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3,776,829

AMINATED CARBON FIBERS

John Cecil Goan, Johnson City, Tenn., assignor to Great Lakes Carbon Corporation, New York, N.Y.

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1 Claim

ABSTRACT OF THE DISCLOSURE

Carbon fibers are reacted with ammonia plasma to form amino groups on the surface, useful in preparing carbon fiber-epoxy resin composite.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a division of pending application Ser. No. 15,281, filed Feb. 27, 1970, now abandoned.

BACKGROUND OF THE INVENTION

Composite materials, for use in the aerospace industry, are well known to the art. Such materials comprise a resinous binder, as for example a polymerized epoxide and a filler, as for example asbestos, glass fibers, or carbon fibers.

Of the above named fillers, carbon fibers have received attention due to their high corrosion and temperature resistance, low density, high tensile strength and high modulus of elasticity.

Uses for such carbon-fiber reinforced composites include aerospace structural components, rocket motor casings, deep submergence vehicles, and ablative materials for heat shields on re-entry vehicles.

The incorporation of carbon or graphite particles in resin bases in amounts of up to 60 percent by volume will impart a heat-conducting property but not an electrical conductivity to the component. Litant, in U.S. 3,406,126, teaches the addition of carbon yarn in as little as 0.05 percent by volume to the resinous matrix to impart electrical conductivity to the resulting composite. Such composites can be prepared from polyesters, polyvinyl chloride, polyepoxides, or like resins, and carbonized rayon, polyacrylonitrile, or like fibers.

High modulus composites usually have low interlaminar shear strengths of about 3000 to 4000 p.s.i. The low shear strengths are probably due to poor bonding between the carbon fibers and the matrix. Attempts to improve this bonding, particularly between rayon-based carbon fiber fillers and an epoxy-matrix have been partially successful, but have resulted in a degradation of the ultimate tensile strength of the fiber and also of the fabricated composite.

Improved bonding has been accomplished by plating the fiber with various metals, as for example tantalum, with metal carbides, as for example whiskers of silicon carbide, and with nitrides.

More recently, rayon-based carbon fibers have been treated with various oxidizing agents in order to etch the surface of the fiber. Such oxidizing agents have included air, ozone, concentrated nitric acid, and a 3.3 percent by weight solution of sodium dichromate in concentrated sulfuric acid at 50° C. for 5 minutes. In most cases the oxidative treatment of rayon-based carbon fibers resulted in a decrease in ultimate tensile strength of the fiber and of the fiber-resin composite.

The primary structural properties of fiber-resin composites improves as carbon fiber content is increased up to about 65 volume percent then decreases as the fiber content exceeds that aforementioned figure. The preferred range of carbon fiber content is about 45 to 65 volume percent of fiber in the fabricated composite.

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SUMMARY OF THE INVENTION

This invention relates to carbon fibers containing amine functional groups on the surface thereof. The amine groups act as cross linking agents for an epoxy resin matrix in the preparation of sized fibers, pre-impregnated tapes, and composites containing the fibers.

The carbon fibers of this invention are prepared by contacting the carbon fiber with an ammonia plasma.

DETAILED DESCRIPTION OF THE INVENTION

High modulus carbon fibers are particularly useful for this invention since such fibers have primary structural properties well adapted for structural uses. However, this invention, as herein described and claimed, is not limited thereto and can be used for all carbon fibers.

High modulus acrylic-based carbon fibers are defined as those fibers possessing a tensile strength of greater than 100×10^3 p.s.i. and a Young's modulus greater than 20×10^6 p.s.i. Such fibers can be prepared by the method of Shindo, "Studies in Graphite Fiber, Report No. 317 of the Government Research Industrial Institute," Osaka, Japan, 1961, and Tsunoda, U.S. 3,285,686. Typically, acrylic-fibers can be stretched to about 50 to 100 percent or more of their original length while heating in the presence of water or steam to about 100° C., oxidized in an oxidizing atmosphere at about 200 to 300° C. for a period of up to 4 hours, oxidized in a second stage in an oxidative atmosphere at 200 to 375° C., and pyrolyzed and/or graphitized at 1000 to 3000° C. in a non-oxidizing atmosphere to prepare a carbon fiber possessing a high modulus of elasticity and a high tensile strength.

By the process of this invention the carbon fibers as prepared above are contacted with a plasma of ammonia to yield a new carbon fiber with an aminated surface. The ammonia plasma can be formed by charging a tube containing the fiber with ammonia gas at an absolute pressure of about 0.05 to about 2 torr (mm. Hg) and passing therethrough an electric discharge of from about 10 to about 100 megahertz for from about 15 minutes to about 3 hours. A power level of 10 to 500 watts is generated in the plasma. The treated carbon fiber is then removed from the tube and can be used without further manipulation to prepare epoxy-sized fibers, and pre-impregnated tapes and composites with an epoxy matrix. The amine functions catalyze the curing of the resin and bond thereto providing a direct chemical linkage between fiber and matrix.

Typically, graphitized fiber and ammonia are charged into the tube of a crystal-controlled RF generator—LTA-600 J (Tracerlab, a Division of Laboratory for Electronics, Inc.) at an internal pressure of 0.15 torr. A discharge of 13.56 megahertz is passed through the tube for 1.5 hours. The vacuum is released and the fiber is removed.

Alternatively, the excitation of the ammonia is achieved by employing a microwave source for preparing the ammonia plasma.

The aminated carbon fiber of this invention is incorporated in amounts of about 45 to about 65 percent by volume in an epoxy resin without the further addition of a catalyst and polymerized in a manner well known in the art to give a void free composite. Exemplification of this method has been provided by Rees, U.S. 3,276,931, and Warner, U.S. 3,281,300.

Resins useful for preparing the composites utilizing the treated carbon fibers of this invention are those which will bond to amine functions during curing. They include such resins as epoxy resins, polyimide resins, poly-lower alkylene resins as for example polyethylene and polypropylene resins.