Flame-resistant reinforced bodies are disclosed which are composed of reinforcing fibers, filaments or fabrics in a cured body of bis- and tris-imide resins derived from tris(m-aminophenyl) phosphine oxides by reaction with maleic anhydride or its derivatives, or of addition polymers of such imides, including a variant in which a mono-imide is condensed with a dianhydride and the product is treated with a further quantity of maleic anhydride.

20 Claims, No Drawings
PHOSPHORUS-CONTAINING IMIDE RESINS

ORIGIN OF THE INVENTION

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

This application is a continuation-in-part of our copending application Ser. No. 288,267, filed July 30, 1981, now U.S. Pat. No. 4,395,557 which in turn is a continuation-in-part of application Ser. No. 175,452, filed Aug. 5, 1980, now U.S. Pat. No. 4,276,344 issued June 30, 1981.

TECHNICAL FIELD

This invention relates to addition polyimide resins and to fiber or fabric-reinforced composites made from them.

BACKGROUND

Strong light-weight composites can be made by embedding various types of fibers or fabrics in a resin matrix. The polymer used for such a matrix is generally an epoxy resin, although several other resins such as phenolic, novolac, poly(ether-sulfone), poly(phenyl-sulfone), and bismaleimide resins have also been used for certain applications. As fibers or fabrics, carbon and graphite products have been quite useful in the composite structures.

The search for flame resistant materials to form laminates that can be used with greater safety in places such as aircraft cabins, has led to the selection of high temperature resins such as bismaleimides which have high anaerobic char yield (Scientific & Technological Aerospace Reprints, (1976), 14-16, Abstract N76-25354), and to the inclusion of phosphorus-containing compounds either in a mixture with or as an integral part of the resin used as matrix. Searle, in U.S. Pat. No. 2,444,536, discloses a widely used method for the preparation of maleimide polymers. As to the use of phosphorus-containing compounds, Kourtides et al. (Proceedings of the Adhesives for Industry Conference, El Segundo, CA, June 24-25, 1980) have shown substantial improvement in various properties of certain epoxy resins by preparing them with a bis(3-aminophenyl)methylphosphine oxide or its bisphenol analog, instead of the conventional diamine or phenol monomers or curing agents of the art. In summary, however, it can be stated that while the introduction of phosphorus into organic polymers has generally resulted in reduced flammability, increased adhesion, and better solubility in polar solvents, none of the resins used in the composite art are nonflammable.

In copending application Ser. No. 175,452, filed Aug. 5, 1980, entitled "Phosphorus-Containing Bismide Resins", now U.S. Pat. No. 4,276,344 issued June 30, 1981, bismides are prepared from phosphine oxides by a reaction typified by the following:

The monomers (bisimides) 3 can be used to impregnate fibers and cloth and, upon curing to rigid composites, confer fire resistant qualities to the fiber or fabric reinforcement present in the composites.

It is an object of the present invention to provide improvements upon such monomers, polymers and impregnated fibers and fabrics.

DISCLOSURE OF THE INVENTION

We have found that the trisamino precursor typified by the following:

can be used in place of the bisamino precursor. This results in curing at a lower temperature, e.g., 180° C., with good fire resistance. A further advantage is the greater ease of preparing the trisamino precursors.

We have found an improved method for reducing the nitro precursors of these trisamino compounds, wherein the nitro groups are reduced using hydrazine hydrate as the reducing agent and palladium/charcoal or Raney nickel as a catalyst.

DETAILED DESCRIPTION OF THE INVENTION

Using the triamine 4 and the anhydride 2 as models, and in a variant using also a coupling agent (a dianhydride), the following monomers result.
In the equations above, \( R_1 \) and \( R_2 \) may be \( H \), methyl, chlorine, or such other atoms or groups as are compatible with the respective reactions and with polymerization of the monomers.

If \( X \) is a linking entity which may be a valence bond, a bivalent atom (e.g., \( >O \) or \( >S \) or a bivalent group, [e.g., \(-\text{C}_n\text{H}_{2n}\) (\( n=1, 2, 3 \), etc.)], \( >\text{C}=\text{O} \), \( >\text{C}=\text{S} \), \( >\text{C}(\text{CF}_3)_2 \), \( >\text{SO}_2 \) or any other bivalent group which is compatible with reaction (4) and with polymerization of the monomers, \( R_3 \) is \( -\text{NH}_2 \) or the imide group;

Further, the benzene rings may be substituted by functional and/or non-functional groups provided they do not interfere with the reactions involved in forming the monomers and provided they do not interfere with polymerization and with the thermal stability of the polymers. Examples of substituents are alkyl, e.g., \( C_1 \) to \( C_5 \) straight and branched chain alkyl; chlorine; aryI, e.g., phenyl and tolyl. Condensed ring phosphine oxides may be used.

Polymerization is accomplished thermally or by means of a catalyst such as cobalt or other metal naphthenates together with peroxides. Partial polymerization may be carried out with the monomer; fibers or fabric may then be impregnated with the resulting oligomer or lower polymer; and the impregnated material may then be cured at a higher temperature. The trisimides polymerize by opening of the olefinic double bonds. With the bisimides, which also contain free primary amine groups, nucleophilic addition of the free amino group to the double bond may also occur.

The linking groups illustrated in 10 above result in polymers having diminished cross linking density, hence composites made with these polymers have greater toughness.

The phosphine oxide component of the imides of this invention can be made from the triphenylphosphine oxide by nitration, followed by reduction of the nitro group to the amino group by, for example, stannous chloride dihydrate and concentrated hydrochloric acid, by hydrazine hydrate and palladized charcoal, or by hydrogen under pressure in the presence of a platinum catalyst.

Imides can be prepared by reacting stoichiometric quantities of the reactants in a polar solvent (e.g., dimethylformamide, dimethylacetamide, N-methyl pyrrolidine, etc.) and cyclodehydrating the intermediate amic acid by sodium acetate and acetic anhydride. Alternatively refluxing the reactants in glacial acetic acid and acetic anhydride. The resulting imides can be cured in the temperature range of \( 180^\circ-300^\circ \) C.

The resins produced according to the process just described are suitable for many applications in which good adhesion and excellent resistance to heat, fire, solvents and chemicals are required. In the aerospace industry, the new resins may be used as adhesives and as matrix materials for fiber-reinforced lightweight composites. The fibers employed in such composites may be selected from the reinforcing fibers known in the art. For example, they may be inorganic fibers such as metal fibers; or ceramic fibers such as alumina fibers, silicon carbide fibers, boron nitride fibers, glass fibers or carbon fibers. They may also be organic fibers such as the aramid fibers (for example the aramids marketed under the names Kevlar ®, Nomex ®, Kevlar ®-49, "X-500", and the like). These fibers can be in organized form such as fabrics, yarns, tapes, or the like or can be in disorganized forms such as felts, loose fibers, chopped fibers or the like as is known in the art. The exact form of the reinforcing fibers will in part depend upon the method employed to form the finished composite body which can be selected from the methods known in the art for forming bodies from fiber-reinforced resin including laminating, filament-winding,
impregnated fabric is then dried in a circulating air oven. The yield of resin cured at 232°F for 2 hours was as follows:
The polymer obtained in this manner can further be processed.

When the “varnish” method, the solution is applied to the reinforcing fibers, generally in an amount sufficient to at least impregnate the fiber. This prepreg material is formed into the shape desired for the finished article. This may be done by molding, laminating, pressing, winding, laying up or the like technique appropriate for the particular form of reinforcement employed.

The solvent is removed from the resin solution either before or after the resin/reinforcement material is formed into the desired shape. This can be accomplished by evaporation effected by heat, vacuum or a combination thereof. If heat is employed, it is generally desirable to employ a temperature below the temperature to be used to cure the resin, i.e. a temperature of from about 50°C to about 150°C, preferably about 75°C to about 145°C and more preferably about 100°C to 140°C. In a typical preparation, the solvent is removed by evaporation in an air oven at 125°C to 145°C for about 24 hours. The trisimide was isolated by precipitation in water. The yellow precipitate had a glass transition temperature of 314°C.

In such applications, conventional resin to reinforcement ratios—e.g. 5:1 to 1:5 by weight are employed so long as adequate resin is present to give a continuous resin phase in the composite. To produce such composites, the imide resin is either dry-mixed as a powder with the reinforcement and then melt-cured or dissolved in an appropriate solvent and applied to the reinforcing fibers as a “varnish” and cured. A suitable solvent for the second mode of application is an organic solvent such as a ketone, for example acetone, methyl ethyl ketone or methyl isobutyl ketone or the like or an aprotic organic liquid such as methylene chloride, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), or dimethylacetamide (DMAc). Preferred solvents are the aprotic solvents, especially DMF, DMSO and DMAc. When using the “varnish” method, the solution is applied to the reinforcing fibers, generally in an amount sufficient to at least impregnate the fiber. This prepreg material is formed into the shape desired for the finished article. This may be done by molding, laminating, pressing, winding, laying up or the like technique appropriate for the particular form of reinforcement employed.

The solvent is removed from the resin solution either before or after the resin/reinforcement material is formed into the desired shape. This can be accomplished by evaporation effected by heat, vacuum or a combination thereof. If heat is employed, it is generally desirable to employ a temperature below the temperature to be used to cure the resin, i.e. a temperature of from about 50°C to about 150°C, preferably about 75°C to about 145°C and more preferably about 100°C to 140°C. In a typical preparation, the solvent is removed by evaporation in an air oven at 125°C to 145°C. The layers and the impregnated fiber materials are formed by means of pressure and high temperature into the desired molded laminate. The laminate is then cured at an elevated temperature, for example 150°C-300°C, preferably 160°C-270°C and especially 180°C-250°C. The cure can be done in stages, as is known in the art.

The imide resins according to the present invention have noteworthy advantages over the imide resins of the aforesaid now-issued application. The curing of this resin was done thermally at 180°C, 225°C, and 232°C. An an aerobic char yield of cured resin was found to be 68-70%. Elemental analysis gave the following results: C=65.16%, H=3.54%, N=7.12%, P=4.40%. The values calculated for formula C61H38P2O11N6 are C=67.03%, H=3.47%, N=7.69%, P=5.67%.

EXAMPLE 2
Tris(m-aminophenyl) phosphine oxide 4.27 g, was dissolved in 25 ml DMF and 2.69 g of maleic anhydride added. The solution was stirred at 50°C for one hour. BTDA (2.09 g) was then introduced and solution stirred overnight. The solution was heated at 145°C C=2°C for 45 minutes and refluxed for 10 minutes.

A graphite cloth laminate was cured in a manner similar to that described in Example 1. This material had a glass transition temperature of 314°C as obtained by DMA.

Trisimide monomer could be isolated by precipitation from the DMF solution with water. An aerobic char yield of 62-69% was obtained. Elemental analysis showed the following results: C=64.40%, H=3.6%, N=6.92%, P=5.14%. The values calculated for formula C66H34P2O15N6 are C=66.13%, H=3.03%, N=6.71%, P=4.95%.

EXAMPLE 3
Tris(amino phenyl)phosphine oxide 1.615 g and dichloromaleic anhydride 2.48 g were dissolved separately in glacial acetic acid and mixed. This solution was then refluxed gently for 24 hours. The trisimide was isolated by precipitation in water. The yellow precipitate was dissolved in and recrystallized from chloroform and petroleum ether. The aerobic char yield of the polymer formed from this monomer by curing at 305°C for 30 minutes was found to be 65%.

EXAMPLE 4
Tris(amino phenyl)phosphine oxide 1.61 g and citraconic anhydride 1.12 g were separately dissolved in glacial acetic acid. The two solutions were mixed and gently refluxed for 24 hours. The imide was isolated by precipitation in water. The precipitates were dissolved in acetone and solution was concentrated. The imide was recovered by addition of petroleum ether. Elemental analysis gave the following results: C=65.33%, H=4.45%, N=7.31% and P=5.42%. Calculated values for the formula C23H22PO5N3 C=65.75%, H=4.30%, N=8.21% and P=6.06%. Anaerobic char yield of resin cured at 232°C for 2 hours was 62.5%.
EXAMPLE 8

Imide monomer was isolated by precipitation in water and filtration. The residue was washed several times with 1.85 g of citraconic anhydride and refluxing the imide resin formed by curing at 232°F for 2 hours was added. The solution was stirred as mentioned above. We have also discovered an improved method for reducing tris(nitrophenyl)phosphine oxide, as shown in Example 6. Alternatively, the condensation of the dinitro compound was prepared by dissolving 1.61 g of trinitro oxide in 10 ml of dimethylformamide and adding 1.62 g of maleic anhydride. The solution was stirred at 135°F of amine and by reaching 1.61 g of amine under reduced pressure to a small volume and then concentrated under reduced pressure to add an equal volume of maleic anhydride. The solution was stirred as mentioned above.

EXAMPLE 9

Tris(m-nitrophenyl)phosphine oxide: 245, 440, 322, 323, 93, 65, 229, 182, 230. The infra-red spectra of the amine showed characteristic absorption due to amino and P=O groups.

Elemental analysis of the amine gave the following results: C = 64.7%, H = 5.60%, N = 12.95%, P = 9.58%.

Example of a fiber-reinforced composite material is shown in Example 6 with the following results: C = 64.7%, H = 5.60%, N = 12.95%, P = 9.58%.

For either the tris(nitrophenyl)phosphine oxide or the tris(m-nitrophenyl)phosphine oxide, the mass spectra of these amines M-1 ion was the base peak. Eight most intense peaks, i.e., fragment ion values are listed in order to decreasing relative abundances. The production of a fiber-reinforced composite material is shown in Example 6 with the following results: C = 64.7%, H = 5.60%, N = 12.95%, P = 9.58%.

EXAMPLE 10

The reinforcement and finished form is varied in Table 1.

Table 1

<table>
<thead>
<tr>
<th>Number</th>
<th>Product Form</th>
<th>Reinforcement</th>
<th>Handlable</th>
<th>Finish</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>Phenolic Cloth</td>
<td>Kevlar® Aramid Fiber</td>
<td>Laminate</td>
<td>Laminated Ply</td>
</tr>
<tr>
<td>B</td>
<td>Kevlar® Aramid Fiber</td>
<td>Glass Fiber</td>
<td>Laminate</td>
<td>Laminated Ply</td>
</tr>
<tr>
<td>C</td>
<td>Silicon Carbide-Cored Fiber</td>
<td>Glass Fiber</td>
<td>Laminate</td>
<td>Laminated Ply</td>
</tr>
<tr>
<td>D</td>
<td>Glass Fiber</td>
<td>Glass Fiber</td>
<td>Laminate</td>
<td>Laminated Ply</td>
</tr>
<tr>
<td>E</td>
<td>Chopped Glass Fiber</td>
<td>Glass Fiber</td>
<td>Laminate</td>
<td>Laminated Ply</td>
</tr>
</tbody>
</table>

We claim:

1. A fiber-reinforced imide polymer composite containing reinforcing fiber as an imide polymer via an imide structure selected from Table 1.

2. A fiber-reinforced imide polymer composite containing reinforcing fiber as an imide polymer via an imide structure selected from Table 1.

3. A fiber-reinforced imide polymer composite containing reinforcing fiber as an imide polymer via an imide structure selected from Table 1.

4. A fiber-reinforced imide polymer composite containing reinforcing fiber as an imide polymer via an imide structure selected from Table 1.
The polymer composite of claim 1 wherein said
nitride fibers, aramid fibers, alumina fibers, and silicon
carbide fibers.

3. The polymer composite of claim 1 wherein said
imide has the structure

wherein \( R_1 \) and \( R_2 \) are selected from the group consisting
of chlorine, methyl and hydrogen; \( R_3 \) is the amino
group or an imide group

\[ \text{X is a linking entity selected from the group consisting of a valence bond, } -O-, -S-, -C_nH_{2n} - \text{ wherein } n \text{ is 1, 2, or 3,} \]

4. The polymer composite of claim 3 wherein \( R_3 \) is the
amino group.

5. The polymer composite of claim 4 wherein said
fiber is selected from glass fibers, carbon fibers, boron
nitride fibers, aramid fibers, alumina fibers, and silicon
carbide fibers.

6. The polymer composite of claim 5 wherein \( R_1 \) and
\( R_2 \) are each \( H \).

7. The polymer composite of claim 6 wherein the
fiber is aramid fiber.

8. The polymer composite of claim 3 wherein \( R_3 \) is the
imide group.

9. The polymer composite of claim 8 wherein said
fiber is selected from glass fibers, carbon fibers, boron
nitride fibers, aramid fibers, alumina fibers, and silicon
carbide fibers.

10. The polymer composite of claim 9 wherein \( R_1 \) and
\( R_2 \) are each \( H \).

11. The polymer composite of claim 10 wherein the
fiber is aramid fiber.

12. The polymer composite of claim 1 wherein said
imide has the structure
13. The polymer composite of claim 12 wherein R₃ is the amino group.

14. The polymer composite of claim 13 wherein X is

-\( \text{C} \)-

\( \text{H} \)

\( \text{O} \)

and said fiber is selected from glass fibers, carbon fibers, boron nitride fibers, aramid fibers, alumina fibers, and silicon carbide fibers.

15. The polymer composite of claim 14 wherein R₁ and R₂ are each H and the benzene rings are not substituted.

16. The polymer composite of claim 15 wherein the fiber is aramid fiber.

17. The polymer composite of claim 12 wherein R₃ is the imide group.

18. The polymer composite of claim 17 wherein X is

-\( \text{C} \)-

\( \text{H} \)

\( \text{O} \)

and said fiber is selected from glass fibers, carbon fibers, boron nitride fibers, aramid fibers, alumina fibers, and silicon carbide fibers.

19. The polymer composite of claim 18 wherein R₁ and R₂ are each H and the benzene rings are not substituted.

20. The polymer composite of claim 19 wherein the fiber is aramid fiber.