PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 :
C08K 3/32, C08L 79/06

A1

(11) International Publication Number: **WO 92/10536**

(43) International Publication Date: 25 June 1992 (25.06.92)

(21) International Application Number: PCT/US91/09227

(22) International Filing Date: 6 December 1991 (06.12.91)

(30) Priority data:

624,164	7 December 1990 (07.12.90)	US
668,532	13 March 1991 (13.03.91)	US

(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

(72) Inventors: PIERINI, Peter, E. ; 2262 Ashby Avenue, Berkeley, CA 94705 (US). WESSLING, Ritchie, A. ; 1126 Shattuck Avenue, Berkeley, CA 94707 (US). KIM, Peter, K. ; 48 White Pine Lane, Danville, CA 94506 (US). DIXIT, Thuan, Phung ; 2330 Deer Valley Drive, Midland, MI 48642 (US). DILLINGHAM, R., Giles ; 2154 Sasse Road, Midland, MI 48640 (US). RASPOR, O., Carl ; 6271 Fox Glen Drive-Apartment Number 343, Saginaw, MI 48603 (US).

(74) Agent: MAURER, Charles, J., III; The Dow Chemical Company, Patent Department, P.O. Box 1967, Midland, MI 48641-1967 (US).

(81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD TO MAKE MATRIX COMPOSITES IN WHICH THE MATRIX CONTAINS POLYBENZOXAZOLE OR POLYBENZOTHIAZOLE

(57) Abstract

This application claims a method for using a dope solution that contains polybenzoxazole or polybenzothiazole polymer or copolymer. Fibers are prepregged with the dope, and the prepreg is be contacted with water or another coagulant to coagulate the polymer and form a matrix composite.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CS	Czechoslovakia
DE*	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GN	Guinea
GR	Greece
HU	Hungary
IT	Italy
JP	Japan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
MC	Monaco
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NL	Netherlands
NO	Norway
PL	Poland
RO	Romania
SD	Sudan
SE	Sweden
SN	Senegal
SU+	Soviet Union
TD	Chad
TG	Togo
US	United States of America

\+ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

METHOD TO MAKE MATRIX COMPOSITES IN WHICH THE MATRIX CONTAINS POLYBENZOXAZOLE OR POLYBENZOTHIAZOLE

This invention relates to matrix composites and processes for making them.

A fiber-reinforced composite, or matrix composite, is an article comprising a plurality of fibers (the reinforcement) embedded in a plastic (the matrix). Typically, the fibers give strength and/or stiffness to the composite, and the matrix maintains fiber alignment and transfers load around broken fibers. Matrix composites are described in detail in numerous references, such as Kirk-Othmer Ency. Chem., Tech. - Supp., <u>Composites, High Performance</u>, at 260-281 (J. Wiley & Sons 1984).

A number of fibers are available for use in matrix composites, each having different combinations of tensile and compressive strength and modulus, temperature stability, creep, cost, and other properties. Suitable fibers may contain, for example, aramid (such as Kevlar™ fibers), boron, glass, carbon, gel-spun polyethylenes (such as Spectra™ fiber), polybenzoxazole, polybenzothiazole, or polybenzimidazole.

Suitable fibers and processes for their fabrication are described in numerous references, such as U.S. Patent 4,533,693; 3 Kirk-Othmer Ency. Chem. Tech., Aramid Fibers, 213 (J. Wiley & Sons 1978); Kirk-Othmer Ency. Chem., Tech. - Supp., Composites, High Performance, at 261-263; 11 Ency. Poly. Sci. & Eng., Polybenzothiazoles and Polybenzoxazoles, 601 (J. Wiley & Sons 1988) and W. W. Adams et al., The Materials Science and Engineering of Rigid-Rod Polymers, at 245--312 (Materials Research Society 1989).

A number of matrix materials are also available for use in matrix composites. Examples of polymer matrix materials include polyesters, epoxy resins, polycyanates, polybutadienes, vinyl ester resins and polyimides. Thermoplastic polymers, such as poly(ether ether ketone), are also used as matrix materials in some composites. Some carbon matrix composites have been made. Metal and ceramic matrix composites are also known.

There is a need for improved matrix materials in advanced matrix composites. For example, the flame resistance, chemical resistance, solvent resistance and thermal stability of many polymer matrix materials is much poorer than the same properties of the fiber reinforcement. Stronger polymer matrices could yield stronger composites using the same amount of fiber. Metal matrix materials are heavier than polymers. Ceramic and carbon matrix materials are expensive and brittle. An objective of the present invention is to provide a fiber-reinforced composite having new polymer matrix materials that show improvement over existing thermoset or thermoplastic matrix resins in at least one of the following properties: flame resistance, smoke from exposure to flame, chemical resistance, solvent resistance, thermal stability, tensile strength or tensile modulus.

The present invention is a method of using a dope solution that contains: (i) a polybenzoxazole polymer or copolymer or a polybenzothiazole polymer or copolymer, and (ii) a solvent for the polymer or copolymer, said method being characterized by the steps of:

(1) prepregging a plurality of reinforcing fibers with the dope solution; and

(2) contacting the dope solution with a liquid that causes the polymer or copolymer to coagulate, in a quantity sufficient to cause the polymer or copolymer to coagulate with the fibers embedded therein.

The method of the present invention can be used to synthesize fiber-reinforced composites in which the matrix resin is a polybenzoxazole or polybenzothiazole polymer or copolymer. The polybenzoxazole or polybenzothiazole matrix in the composite can be selected to provide any one of the properties of low flammability, low smoke generation, high temperature stability, high chemical resistance, high solvent resistance, high strength and/or modulus or a combination of those properties. Composites of the present invention and shaped articles containing them are useful for structural materials and parts.

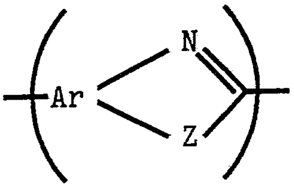
The present invention uses fibers, such as those previously described. The fibers should be a type whose properties are not substantially degraded by contact with the solution of polymer or copolymer and its solvent. The fiber is preferably aramid, carbon, polybenzoxazole or polybenzothiazole. It is most preferably carbon or polybenzoxazole. Polybenzoxazole and polybenzothiazole fibers are preferably heat treated. The tensile strength of the fiber is preferably at least 2.5 GPa, more preferably at least 3.0 GPa and most preferably at least 3.5 GPa. The tensile modulus of the fiber is preferably at least 135 GPa, more preferably at least 200 GPa and most preferably at least 270 GPa.

The fibers may have dimensions that are usual for reinforcing materials in matrix composites. Their average diameter is preferably between 1 µ and 100 µ. It is more preferably no more than 40 µ and most preferably no more than 20 µ. The fiber may be, for instance, in the form of a cloth or in the form of long strands or in the form of a short fiber or fiber pulp suitable for making random fiber composites. A mixture of fibers may be used. For instance, the fibers may contain a mixture of at least one fiber having high tensile properties, such as aramid or polybenzazole, and another fiber having high compressive properties, such as quartz.

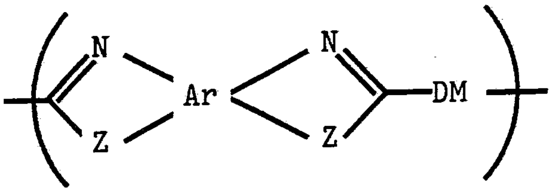
The present invention also uses matrix materials containing polybenzoxazole (PBO) or polybenzothiazole (PBT) or copolymers thereof. Those matrix materials are dissolved in a dope solution with a suitable solvent.

PBO, PBT and random, sequential and block copolymers of PBO and PBT are described in references such as Wolfe et al., Liquid Crystalline Polymer Compositions, Process and Products, U.S. Patent 4,703,103 (October 27, 1987); Wolfe et al., Liquid Crystalline Polymer Compositions, Process and Products, U.S. Patent 4,533,692 (August 6, 1985); Wolfe et al., Liquid Crystalline Poly(2,6-Benzothiazole) Compositions, Process and Products, U.S. Patent 4,533,724 (August 6, 1985); Wolfe, Liquid Crystalline Polymer Compositions, Process and Products, U.S. Patent 4,533,693 (August 6, 1985); Evers, Thermoxadatively Stable Articulated p-Benzobisoxazole and p-Benzobisthiazole Polymers, U.S. Patent 4,359,567 (November 16, 1982); Tsai et al., Method for Making Heterocyclic Block Copolymer, U.S. Patent 4,578,432 (March 25, 1986); 11 Ency. Poly. Sci. & Eng., Polybenzothiazoles and Polybenzoxazoles, 601 (J. Wiley & Sons 1988) and W. W. Adams et al., The Materials Science and Engineering of Rigid-Rod Polymers (Materials Research Society 1989). Other block copolymers of PBO and PBT are described in detail in Harris et al., Copolymers Containing Polybenzoxazole, Polybenzothiazole and Polybenzimidazole Moieties, International Application No. PCT/US89/04464 (filed October 6, 1989), International Publication No. WO 90/03995 (published April 19, 1990) and in Harris et al., Thermoplastic Compositions Containing Polybenzoxazole, Polybenzothiazole and Polybenzimidazole Moieties and Process for Making Shaped Articles from Them, EPO Application 90104963.5 (filed March 16, 1990), EPO Publication 0 388 803 (published September 26, 1990).

The polymer or copolymer contains any one of AB-mer units, as represented in Formula 1(a), and/or AA/BB-mer units, as represented in Formula 1(b)



1(a) AB



1(b) AA/BB

wherein:

Each Ar represents an aromatic group. The aromatic group may be heterocyclic, such as a pyridinylene group, but it is preferably carbocyclic. The aromatic group may be a fused or unfused polycyclic system, but is preferably a single six-membered ring. Size is not critical, but the aromatic group preferably contains no more than 18 carbon atoms, more preferably no more than 12 carbon atoms and most preferably no more than 6 carbon atoms. Examples of suitable aromatic groups include phenylene moieties, tolylene moieties, biphenylene moieties and bis-phenylene ether moieties. Ar in AA/BB-mer units is preferably a

1,2,4,5-phenylene moiety or an analog thereof. Ar in AB-mer units is preferably a 1,3,4-phenylene moiety or an analog thereof.

Each Z is independently an oxygen or a sulfur atom.

Each DM is independently a bond or a divalent organic moiety that does not interfere with the synthesis, fabrication or use of the polymer. The divalent organic moiety may contain an aliphatic group, which preferably has no more than 12 carbon atoms, but the divalent organic moiety is preferably an aromatic group (Ar) as previously described. It is most preferably a 1,4-phenylene moiety or an analog thereof.

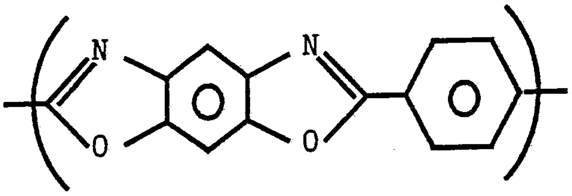
The nitrogen atom and the Z moiety in each azole ring are bonded to adjacent carbon atoms in the aromatic group, such that a five-membered azole ring fused with the aromatic group is formed.

The azole rings in AA/BB-mer units may be in cis- or trans-position with respect to each other, as illustrated in 11 Ency. Poly. Sci. & Eng., supra, at 602.

The polymer or copolymer preferably consists essentially of either AB-PBZ mer units or AA/BB-PBZ mer units, and more preferably consists essentially of AA/BB-PBZ mer units. The polybenzazole polymer may be rigid rod, semi-rigid rod or flexible coil. It is preferably rigid rod in the case of an AA/BB-PBZ polymer or semi-rigid in the case of an AB-PBZ polymer. Azole rings within the polymer are preferably oxazole rings (Z = O), so that the polymer is a polybenzoxazole polymer. Preferred mer units are any one illustrated in Formulae 2 (a)-(h). The polymer more preferably consists essentially of any of the mer units illustrated in 2(a)-(h), and most preferably consists essentially of any of the mer units illustrated in 2(a)-(c).

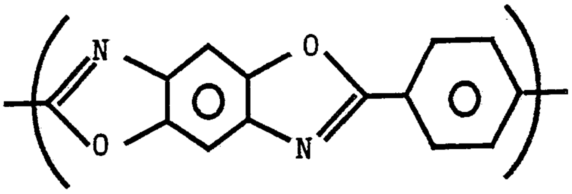
2

(a)



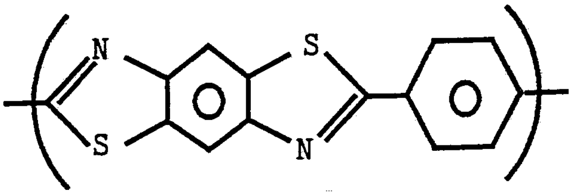
,

(b)



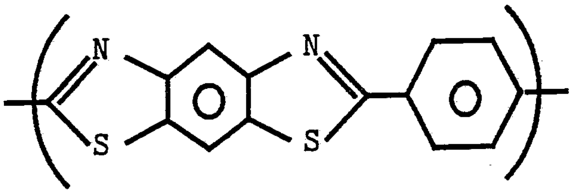
,

(c)



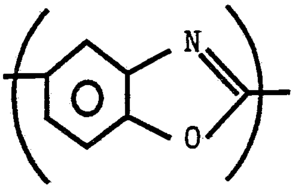
,

(d)

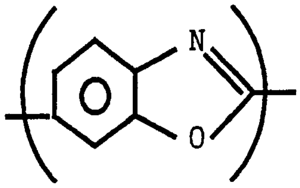


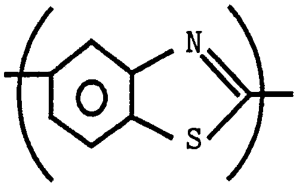
,

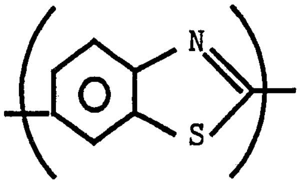
(e)



,

(f)  .

(g)  , and

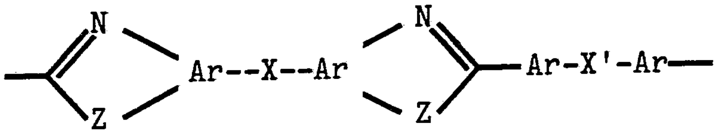
(h)  .

The polybenzoxazole or polybenzothiazole polymer or copolymer may also be a block copolymer in which the previously described repeating units are bonded to blocks of thermoplastic polymer. For example, the thermoplastic block may contain a thermoplastic polyamide, polyimide, poly(aromatic ketone), poly(aromatic sulfone), poly(aromatic ether), or random or sequential copolymer of those polymers with each other or with polybenzazole. The thermoplastic block may also contain a thermoplastic polybenzazole polymer, such as the polymers described in Harris et al., Thermoplastic Compositions Containing Polybenzoxazole, Polybenzothiazole and Polybenzimidazole Moieties and Process for Making Shaped Articles from Them, EPO Application 90104963.5 (filed March 16, 1990), EPO Publication 0 388 803 (published September 26, 1990) and in K.-U. Bühler, Spezialplaste 838-866 (Akademie-Verlag 1978). The thermoplastic block preferably contains any one of:

(a) a thermoplastic polyamide;
(b) a thermoplastic poly(aromatic ether);
(c) a thermoplastic polybenzazole-poly(aromatic ether) copolymer;
(d) a jointed polybenzazole are more preferably represented by Formula 5(a)

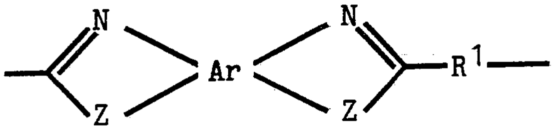
5

(a)



(e) an aliphatic polybenzazole represented by Formula 5(b)

(b)



wherein each X and X' is independently any of an oxygen atom, a carbonyl group, a sulfonyl group, an alkyl group or a perfluoroalkyl group; each Ar is independently an aromatic group as previously described; and R^1 is a substituted or unsubstituted alkyl group that contains at least three carbon atoms, in which the illustrated bonds are not to the same or adjacent carbon atoms.

Each polybenzoxazole or polybenzothiazole polymer or copolymer preferably contains on average at least 25 mer units, more preferably at least 50 mer units and most preferably at least 100 mer units. The intrinsic viscosity of rigid AA/BB-PBZ polymers in methanesulfonic acid at 25°C is preferably at least 10 dL/g, more preferably at least 15 dL/g and most preferably at least 20 dL/g. For some purposes, an intrinsic viscosity of at least 25 dL/g or 30 dL/g may be best. Intrinsic viscosity of 60 dL/g or higher is possible, but the intrinsic viscosity is preferably no more than 40 dL/g. The intrinsic viscosity of semi-rigid AB-PBZ polymers is preferably at least 5 dL/g, more preferably at least 10 dL/g and most preferably at least 15 dL/g.

The polybenzoxazole or polybenzothiazole polymer or copolymer is a preferably a homopolymer. The homopolymer preferably is not thermoplastic - i.e., it does not become flowable or moldable at any temperature below its decomposition temperature. The homopolymer is preferably essentially insoluble in common organic solvents such as halogenated hydrocarbons, alkanes, benzene or toluene. The homopolymer is preferably insoluble in non-acidic aqueous solvents.

The polymer or copolymer is dissolved in a solvent to form a solution or dope. Some polybenzoxazole and polybenzothiazole polymers are soluble in cresol, but the solvent is preferably an acid capable of dissolving the polymer. The acid is preferably non-oxidizing. Examples of suitable acids include polyphosphoric acid, methanesulfonic acid and sulfuric acid and mixtures of those acids. The acid is preferably polyphosphoric acid and/or methanesulfonic acid, and is more preferably polyphosphoric acid. The fiber should be chosen so that its properties do not degrade upon contact with the acid.

The dope should contain a high enough concentration of polymer for the polymer to coagulate to form a solid article. The concentration of polymer in the dope is usually at least 0.5 weight percent, preferably at least 1 percent and more preferably at least two percent. The maximum concentration is limited primarily by practical factors, such as polymer solubility and dope viscosity. The concentration of polymer is seldom more than 30 weight percent, and usually no more than about 20 weight percent. The best concentration within that range varies, depending upon the polymer in the dope.

When the polymer is rigid or semi-rigid, then the concentration of polymer in the dope is preferably high enough to provide a liquid crystalline dope. The concentration of the polymer is preferably at least 7 weight percent, more preferably at least 10 weight percent and most preferably at least 14 weight percent.

On the other hand, a block copolymer that contains rigid or semirigid polybenzazole blocks and thermoplastic polymer blocks is preferably in a lower concentration, so that the dope solution is not liquid crystalline. The total weight percent of rigid or semirigid blocks in the solution is preferably no more than 4 weight percent. Coagulation of the block copolymer from isotropic dopes yields a substantially non-phase-separated matrix that can be thermoformed without phase separation.

Suitable polymers or copolymers and dopes can be synthesized by known procedures, such as those described in Wolfe et al., U.S. Patent 4,533,693 (August 6, 1985); Sybert et al., U.S. Patent 4,772,678 (September 20, 1988); Harris, U.S. Patent 4,847,350 (July 11, 1989); Ledbetter et al., "An Integrated Laboratory Process for Preparing Rigid Rod Fibers from the Monomers," _The Materials Science and Engineering of Rigid-Rod Polymers_ at 253-64 (Materials Res. Soc. 1989); Harris et al., Copolymers Containing Polybenzoxazole, Polybenzothiazole and Polybenzimidazole Moieties, International Application No. PCT/US89/04464 (filed October 6, 1989), International Publication No. WO 90/03995 (published April 19, 1990) and Harris et al., Thermoplastic Compositions Containing Polybenzoxazole, Polybenzothiazole and Polybenzimidazole Moieties and Process for Making Shaped Articles from Them, EPO Application 90104963.5 (filed March 16, 1990), EPO Publication 0 388 803 (published September 26, 1990).

In summary, to make polybenzoxazole or polybenzothiazole homopolymer or random or sequential copolymer, suitable monomers (AA-monomers and BB--monomers or AB-monomers) are reacted in a solution of non-oxidizing and dehydrating acid under non-oxidizing atmosphere with vigorous mixing and high shear at a temperature that is increased in step-wise or ramped fashion from no more than 120°C to at least 190°C. Examples of suitable AA-monomers include terephthalic acid and analogs thereof. Examples of suitable BB--monomers include 4,6-diaminoresorcinol, 2,5-

-diaminohydroquinone, 2,5-diamino-1,4-dithiobenzene and analogs thereof, typically stored as acid salts. Examples of suitable AB-monomers include 3-amino-4-hydroxybenzoic acid, 3-hydroxy-4-aminobenzoic acid, 3-amino-4-thiobenzoic acid, 3-thio-4-aminobenzoic acid and analogs thereof, typically stored as acid salts.

To make a block copolymer, the polybenzoxazole or polybenzothiazole oligomer or polymer may be reacted with: (1) a thermoplastic polymer; or (2) monomers that polymerize to form a thermoplastic polymer. The polybenzoxazole or polybenzothiazole may be end-capped with a reactive group, such as by end-capping with an oxy-bis-(benzoic acid) monomer, to facilitate formation of the block copolymer.

The fiber is prepregged with the dope solution. The optimum procedure for prepregging the fiber in the dope will vary depending upon the fiber, the dope and the desired composite. A less viscous dope, whose viscosity is similar to that of other uncured matrix resins, may be prepregged according to processes used for known matrix resins. Likewise, a fiber or fiber tow or a group of tows may be prepregged with a viscous dope by known means for putting viscous coatings on fibers or wires, such as by extruding the dope on the fiber using a cross-head die.

Such processes ordinarily form a prepregged tape that can be laid up in a desired orientation and shape. Many different fiber configurations are known and may be used. The fibers may run in a single direction to form a unidirectional composite, having great strength in one direction but poorer properties in other directions. The fibers may be laid out in layers directed at different angles with respect to each other to form a multidirectional composite. The prepreg may be laid out flat or filament wound to form a shaped article.

A group of fibers or tows may be prepregged with a dope that is viscous enough to form a film, by forming one or more dope films and either pressing the fibers into a single film of dope or pressing the fibers between two films of dope. Several alternating layers of fiber and dope film may be pressed together to form a composite having several layers of fiber. The fibers pressed into the dope may have unidirectional or multidirectional orientation as previously described. They may be part of a cloth or a non-woven mat. The dope film may be thicker to form a "resin-rich" composite or thinner to form a "resin-starved" composite. The dope film is preferably on average at least 25 μm thick. The temperature should be high enough for the fibers to embed in the dope and for the dope sheets to consolidate.

The film may be uniaxially stretched to provide best properties in a single direction, but it is preferably biaxially stretched to provide good properties in at least two directions. The extrusion of dopes to form films is described in numerous references, such as in Chenevey, U.S. Patent 4,487,735 (December 11, 1984); Lusignea et al., U.S. Patent 4,871,595 (October 3, 1989); Chenevey, U.S. Patent 4,898,924 (February 6, 1990); Harvey et al., U.S. Patent 4,939,235 (July 3, 1990); Harvey et al., U.S. Patent 4,963,428 (October 16, 1990); and Lusignea et al., U.S. Patent 4,966,806

(October 30, 1990). For instance, the dope may be extruded from a slit die, after which it is preferably mechanically stretched before coagulation to impart biaxial orientation. Alternatively, the dope may be extruded in a tubular film that is preferably stretched biaxially by a bubble process to impart biaxial orientation.

The fibers may be short fibers or fiber pulps that are immersed in the dope to form a random fiber composite, similar to those described in U.S. Patents 4,426,470 and 4,550,131.

After prepregging is accomplished and the prepregs are laid up in the desired shape and configuration, the composite is hardened by contacting the dope with a liquid that causes the polymer or copolymer to coagulate. Ordinarily, the liquid is a nonsolvent for the polymer or copolymer that dilutes the solvent. Many nonsolvent liquids have been studied and their effects on polybenzazole coagulation reported. The nonsolvent liquid is preferably volatile. The nonsolvent liquid may be an organic compound, such as an alcohol or a ketone containing no more than 4 carbon atoms. The nonsolvent liquid is preferably aqueous, and more preferably consists essentially of water, at least at the commencement of the coagulation. When the solvent is volatile or contains a volatile component, such as methanesulfonic acid, then the volatile component can be at least partially removed by evaporation to concentrate the polymer before coagulation.

The coagulated polymer is preferably washed for a period of time sufficient to remove substantially all of the remaining solvent. The composite may be dried. It is preferably restrained from shrinking as it is dried. After drying, the composite may be heat treated. Heat treatment is preferably carried out under pressure. The finished composite may be machined into a desired final shape.

The resulting composite has fibers as previously described embedded in a matrix resin containing a polybenzoxazole or polybenzothiazole polymer or copolymer as previously described. The composite should contain a sufficient number of fibers to provide reinforcement for the composite. It should contain a sufficient quantity of matrix material to hold the fibers together and maintain fiber alignment, and preferably to transfer loads around broken fibers.

The composite preferably contains at least 20 volume percent fiber, more preferably at least 40 volume percent fiber and most preferably at least 50 volume percent fiber. It preferably contains at least 20 volume percent matrix and more preferably at least 35 volume percent matrix.

Several variations on the basic composite are possible. For instance, the fiber may receive surface treatment or be coated with an adhesive to improve the adhesion of the fiber to the matrix. The matrix may contain a mixture of more than one polymer, such as several polybenzazole polymers or a mixture of the polybenzazole fiber and a non-polybenzazole polymer, as described in Uy, U.S. Patent 4,810,735 (March 7, 1989). The matrix preferably contains only a single polymer or copolymer. The fiber may be wrapped with another fiber to improve compressive strength (filed August 8, 1990).

The preferred polybenzoxazole and polybenzothiazole matrix resins have one or more of the following advantages over current corresponding thermoset or thermoplastic matrix resins: better flame resistance, lower smoke, good solvent resistance, good chemical resistance, high continuous use temperatures, higher tensile strength and higher tensile modulus. The composite may be fabricated into structural parts for many known uses.

Illustrative Examples

The following examples are given to illustrate the invention and should not be interpreted as limiting the Specification or the Claims. Unless stated otherwise, all parts and percentages are given by weight.

Example 1 - Composite Containing Carbon Fiber and Polybenzoxazole Matrix.

A dope containing 14 weight percent cis-polybenzoxazole (consisting essentially of mer units illustrated in Formula 2(a) - intrinsic viscosity of 25 dL/g to 45 dL/g in methanesulfonic acid at 25°C) in polyphosphoric acid is extruded from a slit die as a 15 mil thick sheet between two sheets of 2 mil thick Teflon™ fluoropolymer. Two 3 inch by 3 inch squares of the dope film are cut, and the Teflon™ sheet is stripped off of one side of each sheet.

A 3 inch by 3 inch piece of Panex™ PWB-6 carbon fiber cloth, available from Stackpole Fibers Inc., is placed between the two dope film samples, with the dope sides against the carbon fiber cloth. The article is pressed at 150°C under 5 tons of pressure for one minute to form a prepreg.

The prepreg is cooled to room temperature, and the Teflon™ sheet is stripped off of each side of the prepreg. The prepreg is placed in a "picture frame" holder to prevent shrinkage along the length and width of the sample but allow shrinkage in the thickness of the sample. The framed prepreg is placed in two liters of water, left in the water for two days, removed from the frame and dried in air at ambient temperature. A composite having carbon fiber reinforcement and a cis--polybenzoxazole matrix results.

The composite is cut in half. One half is placed in a heated press at 150°C and 5000 lbs. pressure for one minute. It is golden yellow in color. One half is placed in a heated press at 300°C and 5000 lbs. pressure for one hour. It is darker yellow with a purple tinge. Both have smooth surfaces with no visible holes. The polybenzoxazole in both adheres firmly to the cloth.

Example 2 - Composite Containing Carbon Fiber and Nonrigid Matrix.

The procedure of Example 1 is followed, except that:

Instead of 14 weight percent cis-polybenzoxazole, the dope contains 12 weight percent of a polymer formed by the reaction of 4,6-diaminoresorcinol bis(hydrogen chloride) and 1,1,3-trimethyl-3-phenylindan-4',5-dicarboxylic acid in polyphosphoric acid, such as is described in Summers et al., Ser. No. 513,316 (filed April 20, 1990);

The sheets pressed together are 2 inches by 3 inches; and

Only one sample is pressed after coagulation at 300°C for 90 minutes under 5000 lbs. pressure. It turns black and sticks to the press.

<u>Example 3</u> - <u>Composite Containing Polybenzoxazole Fiber and Polybenzoxazole Matrix</u>.

The procedure of Example 1 is followed, except that:

The cloth consists essentially of polybenzoxazole fiber and has dimensions of 5 inches by 5 inches;

The dope films have dimensions of 5 inches by 5 inches;

The sample is coagulated in 2 gallons of water.

The resulting composite appears similar to the composite of Example 1.

Example 4 - Composite Containing Two Layers of Carbon Fiber and Polybenzoxazole Matrix.

The procedure of Example 1 is followed, except that:

The cloth and dope film are laid up so that there is from top to bottom: a layer of Teflon™ film, a layer of polybenzoxazole dope, a layer of carbon fabric, a layer of polybenzoxazole dope, a layer of carbon fabric, a layer of polybenzoxazole dope, and a layer of Teflon™ film;

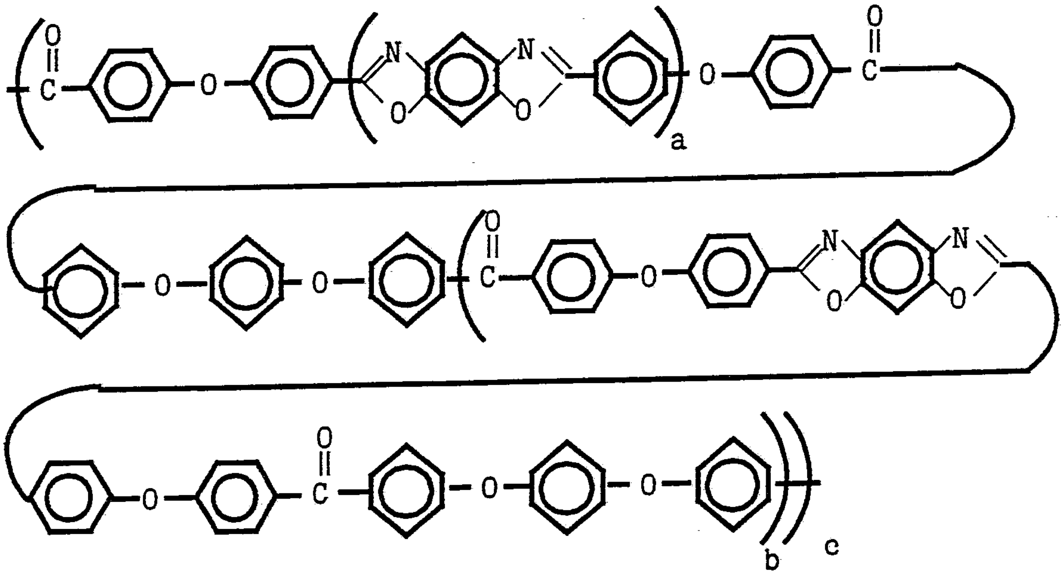
The prepregging is carried out at 150°C and 5000 lbs. pressure for 3 minutes;

The finished composite is pressed under 5000 lbs pressure at a temperature ramped from room temperature to 300°C over 90 minutes and held at 300°C for 30 minutes.

The resulting structures are much stiffer than the structures prepared in Example 1.

Example 5 - Composite Containing Carbon Fiber and Polybenzoxazole/PEEK-PBO Block Copolymer Matrix

A composite is fabricated by the following procedure using (1) a graphite fiber and (2) a dope containing a mixture of methanesulfonic acid and polyphosphoric acid and about 3 weight percent of a block copolymer having rigid rod cis-polybenzoxazole blocks and blocks of thermoplastic cis-PBO/PEEK copolymer. The block copolymer contains about 38 weight percent rigid rod block and about 62 weight percent thermoplastic block. Its average structure is represented by the Formula:



wherein "a", "b" and "c" are each a number of mer units suitable to provide the desired proportions of polymer.

The fiber is passed through a 400°C oven at a rate of 140 inches/min. in order to remove the sizing on the fiber. The fiber passes through several idler rollers and through a resin bath that contains the dope at room temperature. The impregnated fiber passes through a rectangular die 0.120 in. x 0.008 in. to clean off excess dope.

The prepreg is wound around a rotating 70 inch drum such that each wrap is immediately adjacent to the previous wrap without overlapping. The prepreg is cut into seven 7 inch x 7 inch panels, which are stacked to form a seven-ply unidirectional laminate. The laminate is placed in a porous Teflon™ fluoropolymer bag, clamped between perforated aluminum plates and immersed in running water at room temperature for 24 hours.

The resulting wet composite is pressed at 80°C and 100 psi for 4-1/2 hours and is placed in a vacuum oven at 90°C for 24 hours to dry. It is then compressed for 6 minutes at 400°C and 50 psi, for 15 minutes at 400°C and 1000 psi, and for a time sufficient to cool at 1000 psi to consolidate. The resulting composite is rigid with individual plies bonded firmly together.

Example 6 - Composite Containing Carbon Fiber and Polybenzothiazole Matrix

The procedure of Example 1 is repeated, except that the dope solution contains trans-polybenzothiazole polymer. Similar results will be obtained.

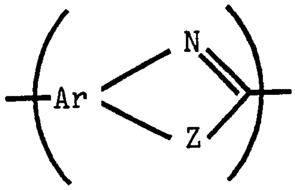
Claims :

1. A method of using a dope solution that contains: (i) a polybenzoxazole polymer or copolymer and/or a polybenzothiazole polymer or copolymer, and (ii) a solvent for the polymer or copolymer, said method being characterized the steps of:

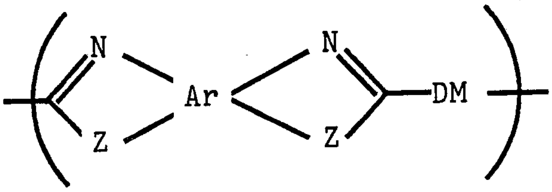
(1) prepregging a plurality of reinforcing fibers with a the dope solution that contains: (i) a polybenzoxazole polymer or copolymer or a polybenzothiazole polymer or copolymer, and (ii) a solvent for the polymer or copolymer; and

(2) contacting the dope solution with a liquid coagulant that causes the polymer or copolymer to coagulate, in a quantity sufficient to cause the polymer or copolymer to coagulate with the fibers embedded therein.

2. A method as described in Claim 1 wherein the polymer or copolymer is not thermoplastic and contains repeating units that are each individually represented by any of the following Formulae:



1(a) AB



1(b) AA/BB

wherein:

Each Ar represents an aromatic group that contains no more than 18 carbon atoms.

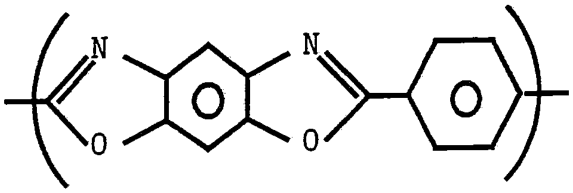
Each Z is independently an oxygen or a sulfur atom.

Each DM is independently a bond or an aromatic group as previously described.

3. A method as described in any of the preceding Claims wherein the polymer or copolymer contains repeating units that are represented by any of the following Formulae:

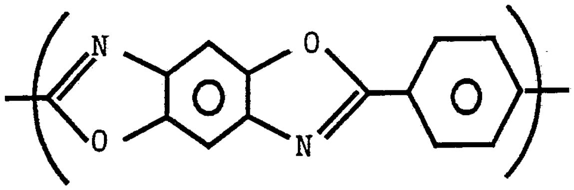
2

(a)



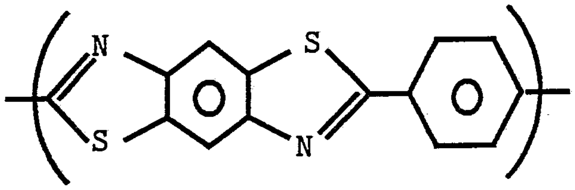
,

(b)



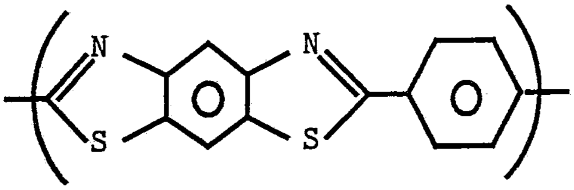
,

(c)



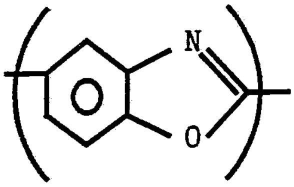
,

(d)



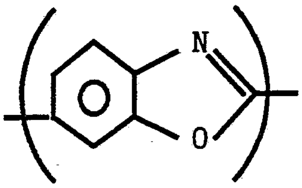
,

(e)

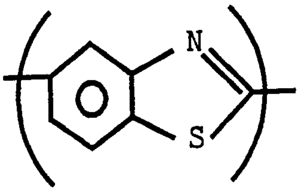


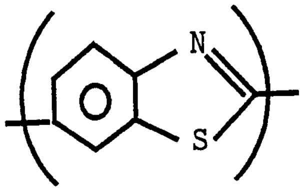
,

(f)



.

(g)  , and

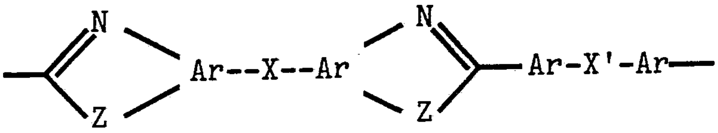
(h)  .

4. A method as described in any of the preceding Claims wherein the dope solution contains 7 to 20 weight percent polymer or copolymer.

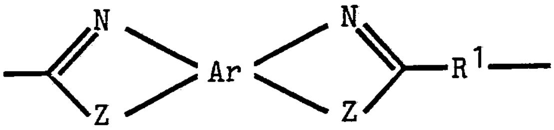
5. A method as described in Claim 1 wherein the polymer or copolymer is a block copolymer that contain blocks of polybenzoxazole or polybenzothiazole polymer and blocks of thermoplastic polymer.

6. A method as described in any one of Claims 1, 3 or 5 wherein the polymer or copolymer is a block copolymer containing blocks of any of the following thermoplastic polymers:

(a) a thermoplastic polyamide;
(b) a thermoplastic poly(aromatic ether);
(c) a thermoplastic polybenzazole-poly(aromatic ether) copolymer;
(d) a jointed polybenzazole represented by the Formula:

(a) 

(e) an aliphatic polybenzazole represented by the Formula:

(b) 

wherein each X and X' is independently any of an oxygen atom, a carbonyl group, a sulfonyl group, an alkyl group or a perfluoroalkyl group; each Ar is independently an aromatic group as previously described; and R^1 is a substituted or unsubstituted alkyl group that contains at least three carbon atoms, in which the illustrated bonds are not to the same or adjacent carbon atoms.

7. A method as described in any one of Claims 1, 3, 5 or 6 wherein the dope solution contains from 1 to 4 weight percent polymer or copolymer.

8. A method as described in any of the preceding Claims wherein the solvent in the dope solution is polyphosphoric acid or methanesulfonic acid.

9. A method as described in any of the preceding Claims wherein the fiber is an aramid, boron, glass, carbon, gel-spun polyethylene, polybenzoxazole, polybenzothiazole, or polybenzimidazole fiber.

10. A method as described in any of the preceding Claims wherein the fiber is prepregged with sufficient dope solution to make a composite containing at least 20 weight percent fiber and at least 20 weight percent matrix polymer.

11. A method as described in any of the preceding Claims wherein the prepregged fibers are continuous fibers that are laid up as any one of:

(a) a unidirectional composite; or
(b) a multidirectional composite,

before the polymer or copolymer is coagulated.

12. A method as described in any of Claims 1 through 10 wherein the prepregged fibers are short fibers or fiber pulps that are mixed with the dope solution to form a random fiber composite on coagulation.

13. A method as described in any of the preceding Claims wherein the coagulant liquid is water or an aqueous solution.

14. A method as described in any of the preceding Claims wherein the polymer or copolymer is a polybenzoxazole polymer or copolymer.

15. A method as described in any of Claims 1 through 14 wherein the polymer or copolymer is a polybenzothiazole polymer or copolymer.

INTERNATIONAL SEARCH REPORT

PCT/US91/09227
International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): C08K 3/32; C08L 79/06
U.S. CL. 524/417, 494; 528/176, 179

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	428/288, 408; 524/417, 494; 528/176, 179

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US, A, 4,533,692 (WOLFE ET AL.) 06 AUGUST 1985; See entire document.	1-3 & 5
Y	US, A, 4,533,693 (WOLFE ET AL.) 06 AUGUST 1985; See entire document.	1-3 & 5
Y,P	US, A, 4,996,281 (SO) 26 FEBRUARY 1991; See entire document.	1-3 & 5

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2] 14 FEBRUARY 1992	Date of Mailing of this International Search Report [2] 20 APR 1992
International Searching Authority [1] ISA/US	Signature of Authorized Officer [20] Edward Cain Edward Cain

Form PCT/ISA/210 (second sheet) (May 1986)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☒ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers , because they relate to subject matter [1] not required to be searched by this Authority, namely:

2. ☐ Claim numbers , because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [1], specifically:

3. ☒ Claim numbers 4 & 6-15, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application [illegible]

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report [illegible] of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international [illegible] those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search [illegible] the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Search [illegible] invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.