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(54) Preparation of articles based on thermoplastic polymers reinforced with glass fibres

(57) Polymeric articles reinforced with glass fibres are prepared according to methods suited to paper manufacture, starting from dispersions of glass fibres with polyolefinic fibrils having a high surface area, by deposition in sheets, drying and pressure moulding, optionally after bonding the sheets with an intermediate thermoplastic polymeric plate, not containing glass fibres, and having a flexural modulus less than that of the glass fibres contained in such sheets, so as to thermoweld the plate to the sheets.

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SPECIFICATION

Preparation of articles based on thermoplastic polymers reinforced with glass fibres

This invention relates to the preparation of articles based on thermoplastic polymers reinforced with glass fibres, and more particularly to a process for preparing sheets or laminae of olefinic polymers containing a glass fibre reinforcement; furthermore the invention relates to multilayer shaped bodies of polymeric material containing such sheets as components.

It is known to enhance the mechanical properties of manufactured articles based on polymeric plastics materials by incorporating therein reinforcing fibrous materials having a high elastic flexural modulus, such as fibres of glass, cellulose, asbestos, or carbon.

Methods employed for preparing articles so reinforced are those based on pressure injection of mixtures of molten polymer and fibres, which however are most suitable for preparing small-size articles and involve non-homogeneity of the article reinforcement at bent areas thereof, or methods comprising inpregnating fibre layers with polymeric latexes followed by hot moulding of the resulting panels. In the latter case, the fibrous material is predominantly located in the central area of the article and does not contribute to the reinforcement.

A defect common to both such methods is the poor finish of the article surface, due to the presence of the fibrous material on the surface.

The present invention in one aspect provides a process for preparing an article based on thermoplastic polymeric material containing glass fibres as reinforcing material, comprising:

(a) preparing a dispersion, in an aqueous or in an inert liquid medium, of a mixture of glass fibres longer than 1 mm with fibrils of at least one olefinic thermoplastic polymer having a surface area of at least 1 m^2/g, with a glass fibre/olefinic polymer weight ratio of from 3/97 to 95/5;

(b) forming a sheet by deposition of the dispersion onto a porous surface, as a result of which there occurs substantial elimination of the liquid medium, with deposition of the glass fibres onto a plane substantially parallel to the principal plane of the sheet;

(c) drying the sheet; and

(d) heating the sheet at a temperature equal to or higher than the melting temperature of the olefinic polymer constituting the fibrils, or of the olefinic polymer having the highest melting temperature, with application of pressure, for a time period sufficient to melt the said fibrils.

The process according to the invention permits the preparation of manufactured articles from thermoplastic polymeric material, containing glass fibres as reinforcing material, having an excellent surface finish, and in which such fibres are fully homogeneously distributed in the entire article.

The term fibrils generally means fibrous structures, having a morphology similar to that of cellulose fibres, having an appearance which is sometimes also pellicular as well as tubular, the length of which generally ranges from 0.5 to 50 mm, and the apparent (mean) diameter or smaller dimension of which ranges from 1 to 500 μ.

Fibrils having a surface area equal to or greater than 1 m^2/g have long been known and are mostly employed as partial or total substituents for cellulose fibres in the manufacture of paper or of related products. They can be prepared according to various methods described in the literature.

According to British Patent No. 868 651, such structures can be prepared by adding a solution of a polymer to a non-solvent of the polymer, whilst simultaneously subjecting the precipitated polymer, or the swollen polymer, to the action of cutting. A similar process is also described in German Patent Application No. 2 208 553.

According to British Patent No. 1 287 917, structures having an analogous morphology are obtained by polymerizing alpha-olefins in the presence of coordination catalysts, under the action of cutting stresses exerted in the reaction medium.

Further processes, by means of which fibrous structures having the characteristics and applicative properties described above are obtained in the state of more or less coherent aggregates, or of fibrillar filament structures (plexifilaments), comprise extruding through an orifice solutions, emulsions, dispersions or suspensions of synthetic polymers in solvents, emulsifiers or dispersants, or mixtures thereof, in conditions of almost immediate evaporation of the solvent or of the existing liquid phase (flash-spinning processes).

Such processes are described for example in British Patent Nos. 891 943 and 1 262 531, in U.S. Patent Nos. 3 770 856, 3 740 383 and 3 808 091, in Belgian Patent No. 789 808, in French Patent No. 2 176 858 and in German Patent Application No. 2 343 543.

The fibrous aggregates or plexifilaments obtained according to such processes can be easily disaggregated by cutting or refining, until there are obtained elementary fibrous structures, having a surface area of at least 1 m^2/g and suitable for use in the manufacture of paper or of similar products.

British Patent No. 891 945 describes, for example, how to prepare such plexifilament fibrils by disaggregation of plexifilaments obtained by flash-spinning of polymeric solutions.

Finally, fibrils of fibrous structures having analogous applicative charactistics can be advantageously prepared by subjecting a solution, a suspension, an emulsion or a dispersion of a polymer in a solvent and/or emulsifier or dispersant, while it is being extruded in conditions of rapid evaporation of the liquid phase, to the cutting action of a gaseous fluid having a high velocity and directed angularly with respect to the extrusion direction.

Such processes are described in Italian Patent Nos. 947 919 and 1 030 809.

For the purpose of the present invention use is made of fibrils of olefinic polymers, such as low or high density polyethylene, polypropylene, ethylenepropylene copolymers of the statistic or block type, poly-butene 1 and poly-4-methyl-1-pentene.

The preparation of the mixture of glass fibres and fibrils can be easily effected by dispersing together the two types of fibres in an inert liquid, preferably water, under stirring, according to the methods usually employed in the preparation of pulps for paper. The dispersion of fibres, or the polyolefinic fibrils, should preferably contain a wetting agent, in order to enhance their dispersibility in water and thorough mixing with the glass fibres. Methods of rendering the synthetic polymer fibres wettable by addition of wetting agents are described for example in Belgian Patent No. 787 060 and in German Patent Application No. 2 208 553, as well as Italian Patent No. 1 006 878.

Prior to the forming of the sheet, to the fibre dispersion can be also added a cohesion agent, such as a ureic, acrylic or aminic resin, which facilitates the forming of the sheet.

The preparation of the sheet by means of the dispersion can be also prepared in step (a) can be effected by a method and an apparatus utilized in the paper industry for preparing cellulose paper sheets, by which it is possible to easily attain an arrangement of the glass fibres in the sheet in a substantially horizontal plane, or in a plane parallel with the sheet plane.

When forming the sheet, the excess liquid contained in the fibre mixture can be removed, besides by gravity, by suction under vacuum, which promotes stabilization of the orientation assumed by the glass fibres in the feeding direction of the dispersion to the porous surface, or in the direction of the carrying liquid flow.

Drying of the sheet according to the step (c) can be effected according to a conventional technique used in the paper industry (on cylinders, belts, nets etc.) and is preferably conducted to a dry content in the sheet of almost 100%.

The heating step (d) can be carried out under pressure, continuously in a calender, or discontinuously in a plate press. Preferably the sheet is heated at a temperature higher than the melting temperature of the thermoplastic fibrils present therein, in the absence of pressure, and by successively cooling the sheet under pressure in a cold press or in moulds.

Generally it is possible to obtain a sheet or film having a compact, non-porous structure, in which the preeexisting polymeric fibrils are no longer identifiable.

According to a further embodiment of the process according to the invention, prior to the heating step (d), at least two sheets obtained from step (b) or (c) are sandwiched on the two faces of a lamina of a thermoplastic polymer, free or substantially free from incorporated glass fibres, and are then subjected to heating step (d) while in contact with the lamina, at a temperature at least equal to the softening point of the thermoplastic polymer constituting such lamina, for a time period sufficient to cause the melting of the fibrils and the adhesion of the lamina to the sheets.

The thermoplastic polymer constituting the lamina possesses a flexural modulus lower than that of the glass fibres present in the sheets, and is compatible with the olefinic polymer constituting the fibrils employed.

By saying that the thermoplastic polymer constituting the lamina is substantially free from glass fibres it is meant that such fibres may be optionally present, but only in such amounts as not to essentially modify the value of the flexural modulus of the polymer itself, for example by not more than 10% of such value.

The polymer comprising the lamina may be suitably polyethylene, polypropylene, an ethylene-propylene copolymer, polystyrene, a polyurethane, a styrene-butadieneacrylonitrile terpolymer, or a mixture thereof.

The internal structure of the utilized lamina can be either compact, or cellular or expanded. The polymer or the polymeric material constituting the lamina preferably has a melting temperature in the range of from 135° to 172°C.

Thus there may be obtained polymeric manufactured articles containing glass fibre reinforcement, comprising a structure made up of 3 compact layers, two of which are prepared from an olefinic polymer with incorporated glass fibres, and are thermowelded to the third layer which is intermediate them, which third layer is prepared from a thermoplastic polymer compatible with the olefinic polymer of the other two layers, is totally or substantially free from incorporated glass fibres, and possesses a flexural modulus lower than that of the glass fibres contained in the other two layers.

Such articles possess, the incorporated glass fibres content, shape and total thickness being the same, mechanical properties, especially flexibility and impact resistance, far higher than those of the articles prepared from analogous polymers, in which the fibre reinforcement is homogenously dispersed in the whole mass of the article, or prevailingly in the inside of such mass.

The complete process for preparing such composite articles comprises the following consecutive steps:

(A) preparing a dispersion, in an aqueous or in another inert liquid medium, of a mixture of glass fibres having a length exceeding 1 mm with fibrils of at least one olefinic thermoplastic polymer having a surface area of at least 1 m^2/g, with a glass fibre/olefinic polymer weight ratio of from 3/97 to 95/5;

(B) forming a sheet by deposition of such dispersion onto a porous surface, as a result of which there occurs substantial elimination of the liquid medium, with deposition of the glass fibres onto a plane substantially parallel to the principal plane of the sheet;

(C) drying the sheet;

(D) sandwiching at least two such sheets onto a lamina of a thermoplastic polymer compatible with the olefinic polymer constituting the fibrils, substantially free from incorporated glass fibres, having a flexural modulus lower than that of the glass fibres present in such sheets, by deposition of such sheets onto the faces of such lamina; and

(E) heating the sheets, at a temperature at least equal to the melting temperature of the olefinic polymer constituting the fibrils existing in the sheets, and at least equal to the softening temperature of the thermoplastic polymer constituting the lamina, by application of pressure, for a time sufficient to cause the melting of such fibrils and at least superficial softening of the lamina, with consequent adhesion of such sheets to the lamina.

The drying step (C) can represent an operation not separate from the bonding step (D), and can be carried out during or after the bonding of the sheets with the polymeric lamina, prior to the heating step (E) of the whole body.

The step (D) can be easily carried out for example by preparing the lamina by extrusion, between two sheets obtained from step (C) or (B). Successively, the step (E) can be carried out by heating the bonded article under pressure, for example in a plate press.

The invention in another aspect provides an article based on thermoplastic polymers, comprising a three-layer structure two layers of which are prepared from fibrils of an olefinic polymer containing 3 to 95% by weight of glass fibres longer than 1 mm, and arranged in a plane substantially parallel with the principal plane of the layers, the said two layers being thermowelded to the third layer, which is intermediate the said two layers and is prepared from a thermoplastic polymer compatible with the olefinic polymer of the said two layers, is substantially free from incorporated glass fibres, and possesses a flexural modulus lower than that of the glass fibres contained in the said two layers.

The invention will now be further described with reference to the following illustrative Examples.

EXAMPLE 1

Preparing polyethylene sheets containing glass fibres as a reinforcement.

In a mixer there was prepared an aqueous dispersion of 7 kg of high density polyethylene fibrils (M.I. = 7, M.T. = 135°C), having a surface area of 6 m^2/g and pretreated with acetalized polyvinyl alcohol according to the method described in Italian Patent No. 1 006 878, and 3 kg of glass fibres having a length of 6 mm, a diameter of about 14 μ, a density of 2.54 g/cc and a flexural modulus of about 826,000 kg/cm^2.

This dispersion was diluted with water to a volume of 1,000 liters and then refined in an open-blade conical refiner for 25 minutes. After refining, the glass fibres had an average length of about 4 mm. The suspension was then further diluted to a fibre concentration of 5 g/l and transformed into a sheet on a continuous paper machine at a speed of 40 m/minute.

After pressing and drying at 120°C for 5 minutes the sheet so obtained (sheet (a)) was calendered at a temperature ranging on average from 135° to 150°C under a pressure of 90 kg/cm^2 for 15 seconds, at a speed of 4 m/minute, so obtaining a sheet or film of compact structure.

Operating in the same manner, but using fibrils of polyethylene having a M.I. of 0.3 and 5 respectively, and a melting temperature of 135°C, two other sheets (b) and (c) were prepared which, after calendering under the conditions employed for sheet (a), appeared as sheets or films of compact structure.

The characteristics of the three products after calendering are given in Table I below.

Preparing a laminate according to the invention.

Utilizing a plate press, which operated at a pressure of 5—20 kg/cm^2 and at a temperature of 150°C, 7 layer structures were prepared by causing to adhere to the two main faces of a plate made of high density polyethylene (M.I. = 5, melting temperature = 135°C) having a flexural modulus of 17,000 kg/cm^2 and a thickness of about 1.3 mm, in an equal amount on each face, an increasing number of previously prepared sheets of type (a) and (b) respectively.

The properties of the structures so obtained are given in Table II below.

EXAMPLE 2 (COMPARATIVE TEST)

Polyethylene of the type utilized for preparing sheet (a) of the preceding example was mixed with 30% by weight (referred to the mixture) of glass fibres like those in Example 1. The mixture was extruded at 205°C in a double screw Pasquetti extruder and the extruded product was granulated and then formed into small plates by treatment for 5 minutes at 180°C in a plate press.

The same granulate was also used to prepare a plate by pressure injection at 225°C in a pressure-injector type GBF. The characteristics of the plates are given in Table III below.

EXAMPLE 3

Preparation of the layer structures described in Example 1 was repeated, except that a thermal treatment in the absence of pressure was first carried out, placing the polyethylene lamina bonded to the sheets of type (a) and (b) into a oven at 180°C, and then transferring the whole into a cold plate press operating at 200 kg/cm^2, for a time of 10 seconds. The properties of the resulting structures are analogous with those of the layer structures of Example 1.

EXAMPLE 4

Operating in the same manner and using the same polyethylene fibrils and the same glass fibres as used for sheet (a) of Example 1, sheets were prepared containg 50% by weight of glass fibres and having, after drying, the following characteristics:

thickness = 208 μ
weight = 220 g/m^2
density = 1.07 g/cm^3

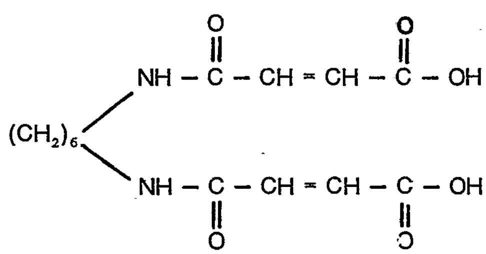
transverse tensile strength = 1.40 kg
longitudinal tensile strength = 1.95 kg

An increasing number of sheets was placed, in equal amounts, on the two faces of a high density polyethylene plate similar to the one of Example 1, and a laminate was formed according to the method employed in Example 3.

The properties of the multilayer structure so obtained are given in columns 1 and 2 of Table IV below.

EXAMPLE 5

Example 4 was repeated using a 1.3 mm thick lamina of polyethylene having a M.I. of 0.4 and a flexural modulus of 17,000 kg/cm^2, except that the sheets containing the glass fibres had been impregnated, prior to their bonding with the polyethylene lamina, with an aqueous solution containing 0.5% by weight of γ-aminopropyltriethoxysilane hydrolyzed at a pH of 3.4 with acetic acid, and 1% of a derivative of maleic anhydride having the structure:



and were seccessively dried.

The properties of the structures are given in column 3 of Table IV below.

TABLE I

	Sheets			Characterization method.
	(a)	(b)	(c)	
Sheet thickness (μ)	195	208	305	
Weight (g/m²)	185	192	219	(1)
Density (g/m³)	0.95	0.923	0.717	
Longitudinal tensile strength (kg)	4.46	4.79	3.36	(2)
Transverse tensile strength (kg)	3.24	3.88	2.60	(2)
Longitudinal flexural rigidity (g/cm)	57.1	39.3	44.9	(3)
Transverse flexural rigidity (g/cm)	48.1	30.8	37.0	(3)

(1) Tappi 420
(2) Tappi 494
(3) Tappi 489

TABLE II

	Bonded article with use of sheets (a)					Bonded article with use of sheets (b)		measuring method
Total thickness of the sandwich-bonded article (cm)	0.188	0.213	0.237	0.250	0.314	0.249	0.207	
Total thickness of sheets on each face of the polyethylene plate (cm)	0.0272	0.0400	0.0544	0.0800	0.0928	0.0656	0.0864	
Total content of glass fibres in the bonded article (%)	9.5	12.65	15.20	18.95	19.1	17.3	19.4	
Flexural modulus of elasticity (kg/cm^2)	25,900	31,400	34,550	39,800	41,900	42,200	44,950	(1)
Flexural tensile strength (kg/cm^2)	329	394	413	480	484	541	731	(2)
Density (g/cm^3)	1023	1,041	1,058	1.090	1.085	1.075	1.090	
Total energy of fracture (kg.cm/cm)	133	162	126	202	194	194	256	(3)
Creep resistance under load, at 80°C and 60 kg/cm^2: deformation after 24 h (%)	1.75	1.70	0.92	0.92	0.90	0.87	0.38	(4)
Endurance strength (10^3 cycles)	564	444	100	92	61	437	20	(5)
Load at the beginning of proof (kg/cm^2)	468	510	653	527	665	747	671	
Load at the end of proof (kg/cm^2)	304	312	407	309	432	293	162	

(1) ASTM–D–790
(2) ASTM–D–790
(3) "Ball drop" tests (biaxial impact) with constrained test piece; autographic ram; weight of the ram = 10.4 kg; height of fall = 1 m; resting ring Ø = 33 mm; punch diameter = 12.6 mm.
(4) ASTM–D–2990
(5) Standard DIN 50142, on plane machine PWO–0310 "WEBI".

TABLE III

	Method of preparing the plate	
	Pressure moulding	Pressure injection
Fibre content (%)	30	30
Thickness (cm)	0.179	0.296
Density (g/cm^3)	1.18	1.18
Flexural modulus of elasticity (kg/cm^2)	24,920	37,550
Flexural tensile strength (kg/cm^2)	269	360
Total energy of fracture (kg.cm/cm)	119	198
Creep resistance under load, at 80°C and 60 kg/cm^2: deformation after 24 hours (%)	1.44	1.55
Endurance strength: No. of cycles × 10^3	477	36
– load at the beginning of proof (kg/cm^2)	419	595
– load at the end of proof (kg/cm^2)	322	284

TABLE IV

	1	2	3
Total thickness of the multi-layer structure (cm)	0.161	0.272	0.272
Total thickness of the sheets on each face of the plate (cm)	0.018	0.065	0.065
Total content of glass fibres in the structure (%)	17.3	31.3	31.3
Flexural modulus of elasticity (kg/cm^2)	39,880	60,690	68,000
Flexural tensile strength (kg/cm^2)	495	709	1,000
Density (g/cm^3)	1.065	1.19	1.21
Total energy of fracture (kg. cm/cm)	273	319	417
Creep resistance under load, at 80°C and 60 kg/cm^2: deformation after 24 hours (%)	0.707	0.406	0.215

CLAIMS

1. A process for preparing an article based on thermoplastic polymeric material containing glass fibres as reinforcing material, comprising:

(a) preparing a dispersion, in an aqueous or in an inert liquid medium, of a mixture of glass fibres longer than 1 mm with fibrils of at least one olefinic thermoplastic polymer having a surface area of at least 1 m/g², with a glass fibre/olefinic polymer ratio of from 3/97 to 95/5;

(b) forming a sheet by deposition of the dispersion onto a porous surface, as a result of which there occurs substantial elimination of the liquid medium, with deposition of the glass fibres onto a plane substantially parallel to the principal plane of the sheet;

(c) drying the sheet; and

(d) heating the sheet at a temperature equal to or higher then the melting temperature of the olefinic polymer constituting the fibrils, or of the olefinic polymer having the highest melting temperature, with application of pressure, for a time period sufficient to melt the said fibrils.

2. A process as claimed in Claim 1, in which, prior to the heating step (d), at least two sheets obtained from step (b) or (c), are sandwiched on the two faces of a lamina of a thermoplastic polymer, substantially free from incorporated glass fibres, and possesses a flexural modulus lower than that of the having a flexural modulus less than that of the glass fibres present in such sheets, and in which the heating step (d) of the sheets is carried out at a temperature at least equal to the melting temperature of the fibrils, and at least equal to the softening temperature of the polymer forming the said lamina, with application of pressure, for a time period sufficient to cause the melting of the fibrils and at least superficial softening of the lamina, with consequent adhesion of the lamina to the sheets.

3. A process according to Claim 1, substantially as herein described in any of the foregoing Examples 1, 3, 4 and 5.

4. An article based on thermoplastic polymers, comprising a three-layer structure two layers of which are prepared from fibrils of an olefinic polymer containing 3 to 95% by weight of glass fibres longer than 1 mm, and arranged in a plane substantially parallel with the principal plane of the layers, the said two layers being thermowelded to the third layer, which is intermediate the said two layers and is prepared from a thermoplastic polymer compatible with the olefinic polymer of the said two layers, is substantially free from incorporated glass fibres, and possesses a flexural modulus lower than that of the glass fibres contained in the said two layers.

5. An article according to Claim 4, substantially as herein described in any of the foregoing Examples 1, 3, 4 and 5.

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