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(54) Process for improving carbon fibers.

(57) A process for producing a carbon fiber having very high Young's modulus includes a post heat treatment for a carbon fiber wound onto a bobbin.

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The invention relates to carbon fibers and particularly, a process for improving the mechanical properties of a carbon fiber.

The invention relates to polyacrylonitrile (PAN)-based carbon fibers and mesophase pitch-based carbon fibers. These carbon fibers have found considerable commercial value because of the mechanical properties they possess. In particular, carbon fibers having high values of Young's Moduli are in greater demand for specialized products.

Generally, a PAN-based carbon fiber is produced by spinning polyacrylonitrile into a fiber, infusibilizing the fiber by raising it to an elevated temperature in air, and thereafter carbonizing the infusibilized fiber at an elevated temperature in an inert atmosphere under tension in a threadline to produce a carbon fiber.

Generally, a mesophase pitch-based carbon fiber is produced by spinning a mesophase pitch into a fiber, infusibilizing the fiber by raising it to an elevated temperature in air, and thereafter carbonizing the infusibilized fiber at an elevated temperature in an inert atmosphere.

Typically, the temperatures used for carbonizing mesophase pitch based carbon fibers are at least greater than about 1000°C and usually more than 1000°C and usually more than 1500°C. PAN-based fibers are usually carbonized at about 1300°C. A carbon fiber having a very high value of Young's Modulus requires elevated temperatures greater than about 2300°C and preferably greater than about 2700°C.

According to the prior art, the carbonizing step for PAN-based fibers and mesophase pitch-based fibers is carried out in a threadline operation. Typically, a threadline operation is carried out by passing an infusibilized fiber along a linear path through a heated chamber. The heated chamber, commonly referred to as a furnace, must be maintained at a positive pressure in order to exclude air. Typically, the infusibilized fiber moves at the rate of several feet per minute so that the residence time at the elevated temperature is relatively short.

Moreover, it has been found that the furnace used for such operations degrades rapidly at elevated temperatures greater than about 2700°C.

This substantially increases the cost of manufacturing high modulus carbon fibers.

It has now been discovered that a carbon fiber can be substantially improved as to its Young's Modulus by carrying out an additional carbonizing step in accordance with the instant invention.

In its broadest embodiment, the invention relates to a process for improving a carbon fiber, comprising the steps of winding the carbon fiber onto a bobbin which is thermally and mechanically stable at temperatures greater than 2000°C and which is chemically compatible with the carbon fiber, and thereafter, subjecting the carbon fiber to a heat treatment at a temperature greater than 2000°C.

Typically, the temperature rate for carrying out the heat treatment can be as high as from about 200°C to 500°C per hour with the final temperature being maintained for a period of from one to two hours. A temperature rate of from about 50°C to about 100°C per hour would enable the holding time at the final temperature to be reduced to one half hour and possibly less.

After the heat treatment, the fiber should be maintained in the inert atmosphere until it has been cooled to a temperature at least below about 200°C to minimize the oxidation of the carbon fiber upon exposure to air.

Preferably, the final temperature for the heat treatment should be greater than about 2700°C.

The bobbin for carrying out the new process comprises a cylindrical body made of material such as stainless steel, or refractory oxides or boron nitride, or graphite. Optionally, a layer of a compressible resilient carbon mater such as carbon felt can be positioned on the outside surface of the cylindrical body to receive the carbon fiber and thereby minimize the stresses on the carbon fiber during the heat treatment.

The bobbin can be with or without end flanges. Preferably, the bobbin should have end flanges and more preferably, the end flanges should be movable so that after the heat treatment the end flanges can be moved to abut the carbon fibers because it is known that the heat treatment results in the shrinkage of the longitudinal space occupied by the carbon fiber. Moving the flanges to abut the carbon fiber simplifies the unwinding of the carbon fiber from the bobbin.

Typically, the cylindrical body of the bobbin can have an inside diameter of three inches and outside diameter of about three and a half inches with an overall length of about eleven inches.

Preferably the carbon felt should have a thickness of about 1/4 inch to about 1/2 inch thick.

If the carbon felt is not used, the layers of the carbon fiber adjacent to the bobbin are damaged, but it may be advantageous to sustain the damage of a portion of the carbon fibers and thereby avoid the use of carbon felt.

The wind angle of the carbon fiber onto the bobbin can be generally from about 0.1° to about 2.5° and preferably less than about 0.4° for a bobbin having flanges. Generally, the tension used for winding the carbon fiber onto the bobbin should be less than about 200 g.

In commercial practice, fibers are spun from a spinneret which produces usually about two thousand continuous filaments and these fibers are brought together and handled together during additional operations. The bundle of filaments is referred to as "yarn". As used herein, the process applying to a carbon fiber also applies to yarn comprising a plurality of carbon fibers.

Illustrative, non-limiting examples of the practice of the invention are set out below. Numerous other examples can readily be evolved in the light of the guiding principles and teachings contained herein. The examples herein are intended to illustrate the invention and not in any sense to limit the manner in which the invention can be practiced.

EXAMPLE 1

Forty pounds of carbon yarn was produced from mesophase pitch in accordance with conventional processes. The yarn comprised two thousand filaments, each filament having a diameter of 10 microns. The yarn was carbonized in a threadline furnace in accordance with conventional practice at a temperature of 2400°C and thereafter, wound on to four separate graphite bobbins with a wind angle of 0.4 degrees. Each bobbin comprised threaded flanges on a threaded portion of the bobbin. The carbon yarn substantially filled the space between the flanges of each bobbin.

Tests on the fibers of the carbon yarn indicated that the average tensile strength was approximately 300 Kpsi and the average Young's Modulus was 55 Mpsi. There was about ten pounds of carbon yarn on each bobbin.

The four bobbins were then loaded onto a graphite rack so that each bobbin was mounted in a horizontal position. The rack was placed in a graphite-susceptor induction furnace and heated under an argon atmosphere at the rate of 100°C per hour to 2950°C. The final temperature was maintained for two hours and then the furnace was allowed to cool to room temperature.

After the bobbins were removed from the furnace, the flanges on each bobbin were screwed inwardly to abut the carbon yarn and eliminate gaps which had formed between the flanges and the carbon arm. The yarn was unwound at the rate of 20 feet per minute with a tension of 150 g.

Strand tensile tests on the carbon fibers after the heat treatment resulted in the average properties set forth in the table.

	Tensile Strength (Kpsi)	Young's Modulus (Mpsi)	Fiber Density (Mg/m^3)
Spool A	317	123	2.14
Spool B	306	111	2.13
Spool C	295	117	2.13
Spool D	338	128	2.17

Surprisingly, the average Young's Modulus for the fibers taken from each of the spools A, B, C, and D was greater than 100 Mpsi. Furthermore, tests show that there was reasonable uniformity in the properties of samples of the fibers taken from different locations in each bobbin. In addition, the fiber density was measured to be approximately 99% of the theoretical value.

In summary, the Young's Modulus and density were much higher than the values which would have been obtained for the heat treatment if it had been carried out by conventional threadline carbonization.

In addition, it is significant that the fibers removed from the spools A, B, C, and D were straight and were collimated. It could be expected that wrinkles or deformation might arise due to the pressures caused by the shrinkage of the fibers at the elevated temperatures. The deformations substantially degrade mechanical properties.

The excellent physical condition of the fibers is due to the use of the low winding angle of 0.4°. This angle and smaller angles are important for fibers being subjected to temperatures greater than $2700^{\circ}C$.

EXAMPLE 2

A PAN-based yarn having 6,000 filaments was used in this example. The PAN-based yarn was prepared so that its nitrogen content was less than about 1% by weight. It is important to have a low nitrogen content for the PAN-based yarn used in the instant process so that the elevated temperatures do not cause damage to the yarn as the nitrogen being pyrolyized out of the yarn.

The PAN-based yarn was prepared as follows:

A PAN-based infusibilized yarn was used. The fibers in the yarn had a composition of 64.0% carbon, 3.9% hydrogen, 6.2% oxygen, and 25.1% nitrogen. The yarn was wound on a bobbin used in commerical production. The yarn was unwound from the bobbin and rotated at 500 revolutions per minute while being unwound at the rate of 63 feet per minute so that a twist of 0.7 turns per inch was established. The twisted yarn was rewound with a tension of 250 grams onto a graphite bobbin having dimensions of 3.5 inches in diameter and 11 inches long. The graphite bobbin had a layer of one quarter inch of graphite felt on the cylindrical portion to receive the yarn. A wind angle of 23 degrees was used and the package pressure was 3 lbs with a transverse length of ten inches. The rewound yarn amounted to 23,500 feet of yarn and was in the form of a square-sided package.

The package was placed horizontally in a graphite tube induction furnace which was purged with nitrogen and fired at the rate of 50°C per hour to 800°C and thereafter temperature was raised at 250°C per hour to 1300°C. The final temperature was maintained for two hours and the package was allowed to cool back to room temperature. As a result of the heat treatment, the package had shrunk longitudinally about 1.5 to 2 inches from its original ten inch length.

The package was then mounted horizontally on a tension-loaded payoff creel, and the yarn was unwound under a tension of approximately 50 grams, passed through a grooved-reel, tension-controlled drive system maintained at a tension of about 1,825 grams and thereafter through graphite tube electric resistance furnace having a hot zone maintained at a temperature of about 1830°C and five feet long. The yarn exiting the furnace was then subjected to a finish treatment in accordance with the prior art and wound onto bobbins made of cardboard in one thousand foot lengths. Twenty-two samples of the yarn were taken at about 1,000 foot intervals.

The average tensile strength of the resulting fiber was 500,000 psi with a coefficient of variation of 1.3%. The average Young's modulus for the resulting fiber was about 41.2 million psi with a coefficient of variation of 2.9%. The average density of the fibers was 1.766 Mg per cubic meter with a coefficient of variation of 0.6%. The average yield was 3571 feet per pound with a coefficient of variation of 2.1%.

This carbon yarn was the PAN-based yarn used in the instant process.

About 4700 feet of the PAN-based yarn was wound onto a flanged graphite bobbin with a wind and of about 0.4°. The bobbin had a diameter of 4.5 inches, a length of 7 inches, and no carbon felt was used.

The loaded bobbin was subjected to a heat treatment in a graphite tube induction furnace. The furnace was purged with argon and the temperature was raised at a rate of about 100°C per hour to 2950°C. The final temperature was maintained for two hours and then the furnace was allowed to cool to ambient temperature.

The yarn obtained had excellent physical appearance, no wrinkles or the like, and excellent mechanical properties. The average strand properties were: 360 Kpsi tensile strength, 96.9 Mpsi meter.

EXAMPLE 3

A commercially available PAN-based carbon yarn was used in the post heat treatment of the invention. The yarn used had an average strand Young's modulus of about 33 Mpsi and an average tensile strength of about 400 Kpsi. The heating schedule and bobbin of Example 2 were used.

After the heat treatment, the yarn had an excellent physical appearance and had an average strand Young's modulus of 70 Mpsi and tensile strength of 340 Kpsi.

CLAIMS

1. A process for an improved carbon fiber, comprising the steps of winding a carbon fiber onto a bobbin which is thermally and mechanically stable at temperatures greater than 2000°C and which is chemically compatible with the carbon fiber, and thereafter, subjecting the carbon fiber to a heat treatment at a temperature greater than 2000°C.

2. The process of Claim 1, wherein the heat treatment is carried out by raising the temperature at a rate from about 200°C to 500°C per hour.

3. The process of Claim 1, wherein the heat treatment is carried out by raising the temperature at a rate from about 50°C to 100°C per hour.

4. The process of Claim 1, wherein the heat treatment is carried out by raising the temperature to more than 2700°C.

5. The process of Claim 1, wherein the heat treatment is carried out so that the carbon fiber has a Young's modulus greater than about 100 Mspi.

6. The process of Claim 1, wherein the heat treatment is carried out so that the carbon fiber has a Young's modulus greater than about 90 Mpsi.

7. The process of Claim 1, wherein the heat treatment is carried out so that the carbon fiber has a Young's modulus greater than about 75 Mpsi.