

Description

THIS INVENTION relates to sizing agents for carbon fibers.

Carbon fibers reinforced plastics (CFRP), which are composites of carbon fibers with matrix resins such as epoxy resins, unsaturated polyester resins and polyamide resins, are among the most desirable materials from the point of view of specific modulus and specific strength and are rapidly coming into use in aerospace and other industries because of their superior qualities and light weight.

Carbon fibers which are used for the production of CFRP are unidirected into the form of filaments or tows and are combined with matrix resin after they are made into strands or woven or knitted into sheets.

10 Since carbon fibers are basically brittle and do not elongate easily, fluffs tend to be produced by mechanical friction during processing if the fibers are used directly without any pretreatment. Difficulty of handling becomes a problem and the mechanical properties of the CFRP obtained from damaged fibers is also adversely affected.

15 It is therefore a common practice to coat such carbon fibers with a sizing agent in order to improve their cohesiveness and abrasion resistance. This invention relates to such sizing agents for carbon fibers which will subsequently be combined with an unsaturated polyester matrix resin.

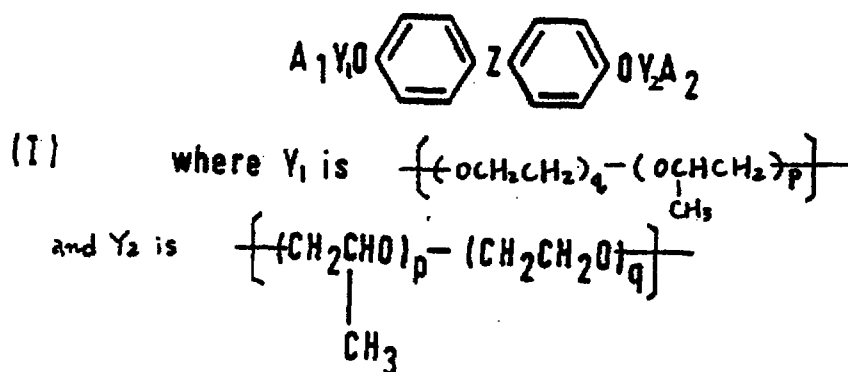
20 Examples of prior art sizing agents for coating carbon fibers include those which use epoxidized polybutadiene (JP-B-56-4335), those which use a mixture of bisphenol diglycidyl ether and a prepolymer derived from diallyl phthalate (JP-B-59-228083), those of a water emulsion type having as indispensable constituents an epoxy resin, a condensation product of an unsaturated dibasic acid and oxyalkylated bisphenol, and oxyalkylene derivative of phenol (US-A-4 167 538), those using an unsaturated epoxy compound as a coupling agent (US-A-4 163 003), and those which use a sizing agent obtained from the reaction of bisphenol-alkylene oxide adduct between alkylene oxide and maleic anhydride (JP-A-63092780).

25 Although these prior art sizing agents have advantages, they still give rise to serious problems, because of poor mechanical properties (such as fluffs and yarn breakage) at the time of weaving. These arise because of the low cohesiveness and abrasion resistance of the carbon fibers. There is also danger of toxicity and flammability because an organic solvent is used. Subsequently, the prior art sizing agents give low interlaminar shear strength (ILSS) of the CFRP produced because of the poor adhesiveness between carbon fibers and unsaturated polyester matrix resins.

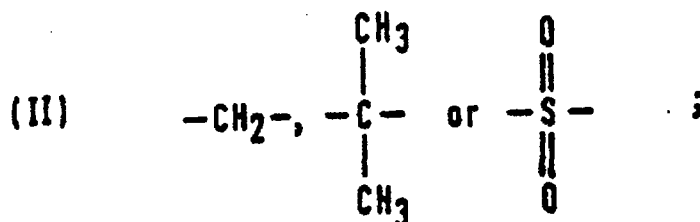
30 The present invention sets out to provide a new sizing agent for carbon fibers with which the problems discussed above can be reduced or eliminated.

The present invention is based on the discovery that bisphenol-polyalkylene glycol etherester copolymers of a special kind are desirable compounds in sizing agents.

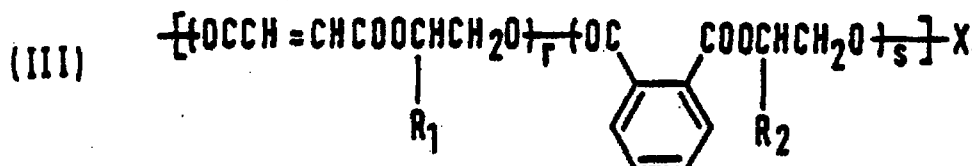
35 This invention relates to sizing agents for coating carbon fibers to be used in preparing composites based on an unsaturated polyester matrix resin. The sizing agent contains a bisphenol-polyalkylene glycol etherester copolymer shown by the following formula:



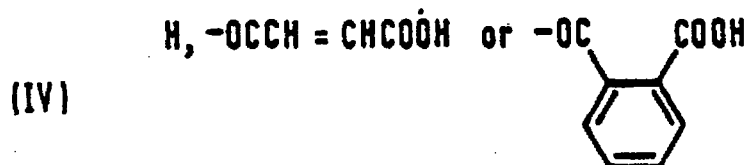
the segments inside parentheses in Y_1 and Y_2 being in each case a block or random copolyether when p is an integer 1-10 and q is an integer 1-20, or a homopolyether when p or q is 0; and $(p+q)$ being equal to or greater than 1; and Z is



10 characterised in that A_1 and A_2 may be identical or different and are



20 R_1 and R_2 being identical or different and H or CH_3 ; X being



30 the segments inside parentheses of A_1 or A_2 being in each case a block or random copolyester when r is an integer 1 - 14, or a homopolyester when r is 0; s being an integer 1-15; and $(r+s)$ being equal to or smaller than 15 and equal to or greater than 1.

Compounds of the present invention shown by the aforementioned formula are polyesters synthesizable from polyoxyalkylene bisphenol ether, maleic acid anhydride and/or phthalic acid anhydride and alkylene oxide. In the formula, propylene oxide (abbreviated as PO) and ethylene oxide (abbreviated as EO) in Y (that is, the polyoxyalkylene part) are block and random copolyethers. The repetition number r of the polyester part may be zero or in the range of 1 - 14 and the repetition number s of the polyester part may be in the range of 1 - 15 but their preferable range is 2- 6 in order to satisfy both requirements of affinity with unsaturated polyester matrix resins and wettability of carbon fibers.

40 In addition to a bisphenol-polyalkylene glycol etherester of the type shown above, the sizing agent according to the present invention may also contain, if necessary, a prior art sizing agent, a lubricant, an emulsifier and the like appropriately as long as the effects achievable by the present invention are not affected. Examples of prior art sizing agent which may be contained include epoxy compounds such as bisphenol -A diglycidyl ethers, epoxy phenol novolac resins, and N,N,N',N'-tetraglycidyl diaminodiphenylmethane. Examples of lubricant include aliphatic esters such as stearyl laurate and oleyl oleate. Examples of emulsifier include those obtainable by block or random addition of EO and/or PO to a phenol compound such as alkyl phenol, phenylethylated phenol, phenylethylated phenylphenol, phenylethylated cumylphenol, phenylmethylated phenol and phenylmethylated cumylphenol. More specifically, examples of emulsifier include non-ionic surfactants such as polyoxyethylene (6mol) nonylphenylether, polyoxyethylene (70mol) styrenated (5mol) cumylphenylether, and polyoxyethylene (30mol) tribenzylated phenylether. The sizing agent of the present invention typically contains a compound shown by aforementioned formula in an amount of 50wt% or greater (more preferably 70wt% or greater) and an emulsifier of the aforementioned type in an amount of 30wt% or less.

55 Matrix resins to which the sizing agent of the present invention is applicable are unsaturated resins with polyester linkages and include α,β - unsaturated polyester resins and vinyl ester resins. The afore-mentioned α,β -unsaturated polyester resins can be obtained by dissolving in a styrene monomer or another vinyl monomer an unsaturated polyester obtainable by condensation of α,β -unsaturated dicarboxylic acid and glycol. Saturated dicarboxylic acid or aromatic dicarboxylic acid may be used supplementarily as the dibasic carboxylic acid.

Examples of α,β -unsaturated dicarboxylic acid include maleic acid, fumaric acid, itaconic acid, citraconic acid and anhydrides of these dicarboxylic acids. Examples of dicarboxylic used supplementarily include succinic acid, phthalic anhydride, o-phthalic acid, isophthalic acid and terephthalic acid.

Examples of glycol include ethylene glycol, 1,2-propylene glycol and 1,3-propylene glycol.

Examples of olefinic unsaturated monomer include styrene, vinyl toluene, divinyl benzene and esters of acrylic acid or methacrylic acid such as methyl methacrylate, butyl acrylate, and trimethylolpropane trimethacrylate.

The aforementioned vinyl ester resins can be obtained by esterification of epoxy resin and acrylic acid or methacrylic acid. Examples of epoxy resins are diglycidyl ethers of bisphenol A derived from bisphenol A and epichlorohydrin, cresol-novolac epoxy resins and phenol-novolac epoxy resins. Novolac resins are produced by reacting phenol or a substituted phenol with formaldehyde in acid solution. The novolacs suitable for reaction with epichlorohydrin contain from about 2 to 6 phenolic hydroxyl groups.

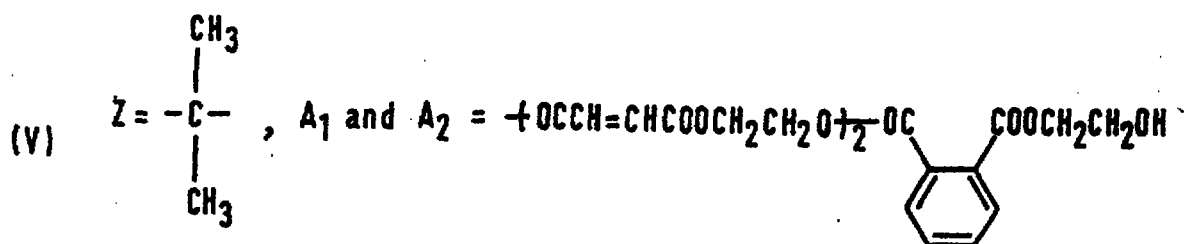
These vinyl ester resins have acrylate or methacrylate groups on its terminals. The main chain of these vinyl ester resins is constituted from a bisphenol or novolac molecular structure.

The proportion at which a sizing agent of the present invention would be attached to carbon fibers is generally 0.1-5.0wt% with respect to the carbon fibers and more particularly 0.5-3.0wt%. Application in the form of a water dispersant is favourable but use may also be made of appropriate organic solvents. The preferred concentration of sizing solution, when it is used, is 0.5-5wt%. The amount finally attached to carbon fibers may be controlled by a mangle roller after impregnation or by the rotational velocity of an oiling roller and the coating density. After attachment, an appropriate method may be used for drying to complete a sizing process.

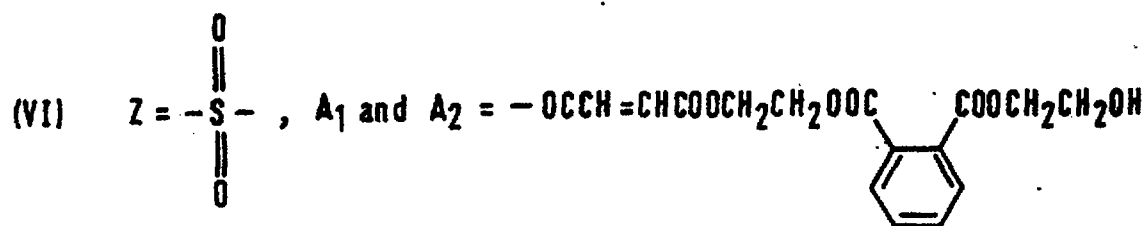
Sizing agents of the present invention are particularly effective on carbon fibers from pitch and carbon fibers obtained by heating a precursor of acrylic filaments. They can eliminate or greatly reduce the problems of prior art agents and significantly improve the processability of carbon fibers in later processing steps. For example, they can reduce fluffs and yarn breakage while carbon fiber filaments and tows are wound up or during a weaving process although they are bent repeatedly by guides and rollers. Being thus provided with superior cohesiveness and lubricity, the treated carbon fiber yarns can be wound and woven more speedily and this contributes to improved productivity. Moreover, no organic solvent is needed and the sizing agents can be applied to carbon fibers directly or as a uniform stable aqueous emulsion with only a small amount of non-ionic surfactant. This makes them advantageous from the point of view of hygiene and operator safety. In addition to these advantages, sizing agents of the present invention have superior adhesiveness to carbon fibers and matrix resins and hence can improve the interlaminar shear strength of the produced CFRP.

In what follows, test results are described in order to show the effects of the present invention more clearly. For this purpose, the following ten bisphenol-polyalkylene glycol etherester copolymers (P-1 through P-10) defined by the formula given above were prepared:

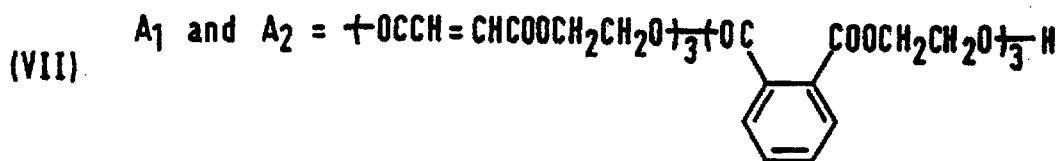
(i) P-1 with $p=0, q=5$,



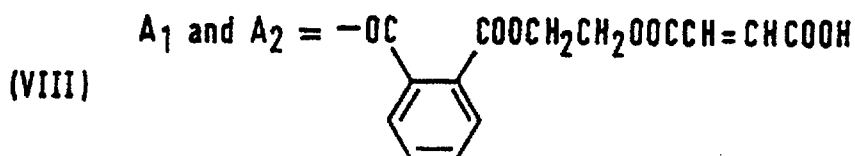
(ii) P-2 with $p=2, q=7$, random



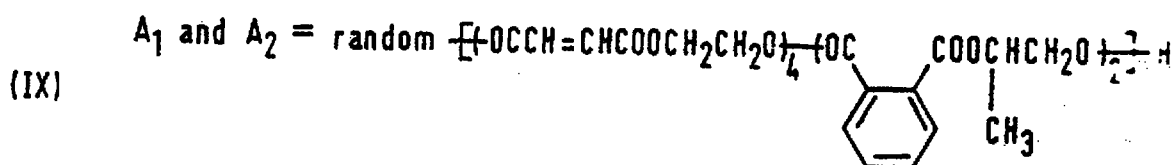
(iii) P-3 h with $p = 0, q = 5$ as in P-1,



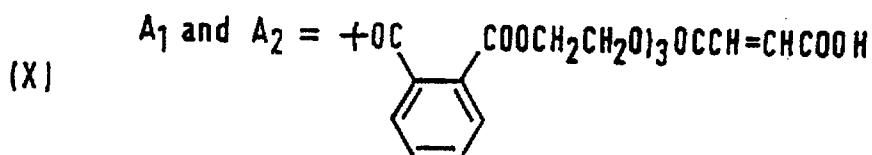
(iv) P-4 with $p = 0, q = 4, Z$ as in P-1,



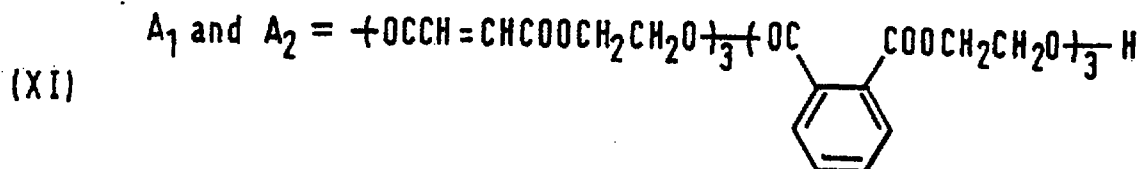
(v) P-5 with $p = 0, q = 5, z$ as in P-1,



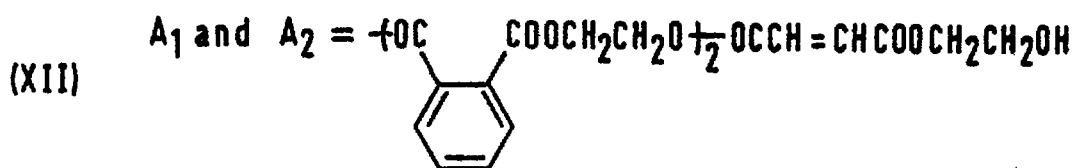
(vi) P-6 with $p = 0, q = 2, Z$ as in P-1,



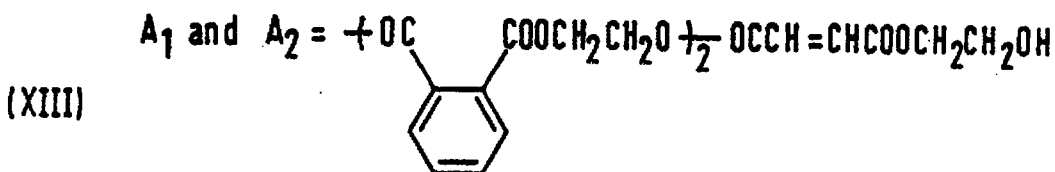
(vii) P-7 with $p = 5, q = 8, \text{random}, Z$ as in P-1,



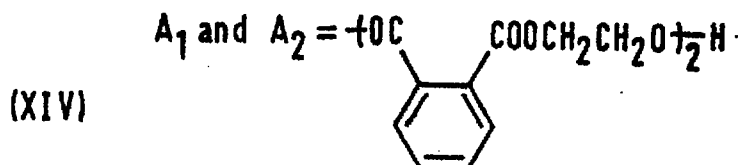
(viii) P-8 with $p = 2, q = 0, Z$ as in P-1,



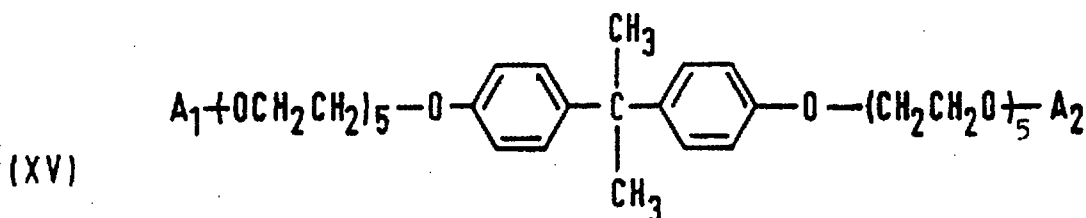
(ix) P-9 with $p=2, q=4$, block X as in P-1,



(x) P-10 with $p=1, q=0, Z$ as in P-1,



The chemical formula for P-5 for example, is



where A_1 and A_2 are groups as shown above with a random linkage inside the outer parentheses.

Synthesis of P - 1:

1335g (2.0 mol) of EO (10mol) adduct of bisphenol-A, 592g (4.0mol) of phthalic acid anhydride, 784g (8.0mol) of maleic acid anhydride and 1.0g of tetramethyl ammonium bromide as catalyst were placed inside a 5-liter autoclave and agitated at 120-125 °C for 30 minutes. Thereafter, 535g (12.16mol) of EO was infused at 125 °C over a period of four hours for a reaction and a light brown viscous liquid (A-1) was obtained as reaction product. Its acid value was 3.6 and its (polystyrene-converted) average molecular weight by GPC (gel permeation chromatography) was 1700. P-2 through P-10 were also synthesized in similar manners and sizing liquids (Test Examples 1 - 10 and Comparison Examples 1 - 4) shown in Table 1 were prepared therefrom for testing. Tests conducted therewith are described below and results are shown in Table 2.

To test stability of emulsion, each sizing liquid with 20 percent solid component (Comparison Example 4 having been adjusted to 20 percent solid component) was left for seven days at 20 °C and their separation conditions were evaluated as follows:

A = no separation

B = creamy separation floating,

C = precipitation,

D = both creamy separation and precipitation

Unsize carbon fibers obtained by heating a precursor of acrylic filaments (7μ/6000 filaments) were impregnated by each sizing liquid by dipping such that the attached effective component was 1.3wt%. After they were squeezed by rollers and dried, they were subjected to a heat treatment inside an oven at 150 °C for 30 minutes. Fiber-metal rubbing friction was tested with each of these sized carbon fibers by means of a TM type yarn friction and rubbing tester (product of Dalei Kagaku Seiki Company) with a load of 110g/6000 filaments, $\theta = 150^\circ$, rubbing distance = 30mm and by moving a metallic comb 500 times reciprocatingly at the rate of 150 times/min. In addition, a rubbing tester (product of Toyo Seiki Company) was used with internal angle about 35°, one twist, running distance = 20 mm and by 500 times of reciprocating motion at

the rate of 100 times/min. to examine fiber-fiber friction. Results of these examinations were evaluated as follows:-

- A = hardly any fluffs or yarn breakages
- B = fluffs appearing only singly
- C = fluffs and yarn breakages appearing collectively
- D = many fluffs and yarn breakages with a cut at one place
- E = 6000 filaments cut

Carbon fibers which has been sized as above were unidirected and impregnated uniformly with a resin mixture composed of 100 weight parts of RIPOXY R - 802 (produced by Showa Kobunshi Company) which is a vinyl ester resin, 1 weight part of tertiary butylperbenzoate and 1 weight part of butylbenzoate peroxide to produce unidirected composites by a molding method ($130^{\circ}\text{C} \times 7\text{kgcm}^2 \times 1\text{ hour}$). Their carbon fiber contents were 60 volume percent and their dimensions were 2.5mm (thickness) $\times$ 6mm (width) $\times$ 17mm (length). The interlaminar shear strength of each composite was measured with the ratio of span/thickness = 5.

The results demonstrated in Table 2 clearly show that sizing agents according to the present invention have superior emulsion stability, provide significantly reduced fluffs and yarn breakages, confer improved processability of carbon fibers and result in increased interlaminar shear strength of the CFRP produced from sized carbon fibers.

TABLE 1

	Test Examples										Comparison			
	1	2	3	4	5	6	7	8	9	10	1	2	3	4
P-1	18													
P-2		20												
P-3			17											
P-4				19										
P-5					19									
P-6						18								
P-7							17,5							
P-8								16						
P-9									18					
P-10										18				
*1											1.7			
*2												2.0		
*3													1.0	30
*4													0.5	
*5														20
*6														5
*7							0.5	1						
*8	2		2	1	1	2	2.0	3	2	2				
water	80	80	80	80	80	80	80	80	80	80				45
acetone											98.3		98.5	
*9												98.0		

Notes: Numbers in table represent wt%

- *1: Epoxidized polybutadiene (BF-1000 produced by Adeka Argus Chemical).
- *2: Allyl glycidyl ether
- *3: Bisphenol-A diglycidyl ether (Epikote 828 produced by Yuka Shell Chemical : Epoxy equivalent of 190).
- *4: Diallyl phthalate prepolymer (Daisodap A produced by Osaka Soda.
- *5: Condensate of 2.0mol of polyethylene glycol (2mol) added bisphenol A, 1.5mol of maleic acid and 0.5mol of sebacic acid.
- *6: Polyoxyethylene (70mol) penta (phenyl ethylated) cumyl phenyl ether.
- *7: Polyoxyethylene (6mol) nonylphenyl ether
- *8: Polyoxyethylene (30mol) tribenzylated phenol
- *9: Ethylene dichloride

TABLE 2

Fluffs, Yarn Breakage				
Examples	TM Test	Rubbing Test	ILSS (Kg/mm ²)	Emulsion Stability
Test				
1	A	B	8.2	A
2	A	A	8.5	A
3	B	A	8.5	A
4	A	A	8.6	A
5	A	A	8.4	A
6	A	A	8.6	A
7	A	A	8.5	A
8	A	B	8.5	A
9	A	A	8.5	A
10	B	A	8.4	A
Comparison				
1	D	D	7.0	-
2	E	E	6.8	-
3	C	B-C	7.0	-
4	C	B	7.5	A

Claims

1. A sizing agent for carbon fibers, the sizing agent containing a bisphenol-polyalkylene glycol etherester copolymer shown by the following formula:



(I) where Y_1 is $\left[\text{-(OCH}_2\text{CH}_2\text{)}_q \text{-(OCH(CH}_3\text{)}\text{CH}_2\text{)}_p \right]$

and Y_2 is $\left[\text{-(CH}_2\text{CHO)}_p \text{-(CH}_2\text{CH}_2\text{O)}_q \right]$

the segments inside parentheses in Y_1 and Y_2 being in each case a block or random copolyether when P is an integer 1-10 and q is an integer 1-20, or a homopolyether when p or q is 0; and $(p+q)$ being equal to or greater than 1; and Z is



TABLE 2

Fluffs, Yarn Breakage				
Examples	TM Test	Rubbing Test	ILSS (Kg/mm ²)	Emulsion Stability
Test				
1	A	B	8.2	A
2	A	A	8.5	A
3	B	A	8.5	A
4	A	A	8.6	A
5	A	A	8.4	A
6	A	A	8.6	A
7	A	A	8.5	A
8	A	B	8.5	A
9	A	A	8.5	A
10	B	A	8.4	A
Comparison				
1	D	D	7.0	-
2	E	E	6.8	-
3	C	B-C	7.0	-
4	C	B	7.5	A

Claims

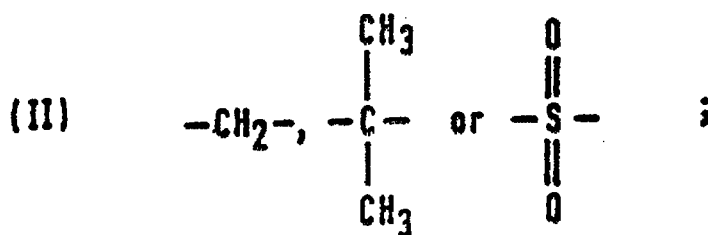
1. A sizing agent for carbon fibers, the sizing agent containing a bisphenol-polyalkylene glycol etherester copolymer shown by the following formula:



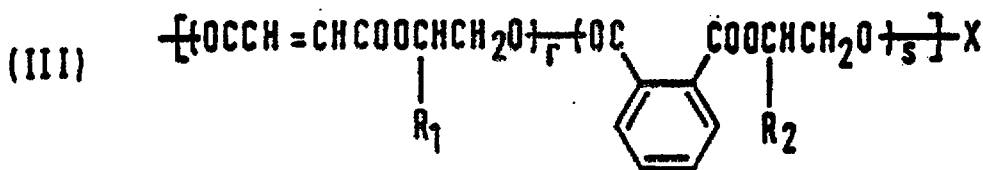
(I) where Y_1 is $\left[(-OCH_2CH_2)_q - (OCH(CH_3)CH_2)_p \right]$

and Y_2 is $\left[(CH_2CHO)_p - (CH_2CH_2O)_q \right]$

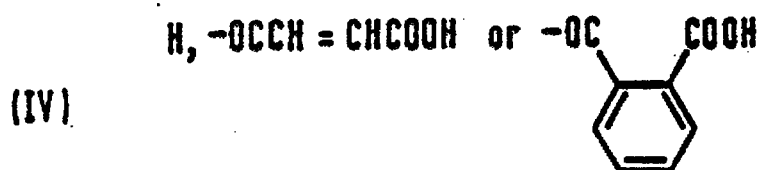
the segments inside parentheses in Y_1 and Y_2 being in each case a block or random copolyether when P is an integer 1-10 and q is an integer 1-20, or a homopolyether when p or q is 0; and $(p+q)$ being equal to or greater than 1; and Z is



characterized in that A₁ and A₂ may be identical or different and are



R₁ and R₂ being identical or different and H or CH₃;
X being



the segments inside parentheses in A₁ and A₂ being in each case a block or random copolyester when r is an integer 1 - 14, or a homopolyester when r is 0; s being an integer 1 - 15; and (r+s) being equal to or smaller than 15 and equal to or greater than 1.

2. A sizing agent as claimed in claim 1 characterized in that both r and s are from 2 to 6.

3. A sizing agent as claimed in claim 1 or 2 characterized by further containing one or more of prior art sizing agents, lubricants or emulsifiers.

4. A sizing agent as claimed in claim 3 characterized by containing at least 70% by weight of the said bisphenol-polyalkylene glycol etherester copolymer and correspondingly not more than 30% by weight of the said emulsifier

5. A carbon fibre material characterized by having attached thereto 0.1 to 5.0% by weight of a sizing agent as claimed in any one preceding claim.

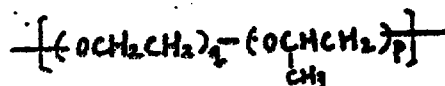
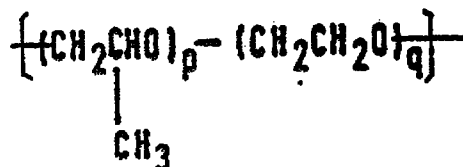
6. A CFRP (carbon fibers reinforced plastics) composite characterised by comprising the carbon fibre as claimed in claim 5 with an α,β-unsaturated polyester resin or a vinyl ester resin.

Patentansprüche

1. Schlichtemittel für Kohlefasern, wobei das Schlichtemittel ein Bisphenol-Polyalkylenglykolether/Polyalkylenglykolester-Copolymer der folgenden Formel enthält:

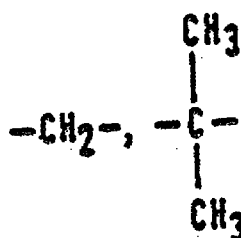


(I)

worin Y_1 bedeutet und Y_2 

bedeutet, wobei das Segment innerhalb der Klammern von Y_1 und Y_2 jeweils ein Blockcopolyether oder ein Copolyether mit zufälliger Verteilung ist, wenn p eine ganze Zahl von 1 bis 10 und q eine ganze Zahl von 1 bis 20 ist, oder ein Homopolyether, wenn p oder q gleich 0 ist, und wobei $(p + q)$ gleich oder größer 1 ist; und worin Z

(II)

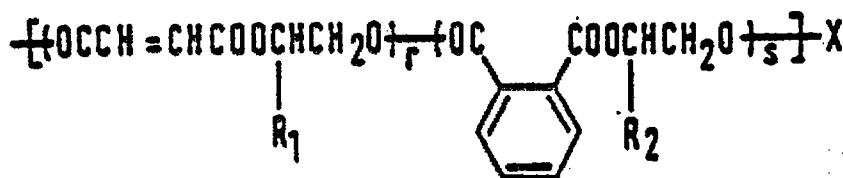


oder



ist, dadurch gekennzeichnet, daß A_1 und A_2 gleich oder verschieden sein können und

(III)



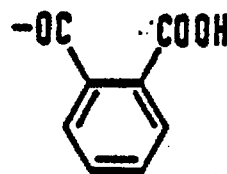
sind, wobei R_1 und R_2 gleich oder verschieden sind und H oder CH_3 bedeuten, und X



(IV)



oder

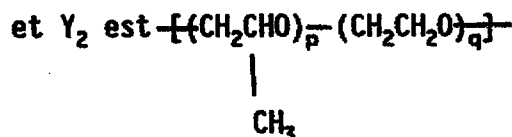
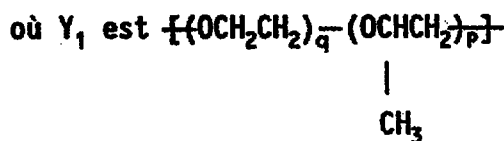


ist, wobei das Segment innerhalb der Klammern von A_1 und A_2 jeweils ein Block-Copolyester oder ein Copolyester mit zufälliger Verteilung ist, wenn r eine ganze Zahl von 1 bis 14 ist, oder ein Homopolyester, wenn r gleich 0 ist, und wobei s eine ganze Zahl von 1 bis 15 und $(r+s)$ gleich oder kleiner als 15 und gleich oder größer als 1 ist.

2. Schlichtemittel nach Anspruch 1, dadurch gekennzeichnet, daß sowohl r als auch s eine ganze Zahl von 2 bis 6 bedeuten.
3. Schlichtemittel nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß es ferner bekannte Schlichtemittel, Schmiermittel und/oder Emulgatoren enthält.
4. Schlichtemittel nach Anspruch 3, dadurch gekennzeichnet, daß es wenigstens 70 Gew.-% Bisphenol-Polyalkylenglykoether/Polyalkylenglykolester-Copolymer und dementsprechend nicht mehr als 30 Gew.-% Emulgator enthält.
5. Kohlefasermaterial, dadurch gekennzeichnet, daß 0,1 bis 5 Gew.-% eines Schlichtemittels gemäß einem der vorstehenden Ansprüche darauf aufgebracht sind.
6. CFRP (Kohlefaserverstärkter Kunststoff)-Verbundwerkstoff, dadurch gekennzeichnet, daß der Verbundwerkstoff die Kohlefaser gemäß Anspruch 5 und ein α,β -ungesättigtes Polyesterharz oder ein Vinylsterharz umfaßt.

Revendications

1. Agent d'ensimage pour les fibres de carbone, l'agent d'ensimage contenant un copolymère de bisphénol-polyalkylène glycol à fonctions éther et ester représenté par la formule suivante:



les segments entre parenthèses dans Y_1 et Y_2 étant, dans chaque cas, un copolyéther bloc ou aléatoire lorsque p est un nombre entier de 1-10 et q est un nombre entier de 1-20, ou un homopolyéther lorsque p ou q est 0 et l'ensemble $(p+q)$ étant égal à ou supérieur à 1; et Z est


$$\text{---} \left[\text{OCCCH}=\text{CHCOOCHCH}_2\text{O} \right]_r \text{---} \left[\text{OC} \begin{array}{c} \text{COOCHCH}_2\text{O} \\ | \\ \text{R}_2 \end{array} \text{---} \text{C}_6\text{H}_4 \text{---} \text{C} \begin{array}{c} | \\ \text{R}_1 \end{array} \right]_s \text{---} \text{X} \quad (\text{III})$$

H, $-\text{OCCH}=\text{CHCOOH}$ ou  (IV)

2. Agent d'ensimage tel que revendiqué dans la revendication 1, caractérisé en ce que r et s sont tous les deux de 2 à 6.
3. Agent d'ensimage tel que revendiqué dans la revendication 1 ou 2, caractérisé en ce qu'il contient en outre un ou plusieurs agents d'ensimage, lubrifiants ou émulsifiants de la technique antérieure.
4. Agent d'ensimage tel que revendiqué dans la revendication 3, caractérisé en ce qu'il contient au moins 70% en poids dudit copolymère de bisphénol-polyalkylène glycol à fonctions éther et ester et, à l'avenant, pas plus de 30% en poids dudit émulsifiant.
5. Matériau en fibre de carbone caractérisé en ce qu'il contient y attaché de 0.1 à 5.0% en poids d'un agent d'ensimage tel que revendiqué dans l'une quelconque des revendications précédentes.
6. Composite CFRP (matières plastiques renforcées par des fibres de carbone) caractérisé en ce qu'il comprend la fibre de carbone telle que revendiquée dans la revendication 5 avec une résine de polyester α, β -non saturé ou une résine d'ester vinylique.