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(54) **Process for the preparation of moisture resistant vegetable fibres**

Verfahren zur Herstellung von feuchtigkeitsbeständigen Pflanzenfasern

Procédé de préparation de fibres végétals résistants à l'humidité

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Description

The present invention relates to a process for the preparation of vegetable fibres having an improved moisture resistance, and more in particular to the preparation of long multicelled vegetable fibres having an improved moisture resistance; to the moisture resistant vegetable fibres prepared by said process and to their use as fibre reinforcement in polymer matrices.

Vegetable fibres form a class of very desirable products for a wide range of applications, for reasons of cost and performance. For example, the mechanical performance properties of flax, which is a well-known example of a long multicelled vegetable fibre, are comparable to those of glass and metal fibres, when taken on weight basis. The vegetable fibres not only have a much lower density than glass and metal, but are moreover also considerably cheaper. Due to their lower rigidity or higher flexibility it can be expected that the vegetable fibres will result in a more favourable processability compared to glass, especially with regard to abrasion of equipment and to fibre-breakage, e.g. during fibre dispersion.

A field of application wherein the hereinbefore mentioned characteristics of vegetable fibres may play an important part, is their use as reinforcing fibres, for example in polymer composites.

Notwithstanding the hereinbefore described positive characteristics of vegetable fibres, their use as reinforcing fibres has one serious drawback when compared with that of e.g. glass, i.e. their sensitivity to moisture. When vegetable fibres are contacted with water or employed in a moist atmosphere, they tend to absorp water and swell, which phenomenon may also occur when they are employed as fibrous reinforcement in e.g. polymer composites, thereby affecting the dimension stability of said composites.

The vegetable fibres belong to the class of lignocellulosic materials, which materials have three major components in common, i.e. cellulose, hemicellulose and lignin. Cellulose is a high molecular weight linear polysaccharide, which as result of its high molecular weight is insoluble at room temperature in water and dilute acids and alkali. It is a substantially crystalline material and the major structural component of the cell wall of said lignocellulosic materials, such as the vegetable fibres, and is primarily responsible for the strength of these fibrous materials. Hemicellulose, on the other hand, is a poorly ordered, non-crystalline, relatively low chain length non-cellulosic polysaccharide, and occurs in close association with the cellulose in the cell wall as well as with lignin between the cells. Lignin is chemically speaking a totally different type of compound, being a phenol-based aromatic polymer comprising phenyl-propane units. It occurs mainly as an encrusting agent between the fibres and on the outer wall of the cell.

It is generally accepted that hemicellulose is not only the most hygroscopic of the three components mentioned hereinbefore but moreover also the most accessible. Hence the hemicellulose component present in the lignocellulosic materials, is generally considered to be the cause of their dimension instability due to moisture absorption.

Cellulose is also hygroscopic, but contrary to hemicellulose it hardly swells, if at all, as a result of moisture absorption and hence does not contribute to the dimension instability of vegetable fibres.

Lignin does not play a part in the process of moisture absorption.

Processes for treating lignocellulosic materials and comprising an at least partial removal and decomposition of the hemicellose component, are known from numerous publications. For example a method for treating green vegetable fibres is known from GB-A- 388 561, which describes a process wherein vegetable fibres are submitted to a steam treatment at high temperatures and pressure for a relatively short time, followed by extrusion under pressure from the reaction chamber through one or more orifices. The latter treatment causes the fibres to be rent apart by expansion of the steam and ultimately results in loose free fibres i.e. materials wherein the cellulose walls have been ruptured. When the steam treatment is prolonged the fibres are converted to a more or less pulpy condition.

In GB-A- 476 569, a similar process is described wherein the steam/water treatment is conducted in two-stages, the pressure in the second stage being lower than in the first. With both processes the disintegrated fibrous materials are purified by washing and used e.g. as packing material or for board-making.

In WO-A-8704194 a process is described for the preparation of modified fibrous flax, which comprises subjecting a fibrous plant to the action of high pressure steam followed by expansion to atmospheric pressure and finally washing the thus obtained fibrous materials. Said fibrous materials, before spinning and after carding, essentially consist of elementary fibres which are free from encrusting materials; and thus lack mechanical strength.

In EP-A- 0 161 766, a process is described for the preparation of composite products from ligno-cellulosic materials, which comprises treating the lignocellulosic material in divided form with steam to heat the lignocellulosic material to a temperature high enough to release hemicellulose and for a time sufficient to decompose and hydrolyse hemicellulose. The thus treated lignocellulosic material is subsequently formed into a mat and compressed at a temperature not exceeding the temperature at which the mat would char, and at a pressure and for a time sufficient to transfer the hemicellulose decomposition products into a polymeric substance, which adhesively bonds together the lignocellulosic material. In the thus obtained boards the cellulose cell walls of the vegetable fibres are irreversibly deformed, i.e. flattened, and due to a combination of compression and reaction of the hemicellulose decomposition products, said vegetable fibres have permanently lost the characteristics of individual vegetable fibres. It is mentioned that the treated

materials are almost completely free from hemicellulose and hence have a better dimension stability. In one embodiment of said process, which appears to be preferentially applied to selected agricultural fibrous materials, the steam pressure is suddenly released upon completion of the steam treatment, which treatment is known to explode and shred the treated material into a fibrous lump.

In EP-A- 0 373 726 a process is described for the preparation of a fibrous aggregate wherein a section of cellulosic fibrous material, i.e. softwood, is exposed to the action of an aqueous softening agent at a temperature in the range of from 150 to 220°C at a pressure which is at least the equilibrium pressure of the softening agent at the operating temperature, thereby at least partially disproportionating and hydrolyzing the hemicellulose and the lignin present in the cellulosic material, and a curing stage comprising drying the product of the softening stage at a temperature in the range of from 100 to 200°C, preferably in a mould under pressure, to yield a shaped cross-linked cellulosic matrix.

The vegetable fibres which have been treated by anyone of the hereinbefore mentioned processes have in common that at least part of their hemicellulose has been removed by means of hydrolysis and hence it can be expected that this will result in an improvement of their moisture resistance. Regarding the end products formed there is a considerable difference. With some of the processes the end products are loose fibrous materials of which the cellulosic cell walls have been ruptured, while with other processes the end products are composite products or aggregates wherein the cellulosic cell walls have frequently been ruptured and/or the characteristics of the individual fibres have disappeared altogether.

As known from numerous textbooks on the subject of lignocellulosic fibres, such as "Structural Biomaterials", Julian F.V. Vincent, The Macmillan Press Ltd., London and Basingstoke (1982), "Cellular Solids - Structure and Properties", Lorna J. Gibson and Michael F. Ashby, Pergamon Press. Oxford 1988, and "Wood Chemistry-Fundamentals and Applications", Eero Sjöström, Acadamic Press, New York (1981), the high level of performance properties of these natural fibres, such as the vegetable fibres, are directly attributed to the presence of specific cellulosic cell structures in these fibrous materials, moreover, any distortion of or damage to said cell structures resulting from e.g. mechanical and/or chemical action, will be reflected in the level of performance properties, e.g. by an appreciable reduction in mechanical strength.

Hence it can be concluded that the methods for treating the vegetable fibres as described hereinbefore, and which result in the production of aggregate and non-aggregate fibrous materials having potentially improved moisture resistance, and wherein at least an appreciable amount of the cellulosic structures have been damaged or distorted, are not suitable for the production of vegetable fibres which combine increased dimension stability with high strength.

As there is considerable need to make such dimension-stable fibres available, the problem underlying the present invention is to develop a suitable process for the production of these fibres, i.e. fibres having an improved dimension stability as a result of reduced moisture absorption combined with good mechanical performance properties, i.e. fibres wherein the original cellulose cell wall has essentially been maintained.

As a result of extensive research and experimentation it has surprisingly been found possible to prepare vegetable fibres having the desirable characteristics as described hereinbefore by a process wherein long, multicelled vegetable fibres are consecutively submitted to a steam treatment, a decompression/ cooling step and a curing step.

Accordingly the invention provides a process for upgrading long, multicelled vegetable fibres or assemblies thereof, which comprises the steps of a submitting long multicelled vegetable fibres or an assembly based thereon, to a water and/or steam treatment at a temperature in the range of from 130 to 250°C and at a pressure which is at least the equilibrium pressure of the operating temperature and for a time sufficient to decompose at least part of the hemicellulose present in said fibres, b) a controlled decompression/cooling of the reactor contents, c) isolating the fibres or assemblies thereof, and d) submitting the isolated fibres or assemblies thereof in a heating chamber to a temperature in the range of from 140 to 200°C to cure said fibres or assemblies thereof without aggregating them.

The nature of the vegetable fibres which may be employed in the process of the present invention is not critical and may include long, multicelled vegetable fibres which originate from the leaves, stem and bark of plants. They may be employed as harvested or after having been submitted to a subsequent treatment which leaves the cellulosic cell wall essentially unaffected, such as drying, retting, hackling, stripping, scraping and carding.

The vegetable fibres may be employed in the form of individual fibres, i.e. the fibres as harvested or as obtained by anyone of the treatments as described hereinbefore, but also in the form of a fibre assembly, i.e. individual fibres which have for example been converted to woven and non-woven fabrics, yarns, cords and paper sheet.

In the context of the present invention the term fibres or individual fibres refers to bundles of single fibrous cells, wherein each cell contains a variety of layers which together form a basically cylindrical arrangement, hence the term multicelled fibre.

Examples of suitable leaf fibres include abaca, bowstring hemp, pineapple and sisal; examples of bast fibres include jute, flax, hemp, kenaf and ramie, while suitable stem fibres include common bamboo, banana stalk and coconut.

As mentioned hereinbefore, the fibres may be employed as harvested but also in a dried form. Advantageously the vegetable fibres are presoaked in water to obtain fibres which are saturated with water, before being introduced

into the reactor. In said reactor the fibres are contacted with water in a water/fibre weight ratio which generally is in the order of at least 1 when working batchwise, whereas the water/fibre ratio will typically be >10 and preferably >20 when operating continuously under slurry conditions. Subsequently the reactor contents are treated at a temperature in the range of from 130 to 250°C and a pressure which is at least equal to the equilibrium vapour pressure at the temperature of operation, and for a time sufficient to decompose at least part of the hemicellulose present in said vegetable fibres. Simultaneously with the decomposition of the hemicellulose, lignin can also be partially decomposed, which results in the formation of fenol type or fenol derivative type of decomposition products. A complete decomposition of the lignin would require a temperature which is considerably higher than the temperature at which the process of the present invention is conducted. Preferably the temperature for treating the fibres is in the range of 160-190°C. When the vegetable fibres have a high lignin content, such as bamboo, cocos and jute fibres said temperature will be in the range of from 180-190°C, while for low-lignin fibres such as abaca, flax and linen, said temperature will be in the range of from 160-170°C. In general very good results were obtained when the vegetable fibres had been submitted to a heat treatment at a time/temperature in the range of from 60 min/160°C to 15 min/180°C, although shorter and longer exposure times at the indicated temperatures should not be excluded.

One of the hemicellulose decomposition products which may be formed in addition to sugars and aldehydes when exposing vegetable fibres to water/steam as described hereinbefore, is acetic acid, and will result in a drop in the pH of the reaction medium. The presence of acetic acid may accelerate the hemicellulose decomposition, simultaneously in a partial decomposition of the cellulose.

Should, however, the formation of acetic acid and the related phenomena be unacceptable, it can be counteracted by conducting the water/steam treatment of the vegetable fibres in the presence of a pH buffer. Suitable buffering agents have a pH in the range of from 4-7 and more preferably from 4.5 - 6.5.

The buffering agent is suitably a mixture of a base or an acid, and a salt of an organic acid. The buffering agent is preferably a mixture of acetic acid and an ammonium or alkali metal salt thereof; alkaline earth metal salts such as magnesium and calcium salts may also be used. Preferred alkali metal salts are sodium and potassium salts. The concentration of the buffering agent in water is suitably between 0.01 and 5 mol/litre and preferably between 0.05 and 2 mol/litre, and wherein the concentration of the buffer is considered to be the joint-concentration of the salt and acid or base. Should an aqueous buffering solution be used in the process of the present invention, it may, when appropriate, already be present during the presoaking of the vegetable fibres as described hereinbefore. As an alternative to the addition of the complete pH buffer, e.g. the acid and alkali metal salt thereof, it is also possible to add only the alkali metal salt, e.g. sodium acetale, and use the in situ generated acetic acid as the acid part of said pH buffer.It will be appreciated that the use of a pH buffer in the process of the present invention is especially advantageous when conducting said process on a large scale.

As mentioned hereinbefore the water/steam treatment of the vegetable fibres is followed by a controlled cooling/decompression step. Depending on the type of reactor employed for the water/steam treatment of the vegetable fibres, the cooling of the reactor contents can be accomplished by means of external and/or internal cooling. A further possibility to lower the temperature of the reactor contents is via decompression of the reactor, which will result in "adiabatic" evaporation of the liquid phase and hence in a reduction of the temperature thereof. When the decompression mode of cooling is applied, care should be taken that it is a very gradual and well controlled decompression which allows evaporation and diffusion of moisture within the fibres, but does not result in rupture of the cell walls due to an explosive evaporation of the liquid phase within the fibres. At any one moment the pressure within the reactor as a result of the decompression should not be very different to that of the equilibrium vapour pressure at the prevailing temperature. Advantageously cooling and decompression are applied simultaneously to reduce the temperature of the reactor contents.

When the temperature in the reactor is below 100°C and the pressure within the reactor equals the atmospheric pressure the vegetable fibres, of which at least part of the hemicellulose has been decomposed, may be isolated from the aqueous reaction medium via known techniques such as filtration and decantation.

Subsequently the isolated fibres are heated at a temperature in the range of from 140 - 200°C. During this treatment, which will be referred to as the curing step, it is believed that a reaction will occur between the various decomposition products, which will increase the moisture resistance and the dimension stability of the treated vegetable fibres. This curing step is conducted in a heating chamber. In order to achieve the highest possible degree of reaction during said curing step, care should be taken to reduce the loss of reactive decomposition products. In this context it is considered advantageous to dewater and dry the isolated fibres, preferably at ambient temperature, with the aid of a drying agent, prior to the curing step. Suitable drying agents include silicagel, magnesium sulfate and calcium chloride.

The time during which the fibres are submitted to the curing step is largely determined by the actual cure temperature. Conveniently the cure time may vary from 0.25 - 10 hours at a temperature in the range of from 200 - 145°C respectively. When green fibres, i.e. fibres which have not undergone any treatment, are used in the preparation of the vegetable fibres having improved moisture resistance and dimension stability, it is possible that the ultimate products are coloured and/or soiled. Should this be unacceptable for certain applications, then the steam/water treated fibres

may be submitted to an aqueous washing procedure for which generally water having a temperature in the range of from room temperature to 65°C is used, prior to being cured. The resulting cured fibres will generally have a considerably lighter colour.

However, it should be borne in mind that during the aqueous wash certain reactive organic compounds, especially water-soluble compounds, may be removed or extracted from the fibres. Hence it is possible that these fibres will have a somewhat lower moisture resistance and dimension stability after curing than the corresponding non-washed fibres, although still being considerably superior in this respect than untreated or green fibres.

The long, multicelled vegetable fibres as described in claim 9 and prepared according to the process of the present invention were indeed found to have improved moisture resistance and dimensionstability when compared with the corresponding untreated fibres.

These improved fibre characteristics can be determined by measuring the moisture take up of the fibres after having been exposed to moisture under varying conditions or after having been soaked in water, and subsequently measuring the corresponding degree of swell of the exposed fibres. Said degree of swell being a useful yardstick for the dimensionstability of the vegetable fibres. Moisture take up can conveniently be determined by measuring the weight increase of the exposed fibres.

A suitable method for measuring the degree swell of the exposed fibres is comparing the diameter of the fibres before and after exposure to moisture with the aid of a microscope having sufficiently large magnification, e.g. 52 x. A further method for measuring the degree of swell is with the aid of a so-called dedicated image analyzer (Vidas, ex Kontron, Germany). With this technique, which is considerably faster than the microscopic route, the volume of the fibre is projected on a screen. By comparing the size of the images of the fibres before and after exposure, it is possible to calculate the dimension stability.

With the aid of Confocal Laser Scanning Microscopy it was demonstrated that with the fibres prepared according to the process of the present invention the original cellulose cell structure had essentially been maintained, i.e. the cell walls had remained intact during the upgrading of the moisture resistance, and had not been ruptured. Occasionally some of the cross sections of the cells deviated slightly from those of the untreated fibres.

Moreover with the same technique it was also demonstrated that with fibres which had been submitted to a process which comprized a steam treatment step followed by a sudden decompression, no trace of any cellulose cell structure and/or cell wall could be observed. Confocal Laser Scanning Microscopy is a novel form of optical microscopy having an advantage over the conventional light- and electronmicroscopy in that it possesses a large depth of focus, and moreover rejects all out of focus information.

The images of the fibre cell structures and walls produced via the hereinbefore described confocal laser technique, can be made visible by projection on e.g. a screen or on photographic paper. The latter mode of operation having the advantage in that it makes comparing the different images a lot easier, and moreover also allows said results to be saved.

The long, multicelled vegetable fibres having improved moisture resistance and dimension stability and wherein moreover the original cellulose cell structure has been essentially maintained, as described hereinbefore, are novel products and form another aspect of the present invention. In view of the presence of the original cell structures it can be expected that said fibres will also have maintained their mechanical performance properties, thus making them valuable materials e.g. for use as fibre reinforcement in polymer matrices.

The use of the vegetable fibres which can be made via the process of the present invention and especially their use as fibre reinforcement in polymer matrices as described in claim 10 is another aspect of the present invention.

The method or process used for the preparation of the fibre-reinforced polymer matrices or composites as they will be referred to hereinafter, is not critical, but will of course be governed by the nature of the polymer(s) used, i.e. be it a thermoplastic or thermosetting polymer. In general any process used for the preparation of fibre reinforced composites employing conventional fibrous reinforcements, e.g. glass fibres or green vegetable fibres, can also be used when the fibrous reinforcement comprises the vegetable fibres having improved moisture resistance and dimension stability as described hereinbefore. Well-known examples of such processes include melt-mixing, laminating and pultrusion.

Melt-mixing will generally be conducted by mixing the loose vegetable fibres and polymer at a temperature at which the polymer is in the molten form. Conveniently melt-mixing can be conducted in an extruder wherein the polymer and fibrous reinforcement can be fed separately or jointly. In the latter case the joint polymer and fibre addition may be preceded by a dry blending step. The ultimate fibre containing polymer melt or extrudate can be employed in e.g. moulding operations for the preparation of shaped articles.

When the preparation of the fibre reinforced composites is conducted via a laminating technique, which composites are generally referred to as laminates, both loose fibres and fibre assemblies can be used. The general procedure for the preparation of such laminates comprises stacking alternating layers of polymer and reinforcement, e.g. in a mould; heating the contents of the mould to melt the polymer, evacuating the air from the mould followed by cooling and compressing the mould contents to obtain the laminate. The polymer may be used in powder form but advantageously

the polymer is employed in the form of a film or sheet. Suitable fibre assemblies which may be employed include woven and non-woven cloth based on vegetable fibres as described hereinbefore.

With pultrusion the fibre reinforcement, is conveniently is contacted with the molten polymer by drawing the fibre reinforcement with the molten polymer through an orifice or die, followed by cooling of the resulting product. The resulting coated yarn can then be cut to the desired fibre length, and the resulting granules, each containing the correct blend of fibre and polymer, can be applied in further processing to provide the final fibre-reinforced article.

Generally the fibre reinforcement used in the preparation of the fibre-reinforced composites as described hereinbefore will be based on a single type of vegetable fibre. It is of course also possible or sometimes even advantageous to use blends of two or more types of vegetable fibres or use fibre assemblies based on more than a single type of vegetable fibre. In general the fibres will comprise in the range of from 10 to 90%W of the total reinforced composite, and preferably from 20 to 80%W.

As mentioned hereinbefore the polymer matrix of the fibre reinforced composites may be based on both thermoplastic and on thermosetting polymers. Examples of suitable thermoplastic polymers include polyethylene, polypropylene, polybutylene, polystyrene, polyamides, polyethyleneteraphthalate, polycarbonate, polyketones, polyphenyleneoxides, polyesters such as polymethacrylates, functionalized, polyolefins such as those which have been modified to carry one or more polar groups via grafting or copolymerization; preferred polar groups being acid groups and especially carboxylic acid groups or derivatives thereof. The composites may be based on a single thermoplastic polymer or blends of two or more thermoplastic polymers. It is moreover feasible that when employing a laminating technique that the composites may combine polymer sheets or films from different polymers.

Examples of suitable thermosetting polymer systems include polyepoxides in combination with a wide range of curing agents, unsaturated polyesters, phenolic resins and isocyanate curable systems.

The fibre reinforced composites based on the vegetable fibres or assemblies thereof as described hereinbefore as well as in claim 11, are part of the invention.

The use of said vegetable fibres as fibre-reinforcement in the polymer composites as described hereinbefore allows said composites to be prepared via a fully integrated process, i.e. a process wherein the heattreatment or cure step of the vegetable fibres takes place during the moulding operation of the composites. Under said circumstances it is required that the isolated non-cured vegetable fibres should be dry, i.e. water free.

The invention will be illustrated with the following examples for which the following information is provided.

Reactors

1. The small-scale water/steam treatment of the vegetable fibres was conducted in 20 cm^3 pipe reactors. The closed reactors were placed in an oil bath of sufficient heat capacity to allow heating of the reactor contents to a temperature in the range of from 165-180°C within approximately 2 minutes. Likewise cooling of the reactors was accomplished by placing them in a cold bath.

2. Larger scale batch experiments were conducted in a 13 l autoclave containing a 5 l stainless steel wire basket as sample holder. Between basket and reactor wall a thermal shield was positioned, comprising a highly efficient copper cooling spiral, which could be water cooled, or when so required could be drained with compressed air. The autoclave was furthermore equipped with a facility to allow steam to be introduced and a possibility to drain off a liquid phase.

Test procedures

Water absorption was determined by measuring the weight increase of fibres after having been exposed to moisture.

Degree of swell was determined with the aid of a so-called dedicated image analyzer (Vidas, ex Kontron, Germany) by projecting the volume of a fibre on a screen and measuring the dimensions of the projection before and after exposure to moisture.

Composite preparation via compression moulding (stacking method)

Reinforcement and polymer film were cut in the dimensions of the cavity of a positive mould and 14 layers of polymer film and 13 layers fibre based mats were stacked in alternating layers. The stacked layers were compression moulded to a sheet of 4 mm thickness using the following moulding conditions: preheating for 1 minute at 200°C and 4 bar, subsequently evacuating the air from the mould followed by heating for 2.5 min at 200°C and 80 bar and cooling to room temperature at 80 bar.

Composite preparation via wet deposition

10.5 g of disintegrated fibres, 24.5 g of polymer powder and 2 g of Triton X-45 were mixed for about 10 minutes in 20 l of demi water and the resulting slurry was drained to form a sheet. The sheet was dried in a vacuum oven between filter paper for at least 24 h at 40°C under a nitrogen stream.

The dried sheet was further converted to composites via the compression moulding technique described hereinbefore.

Example 1

3 g size samples of ovendry abaca thread (ex Langman, the Netherlands) were placed in a pipe reactor as described hereinbefore and allowed to soak in 7.5 g of demiwater for 10 min. Subsequently the reactor was closed and heated to the temperature and for the time as indicated. After cooling, the reactor was opened, and the fibres were removed, dried, and cured at 140°C for 2 hours.

With some of the experiments the water contained 0.05 mol/l of sodium acetate. A further variable in the process condition was submitting the fibres to a water wash before cure, to which end the fibres were stirred in an excess of demi water at approximately 50°C. The thus obtained fibres were tested for water absorption after having been placed in an environment of 98% RH at room temperature.

From the resulting data which have been collected in Table 1 and also includes the corresponding data of the non-treated fibres, it can be observed that the fibres prepared according to the present process, show only a marginal reduction in moisture absorption. It should however be remembered, as mentioned hereinbefore, that the cellulose also contributes to the moisture absorption. As this fibre component is not affected by the process of the present invention, its moisture absorption is likewise not affected.

Moreover it is also apparent that the influence of the use of a pH buffer and/or of washing the fibres before cure is not very clear with these small scale experiments. Confocal Laser Scanning Microscopy confirmed that the original cellulose cell structures had been essentially maintained.

TABLE 1

exp. steam treatment buffer washing pH after water absorption (%w)						
no.	conditions			reaction after		
					7 days	16 days
1	15'180°C	+	+	4.5	18.8	19.7
2	"	+	-	4.5	22.0	24.2
3	"	-	+	3.5-4	17.8	18.9
4	"	-	-	4	20.0	22.4
5	1h 165°C	+	+	4.5	18.8	19.7
6	"	+	-	4.5	21.6	22.7
7	"	-	+	3.5-4	17.1	18.1
8	"	-	-	3.5-4	19.2	19.8
ref	-	-	-	-	23.4	24.3

Example 2

The procedure of example 1 was repeated using green flax and abaca but restricting the steam treatment to 165°C for 1 hour, followed by a wash step at 50°C and cure at 140°C for 2 hours.

The resulting fibres were tested for moisture absorption and swelling after having been exposed in air of 98% RH for 650 hours, which provided the following data

green flax	moisture absorption 26% swelling 60%
treated flax	moisture absorption 19% swelling 6%
abaca	moisture absorption 26% swelling 40%
treated abaca	moisture absorption 19% swelling 6%

The results obtained in the experiments described in this example clearly demonstrate the very large reduction in

the degree of swelling which can be achieved by the process of the present invention. The moisture absorption improvement is considerably less impressive and confirm the results of the previous example.

Furthermore the presence of the original cellulose cell structures was again confirmed.

Example 3

In a number of consecutive experiments 2 kg size wet samples of flax fibres, non-woven flax, abaca fibres, woven jute (burlap) and woven linen (muslin), which samples corresponded with approximately 1 kg of dry material, were placed in the sample holder of the autoclave described hereinbefore. The reactor walls had already been heated to the temperature required for treating the fibrous material and full cooling had been put on the thermal shield. The reactor was closed, the cooling switched off, water drained from the thermal shield and simultaneously a sufficient amount of saturated steam having the required temperature for conducting the fibre treatment was supplied to the reactor. Upon completion of the steam treatment the steam supply was closed and cooling of the thermal shield switched on. When the reaction contents had reached a temperature < 100°C the slight overpressure in the reactor was neutralized by careful decompression of the reactor. The treated fibres were dewatered and cured as indicated in Table 2 hereinafter.

The thus treated flax and abaca fibres were used for the preparation of polypropylene composites having a fibre content of 30% w (20% v) via the wet deposition procedure as described hereinbefore.

Via the same procedure but omitting the polypropylene powder and the compression moulding step, abaca "paper" sheets were prepared.

The abaca "paper" sheet, the treated non-woven flax, the woven jute and linen were each used in combination with polypropylene film for the preparation of fibre-reinforced polypropylene composites having a fibre content of 30% w (20% V), via the stacking method described hereinbefore. Reference composites based on the corresponding non-treated fibres were prepared likewise.

The thus prepared composites were submerged at room temperature in water for 650 hours, which was followed by measuring the weight increase and degree of swell. The resulting data have been collected in Table 2. It can be observed that the composites based on the vegetable fibres prepared following the process of the present invention show a considerable reduction in swell when exposed to moisture and also a reduced moisture uptake.

The flexural properties (Modulus and Strength) of the thus prepared composites were determined on a fully computerized Instron testing machine using standard test specimens having a thickness of 4 ± 0.2 mm and a width of 10 ± 0.5 mm. Testing conditions: span 64 mm, crosshead speed 20 mm/min and straining rate 0.01 min^{-1}.

From the results collected in Table 3, it can be observed that the use of the vegetable fibres having improved moisture resistance results in composites of which the flexural properties are very simular to those of corresponding composites based on the untreated fibres. Moreover it can be observed that the flexural properties of linen based composites are on a considerably lower level compared to those based on the other types of vegetable fibres, this applies to both the treated and untreated linen fibres.

TABLE 2

Fibre	treated	conditions of treatment	cure	weight increase %	swelling %
abaca	+	60'-170°C	2h-165°C	7.9	1.6
abaca	-			9.0	3.7
jute	+	15'-185°C	1h-190°C	7.2	1.2
jute	-			11.9	4.9
flax	+	60'-170°C	10h-145°C	6.9	1.0
flax	-			9.0	2.8
linen	+	60'-165°C	3h-160°C	4.7	0.7
linen	-			6.1	2.4

TABLE 3

Composite preparation	Flexural properties			
	Modulus, (GPa)		Strength, (MPa)	
	Untreated	Treated*	Untreated	Treated*
Wetdeposited				
abaca	5.4	5.4	84	87
flax	4.9	5.1	66	70
Stacked				
jute, woven	5.3	5.2	70	
linen, woven	3.6	3.0	65	62
flax, non-woven	4.9	4.7	61	66
abaca paper	4.3	4.1	75	72
Non-reinforced Polypropylene	1.7		48	

* Conditions are given in Table II.

Claims

1. A process for upgrading long, multicelled vegetable fibres or assemblies thereof, which comprises the steps of

   a) submitting long, multicelled vegetable fibres or an assembly based thereon, to a water and/or steam treatment at a temperature in the range of from 130 to 250°C, and at a pressure which is at least the equilibrium pressure of the operating temperature, and for a time which is sufficient to decompose at least part of the hemicellulose present in said fibres,
   b) a controlled decompression/cooling of reactor contents,
   c) isolating the fibres or assemblies thereof, and
   d) submitting the isolated fibres or assemblies thereof in a heating chamber to a temperature in the range of from 140 to 200°C to cure said fibres or assemblies thereof without aggregating them.

2. A process as claimed in claim 1, wherein the fibres to be submitted to the heat treatment are presoaked in water.

3. A process as claimed in claim 1 or 2, wherein the water/fibre weight rate is ≥ 1 for a batchwise operated process, and >10 and preferably >20 when operating the process continuously under slurry conditions.

4. A process as claimed in anyone of claims 1-3, wherein the water and/or steam treatment is conducted in the presence of an aqueous buffering system.

5. A process as claimed in claim 4, wherein buffering solution has a pH in the range of from 4-7 and preferably in the range of from 4.5-6.5.

6. A process as claimed in claim 4 or 5, wherein the buffering agent is a mixture of acetic acid and an ammonium or alkali metal salt thereof.

7. A process as claimed in anyone of claims 4-6, wherein the concentration of the buffering agent in water is in the range of from 0.01 to 5 and preferably from 0.05 to 2 mol/litre.

8. A process as claimed in anyone of claims 1-7, wherein the water and/or steam treatment is conducted at a temperature in the range of from 160-190°C.

9. Non-aggregated upgraded long multicelled vegetable fibres or assemblies thereof having improved moisture resistance and dimension stability, wherein the original cellulose cell structure has been essentially maintained, obtainable by a process as claimed in any of claims 1-8.

10. The use of the vegetable fibres or assemblies thereof claimed in claim 9, as fibre reinforcement in polymer matrices.

11. Fibre reinforced polymer composites, wherein the fibre reinforcement is based on the long multicelled vegetable fibres or assemblies thereof, as claimed in claim 9.

12. Fibre reinforced composites as claimed in claim 11, wherein the fibre content is in the range of from 10 to 90% w and preferably from 20 to 80% w.

Patentansprüche

1. Verfahren zur Verbesserung langer, mehrzelliger Pflanzenfasern oder Gruppen davon, umfassend die Schritte:

   a) des Aussetzens langer, mehrzelliger Pflanzenfasern oder Gruppen davon einer Wasser- und/oder Dampfbehandlung bei einer Temperatur im Bereich von 130 bis 250°C, und bei einem Druck, der mindestens dem Gleichgewichtsdruck der Betriebstemperatur entspricht, und für eine Zeitdauer, die ausreicht, um mindestens einen Teil der in den Fasern vorhandenen Halbcellulose zu zersetzen;
   b) einer kontrollierten Dekompression/Abkühlung des Reaktorinhalts;
   c) des Isolierens der Fasern oder Gruppen davon; und
   d) des Aussetzens der isolierten Fasern oder Gruppen davon in einer Wärmekammer bei einer Temperatur im Bereich von 140 bis 200°C zur Aushärtung der Fasern oder Gruppen davon ohne Verklumpung derselben.

2. Verfahren nach Anspruch 1, wobei die der Wärmebehandlung zu unterziehenden Fasern in Wasser voreingeweicht werden.

3. Verfahren nach Anspruch 1 oder 2, wobei das Wasser/Fasergewichtsverhältnis für einen stapelweise betriebenen Prozeß ≥ 1 ist, und >10 und vorzugsweise >20 ist, wenn der Prozeß kontinuierlich unter Schlammbedingungen ausgeführt wird.

4. Verfahren nach einem der Ansprüche 1-3, wobei die Wasser- und/oder Dampfbehandlung bei Vorhandensein eines wäßrigen Puffersystems durchgeführt wird.

5. Verfahren nach Anspruch 4, wobei die Pufferlösung einen pH-Wert im Bereich von 4-7 und vorzugsweise im Bereich von 4,5-6,5 aufweist.

6. Verfahren nach Anspruch 4 oder 5, wobei es sich bei dem Puffermittel um eine Mischung aus Essigsäure und einem Ammonium- oder Alkalimetallsalz davon handelt.

7. Verfahren nach einem der Ansprüche 4-6, wobei die Konzentration des Puffermittels in Wasser im Bereich von 0,01 bis 5 und vorzugsweise von 0,05 bis 2 Mol/Liter liegt.

8. Verfahren nach einem der Ansprüche 1-7, wobei die Wasser- und/oder Dampfbehandlung bei einer Temperatur im Bereich von 160-190°C durchgeführt wird.

9. Nicht verklumpte, verbesserte, lange, mehrzellige pflanzenfasern oder Gruppen davon mit verbesserter Feuchtigkeitsbeständigkeit und Formstabilität, wobei die ursprüngliche cellulose Zellstruktur im wesentlichen erhalten bleibt, wobei dies durch ein Verfahren nach einem der Ansprüche 1-8 erzielbar ist.

10. Verwendung der Pflanzenfasern oder Gruppen davon, wie sie in Anspruch 9 beschrieben werden, als Faserverstärkung in Polymermatrizen.

11. Faserverstärkte Polymerverbundstoffe, wobei die Faserverstärkung auf den langen, mehrzelligen Pflanzenfasern oder Gruppen davon nach Anspruch 9 beruht.

12. Faserverstärkte Verbundstoffe nach Anspruch 11, wobei der Fasergehalt im Bereich von 10 bis 90 Gew.% und vorzugsweise 20 bis 80 Gew.% liegt.

Revendications

1. Procédé pour améliorer la qualité de fibres végétales longues à cellules multiples ou d'ensembles formés de ces fibres, qui comprend les étapes :

   a) d'exposition de fibres végétales longues à cellules multiples ou d'un ensemble à base de ces fibres à un traitement à l'eau et/ou à la vapeur d'eau à une température comprise dans la plage de 130 à 250°C et à une pression qui est au moins la pression à l'équilibre de la température de travail, et pendant une durée qui est suffisante pour décomposer au moins une partie de l'hémicellulose présente dans ces fibres,
   b) de décompression/refroidissement contrôlés du contenu du réacteur,
   c) d'isolement des fibres ou des ensembles qui en sont formés et
   d) d'exposition des fibres isolées ou des ensembles formés de ces fibres dans une chambre de chauffage à une température comprise dans la plage de 140 à 200°C pour durcir ces fibres ou ensembles de fibres sans les agréger.

2. Procédé suivant la revendication 1, dans lequel les fibres devant être soumises au traitement à la chaleur sont préalablement trempées dans l'eau.

3. Procédé suivant la revendication 1 ou 2, dans lequel le rapport en poids eau/fibres est égal ou supérieur à 1 pour un procédé mis en oeuvre en discontinu et il est supérieur à 10 et de préférence supérieur à 20 lorsque le procédé est mis en oeuvre dans des conditions continues en suspension.

4. Procédé suivant l'une quelconque des revendications 1 à 3, dans lequel le traitement à l'eau et/ou à la vapeur d'eau est conduit en présence d'un système tampon aqueux.

5. Procédé suivant la revendication 4, dans lequel la solution tampon a un pH compris dans la plage de 4 à 7 et de préférence dans la plage de 4,5 à 6,5.

6. Procédé suivant la revendication 4 ou 5, dans lequel l'agent tampon est un mélange d'acide acétique et d'un sel d'ammonium ou de métal alcalin de l'acide acétique.

7. Procédé suivant l'une quelconque des revendications 4 à 6, dans lequel la concentration de l'agent tampon dans l'eau se situe dans la plage de 0,01 à 5 et de préférence de 0,05 à 2 moles/litre.

8. Procédé suivant l'une quelconque des revendications 1 à 7, dans lequel le traitement à l'eau et/ou à la vapeur d'eau est conduit à une température comprise dans la plage de 160 à 190°C.

9. Fibres végétales longues à cellules multiples de qualité améliorée, non agrégées, ou ensembles formés de ces fibres, perfectionnées quant à leur résistance à l'humidité et à leur stabilité dimensionnelle, dans lesquels la structure cellulaire originelle de la cellulose a été essentiellement maintenue, à obtenir par un procédé suivant l'une quelconque des revendications 1 à 8.

10. Utilisation de fibres végétales ou d'ensembles formés de ces fibres suivant la revendication 9 comme armature fibreuse de renforcement dans des matrices de polymères.

11. Composites de polymères renforcés par des fibres, dont l'armature fibreuse de renforcement est à base des fibres végétales longues à cellules multiples ou d'ensembles formés de ces fibres suivant la revendication 9.

12. Composites renforcés par des fibres suivant la revendication 11, dans lesquels la teneur en fibres se situe dans la plage de 10 à 90 % en poids et de préférence de 20 à 80 % en poids.