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NASA CASE NO. LEW-12876-2

PRINT FIG. 1

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(NASA-Case-LEW-12876-2) LOW TEMPERATURE
CROSS LINKING POLYIMIDES Patent Application
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AWARDS ABSTRACT

NASA CASE LEW 12,876-2

LOW TEMPERATURE CROSS LINKING POLYIMIDES

Low temperature-curing polyimide resins are provided by reacting a polyfunctional amine, a polyfunctional ester, and a styrene derivative end-capping agent to form a prepolymer. The prepolymer can be cross-linked at a relatively low temperature. This provides a distinct advantage over previously known systems which require higher temperature for cross linking.

Polyimide resins are noted for their high thermal and oxidative stability, high strength at elevated temperatures, and for many outstanding physical and chemical properties useful in high temperature applications. A distinctly advantageous system, previously known, involves reacting, in solution in an organic solvent, a polyfunctional amine, a polyfunctional ester, and an end-capping agent to form a prepolymer which can be cross-linked by heating to form a polyimide resin. This system permits facile impregnation of fabric with the prepolymer for fabricating polyimide resin-reinforced fibrous materials. It is a distinct advantage of the previously known system that the prepolymer is soluble in organic solvent. A disadvantage of the earlier system is the requirement for a relatively high cure temperature of over 250°C. The present system has all the advantages of the previously known system with the added advantage of a low temperature cure.

Novelty appears to reside in the selection of a styrene derivative as an end-capping agent. Suitable end-capping agents include m-aminostyrene and are readily obtained. Selection of this type of end-capping agent provides, for the first time, a polyimide system which is cross-linkable at relatively low temperature and which retains the advantageous properties of otherwise similar previously known polyimide resins.

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SERIAL NO.: ~~161,299~~ 393,583

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POLYFUNCTIONAL AMINE, POLYFUNCTIONAL ESTER
AND STYRENE DERIVATIVE END-CAPPING AGENT
DISSOLVED IN SOLVENT TO FORM IMPREGNATING
SOLUTION.



SOLUTION IMPREGNATED INTO FIBROUS MATERIAL



SOLVENT REMOVED FROM IMPREGNATED FIBROUS
MATERIAL.



DRIED FIBROUS MATERIAL CUT INTO PLURALITY
OF PIECES WHICH ARE THEN STACKED



STACKED PIECES OF FIBROUS MATERIAL HEATED
AT 120°C TO FORM POLYIMIDE PREPOLYMER IN
FIBROUS MATERIAL



FURTHER HEATING AT 200°C TO FORM POLYIMIDE-
REINFORCED FIBROUS MATERIAL

393,583

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LOW TEMPERATURE CROSS LINKING POLYIMIDES

ORIGIN OF THE INVENTION

5 The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

TECHNICAL FIELD

The present invention relates to compositions for making polyimide prepolymers and resins and for making resin-reinforced fabrics and to methods of making such fabrics. More particularly, the invention relates to an improvement of such compositions and methods disclosed in U.S. Patent 3,745,149, issued July 10, 1973, and herein incorporated by reference.

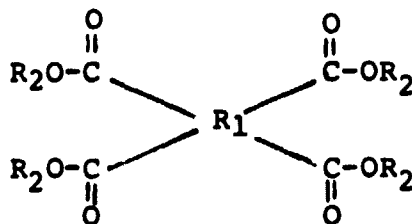
BACKGROUND ART

The polyimide resins to which the invention relates are noted for their high thermal and oxidative stability, high strength at elevated temperatures, and which exhibit many other outstanding physical and chemical properties useful in high temperature applications.

U.S. Patent 3,528,950 discloses a method for preparing addition-type polyimides, in which an end-capped, low molecular weight prepolymer is prepared in a refluxing solvent. The prepolymer is isolated and then heated to a temperature of 200° to 350°C to form polyimide macromolecules. The prepolymer has a very limited solubility in organic solvents, and thus does not allow facile impregnation of fibers for fabrication of fiber-reinforced polyimide composite articles.

An improved method for preparing high molecular weight addition-type polyimides is described in U.S. Patent 3,745,149. In this method, the polyimides are synthesized from a mixture of a polyfunctional amine, a polyfunctional ester, and an end-capping agent.

The polyfunctional ester (a) has the formula:



wherein R_1 is a tetravalent aryl radical and R_2 is alkyl or hydrogen, at least two R_2 groups being alkyl.

The polyfunctional amine (b) has the formula:

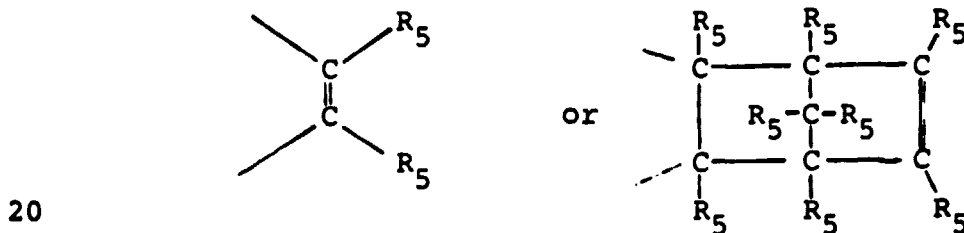


wherein R_3 is a divalent aryl radical.

The end-capping agent (c) has the formula:



15 wherein R_2 is alkyl or hydrogen, at least one R_2 group being alkyl, and R_4 is a divalent radical of the formula:



wherein R_5 is hydrogen or lower alkyl of one to four carbon atoms, preferably methyl.

The molar ratio of a:b:c is n:n+1:2 wherein n has a value of 1-20. The compounds are preferably present in an amount of 30 to 70% by weight of the solution.

A solution of the foregoing components is used for the preparation of reinforced fibers or fabric. The solution is impregnated into the fibers and then heated at a temperature of up to about 210°C to remove solvent and to form a prepolymer in the fibers or fabric and the thus prepared "prepreg" material is subsequently heated at a temperature of about 275 to 350°C to form the polyimide resin in the fibers or fabric. Usually, solvent removal is effected at a temperature of about about 50 to 120°C and prepolymerization is subsequently

5 effected at a temperature of about 125 to 210°C. The prepolymer has a molecular weight of about 400 to 10,000 and the polyimide resin has a molecular weight of over 10,000. Further details concerning the composition and its use will be found in the disclosure of U.S. Patent 3,745,149.

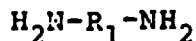
10 One of the advantages of the composition and method described in U.S. Patent 3,745,149 is that there is no need for prior synthesis of the polyimide precursors. However, one limitation of the method is that it requires relatively high cure temperatures of up to 350°C.

15 It is an object of the present invention to provide novel compositions and methods for forming polyimide prepolymers, polyimide resins, and polyimide resin-reinforced fibers or fabric. It is a further object to provide such compositions wherein, at a "prepreg" state, the prepreg material is curable at relatively low temperature.

20 SUMMARY OF THE INVENTION

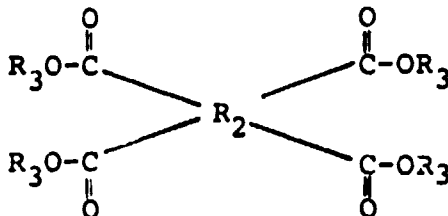
The foregoing and other objects which will be apparent to those of ordinary skill in the art are achieved, in accordance with the present invention, by providing a composition comprising a solution, in an organic solvent, of the following compounds:

25 a) a polyfunctional amine having the formula:



wherein R_1 is a divalent aryl radical; and

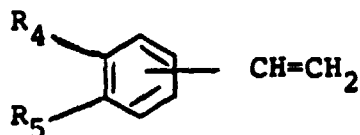
b) a polyfunctional ester having the formula:



where in R_2 is a tetravalent aryl radical and R_3 is alkyl or hydrogen, at least two R_3 groups being alkyl; and

c) an end-capping agent having the formula:

5



10

wherein R_4 is NH_2 and R_5 is hydrogen, or R_4 and R_5 are each $COOR_6$, wherein R_6 is alkyl or hydrogen, at least one R_6 group being alkyl;

the molar ratio of a:b:c being n:n+1:2 when R_4 is NH_2 and R_5 is hydrogen and being n+1:1:2 when R_4 and R_5 are each $COOR_6$, n having a value of 1-20.

15

In accordance with the present invention, the composition is heated at an elevated temperature to form a polyimide prepolymer having a molecular weight of about 400 to 10,000. The prepolymer material is subsequently heated at a higher temperature of about 150 to 245°C to effect formation of the polyimide resin having a molecular weight of about 10,000. In the formation of resin-reinforced fibrous material, the composition is impregnated into a fibrous material and the prepolymer and polyimide resin are formed in situ by carrying out the heating steps just described.

20

25

The solvent is conveniently removed by relatively gentle heating at a suitable temperature such as about 50 to 120°C. Formation of the prepolymer is preferably effected at a temperature of about 50 to 150°C. The inclusion of the end-capping constituent in accordance with the present invention results in a prepolymer material which is curable at relatively low temperature.

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BRIEF DESCRIPTION OF THE DRAWING

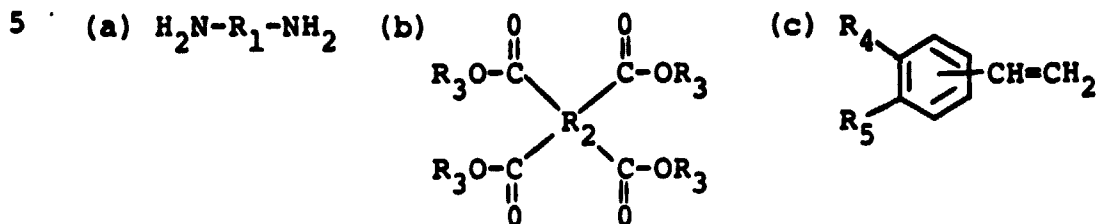
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The drawing is a block diagram flowsheet illustrating the steps in a preferred embodiment of the invention directed to the formation of a polyimide resin-

reinforced fibrous material.

DETAILED DESCRIPTION

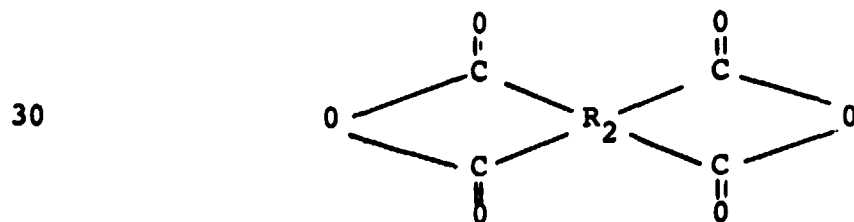
The three types of monomers of the present composition are represented by the formulas:



10 Where R_1 is a divalent aryl radical, R_2 is a tetravalent aryl radical, R_3 is an alkyl radical (preferably lower alkyl, more preferably methyl) or hydrogen, and at least two R_3 radicals are alkyl, R_4 is an $-NH_2$ group, R_5 is hydrogen, or, alternately, R_4 and R_5 are $-COOR_6$,
15 groups where R_6 is alkyl (preferably lower alkyl, more preferably methyl), and at least one R_6 is alkyl (preferably lower alkyl, more preferably methyl).

Representative of the many diamines of the type defined in (a) above which may be employed are benzidine, 4,4'-methylenedianiline, 4,4'-oxydianiline, 4,4'-sulfonyldianiline, 4,4'-thiodianiline, p-phenylenediamine, m-phenylenediamine. Others are mentioned in U.S. Patents 3,528,950 and 3,745,149.

25 The esters of the tetracarboxylic acid defined in (b) above may be readily prepared according to the known methods from the corresponding dianhydrides of the formula:



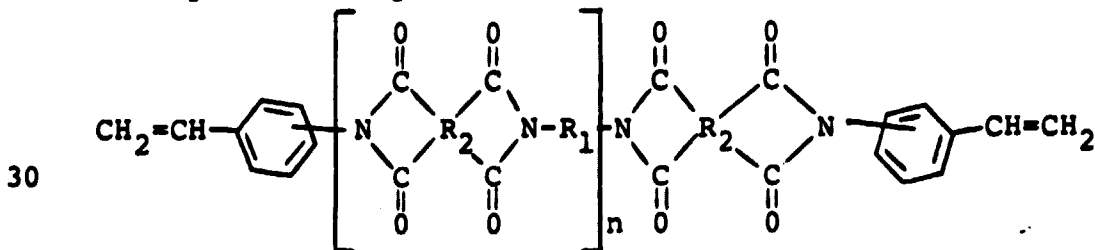
wherein R_2 is as defined above. Representative of the dianhydrides which may be employed include pyromellitic dianhydride, 3,3', 4,4'-benzophenonetetracarboxylic
35

dianhydride, 4,4'-(hexafluoroisopropylidene)-bis
 (phthalic anhydride), bis(3,4-carboxyphenyl) sulfone
 dianhydride, bis(3,4-dicarboxyphenyl) ether dianhydride,
 1,2,5,6-napthalene tetracarboxylic dianhydride, 2,3,6,
 5 7-napthalene tetracarboxylic dianhydride. Others are
 mentioned in U.S. Patents 3,528,890 and 3,745,149.
 Several suitable esters are disclosed in U.S. Patent
 3,745,149.

10 The end-capping groups defined in (c) above can
 be readily prepared according to known methods.

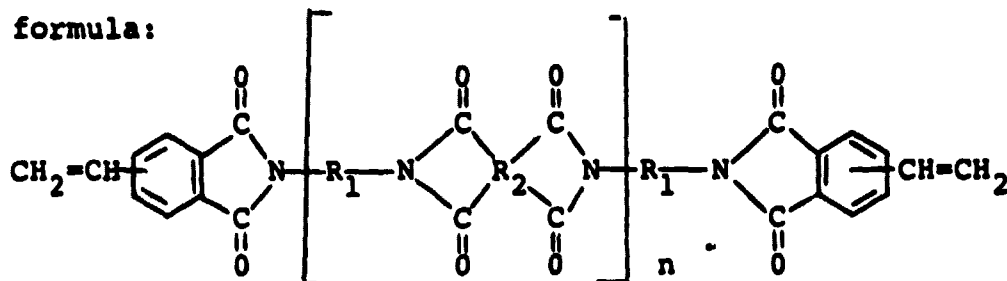
An organic solvent is employed to dissolve the
 three types of monomers. The solvent is one which must
 not react with the ester or amines during the proces-
 15 sing conditions. Representative examples of suitable
 solvents are aliphatic alcohols (preferably methanol
 or ethanol), aliphatic alcohol ethers, or aprotic sol-
 vents such as N,N-dimethyl formamide. Mixtures of two
 or more of such solvents may be employed. The solu-
 20 tion of monomers is prepared with a solids content of
 30 to 70% by weight.

When the monomer solutions are heated at tempera-
 25 tures of 50°C to 150°C, the monomers react to form low
 molecular weight end-capped prepolymers. If an end-
 capping monomer is selected where R₄ is an -NH₂ group
 and R₅ is hydrogen, the structure of the prepolymer can
 be represented by the formula:



wherein n is an integer of from 1 to 20, and R₁ and R₂
 are as defined above. The molecular weight of such
 end-capped prepolymers can be adjusted to desired val-
 35 ues by varying the value of the number n between 1 and

20, provided a molar ratio of $n : (n+1) : 2$ is maintained for the relationship of $a : b : c$. If an end-capping monomer is selected where R_4 and R_5 are $-COOR_3$ groups, the structure of the prepolymer can be represented by the formula:



wherein n, R_1 and R_2 are as defined above. A molar ratio of $(n+1) : n : 2$ must be maintained for the relationship of $a : b : c$.

The end-capped prepolymers are stable below 175°C . When heated at from about 175°C to about 245°C , the end-capped portion of the molecule becomes reactive and chain extension and cross-linking occur to form high molecular weight thermally stable polyimides.

An important advantage of the present invention is that a significantly lower final cure temperature of 175° to 245°C is employed to obtain the high molecular weight polyimide compared to a final cure temperature of 275° to 350°C described in U.S. Patent 3,745,149. The final cure is accomplished within 30 minutes to 1 hour without the evolution of volatile material to obtain polyimides with thermal and oxidative stability comparable to those described in U.S. Patent 3,745,149.

EXAMPLE 1

A mixture of 2.38 g of *m*-aminostyrene, 3.96 g of 4,4'-methylenedianiline, and 11.58 g of 3,3',4,4'-benzophenonetetracarboxylic acid dimethyl ester is dissolved in 17.9 g of methanol by stirring at $50-60^\circ\text{C}$. The solution is then heated in vacuum at 150°C for 1 hour. The solid prepolymer is ground into a fine powder. The yield of molding powder is 14.2 to 14.8g.

It has a formulated molecular weight of 1492. The value of n is 2.00.

5 Approximately 3.5 g of the molding powder are placed into a matched circular metal die having a diameter
of one inch, preheated to 150°C. The mold is closed, and contact pressure maintained for 5 minutes, then
2000 psi pressure is applied and the temperature is increased to 200°C at a rate of 5° per minute. After
10 1 hour at 200°C and 2000 psi, the pressure is released and the mold slowly cooled to room temperature. The
resulting molded polyimide plug is postcured for 1 hour at 316°C. The polyimide exhibits a glass transition
temperature in excess of 350°C.

EXAMPLE 2

15 A mixture of 3.67 g of *m*-aminostyrene, 6.07 g of 4,4'-methylenedianiline, and 17.83 g of 3,3', 4,4'-
benzophenonetetracarboxylic acid dimethyl ester is dissolved in 27.6 g of methanol by stirring at room
temperature. The solids dissolve within 30 minutes.
20 The resulting solution contains 50 percent monomers by weight and will yield an imidized end-capped prepolymer
having a formulated molecular weight of 1492. The value of n is 2.00.

25 Approximately 34 g of graphite fiber are impregnated with the above solution by first winding the
graphite fiber onto a mandrel, then applying the solution evenly to the fiber with a brush. The impreg-
nated fiber is then dried at 50°C for 1 hour to reduce the solvent content to 5 to 10 percent by weight. The
30 impregnated fiber at this point is easily cut and shaped into various forms.

Twelve plies of 3 by 7-7/8 inches are cut and
stacked unidirectionally in a preforming mold and staged for 2 hours at 120°C under an applied pressure of 0.1
35 psi. The staged prepreg is then inserted into a matched

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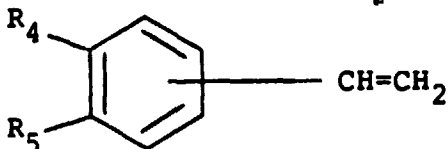
metal die preheated to 150°C. The mold is closed, and contact pressure maintained for 5 minutes, then 500 psi pressure is applied and the temperature is increased to 200°C at a rate of 5° per minute. After 1 hour at 200°
5 C and 500 psi, the pressure is released and the mold slowly cooled to room temperature. The resulting polyimide-graphite fiber composite is essentially void-free and exhibits excellent mechanical properties.

What is claimed is:

LOW TEMPERATURE CROSS LINKING POLYIMIDES

ABSTRACT

A polyimide is formed by cross linking a prepolymer formed by reacting a polyfunctional ester, a polyfunctional amine, and an end-capping unit. By providing an end-capping unit having the formula:



wherein R₄ is NH₂ and R₅ is hydrogen, or wherein R₄ and R₅ are each COOR₆ wherein R₆ is alkyl or hydrogen at least one R₆ being alkyl, the prepolymer is curable at a relatively low temperature of about 175 to 245°C.