

1

3,412,062

PRODUCTION OF CARBON FIBRES AND COM-
POSITIONS CONTAINING SAID FIBRES

William Johanson, Leslie Nathan Phillips, and William
Watt, Farnborough, England, assignors to National Re-
search Development Corporation, London, England, a
British company

No Drawing. Filed Apr. 19, 1965, Ser. No. 449,320
Claims priority, application Great Britain, Apr. 24, 1964,
17,128/64
17 Claims. (Cl. 260—37)

ABSTRACT OF THE DISCLOSURE

According to the invention carbon fibres having high
tensile strength and high Young's modulus are made by
the conversion of organic polymer fibre, such as poly-
acrylonitrile, by the combined effect of heating in a non-
oxidising atmosphere to a carbonising temperature of up
to about at least 1000° C. and the application of longi-
tudinal tension at some stage of the conversion. The pro-
cess preferably includes a preliminary step of heating the
polymer fibre in an oxidising atmosphere at from 200-
250° C. for sufficient time to achieve complete permea-
tion of oxygen throughout the fibre whilst held under
tension such that during oxidation there is little or no
longitudinal shrinkage of the fibre. The oxidised fibre may
subsequently be carbonised and heat treated without ten-
sion to give carbon fibre in some cases having an ultimate
tensile strength of 260×10^3 lb. per square inch of a
Young's modulus of 60×10^6 lb. per square inch.

This invention relates to the production of carbon fibres.
Generally speaking, carbon fibres are members of a class
of non-metallic fibres the use of which has been proposed
as a high strength and/or a stiffening element of composite
materials of which the matrix material may or may not
be metal. It may be shown that such fibres, particularly
carbon fibres, usually have their highest specific strength
when their diameter is smallest. Now the production of
non-metallic fibres, particularly the very small diameter
very high strength fibres of which carbon is an example,
presents numerous problems. One problem is that of
devising means and a process for manufacturing and
harvesting fibres of sufficient length that in the composite
material, they will bear and enable the composite mate-
rial to withstand, loads comparable with their individual
strength.

In connection with carbon fibres, it has previously been
proposed that these should be manufactured by the car-
bonising of organic materials, such as, for example, cot-
ton-wool and fibres and filaments of synthetic resinous
materials. Among the latter materials in particular, poly-
acrylonitrile fibres have been the proposed subject of
experiment but it would appear that only limited success
has been achieved.

It is to be noted that the term polyacrylonitrile fibres
is used by those skilled in this art to include co-polymers
or ter-polymers of acrylonitrile with other monomers e.g.
methyl methacrylate or vinyl acetate, either alone or to
which have been added polymers compatible with them
for example phenolic resins or Friedel-Crafts condensates.
It is in this sense that the term polyacrylonitrile fibres is
used throughout the specification.

According to the present invention a process of pro-
ducing carbon fibres comprises heating fibres of poly-
acrylonitrile while held under tension to a relatively high
carbonising temperature under non-oxidising conditions.

Also in accordance with the invention the process

2

comprises a preliminary low temperature oxidising step
which, for example, is performed by heating in air.

The high temperature carbonising is performed under
vacuum or in a non-oxidising atmosphere such as hydro-
gen.

In cases where the preliminary low temperature oxidis-
ing step forms part of the process, if this step is of too
short duration the fibres are left with a soft core and upon
subsequent high temperature heat treatment holes are
formed in the resulting fibres.

In a further embodiment according to the present in-
vention a process of producing carbon fibres comprises
initially heating fibres of polyacrylonitrile whilst held
under tension in an oxidising atmosphere at from 200-
250° C. for sufficient time to permit substantially complete
permeation of oxygen throughout the individual fibres
and subsequent further heating of the fibres so formed
to a carbonising temperature of at least 1000° C. under
non-oxidising conditions.

The duration of the initial heating required will depend
to a large extent on the diameter of the fibres concerned
but for a temperature of 220° C. complete oxygen per-
meation of the fibres takes place after heating for about
24 hours for 2½ denier fibres and after about 50 hours
for 4½ denier fibres.

The fibres are tensioned so that longitudinal shrinkage
which normally takes place during this initial heating is
reduced, eliminated or is such as to cause the fibres to
elongate.

Further improvements in the characteristics of the fibres
produced are achieved if, subsequent to carbonising to
about 1000° C. the fibres are further heat treated to above
2000° C. in a non-oxidizing atmosphere.

The tensioning of fibres may also be maintained during
the subsequent carbonising and/or heat treatment.

Several examples of the invention will now be described
for the purpose of illustration only.

In each example the raw material was in the form of a
multi-filament polyacrylonitrile yarn of which the indi-
vidual filaments were continuous.

Example 1

Raw material in the form of a 4½ denier bundle of
about 500 polyacrylonitrile fibres each about 27 microns
diameter and about 5 inches long was suspended in a
vertical furnace tube with weights totalling 10 grams
attached so as to apply tension to the fibres. The furnace
was evacuated and evacuation pumping was continu-
ously maintained thereafter during heat treatment. The
heat treatment consisted of raising the temperature of the
furnace to 1,000° C. at a rate of 15° C. per hour. After
this treatment the carbonised fibres had the following
properties:

Carbonised density	-----gram/cc--	1.6
Final carbon filament diameter	---- microns--	11-13
Tensile strength of individual fibres	---- p.s.i.--	110×10^3
Young's modulus	-----do-----	16.5×10^6
Failing strain	-----percent--	0.7

As a further step the carbon fibres were heated up to a
temperature of 2500° C. for 1 hour under argon gas at
one atmosphere pressure. After this treatment, during
which the fibres shrank in the diametric direction but not
in the direction of the fibre axis, the density had changed
from 1.70 gm./cm.³ to 1.90 g./cm.³. The Young's modu-
lus of the fibres as a result of this treatment changed from
 16.5×10^6 p.s.i. to an average value of 35×10^6 p.s.i. The
average tensile strength after the high temperature treat-
ment was 200×10^3 p.s.i.

3

Example 2

In this example material as in Example 1 was used and the heat treatment procedure was similar, but instead of carbonising the filaments under vacuum an atmosphere of hydrogen was maintained in the furnace at a pressure of 5 cm./Hg. The properties of the carbonised filaments after treatment were as follows:

Density of the carbonised fibres ---grams/cc---	1.6
Final carbon filament diameter ----microns---	11-14
Tensile strength -----p.s.i.---	135×10^3
Young's modulus -----p.s.i.---	12.9×10^6
Failing strain -----percent---	1

In the examples above described it has been found that the individual filaments shrink whilst their original circular cross-section is maintained. The data given indicates that the diameter is halved approximately.

Examples 3, 4, 5 and 6 which follow describe the use of carbon fibres produced according to Examples 1 and 2 as strengthening elements in composite materials.

Example 3

The following constituents were compounded in a rubber mill:

	Grams
Fluoroelastomer co-polymer of vinylidene fluoride and hexafluoro propylene (Viton B) -----	100
Magnesium oxide -----	15
Dicinnamylidene hexamethylene diamine (curing agent) -----	3
Carbon fibres produced as in Example 1 -----	20

The fibres were fed into the charge at the nip of the rolls where they broke into short lengths about $\frac{1}{8}$ of an inch long and thereafter became uniformly distributed throughout the charge by the compounding. The compounded charge was shaped by moulding and cured in the mould by heating at 160° C. for 1 hour and further heat treated at 250° C. for 24 hours. The end product was a dense composite rubber of great toughness and having good strength retaining properties at elevated temperatures.

Example 4

A bundle of unbroken carbon fibres about 4 inches long produced according to Example 2 was tightly packed in a test tube of $\frac{3}{8}$ " internal diameter and a cold setting catalysed polyester resin poured over them. The resin consisted of polyester resin mixed with methyl ethyl ketone peroxide and a 6% solution of cobalt naphthenate in white spirit in proportions thus: 100 parts of the resin to 3 parts by weight of each of the other two constituents.

The fibres were evenly wetted by the resin mixture and constituted a longitudinal reinforcement in the high strength rigid composite resin/fibre formed by the curing and setting of the resin at room temperature.

Example 5

The procedure of Example 4 was repeated using an epoxy resin mixture consisting of:

	Parts by weight
Epoxy resin -----	60
Polyamide hardener (Versamid 125) -----	40

4

The room temperature curing step led to the production of a product similar in properties to that resulting from Example 4.

Example 6

A bundle of carbon fibres produced as in Example 1 were impregnated with a solution of a Friedel-Craft type resin, in particular a diphenyl oxide based resin made by reacting the constituents in the following proportions:

1 mol diphenyl oxide
1.2 mols para-dichloroxylylene

in a dichloroethane solution sufficient to give 40% solid content in the mixed resin. A Friedel-Crafts type resin is formed from an aromatic compound with an aromatic linking agent which has two chloromethyl or methoxymethyl groups attached to an aromatic nucleus by means of a polycondensation reaction involving the nuclear hydrogen atoms and may be aided by the presence of a small amount of Friedel-Craft type catalyst such as stannic chloride. After evaporation of the dichloroethane, the impregnated fibrous mass was shaped and heat cured at 180° C. for 2 hours under a pressure of 500 p.s.i. to form a high strength fibre reinforced hard stiff composite article.

Among the advantages offered by the process of the invention are the superior strength of the carbonised filaments compared with those produced from regenerated cellulose fibres, the latter in general having a tensile strength of about 50×10^3 p.s.i., also that the fibres have a particularly smooth surface making them more suitable than those made from regenerated cellulose as reinforcement in composite materials.

Example 7

$2\frac{1}{2}$ denier polyacrylonitrile fibres heated to achieve complete permeation of oxygen throughout the fibres for 24 hours at 220° C. in air, then carbonised in a non-oxidising atmosphere to 1000° C. and heat treated to 2500° C. resulted in fibres having a tensile strength of 250×10^3 p.s.i., whereas when the initial heating at 220° was only applied for 2 hours the resulting fibre strength was only 100×10^3 p.s.i.

When treated in the above manner the fibres shrink during the initial heating to 220° C. in air by as much as 40% and whilst the carbon fibre obtained by subsequent carbonising and heat treating to 2,500° C. has a tensile strength which may be satisfactory for certain circumstance the Young's modulus is relatively low. If tension is applied to the fibres during the initial heat treatment to 220° C. both the tensile strength and Young's modulus can be increased as is shown by the following table:

Load applied to a yarn of 100 filaments of $2\frac{1}{2}$ denier polyacrylonitrile fibres, for 24 hours at 220° C., grams	Length change during 220° C. treatment, percent	Properties of the fibre after carbonising to 1,000° C. in an inert atmosphere		Properties of the fibre after heat treating to 2,500° C. in an inert atmosphere	
		Tensile strength, p.s.i.	Young's modulus axially of fibre, p.s.i.	Tensile strength, p.s.i.	Young's modulus axially of fibre, p.s.i.
Nil-----	-40	100×10^3	13×10^6	80×10^3	30×10^6
10-----	-12	100×10^3	16×10^6	100×10^3	38×10^6
20-----	+2	120×10^3	20×10^6	120×10^3	47×10^6
30-----	+15	200×10^3	21×10^6	200×10^3	53×10^6
40-----	+36	200×10^3	21×10^6	200×10^3	60×10^6

Example 8

Fibres of polyacrylonitrile were wound on to a carbon former under slight tension and heated to 220° C. in air for 22 hours. The fibre was in the form of yarn comprising 100 filament $2\frac{1}{2}$ denier polyacrylonitrile with 20 yarns per side of the former and this was secured to the former so that the tension was maintained. After this initial heat treatment the yarns were cut into 5 inch lengths and carbonised by heating at a linear rate of temperature increase from 200-1000° C. in 24 hours in an atmosphere of hydrogen at 15 cms. pressure.

5

The properties of some of the fibres were then measured and the remainder heated to 2500° C. in a carbon tube furnace under one atmosphere pressure of argon.

A further selection of the resulting fibres were tested and the remainder heated to 2900° C. under the same 1 atmosphere of argon conditions. The properties of the fibres resulting from this final treatment were then measured.

The results were as follows:

Treatment	Properties of resulting fibres	
	Tensile strength, p.s.i.	Young's modulus, p.s.i.
1. Fibres heated 22 hours in air at 220° C. with fibres held under tension on former.....		
2. After 1. Fibres heated from 200° C. to 1000° C. over 24 hours in atmosphere of hydrogen at 15 cms. pressure.....	260×10 ³	20×10 ⁶
3. After 2. Fibres heated to 2,500° C. in argon for 2 hours at 1 atmosphere pressure.....	260×10 ³	50×10 ⁶
4. After 3. Fibres heated to 2,900° C. under argon at 1 atmosphere pressure for ¼ hour.	260×10 ³	60×10 ⁶

We claim:

1. A method of making carbon fibers having a Young's modulus parallel to the fiber axis of not less than 16×10⁶ pounds per square inch comprising the steps of oxidizing an organic polymer fiber by simultaneously heating the fiber in an oxidizing atmosphere at a temperature of from about 200° C. to 250° C. for a time sufficient to permit substantially complete permeation of oxygen throughout the core of the fiber while the fiber is held under longitudinal tension, said tension being sufficient at least to limit shrinkage of the fibers during heating to not more than about 12% of the length of the fiber, and carbonizing the fiber by heating the oxidized fiber in a non-oxidizing atmosphere to a temperature of up to about at least 1000° C.

2. A method according to claim 1 wherein said organic polymer is polyacrylonitrile.

3. A method according to claim 2 wherein longitudinal tension is applied to said fiber during said oxidizing step such that the change in length of the fiber during oxidizing is within the range of 12% shrinkage to 36% extension based on the length of the fiber before oxidizing.

4. A method according to claim 2 wherein said fiber

6

is stretched during said oxidizing step up to about 36% based on the length of the fiber before oxidizing.

5. A method according to claim 2 including a further heat treatment comprising heating the carbonized fiber in a non-oxidizing atmosphere at a temperature above said carbonizing temperature and up to about 3000° C.

6. A method according to claim 2 wherein said fiber is heated during said oxidizing step for at least 24 hours.

7. A method according to claim 1 wherein said oxidized fiber is held under tension during said carbonizing step.

8. A method according to claim 5 wherein said carbonized fiber is held under tension during said further heat treatment.

9. Carbon fiber made by the process of claim 1 and having a Young's modulus parallel to the fiber axis of not less than 16×10⁶ pounds per square inch.

10. Carbon fiber made by the process of claim 5 having a Young's modulus parallel to the fiber axis of not less than 38×10⁶ pounds per square inch.

11. A composite material comprising a matrix containing a plurality of carbon fibers as claimed in claim 9 distributed therein.

12. A composite material according to claim 11 wherein said matrix comprises rubber.

13. A composite material according to claim 12 wherein said rubber comprises fluoroelastomer.

14. A composite material according to claim 11 wherein said matrix comprises synthetic resin.

15. A composite material according to claim 14 wherein said resin comprises polyester.

16. A composite material according to claim 14 wherein said resin comprises an epoxy resin.

17. A composite material comprising a matrix containing a plurality of carbon fibers as claimed in claim 10 distributed therein.

References Cited

UNITED STATES PATENTS

2,796,331	1/1957	Kauffman et al.	23—209.1
2,799,915	7/1957	Barnett et al.	23—209.1
3,285,696	11/1966	Tsunoda	23—209.1

ALLAN LIEBERMAN, Primary Examiner.