

(9)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 312 770
A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **88115107.0**

(51) Int. Cl.4: **C08L 101/00 , C08L 79/08 ,
C08L 63/00 , C08G 77/38**

(22) Date of filing: **15.09.88**

(30) Priority: **24.09.87 US 100652**

(43) Date of publication of application:
26.04.89 Bulletin 89/17

(84) Designated Contracting States:
CH DE ES FR GB IT LI NL

(71) Applicant: **BASF Aktiengesellschaft
Carl-Bosch-Strasse 38
D-6700 Ludwigshafen(DE)**

(72) Inventor: **Ryang, Hong-Son
2012 El Rancho Drive
Camarillo California 93010(US)**

(54) **Curable resin systems containing cyanate ester functional oxazolinylpolysiloxanes.**

(57) Cyanate-functional oxazolinylpolysiloxanes are useful for toughening high performance resin systems such as cyanates, epoxies, and bismaleimides without substantial loss of heat resistance.

EP 0 312 770 A1

CURABLE RESIN SYSTEMS CONTAINING CYANATE ESTER FUNCTIONAL OXAZOLINYLPOLYSILOXANES

The subject invention relates to high performance thermosetting resin systems. More particularly, the subject invention relates to heat-curable resin systems containing cyanate ester-functional oxazolinyl-polysiloxanes.

High performance thermosetting resins based upon cyanate esters find application in many areas where high strength and heat resistance are important. Such resins, which contain monomers having two or more cyanate ester (cyanate) groups, polymerize to form highly crosslinked triazine structures. Unfortunately, the high strength and heat resistance which results from the polymer structure also causes the polymer to be brittle, and subject to impact induced damage.

Modification of these resin systems to improve their flexibility and reduce susceptibility to impact induced damage has been but partially successful. Co-polymerization with epoxy resins, bismaleimide resins, and modification with cyanate-reactive acrylonitrile-butadiene elastomers have imparted greater toughness to cyanate resin systems, but generally with considerable loss of heat resistance.

It has now been discovered that cyanate resins and other resin systems may be successfully modified through incorporation of a cyanate-functional oxazolinylpolysiloxane into the resin system. The resulting toughened resin systems show a considerable increase in flexibility without a concomitant decrease in heat resistance.

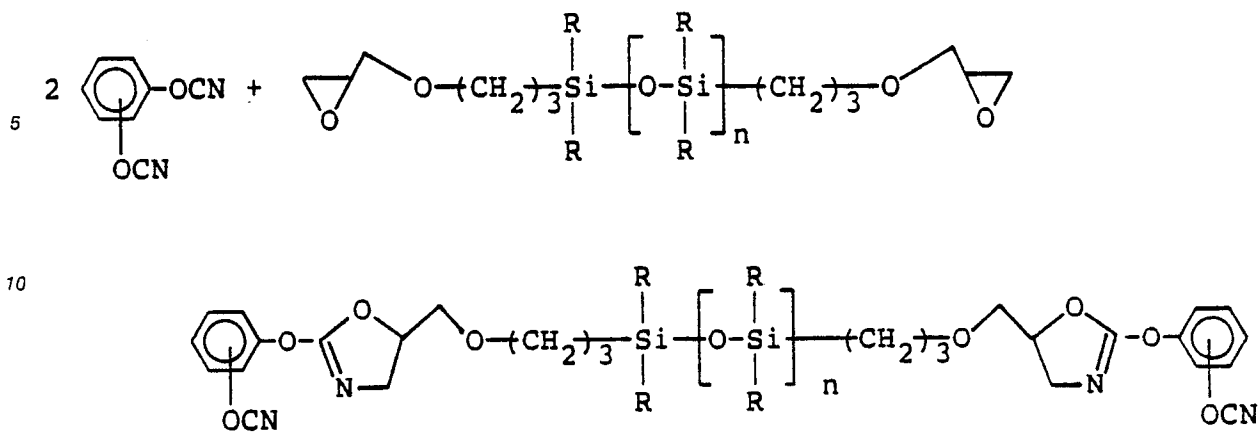
The cyanate-functional oxazolinylpolysiloxanes of the subject invention are readily prepared by the catalyzed or uncatalyzed reaction of at least a molar equivalent of a di- or polycyanate functional monomer with an epoxy-functional polysiloxane.

The cyanate-functional monomers are well known to those skilled in the art. These monomers are generally prepared by reacting a cyanogen halide with a di- or polyhydric phenol or similar compound. Examples of phenols which are commonly used to prepare the cyanate resins include mononuclear phenols such as hydroquinone and resorcinol; the various bisphenols, i.e. bisphenol A, bisphenol F and bisphenol S; and the various phenol and cresol based novolac resins. Examples of the method of preparation and of specific cyanate functional monomers may be found in U.S. patents 3,448,079, 3,553,244 and 4,663,398. Particularly preferred are the cyanates of hydroquinone, bisphenol A, bisphenol F, 2,2',6,6'-tetramethyl-bisphenol F, bisphenol S, and the phenolic novolac resins, and the di- and polyphenols which are derived from the reaction products of phenol and dicyclopentadiene in the presence of Friedel-Crafts catalysts as disclosed in U.S. Patent 3,536,734, hereinafter referred to as phenolated dicyclopentadiene. The cyanate functional resins are generally used in an amount at least equivalent to the number of moles of epoxy groups in the epoxy-functional siloxane and preferably in excess. For example, to one mole of a linear siloxane or polysiloxane terminated at both ends with epoxy functionality will be added two moles or more of a dicyanate. The amount of excess cyanate may be adjusted depending upon the particular application or the degree of toughness required.

The epoxy-terminated siloxanes may be prepared by methods well known to those skilled in the art. See, for example, J. Riffle, et. al., Epoxy Resin Chemistry II, ACS Symposium Series No. 221, American Chemical Society, pp. 24-25. Generally speaking, the epoxy functional polysiloxanes are prepared by the equilibrium polymerization of the readily available bis (3-glycidoxypropyl)tetramethyldisiloxane with a cyclic siloxane oligomer, preferably octamethylcyclotetrasiloxane or octaphenylcyclotetrasiloxane.

The equilibrium polymerization generally proceeds in the presence of a catalyst such a tetramethylammonium or tetrabutylammonium hydroxide or the corresponding siloxanolate. Particularly preferred is tetramethylammonium siloxanolate. The reaction proceeds readily at temperatures from about 50 °C to about 200 °C, preferably from about 80 °C to about 150 °C.

Reaction of the cyanate-functional monomer with the epoxy-functional siloxane occurs at elevated temperatures, e.g. from about 80 °C to about 250 °C, preferably from about 100 °C to about 160 °C to yield a cyanate-functional oxazolinylpolysiloxane. The reaction sequence may be illustrated as follows:



wherein each R may be, for example, a C₁-C₆ lower alkyl, C₁-C₆ lower alkoxy, C₁-C₆ haloalkyl, vinyl, allyl, allyloxy, propenyl, propenyloxy, acetoxy, C₅-C₁₀ cycloalkyl, or aryl radical.

Catalysts are not necessary for the reaction between the cyanate monomer and the epoxy-functional polysiloxane. However, if desirable, metal catalysts such as tin octoate, dibutyltin diacetate, or compounds of lead or zinc which catalyze triazine formation from cyanates may be used. Other catalysts which may be useful include metal acetylacetonates, metal alkyls such as butyl titanate and propyl aluminum, metal chlorides such as tin(IV) chloride; imidazoles, particularly 2-substituted and 2,4-disubstituted imidazoles, and tertiary amines such as N,N-dimethylbenzylamine, triethylenediamine, N-methylmorpholine and the like. The catalysts, when utilized, are generally present to the extent of from about 1.0x10⁻⁶ to about 2.0 wt. percent, preferably from about 1.0x10⁻³ to about 0.5 weight percent, and most preferably from about 1.0x10⁻² to about 0.5 weight percent.

The cyanate-functional oxazolinylpolysiloxane modifiers of the subject invention may be used to toughen a number of high performance resin systems. Due to the variety of reactions in which the cyanate radical may take part, these modifiers may be used, for example, in epoxy resin systems, cyanate resin systems, and bismaleimide resin systems, to name a few. Such resin systems are well known to those skilled in the art.

The modifiers of the subject invention may be present in the resin systems in an amount of 1 to 50%, preferably 3 to 30% by weight.

The toughened resin systems find use as laminating resins, as matrix resins in high performance, fiber reinforced preregs, as potting and encapsulating resins, and as structural adhesives. When used in preregs, traditional fiber reinforcement such as carbon/graphite, fiberglass, boron, and other fibers may be used in woven or non-woven form, as a mat, or as collimated fiber tows. Rovings and yarns may also be used. The use of such fiber reinforcement is commonplace in the aerospace and transportation industries.

The examples which follow illustrate the practice of the subject invention. These examples are by way of illustration only, and should not be interpreted as limiting the scope of the invention in any way.

Example 1

Preparation of Tetramethylammonium Siloxanolate

Into a 250 ml three neck round bottom flask equipped with a mechanical stirrer and reflux condenser are placed 118.6g (0.4mol) octamethylcyclotetrasiloxane and 18.1g (0.1mol) tetramethylammonium hydroxide pentahydrate. The mixture is stripped of water over a period of 48 hours by means of a flow of nitrogen while stirring at 70°C. The resulting viscous syrup is used as a polymerization catalyst without further purification.

Example 2

Preparation of Epoxy-Functional Polysiloxane Copolymer

To a 2 liter three neck round bottom flask equipped with a mechanical stirrer and reflux condenser are
 5 charged 534.4g octamethylcyclotetrasiloxane, 534.4g octaphenylcyclotetrasiloxane, 90.7g bis[3-
 glycidoxypropyl]-tetramethyldisiloxane, and 12.0g tetramethylammonium siloxanolate from Example 1. The
 resulting mixture is stirred at 80 °C for 48 hours under nitrogen. During this period, the viscosity is observed
 to increase and then reach a stable value. The catalyst is then destroyed by heating to 150 °C for 4 hours.
 10 After cooling to room temperature, the filtered reaction mixture is extracted twice with methanol (300 ml x 2)
 to remove unreacted cyclic oligomers. The product is then dried in vacuo at 1 torr and 150 °C. The product
 is a viscous oil (1100g) having an epoxy equivalent weight (EEW) of 1210>

Example 3

15

Preparation of Epoxy-Functional Polydimethylsiloxane

20

Using the procedure of Example 2, a reactor is charged with 18.3g bis[3-glycidoxypropyl]-
 tetramethyldisiloxane, 182.0g octamethylcyclotetrasiloxane, and 1.4g tetramethylammonium siloxanolate.
 The product is a colorless, viscous oil (180g, EEW = 2200).

25

Example 4

30

Heat-Curable Resin Adhesive

A heat-curable resin adhesive composition is prepared by mixing 20.0g of the epoxy-functional
 polysiloxane from Example 2 with 180.0g 2,2',6,6'-tetramethylbisphenol F dicyanate in a 500 ml glass
 35 reactor. The mixture is heated, with vigorous stirring, to 150 °C and maintained at that temperature for 5
 hours under nitrogen. After cooling to 70 °C, 5.25g of fumed silica (CAB-O-SIL® M-5, a product of the
 Cabot Corporation), 0.6g copper acetylacetonate and 8.0g of a novolac epoxy resin (DEN® 431, a product
 of the Dow Chemical Company) are added. The homogenous mixture is coated on a 112 fiberglass carrier.

40

Comparison Example A

45

Heat-Curable Resin Adhesive

A resin composition similar to that of example 4, but without the cyanate-functional oxazolinylpolysilox-
 ane modifier, is prepared by admixing 180g 2,2',6,6'-tetramethylbisphenol F dicyanate, 5.25g CAB-O-SIL®
 50 M-5, 0.6g copper acetylacetonate, and 8.0g DEN® 431.

The adhesives prepared in Example 4 and Comparison Example A are used to bond aluminum sheets.
 The resins are cured by heating for 4 hours at 177 °C, 2 hours at 220 °C and 1 hour at 250 °C. Single lap
 shear strengths are measured by ASTM method D-1002. Results are presented in Table I below.

55

Table I

Adhesive Formulation	Single Lap Sheer Strength (psi)	
	20 ° C	177 ° C
Example 4	3100	3300
Comparison Example A	2000	2510

Example 5Heat-Curable Resin Adhesive

A heat-curable composition is prepared by first admixing 10.0g of the epoxy-functional polysiloxane of Example 2 with 70.0g 2,2',6,6'-tetramethyl bisphenol F dicyanate in a 500 ml reactor. After heating at 150 ° C for 5 hours with vigorous stirring, 10.0g of the bismaleimide of 4,4'-diaminodiphenylmethane is added. After stirring for 30 minutes, the mixture is allowed to cool to 70 ° C and 3.2g CAB-O-SIL® M-5, 0.43g zinc naphthenate, and 2.0g benzylalcohol are added. After coating onto a 112 glass fabric, the adhesive is used to bond aluminum. The cure cycle is identical to that used previously for Example 4 and Comparison Example A. Single lap shear strength (ASTM D-1002) are as follows:

Table II

Temp	Shear Strength (psi)
20 ° C	2890
177 ° C	3060
205 ° C	3270

Example 6Heat-Curable Resin Formulation

A heat-curable cyanate resin formulation is prepared by stirring together 6g of bisphenol A dicyanate and 16.0g of the epoxy functional silicone of Example 3 at 150 ° C under nitrogen for 5 hours. To the resulting homogeneous but opaque mixture is added 0.079g zinc octoate. The resulting mixture is cured at 177 ° C for 4 hours, then 205 ° C for an additional 4 hours. The resin showed good adhesion to both aluminum and glass. Thermogravimetric Analysis (TGA) of the cured elastomer and of cured bisphenol A dicyanate are presented in Table III which indicates that despite large quantities of modifier, the finished elastomer has virtually the same heat resistance as the polymerized cyanate resin itself.

Table III

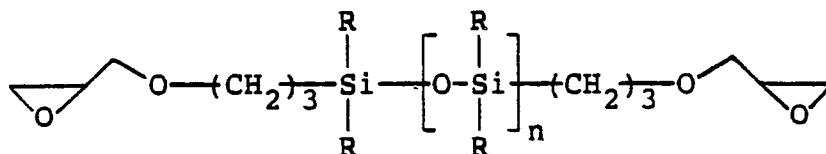
Resin	TGA (° C) in Air	
	5% Wt. Loss	10% Wt. Loss
Modified Cyanate of Example 6	430	440
Bisphenol A dicyanate	440	445

Claims

1. A heat-curable resin system containing a cyanate-functional oxazolinylpolysiloxane modifier which is the reaction product of an epoxy-functional polysiloxane and a di- or polycyanate-functional monomer

2. The resin system of claim 1 wherein said epoxy-functional polysiloxane is a bis[3-glycidoxypropyl]-polysiloxane.

3. The resin system of claim 2 wherein said epoxy-functional polysiloxane corresponds to the formula



wherein each R is individually selected from the group consisting of C₁-C₆ lower alkyl, C₁-C₆ lower alkoxy, C₁-C₆ haloalkyl, vinyl, allyl, allyloxy, propenyl, propenyloxy, acetoxy, C₅-C₁₀ cycloalkyl, and aryl radicals and wherein n is an integer from 1 to about 10,000.

4. The resin system of claim 3 wherein each R is individually selected from the group consisting of methyl and phenyl radicals.

5. The resin system of claim 1 wherein said cyanate monomer is selected from the group consisting of the cyanates of hydroquinone, bisphenol A, bisphenol F, bisphenol S, 2,2',6,6'-tetramethylbisphenol F and phenolated dicyclopentadiene.

6. The resin system of claim 1 wherein the mole ratio of cyanate groups in the cyanate-functional monomer to epoxy groups in the epoxy-functional polysiloxane is at least 2:1.

7. The resin system of claim 1 containing 1 to 50% by weight of said modifier.

8. The resin system of claim 1 comprising cyanate resins, epoxy resins, bismaleimide resins and mixtures thereof.

9. Structural adhesives comprising the resin system of claim 1.

10. High performance preregs, comprising the resin system of claim 1 and reinforcing fibers.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 167 (C-177)[1312], 22nd July 1983; & JP-A-58 74 749 (MITSUBISHI GAS KAGAKU K.K.) 06-05-1983 * Abstract * ---	1	C 08 L 101/00 C 08 L 79/08 C 08 L 63/00 C 08 G 77/38
A	PATENT ABSTRACTS OF JAPAN, vol. 3, no. 118 (C-60), 4th October 1979, page 60 C 60; & JP-A-54 97 700 (MITSUBISHI GAS KAGAKU K.K.) 01-08-1979 * Abstract * ---	1	
A,D	US-A-4 663 398 (R.E. HEFNER) * Claim 1 * ---	1	
A	US-A-4 659 777 (J.S. RIFFLE) * Claim 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 G C 08 L C 09 J
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-02-1989	Examiner DEPIJPER R.D.C.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			