varnish was applied to a glass silk fabric by pulling the glass silk fabric through a resin bath containing the varnish and then through a doctor bar set at about 0.5 to 1.3 mm and then through three air heated zones to a temperature of from 150 °C to 170 °C. The total length of all three heating zones was 3 meters. The glass silk fabric passed through the resin bath and heating zones at a rate of 0.5 to 2.5 m/min.

5 The treater parameters were adjusted to produce prepreg with the following characteristics:

		Test method
Rest gel time at 175 °C	100-200 sec	NEMA LI 1-12.19
Flow at 170 °C	12- 20 %	NEMA LI 1-14.32
Volatile	< 1 %	
Resin content	40-44 %	NEMA LI 1-12.16

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except for Examples III and XII, in which the parameters were adjusted to produce the following characteristics:

Rest gel time at 170 °C	60 - 100 sec
Flow at 170 °C	10 - 25%

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The prepregs were then fabricated into "FR-4" and "G-10" type electrical laminates by placing 8 plies of prepreg between 2 sheets of copper foil and pressing in a laboratory press (LAUFFER) following the press cycle:

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0 - 30 min. low pressure (14 kg/cm²) R.T. to 170 °C

30 - 120 min. high pressure (45 kg/cm²) at 170 °C

120 - 150 min. cooling (by water) 170 °C to R.T.

The press was loaded at room temperature.

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Composition of the epoxy resin varnishes and various physical and mechanical properties of the cured resins, prepregs and laminates are set out in Table 1 below.

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Table 1
COMPOSITIONS - CURED RESINS, PREPREGS AND LAMINATES
PROPERTIES

Varnish and Laminate Examples	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII (2)
VARNISH COMPOSITION (parts by weight)												
RESINS (parts based on solid)												
Resin 1	80											
Resin 2					75.9					58.4	91.3	
Resin 3						100						
Resin 4		100										
Resin 5							100	72.4	67.4			
Resin 6			100									
Resin 7				100								
Resin 9												100
DER* 542									32.6			
HARDENERS												
DICY solution (1)	53.3	25	50.7	28	40	45.3	53.3	26.7	60		44	
Bisphenol A											8.7	
TBBA					24.1			27.6		31		

Table I (continued)

Examples	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Phenolic Novolac										10.6		
CATALYSTS												
2-methyl-imidazole	0.08	0.1	0.08	0.11	0.07	0.075	0.1	0.05	0.1	0.08	0.066	0.06
SOLVENTS												
Methyl-ethyl-ketone	20	67	33	33.3	33.3	38.3	25	33.3	33.3	33.3	25	33
RESIN PROPERTIES												
Geltime, 175° C, sec.	256	215	240	205	146	272	230	250	221	218	167	279
Tg of film, deg C (cure: 90 min, 175° C)	168	170	175	148	164	139	168	150	175	152	150	193
Viscosity (Ford Cup #4, sec.)			27		34	60	45	56	25	65	41	20
PREPREG PROPERTIES												
% Resin content			42		42.5	45	41	40.5	41	42	41	46
% Volatiles			0.1		0.2	NA	NA	NA	NA	NA	0.38	0.2
Geltime, 175 C, sec.			88		65	91	103	152	105	103	60	101
% Flow			16.5		18.7	NA	23	8.1	17.7	19.8	24.4	11.3

Table I (Continued)

Examples	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
LAMINATE PROPERTIES												
Tg, deg C			168		164	136	168	149	175	146	147	190
Chemical Resistance (% NMP pick-up)			0.1		0.06	0.3	0.03	0.75	0.03	0.34	0.09	0.1
Blister Resistance (P.T.C., min.)			120		60	60	120	90	120	90	60	120
Copper peel Strength (N/cm.)			15		14.2	15	14.4	18.8	14.8	13.8	12.6	14.8

(1) DICY solution: Dicyandiamide 7.5%

Propylene glycol

monomethyl ether 69.9%

Dimethylformamide 22.6%

(2) Pressure cycle: RT - 175°C Low pressure 15 min.

175°C High pressure 60 min.

175°C to 30°C pressure 15 min.

Laminates produced from standard commercial grades of NEMAG-10 (Non Brominated) and NEMA FR-4 (Brominated) resins have properties set out in Table II below.

Table II

Standard Laminate Properties		
Laminate Type*	NEMA G-10*	NEMA FR-4*
St. Resin Type	Epoxy Resin E*	Epoxy Resin F*
Tg °C	110	127
Chemical Resistance (% NMP Pick-up)	2.0	1.6

* Not an example of the present invention.

Note: The resins are cured according to standard practice in the industry with dicyandiamide.

The data in Table I and Table II clearly demonstrate surprisingly improved properties of the laminates incorporating the epoxy-terminated polyoxazolidones of the present invention, especially the improved heat resistance (Tg) and chemical resistance (percent NMP pick-up) properties.

Claims

1. A process for the preparation of an epoxy-terminated polyoxazolidone having, when cured, a glass transition temperature greater than 135°C and N-methylpyrrolidone pick-up of less than 0.5 percent, which process comprises reacting a polyepoxide compound with a polyisocyanate compound in the presence of a catalyst for the reaction of the epoxy and isocyanate groups at an elevated temperature, said process being characterized in that
 - A) the catalyst is an imidazole compound;
 - B) (1) from 5 to 30 weight percent of the polyisocyanate compound is added within a period of time of from 3 to 90 minutes to (2) a mixture comprising (a) from 70 to 95 weight percent of the polyepoxide compound and (b) from 0.01 to 2 weight percent of the catalyst, said weight percentages being based on the combined weight of the polyepoxide compound and polyisocyanate compound;
 - C) the reaction mixture obtained in step B is heated to a temperature of from 110°C to 200°C, for a period of time of from 5 to 180 minutes; so as to obtain an epoxy-terminated polyoxazolidone having from 50 to 100 percent of the original isocyanate groups converted to oxazolidone rings and from 0 to 50 percent of the original isocyanate groups converted to isocyanurate rings; and
 - D) the reaction is carried out in the absence of a solvent or other reaction diluent.
2. The process of Claim 1 for the preparation of an epoxy-terminated polyoxazolidone, characterized in that in step (B) from 0.02 to 0.1 weight percent of the catalyst is employed.
3. The process of Claim 1 or 2, characterized in that in step (B) the polyisocyanate compound is added to a mixture of the polyepoxide compound and the catalyst within a period of time of from 20 to 45 minutes.
4. The process of any one of Claims 1 to 3, characterized in that in step (C) the reaction mixture is heated to a temperature of from 140°C to 160°C.
5. The process of any one of the preceding Claims, characterized in that the imidazole compound is 2-phenylimidazole, 2-methylimidazole, 2-ethyl-4-methylimidazole, 4,4'-methylene-bis(2-ethyl-5-methylimidazole).
6. The process of anyone of the preceding Claims, characterized in that the polyepoxide used has the following general formula

Table II

Standard Laminate Properties		
Laminate Type*	NEMA G-10*	NEMA FR-4*
St. Resin Type	Epoxy Resin E*	Epoxy Resin F*
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* Not an example of the present invention.

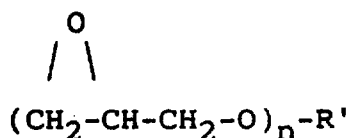
Note: The resins are cured according to standard practice in the industry with dicyandiamide.

The data in Table I and Table II clearly demonstrate surprisingly improved properties of the laminates incorporating the epoxy-terminated polyoxazolidones of the present invention, especially the improved heat resistance (Tg) and chemical resistance (percent NMP pick-up) properties.

Claims

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 - C) the reaction mixture obtained in step B is heated to a temperature of from 110°C to 200°C, for a period of time of from 5 to 180 minutes; so as to obtain an epoxy-terminated polyoxazolidone having from 50 to 100 percent of the original isocyanate groups converted to oxazolidone rings and from 0 to 50 percent of the original isocyanate groups converted to isocyanurate rings; and
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6. The process of anyone of the preceding Claims, characterized in that the polyepoxide used has the following general formula

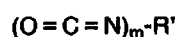




wherein R' is substituted or unsubstituted aliphatic, cycloaliphatic, aromatic or heterocyclic polyvalent group and n has an average value of from greater than 1 to less than 5.

7. The process of Claim 6, characterized in that the polyepoxide used is 2,2-bis(4-hydroxyphenyl)propane and/or 2,2-bis(3,5-dibromo-hydroxyphenyl)propane.

8. The process of any one of the preceding Claims, characterized in that the polyisocyanate compound used has the following general formula



wherein R' is substituted or unsubstituted aliphatic, cycloaliphatic, aromatic or heterocyclic polyvalent group and m has an average value of from greater than 1 to less than 5, preferably from 1.5 to 4, most preferably from 2 to 3.

9. The process of Claim 8, characterized in that the polyisocyanate is 4,4'-methylene-bis-(phenylisocyanate) or an isomer thereof, polymeric MDI or toluene diisocyanate, or a mixture of two or more thereof.

10. A process for the preparation of an epoxy varnish composition, comprising preparing an epoxy-terminated polyoxazolidone resin by a process as claimed in any one of Claims 1 to 9, and mixing the epoxy resin, a hardener for the epoxy resin, an organic solvent and, optionally an accelerator and other conventional adjuncts.

11. A process according to Claim 10, wherein the epoxy resin constitutes from 40 to 60 weight percent of the varnish composition.

12. A process for preparing an electrical laminate which process comprises the steps of:

A) forming a prepreg by impregnating a reinforcing web with an epoxy resin varnish composition, a hardener for the epoxy resin and an organic solvent;

B) heating the prepreg to a temperature sufficient to partially react the epoxy resin with the hardener; and

C) laminating at least one layer of the prepreg with electrically conductive material and heating the so prepared laminate to cure the epoxy resin, characterized in that the epoxy resin varnish used is an epoxy resin varnish composition prepared by a process as claimed in Claim 10 or Claim 11.

13. The process of Claim 12, characterized in that in step (B) the partial reaction of the epoxy resin with the hardener is conducted at a temperature of from 100°C to 230°C and the laminating step (C) is conducted at a temperature of from 130°C to 230°C and a pressure of from 34 kPa to 6.9 MPa.

Patentansprüche

1. Verfahren zur Herstellung eines Polyoxazolidons mit Epoxyendgruppen, das, wenn es gehärtet ist, eine Glasübergangstemperatur von mehr als 135°C und eine N-Methylpyrrolidonaufnahme von weniger als 0,5 Prozent hat, welches Verfahren umfaßt das Umsetzen einer Polyepoxidverbindung mit einer Polyisocyanatverbindung in der Anwesenheit eines Katalysators für die Reaktion der Epoxid- und Isocyanatgruppen bei einer erhöhten Temperatur; wobei das Verfahren

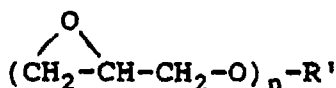
dadurch gekennzeichnet ist, daß

A) der Katalysator eine Imidazolverbindung ist;



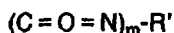
B) (1) von 5 bis 30 Gew.-% der Polyisocyanatverbindung innerhalb eines Zeitraums von 3 bis 90 Minuten zu (2) einem Gemisch, umfassend (a) von 70 bis 95 Gew.-% der Polyepoxidverbindung und (b) von 0,01 bis 2 Gew.-% des Katalysators zugegeben werden, wobei die Gewichtsprozentangaben auf das Gesamtgewicht der Polyepoxidverbindung und der Polyisocyanatverbindung bezogen sind, C) das in Schritt B) erhaltene Reaktionsgemisch auf eine Temperatur von 110°C bis 200°C für einen Zeitraum von 5 bis 180 Minuten erhitzt wird, um ein Polyoxazolidon mit Epoxyendgruppen zu erhalten, bei dem von 50 bis 100 Prozent der ursprünglichen Isocyanatgruppen in Oxazolidonringe umgewandelt sind und von 0 bis 50 Prozent der ursprünglichen Isocyanatgruppen in Isocyanuratringe umgewandelt sind und D) die Reaktion in Abwesenheit eines Lösungsmittels oder eines anderen Reaktionsverdünnungsmittels durchgeführt wird.

2. Verfahren nach Anspruch 1 zur Herstellung eines Polyoxazolidons mit Epoxyendgruppen, dadurch gekennzeichnet, daß in Schritt (B) von 0,02 bis 0,1 Gew.-% des Katalysators verwendet werden.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß in Schritt (B) die Polyisocyanatverbindung zu einem Gemisch aus der Polyepoxidverbindung und dem Katalysator innerhalb eines Zeitraums von 20 bis 45 Minuten zugegeben wird.
4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß in Schritt (C) das Reaktionsgemisch auf eine Temperatur von 140°C bis 160°C erhitzt wird.
5. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Imidazolverbindung 2-Phenylimidazol, 2-Methylimidazol, 2-Ethyl-4-methylimidazol, 4,4'-Methylen-bis(2-ethyl-5-methylimidazol) ist.
6. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das verwendete Polyepoxid die folgende allgemeine Formel hat

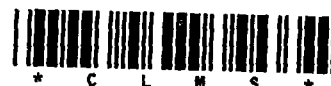


wobei R' eine substituierte oder unsubstituierte aliphatische, cycloaliphatische, aromatische oder heterocyclische polyvalente Gruppe ist und n einen Durchschnittswert von mehr als 1 bis weniger als 5 hat.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das verwendete Polyepoxid 2,2-bis(4-Hydroxyphenyl)propan und/oder 2,2-bis(3,5-Dibromhydroxyphenyl)propan ist.
8. Verfahren nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die verwendete Polyisocyanatverbindung die folgende allgemeine Formel hat



wobei R' eine substituierte oder unsubstituierte aliphatische, cycloaliphatische, aromatische oder heterocyclische polyvalente Gruppe ist und m einen Durchschnittswert von mehr als 1 bis weniger als 5 hat, bevorzugt von 1,5 bis 4, am meisten bevorzugt von 2 bis 3.



9. Verfahren nach Anspruch 8,
dadurch gekennzeichnet,
daß das Polyisocyanat 4,4'-Methylen-bis(phenylisocyanat) oder ein Isomer davon, polymeres MDI oder Toluoldiisocyanat oder ein Gemisch von zwei oder mehreren davon ist.
10. Verfahren zur Herstellung einer Epoxylackzusammensetzung, umfassend das Herstellen eines Polyoxazolidonharzes mit Epoxyendgruppen durch ein Verfahren nach einem der Ansprüche 1 bis 9 und das Mischen des Epoxidharzes, eines Härter für das Epoxidharz, eines organischen Lösungsmittels und gegebenenfalls eines Beschleunigers und anderer herkömmlicher Zusätze.
11. Verfahren nach Anspruch 10, wobei das Epoxidharz von 40 bis 60 Gew.-% der Lackzusammensetzung ausmacht.
12. Verfahren zum Herstellen eines elektrischen Laminats, wobei das Verfahren die Schritte umfaßt:
A) Bilden eines Prepregs durch Imprägnieren eines Verstärkungsgewebes mit einer Epoxidharzlackzusammensetzung, einem Härter für das Epoxidharz und einem organischen Lösungsmittel
B) Erhitzen des Prepregs auf eine ausreichende Temperatur, um das Epoxidharz teilweise mit dem Härter umzusetzen und
C) Laminieren mindestens einer Schicht des Prepregs mit einem elektrisch leitfähigen Material und Erhitzen des derart hergestellten Laminats um das Epoxidharz zu härten,
dadurch gekennzeichnet,
daß der verwendete Epoxidharzlack eine Epoxidharzlackzusammensetzung ist, die hergestellt wurde durch ein Verfahren nach Anspruch 10 oder Anspruch 11.
13. Verfahren nach Anspruch 12,
dadurch gekennzeichnet,
daß in Schritt (B) die Partialreaktion des Epoxidharzes mit dem Härter bei einer Temperatur von 100 °C bis 230 °C durchgeführt wird und der Laminierungsschritt (C) bei einer Temperatur von 130 °C bis 230 °C und einem Druck von 34 kPa bis 6,9 MPa durchgeführt wird.

Revendications

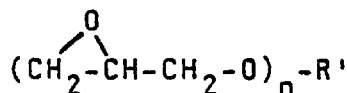
1. Procédé de préparation d'une polyoxazolidone à terminaison époxy, ayant, lorsqu'elle est durcie, une température de transition vitreuse supérieure à 135 °C et une fixation de N-méthylpyrrolidone inférieure à 0,5 %, procédé comprenant la réaction d'un composé polyépoxyde avec un composé polyisocyanate, en présence d'un catalyseur pour la réaction des groupes époxy et isocyanate, à température élevée, ce procédé étant caractérisé en ce que :
- (A) le catalyseur est un composé imidazole ;
(B) (1) de 5 à 30 % en poids de composé polyisocyanate sont ajoutés, en l'espace de 3 à 90 minutes à (2) un mélange comprenant (a) de 70 à 95 % en poids de composé polyépoxyde et (b) de 0,01 à 2 % en poids de catalyseur, ces pourcentages en poids étant calculés sur le poids combiné du composé polyépoxyde et du composé polyisocyanate ;
(C) le mélange obtenu dans l'étape B est chauffé à une température de 100 à 200°C, pendant un laps de temps de 5 à 180 minutes, de façon à obtenir une polyoxazolidone à terminaison époxy dans laquelle de 50 à 100 % des groupes isocyanate d'origine sont transformés en noyaux oxazolidone et de 0 à 50 % des groupes isocyanates d'origine sont transformés en noyaux isocyanurate ; et
(D) la réaction est mise en oeuvre en l'absence d'un solvant ou d'un autre diluant de réaction.
2. Procédé selon la revendication 1 pour la préparation d'une polyoxazolidone à terminaison époxy, caractérisé en ce qu'on utilise dans l'étape B de 0,02 à 0,1 % en poids de catalyseur.
3. Procédé selon la revendication 1 ou 2, caractérisé en ce qu'on ajoute dans l'étape (B) un composé polyisocyanate à un mélange du composé polyépoxy et du catalyseur, pendant un laps de temps de 20 à 45 minutes.



4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce qu'on chauffe dans l'étape (C) le mélange réactionnel à une température de 140 à 160 °C.

5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le composé imidazole est le 2-phénylimidazole, le 2-méthylimidazole, le 2-éthyl-4-méthylimidazole, le 4,4'-méthylène-bis(2-éthyl-5-méthylimidazole).

6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la polyépoxyde utilisée à la formule générale :



dans laquelle R' est un groupe polyvalent aliphatique, cycloaliphatique, aromatique ou hétérocyclique, substitué ou non substitué et n a une valeur moyenne comprise entre une valeur supérieure à 1 et une valeur inférieure à 5.

7. Procédé selon la revendication 6, caractérisé en ce que le polyépoxyde utilisé est le 2,2-bis(4-hydroxyphényl)propane et/ou le 2,2-bis(3,5-dibromo-hydroxyphényl)propane.

8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le composé polyisocyanate utilisé à la formule générale :



dans laquelle R' désigne un groupe polyvalent aliphatique, cycloaliphatique, aromatique ou hétérocyclique, substitué ou non substitué, m a une valeur moyenne comprise entre une valeur supérieure à 1 et une valeur inférieure à 5, et de préférence comprise entre 1,5 et 4 et plus préférablement comprise entre 2 et 3.

9. Procédé selon la revendication 8, caractérisé en ce que le polyisocyanate est le 4,4'-méthylène-bis(phénylisocyanate) ou un isomère de ce dernier, un polymère de diphenylméthane 4,4-diisocyanate (MDI) ou de toluène diisocyanate ou un mélange de deux ou plus de deux des isocyanates ci-dessus.

10. Procédé de préparation d'une composition de vernis époxy, comprenant la préparation d'une résine polyoxazolidone à terminaison époxy, par un procédé tel que revendiqué dans l'une quelconque des revendications 1 à 9, et le mélange de la résine époxy, d'un durcisseur pour une résine époxy, d'un solvant organique, et, à titre facultatif, d'un accélérateur et d'autres additifs conventionnels.

11. Procédé selon la revendication 10, dans lequel la résine époxy constitue de 40 à 60 % en poids de la composition de vernis.

12. Procédé de préparation d'un stratifié électrique, procédé comprenant les étapes suivantes :

(A) formation d'une feuille préimprégnée (prepreg) par imprégnation d'un tissu de renfort avec une composition de vernis de résine époxy, un durcisseur pour la résine époxy et un solvant organique ;

(B) le chauffage du prepreg à une température suffisante pour faire réagir partiellement la résine époxy avec le durcisseur ; et

(C) la stratification d'au moins une couche de prepreg avec un matériau conducteur d'électricité et chauffage du stratifié ainsi préparé pour durcir la résine époxy, caractérisé en ce que le vernis de résine époxy utilisé est une composition de vernis de résine époxy préparé par un procédé tel que revendiqué dans la revendication 10 ou 11.

13. Procédé selon la revendication 12, caractérisé en ce que dans l'étape (B) on conduit la réaction partielle de la résine époxy avec le durcisseur, à une température comprise entre 100 et 230 °C et qu'on conduit l'étape de stratification (C) à une température de 130 à 230 °C et à une pression de 34



kPa à 6,9 MPa.

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