

United States Patent [19]
McKee

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[54] **METHOD OF TREATING HIGH STRENGTH CARBON FIBERS**

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[51] **Int. Cl.** **C01b 31/07**

[58] **Field of Search** 8/115.5, 116, 115.6; 423/447, 448; 117/137, 8, 169 R, 47 R, DIG. 11; 264/DIG. 19

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[57] **ABSTRACT**

A method of treating high strength carbon fibers comprises treating such fibers with an aqueous solution of the formate, acetate and nitrate salts of copper, lead, cobalt and cadmium, and vanadium pentoxide, and subsequently mildly oxidizing the fibers in air or oxygen at a temperature in the range of from 200° to 600°C. This method uniformly roughens the fiber surfaces thereby providing a desirable fiber structure for employment in a carbon-polymer composite.

3 Claims, No Drawings

METHOD OF TREATING HIGH STRENGTH CARBON FIBERS

This is a continuation-in-part of my copending application, Serial No. 31,743, filed Apr. 24, 1970 and now abandoned.

This invention relates to a method of treating high strength carbon fibers and more particularly to such a method wherein the surface is roughened in a uniform manner.

As used hereinafter, the term "high strength carbon fibers", which include both carbon fibers and graphite fibers signifies carbon fiber having a tensile strength of at least 200,000 psi and a modulus of at least 20×10^6 psi. Composites can be prepared generally by mixing together 50-70 weight percent of carbon fibers with 50-30 weight percent conventional polymer binder such as epoxy resin as the matrix material. These structures are then prepared in a conventional manner by a heat, vacuum, pressure cycle resulting in composites which are lightweight but exhibit excellent flexural strength. However, a major problem exists in the use of such carbon-polymer composites in that these composites exhibit low interlaminar shear strength caused by poor bonding between fibers and polymer matrix.

One approach, which has been made to improve the bonding characteristics of carbon fibers to a polymer resin matrix, has been to subject initially the fibers to oxidation in air. However, such oxidation has resulted in etch pitting of fiber surfaces. Another approach has been to etch mildly the fiber surfaces by subjecting the fibers to a prolonged treatment in nitric acid. While the resultant fibers are suitable, the process is time consuming and the results are non-uniform unless the process is controlled carefully. The above methods are discussed, for example, in an article entitled "Silane Coupling in Fibre-Reinforced Polyester Resin" by Harris et al. in the "Journal of Materials Science" 4 (1969) at pages 432-438.

The present invention is based on the discovery that improved interlaminar shear can be achieved between carbon fiber and polymer matrix by contacting the carbon fiber with an aqueous solution or dispersion of organic or inorganic acid salts of copper, lead, cobalt, and cadmium and certain metal oxides such as vanadium pentoxide, after which the fibers are heated in an oxygen containing atmosphere. My improved method results in the fibers having a uniformly roughened surface as opposed to a surface with deep etch pitting and resultant structural weakness.

I found also that organic acid salts of other metals such as silver, titanium and boron do not give the desirable features of my invention but promote etch pit formation. As mentioned above the etch pitting tends to weaken the fiber structure and thus is unsuitable for use in carbon-polymer composites since it leads to a decline in the interlaminar shear strength.

There is provided by the present invention a method for treating high modulus graphite fiber to improve the bonding characteristics of said fiber to a resin matrix which comprises

1. Coating the fiber with about 0.01 to about 10 percent by weight of a coating compound selected from the class consisting of organic acid salts of copper, lead, cobalt, and cadmium, inorganic salts of copper, lead, cobalt and cadmium and vanadium pentoxide.

2. Heating the fiber at a temperature in the range of from 200° to 600°C. in an oxygen containing atmosphere, and

3. Effecting the removal of the coating compound from the surface of the fiber.

Various organic and inorganic acid salts of the above types are useable in my process. For example, suitable salts include cupric acetate, copper formate, copper nitrate, lead acetate, lead nitrate, cobalt acetate, cobalt nitrate, cobalt formate, cadmium acetate, cadmium nitrate, cadmium formate, etc.

For the mild oxidation following the treatment with one of the above salts or with vanadium pentoxide, the oxidant can be oxygen or air. The period of time for such oxidation can be varied over a wide range but it is preferred to employ a time period from about 5 to 30 minutes. Experience has shown that the use of oxygen reduces the time period.

After the oxidation of the fiber, it is desirable to use a dilute acid which is compatible with the previously used salt to remove any remaining salt. The retention of salt on the fiber can lead to degradation of the polymer employed as the matrix in the composite. After the acid treatment the fiber is dried.

Such fibers can then be made into a composite in a conventional manner by mixing together 50-70 weight percent of carbon fibers with 50-30 weight percent of a generally employed polymer resin such as an epoxy, polyimide, maleimide, etc., and subjecting the mixture to a heat, vacuum and pressure cycle.

Examples of carbon fibers treated in accordance with my method are carbon fibers derived from carbonized polyacrylonitrile, cellulose acetate, cellulose nitrate, etc. such as Morganite Type I and II, Thornel 25, 40, 50 etc., fiber made from molten polyvinyl chloride pitch, etc.

In order that those skilled in the art will be better able to practice the invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight.

EXAMPLE 1

A 0.1% cupric acetate solution was prepared and heated to a temperature of 80°C. in a beaker. A plurality of commercially available high strength carbon fibers were immersed for 15 minutes in the hot cupric acetate solution. The fibers were then removed from the solution and dried in air for a period of 30 minutes. The fibers were then heated in air at 500°C. for 30 minutes. After cooling the fibers were washed with a 10% dilute acetic acid solution. This washing was followed by a washing with distilled water. The fibers were then allowed to dry in air.

EXAMPLE 2

A solution of 0.1% copper acetate was prepared and heated to a temperature of 80°C. in a beaker. A plurality of commercially available high strength carbon fibers were immersed in the solution for a period of 15 minutes. The fibers were then removed from the solution and dried in air. These fibers were heated in oxygen in a tube furnace for 60 minutes. The fibers were then washed with a 10% dilute acetic acid after which they were subjected to a second washing with distilled water. The fibers were then dried in air.

EXAMPLE 3

A solution of 0.1% lead acetate was prepared and heated in a beaker to a temperature of 80°C. A plurality of commercially available carbon fibers were immersed in the solution for a period of 15 minutes. The fibers were then removed and dried in air. The fibers were then heated in air at a temperature of 400°C. for 30 minutes. After cooling, the fibers were washed in a 10% dilute acetic acid. Subsequently the fibers were washed with distilled water. The fibers were then dried in air.

EXAMPLES 4-13

Ten carbon-epoxy composites were prepared in bar form with dimensions of 1.5 × 0.080 × 0.050 inch. Each composite was prepared from 50 weight percent of fibers and 50 weight percent conventional epoxy resin mixture. The epoxy resin mixture was a mixture of Epon epoxy 823 and Epon epoxy 1031 which are manufactured by Shell Chemical Company, New York, New York. The first bar which is identified as Example 4 was prepared by using commercially available carbon fibers which had not been treated in accordance with my invention. Examples 5-7 employed fibers from Example 1. Examples 8-10 contain fibers from Example 2. Examples 11-13 contained fibers from Example 3.

These composites were tested and the mechanical properties are listed below in Table 1.

Table 1

Examples	Flexural Strength × 10 ³ psi	Flexural Modulus × 10 ⁶ psi	Interlaminar Shear Strength × 10 ³ psi
4	45 - 100	20 - 32	3 - 4
5	84	29.9	6.81
6	80	25.7	6.20

7	89	28.0	6.46
8	118	30.0	4.38
9	114	30.0	4.94
10	104	27.1	5.00
11	118	28.7	4.27
12	121	30.4	4.75
13	116	28.0	4.09

While other modifications of the invention and variations thereof which may be employed within the scope of the invention have not been described, the invention is intended to include such as may be embraced within the following claims.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A method for treating high strength carbon fiber having a tensile strength of at least 200,000 psi and a modulus of at least 20 × 10⁶ psi to improve the bonding characteristics of the fiber to resin matrix which comprises:

1. coating the fiber with about 0.01 to about 10 percent by weight of the formate, acetate and nitrate salts of a metal selected from the class consisting of copper, lead, cobalt and cadmium, and vanadium pentoxide
2. heating the fiber at a temperature in the range of from 200° to 600°C in an oxygen containing atmosphere, and
3. treating the surface of the fiber with an aqueous acid solution to effect the removal of the coating of metal salt.

2. A method as in claim 1 wherein the salt is cupric acetate, the oxygen containing atmosphere is air, the heating temperature is about 500°C.

3. A method as in claim 1, wherein the salt is lead acetate, the oxygen containing atmosphere is air, the heating temperature is about 400°C.

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