

Description

The present invention relates to the use of a glass fiber product in the reinforcement of fluororesin which is improved in adhesiveness to fluoroplastic.

Fluororesins are different from other plastic materials in that they have an excellent heat resistance, chemical resistance and dielectric property. For this reason, fluoroplastics are used in various fields.

Originally, a fluororesin is a soft material. In order to compensate for this softness, inorganic fillers such as glass fibers, graphite or molybdenum disulfide are used. Among these inorganic fillers, glass fibers are most conventionally used in the field of electrical industry, because they are inexpensive and have excellent electrical properties. Further, glass fibers greatly improve the mechanical characteristics such as abrasion resistance, creep resistance and elastic modulus. However, glass fibers are disadvantageous in that the minute gap formed at the interface between the glass fibers and fluoroplastic causes a deterioration in insulation resistance.

The problem of deterioration in insulation resistance makes the greatest trouble in expanding the use of this material in the field of electrical industry.

With the aim of overcoming this disadvantage, various attempts have been made up to today. They are:

(1) An attempt to use glass fibers in the state of carrying greige goods on its surface, expecting that the interfacial adhesion will be improved owing to the baking effect (the so-called scorching) of the greige goods at the molding temperature of fluoroplastics (350 °C to 400 °C).

(2) An attempt to use greige goods of glass fibers in a state of appropriate scorching without burning them completely, expecting that the adhesion will be improved by the same effect as in (1).

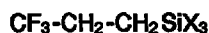
(3) An attempt to apply the hitherto known general silane couplers (for example, a blend of silane couplers, a blend of a silane coupler and a primer such as a silicone resin primer or a fluororesin primer).

However, none of these attempts could exhibit any significant effect.

A glass fibre product which is pre-treated with perfluoroalkylsilane is already known from GB-A-1 107 443.

It is the object of the present invention to provide a glass fiber for use in the reinforcement of fluororesin, which is improved in the adhesiveness to fluororesin.

The present invention is directed to the use of a glass fibre product which is pretreated with a perfluoroalkylsilane represented by the following formula:



wherein X represents a hydrolyzable group such as an alkoxy group having 1 to 4 carbon atoms for the reinforcement of a fluororesin.

The present invention makes it possible to improve the adhesion of glass fibers to fluororesin to a great extent and to prevent the deterioration in insulation resistance.

The perfluoroalkylsilanes which can be employed in the present invention include 3,3,3-trifluoropropyltrimethoxysilane, 3,3,3-trifluoropropyltriethoxysilane, 3,3,3-trifluoropropyltri(β-methoxyethoxy)silane. As the "X₃", -Cl₃ is also usable in place of said alkoxy groups having 1 to 4 carbon atoms.

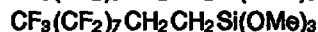
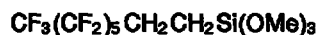
The amount of perfluoroalkylsilane used in the invention varies depending on the kind of glass fiber product. However, it is usually 0.2 to 3.0% (by weight, hereinafter the same) and preferably 0.5 to 2.0%, as expressed in terms of the concentration of the treating solution. Further, the amount is usually 0.06 to 0.50% and preferably 0.10 to 0.35%, as expressed in terms of the amount attached to the glass fibers. In carrying out the surface treatment, some contrivance, such as preparing a solution of the perfluoroalkylsilane in an organic solvent is necessary, because these perfluoroalkylsilanes are relatively poor in water-solubility. The pH should be 4 or below, and preferably in the range of 2 to 4. As the organic solvent, methanol is particularly preferable. The concentration of the organic solvent in the solution is preferably 30 to 40% by weight. Ordinary surface treatment processes for glass fibers, such as dipping, roll coating, or spraying, may be adopted in the invention.

As the glass fiber usable in the invention, E glass (non-alkali glass for electrical use), S glass (high strength glass), D glass (low dielectric constant glass), quartz glass, A glass (acid resistant glass) and C glass (alkali-containing glass for chemical use) can be referred to.

As the glass fiber product, glass fabric, glass tape, glass yarn, glass mat, glass paper and glass powder can be referred to.

Although there are known several kinds of perfluoroalkylsilane compounds resembling the perfluoroalkylsilane used in the present invention, they are all unsatisfactory from the viewpoint of production process,

cost, water-solubility at the time of surface treatment or effect as a surface treating agent. For example, perfluoroalkylsilanes represented by the following formulas:



lack water-solubility and surface treatment with their methanolic solutions exhibit no effect.

At the time of the surface treatment, some additives (surfactant, other silane coupler) may be added to the surface treating solution to increase the flexibility of the glass fibers, thereby promoting the physical permeation of the tetrafluorocarbon resin into the interstices of the glass fiber filaments.

Said perfluoroalkylsilanes are excellent in affinity and compatibility with fluororesins. According to the invention, the surface of a glass fiber product is treated with such a perfluoroalkylsilane, thereby improving affinity and adhesiveness between the glass fiber product and the fluororesin.

(1) The organic functional group ($\text{CF}_3\text{CH}_2\text{CH}_2$) of the perfluoroalkylsilane ($\text{CF}_3\text{CH}_2\text{CH}_2\text{-SiX}_3$) takes part in the affinity and adhesion with the fluororesin. Further, an inter-polymer network (I. P. N.) seems to be formed between the fluororesin and the molecular chain of the organic functional group moiety.

(2) The hydrolyzable group X of the silane compound is hydrolyzed under specified conditions (at a pH value of 4 or below) in order that the glass fiber surface treated with the perfluoroalkylsilane exhibits sufficient adhesiveness or bonding force, and the resulting silanol group forms a siloxane linkage with the glass surface.

The effect of the invention is exhibited by the above-mentioned mechanism. Regarding the affinity and adhesion between a perfluoroalkylsilane and a fluoroplastic, occurrence of the following phenomenon is also assumable, in addition. That is, in the high temperature process at 350°C to 400°C , a part of the fluoroplastic forms radicals which cause a crosslinking reaction.

The perfluoroalkylsilane takes part in this reaction at least partially. Due to this reaction in addition to the I. P. N., it forms a linkage with fluororesin.

Example 1

1) Treating solution

3,3,3-Trifluoropropyltriethoxysilane (FTS-E manufactured by Chisso K.K.)	1.0%
Acetic acid	0.2%
Methyl alcohol	30.0%
Water	68.8%
Total	100%

2) Glass fabric

WE-116^F (a glass fiber fabric manufactured by Nitto Boseki K.K.) was degreased by heat cleaning and put to use.

3) Surface treatment

The glass fabric of 2) was dipped into the treating solution of 1) and squeezed by means of squeezing rolls. Then, it was dried in an oven at 110°C for 5 minutes.

4) Preparation of a laminate

The surface-treated glass fabric was dipped into a tetrafluoroethylene resin dispersion (Teflon 30-J, manufactured by Mitsui Fluorochemical K.K.) and air-dried, after which it was dried at 370°C for 2 minutes.

This procedure was repeated twice to obtain a prepreg having a resin content of 55%.

Sixteen sheets of the prepreg were stacked. After superposing a copper foil ($35\text{ }\mu\text{m}$ in thickness) on both sides of it, the whole was compression-molded at 400°C under a pressure of 50 bar (kg/cm^2) for 60

minutes to prepare a copper foil-lined laminate.

5) Testing method

Electrical insulation resistance was measured according to the testing method of JIS-C-6481, after boiling a test piece at 100° C for 2 hours.

Example 2

1) Treating solution

3,3,3-Trifluoropropyltrimethoxysilane (XC95-418, manufactured by Toshiba Silicone K.K.)	1.0%
Acetic acid	0.2%
Methyl alcohol	30.0%
Water	68.8%
Total	100%

The other conditions were the same as in Example 1.

Comparative Example 1

As the glass fabric, WE 116^E not subjected to heat cleaning and carrying a greige good was used.

Comparative Example 2

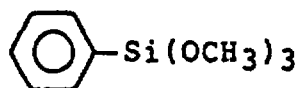
As the glass fabric, WE 116^E which had been subjected only to a preliminary degreasing at 400° C for 20 to 30 seconds until the greige good was appropriately scorched was used.

Comparative Example 3

General silane coupler blend

As the glass cloth, WE 116^E which had been degreased by heat cleaning and then treated with a treating solution having the following formulation was used.

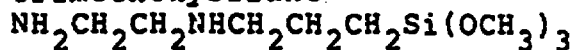
Phenyltrimethoxysilane



(AX43-040, manufactured by Toray Silicone K.K.)

0.8%

γ-(2-Aminoethyl)-aminopropyl-trimethoxysilane



(SH 6020 manufactured by Toray Silicone K.K.)

0.2%

Acetic acid

2.0%

Water

97.0%

Total

100%

Comparative Example 4

5 A perfluorosilane $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$ (3,3-4,4-5,5-6,6-7,7-8,8,8-tridecafluorooctyltrimethoxysilane (XC95-468, manufactured by Toshiba Silicone K.K.), i.e. a perfluorosilane resembling the perfluorosilane of the present invention in structure, was used in the surface treatment.

XC95-468	1.0%
Methanol	95.0%
Water	3.5%
Acetic acid	0.5%
Total	100%

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15 The samples of Examples 1 and 2 and Comparative Examples 1 to 4 were examined for electrical insulation resistance. The results are summarized in Table 1.

Table 1

	Example		Comparative Example			
	1	2	1	2	3	4
Surface treatment agent and the others	3,3,3-Tripropyltriethoxysilane 1.0% solution	3,3,3-Tri-fluoropropyltrimethoxysilane 1.0% solution	Greige good of glass fiber	Preliminary degreasing of greige good of glass fiber	Blend of general silane couplers	Perfluoro-resembling that of this invention (3,3-4,4-5,5-6,6-7,7-8,8,8-tridecafluoro-octyltrimethoxysilane) 1.0% solution
Amount of treating agent attached (%)	0.16	0.14	3.2*	0.28*	0.14	0.14
Thickness of laminate (mm)	1.56	1.57	1.60	1.57	1.57	1.60

Table 1 (cont'd)

Electrical insulation resistance (ohms after boiling at 100°C for 2 hrs.)	2.4×10^{13}	1.2×10^{13}	$< 10^9$	$< 10^9$	5.1×10^{10}	5.5×10^{10}
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* Not containing coupling agent.

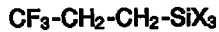
A fluoroplastic molding material filled and reinforced with the glass fiber product of the invention is not only improved in abrasion resistance, creep resistance and elastic modulus, but also markedly prevented from the deterioration of insulating resistance which is a side effect having been unavoidable according to the prior techniques.

Particularly, printed circuit boards made of fluoroplastic reinforced with the glass fabric of the invention do show only a small deterioration in insulation resistance after being boiled, so that their usefulness is very

high and they are useful in the field of multi-layered print circuit boards where these types of products have hitherto been unemployable because of the deterioration in insulation resistance.

Claims

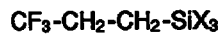
1. Use of a glass fibre product which is pretreated with a perfluoroalkylsilane represented by the following formula:



wherein X represents a hydrolyzable group such as an alkoxy group having 1 to 4 carbon atoms, for the reinforcement of a fluororesin.

Patentansprüche

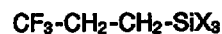
1. Verwendung eines Glasfaserproduktes, das mit einem Perfluoroalkylsilan der folgenden Formel vorgehandelt wurde:



worin X eine hydrolysierbare Gruppe, wie eine Alkoxygruppe mit 1 bis 4 Kohlenstoffatomen darstellt, zur Verstärkung eines Fluorharzes.

Revendications

1. Utilisation d'un produit en fibre de verre qui est traité avec un perfluoroalkylsilane représenté par la formule suivante :



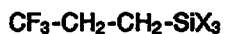
dans laquelle X représente un groupe pouvant être hydrolysé tel qu'un groupe alcoxy ayant 1 à 4 atomes de carbone, pour le renforcement d'une résine fluorée.



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Claims

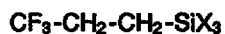
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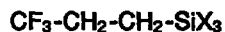
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worin X eine hydrolysierbare Gruppe, wie eine Alkoxygruppe mit 1 bis 4 Kohlenstoffatomen darstellt, zur Verstärkung eines Fluorharzes.

Revendications

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1. Utilisation d'un produit en fibre de verre qui est traité avec un perfluoroalkylsilane représenté par la formule suivante :



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dans laquelle X représente un groupe pouvant être hydrolysé tel qu'un groupe alcoxy ayant 1 à 4 atomes de carbone, pour le renforcement d'une résine fluorée.