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(54) Carbon fibers sized with a sizing agent.

(57) Petroleum pitch-derived carbon fibers coated with a sizing agent are disclosed. The sizing agent includes the following ingredients (a)-(c):

(a) an epoxy resin having a number average molecular weight of 550-1600 wherein the content of epoxy resin components which are equivalent to polystyrenes having a molecular weight of 10000 or more with respect to retention time in gel permeation chromatography is less than 5 mol %,

(b) at least one ether compound of the general formula:

X - O - Y

wherein X represents a polyoxyalkylene group and Y represents an aromatic group; and

(c) an ester compound selected from unsaturated fatty acid esters of an aliphatic monohydric alcohol and aliphatic monocarboxylic acid esters of an unsaturated aliphatic monohydric alcohol, wherein the amounts of ingrdients (a)-(c) are 55-84 %, 15-35 % and 1-25 %, respectively, based on the total weight of ingredients (a)-(c).

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CARBON FIBERS SIZED WITH A SIZING AGENT

This invention relates to carbon fibers sized with a sizing agent.

Because of their excellent strength, modulus and heat resistance, carbon fibers are now utilized in a variety of applications. Carbon fibers, however, pose a problem because they are apt to be damaged during processing which includes repeated bending and repeated frictional contact with, for example, guide rollers, thereby causing cleavage of filaments and fluff of the fibers. In the preparation of fiber-reinforced composite material, the fluff of carbon fibers impede the compatibility thereof with a matrix resin so that the composite material fails to exhibit satisfactory mechanical properties. To cope with this problem, a method is proposed for treating carbon fibers with a sizing agent.

Known sizing agents include organic solutions or aqueous emulsions containing binder resins such as vinyl acetate polymers, acrylic polymers, polyurethanes, epoxy resins and polystyrenes. These conventional sizing agents, however, are not entirely satisfactory with respect to anti-spreading or fluff-preventing property, especially when they are used for the treatment of petroleum pitch-derived carbon fibers.

It is an object of the present invention to provide petroleum pitch-derived, sized carbon fibers which are excellent in anti-spreading property, lubricity and flexibility and, therefore, are free of occurrence of fluff and filament cleavage during processing such as weaving.

In accordance with the present invention there is provided petroleum pitch-derived carbon fibers coated with a sizing agent comprising the following ingredients (a)-(c):

(a) an epoxy resin having a number average molecular weight of 550-1600 wherein the content of epoxy resin components which are equivalent to polystyrenes having a molecular weight of 10000 or more with respect to retention time in gel permeation chromatography is less than 5 mol %,

(b) at least one ether compound of the general formula:

X - O - y

wherein X represents a polyoxyalkylene group and Y represents an aromatic group; and

(c) an ester compound selected from the group consisting of unsaturated fatty acid esters of an aliphatic monohydric alcohol and aliphatic monocarboxylic acid esters of an unsaturated aliphatic monohydric alcohol, wherein the amounts of ingrdients (a)-(c) are 55-84 %, 15-35 % and 1-25 %, respectively, based on the total weight of ingredients (a)-(c).

In another aspect, the present invention provides a product obtained by a method comprising the steps of:

providing carbon fibers derived from petroleum pitch;

contacting said carbon fibers with an aqueous emulsion containing the following ingredients (a)-(c):

(a) an epoxy resin having a number average molecular weight of 550-1600 wherein the content of epoxy resin components which are equivalent to polystyrenes having a molecular weight of 10000 or more with respect to retention time in gel permeation chromatography is less than 5 mol %,

(b) at least one ether compound of the general formula:

X - O - Y

wherein X represents a polyoxyalkylene group and Y represents an aromatic group; and

(c) an ester compound selected from the group consisting of unsaturated fatty acid esters of an aliphatic monohydric alcohol and aliphatic monocarboxylic acid esters of an unsaturated aliphatic monohydric alcohol, wherein the amounts of ingrdients (a)-(c) are 55-84 %, 15-35 % and 1-25 %, respectively, based on the total weight of ingredients (a)-(c), thereby coating said carbon fibers with said aqueous emulsion; and

drying said aqueous emulsion coating.

The present invention will now be described in detail below.

The present invention is characterized in that petroleum pitch-derived carbon fibers are treated and coated with a specific sizing agent in the form of an aqueous emulsion including ingredients (a)-(c). These ingredients will be described below.

Ingredient (a):

is an epoxy resin having a number average molecular weight of 550-1600, preferably 600-900. When the number average molecular weight of the epoxy resin is below 550, the resulting sized fibers are sticky and high in frictional resistance. Further, the anti-spreading property becomes insufficient. As a result, the fibers tend to fluff upon running contact with guide rollers. This is particularly outstanding when the fibers are pitch-derived carbon fibers having a high elastic modulus of more than 40 ton/mm^2. When the number

average molecular weight exceeds 1600, on the other hand, the emulsion becomes so unstable that sizing treatment cannot be efficiently performed.

It is important that the content of epoxy resin components of ingredient (a) which are equivalent to polystyrenes having a molecular weight of 10000 or more with respect to ellution characteristics (retention time), namely with respect to molecular weight, in gel permeation chromatography is less than 5 mol %, since otherwise the emulsion is unstable and becomes heterogeneous so that it is impossible to effect the sizing treatment.

Any epoxy resin may be used as long as the above requirements are satisified. Thus, bisphenol type epoxy resins, phenol novolak epoxy resins, cresol novolak epoxy resins and diaminodiphenylmethane epoxy reins may be used as the epoxy resin of ingredient (a). Suitable epoxy resins may be obtained by blending the following epoxy resins and their homologues:

Epoxy Resins	Number Average Molecular Weight
EPIKOTE 828 (bisphenol A diglycidyl ether)	380
EPIKOTE 834 (bisphenol A diglycidyl ether)	470
EPIKOTE 1001 (bisphenol A diglycidyl ether)	900
EPIKOTE 1002 (bisphenol A diglycidyl ether)	1060
EPIKOTE 1004 (bisphenol A diglycidyl ether)	1600
EPIKOTE 1007 (bisphenol A diglycidyl ether)	2900
EPIKOTE 152 (phenol novolak epoxy resin)	370
EPIKOTE 154 (phenol novolak epoxy resin)	650
EPIKOTE 604 (DDM epoxy resin)	480

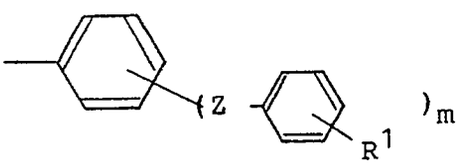
For example, a blend of EPIKOTE 828 and EPIKOTE 1001 (weight ratio of EPIKOTE 828/EPIKOTE 1001 of 46:54 to 0:100), a blend of EPIKOTE 828 and EPIKOTE 1002 (weight ratio of EPIKOTE 828/EPIKOTE 1002 of 47:53 to 0:100) and a blend of EPIKOTE 828 and EPIKOTE 1004 (weight ratio of EPIKOTE 828/EPIKOTE 1004 of 59:41 to 25:75) are suitably used as ingredient (a).

Ingredient (b):

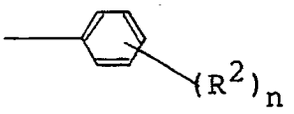
is at least one ether compound of the general formula:

X - O - Y

wherein X represents a polyoxyalkylene group and Y represents an aromatic group. Examples of the polyoxyalkylene group X include a polyoxyethylene, a polyoxypropylene or a copolymer of ethylene oxide and propylene oxide. Examples of the aromatic group Y include:

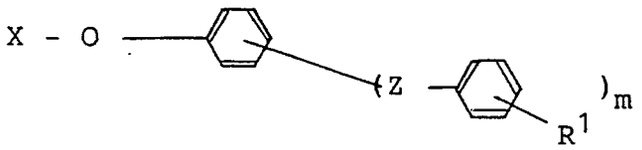


where Z is an alkylene
group such as methylene, ethylene, propylene or isopropylene, an alkenylene group such as vinylene, R^1 is hydrogen a hydroxyl group or an alkyl group and m is an integer of 1-5;

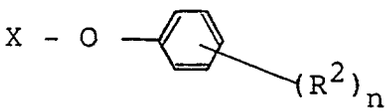


where R^2 is an alkyl group and n is an integer of 1-5; and
a polycondensed ring aromatic group such as naphthyl or alkylnaphthyl.

Thus, the ingredient (b) is preferably one or more of the following ether compounds:
(b-1): an ether of the formula:



where X, 2, R^1 and m are as defined above;
(b-2): an ether of the formula:



where X, R^2 and n are as defined above; or
(b-3): an ether of a polyoxyalkylene and a polycondensed ring aromatic alcohol.

Examples of ethers (b-1) include polyoxyalkylene ethers of styrenated phenols such as polyoxyalkylene monostyrylphenyl ether, polyoxyalkylene distyrylphenyl ether, polyoxyalkylene tristyrylphenyl ether and polyoxyalkylene polystyrylphenyl ether; polyoxyalkylene ethers of benzylated phenols such as polyoxyalkylene monobenzylphenyl ether, polyoxyalkylene dibenzylphenyl ether, polyoxyalkylene tribenzylphenyl ether, polyoxyalkylene tetrabenzylphenyl ether and polyoxyalkylene pentabenzylphenyl ether; and polyoxyalkylene ethers of bisphenols such as bispenol A polyoxyalkyl ether and bisphenol F polyoxyalkyl ether.

Examples of ethers (b-2) include polyoxyalkylene ethylphenyl ether, polyoxyalkylene propylphenyl ether, polyoxyalkylene butylphenyl ether, polyoxyalkylene pentylphenyl ether, polyoxyalkylene hexylphenyl ether, polyoxyalkylene heptylphenyl ether, polyoxyalkylene octylphenyl ether, polyoxyalkylene nonylphenyl ether, polyoxyalkylene decylphenyl ether and polyoxyalkylene dodecylphenyl ether.

It is preferred that a mixture of an ether (b-l) with an ether (b-2) or a mixture of an ether (b-2) with an ether (b-3) be used as ingredient (b).

Ingredient (c):

is an ester compound selected from the group consisting of unsaturated fatty acid esters of an aliphatic monohydric alcohol and aliphatic monocarboxylic acid esters of an unsaturated aliphatic monohydric alcohol.

Examples of ingredient (c) include octyl oleate, lauryl oleate, stearyl oleate, isotridecyl oleate, oleyl oleate, oleyl stearate, oleyl laurate, oleyl isostearate, oleyl palmitate and oleyl octalate.

It is necessary that the amounts of ingrdients (a)-(c) should be 55-84 %, 15-35 % and 1-25 %, respectively, based on the total weight of ingredients (a)-(c). Preferred amounts of ingrdients (a)-(c) are 60-75 %, 20-30 % and 5-10 %, respectively, based on the total weight of ingredients (a)-(c).

An amount of ingredient (a) below 55 % by weight causes deterioration of anti-spreading property of the carbon fibers so that the fibers tend to fluff when subjected to repeated frictional forces. When the amount of ingredient (a) exceeds 84 % by weight, the emulsion of the sizing agent becomes unstable and homogeneous elulsion cannot be obtained. This also applies to the case where the amount of ingredient (b) is below 15 % by weight. Too large an amount of ingredient (b) in excess of 35 % by weight, on the other hand, is disadvantageous because the anti-spreading property of the carbon fibers is deteriorated so that the fibers tend to fluff when subjected to repeated frictional forces. When the amount of ingredient (c) is below 1 % by weight, the sized fibers become poor in lubricity and tend to fluff when subjected to repeated frinctional forces. Too large an amount of ingredient (c) in excess of 25 % by weight adversely affects the

adhesion of the fibers to a matrix resin of a composite material.

The above ingredients (a)-(c) are emulsified in water to obtain a sizing agent in the form of an emulsion. The total concentration of ingredients (a)-(c) in the emulsion is generally 0.2-10 % by weight. The emulsion is used for the sizing treatment of petroleum pitch-derived carbon fibers.

Petroleum pitch is a carbonaceous pitch obtained from heavy hydrocarbon oils such as atmospheric pressure distillation residues, vacuum residues, vacuum distillation heavy distillates, catalytic cracking heavy distillates (e.g. recycle oils), catalytic cracking residual oils (including tar), steam cracking heavy distillates, steam cracking residual oils (including tar), and other heavy oils obtained in petroleum refining processes. If desired, these heavy hydrocarbon oils may be subjected to filtration, solvent extraction or other pretreatment before conversion into pitch. The petroleum-derived pitch may be used in conjunction with a coal tar pitch obtained from coal-derived heavy oils (including liquified coal oils) or coal tar, or with a synthetic pitch obtained from aromatic compounds or polynuclear condensed compounds. Carbon fibers may be obtained from the above pitch by any known manner.

The petroleum pitch-derived carbon fibers, which may be in the form of a tow, are sized with the above-described emulsified sizing agent by any known method such as a roller sizing method, a roller immersion method or a spray coating method so that the sizing agent is coated over the fibers in an amount of 0.1-5.0 % by weight, preferably 0.5-3.0 % by weight (on dry basis) based on the weight of the fibers.

The following examples will further illustrate the present invention.

Example 1

A first glycidyl ether of bisphenol A (EPIKOTE 828 manufactured by Yuka-Shell Epoxy Inc.) was mixed with a second glycidyl ether of bisphenol A (EPIKOTE 1001 manufactured by Yuka-Shell Epoxy Inc.) to obtain Ingredient (a) having a number average molecular weight of 670. GPC analysis revealed that Ingredient (a) had a content of components having a molecular weight (PS equivalent molecular weight) of 10,000 of less than 0.5 mole %. The GPC analysis was conducted by Gel Permeation Chromatogram GPC LC-6A (manufactured by Shimadzu Ltd.) equipped with three 30 cm columns (HGS-40H, 20H and 15H) using tetrahydrofuran as an elution solvent.

Into pure water were emulsified 75 parts by weight of Ingredient (a), 14 parts of Ingredient (b-1)which was polyoxyalkylene(3 mol, PO/EO molar ratio: 1/3)polyoxyethylene(20 mol) tristyryl phenyl ether (PO represents polyoxypropylene and EO represents polyoxyethylene), 6 parts of Ingredient (b-2) which was polyoxyethylene(8 mol) nonylphenyl ether and 5 parts of Ingredient (c) which was lauryl oleate to obtain an aqueous emulsion having a total concentration of Ingredients (a)-(c) of 2 % by weight. This emulsion was found to be stable and to remain homogeneous after being allowed to stand for 5 hours.

Carbon fibers (derived from petroleum pitch, modulus: 50 ton/mm^2, filament number: 3000) in the form of a thread were subjected to a sizing treatment using the thus obtained aqueous emulsion as a sizing agent. Thus, the fibers were immersed in the aqueous emulsion and squeezed so that the amount of the emulsion contained in the fibers was adjusted to 1 g per 1 g of the fibers. The thus treated fibers were then dried with a hot wind blow at 110 $^\circ$C.

The treated carbon fibers were then tested for running friction force to give the following results:

Fiber-Fiber (F/F) frictional force: 105 g

Fiber-Metal (F/M) frictional force: 220 g

The frictional force was measured as follows:

F/F Frictional Force:

A running friction force tester composed of two tension meters, guide rollers and a thread feeder is used. An increase in tension due to the friction between the threads is measured with the tension meters. The twist angle is 540°, the crossing angle is 30° and the running speed is 2.0 m/minute. The difference in frictional force between the two tension meters represents the F/F frinctional force. The initial load applied is 20 g.

F/M Frictional Force:

A running friction force tester composed of two tension meters, guide rollers, a metal friction bar and a thread feeder is used. An increase in tension due to the friction between the running thread and the bar is measured with the tension meters. The difference in frictional force between the two tension meters represents the F/M frictional force.

The carbon fibers treated with the sizing agent were found to exhibit good anti-spreading tendency. As expected from the low F/F and F/M frictional forces, the fibers scarecely fluffed even when they are rubbed with each other or with a metal bar.

The sized fibers were also tested for their adhesion to epoxy resin. Thus, a carbon fiber-reinforced plate (Vf: 60%) in which the carbon fibers were uniaxially oriented within a matrix of a hardened epoxy resin was prepared. The matrix resin was formed by hardening a composition containing 100 parts by weight of an epoxy resin (EPIKOTE 828 manufactured by Yuka-Shell Epoxy Inc.), 85 parts by weight of an acid anhydride curing agent (HN-5500 manufactured by Hitachi Chemical Co., Ltd.) and 1 part by weight of a curing promoter (ethylmethylimidazole) at 120 °C for 1 hour followed by post curing at 180 °C for 1 hour. The thus prepared plate was subjected to a short beam three-point bending (length/height: 4) test to measure the interlaminar shear strength (ILSS). The interlaminar shear strength was 7.8 kg/mm^2.

Examples 2-6

Example 1 was repeated in the same manner as described except that the kinds and/or amounts of Ingredients (a)-(c) were varied as indicated in Table 1 below. The results are summarized in Table 2 together with those of Example 1.

Comparative Examples 1-5

Example 1 was repeated in the same manner as described except that the kinds and/or amounts of Ingredients (a)-(c) were varied as indicated in Table 1 below. The results are summarized in Table 2 together with those of Example 1.

As will be appreciated from the results summarized in Table 2, the carbon fibers treated with the sizing agent according to the present invention exhibit low friction, small anti-spreading tendency, small fluffing tendency and high adhesivity to epoxy resin matrix. In contrast, the carbon fibers treated with the sizing agents of Comparative Examples are not fully satisfactory.

Remarks In Table 1:

*1: Bisphenol A diglycidyl ether

*2: Content of epoxy resins equivalent in molecular weight to polystyrenes having a molecular weight of 10,000 or more with respect to retention time in gel permeation chromatography

*3: R: Polyoxyalkylene(3 mol, PO/EO molar ratio: 1/3)polyoxyethylene(20 mol) tristyryl phenyl ether

*4: S: Polyoxyalkylene(3 mol, PO/EO molar ratio: 1/4)polyoxyethylene(30 mol) tribenzyl phenyl ether

*5: T: Polyoxyethylene(60 mol) pentastyrylcumylphenyl ether

*6: U: Polyoxyethylene(8 mol) nonylphenyl ether

*7: V: Polyoxyethylene(10 mol) laurylphenyl ether

*8: W: Polyoxyethylene(6 mol) octylphenyl ether

*9: X: Lauryl oleate

*10: Y: Oleyl stearate

*11: Z: Oleyl oleate

Table 1

Example	Ingredient (a)						Ingredient (b)				Ingredient (c)	
	Composition (weight %)					Content over 10000*2 (mol %)	Number average molecur weight	Ingredt. b-1 Amount (weight %)		Ingredt. b-2 Amount (weight %)		Amount (weight %)
	EPIKOTE *1							R*3	S*4 T*5	U*6 V*7 W*8		X*9 Y*10 Z*11
	828	1001	1002	1004								
1	18.7	56.3				<0.5	670	14		6		5
2	37.5			37.5		2.0	614	14		6		5
3	37.5		37.5			<0.5	560	14		6		5
4	32.5			32.5		2.5	614	14		6		5
5	17.5			52.5		4.0	888	24		6		10
6	18.7	56.3				<0.5	670	22		8		5
Comp.1	20	60				<0.5	670	14		6		
Comp.2	40			40		2.5	614	14		6		
Comp.3	75					<0.5	380	14		6		5
Comp.4	56			19		<0.5	471	14		6		5
Comp.5	25			25		2.5	614	14		6		30

Table 2

Example	Stability of Emulsion	Running Friction Force		Anti-Spreading Tendency	Fluff	Flexibility	ILSS (kg/mm^2)
		F/F	F/M				
1	good	105	220	good	minimum	good	7.8
2	good	105	220	good	minimum	good	7.6
3	good	100	210	good	minimum	good	7.5
4	good	90	190	good	minimum	good	7.7
5	good	110	240	good	minimum	good	7.5
6	good	100	200	good	minimum	good	7.8
Comp. 1	good	180	250	good	fair	good	7.7
Comp. 2	good	180	250	good	fair	good	7.6
Comp. 3	good	90	220	poor	considerable	good	7.5
Comp. 4	good	100	230	poor	considerable	good	7.7
Comp. 5	good	80	150	poor	considerable	good	6.5

Comparative Examples 6-9

Emulsions were prepared in the same manner as described in Example 1 using Ingredients (a)-(c) indicated in Table 3. After 5 hours from the preparation, the emulsions were found to form precipitates and

become non-uniform. Stable emulsions were not obtained.

Remarks in Table 3:

*1, 2, 3, 4, 6, 9: the same as above

*12: 35 % by weight methyl ethyl ketone solution of

*13: content of solids

*14: Ingredients b-1 and b-2 were replaced by 25 % by weight of a nonionic surfactant (polyoxyethylene(10 mol) dodecyl ether, $C_{12}H_{25}-O\{CH_2-CH_2-O\}_{10}H$)

Table 3

Comparative Example	Ingredient (a) Composition (weight %)						Content over 10000*2 (mol %)	Number average molecular weight	Ingredient (b) Ingredt. b-1 Amount (wt. %)	Ingredt. b-2 Amount (wt. %)	Ingredient (c) Amount (wt. %)
	EPIKOTE*1					EP-OL					
	828	1001	1002	1004	1007	53-BH			R*3	U*6	X*9
6	42.5			42.5		-35*12	2.5	614	7	3	5
7				60	10		15	1710	18	7	5
8	35					35*13	47	755	18	7	5
9	17.5	52.5					<1	670	-*14	-*14	5

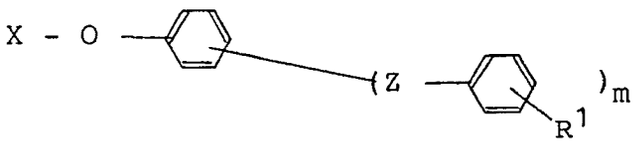
Claims

1. Petroleum pitch-derived carbon fibers ccated with a sizing agent comprising the following ingredients (a)-(c):

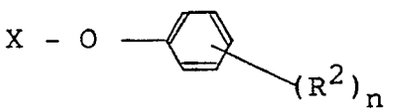
   (a) an epoxy resin having a number average molecular weight of 550-1600 wherein the content of

epoxy resin components which are equivalent to polystyrenes having a molecular weight of 10000 or more with respect to retention time in gel permeation chromatography is less than 5 mol %,
(b) at least one ether compound of the general formula:
X - O - Y
wherein X represents a polyoxyalkylene group and Y represents an aromatic group; and
(c) an ester compound selected from the group consisting of unsaturated fatty acid esters of an aliphatic monohydric alcohol and aliphatic monocarboxylic acid esters of an unsaturated aliphatic monohydric alcohol, wherein the amounts of ingrdients (a)-(c) are 55-84 %, 15-35 % and 1-25 %, respectively, based on the total weight of ingredients (a)-(c).

2. Carbon fibers according to claim 1, wherein ingredient (b) is at least one ether compound selected from the group consisting of (b-1), (b-2) and (b-3),
(b-1) being an ether of the formula:



where X is as defined above, Z is an alkylene group or an alkenylene group, R^1 is hydrogen, a hydroxyl group or an alkyl group and m is an integer of 1-5,
(b-2) being an ether of the formula:

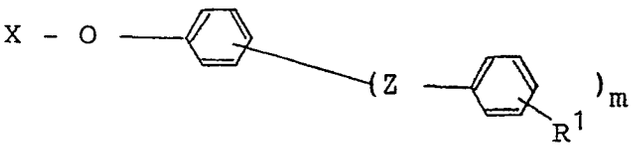


where X is as defined above, R^2 is an alkyl group and n is an integer of 1-5, and
(b-3) being an ether of a polyoxyalkylene and a polycondensed ring aromatic alcohol.

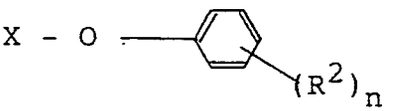
3. Carbon fibers according to claim 2, wherein ingredient (b) is a mixture of an ether compound (b-1) with an ether compound (b-2) or a mixture of an ether compound (b-2) with an ether compound (b-3).

4. A product obtained by a method comprising the steps of:
providing carbon fibers derived from petroleum pitch;
contacting said carbon fibers with an aqueous emulsion
containing the following ingredients (a)-(c):
(a) an epoxy resin having a number average molecular weight of 550-1600 wherein the content of epoxy resin components which are equivalent to polystyrenes having a molecular weight of 10000 or more with respect to retention time in gel permeation chromatography is less than 5 mol %,
(b) at least one ether compound of the general formula:
X - O - Y
wherein X represents a polyoxyalkylene group and Y represents an aromatic group; and
(c) an ester compound selected from the group consisting of unsaturated fatty acid esters of an aliphatic monohydric alcohol and aliphatic monocarboxylic acid esters of an unsaturated aliphatic monohydric alcohol, wherein the amounts of ingrdients (a)-(c) are 55-84 %, 15-35 % and 1-25 %, respectively, based on the total weight of ingredients (a)-(c), thereby coating said carbon fibers with said aqueous emulsion; and
drying said aqueous emulsion coating.

5. A product according to claim 4, wherein ingredient (b) is at least one ether compound selected from the group consisting of (b-1), (b-2) and (b-3),
(b-I) being an ether of the formula:



where X is as defined above, Z is an alkylene group or an alkenylene group, R^1 is hydrogen, a hydroxyl group or an alkyl group and m is an integer of 1-5,
(b-2) being an ether of the formula:



where X is as defined above, R^2 is an alkyl group and n is an integer of 1-5, and
(b-3) being an ether of a polyoxyalkylene and a polycondensed ring aromatic alcohol.

6. A product according to claim 5, wherein ingredient (b) is a mixture of an ether compound (b-1) with an ether compound (b-2) or a mixture of an ether compound (b-2) with an ether compound (b-3).