(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 214 509**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: 86111427.0

(22) Date of filing: 19.08.86

(51) Int. Cl.4: D04H 1/42 , A41D 13/00

(30) Priority: 26.08.85 JP 188275/85

(43) Date of publication of application:
18.03.87 Bulletin 87/12

(84) Designated Contracting States:
DE FR GB

(71) Applicant: SUMITOMO CHEMICAL COMPANY, LIMITED
15 Kitahama 5-chome Higashi-ku
Osaka-shi Osaka 541(JP)
Applicant: JAPAN EXLAN COMPANY, LTD.
2-8, Dojimahama-2-chome Kita-ku
Osaka-shi Osaka 530(JP)

(72) Inventor: Kobashi, Toshiyuki
1-6, Saidaijikami-3-chome
Okayama-shi(JP)
Inventor: Sugimoto, Hiroaki
13-5, Kawanishicho-1-chome
Takatsuki-shi(JP)
Inventor: Hayatsu, Kazuo
11-8, Kamihozumi-2-chome
Ibaraki-shi(JP)

(74) Representative: Henkel, Feiler, Hänzel & Partner
Möhlstrasse 37
D-8000 München 80(DE)

(54) **Protective material.**

(57) Protective material light in weight and excellent in fundamental properties for protective material such as abrasion resistance, impact strength, cutting resistance and the like and further excellent in thermal resistance, nonhygroscopicity, electrical insulation and the like, can be obtained by use of a fiber obtained by melt spinning an aromatic polyester exhibiting anisotropy in its molten state.

EP 0 214 509 A2

PROTECTIVE MATERIAL

FIELD OF THE INVENTION

This invention relates to a protective material.

BACKGROUND OF THE INVENTION

In the field of use for dangerous works, crime prevention, and defence, metal plate, metal net, and metal chain etc. have been used as protective material for human body and equipments. But the safety protector made of metal material is so heavy that feeling of physical disorder is given on wearing and movability is poor.

At the recent year, glassfiber reinforced plastics and composite materials have been used for the purpose of decreasing the weight. But the density of glassfiber itself is about 2.5 g/cc which is large as compared with that of high polymer of matrix. Further, since content of the glass fiber is about 30 -70% by weight, it is not sufficient for the purpose of decreasing the weight.

Also recently, in place of glassfiber, protective materials comprising organic fiber of high strength is proposed. However, in the application of high strength polyolefin fiber, (Japanese Patent Application Laid-open No. Sho 58-180653, (1983)) because of melting point of the fiber itself as low as about 140°C, the fiber may be often melted by high energy caused of collision. In the case of high strength aromatic polyamide the fiber is poor in abrasion resistance and in strength in wet state, and thus, it may cause trouble in application process.

SUMMARY OF THE INVENTION

The purpose of this invention is to provide protective material excellent in the abrasion resistance, impact strength and cutting resistance. Further, this invention provides a protective material characterized by using fiber which is obtained by melt-spinning an aromatic polyester exhibiting anisotropy in its molten state.

DETAILED DESCRIPTION OF THE INVENTION

The polyester which exhibits anisotropy in its molten state referred to in this invention means one which has a property of allowing the transmission of light at a temperature region in which it is flowable when the powder sample of the polyester is placed on a heating sample stage positioned between two polarizing plates crossed at an angle of 90° and the temperature of the sample is increased. Such polyesters are those formed of aromatic dicarboxylic acids, aromatic diols and/or aromatic hydroxycarboxylic acid, and the derivatives thereof, disclosed in Japanese Patent Application Kokoku (Post-Exam. Publn.) Nos. 18016/81 and 20008/80, and optionally include copolymers of these with alicyclic dicarboxylic acids, alicyclic diols, aliphatic diols, and the derivatives thereof.

Examples of the aromatic dicarboxylic acids include terephthalic acid, isophthalic acid, 4,4'-dicarboxydiphenyl, 2,6-dicarboxynaphthalene, 1,2-bis(4-carboxyphenoxy)ethane, and the nuclear-substituted products thereof with an alkyl, aryl, alkoxy, or halogen group.

Examples of the aromatic diols include hydroquinone, resorcin, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxybenzophenone, 4,4'-dihydroxydiphenyl-methane, 4,4'-dihydroxydiphenylethane, 2,2-bis(4-hydroxyphenyl)propane, 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxydiphenyl sulfide, 2,6-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, and the nuclear-substituted products thereof with an alkyl, aryl, alkoxy, and halogen group.

Examples of the aromatic hydroxycarboxylic acids include p-hydroxybenzoic acid, m-hydroxybenzoic acid, 2-hydroxynaphthalene-6-carboxylic acid, 1-hydroxynaphthalene-5-carboxylic acid, and the nuclear-substituted products thereof with an alkyl, aryl, alkoxy, and halogen group.

Examples of alicyclic dicarboxylic acids include trans-1,4-dicarboxycyclohexane, cis-1,4-dicarboxycyclohexane and the substituted products thereof with an alkyl, aryl, and halogen group.

Examples of the alicyclic and aliphatic diols include trans-1,4-dihydroxycyclohexane, cis-1,4-dihydroxycyclohexane, ethylene glycol, 1,4-butanediol, and xylylene diol.

Among the combinations of the aforesaid materials, there may be mentioned as examples of a preferable aromatic polyester to be used in this invention:

(I) a copolyester comprising 40 to 70% by mole of p-hydroxybenzoic acid residue, 15 to 30% by mole of an above-mentioned aromatic dicarboxylic acid residue, and 15 to 30% by mole of an aromatic diol residue;

(2) a copolyester formed of terephthalic acid and/or isophthalic acid and chlorohydroquinone, phenylhydroquinone and/or hydroquinone; and

(3) a copolyester comprising 20 to 80% by mole of p-hydroxybenzoic acid residue and 20 to 80% by mole of 2-hydroxynaphthalene-6-carboxylic acid residue.

To attain the polyesters to be used in this invention by using these starting materials, they are subjected to polycondensation as they are or after esterified by an aliphatic or aromatic monocarboxylic acid or the derivative thereof, or an aliphatic alcohol, a phenol, or the derivative thereof.

The polycondensation can be carried out by using a known method including mass polymerization, solution polymerization and suspension polymerization. It may be conducted at 150 to 360°C under normal pressure or a reduced pressure of 10 to 0.1 Torr optionally in the presence of polymerization catalyst such as a Sb, Ti and Ge compound, a stabilizer such as a phosphorus compound, and fillers such as TiO_2, $CaCO_3$, and talc, added thereto. The polymer thus obtained is heat-treated, as it is or in a pulverized form, in an inert gas or under reduced pressure to give a sample material for spinning. It can also be used after once granulated through an extruder.

In this invention, conventional apparatus for the melt spinning can be used. The spinning temperature is usually 280°C -420°C, preferably, 300 - 400°C. If the temperature is lower than the scope, load on the apparatus becomes too much and uniformity of the molten material is not sufficient.

On the contrary, if the temperature is higher than the scope, a decomposition reaction is caused and stable spinning can not be carried out.

The fibers obtained by melt spinning as mentioned above are then taken up or drawn down, as they are or after adhereing a textile oil and a treating agent thereto. The obtained fiber can be used, as it is, and further, stretching, and heat treatment or combination of them may optionally applied.

The protective material of this invention is constituted of structural material comprising aromatic polyester fiber obtained as mentioned above. As shape of the structural material, net structure is preferable. As concrete example of the net structure, there are woven fabric cloth, knitting goods, net cloth, nonwoven cloth and fiber-reinforced composite materials of multi-layer structure, each layer of which is constituted of fibers directed to one direction or directed to multi-direction.

The woven fabric cloth may be of any of various patterns such as plain fabric, twill, satin etc., and it is preferable to change density of fabric depending on its use. The fiber used for fabric may be sized in advance. It may be also admitted to change handling, color and the like by covering with other thermoplastic resin or thermosetting resin.

As the knitting fabrics, there are many kind of the knitting goods, circular knitt, combined knitt and so on. As the net fabrics, there is coarse cloth of netting fabrics.

As the nonwoven fabric, there are a sheet made of short fiber which is obtained by piling up card webs, blowing the fiber on a drum or scooping up the fiber floating in water by using a net and a sheet which is obtained by piling up looped filaments.

The fiber reinforced composite material having multilayer structure in which comprises fibers directed to one direction may be produced, for example, by winding continuously fibers containing resin on a mandrel to form a sheet and by curing combined sheets obtained as above. The reinforced composite material with fiber of multidirection is produced, for example, by impregnating resin into a material having net structure such as fabric, knitted good, net cloth and the like or combination of them.

The resins to be impregnated are, for example, thermosetting resins such as epoxy resin, unsaturated polyester, phenol resin, polyurethan, silicon resin, rubber and others, and thermoplastic resins such as polyolefin, polyamide, polyester, polyether, polysulphone, polyether ketone, and various elastomers. For impregnating the resin, there is used resin solution, molten material, film and the like of the resin.

Thus, the protective material of this invention can be produced. The protective material of this invention is very light and is excellent is fundamental properties such as abrasion resistance, impact strength, cutting resistance and the like and further, excellent in heat resistance, water resistance, electric insulation and the like.

Therefore, the protective material of this invention is used for work treating dangerous material, work treating explosive material, cutting and processing of metal, meat producing work, cutting and processing of timber, work at height and so on, as safety tool and wear such as helmet, glove, legprotector and the like, bulletproof jacket, escape chute, safety net and the like.

The present invention is illustrated in detail with reference to Examples but is not limited to them.

Referential Example 1

Into a polymerization vessel having a comb-type stirrer, were placed 7.20 kg (40 moles) of p-acetoxybenzoic acid, 2.49 kg (15 moles) of terephthalic acid, 0.83 kg (5 moles) of isophthalic acid, and 5.45 kg (20.2 moles) of 4,4'-diacetoxydiphenyl, and the resulting mixture was brought to elevated temperature with stirring under a nitrogen gas at-

mosphere and polymerized at 330°C for 3 hours. During the period, acetic acid formed was removed and the polymerization was carried out with powerful stirring. Thereafter, the system was gradually cooled and the polymer formed was taken out at 200°C from the system. The yield of polymer was 10.88 kg, 97.8% of theoretical yield. The polymer was pulverized in a hammer mill to give particles of 2.5 mm or less. The polymer was then treated in a rotary kiln in nitrogen atmosphere at 280°C for 5 hours. The resulting polymer showed optical anisotropy at a temperature of 350°C or higher.

The polymer obtained above was melt-spun by using a screw type extruder of 30 mmØ. In the melt-spinning the spinneret with a hole diameter of 0.07 mm, a hole length of 0.14 mm and a number of holes of 308 was used. Melt-spinning was conducted at 365°C and light yellowish transparent fiber was obtained without break of filament, and thus stable spinning was carried out. When the fiber obtained was heat treated in a nitrogen gas atmosphere at 320°C for 3 hours, the fiber produced had diameter of 16.2 μm, strength 29.2 g/d, elongation 2.9% and modulus of elasticity 1030 g/d and melting point of this fiber showed at 450°C or higher, water absorption of 0.0%.

Example 1

The fiber obtained in Referential Example 1 was used and plain fabric was woven by automatic weaving machine manufactured by Tsudakoma Kogyo Co., Ltd. The warp density and weft density were both 25 yarn/2.54 cm, and basis weight of the fabric was 172 g/m².

Comparative Example 1

A plain fabric was woven in the same manner as in Example 1 except that poly-p-phenylene terephthalamide fiber was used. Of the fabric woven, warp density and weft density were both 15 yarns/2.54 cm, and basis weight was 187 g/m². The fiber used had diameter of 12.0 μm, strength of 23.0 g/d, elongation of 2.7%, modulus of elasticity of 860 g/d and hydroscopic degree of 3.2%.

Comparative Example 2

A plain fabric was woven in the same manner as in Example 1 except that polyethylene terephthalate fiber was used and warp density and weft density of the fabric were both 102 yarns/2.54 cm and basis weight was 176 g/m². The fiber used had diameter of 17 μm, strength of 6.3 g/d, elongation of 10.7% and modulus of elasticity of 108 g/d.

Cutting test

The fabric each obtained in Example 1, Comparative Example 1 and Comparative Example 2 was fixed in a metal frame and a NT cutter A-300 manufactured by Nihon Tenshashi Co. was set in 45° angle to the fabric. A load was applied on the fabric by putting a weight on the upper of blade of the cutter, and the fabric was moved in a length of 15 cm in a rate of 5 cm/minute. Each fabric thus cut was examined. Results thereof are shown in Table 1. From Table 1, it is known that the fabric of Example 1 is superior to those of Comparative Examples 1 and 2 in resistance to cutting.

Cutting test after fatigue test

Both surfaces of the fabric each obtained in Example 1, Comparative Examples 1 and 2 was subjected to twenty rounds abrasion with sandpaper CC-1500 manufactured by Riken Corundum Co. Thereafter, the cutting test was carried out in the same manner as above on the fabric. Results thereof are shown in Table 1. It is apparent that the fabric of Example 1 is remarkably superior to the others in resistance to cutting.

Table 1 Result of Cutting Test

Example	fiber	Weight (g)									
		50	100	150	200	300	400	500	600	800	900
Example 1	a fiber obtained from polyester exhibiting anisotropy in its molten state	◎ (◎)	◎ (◎)	◎ (◎)	◎ (○)	◎ (Δ)	○ (X)	Δ	Δ	Δ	X
Comparative Example 1	aramide fiber	◎ (○)	◎ (Δ)	◎ (X)	○	Δ	Δ	X			
Comparative Example 2	Polyethylene terephthalate fiber	○ (X)	○	X							

(Note) (1) The symbols have the following means:

◎ Blade was moved without being cut.

○ Less than 20% of filaments of the fabric were cut.

Δ Less than 50% of filaments of the fabric were cut.

X 50% or more of filaments of the fabric were cut.

(2) The symbols in parenthesis show results of cutting test after fatigue test.

0 214 509

Example 2

The fabric obtained in Example I was cut in size of 20 cm × 20 cm and the cut piece was dipped at 120°C in 2% toluene solution of "Sumikathene L 705" (MI=7) (low density polyethylene produced by Sumitomo Chemical Co., Ltd.) and dried. Increase in the weight was 28%.

Comparative Examples 3 and 4

Example 2 was repeated except that the fabric each obtained in Comparative Examples I and 2 is used to obtain a fabric impregnated with resin.

Measurement of amount of absorbed energy

Of the fabric each obtained Example 2 and Comparative Examples 3 and 4, namely, the fabric obtained by impregnation with resin of the fabric each obtained in Example I, Comparative Examples I and 2, amount of absorbed energy was measured. The fabric impregnated with resin was cut in size of 5 cm × 5 cm and each piece was fixed on circular frame 25.4 mm in inner diameter. An iron drop weight which is a hemishere 12.7 mm in diameter having a column 8 mm in diameter and 20 mm in length, was shot down from height of 2 m above the tested fabric, turning down the hemisherical side of the drop weight, by means of compressed air. Load falling on the tested fabric was measured to obtain amount of absorbed energy. Further, in the same manner as above, amount of absorbed energy of polyethylene film similar to that used in Example 2 having a thickness of 80 μm was measured. From this amount obtained, amount of absorbed energy of the polyethylene used for impregnation was calculated in term of thickness. This value thus obtained was substrated from the amount of absorbed energy per unit area density of the fabric of Example I was 54.8 J m²/kg, and those of Comparative Examples I and 2 were 35.7 J m²/kg and 7.0 J m²/kg, respectively.

From the above, it may be understood that the fabric according to this invention is excellent in impact resistance.

Example 3

Knitting of the fiber obtained in the Referential Example I was carried out by use of home knitting machine, "palie 8" manufactured by Brother Co. Cutting test of knitted goods was carried out.

Under the weight of less than 800 g, only less than 20% of the knitted goods were cut and under that of I.I kg, 50% or more thereof were cut.

Claims

I. Protective material comprising fiber obtained by melt spinning an aromatic polyester exhibiting anisotropy in its molten state.

2. Protective material according to Claim I, wherein the protective material is a net structural material.

3. Protective material according to Claim 2, wherein the net structural material is a fabric comprising a fiber obtained by melt spinning an aromatic polyester exhibiting anisotropy in its molten state.

4. Protective material according to claim 2, wherein the net-structural material is a knitted good comprising a fiber obtained by melt spinning an aromatic polyester exhibiting anisotropy in its molten state.

5. Protective material according to Claim 2, wherein the net-structural material is a net comprising a fiber obtained by melt spinning an aromatic polyester exhibiting anisotropy in its molten state.

6. Protective material according to Claim 2, wherein the net-structural material is a non-woven fabric comprising a fiber obtained by melt spinning an aromatic polyester exhibiting anisotropy in its molten state.

7. Protective material according to Claim 2, wherein the net-structural material is a fiber-reinforced composite material containing as reinforcing fiber, a fiber obtained by melt spinning an aromatic polyester exhibiting anisotropy in its molten state.