United States Patent

Ray et al.

[15] 3,671,411

[45] June 20, 1972

[54] **TREATMENT OF CARBON OR GRAPHITE FIBERS AND YARNS FOR USE IN FIBER REINFORCED COMPOSITES**

[72] Inventors: **James D. Ray**, Springfield; **Samuel Steingiser**; **Robert A. Cass**, both of Dayton, all of Ohio

[73] Assignee: **The United States of America as represented by the Secretary of the Air Force**

[22] Filed: **March 3, 1970**

[21] Appl. No.: **16,251**

[52] **U.S. Cl.** 204/130

[51] **Int. Cl.** B01k 1/00

[58] **Field of Search** 204/130, 294

[56] **References Cited**

UNITED STATES PATENTS

3,323,869 6/1967 Olstowski 204/130

2,807,577 9/1957 Antonsen....................204/130

Primary Examiner—John H. Mack

Assistant Examiner—R. L. Andrews

Attorney—Harry A. Herbert, Jr. and Cedric H. Kuhn

[57] **ABSTRACT**

Carbon fiber or yarn as used in fiber reinforced composites is electrolytically treated to improve the surface characteristics and thereby to improve its bonding or adhesion to the matrix material. By this improved bonding, shear strengths of resultant fiber resin or plastic composites have been more than doubled. The electrolytic treatment is conducted by using the fiber or yarn as the anode and using en electrolyte such as an aqueous caustic solution.

5 Claims, No Drawings

TREATMENT OF CARBON OR GRAPHITE FIBERS AND YARNS FOR USE IN FIBER REINFORCED COMPOSITES

BACKGROUND OF THE INVENTION

1. Field of the Invention.

This invention relates to carbon or graphite fiber or yarn reinforcing materials. In one aspect it relates to the treatment of the reinforcing fibers or yarns to improve the adhesion between the fiber surface and a matrix material.

2. Description of the Prior Art.

There has been an increasing demand for materials of construction of high strength to weight ratio and high modulus to weight ratio for use in aerospace vehicles and devices, particularly for materials which also have good thermal stability and good shear strength.

Specifically, there has been a demand for improved reinforcing fibers to be embodied in structural composites which form the components of the leading edges of high speed aircraft, the nose cones or heat shields for reentry vehicles, rocket engine components, and the like.

High strength and high modulus carbon fibers and yarns, particularly those composed essentially of graphite and generally referred to as graphite fibers and yarns, have already been used as reinforcing agents in composite materials for aerospace structures. However, the bonding of resins or plastics to the carbon fibers in such composites has not been entirely satisfactory, and, as a result, the shear strengths of the resultant composites have been less than desired.

Attempts have been made to improve the surface adhesion properties by heating the fibers in an oxidizing atmosphere. However, this method has been found to produce pitting and uneven results with over-oxidation and resultant weakening of the fibers in the easily accessible or preferential areas and insufficient oxidation and poor adhesion in other areas.

SUMMARY OF THE INVENTION

The present invention resides in a process whereby the bonding properties of carbon and graphite fibers or yarns are improved to a surprising extent, in the improved fibers per se, and in the compositions incorporating the fibers. Broadly, the process comprises the step of subjecting a carbon or graphite fiber to an electrolytic reaction in an aqueous electrolyte whereby negative ions are attracted to the surface of the fiber acting as an anode, thereby modifying the fiber surface. As a result of this modification, subsequent bonding to plastics and resins is improved to such an extent that the shear strengths are increased in many cases to more than double the values obtained without this particular pretreatment with little or no loss in tensile strength.

During the electrolytic reaction, nascent oxygen forms at the anode and oxidizes the fiber surface. The improvement obtained by the present process results from the uniformity of the fiber surface oxidation and the accuracy with which the degree of oxidation can be controlled. In addition to the carbon to oxygen bonds that are formed at the fiber surface, it appears that hydroxyl groups and carboxyl groups also become attached to the surface and contribute to a marked extent to the improvement in bonding properties.

In general, any electrolyte which will generate nascent oxygen at the anode can be used in the practice of this invention. Examples of suitable electrolytes include aqueous solutions of sodium hydroxide, potassium hydroxide, phosphoric acid, nitric acid, sulfuric acid, and the like. It is usually preferred to employ aqueous sodium hydroxide or aqueous phosphoric acid solutions. It is to be understood that the concentration of the solutions will have an effect on the rate of generation of nascent oxygen. For a practical rate of generation, it has been found to be advantageous to use as the electrolyte a solution having a concentration of 0.5 to 20, preferably 1 to 10, weight percent.

In effecting the electrolytic treatment, the carbon fiber or yarn is used as the anode as stated, and the cathode can be an electrode of graphite or other carbon form, or can be any metal or other material suitable for cathode purposes. The process can be applied either as a batch or continuous operation. In the latter case, a continuous carbon fiber or yarn is passed over or under rolls to guide the fiber through the solution, and connection with the current source is applied to the fiber either through one of the rolls in contact with the fiber, or by any other convenient means.

The length, thickness or other dimensions of the fibers are not critical and are determined by other considerations in the ultimate purpose for which the product is to be used.

The temperature used is not critical except as it may affect the rate of nascent oxygen reaction with the fiber surface. However, in such cases, slower rates of reaction can be compensated for by prolonged treatment. Therefore, whatever temperature is convenient, such as 20°–50°C., is found to be most practical.

In accordance with the broad concept of this invention, any current density can be employed which is sufficient to produce nascent oxygen at the anode in an amount great enough to modify the surface of the fiber so as to improve the bonding properties of the fiber. In general, a current density in the approximate range of 0.0005 to 0.005 ampere per square centimeter (amp/cm^2) of the surface area of the yarn or fiber to be treated has been found to be satisfactory. It is usually preferred to employ a current density in the range of about 0.001 to 0.003 amp/cm^2. Any convenient voltage can be used in the electrolysis that will give the desired current density. It is generally preferred to utilize a voltage between about 10 and 150 volts. The period of the electrolytic reaction, referred to in the tables hereinafter as dwell or residence time, usually ranges from about 25 to 500 seconds, preferably from about 75 to 250 seconds. As previously mentioned, the temperature of the electrolyte can conveniently range from about 20° to 50°C.

The improvement in adhesion properties or bonding properties of the fibers of this invention occurs with any type of resin with which the fiber is mixed. Improvements in shear strengths occur for carbon fiber composites in which the resin components include phenolic resins, epoxy resins, polyester resins, polyimide resins, polyamide resins as well as elastomers such as natural rubber, polybutadienes, polyisoprenes, butadiene-styrene copolymers, polyurethanes, and plastics such as polyethylene, polypropylene, and the like. The composite generally contains in the range of about 25 to 75 volume percent of the treated carbon fibers.

However, since the high strength high modulus carbon fibers are relatively expensive and used only for particular purposes, such as in aerospace vehicles and devices, it is most practical to use resins which are also suitable for such purposes. For that reason epoxy resins and other types of resins, such as phenolic resins, that are particularly suitable for use in aerospace applications, are the ones preferred in making composites with the improved fibers of this invention.

Various methods of preparing carbon and graphite fibers are described in the literature and various commercial products of this type are available.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The practice of this invention is illustrated by the following examples. These examples are given merely for purpose of illustration and are not intended to be unduly limitative of the invention. Unless specifically indicated otherwise, parts and percentages are given by weight.

EXAMPLE I

Several samples of commercial graphite yarn were taken from the same bobbin so as to have yarn as identical as possible for use in conducting comparative tests. The graphite yarn used in this and succeeding examples was composed of two plies, each ply consisting of 720 filaments. The yarn denier per ply was 351 (g/9,000 m). The filament surface area was 1 square meter per gram.

The electrolytic tests were conducted in a bath containing 5 percent aqueous sodium hydroxide solution as the electrolyte and maintained at 25°C. The cathode was a carbon electrode supported horizontally near the bottom of the tank and connected to a direct current source. The respective samples of yarn were submerged in the electrolyte by passing them individually under two rollers supported completely submerged in the bath. The positive pole of the direct current source was connected to the continuous yarn being fed into the bath by means of a graphite contact roll over which the yarn was passed prior to its entry into the electrolyte bath. In each run the dwell or residence time of the yarn in the bath was 150 seconds. The graphite yarn had a specific gravity of 1.85 g./cc. After the electrolysis, each yarn was used as the reinforcement in a laminate prepared with an epoxy resin having a specific gravity of 1.21 g./cc. The particular epoxy resin used was a commercially available product which was supplied as a two-package system, one containing a mixture of bis-diglycidol ether of bisphenol A and bis-2,3-epoxycyclopentyl ether and the other meta-phenylenediamine (hardening agent). The composite was cured at 80°C for 2 hours and 150°C for 4 hours at a pressure of approximately 100 psi. As indicated in the results tabulated below in table I, there was a small loss in the tensile strength, but there was a tremendous improvement in the shear strength. The shear test results are an average of four different tests made on each sample.

TABLE II

Physical Properties of 0° Composites

Current density, amp/cm²	0.0013	0.0016	0.0030	0.0030	0.0041
Short Beam Shear S_H(max); psi,					
L/d:3/1	—	9500	10100	9600	9100
4/1	8200	8600	9700	9100	8900
6/1	—	7700	8300	8200	8400
Fiber Properties					
Untreated Tensile Strength, kpsi	327	327	302	295	305
Treated Tensile Strength, kpsi	265	269	197	197	270
Normalized to 60 vol. % from Indicated vol. %	58	60	65	68	55
Dwell time (seconds)	143	143	143	143	53

The data in the foregoing table show that very high shear strength values were obtained when graphite yarn treated according to the process of this invention at various current densities was used to reinforce the resin.

TABLE I

	Fiber properties		Composite properties					
Current density, amp./cm.[2]	Tensile strength, k.p.s.i.	Weight change, percent	Sp. gr.[1] g./cm.[3]	Fiber volume, percent	Thick., in.	Width, in.	S_H, p.s.i.,[3] L/d:6/1, max.	L/d:4/1,[2] max.
0.0	418	0.0	1.415	48	0.077	0.080	4,300	5,500
.0015	356	−7.4	1.461	58	0.079	0.077	7,800	10,800
.0025	308	−3.7	1.442	55	0.070	0.077	7,700	9,100

[1] Specific gravity.
[2] Length/depth.
[3] Short beam shear strength.

EXAMPLE II

A series of comparative tests was made, following the procedure of example I and using a number of strands of graphite yarn all from a different bobbin from that used in example I. In preparing the resin composite, the proportion was adjusted to 60 volume percent fiber. The axes of the fibers in the composites were parallel to one another (0° composites). The results are tabulated below in table II.

EXAMPLE III

A series of experiments was conducted using the procedure of example I and varying the current density. The properties of the treated fibers and the resin-fiber composites are reported in table III. In each run the dwell or residence of the yarn in the electrolyte bath was 150 seconds.

TABLE III

[Short beam shear strength of 0° composite]

	Fiber properties			Composite properties				
	Tensile							
Current density, amp./cm.[2]	Strength, k.p.s.i.	Mod., M.p.s.i.	Weight change, percent	Sp. gr.,[1] g./cm.[3]	Fiber volume, percent	Thick., in.	Width, in.	S_H, p.s.i., L/d:4/1, max.
0	285	38.4	0	1.430	51	0.079	0.113	6,200
0	274	38.0	−1.0	1.430	51	0.079	0.118	6,800
0.0002	314	45.1	−5	1.410	45	0.079	0.110	7,900
0.0005	228	40.6	−1.5	1.390	41	0.079	0.121	8,200
0.0007	234	41.9	0	1.400	44	0.079	0.119	8,800
0.0010	252	43.7	−6	1.38[illegible]	40	0.080	0.101	10,300
0.0010	309	41.7	−0.2	1.409	45	0.080	0.113	13,300
0.0018	266	39.8	−2	1.386	40	0.081	0.116	12,900
0.0025	208	37.4	−5	1. 16	47	0.078	0.125	9,690
0	309	41.6	0	1.411	46	0.079	0.114	6,600
0	303	41.4	0	1.405	45	0.080	0.113	6,900
0	298	40.0	0	1.401	44	0.079	0.113	7,100

[1] Specific gravity.
[2] Length/depth.
[3] Short beam shear strength.

The data in the foregoing table demonstrate the improvement obtained in composite properties when using the treated fibers of this invention as the reinforcing material as compared to the use of untreated fibers. The data also show that maximum shear strength values were obtained at current densities of about 0.0010 and 0.0018 amp/cm^2.

EXAMPLE IV

The procedure of example I is repeated a number of times using in place of the epoxy resin an equal weight respectively of phenol-formaldehyde resin, a polyimide resin, nylon, polyurethane, polyethylene and polystyrene. In each case improvement in shear strength occurs as compared to use of untreated fibers.

EXAMPLE V

The procedure of example I was repeated with similar results using a 5 percent aqueous phosphoric acid solution instead of the sodium hydroxide solution. Improvements also occur when aqueous solutions of nitric acid, boric acid or sulfuric acid are used as the electrolyte.

EXAMPLE VI

Similar improvements occur when a bundle of carbon fibers is suspended in the bath and other conditions applied as in example I with the anode charge being applied to the bundle of carbon fibers.

In the foregoing examples, the physical property data were obtained according to the following test methods:

1. Tensile strength—in determining tensile strength, the strand of yarn was impregnated with a liquid matrix resin to hold the plies in place. Any excess resin was wiped off after which the strand was placed in an oven at 150°C. for 15 minutes. At least one plastic bead was then threaded onto each end of the strand. The beads were fastened in place on the resin by injecting adhesive inside the hole in the bead. The adhesive was cured by heating at 100°C for 30 minutes. Each end of the strand was then placed in a holding device having a slot with a diameter smaller than the beads. Each holding device was attached to an Instron tensile testing machine and the breaking load was determined. The tensile strength (S_t) was then computed according to the following equation:

$$S_t = \frac{\text{Breaking load, lbs.}}{\text{Number of filaments} \times \text{avg. filament cross-section area, in.}^2}$$

2. Short beam shear strength—determined according to the test method ASTM D2344-67-T.

We claim:

1. A process for improving the bonding properties of a carbon or graphite fiber to a resin or plastic matrix which comprises the steps of subjecting a carbon or graphite fiber to an electrolytic reaction for a period in the range of about 25 to 500 seconds whereby negative ions of an aqueous electrolyte with which said fiber is in contact are attracted to said fiber acting as an anode and nascent oxygen is produced at the surface of said fiber, thereby modifying the fiber surface; and controlling current density used in the electrolytic reaction so that it is in the range of about 0.0005 to 0.005 ampere per square centimeter of surface area of said fiber in contact with said electrolyte.

2. The process according to claim 1 in which said fiber is passed through said electrolyte as a continuous strand.

3. The process according to claim 1 in which said current density is in the range of about 0.001 to 0.003 ampere per square centimeter.

4. The process according to claim 1 in which said electrolyte is an aqueous solution of a compound selected from the group consisting of sodium hydroxide, potassium hydroxide, phosphoric acid, nitric acid, boric acid and sulfuric acid and the concentration of said compound in said solution is in the range of about 0.5 to 20 weight percent.

5. A process for improving the bonding properties of a carbon or graphite fiber to a resin or plastic matrix which comprises passing a continuous strand of said fiber through a bath containing an aqueous electrolyte, said electrolyte having an electrode immersed therein and connected to a negative pole of a direct current source and said strand prior to entry into said bath passing over a graphite roller connected to a positive pole of said direct current source; controlling the speed at which said strand is passed through the electrolyte so that it is in contact therewith and subjected to an electrolytic reaction for a period in the range of about 25 to 500 seconds whereby negative ions of the electrolyte are attracted to said fiber and nascent oxygen is produced at its surface, thereby modifying the fiber surface; and controlling current density used in the electrolytic reaction so that it is in the range of about 0.0005 to 0.005 ampere per square centimeter of surface area of the fiber in contact with said electrolyte.

* * * * *