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THE PRODUCTION THEREOF, USE OF THE  
SAME, AND COMPOSITION COMPRISING  
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OIE FRANCE (FR)(57) **ABSTRACT**(21) Appl. No.: **11/597,629**

Filled polymer fiber containing additives within it, the filled polymer fiber having a Young's modulus greater than that of an unfilled polymer fiber and said additives including mineral additives having at least one submicron dimension.

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**LOADED POLYMER FIBRE, METHOD FOR THE PRODUCTION THEREOF, USE OF THE SAME, AND COMPOSITION COMPRISING SUCH FIBRES**

[0001] The present invention relates to the field of fibers, and more particularly relates to a filled polymer fiber.

[0002] Polymer fibers find application in numerous fields. Reference may be made, for example, to the article entitled "Textile applications of polypropylene fibers" by M. Jambrich and P. Hodul enclosed in the book "Polypropylene—an A-Z reference" edited by J. Karger-Kocsis, published by Kluwer Academic Publisher, 1999.

[0003] The polymer fibers are used alone for their own characteristics or also in combination with other materials and/or other fibers, incorporated into diverse matrices (mineral, polymer, etc), especially for a reinforcing purpose.

[0004] Moreover, these fibers are used for the manufacture of products of varied form: fleece, fabric, mat, unidirectional product, etc.

[0005] Also, there is a demand for a polymer fiber having good mechanical properties.

[0006] Document U.S. Pat. No. 6,331,265 discloses a fiber of polypropylene filled by means of 3% of carbon nanotubes introduced into the mass of polypropylene. These carbon nanotubes are about 1  $\mu\text{m}$  long and have a diameter of 1 to 50 nm. This filled polypropylene fiber has a linear titer of 1 dtex, a high tenacity and a Young's modulus greater than that of an unfilled polypropylene fiber. This fiber is proposed as reinforcement for mortars, concretes or cement pastes.

[0007] It is currently difficult to have a high purity of carbon nanotubes. In fact, catalyst residues may form micron-sized impurities that are able to decrease the properties of the end fiber. Moreover, it is difficult to produce carbon nanotubes in large quantities, which is reflected in the cost of the fiber.

[0008] In addition, this filled polymer fiber was made under laboratory conditions, without taking into account the industrial constraints, especially in terms of reliability and output. The proposed manufacturing process is therefore not realistic for industrial production.

[0009] The present invention proposes to supply a polymer fiber that has good mechanical properties, in particular a high Young's modulus, whilst being easy to manufacture on an industrial scale.

[0010] In this respect, the first subject of the invention is a filled polymer fiber comprising additives within it, the filled polymer fiber having a Young's modulus greater than that of an unfilled polymer fiber and the additives comprising mineral additives having at least one submicron dimension.

[0011] The combination of a polymer and mineral additives having at least one submicron dimension according to the invention makes it possible to obtain a fiber having an increased Young's modulus relative to an unfilled fiber based on the same polymer.

[0012] In addition, the mineral additives according to the invention are readily available in nature or are easily synthesized, and if necessary, easily purified. These additives also have the advantage of not being very expensive.

[0013] The manufacture of the fiber according to the invention is compatible with industrial requirements.

[0014] In the present application, the term "submicron dimension" according to the invention is understood to mean the submicron dimension of the mineral additives, taken as an average. The submicron dimension corresponds, for example, to a diameter or a thickness.

[0015] In the present application, the term "fiber" is defined in the broad sense. Without another adjective or specification added, the term "fiber" denotes both a undrawn fiber (in the solid phase) and also a drawn fiber (drawn one or more times). The term "fiber" denotes both a yarn or monofilament and also a set of filaments (of textile fiber type), that are identical to or different from each other. The fiber may be continuous or chopped, short or long.

[0016] Advantageously, the submicron dimension of the mineral additives may be less than 500 nm, and preferably less than 100 nm.

[0017] The mineral additives may be of spherical, rod-shaped or lamellar-type structure.

[0018] Naturally, a combination of additives with different structures can be envisaged.

[0019] Preferably, the mineral additives may have an aspect ratio greater than 5, and preferably greater than 50.

[0020] It can be recalled that the aspect ratio is defined as the ratio of the largest dimension to the smallest dimension.

[0021] A high aspect ratio ensures a high tenacity, in particular when the large dimension of the additives according to the invention is approximately parallel to the axis of the fiber.

[0022] The mineral additives may be metal oxides or clays.

[0023] Among the metal oxides, mention may be made of aluminas, barium oxides, titanium oxides, zirconium oxides, manganese oxides, talc, magnesia and calcium carbonate.

[0024] The clays may be lamellar, that is to say as platelets, or fibrous.

[0025] The mineral additives may comprise an exfoliable lamellar clay preferably chosen from synthetic and natural phyllosilicates, smectite clays such as montmorillonite, nontronite, beidellite, hectorite, saponite, sauconite, vermiculite and the equivalents, and also magadiite, kenyaite, stevensite, halloysite, aluminate oxides, hydrotalcite and the equivalents.

[0026] Preferably, the clays may have a negative surface charge of at least 20 milliequivalents, preferentially of at least 50 milliequivalents, and more preferentially between 50 and 150 milliequivalents, per 100 grams of said additives.

[0027] The clays may thus be modified by organic molecules that are able to be absorbed within the minerals, for example between clay platelets, which allows their exfoliation. Even though the clay may have any cationic exchange capacity, it is nevertheless preferable that the clay exfoliate correctly.

[0028] Preferably, the mineral additives may be chosen from montmorillonite and boehmite.

[0029] Boehmite is based on alumina monohydrate  $\text{Al—O—OH}$ . Boehmite is for example in rod form.

[0030] Montmorillonite has exfoliable platelets and may be distributed uniformly within the filled polymer fiber according to the invention.

[0031] Montmorillonite and boehmite have, moreover, a particularly high Young's modulus, greater than 100 GPa.

[0032] The mineral additives may be surface-modified by one at least of the following agents: cationic surfactants, amphoteric agents, derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines and sulfides, and preferably ammonium, sulfonium or phosphonium salts.

[0033] These agents are used as intercalants for clays in platelet form.

[0034] Furthermore, these agents also favor the dispersion of the mineral additives according to the invention.

[0035] The mineral additives may also be modified by an adhesion promoter that is preferably an organosilane compound, and still more preferentially a silane, an aminosilane, a vinylsilane and mixtures thereof.

[0036] The weight content of mineral additives relative to the total weight of the fiber may be preferably less than 10%, still more preferentially less than 5%.

[0037] The filled polymer fiber may be based on a polymer for example chosen from polyolefins, polyamides, polyesters, polyacrylonitrile and polyvinyl alcohols and copolymers thereof.

[0038] Advantageously, the filled polymer fiber may be a fiber of filled polyolefin, such as polyethylene or polypropylene, and still more preferentially of filled polypropylene.

[0039] The fiber may contain, moreover, a blend of a polyolefin and a polyolefin having polar functional groups, which is preferably a polyolefin grafted by maleic anhydride, glycidyl methacrylate, vinyl pyrrolidone, styrene-methacrylate, acrylates or acetates, the weight content of the polyolefin having polar functional groups relative to the total weight of the filled polymer fiber being preferably less than 10% and still more preferentially less than 5%.

[0040] The polyolefin having polar functional groups may be grafted before or after synthesis. The latter favors the dispersion of a blend to be spun and the drawing of the fiber. The percentage of polyolefin having polar functional groups may be limited for a greater increase in the Young's modulus.

[0041] The linear density of the filled polymer fiber may be between 0.5 to 10 dtex, more advantageously between 0.5 to 2 dtex.

[0042] A reinforcing effect that is particularly advantageous in the composites may be obtained with a fiber (monofilament) of relatively small cross section.

[0043] The cross section of a filled polymer fiber according to the invention is not necessarily circular and may have an irregular or multilobal shape.

[0044] The filled polymer fiber according to the invention may have a tenacity equal to at least 80% of that of the unfilled fiber.

[0045] In a particularly advantageous embodiment, the filled polymer fiber has a high tenacity of at least 4 cN/dtex, preferably at least 5 cN/dtex, very preferentially at least 7 cN/dtex, and in particular 8 to 9 cN/dtex.

[0046] This tenacity range may be achieved by regulating the spinning and drawing process in a suitable manner. By way of example, a polyolefin base material with a suitable molecular weight distribution may be specifically chosen.

[0047] The filled polymer fiber may preferably contain, on the surface, a sizing that contains an amine or polyamine, phosphoric or polyphosphoric compound, more preferably an ester of phosphoric acid based on a fatty chain.

[0048] A simple modification of the exposed surface of the fiber by a sizing makes it possible to effectively and durably improve the interaction between the fiber and a cement matrix.

[0049] The surface properties of the polymer fiber are modified by one or more sizing agents providing the function of assisting the spinning process.

[0050] The function of assisting the spinning process consists in facilitating the formation of the polymer fiber in at least one stage of the spinning: especially, it is to lubricate the fibers (monofilaments at this stage) so as to improve their handling by transport devices at various stages of the production, to minimize the electrostatic charges carried by the fiber.

[0051] For example, a product may be chosen from the products sold under the names SILASTOL Cut 5A and Cut 5B from Schill & Seilacher, SYNTHESIN 7292 from Dr Boehme, KB 144/2 from Cognis, STANTEX S6077 from Cognis and STANTEX S6087/4 from Cognis.

[0052] The sizing may be present on the fiber at a quantity of 0.05 to 5% by weight of solids relative to the dry weight of the fiber.

[0053] For hydraulic-setting matrix applications, the sizing also provides a function of wettability by the hydraulic binder-based composition, of promoting adhesion to the hydraulic-setting matrix and conferring on the fiber-cement composite further improved mechanical properties.

[0054] The function of wettability by the hydraulic binder-based composition consists in facilitating the dispersion of polymer fibers in the matrix, resulting from the good dispersion of the fibrous material within the initial binder/water mixture from which the product is manufactured. This function principally relies on the surface polarity of the fibrous material to make it hydrophilic.

[0055] The function of promoting adhesion to the hydraulic-setting matrix consists in strengthening the interaction between the fibrous reinforcement and the hardened product matrix. The latter function also relies on the presence of polar functional groups on the surface of the fibers.

[0056] These functions may be provided by one or more agents chosen from lubricants, antistatic agents, surfactants, fatty chain compounds and polymers having polar functional groups, in which a lubricant may be a fatty chain compound, likewise a surfactant may be a fatty chain compound, or an antistatic agent may be a polymer having polar functional groups.

[0057] A drawn fiber may be in the form of a chopped yarn with a length of around 2 to 20 mm, in particular 5 to 12 mm.

[0058] Another subject of the present invention is the use of a filled polymer fiber as described above, as a reinforcing fiber in a fiber-based product.

[0059] Therefore yet another subject of the present invention is a fiber-based product characterized in that it comprises filled polymer fibers as defined above.

[0060] Advantageously, the product is in the form of a fabric, fleece, long fiber mat, chopped fiber mat, unidirectional product, nonwoven product, cord, net, ribbon, webbing or strip, or else in the form of a mixture of said fibers with fibers of a different type, and preferably in commingled fiber form.

[0061] An example of a commingled fiber is the fiber sold under the trademark TWINTEX by Saint-Gobain that contains polypropylene filaments and glass filaments.

[0062] Multiple fields of application are possible for the filled polymer fiber according to the invention: carpets, hygienic applications, ribbons, cords and twines, the textile industry (clothing, yarns, etc.), domestic textiles (nonwoven for decoration, woven for walls, etc.), geotextiles, agrotexiles, packaging, medical textiles, bioactive fibers, multi-component fibers, high-performance yarns or high strength monofilaments (seat belts, safety nets, fishing nets, etc.).

[0063] Naturally, the filled polymer fiber according to the invention may be solid or predominantly solid, that is to say it may for example comprise a hollow core along the axis of the fiber.

[0064] Naturally, the (sized or unsized) filled polymer fiber according to the invention may be coated.

[0065] The fiber may be incorporated, in various forms, into products derived from oil, into bitumen products and, for example in mat form, into asphalt-based products such as roofing components.

[0066] The fiber, in various forms, may also be thermofomed.

[0067] In a first advantageous embodiment of the invention, the product comprises a mineral matrix, preferably a hydraulic-setting substance, and the product is preferably chosen from adhesives, mortars, concretes, grouts and fiber cements.

[0068] The hydraulic-setting substance is constituted from a hydraulic-setting binder, chosen mainly from various existing cements, which possibly have inert or active filler additives.

[0069] Among the fillers and additives, mention may be made of rheology modifiers (dispersing agents, plasticizers, superplasticizers and flocculants), mineral fillers (silica, fly ash, slag, pozzolana and carbonates), and also supporting or reinforcing fibers for filtration or dewatering processes (natural fibers, especially cellulose, or synthetic fibers).

[0070] During bending tests, the known products of this type very often perish on reaching the compressive strength level in what is commonly known as the upper zone.

[0071] The Applicant has determined that this situation results from a too important "deformability" of the fibers

taking up the tension in the lower zone, crack progressing even further as the fibers elongate.

[0072] Also, the reduction in the elongation of the fibers on the side intension is obtained by the high Young's modulus of the filled fibers according to the invention.

[0073] The increase in the Young's modulus of the filled fibers makes it possible, therefore, to limit the deformation of the lower zone. This limits the displacement of the neutral axis and therefore limits the increase of the compressive stress in the upper zone.

[0074] Thus, these hydraulic-setting products have a particularly high breaking load.

[0075] The fibers according to the invention are particularly effective as reinforcement for fiber cements, in quantities of around 0.2 to 5 wt % of fibers relative to the total dry weight of the initial mixture.

[0076] The fibers according to the invention are particularly effective as reinforcement for mortars, in quantities of around 0.01 to 0.2 wt % of fibers relative to the total dry weight of the initial mix for an "anticrack" effect and 0.2 to 5% for structural effects.

[0077] In this first embodiment, the fibers may be chopped yarns having a length between 2 and 20 mm and more particularly between 5 and 12 mm.

[0078] The product may have various shapes (hollow, tubular) and preferably is in the shape of a flat or corrugated sheet.

[0079] The hydraulic binder-based articles shaped into sheets may be manufactured by a technique of filtering an aqueous suspension comprising a hydraulic-setting binder, reinforcing fibers and possibly fillers.

[0080] A commonly used process based on this technique is known as the Hatschek process: a very dilute aqueous suspension is contained in a tank fitted with means for ensuring a homogenous distribution of the constituents within the volume of the tank; a filter drum is partially immersed in the tank and its rotation causes a thin layer of material (fibers and hydrated binder) to be deposited on its surface; this layer is carried by a felt towards a size roll onto which it is continuously wound up; when the layer has reached the desired thickness, it is cut so as to unwind from the roll an individual sheet of hydraulic-setting material. The sheet may then be made in the form of a shaped product and it acquires its final characteristics by the curing of the binder. A product of greater thickness may be obtained by superposing a suitable number of sheets and by pressing them together in order to ensure cohesion of the assembly.

[0081] Such boards are used as roofing or facade components.

[0082] In a second embodiment of the invention, the product may comprise a polymer matrix that is chosen preferably from a polyethylene, polypropylene, polyamide, polyester, epoxy or phenolic matrix.

[0083] The main fields of application for composites, for example based on polypropylene, are: transport (parts under the hood, parcel shelf, etc.), electrical applications, domestic and consumer goods, buildings and public works and industrial goods.

[0084] An additional subject of the present invention is a method of manufacturing a filled polymer fiber as defined above comprising a step of spinning a polymer composition comprising mineral additives having at least one submicron dimension.

[0085] The additives according to the invention are easily dispersible and do not significantly modify the rheological properties (viscosity, etc.) of the polymer composition to be spun.

[0086] The polymer composition may be obtained by extrusion. The extrusion temperature is to be adjusted depending on the polymer and said additives. By way of example, the spinning temperature may be between 250° C. and 300° C. for filled polypropylene.

[0087] The spinning step may comprise a cooling operation, preferably in suitably cooled and humidified air, for a good heat exchange capacity, and a radial cooling operation.

[0088] In a preferred embodiment, the method comprises a step of drawing at below the melting point, immediately after spinning or subsequently.

[0089] Preferably, the method may comprise a fiber tapering step by continuous drawing means.

[0090] This step may be achieved with the aid of rolls at various temperatures and with different speeds and with the aid of ovens.

[0091] In a preferred embodiment, the method comprises a step of preparing said composition, comprising at least one filtration operation.

[0092] In this way, potential aggregates and impurities are eliminated before spinning, for example with the aid of a filter at the extruder outlet.

[0093] Moreover, for a better control of the process (in terms of concentration, dispersion, compatibility, etc), the preparation step of the composition can include the realization of a premix transformed then in pellets, to dilute with the polymer and optionally with modified polymer. This premix is obtained by dilution in the polymer of a master batch in pellets and in preference non commercial which contains the mineral additives according to the invention. During its preparation, the master batch can be filtered.

[0094] A sizing step may be added in the spinning step.

[0095] A sizing step may be added after drawing and be followed by a step of drying with the aid of air oven(s).

[0096] The size may be applied neat or as an aqueous solution, dispersion or emulsion, or one based on another suitable carrier liquid.

[0097] A subject of the invention is also a method of manufacturing a product based on filled fibers as defined above and on a hydraulic-setting substance.

[0098] According to this method, an initial mixture is prepared, based on hydraulic binder, water and fibers as defined above, the fibers are filtered over a stationary or moving support in order to form a wet elementary sheet, possibly a plurality of elementary sheets are superposed to form a wet intermediate product and the board or the wet intermediate product is dried.

[0099] A subject of the invention is also a composition for a hydraulic-setting material comprising a hydraulic binder and fibers as described above. These compositions may be cement preparations to be put into suspension for the dewatering process, or cement preparations for mortars for other forming processes.

[0100] A final subject of the invention is a composition comprising a polymer matrix and fibers as described above.

[0101] Such matrices may be preferably thermoplastic matrices, thermosetting matrices, and preferably polyethylene, polypropylene, polyamide, polyester, epoxy or phenolic matrices.

[0102] The invention will now be described in a nonlimiting manner in the following examples.

#### EXAMPLE 1

##### Reference

[0103] The reference fiber was an unfilled high-tenacity small-diameter (1 dtex) fiber obtained, without mineral additives, according to the invention from polypropylene resin HF445FB from Borealis, having a melt flow index of 18 g/10 min measured at 230° C. and 2.16 kg.

[0104] On exiting the spinneret—which has holes approximately 0.35 mm in diameter—the fiber, that is to say, all monofilament, will freeze after a rapid cooling and with a cooling air that is temperature and speed controlled.

[0105] During the spinning, a sizing having the reference SYNTHESIN 7292, sold by Dr Boehme, was deposited onto the polypropylene fiber as it exited the spinneret, in an amount of 0.45 wt % of polypropylene fiber solids.

[0106] The fiber was then wound onto a reel, then unwound and drawn continuously in a drawing zone comprising various series of heated rolls rotating at increasing rotation speeds. Hot-air or steam ovens were interposed between the various series of rolls. At the end of the drawing zone, the fiber was cooled.

[0107] The fiber was then chopped into 30 mm lengths to carry out the tests.

#### EXAMPLE 2

[0108] A filled polypropylene fiber was manufactured from the following polymer composition, expressed in wt % of material relative to the total weight of the fiber:

[0109] 5.5% of the product NANOMER C44PA manufactured by Nanocor, and containing about 45% of montmorillonite and polypropylene (PP);

[0110] 94.5% of Borealis HF445FB PP.

[0111] Montmorillonite is a clay whose platelets have a nanoscale average thickness and an average length of several hundred nanometers, giving an aspect ratio greater than 50.

[0112] The polymer composition was produced in a single-screw extruder at a temperature of about 250° C. and was fed into a spinneret having holes 0.35 mm in diameter. The viscosity of the composition was comparable to that of the polymer used.

[0113] During the spinning, a sizing having the reference SYNTHESIN 7292, sold by Dr Boehme, was deposited onto the filled polypropylene fiber as it exited the spinneret, in an amount of 0.45 wt % of filled polypropylene fiber solids.

## EXAMPLE 3

[0114] A filled polypropylene fiber was manufactured from the following polymer composition, expressed in wt % of material relative to the total weight of the fiber:

[0115] 40% of a premix concentrated to 5% of montmorillonite and in pellet form, this premix being obtained from 87.5% of Borealis HF445FB PP and 12.5% of NANO-BLEND 1001 sold by Polyone which contains about 40% of montmorillonite and PP;

[0116] 60% of Borealis HF445FB PP.

[0117] The clay platelets had a nanoscale average thickness and an average length of several hundred nanometers, giving an aspect ratio greater than 50.

[0118] The premix was produced in a corotating twin-screw extruder at a temperature of 220° C., was passed through a filter having holes of about 40  $\mu$ m diameter and was then fed into a spinneret having holes 3 mm in diameter in order to manufacture pellets.

[0119] The polymer composition was produced in a single screw extruder at a temperature of about 250° C. and was fed into a spinneret having holes 0.35 mm in diameter. The viscosity of the composition was comparable to that of the polymer used.

[0120] During the spinning, a sizing having the reference SYNTHESIN 7292, sold by Dr Boehme, was deposited onto the filled polypropylene fiber as it exited the spinneret, in an amount of 0.45 wt % of filled polypropylene fiber solids.

## EXAMPLE 4

[0121] A filled polypropylene fiber was manufactured from the following polymer composition, expressed in wt % of material relative to the total weight of the fiber:

[0122] 40% of a premix concentrated to 5% of montmorillonite and in pellet form, this premix being obtained from 87.5% of Borealis HF445FB PP and 12.5% of NANO-BLEND 1001;

[0123] 58% of Borealis HF445FB PP; and

[0124] 2% of polypropylene grafted with 1% maleic anhydride, known as PPgMA, of reference POLYBOND3200 from Crompton.

[0125] The clay platelets had a nanoscale average thickness and an average length of several hundred nanometers, giving an aspect ratio greater than 50.

[0126] The fiber was manufactured under conditions similar to those in example 3.

## EXAMPLE 5

[0127] A filled polypropylene fiber was manufactured from the following polymer composition, expressed in wt % of material relative to the total weight of the fiber:

[0128] 60% of a premix concentrated to 5% of montmorillonite and in pellet form, this premix being obtained from 87.5% of Borealis HF445FB PP and 12.5% of NANO-BLEND 1001;

[0129] 37% of Borealis HF445FB PP; and

[0130] 3% of PPgMA of reference POLYBOND3200 from Crompton.

[0131] The clay platelets had a nanoscale average thickness and an average length of several hundred nanometers, giving an aspect ratio greater than 50.

[0132] The fiber was manufactured under conditions similar to those in example 3.

## EXAMPLE 6

[0133] A filled polypropylene fiber was manufactured from the following polymer composition, expressed in wt % of material relative to the total weight of the fiber:

[0134] 60% of a premix concentrated to 5% of montmorillonite and in pellet form, this premix being obtained from 87.5% of Borealis HF445FB PP and 12.5% of NANO-BLEND 1012 sold by Polyone containing about 40% of montmorillonite and PP;

[0135] 37% of Borealis HF445FB PP; and

[0136] 3% of PPgMA of reference POLYBOND3200 from Crompton.

[0137] The clay platelets had a nanoscale average thickness and an average length of several hundred nanometers, giving an aspect ratio greater than 50.

[0138] The fiber was manufactured under conditions similar to those in example 3.

## EXAMPLE 7

[0139] A filled polypropylene fiber was manufactured from the following polymer composition, expressed in wt % of material relative to the total weight of the fiber:

[0140] 20% of a premix concentrated to 5% of montmorillonite and in pellet form, this premix being obtained from 84.5% of Borealis HF445FB PP and 15.5% of the product PL19315 sold by Multibase and which contains about 32% of montmorillonite and PP;

[0141] 79.5% of Borealis HF445FB PP; and

[0142] 0.5% of PPgMA of reference POLYBOND3200 from Crompton.

[0143] The clay platelets had a nanoscale average thickness and an average length of several hundred nanometers, giving an aspect ratio greater than 50.

[0144] The fiber was manufactured under conditions similar to those in example 3.

## EXAMPLE 8

[0145] A filled polypropylene fiber was manufactured from the following polymer composition, expressed in wt % of material relative to the total weight of the fiber:

[0146] 60% of a premix concentrated to 5% of modified montmorillonite and in pellet form, this premix being obtained from 90% of PP, 5% of PPgMA and 5% of modified montmorillonite containing about 62% of montmorillonite and alkyl ammonium,

[0147] 40% of Borealis HF445FB PP.

[0148] The clay platelets had a nanoscale average thickness and an average length of several hundred nanometers, giving an aspect ratio greater than 50.

[0149] The premix was produced in a corotating twin-screw extruder at a temperature of 180° C., was passed through a filter having holes of about 40  $\mu$ m diameter and was then fed into a spinneret having holes 3 mm in diameter in order to manufacture pellets. This premix is a diluted mix 80% of Borealis HF445FB PP, with 20% of a non commercial master batch in pellet form and which contains 50% of Borealis HF445FB PP, 25% of PPgMA of reference POLYBOND3200 from Crompton and 25% of modified montmorillonite in powder of reference Cloisite C20A sold by Southern Clay Products. The master batch realized in a corotating twin-screw extruder at a temperature of 180° C., was passed through a filter having holed of about 40  $\mu$ m diameter and was then fed into a spinneret having holes 3 mm in diameter in order to manufacture pellets of the master batch.

[0150] The polymer composition was produced in a single screw extruder at a temperature of about 250° C. and was fed into a spinneret having holes 0.35 mm in diameter. The viscosity of the composition was comparable to that of the polymer used.

[0151] During the spinning, a sizing having the reference SYNTHESIN 7292, sold by Dr Boehme, was deposited onto the filled polypropylene fiber as it exited the spinneret, in an amount of 0.45 wt % of filled polypropylene fiber solids.

#### EXAMPLE 9

[0152] A filled polypropylene fiber was manufactured from the following polymer composition, expressed in wt % of material relative to the total weight of the fiber:

[0153] 70% of a premix based on modified boehmite concentrated to 3% and in pellet form, this premix being obtained from 94% of Borealis HF445FB PP, 3% of PPgMA

of reference POLYBOND3200 and 3% of boehmite sold under the name CAM9010 by SAINT-GOBAIN and surface-modified with 0.5% of  $\gamma$ -aminopropyltriethoxysilane sold under the name A1100 by Aldrich, and

[0154] 30% of Borealis HF445FB PP.

[0155] This boehmite was in the form of rods having an average diameter of about 20 nm and an average length between 100 and 200 nm, and thus an aspect ratio greater than 5.

[0156] The fiber was manufactured under conditions similar to those in example 3.

[0157] Tests

[0158] The results of the reference fiber no. 1 and the filled fibers no. 2 to no. 8 before drawing (continuous cold drawing) are recorded in Table 1 below.

[0159] The results of reference fiber 1 and filled fibers 2 to 8 after drawing (continuous cold drawing) are recorded in Table 2 below.

[0160] The Young's modulus is defined as being the secant modulus, equal to the ratio of a stress to a nominal strain respectively 1, 5 or 10%.

[0161] The Young's moduli were calculated from tenacity-elongation curves obtained on a single fiber using a Fafegraph tensile testing machine sold by Textechno. The diameters were measured using a Vibromat sold by Textechno. The measurement conditions were determined by the ISO5079 standard. The distance between the jaws was 10 mm for the fibers before drawing and 20 mm after drawing, there being drawn continuously in the solid state to the maximum draw ratio while preventing the fibers (continuous yarns at this stage) from breaking.

TABLE 1

| Examples of fibers before cold drawing | Weight content of mineral additives (%) | Spinning linear density (dtex) | Elongation at break (%) | Tenacity (cN/dtex) | Modulus at 1% (GPa) | Gain in modulus at 1% |
|----------------------------------------|-----------------------------------------|--------------------------------|-------------------------|--------------------|---------------------|-----------------------|
| 1 (ref)                                | 0                                       | 4.9                            | 470                     | 1.5                | 1.08                | —                     |
| 2                                      | 2.5                                     | 4.8                            | 520                     | 1.4                | 1.45                | 34%                   |
| 3                                      | 2                                       | 4.8                            | 510                     | 1.4                | 1.61                | 49%                   |
| 4                                      | 2                                       | 5.1                            | 500                     | 1.4                | 1.54                | 42%                   |
| 5                                      | 3                                       | 5.1                            | 460                     | 1.4                | 1.56                | 44%                   |
| 6                                      | 3                                       | 4.6                            | 490                     | 1.3                | 1.59                | 47%                   |
| 7                                      | 1                                       | 5                              | 470                     | 1.4                | 1.41                | 31%                   |
| 8                                      | 3                                       | 4.7                            | 530                     | 1.3                | 1.55                | 43%                   |
| 9                                      | 2                                       | 5.1                            | 500                     | 1.2                | 1.39                | 29%                   |

[0162]

TABLE 2

| Examples of cold drawn fibers | Weight content of mineral additives (%) | Linear density (dtex) | Elongation at break (%) | Tenacity (cN/dtex) | Modulus at 5% (GPa) | Gain in modulus at 5% | Modulus at 10% (GPa) | Gain in modulus at 10% |
|-------------------------------|-----------------------------------------|-----------------------|-------------------------|--------------------|---------------------|-----------------------|----------------------|------------------------|
| 1 (ref)                       | 0                                       | 1                     | 23                      | 9.3                | 6                   | —                     | 5.4                  | —                      |
| 2                             | 2.5                                     | 0.9                   | 18                      | 9.1                | 7.5                 | 25%                   | 6.4                  | 19%                    |

TABLE 2-continued

| Examples of cold drawn fibers | Weight content of mineral additives (%) | Elongation            |              |                    | Modulus at 5% (GPa) | Gain in modulus at 5% | Modulus at 10% (GPa) | Gain in modulus at 10% |
|-------------------------------|-----------------------------------------|-----------------------|--------------|--------------------|---------------------|-----------------------|----------------------|------------------------|
|                               |                                         | Linear density (dtex) | at break (%) | Tenacity (cN/dtex) |                     |                       |                      |                        |
| 3                             | 2                                       | 0.9                   | 19           | 9.0                | 6.9                 | 15%                   | 5.9                  | 9%                     |
| 4                             | 2                                       | 0.9                   | 19           | 9.0                | 6.8                 | 13%                   | 6.1                  | 13%                    |
| 5                             | 3                                       | 0.9                   | 18           | 9.4                | 7.8                 | 30%                   | 6.7                  | 24%                    |
| 6                             | 3                                       | 0.9                   | 18           | 9.7                | 7.5                 | 25%                   | 6.5                  | 20%                    |
| 7                             | 1                                       | 1.1                   | 20           | 8.9                | 6.6                 | 10%                   | 5.8                  | 8%                     |
| 8                             | 3                                       | 0.9                   | 19           | 8.5                | 7.2                 | 20%                   | 6.0                  | 12%                    |
| 9                             | 2                                       | 0.8                   | 16           | 8.5                | 7                   | 17%                   | 6.1                  | 13%                    |

[0163] The Young's modulus of the undrawn and drawn fibers 2 to 9 is clearly higher than that of the respectively undrawn and drawn reference fiber 1. Moreover, the drawn fibers 2 to 9 retain a high tenacity.

[0164] The following examples illustrate the application of various filled polypropylene fibers according to the invention to the manufacture of a cement product.

#### EXAMPLE 10

[0165] A cement product was manufactured by filtration, by a laboratory method reproducing quite faithfully the main characteristics of the products obtained by industrial methods such as the Hatschek technique.

[0166] Two cement compositions were prepared based on the following cement matrix, put into suspension with a large excess of water:

| Constituents                                                 | Mass (in g) |
|--------------------------------------------------------------|-------------|
| CPA cement (95% clinker)                                     | 79.2        |
| Calcium carbonate                                            | 15.5        |
| <i>Pinus Radiata</i> cellulose                               | 3.5         |
| Unfilled polypropylene fibers or filled polypropylene fibers | 1.8         |
| BASF AE70 flocculent                                         | 400 ppm     |
| TOTAL                                                        | 100         |

[0167] Thus a first reference cement composition was prepared with filled polypropylene fibers identical to the reference fiber of example 1. These fibers were also manufactured in a similar way to that of example 1 but with an additional post-sizing step, carried out after drawing, in an amount of 0.4 wt % of filled polypropylene fiber solids.

[0168] Thus a second cement composition was prepared with filled polypropylene fibers identical to the fiber of example 5. These fibers were also manufactured in a similar way to that of example 5 but with an additional post-sizing step, carried out after drawing, in an amount of 0.4 wt % of filled polypropylene fiber solids.

[0169] The fibers were chopped into 10 mm lengths.

[0170] For each composition, the composition was filtered through a metal grid to form a single layer of about 1 mm thickness. Six individual layers were superposed and sub-

jected to a pressing cycle in order to obtain a material containing, before setting, about 50 wt % of water relative to the weight of cement, and a thickness of about 6 mm.

[0171] This laboratory material underwent a curing of 6 days at 40° C. in a waterproof bag, before being cut into test pieces that were 20 mm wide with lengths greater than 260 mm. The test pieces were put into cold water for 24 hours in order to be mechanically stressed under tension.

[0172] The tensile tests were carried out by fixing the test pieces between the clamps of a tensile testing machine with a distance between the clamps of 180 mm. The tensile test was carried out at a pull rate of 1.2 mm/min.

[0173] The test samples 10a correspond to the reference test pieces (with unfilled fibers). The test pieces 10b correspond to the test pieces according to the invention (with filled fibers).

[0174] The force-displacement curve was plotted. This had a behaviour that was typical of the results observed with products obtained by the Hatschek technique.

[0175] At the start of the displacement, the force increased rapidly, then a plateau was observed where the force increased slowly, corresponding to multicracking of the test sample, until the appearance of a macrocrack, after which the force dropped by the slip effect during opening of the macrocrack.

[0176] The length of the multicracking plateau reflected the effect of the board reinforcement by all the fibers.

[0177] In particular, it was observed that the breaking force, defined as the force divided by the width of the test sample and shown in Table 3 was especially high for each test sample 10b and moreover was greater than the breaking force of the reference test pieces 10a.

TABLE 3

| Test samples    | Breaking strength (N/mm) | Gain in breaking strength (%) | Length of the multicracking plateau (mm) | Gain in length of the multicracking plateau (%) |
|-----------------|--------------------------|-------------------------------|------------------------------------------|-------------------------------------------------|
| 10a (reference) | 24                       | —                             | 9                                        | —                                               |
| 10b             | 28                       | 17                            | 12                                       | 33                                              |

[0178] In an embodiment variant, the amount of calcium carbonate was increased to 60%, even 80%, and conversely the amount of cement was significantly reduced.

[0179] In a similar way, test samples containing fibers identical to the fibers of examples 2 to 4 or 6 to 9 may also be produced.

#### EXAMPLE 11

[0180] This example 11 illustrates the application of filled fibers according to the invention to the manufacture of a cement product by the Hatschek process.

[0181] Aqueous suspensions based on a matrix identical to that with the filled fibers of example 10 were prepared. Each suspension was introduced into the tank of a Hatschek machine, for the formation of a film and for the winding onto a size roll of a sheet of hydrated cement material of about 1 mm thickness. After cutting, sheets of hydrated material were superposed on a former so as to form plane or corrugated sheets having a thickness of 6 mm.

[0182] The sheets were subjected to mechanical tests after 28 days of curing at room temperature.

[0183] Test samples having the same dimensions as those in example 10 were subjected to tensile tests under the same conditions. The force-displacement curves were of similar behaviour, with a multicracking plateau and a decrease after pull-out.

[0184] It was observed that the breaking strength was particularly high for each test sample.

[0185] In a similar way, test samples containing fibers that are identical to the fibers of examples 2 to 4 or 6 to 9 may also be produced.

#### [0186] Other Uses of Filled Polymer Fibers

[0187] The filled polymer fibers according to the invention, for example filled polypropylene fibers similar to the fibers of examples no. 2 to no. 9 or filled polymer fibers having a greater linear titer, may be used as technical yarns or high strength monofilaments to manufacture seat belts, packaging, safety nets, fishing nets, etc.

[0188] Thus the filled polymer fibers according to the invention may be used to manufacture unidirectional or mat-type fabrics that are also hot compactable following the methods described in the articles entitled "The Hot Compaction behaviour of woven oriented PP fibres and tapes. I. Mechanical Properties", by P. J. Hine et al., published in *Polymer*, 44, 2003, pp 1117-1131, and "The hot compaction of high modulus melt-spun polyethylene fibres" by P. J. Hine et al., published in *Journal of Materials Science*, 28, 1993, pp 316-324.

[0189] The filled polypropylene fibers according to the invention may also be used to manufacture agrotexiles and geotextiles according to the method described in the article entitled "Geotextiles and geomembranes", by K. Chan in the book "Polypropylene: an A-Z reference", edited by J. Karger-Kocsis, published by Kluwer Academic Publisher, 1999.

[0190] Filled polypropylene fibers according to the invention may also be used to manufacture all-polypropylene (PP) thermoformed composites, filament windings of PP yarns, all-PP sandwich panels composed at the surfaces of PP fiber fabrics or mats and at the core of a PP honeycomb or a PP foam. Reference may be made to the article entitled "Composites for recyclability", by T. Pejris, published in *Materials*

Today, 2003, pp 30-35. Such a composite has the advantage of being completely recyclable.

[0191] The filled polypropylene fibers according to the invention may also be used to manufacture:

[0192] bundles of impregnated yarns following the method described in "Impregnation techniques for fiber bundles or tow", by A. Lutz et al., in the book "Polypropylene: an A-Z reference", edited by J. Karger-Kocsis, published by Kluwer Academic Publisher, 1999;

[0193] composite boards with a fabric, unidirectionals or a mat of PP fibers, impregnated with thermosetting resin: following the method described in "Melting behavior of gelspun/drawn polyolefins", by C. W. M. Bastiaansen et al., published in *Makromol. Chem., Macromol. Sym.*, 28, 1989, pp 73-84;

[0194] a mixture of PP fibers with glass fibers, for example following the Twintex method of Saint-Gobain.

[0195] In addition, the filled polymer fiber according to the invention may just be a fiber obtained by a continuous one-step drawing process (no subsequent operation).

[0196] In addition, the filled polymer fiber according to the invention may just be a fiber obtained by spinning a polymer composition without prior premixing.

[0197] The filled polymer fiber according to the invention may just be a fiber obtained by solvent spinning (gel spinning or wet spinning) starting from a polymer in solution or from polymer precursors. Reference may be made to the article entitled "Study on gel spinning process of ultra-high molecular weight polyethylene", Y. Zhang, C. Xiao, J. Guangxia, A. Shulin, *Journal of Applied Polymer Science*, 1999, vol. 4, no. 3, pp 670-675.

[0198] The filled polymer fiber according to the invention can also be a fiber from a filled fibrillated ribbon.

1. A filled polymer fiber containing additives within it, the filled polymer fiber having a Young's modulus greater than that of an unfilled polymer fiber, characterized in that the additives include mineral additives having at least one submicron dimension.

2. The filled polymer fiber according to claim 1, characterized in that the submicron dimension of the mineral additives is less than 500 nm, and preferably less than 100 nm.

3. The filled polymer fiber according to any one of the preceding claims, characterized in that the mineral additives are of spherical, rod-shaped or lamellar-type structure.

4. The filled polymer fiber according to any one of the preceding claims, characterized in that the mineral additives have an aspect ratio greater than 5, and preferably greater than 50.

5. The filled polymer fiber according to any one of the preceding claims, characterized in that the mineral additives are chosen from metal oxides, clays and mixtures thereof.

6. The filled polymer fiber according to any one of the preceding claims, characterized in that the mineral additives include an exfoliable lamellar clay preferably chosen from synthetic and natural phyllosilicates, smectite clays, magadiite, kenyaite, stevensite, halloysite, aluminate oxides, hydrotalcite and the equivalents.

7. The filled polymer fiber according to any one of the preceding claims, characterized in that the mineral additives are chosen from montmorillonite and boehmite.

8. The filled polymer fiber according to any one of the preceding claims, characterized in that the mineral additives are surface-modified by one at least of the following agents: cationic surfactants, amphoteric agents, derivatives of aliphatic, aromatic or arylaliphatic amines, phosphines, sulfides and preferably by ammonium, sulfonium or phosphonium salts.

9. The filled polymer fiber according to any one of the preceding claims, characterized in that the mineral additives may be modified by an adhesion promoter that is preferably an organosilane compound.

10. The filled polymer fiber according to any one of the preceding claims, characterized in that the weight content of mineral additives relative to the total weight of the fiber is less than 10%, preferably less than 5%.

11. The filled polymer fiber according to any one of the preceding claims, characterized in that it is a fiber of filled polyolefin, and preferably of filled polypropylene.

12. The filled polymer fiber according to the preceding claim, characterized in that the fiber comprises a blend of a polyolefin and a polyolefin having polar functional groups and which is preferably a polyolefin grafted by maleic anhydride, glycidyl methacrylate, vinyl pyrrolidone, styrene-methacrylate, acrylates or acetates, the weight content of the polyolefin having polar functional groups relative to the total weight of the filled polymer fiber being preferably less than 10%.

13. The filled polymer fiber according to any one of the preceding claims, characterized in that the linear titer of the polymer fiber is between 0.5 and 10 dtex, preferably between 0.5 dtex to 2 dtex.

14. The filled polymer fiber according to any one of the preceding claims, characterized in that it has a tenacity of at least 4 cN/dtex, preferably at least 7 cN/dtex.

15. The filled polymer fiber according to any one of the preceding claims, characterized in that it includes, on the surface, a sizing that contains an amine or polyamine, phosphoric or polyphosphoric compound, preferably an ester of phosphoric acid based on a fatty chain.

16. The use of a filled polymer fiber according to any one of the preceding claims as a reinforcing fiber in a product.

17. A fiber-based product characterized in that it includes filled polymer fibers according to any one of claims 1 to 15.

18. The fiber-based product according to the preceding claim, characterized in that it is in the form of a fabric, fleece, chopped fiber mat, long fiber mat, nonwoven product, unidirectional product, cord, net, ribbon, webbing or strip, or else in the form of a mixture of said fibers with fibers of a different type, and preferably in commingled fiber form.

19. The fiber-based product according to either of claims 17 and 18, characterized in that it includes a mineral matrix, preferably a hydraulic-setting material, and more preferably the product is chosen from adhesives, mortars, concretes, grouts and fiber cements.

20. The fiber-based product according to claim 19, characterized in that the product is a fiber cement and comprises 0.2 to 5 wt % of said fibers relative to the total dry weight of the initial mixture.

21. The fiber-based product according to either of claims 19 and 20, characterized in that it has the shape of a flat or corrugated sheet.

22. The fiber-based product according to either of claims 17 and 18, characterized in that it includes a polymer matrix and that it is chosen preferably from a polyethylene, polypropylene, polyamide, polyester, epoxy or phenolic matrix.

23. A method of manufacturing a filled polymer fiber according to any one of claims 1 to 15, including a step of spinning a polymer composition containing mineral additives having at least one submicron dimension.

24. The method of manufacturing a polymer fiber according to claim 23, characterized in that it includes a step of drawing below the melting point.

25. The method of manufacturing a polymer fiber according to either of claims 23 and 24, characterized in that it includes a step of preparing said composition incorporating at least one filtration operation.

26. A method of manufacturing a product based on fibers and on a hydraulic-setting material, characterized in that:

an initial mixture is prepared, based on hydraulic binder, water and filled polymer fibers defined according to any one of claims 1 to 15;

the fibers are filtered over a stationary or moving support to form a wet elementary layer; and

a plurality of elementary layers are superimposed to form a wet intermediate product and in that the wet intermediate product is dried.

27. A composition for a hydraulic-setting material including a hydraulic binder and filled polymer fibers according to any one of claims 1 to 15.

28. A composition including a polymer matrix and filled polymer fibers according to any one of claims 1 to 15.

29. The composition according to the preceding claim, characterized in that the matrix is a polyethylene, polypropylene, polyamide, polyester, epoxy or phenolic matrix.

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