PATENT SPECIFICATION (11) 1 562 432

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(21) Application No. 39521/76 (22) Filed 23 Sept. 1976
(31) Convention Application No. 7 529 312
(32) Filed 24 Sept. 1975 in
(33) France (FR)
(44) Complete Specification published 12 March 1980
(51) INT CL³ B05D 5/00; B32B 27/08
(52) Index at acceptance
B2E 1305 1319 443T 470T 481S 507T 511T AM
B5N 1704 1710 2706 2712 2730 2736

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(19)

(54) POLYESTER COATED POLYMETHYLMETHACRYLATE ARTICLE, PROCESS FOR ITS MANUFACTURE AND APPLICATIONS THEREOF

(71) We, ALTULOR, a joint stock company duly organised under the laws of France, of 5, Rue du General Foy, Paris 8, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a reinforced laminated composite product, based on polymethacrylate and polyester resin, as well as to its method of manufacture.

French Patent Specification No. 1,152,576 describes a method for manufacturing laminated materials by bonding a surface containing acrylic groups to a polyester surface.

It has been proposed to use an intermediate polyester layer reinforced with fibrous material or silicone fabric. By employing as a cross linking agent of the polyester, a monomer containing acrylic groups, and placing the surfaces to be bonded in contact whilst the polyester surface is still incompletely polymerised, complete polymerisation is then obtained by cross-linking the polyester whilst keeping the two surfaces in contact. The polymerisation operation can be carried out at high temperatures (about 70°C) or at low temperatures (in the presence of cobalt naphthenate). Laminated materials of the aforesaid type are also known in which suitable solvents are sprayed on to the acrylic surface before placing the polyester in position.

US Patent 3,832,268 describes a reinforced plastics structure, comprising a sheet of polymethylmethacrylate on to which a composition of unsaturated polyester methacrylic acid-styrene is sprayed. The methacrylic acid/styrene composition facilitates adherence of the composition to the sheet of polymethylmethacrylate. However, by reason of its composition, the polyester resin used for manufacturing this plastics structure tends to shrink, leading to defective adherence of the individual layers of the structure in numerous applications.

All these known materials have improved mechanical strengths; however, their manufacture is relatively complicated among other things on account of the number of moulds necessary and their cohesion is frequently insufficient to avoid delamination.

It is an object of the invention to overcome these drawbacks and to improve the properties and quality of such composite materials, and to simplify their manufacture.

It is a particular object of the invention to provide a composite material, based on a reinforced and/or filled polyester composition, and on polymethylmethacrylate, the manufacture of which does not involve the use of special solvents.

It is also an object of the invention to provide a laminated material whose composition permits the shrinkage of the layers, liable to arise during manufacture, to be reduced, in order to achieve good adherence of the individual layers of said material.

According to the invention there is provided a laminated material comprising a base sheet of polymethylmethacrylate coated on at least one of its faces with one or more layers of a polyester composition reinforced with glass fibre and/or a filler composition, said polyester composition including a homopolymeric polyester resin, and polyvinyl acetate to reduce the shrinkage of said layer(s).

The polyester composition of the present invention shrinks less after polymerisation, than does a conventional polyester resin. This reduced shrinkage permits the adherence between the polyester composition and the sheet of polymethylmethacrylate to be substantially improved. In the case of conventional polyester resin, the shrinkage is 8%; as a result no cross-linking occurs between the sheet of polymethylmethacrylate and the polyester resin and the adherence is then nil.

Any type of polymethylmethacrylate may be used. In fact, the quality of polymethylmethacrylate sheet does not effect the

adherence of the polyester composition. The polymethylmethacrylate may be, for example, that manufactured and marketed under the trade mark "ALTUGLAS" by the applicants. It is advantageously of the "ALTUGLAS — series 8000" type suitable for deep thermoforming. The polymethylmethacrylate preferably has a molecular weight of the order of 800,000.

The amount of polyvinyl acetate contained in the polyester is not critical. However, in order to avoid problems due to increased viscosity of the polyester composition, said composition preferably contains not more than 10% by weight of polyvinyl acetate.

In a preferred embodiment, the polyester composition contains, by weight, 67% of polyester resin, 27% of styrene and 6% of polyvinyl acetate. The polyester composition then has a shrinkage not exceeding 3%. The polyester resin proper may be obtained in known manner, for example, from a mixture of monomers containing maleic anhydride, phthalic anhydride, propylene glycol and diethylene glycol.

The reinforcing fibre is preferably fibre glass cut to a length of, for example, between 30 and 40 mm. The glass fibre may be in the form of a fabric and/or a mat of, for example, the glass rovings type. The glass fibre is preferably present in the proportion of up to 30% by weight of polyester composition.

According to another feature of the invention, the laminated material advantageously contains a filler, for example calcium sulphate, in the proportion of 19 to 25% by weight of polyester, which improves the bonding of the layers.

The polyester composition contains preferably also a catalyst and an accelerator which are used to induce bonding of the polyester composition on to the polymethyl, methacrylate surface, and which can be respectively benzoyl peroxide and dimethylaniline. Methylethylketone peroxide and cobalt naphthenate should preferably be avoided as catalyst and accelerator respectively since they do not give a sufficiently rapid bonding of the polyester composition to the polymethylmethacrylate surface to be industrially practical, and above all, they result in a tensile strength of the order of 30 kg/cm², much below the required standard.

The present invention further provides a method of manufacturing a laminated material, comprising, at ambient temperature of 25 to 30°C, spraying on to a polymethacrylate surface, a first layer of up to 1 mm thickness of polyester composition reinforced with glass fibre and/or a filler material, wherein the polyester composition contains polyvinyl acetate and a catalyst and accelerator, then spraying a second layer of 1 to 2 mm of composition, rolling said layer to remove any air bubbles therefrom, successively spraying, at time intervals of between 15 and 30 minutes, additional layers of composition, as necessary to obtain the desired thickness, each layer being carefully rolled, and allowing the laminated material to age for about a week at ambient temperature of about 20°C.

The bond between the laminated polyester composition and the previously thermoformed skin of polymethylmethacrylate has a standard tensile strength of about 45 kg/cm².

In the method of the present invention, there need be no treatment of the acrylic surface by spraying with various solvents in order to effect the spraying of the polyester/reinforcing fibre composition. The absence of this processing step is an advantageous feature of this method.

The polyester composition preferably contains about 1.5% by weight of benzoyl peroxide as catalyst, 1.2% of dimethylaniline as accelerator, 15 to 25% by weight of calcium sulphate as a filler material, up to 30% by weight of reinforcing glass fibres of about 30 to 40 mm length. The calcium sulphate is more preferably present in the proportion of 20% by weight of the polyester composition.

The application of the layers of polyester composition and glass fibres may be effected by conventional methods, for example, by spraying (notably with a spray gun) or by injection. The glass fibre and the polyester composition are preferably sprayed from separate spray guns.

The laminated material of the present invention may be used in the manufacture of moulded articles, such as sanitary articles for example, wash basins, sinks and baths. The articles obtained have very superior mechanical properties whereby the tensile strength of the bond between the laminates of the polyester composition and the polymethylmethacrylate support is about 45 kg/cm².

The invention is illustrated by the following examples:

EXAMPLE 1.

This example relates to an embodiment of the method of the invention by spraying.

A sheet of polymethylmethacrylate of the Altuglas type is previously thermoformed by the usual means.

The polyester resin is NORSODYNE 213 FM (NORSODYNE is a Registered Trade Mark), manufactured by the "CDF CHIMIE" (France) Company. This resin, of the one component type with reduced shrinkage, has the following properties:

a) PHYSICO-CHEMICAL.
Before polymerisation:

Density in the liquid state (20°C)	1.07
Viscosity at 25°C	3.5—4.5 poises
APHA colour	40—150 hazen
SPI Reactivity:	
— Gel	5'30—7'
— Polymerisation	8'—10'
— Exothermic peak	185—200° C
After polymerisation:	
Density in the solid state (20°C)	1.10
Specific shrinkage	3%
Barcol hardness	32—34
b) *MECHANICAL*	
Impact strength (DYNASTAT—CEMP)	2.5 kg/cm/cm³
Bending strength (DYNASTAT—CEMP)	7.6 kg/mm²
Bending modulus (HAAKE)	36000 kg/cm2
Yield temperature under load (ASTM standard 648—56)	91°C

On to the sheet of polymethylmethacrylate is sprayed the polyester composition which contains, by weight, 67% of polyester resin, 27% of styrene and 6% of polyvinyl acetate, and up to 20% of $CaSO_4$. The polyester composition and the glass fibres are then sprayed on and a final layer of glass fibre alone is then applied, to obtain a total thickness for the laminate of 3.9 mm.

EXAMPLE 2.

A sheet of polymethylmethacrylate of the drawn Altuglas type, (manufactured and marketed by the Altulor Company), of 0.8 mm thickness is used. On to this sheet is sprayed polyester composition containing, by weight, 67% of unsaturated polyester resin, 27% of styrene, 6% of polyvinyl acetate, and 20% of $CaSO_4$ filler. This polyester composition and glass fibres are then sprayed on and finally there is applied a layer of glass fibre alone, to obtain a total thickness for the laminate of 3.9 mm.

After complete polymerisation, the laminated material possesses the properties shown in the table below.

EXAMPLE 3.

Lamination is effected in the same manner as in Example 2, except that two layers of glass fibre mat of 450 g/m² are applied to the polymethylmethacrylate sheet before the first layer of polyester composition.

After complete polymerisation, the laminated material whose total thickness is 3.6 mm possesses the properties shown in the table below.

TABLE

Properties	AFNOR Standard	Unit	Laminated material according to the invention	
			Example 1	Example 2
Bending strength	51001	N/mm2	154	134
Bending modulus	51001	N/mm2	5570	4880
Impact strength Charpy	51035	J/cm3	1.8	2.0
Tensile strength	57001	N/mm2	84	79
Elongation on rupture	57001	%	2.6	2.7
Shore hardness D	ISO R 868	–	86	86
Water absorption	51002 A	mg	91	88

EXAMPLE 4.

This example relates to the resistance to mechanical shocks and to thermal shock of the laminated material according to the invention.

On to a sheet of polymethylmethacrylate of 3 mm Altuglas 8000 with a free monomer ratio less than 1%, 0.5% of plasticiser and 0% of lubricant, is applied by the method according to the invention, a layer of 0.3 mm of the polyester composition containing polyvinyl acetate (NORSODYNE 213 FM), then successive layers of this polyester composition plus calcium sulphate filler (20%), more glass fibre (30%), then unwetted glass fibre, up to a total thickness of about 1.2 mm of the polyester/filler/glass complex. Beyond this thickness of about 1.2 mm, the finished complex material develops an "orange peel" or pitted appearance. It is observed that the application of a glass fibre mat substrate of 600 g/m2 or of two glass fibre mat substrates of 400 g/m2 before the spraying operation, as described in the previous examples avoids this defect.

The finished material is practically independent of the grain size of the water content of the calcium sulphate; the Altuglas sheet or skin should itself be preferably cold at the moment of spraying the polyester.

The finished material has an excellent impact strength; it withstands the impact of a weight of 5 kg falling from a height of 1 m. The sample is considered as good if the sheet of polymethylmethacrylate does not show a fracture and if there is no separation of the laminate. Delamination in the zone of the impact point and the whitening of the laminate in the same zone are acceptable.

It should be noted that an enamelled cast iron wash basin is destroyed by a weight of 1 kg falling from 1 m.

The laminated material also has good heat shock resistance. Steam and hot water at 85°C were projected at the rate of a jet every 30 seconds for two hours into tanks. The tanks were then full and the temperature of the water 55°C. No separation between the Altuglas and the laminate was observed.

For application of the method, when the glass fibre and resin are being sprayed from separate jets, it is preferable to provide a fibre deflector to avoid too early a mixing of the fibre jet and of the resin jet and to regulate the axes of the fibre jet and resin jet so as to obtain straddling of the fibres and the resin on the Altuglas sheet.

WHAT WE CLAIM IS:—

1. A laminated material comprising a base sheet of polymethylmethacrylate coated on at least one of its faces with one or more layers of a polyester composition reinforced with glass fibre and/or a filler composition, said polyester composition including a homopolymeric polyester resin, and polyvinyl acetate to reduce the shrinkage of said layer(s).

2. A laminated material according to claim 1 wherein said polyester composition includes up to 10% of polyvinyl acetate.

3. A laminated material according to either of claims 1 or 2 wherein said polyester composition contains, by weight, 67% of polyester resin, 27% of monomeric styrene and 6% of polyvinyl acetate.

4. A laminated material according to any of the preceding claims wherein the polyester composition is reinforced with up to 30% by weight of glass fibre.

5. A laminated material according to any of the preceding claims wherein said filler material is calcium sulphate present in the proportion of from 19 to 25% by weight of said polyester composition.

6. A laminated material substantially as hereinbefore described with reference to the Examples.

7. A method of manufacturing a laminated material according to any of the preceding claims, comprising, at ambient temperature of 25 to 30°C, spraying on to a polymethacrylate surface, a first layer of up to 1 mm thickness of polyester composition reinforced with glass fibre and/or a filler material wherein the polyester composition contains polyvinyl acetate and a catalyst and accelerator, then spraying a second layer of 1 to 2 mm of composition, rolling said layer to remove any air bubbles therefrom, successively spraying, at time intervals between 15 and 30 minutes, additional layers of composition, as necessary to obtain the desired thickness, each layer being carefully rolled, and allowing the laminated material to age for about a week at ambient temperature at about 20°C.

8. A method according to claim 7, wherein a first layer of cut glass fibres unwetted by the polyester composition is applied to the laminated material.

9. A method according to claim 8, wherein said polyester composition contains, 1.5% by weight of benzoyl peroxide (catalyst), 1.2% of dimethylaniline (accelerator) 15 to 25% by weight of calcium sulphate (filler) and up to 30% by weight of glass fibre of 30 to 40 mm length.

10. A method according to either of claims 8 or 9, wherein a glass fibre mat of 600 g/m2 is applied to said polymethylmethacrylate surface before the first layer of polyester composition.

11. A method according to either of claims 8 or 9, wherein two glass fibre mats of 450 g/m2 are applied to said polymethylmethacrylate surface before the first layer of polyester composition.

12. Moulded articles comprising a laminated material according to any one of claims 1 to 6.

13. Sanitary articles, including baths, washbasins and sinks, constituted from a laminated material according to any one of claims 1 to 6.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.