

Description

THIS INVENTION relates to sizing agents for carbon fibers.

Carbon fiber reinforced plastics (hereinafter referred to as CFRP) are made from carbon fiber with resin matrix and are most excellent materials in terms of specific modulus and specific strength. Because of their superior characteristics and light weight, their applications in aerospace industries, for example, are quickly expanding. Carbon fibers used for the production of CFRP are drawn and arranged in the form of filament or a tow and after being formed into strands, sheets, textile, or knit materials, are combined with a resin material and used as a prepreg. Alternatively, filaments or tows may be cut to uniform lengths to produce chopped fibers which are then combined with a resin material, for use as a material for premix, a bulk molding compound or a sheet molding compound. Since carbon fibers are basically brittle, fluffs tend to arise due to mechanical friction in the moulding process before such fibers are made into a prepreg, unless they are pre-treated with a sizing agent. Moreover, such fibers cannot be handled easily and the physical characteristics of the CFRP are also adversely affected. Chopped fibers are usually 1-100 mm long but since thousands or tens of thousands of single fibers constitute the carbon fiber filaments or tows which are processed, the fibers become disheveled and bulky and tend to scatter if they are directly chopped without preprocessing. In order to improve the cohesiveness and abrasion resistance of carbon fibers and to make it easier to handle them while they are manufactured or transported, therefore, it has been a common practice to add a sizing agent to carbon fibers. Since sizing agents eventually become a part of the CFRP produced, it is required that they do not adversely affect the characteristics of the final products.

In view of such requirements as described above, the present invention relates to multi-purpose sizing agents to be combined with a matrix resin and in particular with epoxy resins and unsaturated resins having an ester bond.

As sizing agents for carbon fibers to be used for carbon fiber reinforced epoxy resin, a mixture of liquid and solid bisphenol A diglycidylethers (Japanese Patent Publication Tokko 57-15229, US-A-3914504) and the aromatic glycidylamines (Japanese Patent Publication Tokko 59-11710, US-A-4107128) have previously been proposed. As sizing agents for carbon fibers to be used for carbon reinforced unsaturated polyester resin, on the other hand, epoxized polybutadiene (Japanese Patent Publication Tokkai 56-43335) and a mixture of a diglycidylether derived from bisphenol and epichlorohydrin and prepolymer derived from diarylphthate (Japanese Patent Publication Tokkai 59 -228083) have been proposed. As still another example, sizing agents of the aqueous emulsion type having as indispensable components an epoxy resin; a condensation product of an unsaturated dibasic acid and a bisphenol-type alkylene oxide adduct; and an alkylene oxide adduct of phenol or polycyclic phenol, have also been proposed (Japanese Patent Publication Tokko 57-49675, US-A-4167538).

Although these prior art sizing agents each have advantages, they present problems in the production of CFRP. For example, since carbon fibers have poor cohesiveness and abrasion resistance problems of fluff and yarn breakage occur frequently at the time of their weaving and chopped fibers become disheveled. Some are toxic and flammable when exposed to high temperature because of the use of an organic solvent. Some may improve the adhesion between carbon fibers and epoxy resin matrix, but not between carbon fibers and unsaturated polyester resin matrix, so that interlaminar shear strength (ILSS) of the produced CFRP is adversely affected. Sometimes, attempts at improving multi-purpose characteristics have resulted in insufficient adhesion characteristics for either type of resin.

The present invention provides new sizing agents for carbon fibers which eliminate the conventional and aforementioned problems.

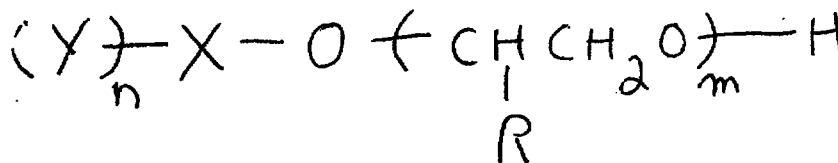
It has now been established that the use of specified copolymer and specified oxyalkylene derivative of substituted phenol together with epoxy resin provides emulsifiable sizing agents for carbon fibers which can improve the processability of the fibers during the fabrication and have substantially equal adhesion characteristics with an epoxy resin matrix or an unsaturated polyester resin matrix.

This invention relates to sizing agents for carbon fibers containing Compound A, Compound B and Compound C to be defined below, as important constituents:

Compound A: an epoxy compound

Compound B: a copolymer having within its molecules one segment (I) which is an oxyalkylene derivative of a polycyclic phenol and one or two segments (II) which are a monoester or a polyester, the segments being interconnected through an ester linkage, said segment of component B which is the monoester or polyester being obtained by alternating ring-opening addition of organic dicarboxylic anhydride and 1,2-epoxide to the oxyalkylene derivative of a polycyclic phenol (segment (I)) in the presence of a catalyst

Compound C: an oxyalkylene derivative of a substituted phenol shown by the general formula



where Y is an alkyl group, phenyl-methyl group or phenyl-ethyl group with 1-12 carbon atoms, X is a benzene residue, diphenyl residue or cumylbenzene residue, R is a hydrogen atom or methyl group, n is an integer in the range of 1-5, and m is an integer in the range of 4-100.

Examples of Component A according to the present invention include straight-chain aliphatic epoxy compounds, glycidylether, glycidylamine, glycidylester, glycidylhydantoin etc. Preferable among these examples are glycidylether and glycidylamine. Particularly preferably examples include bisphenol-A diglycidylether, bisphenol-A diglycidylether polymer, epoxy cresol novolac resins, epoxy phenol novolac resins, N,N,N',N' tetraglycidyl-m-xylylenediamine, N,N,N',N'-tetraglycidyl diaminodiphenylmethane, N,N,N',N'-tetraglycidyl-bis aminomethylcyclohexane and m-N,N'-diglycidylaminophenyglycidylether.

Compound B according to the present invention includes within its molecule one segment which is an oxyalkylene derivative of a polycyclic phenol (B¹) and one or two segments which are a monoester or a polyester (B²), the segments being interconnected through an ester bond. Thus, Component B of the present invention may be expressed as either B¹-B² or B²-B¹-B²

The aforementioned oxyalkylene derivative of a polycyclic phenol can be obtained, for example, by adding an alkyleneoxide to a polycyclic phenol by a known method. Its molecule has a hydroxyl terminal group which provides active hydrogen. Examples of polycyclic phenolalkyleneoxide derivatives that may be advantageous for use in the present invention include polyoxyalkylene poly(phenyl-methylated) phenylether, polyoxyalkylene poly(phenyl-ethylated) phenylether and bisphenol-polyethylene glycol copolymers. They include the following compounds: polyoxyethylene (5 mol) di(phenyl-methylated) cumylphenyl ether, polyoxyethylene (5 mole) tri(phenyl-methylated) diphenyl ether, polyoxy [ethylene (2 mole) propylene (2 mole)] tri(phenyl-ethylated) phenylether, polyoxyethylene (10 mole) tri(phenyl-ethylated) phenylether, polyoxypropylene (4 mole)-added bisphenol A, polyoxyethylene (2 mole)-added bisphenol A, polyoxyethylene (4 mole)-added bisphenol S and polyoxyethylene (6 mole)-added bisphenol A.

The monoester and polyester segments of Component B according to the present invention can be obtained stably in an industrially advantageous manner by alternating ring-opening addition reaction of organic dicarboxylic anhydride and 1,2-epoxide to one of the aforementioned oxyalkylene derivatives of a polycyclic phenol in the presence of a catalyst. In this case, examples of organic dicarboxylic anhydride include aliphatic or ethylenically unsaturated dicarboxylic anhydrides such as succinic anhydride, maleic anhydride and alkenyl succinic anhydride, aromatic dicarboxylic anhydrides such as phthalic anhydride and naphthalene dicarboxylic anhydride, and alicyclic dicarboxylic anhydrides such as cyclohexene dicarboxylic anhydride. Ethylenically unsaturated dicarboxylic anhydrides are particularly preferable. Examples of 1,2-epoxide include aliphatic epoxides such as ethylene oxide, propylene oxide, 1,2-butylene oxide and alkyl or alkenylglycidylether with 1-12 carbon atoms, aromatic or alicyclic epoxides such as phenylene oxide and cyclohexene oxide, and epoxides having aromatic group such as styrene oxide and phenylglycidyl ether. Ethylene oxide, propylene oxide and butylene oxide are particularly preferable. Examples of catalysts include lithium halides such as lithium chloride and lithium bromide and tetra-alkyl quaternary ammonium salts such as tetramethyl ammonium bromide, tetrabutyl ammonium bromide and tetrapropyl ammonium chloride.

The end groups of the monoester and polyester segments thus formed are usually hydroxyl groups, carboxylic groups or a mixture thereof and the ratio thereof as end groups is controlled by the molar ratio between the organic dicarboxylic anhydride and 1,2-epoxide which participated in the reaction. In other words, the ratio of hydroxyl and carboxylic groups as end groups can be varied by selecting the aforementioned molar ratio.

Compounds of Component B having desired characteristics to carry into effect the present invention can be obtained by properly selecting the molecular weights, molecular ratios, structures and compositions of the segment which is a oxyalkylene derivative of a polycyclic phenol and the segment which is a monester or polyester. For example, if the molecular ratio of the segment which is a monoester or polyester is increased, the affinity to a matrix resin based on unsaturated resins having an ester bond can be improved. If on the other hand, the molecular ratio of the other segment i.e. the oxyalkylene derivative of a polycyclic phenol is increased, affinity to a matrix resin which is an epoxy resin can be improved. In order to ensure that Component B is reactive to other components such as Component A, matrix resins and

carbon fibers, various reactive groups may be introduced into the polyester terminal group of Component B. Reactive groups such as ethylenically unsaturated hydrocarbon groups, epoxy groups and isocyanate groups are effective. These reactive groups can be introduced by reacting a reactive substance with the end hydroxyl or carboxylic groups of the polyester segment connected through ether or ester bonds. The end hydroxyl groups of monester or polyester segments can also be modified into carboxylic groups by reacting with a polybase acid (bivalent or greater) or its anhydride. It is effective to have more than 95% of the end groups of monester or polyester segments as a carboxylic group, including such modifications.

Component C according to the present invention is characterised by the general formula given above and serves as an emulsifier component for emulsifying Components A and B in water. In this formula, the polyoxyalkylene segment is a random or block addition of propylene oxide and/or ethylene reaction products of alkyl phenol, phenyl-methylated phenol, phenyl-ethylated phenol, phenyl-ethylated phenylphenol, phenyl-methylated cumylphenol or phenyl-ethylated cumylphenol and propylene oxides and/or ethylene oxide.

The sizing agents of the present invention contain Components A, B and C as important constituents. Depending on the purpose for which they are used, the weight ratios of these components are preferably such that Component A/Component B = 10-90/90-10 and Component C/Component A + B = 10-40/90-60. If necessary, a lubricant and a surfactant may be included to an extent which does not seriously affect the performance of the sizing agent.

The matrix resins to which the sizing agents described above are intended to be applied are epoxy resins include unsaturated polyester means and unsaturated polyester resins. Epoxy resins include the bisphenol A diglycidylether, epoxy novolac resins, tetraglycidylamine and unsaturated polyester resins include unsaturated polyester resins and vinyl ester resins. Unsaturated polyester resins for this purpose are obtained by dissolving in styrene monomer or another polymerizable monomer. More particularly, they are generally polyesters obtainable by using as original material anhydrous maleic acid, orthophthalic acid, isophthalic acid, fumaric acid, ethylene glycol and propylene glycol. Vinyl ester resins have a molecular structure obtainable by a reaction between epoxy resins of bisphenol diglycidylether type or novolac type and acrylic acid or methacrylic acid and are mixed with a styrene monomer or the like.

The amount of the sizing agents of the present invention to be applied to carbon fibers is generally 0.1-10 wt% (with respect to carbon fibers) and preferably 0.5-0.7 wt%. Processing is carried out in the form of a water dispersant and the concentration of the sizing agent in the dispersion should preferably be 0.3-5.0 wt%.

The sizing agents of the present invention are extremely effective on carbon fibers made from pitch materials or carbon fibers from polyacrylonitrile filaments. They can overcome the conventional problems described above and make carbon fibers significantly easier to handle in later processes. Because of their superior cohesiveness and self-lubrication, problems of fluff and fiber breakage are minimised or prevented when carbon fiber filaments and tows are bent many times by guide members and rollers as they are wound or woven, and chopped fibers are prevented from becoming disheveled and scattering around. In summary, the present invention allows carbon fiber yarns to be wound up and woven at a higher speed, makes it easier to cut them cleanly and thereby improves their productivity. Moreover, these sizing agents can be easily applied to carbon fibers as an aqueous emulsion which is uniform and stable, and they are not only safe and hygienically advantageous, but also energy-saving. Carbon fibers processed by the sizing agents of the present invention improve the cohesion not only between the carbon fibers and the epoxy resin matrix but also between the carbon fibers and the unsaturated polyester resin matrix with which prior art sizing agents do not have satisfactory cohesiveness. Thus, sizing agents of the present invention can be used together on these two types of matrix resins to obtain CRFP of superior quality from each.

Test experiments using the sizing agents of the present invention are described below in order to explain the present invention in more detail but the present invention is not intended to be limited by these examples.

Examples of Component B are shown in Tables 1 and 2 and sizing agents both embodying the present invention and for comparison were prepared as shown in Tables 3 and 4. Results of tests thereon are shown in Tables 5 and 6.

EXAMPLE 1: PRODUCTION OF COMPONENT B (B-1)

808 g (2.0 moles) of ethylene oxide (hereinafter abbreviated as EO) 4 moles adduct of bisphenol A 784 g (8.0 moles) of maleic anhydride and 1.0 g of tetramethylammonium bromide as catalyst were placed inside an autoclave and stirred for 30 minutes at 120-125 °C. Next, 464 g (8.0 moles) of propylene oxide (hereinafter abbreviated as PO) was injected thereinto over a period of 4 hours at 125 °C for a reaction and

a light brown viscous liquid (Product B-1) was obtained. For this Product B-1, the acid value was 37, the hydroxyl value was 36 and the molecular weight (hereinafter calculated value) was 1540.

EXAMPLE 2: PRODUCTION OF COMPONENT B (B-7)

After 1540 g (1.0 mole) of Product B-1 and 100 g (1.0 mole) of succinic anhydride were placed inside an autoclave, they were reacted for two hours at 120 -125 °C in the presence of nitrogen gas to obtain a light brown viscous liquid (Product B-7). The ester segment of this Product B-7 has carboxyl terminated polyester segment. Its acid value, hydroxyl value and molecular weight were respectively 67, 2.0 and 1640.

EXAMPLE 3: PRODUCTION OF COMPONENT B (B-10)

After 2349 g (1.0 mole) of Product B-3 obtained in a way similar to Example 1 was dissolved in methylethylketone as a solvent inside a flask. 1.0g of tetramethylammonium bromide as catalyst and 722 g (1.9 moles) of bisphenol A diglycidylether were successively added thereto and stirred for 3 hours at 50-70 °C. Methylethylketone was distilled away under reduced pressure to obtain a light brown viscous liquid (Product B-10). The ester segment of this Product B-10 has epoxy terminated groups and its acid value, hydroxyl value and molecular weight were respectively 1.2, 3.5 and 3116.

EXAMPLES OF COMPONENT B WITHOUT END MODIFICATION

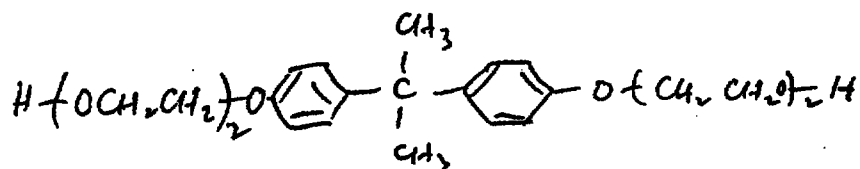
Product B-2 through B-6 were obtained similarly as explained in Example 1 above.

Table 1

Product	Derivative segment Poly-cyclic	Ester segment Component B				
		Organic Dicarboxylic Anhydride (molar ratio)	1,2-Epoxy	Molecular Weight	Wt% of Ester Segment	Molar Ratio of End Groups COOH/OH
B-1	*1 (1 mole)	MA (4 moles)	PO(4.0 moles)	1540	59.6	50.7/ 49.3
B-2	*1 (1 mole)	MA (4.5 moles) FA (4.5 moles)	PO(8.2 moles)	1852	78.2	48.5/ 51.5
B-3	*2 (1 mole)	MA (12 moles)	PO(11.5 moles)	2393	78.2	42.4/ 57.6
B-4	*3 (1 mol)	MA (4 moles) FA (2 moles)	EO(5.5 moles)	1378	69.2	45.3/ 54.7
B-5	*4 (1 mole)	MA (6 moles)	EO(5.5 moles)	1478	57.7	50.2/ 49.8
B-5	*5 (1 mole)	MA (7 moles)	EO(6.5 moles)	1477	67.3	49.5/ 50.5

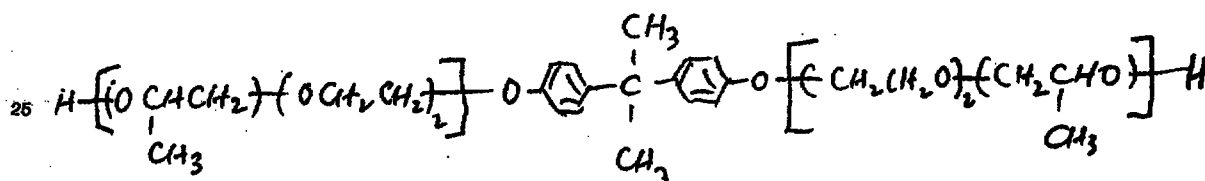
Notes:

*1. Bisphenol-A polyethylene glycol (4 moles) copolymer

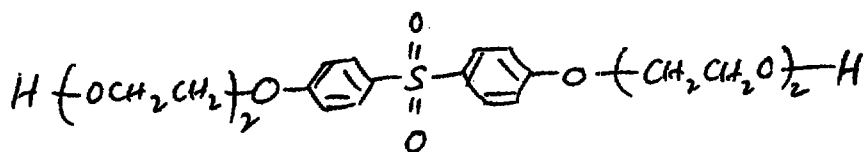


*2. Bisphenol-A polyethylene glycol (4 moles)

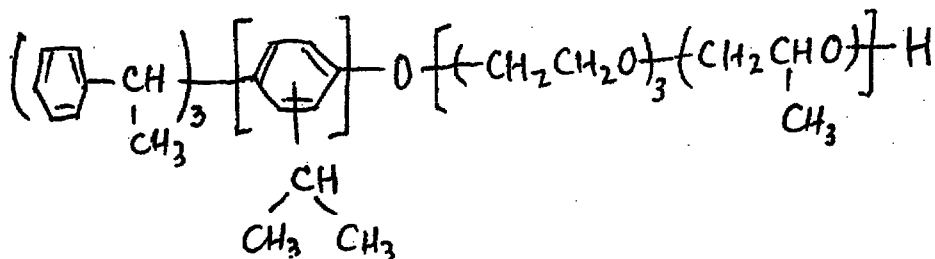
polypropylene glycol (2 moles) random copolymer



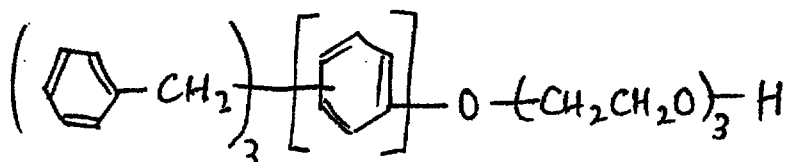
*3. Bisphenol-S polyethylene glycol (4 moles) copolymer



*4. Polyoxyethylene (3 mols) oxypropylene
tri(phenyl-ethylated) cumylphenyl ether



*5. Polyoxyethylene (3 moles) tri(phenyl-methylated)
phenylether



MA: maleic anhydride

PA: phthalic anhydride

EXAMPLES OF COMPONENT B WITH MODIFICATION

Products B-7 through B-11 were obtained similarly as explained in Example 2 or Example 3 above.

TABLE 2

Product	Compound - B (moles)	Terminating Agents (moles)	Terminal group Molar Ratio COOH/OH	Structure
B-7	B - 1 (1 mole)	SA (0.5 mole)	97.0/3.0	- COOH/OH
B-8	B - 1 (1 mole)	MA (0.5 mole)	98.0/2.0	- COOH/OH
B-9	B - 1 (1 mole)	FA (0.5 mole)	97.0/3.0	- COOH/OH
B-10	B - 3 (1 mole)	*6 (2 moles)		$ \begin{array}{c} \text{---CH}_2\text{CH---CH}_2 \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{O} \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}_3 \\ \quad \quad \quad \\ \quad \quad \quad \text{C}=\text{CH}_2 \end{array} $
B-11	B - 3 (1 mole)	*7 (2 moles)		$ \begin{array}{c} \text{---CH}_2\text{CHCH}_2\text{OOC} \\ \\ \text{OH} \end{array} $

Notes:

*6: bisphenol A diglycidyl ether

*7: glycidyl methacrylate

SA: succinic anhydride

Preparation of Sizing Agents

Sizing agents (Test Examples 1-11) shown in Table 3 and those (Comparison Examples 1-9) as shown in Table 4 were prepared.

Table 3

	1	2	3	4	5	6	7	8	9	10	11
5	A-1	4.3	4.0	10.5	5.7	4.5		4.0	5.0	4.0	3.0
	A-2	4.0		2.0			4.0	3.0	4.0	5.0	4.0
	A-3		2.5		5.0	7.0					3.0
10	B-1	9.0									
	B-2		11.0								
15	B-3			6.5							
	B-4				10.0						
	B-5					8.0					
20	B-6						10.0				
	B-7							9.0			
	B-8								9.0		
25	B-9									9.0	
	B-10										9.0
	B-11										10.0
30	C-1	0.2		0.5			0.3	0.3	0.3		
	C-2			2.5							
	C-3	2.5	2.5		2.3	2.5	3.0	2.7	2.7	2.7	3.0
35											
40											
45											
50											
55											

Table 4

	1	2	3	4	5	6	7	8	9
A-1	4.9	15.6		10.0				20.0	10.9
A-2	4.6			10.0					
A-3									
B-1	10.5				20.0				
B-2									
B-3									
B-4									
B-5									
B-6			15.4						
B-7									
B-8									
B-9									
B-10									
B-11									
C-1		0.7							
C-2		3.7							1.9
C-3			4.6			20.0			
*8									7.2
*9							20.0		
*10							80.0		
*11								80.0	

Notes:

Both in Tables 3 and 4, the numbers indicate weight parts.
 Except in Comparison Examples 7 and 8, water comprises
 80 weight parts.

A-1: bisphenol A diglycidylether (Epikote 828 produced by
 Yuka Shell Chemical Company, or Epon 828 produced by Shell Chemical
 Company.

A-2: bisphenol A diglycidylether (Epikote 1002
produced by Yuka Shell Chemical Company or Epon 1002
produced by Shell Chemical Company, epoxy equivalent
630).

A-3: tetraglycidyl diaminodiphenyl methane (Sumiepoxy
ELM 434 produced by Sumitomo Chemical Industries
Company, epoxy equivalent 120).

C-1: polyoxyethylene (6 moles) nonylphenylether

C-2: polyoxyethylene (70 moles) penta
(phenyl-ethylated) cumylphenylether.

C-3: polyoxyethylene (30 moles)
tri(phenyl-methylated) phenyl ether.

*8 condensation product (acid value 50) of 1.0 moles
of EO (2 moles) adduct of bisphenol A, 1.5 moles of
maleic acid, and 0.50 moles of sebacic acid.

*9: epoxidized polybutadiene (BF-1000 produced by
Adeka Argus Chemical Company)

*10: acetone.

*11 methylethyl ketone

55 EVALUATION

By methods to be described below, each sizing agent described above was examined in terms of stability of emulsion, fluffs and fiber breakage in carbon fibers sized therewith and inter-laminar shear

strength (hereinafter abbreviated as ILSS) of such carbon fibers. Results of these tests are shown in Table 5. Sheet molding compounds (SMC) were also prepared with such carbon fibers treated with the sizing agents and bending strength of these composites were measured. Results of these measurements are shown in Table 6.

Table 5

10		Emulsion Stability	Fluffs, Breakage		ILSS (Kg/mm ²)	
			TM	Rubbing	Epoxy Resins	Vinyl Ester Resins
15	1	A	A	A	8.2	8.3
	2	A	A	B	8.2	8.3
	3	A	A	A	8.2	8.3
	4	A	A	A	8.2	8.3
20	5	A	A	B	8.2	8.3
	6	A	A	A	8.2	8.3
	7	A	A	A	8.4	8.5
	8	A	A	A	8.4	8.5
25	9	A	A	A	8.4	8.5
	10	A	A	A	8.5	8.5
	11	A	A	A	8.4	8.6
30	1	**	---	---	---	---
	2	A	D	C	7.7	7.0
	3	B	C	B	7.9	8.2
	4	**	---	---	---	---
35	5	**	---	---	---	---
	6	A	D	D	6.4	6.5
	7	--	D	D	7.5	7.0
	8	--	B	C	7.8	7.1
40	9	A	C	B	7.8	7.9

Note:

** indicates no emulsification

TABLE 6

Test Examples	Bending	
	Strength (kg/cm ²)	Modulus (kg/cm ²)
1	14.5 x 10 ²	8.6 x 10 ⁴
3	14.4 x 10 ²	8.5 x 10 ⁴
8	14.8 x 10 ²	8.8 x 10 ⁴
10	14.8 x 10 ²	8.9 x 10 ⁴
11	15.2 x 10 ²	9.0 x 10 ⁴
Comparison		
Examples		
1	13.5 x 10 ²	6.8 x 10 ⁴
3	13.8 x 10 ²	7.5 x 10 ⁴

Superior effects obtainable by the present invention are clearly demonstrated in Tables 5 and 6.

35 METHODS OF EVALUATION AND MEASUREMENT

(1) Emulsion Stability

Each solution of sizing agent with 20% concentration was allowed to stand for 7 days at 20°C. Its separation was evaluated as follows:

A: No separation

B: Creamy floating substances

(2) Sizing Treatment of Carbon Fibers

(2-1) No-size yarns of carbon fibers (7μ/6000 filaments) were dipped into a solution of each sizing agent for impregnation such that when the effective amount that was attached became 1.2 wt%. After they were wrung by rollers and dried, they were subjected to a heat treatment at 150°C for 10 minutes inside an oven and collected by winding.

(2-2) No-size yarns of carbon fibers (7μ/3000 filaments) were dipped into a solution of each sizing agent for impregnation such that the effective amount that was attached became 3.5wt%. After they were wrung by rollers and dried, they were subjected to a heat treatment at 150°C for 20 minutes inside an oven and chopped to lengths of 1 inch (2.54 cm) to produce chopped fibers.

55 (3) Fluffs and Breakage

A TM type yarn friction and rubbing tester (produced by Daiel Kagaku Seiki Company) was used to test the fiber-metal friction of carbon fibers treating according to (2-1) with a load of 100g/6000 filaments, $\theta = 50$;

length of frictional motion = 30mm and a metallic comb moved 500 times reciprocatingly at the rate of 150 times/min. Separately, a rubbing tester (produced by Toyo Seiki Company) was used to test the fiber-fiber friction with internal angle of about 35°, one twist, length of frictional motion = 20mm and 500 times of reciprocating motion at the speed of 100 times/min. The results of these tests were evaluated as follows:

- 5 A: Hardly any fluffs or yarn breakage
 B: Fluffs appearing only singly
 C: fluffs and breakages occurring in groups
 D: Frequent occurrence of fluffs and yarn breakage and cutting in one part

10 (4) Measurement of ILSS

(4-1) When an Epoxy Resin was used as Matrix Resin

15 After carbon fibers sized according to (2-1) were impregnated with a resinous composition which comprises 80 weight parts of bisphenol A diglycidyl ether monomer (Epikote 828 produced by Yuka Shell Chemical Company or Epon 828 produced by Shell Chemical Company) 20 weight parts of bisphenol A diglycidylether polymer (Epikote 1002 produced by Yuka Shell Chemical Company or Epon 1002 produced by Shell Chemical Company) 5 weight parts of boron trifluoride monomethylamine and 25 weight parts of methylethyl ketone and methylethyl ketone was removed therefrom, they were partially hardened and a unidirectionally reinforced prepreg was produced. The prepreg thus obtained was cut and placed inside a mold and a composite with V_f (volume percentage of carbon fibers therein) = 60% was formed by applying a pressure of 7 kg/cm² (0,7 N/mm²) for 90 minutes at 140°C. The dimensions of the product were 2.5 mm in thickness, 6mm in width and 17 mm in length. ILSS of this product was measured by the short beam method (ratio of span length/thickness = 5).

25 (4-2) When Unsaturated Resin With Ester Bond Was Used As a Matrix Resin

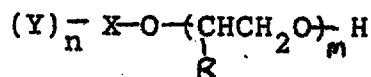
30 After carbon fibers sized according to (2-1) were impregnated uniformly with a resin mixture 100 weight parts of vinyl ester resin (Ripoxy R-802 produced by Showa Kobunshi Company), 1 weight part of tertiary butylperbenzoate and 1 weight part of butylbenzoylperoxide, a pressure of 7kg/cm² (0,7 N/mm²) was applied for 60 minutes at 130°C in a molding production process and a unidirectionally reinforced prepreg with V_f = 60% was produced. The dimensions of this product were 2.5mm in thickness, 6mm in width and 17 mm in length. ILSS of this product was measured by the short beam method (ratio of span length/thickness = 5).

35 (6) Measurement of Bending Strength

40 After 40 weight parts of styrene solution with 35% of rubber-type low shrinkage agent, 60 weight parts of styrene solution with 60% of unsaturated polyester resin (Polyset 9109 produced by Hitachi Kasei Company, phthalic ester-type) 1.5 weight parts of tertiary butylperbenzoate, 3.0 weight parts of zinc stearate, 200 weight parts of calcium carbonate powder and 0.3 weight parts of parabenzoquinone were uniformly mixed, 2.0 weight parts of magnesium oxide were added and a composition for SMC (sheet molding compound) containing 20% of a one-to-one mixture of glass fibers of one inch in length and carbon fibers of one inch in length treated accordingly to (2-1) was prepared. This composition was molded at 45 140°C and bending strength was tested on this molded product.

Claims

- 50 1. A sizing agent for carbon fibers containing Component A, Component B and Component C characterised by Component A being an epoxy compound, Component B being a copolymer based on an oxyalkylene derivative of a polycyclic phenol and Component C being an oxyalkylene derivative of substituted phenol shown by the general formula





length of frictional motion = 30mm and a metallic comb moved 500 times reciprocatingly at the rate of 150 times/min. Separately, a rubbing tester (produced by Toyo Seiki Company) was used to test the fiber-fiber friction with internal angle of about 35°, one twist, length of frictional motion = 20mm and 500 times of reciprocating motion at the speed of 100 times/min. The results of these tests were evaluated as follows:

- A: Hardly any fluffs or yarn breakage
- B: Fluffs appearing only singly
- C: fluffs and breakages occurring in groups
- D: Frequent occurrence of fluffs and yarn breakage and cutting in one part

10 (4) Measurement of ILSS

(4-1) When an Epoxy Resin was used as Matrix Resin

After carbon fibers sized according to (2-1) were impregnated with a resinous composition which comprises 80 weight parts of bisphenol A diglycidyl ether monomer (Epikote 828 produced by Yuka Shell Chemical Company or Epon 828 produced by Shell Chemical Company) 20 weight parts of bisphenol A diglycidylether polymer (Epikote 1002 produced by Yuka Shell Chemical Company or Epon 1002 produced by Shell Chemical Company) 5 weight parts of boron trifluoride monomethylamine and 25 weight parts of methylethyl ketone and methylethyl ketone was removed therefrom, they were partially hardened and a unidirectionally reinforced prepreg was produced. The prepreg thus obtained was cut and placed inside a mold and a composite with V_f (volume percentage of carbon fibers therein) = 60% was formed by applying a pressure of 7 kg/cm² (0.7 N/mm²) for 90 minutes at 140°C. The dimensions of the product were 2.5 mm in thickness, 6mm in width and 17 mm in length. ILSS of this product was measured by the short beam method (ratio of span length/thickness = 5).

(4-2) When Unsaturated Resin With Ester Bond Was Used As a Matrix Resin

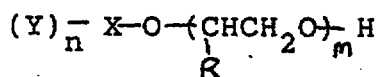
After carbon fibers sized according to (2-1) were impregnated uniformly with a resin mixture 100 weight parts of vinyl ester resin (Ripoxy R-802 produced by Showa Kobunshi Company), 1 weight part of tertiary butylperbenzoate and 1 weight part of butylbenzoylperoxide, a pressure of 7kg/cm² (0.7 N/mm²) was applied for 60 minutes at 130°C in a molding production process and a unidirectionally reinforced prepreg with V_f = 60% was produced. The dimensions of this product were 2.5mm in thickness, 6mm in width and 17 mm in length. ILSS of this product was measured by the short beam method (ratio of span length/thickness = 5).

(6) Measurement of Bending Strength

After 40 weight parts of styrene solution with 35% of rubber-type low shrinkage agent, 60 weight parts of styrene solution with 60% of unsaturated polyester resin (Polyset 9109 produced by Hitachi Kasei Company, phthalic ester-type) 1.5 weight parts of tertiary butylperbenzoate, 3.0 weight parts of zinc stearate, 200 weight parts of calcium carbonate powder and 0.3 weight parts of parabenzoquinone were uniformly mixed, 2.0 weight parts of magnesium oxide were added and a composition for SMC (sheet molding compound) containing 20% of a one-to-one mixture of glass fibers of one inch in length and carbon fibers of one inch in length treated accordingly to (2-1) was prepared. This composition was molded at 140°C and bending strength was tested on this molded product.

Claims

1. A sizing agent for carbon fibers containing Component A, Component B and Component C characterised by Component A being an epoxy compound, Component B being a copolymer based on an oxyalkylene derivative of a polycyclic phenol and Component C being an oxyalkylene derivative of substituted phenol shown by the general formula

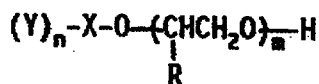




- wherein Y is an alkyl group, phenyl-methyl group or phenyl-ethyl group with 1-12 carbon atoms, X is a benzene residue, diphenyl residue or cumylbenzene residue, R is a hydrogen atom or a methyl group, n is an integer in the range of 1-5 and m is an integer in the range of 4-100; characterised in that the molecules of the copolymer compound B possess a segment (I) which is the oxyalkylene derivative of the polycyclic phenol linked by an ester linkage to at least one segment (II) which is a monoester or polyester obtained by alternating ring-opening addition to Segment (I) of an organic dicarboxylic anhydride and a 1,2-epoxide in the presence of a catalyst for such addition.
2. The sizing agent for carbon fibers as claimed in claim 1 characterized in that Component A includes one or more epoxy compounds selected from the group consisting of bisphenol-A diglycidyl ether, bisphenol-A diglycidyl ether polymer, epoxy cresol novolac resins, epoxy phenol novolac resins N,N,N',N'-tetraglycidyl-m-xylylene diamine, N,N,N',N'-tetraglycidyl diaminodiphenylmethane, N,N,N',N'-tetraglycidyl bis[aminomethyl]cyclohexane and m-N,N,-diglycidyl-aminophenyglycidyl ether.
 3. The sizing agent for carbon fibers as claimed in claim 1 or 2 characterised in that said segment (I) of component B which is an oxyalkylene derivative of a polycyclic phenol is selected from the group consisting of polyoxyalkylene poly(phenyl-methylated)phenylethers, polyoxyalkylene poly(phenyl-ethylated) phenylethers and bisphenol-polyethylene glycol copolymers.
 4. The sizing agent for carbon fibers as claimed in claim 1 characterised in that said organic dicarboxylic anhydride includes an unsaturated dicarboxylic anhydride.
 5. The sizing agent for carbon fibers as claimed in claim 1 or 5 characterised in that said 1,2-epoxide is selected from the group consisting of ethylene oxide, propylene oxide and butylene oxide.
 6. The sizing agent for carbon fibers as claimed in any one preceding claim characterised in that more than 95 molar % of the terminal groups of said monoester or polyester segment (II) of said Component B are carboxylic groups.
 7. The sizing agent for carbon fibers as claimed in any one preceding claim characterised in that terminal groups of said monoester or polyester segment (II) of said Component B are capped by one or more ethylenically groups, unsaturated epoxy groups or isocyanate groups.
 8. The sizing agent for carbon fibers as claimed in any one preceding claim characterised in that the weight ratios are Component A/Component B = 10-90/90-10 and Component C/Component A+B = 10-40/90-60.

Patentansprüche

1. Schlichtemittel für Kohlenstoffasern, das eine Komponente A, eine Komponente B und eine Komponente C enthält, dadurch gekennzeichnet, daß die Komponente A eine Epoxyverbindung, die Komponente B ein Copolymer auf der Basis eines Oxyalkylenderivats eines polyzyklischen Phenols und die Komponente C ein Oxyalkylenderivat von substituiertem Phenol mit der allgemeinen Formel



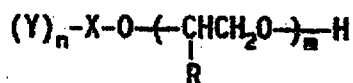
- ist, wobei Y eine Alkylgruppe, eine Phenylmethylgruppe oder Phenylethylgruppe mit 1-12 Kohlenstoffatomen, X ein Benzolrest, Diphenylrest oder Cumylbenzolrest, R ein Wasserstoffatom oder eine Methylgruppe, n eine ganze Zahl im Bereich von 1-5, und m eine ganze Zahl im Bereich von 4-100 ist; dadurch gekennzeichnet, daß die Moleküle der Copolymerverbindung B ein Segment (I) aufweisen, welches das Oxyalkylenderivat des polyzyklischen Phenols ist, das über eine Esterbindung an mindestens ein Segment (II) gebunden ist, welches ein Monoester oder Polyester ist, den man durch alternierende Ringöffnungsanlagerung eines organischen Dicarbonsäureanhydrids und eines 1,2-Epoxids an das Segment (I) in Gegenwart eines Katalysators für diese Anlagerung erhält.



2. Schlichtemittel für Kohlenstoffasern nach Anspruch 1, dadurch gekennzeichnet, daß die Komponente A eine oder mehrere Epoxyverbindungen enthält, die aus der Gruppe ausgewählt sind, die aus Bisphenol-A-diglycidylether, Bisphenol-A-diglycidyletherpolymer, Epoxycresol-Novolakharzen, Epoxyphenol-Novolakharzen, N,N,N',N'-tetraglycidyl-m-xylylendiamin, N,N,N',N'-tetraglycidyl-diaminodiphenylmethan, N,N,N',N'-tetraglycidylbis[aminomethyl]cyclohexan und m-N,N-diglycidyl-aminophenylglycidylether besteht.
3. Schlichtemittel für Kohlenstoffasern nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Segment (I) der Komponente B, das ein Oxyalkylenderivat eines polyzyklischen Phenols ist, aus der Gruppe ausgewählt wird, die aus polyoxyalkylen-poly(phenyl-methylierten) Phenylethern, polyoxyalkylen-poly(phenyl-ethylierten) Phenylethern und Bisphenol-polyethylenglycol-Copolymeren besteht.
4. Schlichtemittel für Kohlenstoffasern nach Anspruch 1, dadurch gekennzeichnet, daß das organische Dicarbonsäureanhydrid ein ungesättigtes Dicarbonsäureanhydrid einschließt.
5. Schlichtemittel für Kohlenstoffasern nach Anspruch 1 oder 5, dadurch gekennzeichnet, daß das 1,2-Epoxyd aus der Gruppe ausgewählt ist, die aus Ethylenoxid, Propylenoxid und Butylenoxid besteht.
6. Schlichtemittel für Kohlenstoffasern nach irgendeinem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß mehr als 95 Mol-% der Endgruppen des Monoester- oder Polyestersegments (II) der Komponente B Carboxylgruppen sind.
7. Schlichtemittel für Kohlenstoffasern nach irgendeinem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß Endgruppen des Monoester- oder Polyestersegments (II) der Komponente B von einer oder mehreren Ethylengruppen, ungesättigten Epoxygruppen oder Isocyanatgruppen abgeschlossen werden.
8. Schlichtemittel für Kohlenstoffasern nach irgendeinem der vorstehenden Ansprüche, gekennzeichnet durch die Gewichtsverhältnisse Komponente A/Komponente B = 10-90/90-10 und Komponente C/Komponente A + B = 10-40/90-60.

Revendications

1. Agent d'apprêtage pour fibres de carbone contenant le Composant A, le Composant B et le Composant C, caractérisé en ce que le composant A est un composant époxy, le Composant B est un copolymère basé sur un dérivé oxyalkylénique d'un phénol polycyclique et le Composant C est un dérivé oxyalkylénique d'un phénol substitué représenté par la formule générale



dans laquelle Y est un groupement alkyle, un groupement phényl-méthyle ou un groupement phényl-éthyle ayant de 1 à 12 atomes de carbone, X est un reste de benzène, un reste de diphenyle ou un reste de cumylbenzène, R est un atome d'hydrogène ou un groupement méthyle, n est un nombre entier dans la plage de 1 à 5 et m est un nombre entier dans la plage de 4 à 100, caractérisé en ce que les molécules du composé copolymère B possède un segment (I) qui est le dérivé oxyalkylénique du phénol polycyclique lié par une liaison ester à au moins un segment (II) qui est un monoester ou un polyester obtenu par addition sur ouverture de cycle alternante au segment (I) d'un anhydride dicarboxylique organique et à un 1,2-époxyde en présence d'un catalyseur pour une telle addition.

2. Agent d'apprêtage pour fibres de carbone tel que revendiqué dans la revendication 1, caractérisé en ce que le Composant A comprend un ou plusieurs composés époxy choisi dans le groupe constitué par le diglycidylether bisphénol-A, le polymère de diglycidylether bisphénol-A, les résines novolaques d'époxy crésol, les résines novolaques d'époxy phénol, la N, N, N', N'-tétraglycidyl-m-xylylène diamine, le N, N,



N', N'-tétraglycidyl diaminodiphénylméthane, le N, N, N', N'-tétraglycidyl bis[aminométhyl] cyclohexane et le m-N, N,-diglycidyl aminophényl-glycidyl éther.

- 5 3. Agent d'apprêtage pour fibres de carbone tel que revendiqué dans la revendication 1 ou 2, caractérisé en ce que ledit segment (I) du composant B qui est un dérivé oxyalkylénique d'un phénol polycyclique est choisi dans le groupe constitué par les poly(phényl-méthyl) phénoxy polypolyalkylènes, les poly-(phényl-éthyl) phénoxy polyoxyalkylènes et les copolymères de bisphénol-polyéthylène et de glycol.
- 10 4. Agent d'apprêtage pour fibres de carbone tel que revendiqué dans la revendication 1, caractérisé en ce que l'anhydride dicarboxylique organique comprend un anhydride dicarboxylique non saturé.
- 15 5. Agent d'apprêtage pour fibres de carbone tel que revendiqué dans la revendication 1 ou 5, caractérisé en ce que ledit 1,2-époxyde est choisi dans le groupe constitué par l'oxyde d'éthylène, l'oxyde de propylène et l'oxyde de butylène.
6. Agent d'apprêtage pour fibres de carbone tel que revendiqué dans l'une quelconque des revendications précédentes, caractérisé en ce que plus de 95% molaires des groupements terminaux dudit segment de monoester ou de polyester (II) dudit Composant B sont des groupements carboxyliques.
- 20 7. Agent d'apprêtage pour fibres de carbone tel que revendiqué dans l'une quelconque des revendications précédentes, caractérisé en ce que les groupements terminaux dudit segment de monoester ou de polyester (II) dudit Composant B sont coiffés par un ou plusieurs groupements à insaturation éthylénique, groupements époxy ou groupements isocyanates.
- 25 8. Agent d'apprêtage pour fibres de carbone tel que revendiqué dans l'une quelconque des revendications précédentes, caractérisé en ce que les rapports pondéraux Composant A/Composant B = 10-90/90-10 et Composant C/Composants A + B = 10-40/90-60.
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