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[54] **PROCESS FOR THE ENHANCEMENT OF LOW MODULUS CARBON FIBERS**

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[56] **References Cited**

UNITED STATES PATENTS

3,023,118	2/1962	Donnet	423/460
3,347,632	10/1967	Parker	423/460
3,660,140	5/1972	Scola	117/47 R
3,746,560	7/1973	Goan	423/447

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[57] **ABSTRACT**

An improved process is provided for modifying the surface characteristics of a low modulus carbonaceous fibrous material to facilitate enhanced adhesion between the fibrous material and a resinous matrix material. The process is carried out in the absence of electrolysis by contacting the carbonaceous fibrous material for a relatively brief residence time with an aqueous solution of sodium hypochlorite (as defined) which is provided at a moderate temperature, and thereafter washing the same. Composite articles of enhanced interlaminar shear strength may be formed by incorporating the fibers modified in accordance with the present process in a resinous matrix material.

11 Claims, No Drawings

PROCESS FOR THE ENHANCEMENT OF LOW MODULUS CARBON FIBERS

BACKGROUND OF THE INVENTION

In the search for high performance materials, considerable interest has been focused upon carbon fibers. The term "carbon fibers" is used herein in its generic sense and includes graphite fibers as well as amorphous carbon fibers. Graphite fibers are defined herein as fibers which consist essentially of carbon and have a predominant x-ray diffraction pattern characteristic of graphite. Amorphous carbon fibers, on the other hand, are defined as fibers in which the bulk of the fiber weight can be attributed to carbon and which exhibit an essentially amorphous x-ray diffraction pattern. Graphite fibers generally have a higher Young's modulus than do amorphous carbon fibers and in addition are more highly electrically and thermally conductive.

Industrial high performance materials of the future are projected to make substantial utilization of fiber reinforced composites, and carbon fibers theoretically have among the best properties of any fiber for use as high strength reinforcement. Among these desirable properties are corrosion and high temperature resistance, how density, high tensile strength, and high modulus. Graphite is one of the very few known materials whose tensile strength increases with temperature. Uses for carbon fiber reinforced composites include recreational equipment such as golf club shafts, aerospace structural components, rocket motor casings, deep-submergence vessels, ablative materials for heat shields on re-entry vehicles, etc.

In the prior art numerous materials have been proposed for use as possible matrices in which carbon fibers may be incorporated to provide reinforcement and produce a composite article. The matrix material which is selected is commonly a thermosetting resinous material and is commonly selected because of its ability to also withstand highly elevated temperatures.

While it has been possible in the past to provide carbon fibers of highly desirable strength and modulus characteristics, difficulties have arisen when one attempts to gain the full advantage of such properties in the resulting carbon fiber reinforced composite article. Such inability to capitalize upon the superior single filament properties of the reinforcing fiber has been traced to inadequate adhesion between the fiber and the matrix in the resulting composite article.

Various techniques have been proposed in the past for modifying the fiber properties of a previously formed carbon fiber in order to make possible improved adhesion when present in a composite article. See, for instance, U.S. Pat. No. 3,476,703 to Nicholas J. Wadsworth and William Watt wherein it is taught to heat a carbon fiber normally within the range of 350°C. to 850°C. (e.g. 500° to 600°C.) in a gaseous oxidizing atmosphere such as air for an appreciable period of time. Other atmospheres contemplated for use in the process include an oxygen rich atmosphere, pure oxygen, or an atmosphere containing an oxide of nitrogen from which free oxygen becomes available such as nitrous oxide and nitrogen dioxide. Such hot gas techniques while effectively improving bonding characteristics have been found, however, commonly to have a tendency to concomitantly decrease the carbon fiber single filament properties which ultimately produces a composite article exhibiting a diminished tensile strength.

More recently, various liquid oxidative surface treatments for carbon fibers have been proposed. Illustrative examples of representative non-electrolytic treatments utilizing an aqueous sodium hypochlorite solution are disclosed in British Pat. No. 1,238,308, and German Pat. Nos. 2,112,455 and 2,147,419. Illustrative examples of electrolytic liquid oxidative surface treatments are disclosed in British Pat. No. 1,257,022, Belgian Pat. No. 747,631, and German Pat. No. 2,048,916. The nonelectrolylic treatments identified above commonly employ elevated processing temperatures, extended treatment times, and relatively unstable solutions with which the carbon fibers are treated. The electrolytic treatments identified above commonly employ highly elevated current densities and relatively unstable solutions with which the carbon fibers are treated.

It is an object of the invention to provide an improved process for efficiently modifying the surface characteristics of low modulus carbon fibers.

It is an object of the invention to provide an improved process for enhancing the ability of low modulus carbon fibers to bond to a resinous matrix material.

It is an object of the invention to provide an improved process for modifying the surface characteristics of low modulus carbon fibers which may be conducted relatively rapidly.

It is an object of the invention to provide an improved process for modifying the surface characteristics of low modulus carbon fibers which is nondegradative to fiber strength.

It is an object of the invention to provide an improved liquid phase oxidation process for modifying the surface characteristics of low modulus carbon fibers.

It is an object of the invention to provide an improved liquid phase oxidation process for modifying the surface characteristics of low modulus carbon fibers wherein the fibers are treated with an aqueous solution of sodium hypochlorite at stable operating conditions.

It is an object of the invention to provide composite articles exhibiting an improved interlaminar shear strength reinforced with low modulus carbon fibers.

These and other objects, as well as the scope, nature, and utilization of the invention will be apparent from the following detailed description and appended claims.

SUMMARY OF THE INVENTION

It has been found that an improved process for enhancing the ability of a carbonaceous fibrous material containing at least about 90 per cent carbon by weight and exhibiting a mean single filament Young's modulus of about 10 to 50 million psi to bond to a resinous matrix material comprises:

a. contacting said fibrous material for about 1 to 60 minutes in the absence of electrolysis with an aqueous solution of sodium hypochlorite provided at about 20° to 35°C. having a pH of about 8 to 12 and an active chlorine concentration of about 3 to 7 per cent by weight,

b. washing the resulting carbonaceous fibrous material to remove residual solution, and

c. drying the same.

The resulting carbon fibers may be incorporated in a resinous matrix material to form a composite article exhibiting an enhanced interlaminar shear strength.

DESCRIPTION OF PREFERRED EMBODIMENTS

The Starting Material

The fibers which are modified in accordance with the present process are carbonaceous and contain at least about 90 per cent carbon by weight. Such carbon fibers may exhibit either an amorphous carbon or a predominantly graphitic carbon x-ray diffraction pattern. In a preferred embodiment of the process the carbonaceous fibers which undergo surface treatment contain at least about 95 per cent carbon by weight, and at least about 99 per cent carbon by weight in a particularly preferred embodiment of the process.

The fibers which are modified in accordance with the present process additionally exhibit a relatively low mean single filament Young's modulus of about 10 to 50 million psi, and preferably a mean single filament Young's modulus of about 20 to 40 million psi. Additionally, the fibers commonly exhibit a single filament tensile strength of at least about 250,000 psi, e.g. about 250,000 to 500,000 psi (or more). The carbon fiber Young's modulus may be determined, for instance, by the procedure of ASTM Designation D–2101–64T.

The carbonaceous fibrous materials may be present as a continuous length in a variety of physical configurations provided substantial access to the fiber surface is possible during the surface modification treatment described hereafter. For instance, the carbonaceous fibrous materials may assume the configuration of a continuous length of a multifilament yarn, tape, tow, strand, cable, or similar fibrous assemblage. In a preferred embodiment of the process the carbonaceous fibrous material is one or more continuous multifilament yarn or tow.

The carbonaceous fibrous material which is treated in the present process optionally may be provided with a twist which tends to improve the handling characteristics. For instance, a twist of about 0.1 to 5 tpi, and preferably about 0.3 to 1.0 tpi, may be imparted to a multifilament yarn. Also, a false twist may be used instead of or in addition to a real twist. Alternatively, one may select continuous bundles of fibrous material which possess essentially no twist.

The carbonaceous fibers which serve as the starting material in the present process may be formed in accordance with a variety of techniques as will be apparent to those skilled in the art. For instance, organic polymeric fibrous materials which are capable of undergoing thermal stabilization may be initially stabilized by treatment in an appropriate atmosphere at a moderate temperature (e.g. 200° to 400°C.), and subsequently heated in an inert atmosphere at a more highly elevated temperature, e.g. 900° to 1000°C., or more, until a carbonaceous fibrous material is formed. The higher the temperature the greater the amount of graphite carbon produced within the same and the higher the Young's modulus.

The exact temperature and atmosphere utilized during the initial stabilization of an organic polymeric fibrous material commonly vary with the composition of the precursor as will be apparent to those skilled in the art. During the carbonization reaction elements present in the fibrous material other than carbon (e.g. oxygen, nitrogen, and hydrogen) are substantially expelled. Suitable organic polymeric fibrous materials from which the fibrous material capable of undergoing carbonization may be derived include an acrylic polymer, a cellulosic polymer, a polyamide, a polybenzimidazole, polyvinyl alcohol, etc. As discussed hereafter, acrylic polymeric materials are particularly suited for use as precursors in the formation of carbonaceous fibrous materials. Illustrative examples of suitable cellulosic materials include the natural and regenerated forms of cellulose, e.g. rayon. Illustrative examples of suitable polyamide materials include the aromatic polyamides, such as nylon 6T, which is formed by the condensation of hexamethylenediamine and terephthalic acid. An illustrative example of a suitable polybenzimidazole is poly-2,2′-m-phenylene-5,5′-bibenzimidazole.

A fibrous acrylic polymeric material prior to stabilization may be formed primarily of recurring acrylonitrile units. For instance, the acrylic polymer should contain not less than about 85 mole per cent of recurring acrylonitrile units with not more than about 15 mole per cent of a monovinyl compound which is copolymerizable with acrylonitrile such as styrene, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl chloride, vinylidene chloride, vinyl pyridine, and the like, or a plurality of such monovinyl compounds.

During the formation of a preferred carbonaceous fibrous material for use in the present process multifilament bundles of an acrylic fibrous material may be initially stabilized in an oxygen-containing atmosphere (i.e. preoxidized) on a continuous basis in accordance with the teachings of U.S. Ser. No. 749,957, filed Aug. 5, 1968, of Dagobert E. Stuetz (now abandoned), which is assigned to the same assignee as the present invention and is herein incorporated by reference. More specifically, the acrylic fibrous material should be either an acrylonitrile homopolymer or an acrylonitrile copolymer which contains no more than about 5 mole per cent of one or more monovinyl comonomers copolymerized with acrylonitrile. In a particularly preferred embodiment of the process the fibrous material is derived from an acrylonitrile homopolymer. The stabilized acrylic fibrous material which is preoxidized in an oxygen-containing atmosphere is black in appearance, contains a bound oxygen content of at least about 7 per cent by weight as determined by the Unterzaucher analysis, retains its original fibrous configuration essentially intact, and is nonburning when subjected to an ordinary match flame. Another preferred stabilization technique is disclosed in commonly assigned U.S. Pat. No. 3,508,874 of Richard N. Rulison.

In accordance with a particularly preferred carbonization and graphitization technique a continuous length of stabilized acrylic fibrous material which is non-burning when subjected to an ordinary match flame and derived from an acrylic fibrous material selected from the group consisting of an acrylonitrile homopolymer and acrylonitrile copolymers which contain at least about 85 mole per cent of acrylonitrile units and up to about 15 mole per cent of one or more monovinyl units copolymerized therewith is converted to a graphite fibrous material while preserving the original fibrous configuration essentially intact while passing through a carbonization/graphitization heating zone containing an inert gaseous atmosphere and a temperature gradient in which the fibrous material is raised within a period of about 20 to about 300 seconds from

about 300°C. to a temperature of about 1200°C. to form a continuous length of carbonized fibrous material, and in which the carbonized fibrous material is subsequently raised from about 1200°C. to a maximum temperature of at least about 1500°C. within a period of about 3 to 300 seconds where it is maintained for about 10 seconds to about 100 seconds to form a continuous length of carbonaceous fibrous material. The equipment utilized to produce the heating zone used to produce the carbonaceous starting material may be varied as will be apparent to those skilled in the art. It is essential that the apparatus selected be capable of producing the required temperature while excluding the presence of an oxidizing atmosphere.

In a preferred technique the continous length of fibrous material undergoing carbonization is heated by use of an induction furnace. In such a procedure the fibrous material may be passed in the direction of its length through a hollow graphite tube or other susceptor which is situated within the windings of an induction coil. By varying the length of the graphite tube, the length of the induction coil, and the rate at which the fibrous material is passed through the graphite tube, many apparatus arrangements capable of producing carbonization or carbonization and graphitization may be selected. For large scale production, it is of course preferred that relatively long tubes or susceptors be used so that the fibrous material may be passed through the same at a more rapid rate while being carbonized or carbonized and graphitized. The temperature gradient of a given apparatus may be determined by conventional optical pyrometer measurements as will be apparent to those skilled in the art. The fibrous material because of its small mass and relatively large surface area assumes essentially the same temperature as that of the zone through which it is continuously passed.

The Surface Treatment

The carbonaceous fibrous material is contacted for a relatively brief residence time in the absence of electrolysis with an aqueous solution of sodiu · hypochlorite as described in detail hereafter which is provided at a moderate temperature, and the resulting fibrous material is washed and dried.

The aqueous solution of sodium hypochlorite has a pH of about 8 to 12, preferably 10.5 to 11.5 (e.g. about 11), and an active chlorine concentration (i.e. an available chlorine concentration) of about 3 to 7 per cent by weight, preferably, 5.025 to 5.35 (e.g. 5.25) per cent by weight. The active chlorine concentration for a given solution of sodium hypochlorite may be determined by adding KI and determining excess iodine by titrating with sodium thiosulfate. Commercially available liquid bleach meeting the above prerequisites may be selected for use in the present process, and is sometimes designated as soda bleach liquor or simply as household bleach solution. Such a solution may be formed, inter alia, by passage of chlorine through a dilute caustic soda solution in either a batch or continuous operation in accordance with techniques known in the art. The sodium hypochlorite solution utilized in the process of the present invention is considerably more stable than common laundry grade commercial bleach solutions which contain 12 to 15 per cent active chlorine. For optimum stability a sodium hypochlorite solution having a pH of about 11 is selected.

The contact between the carbonaceous fibrous material and the aqueous solution of sodium hypochlorite may be accomplished in any convenient manner. In a preferred embodiment of the process the carbonaceous fibrous material is simply immersed in the aqueous solution of sodium hypochlorite for an appropriate residence time. Alternatively, the contact may be made by spraying the carbonaceous fibrous material with the aqueous solution of sodium hypochlorite. The contact may be conducted on a static basis or on a continuous basis. For instance, the carbonaceous fibrous material may be wound on a support and immersed in the solution. Alternatively, a continuous length of the carbonaceous fibrous material may be passed in the direction of its length through a vessel containing the sodium hypochlorite solution.

The solution is provided at the mild temperature of about 20° to 35°C. when contacted with the carbonaceous fibrous material, and is preferably provided at room temperature (i.e. at about 25°C.).

The process of the present invention surprisingly produces the desired surface modification of the carbonaceous fibrous material in the brief residence time of about 1 to 60 minutes in spite of the relatively mild conditions utilized. The exact residence time for optimum results will vary somewhat with the Young's modulus of the carbonaceous fibrous material undergoing treatment. Generally, the higher the mean Young's modulus within the range of 10 to 50 million psi the longer the residence time employed for optimum results. Commonly residence times of about 2 to 45 minutes (e.g. about 4 minutes to 30 minutes or about 5 to 15 minutes) are utilized with a carbonaceous fibrous material having a mean Young's modulus of 20 to 40 million psi. The residence time is considered to be the total time in which the solution is in contact with the fiber surface, and is measured from the time of initial contact to the time the solution is removed by washing or other means.

During the contact with the aqueous solution of sodium hypochlorite adequate solution is provided so that the fiber at least remains wet with a film of the solution upon its surface. No diminution in activity has been observed even if very high ratios of fiber surface to solution volume are utilized.

Following the surface modification treatment heretofore described the resulting carbonaceous fibrous material is washed so as to remove residual quantities of the sodium hypochlorite solution adhering to the same. The washing may be carried out in any convenient manner and should be as exhaustive as possible since residual sodium hypochlorite if left on the fiber will adversely influence the properties of a composite incorporating the same. In a preferred wash technique the wash treatment includes the contact of the resulting carbonaceous fibrous material with a solution of a dilute acid, and a subsequent rinsing the same with water. The acid serves to neutralize any adhering residue and to aid in its expeditious removal. For instance, dilute mineral acids such as hydrochloric acid, etc. may be conveniently utilized. The washing may be carried out on a static or a continuous basis wherein a continuous length of the fibrous material is passed through one or more wash solutions. A simple water rinse may advantageously precede the acid neutralization wash step.

Following washing and prior to utilization as fibrous reinforcement in a composite article, the surface modi-

fied carbonaceous fibrous material is dried to remove any adhering wash solution. Such drying may be simply conducted by placing the same in a circulating air oven provided at about 60° to 80°C.

The theory whereby the carbonaceous fibrous material heretofore defined may be beneficially surface modified under the relatively mild treatment conditions and brief residence times disclosed herein is considered complex and incapable of simple explanation. Additionally, the ability of one to produce the desired surface modification utilizing the conditions heretofore recited is considered to be most surprising when compared with the considerably more severe surface modification conditions employed by others in the prior art.

The surface modification imparted to the carbonaceous fibrous material through the use of the present process has been found to exhibit an appreciable life which is not diminished to any substantial degree even after the passage of 30, or more days. Also, the single filament tensile properties of the carbonaceous fibrous material are not adversely influenced by the surface modification treatment of the present invention, and the surface of the resulting fibrous material is substantially free of pitting.

The surface treatment of the present invention makes possible improved adhesive bonding between the carbonaceous fibers, and a resinous matrix material. Accordingly, carbon fiber reinforced composite materials which incorporate fibers treated as heretofore described exhibit an enhanced interlaminar shear strength, flexural strength, compressive strength, etc. The resinous matrix material employed in the formation of such composite materials is commonly a polar thermosetting resin such as an epoxy, a polyamide, a polyester, a phenolic, etc., or a thermoplastic resin. The carbonaceous fibrous material is commonly provided in such resulting composite materials in either an aligned or random fashion in a concentration of about 20 to 70 per cent by volume.

The following examples are given as specific illustrations of the invention. It should be understood, however, that the invention is not limited to the specific details set forth in the examples.

EXAMPLE I

A high strength-low modulus continuous filament carbonaceous tow derived from an acrylonitrile copolymer tow was selected as the starting material for use in the present process. The acrylonitrile copolymer tow prior to thermal conversion consisted of about 90.8 mole per cent acrylonitrile units, about 9.2 mole per cent methyl acrylate units, and a very minor proportion of copolymerized dye site improving units. The tow which consisted of approximately 40,000 substantially untwisted filaments was stabilized by heating in air at a temperature of about 240°C. for about 360 minutes while in the presence of colloidal graphite in accordance with the teachings of commonly assigned U.S. Pat. No. 3,508,874. The stabilized tow was carbonized by heating to a maximum temperature of about 1500°C. in a circulating nitrogen atmosphere.

The carbonaceous tow prior to treatment in accordance with the present process had a carbon content of about 97.5 per cent by weight, a mean single filament Young's modulus of about 36 million psi, and a mean single filament tenacity of about 440,000 psi (19.5 gpd).

Samples of the carbonaceous tow were immersed in an aqueous solution of sodium hypochlorite in the absence of electrolysis for various residence times as indicated in the following Table I. The sodium hypochlorite solution was provided in a tank, and the tow was treated therein by repeated immersion via a skewed roll equipment configuration. The tow was in continuous contact with the solution regardless of whether it was fully immersed therein. The aqueous solution of sodium hypochlorite was provided at room temperature (i.e. about 25°C.), had a pH of 11, and an active chlorine concentration of 5.25 per cent by weight. The aqueous solution of sodium hypochlorite was obtained under the designation of Clorox household bleach solution.

Following the treatment with the aqueous solution of sodium hypochlorite, the tow was washed by (a) immersing the same in flowing tap water for 15 minutes (b) contacting the same with a 2 per cent hydrochloric acid solution provided in distilled water for about 1 minute, and (c) rinsing the same with deionized water for 15 minutes. The tow was next dried in a forced air circulating oven at 70°C. for approximately 16 hours. The tensile properties of the resulting fibers were unchanged. Composite articles were next formed employing the surface modified tow samples as reinforcing media in epoxy resin matrices. The composite articles were rectangular bars consisting of about 60 per cent by volume of the tow and had dimensions of ⅛ × ¼ × 5 inches. The composite articles were formed by impregnation of the tow in a liquid epoxy resin-hardener mixture at 70°C., followed by unidirectional layup of the required quantity of the impregnated tow in a steel mold, and compression molding of the layup for 2 hours at 200°C., and 2 hours at 400°C. in a heated platen press at about 50 psi pressure. The mold was cooled slowly to room temperature, and the composite article was removed from the mold cavity and cut to size for testing. The resinous matrix material used in the formation of the composite article was provided as a solventless system which contained 100 parts by weight of ERLA 4617 epoxy resin available from Union Carbide Corp., and 24 parts by weight metaphenylene diamine curing agent.

The following Table I summarizes the surface treatment conditions employed and the properties achieved.

TABLE I

Sample	Surface Treatment Contact Time (minutes)	Interlaminar Shear Strength of Composite (psi)	Flexural Strength of Composite (psi)	Flexural Modulus of Composite (psi)
Control	0	9,300	165,000	20,400,000
A	4.33	12,700	221,000	20,400,000
B	7.1	14,600	220,000	21,000,000
C	23.1	14,100	222,000	20,200,000
D	36.3	13,900	200,000	20,000,000

The horizontal interlaminar shear strengths reported were determined by short beam testing of the carbon fiber reinforced composite according to the procedure of ASTM D2344–65T as modified for straight bar testing at a 4:1 span to depth ratio. The flexural strengths and moduli reported were determined by four point bending.

EXAMPLE II

Example I was substantially repeated with the exception that the carbonaceous fibrous material undergoing surface modification was a high strength-low modulus continuous filament yarn derived from an acrylic yarn and commercially available from the Hercules Corporation under the designation Type A carbon fiber.

The carbonaceous yarn prior to surface treatment in accordance with the present process consisted of about 10,000 filaments having a total denier of about 7900, had a carbon content of about 94 per cent by weight, exhibited a mean single filament Young's modulus of about 35.5 million psi, and exhibited a mean single filament tenacity of about 435,000 psi (19 gpd).

The immersion times utilized and the results achieved are summarized in the following Table II.

TABLE II

Sample	Surface Treatment Contact Time (minutes)	Interlaminar Shear Strength of Composite (psi)	Flexural Strength of Composite (pis)	Flexural Modulus of Composite (pis)
Control	0	12,670	305,000	19,500,000
A	4.1	14,525	291,000	19,400,000
B	9.1	16,775	324,000	19,100,000
C	36.3	15,775	not available	not available
D	60.5	16,325	302,000	19,300,00

EXAMPLE III

Example I was substantially repeated with the exception that the carbonaceous fibrous material was a high strength-low modulus continuous filament yarn derived from an acrylic yarn and commercially available from the Great Lake Carbon Corporation under the designation 4T carbon fiber.

The carbonaceous yarn prior to surface treatment in the present process consisted of about 40,000 filaments having a total denier of about 35,000, had a carbon content of about 99 per cent by weight, exhibited a mean single filament Young's modulus of about 38 million psi, and exhibited a mean single filament tenacity of about 355,000 psi (16 gpd).

The immersion times utilized and the results achieved are summarized in the following Table III.

TABLE III

Sample	Surface Treatment Contact Time (minutes)	Interlaminar Shear Strength of Composite (psi)	Flexural Strength of Composite (psi)	Flexural Modulus of Composite (psi)
Control	0	4,290	145,000	21,100,000
A	9.1	12,700	236,000	21,800,000
B	27.9	15,000	232,000	21,600,000
C	33.0	12,800	245,000	22,300,000
D	45.4	12,000	not available	not available

Although the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations are to be considered within the purview and scope of the claims appended hereto.

We claim:

1. An improved process for enhancing the ability of a carbonaceous fibrous material containing at least about 90 per cent carbon by weight and exhibiting a mean single filament Young's modulus of about 10 to 50 million psi to bond to a resinous matrix material comprising:

a. contacting said fibrous material for about 1 to 60 minutes in the absence of electrolysis with an aqueous solution of sodium hypochlorite provided at about 20° to 35°C. having a pH of about 8 to 12 and an active chlorine concentration of about 3 to 7 per cent by weight,

b. washing the resulting carbonaceous fibrous material to remove residual solution adhering the same, and

c. drying the same.

2. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **1** wherein said fibrous material is immersed in said solution of sodium hypochlorite during said contact.

3. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim **1** wherein said aqueous solution of sodium hypochlorite has a pH of about 10.5 to 11.5 and an active chlorine concentration of about 5.025 to 5.35 per cent by weight.

4. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material according to claim **1** wherein said washing is conducted at least in part by contacting said resulting carbonaceous fibrous material with a solution of a mineral acid to neutralize any adhering residue resulting from said contact with said sodium hypochlorite solution, and by subsequently rinsing the same with water.

5. An improved process for enhancing the ability of a carbonaceous fibrous material containing at least about 95 per cent carbon by weight and exhibiting a mean single filament Young's modulus of about 20 to 40 million psi to bond to a resinous matrix material comprising:

a. contacting said fibrous material for about 2 to 45 minutes in the absence of electrolysis in an aqueous solution of sodium hypochlorite provided at about 20° to 35°C. having a pH of about 10.5 to 11.5 and an active chlorine concentration of about 5.025 to 5.35 per cent by weight,

b. washing the resulting carbonaceous fibrous material to remove residual solution, and

c. drying the same.

6. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material according to claim 5 wherein said fibrous material is immersed in said solution of sodium hypochlorite during said contact.

7. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim 5 wherein said fibrous material is contacted with said aqueous solution of sodium hypochlorite for about 4 to 30 minutes.

8. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim 5 wherein said aqueous solution of sodium hypochlorite is provided at about 25°C.

9. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material in accordance with claim 5 wherein said washing is conducted at least in part by contacting said resulting carbonaceous fibrous material with a solution of a mineral acid to neutralize any adhering residue resulting from said contact with said sodium hypochlorite solution, and by subsequently rinsing the same with water.

10. An improved process for enhancing the ability of a carbonaceous fibrous material containing at least about 95 per cent carbon by weight and exhibiting a mean single filament Young's modulus of about 20 to 40 million psi to bond to a resinous matrix material comprising:

a. contacting said fibrous material for about 4 to 30 minutes in the absence of electrolysis in an aqueous solution of sodium hypochlorite provided at about 25°C. having a pH of about 11 and an active chlorine concentration of about 5.25 per cent by weight,

b. rinsing the resulting carbonaceous fibrous material with water,

c. contacting the previously rinsed carbonaceous fibrous material with a dilute aqueous solution of a mineral acid to neutralize said sodium hypochlorite adhering thereto,

d. subsequently rinsing the carbonaceous fibrous material with water, and

e. drying the same.

11. An improved process for enhancing the ability of a carbonaceous fibrous material to bond to a resinous matrix material according to claim 10 wherein said fibrous material is immersed in said solution of sodium hypochlorite during said contact.

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