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(54) Cellulosic fibre - and chitosan-based composite material and a method for the preparation thereof.

(57) The composite material of the invention is a sheet of cellulose fibres impregnated with chitosan of at least 40% deacetylation and further impregnated with a higher fatty acid such as stearic acid by treatment with an organic solution thereof. The composite sheet of the invention differs from conventional paper and films of plastic resins in having a high strength even in a wet condition and still is biodegradable, for example, in wet soils so that no problems of environmental pollution are caused by the waste thereof left in the environment. Therefore, the composite sheet of the invention is useful as a wrapping material for foods, a sheet material for agricultural use and other temporary or seasonal uses.

CELLULOSIC FIBRE - AND CHITOSAN-BASED COMPOSITE MATERIAL AND A METHOD FOR THE PREPARATION THEREOF

The present invention relates to a novel composite material based on cellulosic fibres and chitosan. More particularly, the present invention relates to a composite material basically formed of cellulose fibres and chitosan and which is biodegradable, for example, in the soil. The invention also relates to a method for the preparation of such a composite material.

The composite material of the invention is useful in,a wide variety of applications, mainly but not limited to a sheet form used, for example, as a wrapping sheet for foods, a sheet material for agricultural use, temporary pots for growing young garden trees and seedlings, goods for hydroponics and the like. The services expected for the sheet materials in the above-mentioned applications are mostly of a temporary nature, so that it is desirable that the sheet material can be spontaneously decomposed after use or at the end of the service season without leaving any decomposition products which may cause environmental pollution problems.

Most of the sheet materials for the above-mentioned applications currently in use are made from a film of a plastic material, such as polyvinyl chloride and polyethylene, or a cellulose fibre-based sheet, i.e. paper, coated with a synthetic resin such as a polyethylene, or a melamine resin with the object of enhancing the mechanical strength of the base sheet. The synthetic polymer-based constituents in the conventional sheet materials are not biodegradable, so that a serious problem is sometimes caused by the waste materials after use left in the environment without being properly disposed causing environmental pollution. In consideration of this problem, a photodegradable polymer has been proposed by incorporating a photosensitizer into a certain synthetic polymer. Such a photodegradable polymer is still not free from the problem of environmental pollution because the decomposition product thereof per se is a potential pollutant of the environment when the amount thereof is relatively large. Moreover, the photodegradable polymer cannot be decomposed when the waste thereof is out of reach of light, for example in the soil.

Cellulosic materials, including lignocellulose, pectocellulose and bacteria cellulose, are natural products produced by plants and fungi which are readily available. Cellulosic materials are of course absolutely free from the problem of environmental pollution of the soil by waste thereof as is typically evidenced by the fact that cellulosic materials constitute an important constituent of composts. Accordingly, a cellulose-based sheet material is required having a sufficiently high mechanical strength not only in the dry but also in the wet state which is also biodegradable and thus causes no environmental or soil pollution.

We have now developed a novel sheet material based on cellulose fibres having a sufficiently high mechanical strengths together with boidegradability to meet the above described requirements for sheet materials for temporary use.

Accordingly, the present invention provides a composite material which comprises: (a) cellulose fibres shaped in the form of a sheet; (b) chitosan in an amount in the range of from 1% to 99% by weight based on the amount of cellulose fibres; and (c) a higher fatty acid in an amount in the range of from 0.05% to 1.0% by weight based on the amount of the cellulose fibres.

It is preferred that the higher fatty acid as a treatment agent of the sheet material of the cellulose fibres impregnated with chitosan has at least 12 carbon atoms per molecule and that the amount thereof is in the range of from 0.05% to 1% by weight based on the weight of the cellulose fibres.

The cellulose fibre and chitosan-based composite sheet material of the invention can be prepared by first forming sheets of the cellulose fibres in a process similar to paper making and then soaking the sheet of cellulose fibres with an aqueous solution of a chitosan salt, followed by drying. Alternatively, the composite sheet material can be prepared by forming sheets from an aqueous slurry of cellulose fibres containing chitosan in the form of a salt. The composite sheet comprising a higher fatty acid can be prepared by soaking the composite sheet of cellulose fibres and chitosan with a solution of the higher fatty acid followed by drying.

As is described above, the basic constituents of the inventive composite material are cellulose fibres and chitosan which impregnates a sheet of the cellulose fibres in a limited amount. The cellulose fibres can be obtained from various sources including, mostly, wood and .is avilable in the form of chemical pulp, mechanical pulp and the like.

Chitosan is a deacetylation product of chitin which is a nitrogen-containing polymeric commpound occurring in large quantities in nature and is a principal constituent of the shells of insects, lobsters, crabs and the like as well as a constituent of certain microorganisms. Chitosan may have different degrees of deacetylation depending on the conditions of the deacetylation treatment of chitin. Chitosan, as such, is insoluble in water but can be solubilized when chitosan is converted into the form of a salt with, for example, acetate ions or chlorine ions. The so-called chitinous substances include chitin and chitosans in general. Since chitinous substances belong to a class of natural products, various species of microorganisms are known to decompose the chitinous substances. This fact is evidenced by the tests undertaken by the inventors who collected samples of soils from a number of cultivated lands all over the territory of Japan to test the biodegradability of chitosan therein to find microorganisms capable of decomposing chitosan having a relatively high degree of deacetylation.

Chitosan has previously been used industrially as a flocculating agent in the technology of waste water disposal. In recent years, investigations have been undertaken for the development of a chitinous substance as a bioadaptable material. Further, an attempt has been made to improve the surface strength of paper with chitosan (see, for example, British Patent No. 458,813 and "Proceedings of the 2nd International Conference of Chitin and Chitosan", 1982). No prior art is known, however, of a composite material composed of cellulose fibres and chitosan, in particular, surface-treated with a higher fatty acid.

Needless to say, cellulose fibres in a sheet-like form and chitosan shaped in a sheet, when alone, cannot retain their strength or form in a hydrous soil. Namely, a sheet of cellulose fibres rapidly disintegrates into discrete fibres in a wet condition and a sheet of chitosan is converted into a gel-like material. It is a discovery that, when cellulose fibres and chitosan form a composite, the composite material can retain its shape and mechanical strength even in a hydrous soil for a length of time and thereafter gradually be decomposed by the microorganisms living in the soil. A composite material composed of cellulose fibres and chitosan alone is water-absorptive, but the composite can be provided with water repellency when it is treated with a higher fatty acid so that the stability of the composite material in the wet condition can be further increased without unduly affecting biodegradability.

The treatment of a composite sheet of cellulose fibres and chitosan with a higher fatty acid is performed by bringing the composite sheet into contact with a solution of the fatty acid in a concentration of from 0.1 to 0.5% by weight in a suitable organic solvent, followed by drying. The amount of the higher fatty acid impregnating the composite sheet is in the rage of from 0.05% to 1% by weight or, preferably, in the range of from 0.1% to 0.6% by weight based on the amount of the cellulose fibres. The content of the higher fatty acid has some influence on the biodegradability of the composite sheet in soil. The organic solvent to dissolve the higher fatty acid is not limited, provided that it is inert to chitosan. Methyl alcohol is an example of a suitable organic solvent though not limited thereto. The higher fatty acid is selected from those insoluble in water and should have at least 12 carbon atoms per molecule. Stearic and palmitic acids are preferred in respect of the water repellency imparted to the composite sheets treated therewith.

The composite sheet of cellulose fibres and chitosan can be prepared in several different ways as described below. First, cellulose fibres are shaped into the form of a sheet by a method similar to paper making and then the sheet of cellulose fibres is coated or soaked with an aqueous solution of chitosan acidified with acetic or hydrochloric acid. Secondly, cellulose fibres are first treated with an aqueous solution of chitosan and the thus chitosan-treated cellulose fibres are shaped into a sheet-like form. Thirdly, cellulose fibres are slurried in an aqueous medium containing chitosan and sheet-making is performed from this slurry.

It is important that the average molecular weight and degree of deacetylation of chitosan, as well as the compounding amount thereof with the cellulose fibres, should be selected appropriately in order to control adequately the mechanical properties of the composite material and the biodegradability thereof. For example, the chitosan should have a degree of deacetylation of at least 40% in order to have an adequate sheet-forming power. Further, the chitosan should preferably have an average molecular weight in the range from 2,000 to 500,000. Presumabley, a type of chemical bond is formed between the surface of the cellulose fibres and chitosan so that the composite sheet having biodegradability is imparted with a high mechanical strength whilst still retaining its water-absorptivity. The treatment with a higher fatty acid forms a water-repellent film on the surface of the composite sheet so as to decrease the water-absorptivity of the sheet.

The following Examples are given to illustrate the composite material of the invention and the method for the preparation thereof in more detail although the scope of the invention is not limited thereby in any way. The water absorption in % by weight of composite sheets prepared in Example 4 and treated with a higher fatty acid as a function of the number of carbon atoms per molecule of the fatty acid when the sheet was dipped in water overnight is shown in the single Figure of the drawings.

Example 1

A sheet of paper having a basis weight of 50 g/m^2 and made from a mechnaical pulp was soaked with an aqueous solution of chitosan having an average molecular weight of about 50,000 and a degree of deacetylation of about 99% acidified with acetic acid in different concentrations followed by drying at 105 °C. The contents of chitosan in the thus prepared composite sheets were 1 to 50% by weight based on the cellulose fibres of the paper. The composite sheets were each soaked with 0.1% by weight solution of stearic acid in methyl alcohol followed by drying. The amount of stearic acid picked up by the composite sheet was 0.12% by weight based on the cellulose fibres. These composite sheets were subjected to the determination of the breaking length both in a dry and in a wet condition to give the results shown in Table 1 which also incudes the data obtained by omitting addition of chitosan. Further, the sheets were buried in a soil of a cultivated land containing 60% by weight of water at 25 °C in a depth of 2 to 8 cm from the surface and kept there over months to evaluate the biodegradability for which a measure was given by the number of months taken until the breaking length of the sheet in a wet condition had been decreased to 0.5 km or less.

Table 1

Content of chitosan, %	0	1	3	5	20	50
Breaking length, dry, km	3.2	4.4	5.5	6.1	10.3	10.5
Breaking length, wet, km	0.2	1.3	2.6	4.2	8.3	10.7
Months for decomposition	-	0.5-2	4-8	6-12	10-18	10-18

The results in Table 1 show that the sheet of cellulose fibres can be imparted with an increased strength even in a wet condition by composite-making with chitosan in an amount of 1% by weight or larger. In addition, the biodegradability of the composite sheet is controllable by the amount of chitosan compounded with the cellulose fibres.

Example 2.

Several stearic acid-treated composite sheets of cellulose fibres and chitosan were prepared in substantially the same manner as in Example 1 except that several chitosans having different average molecular weights were used and the compounding amount of the chitosan was always 3% by weight based on the cellulose fibres in the form of a sheet of paper prepared from a mechanical pulp. The composite sheets were subjected to the evaluation test of the biodegradability in the same manner as in Example 1 to give the results shown in Table 2.

Table 2

Molecular weight of chitosan, x 10^3	2	50	200	500
Months for decomposition	0-1	3-6	4-8	6-12

The results in Table 2 show that the molecular weight of chitosan had an influence on the biodegradability of the composite sheets and the length of time taken for biodegradation of the composite sheet was longer when the chitosan had a larger average molecular weight. The biodegradability of the composite sheet was little influenced by the treatment with stearic acid.

Example 3.

Several composite sheets of cellulose fibres and chitosan, each having a basis weight of about 50 g/m², were prepared by sheet-making from an aqueous slurry of fine cellulose fibres after thorough beating with admixture of an aqueous solution of chitosan having a varied degree of deacetylation of 40 to 100% acidified with acetic acid followed by neutralization. The amount of chitosan added to the slurry was 2% by weight based on the amount of the cellulose fibres in the slurry. It was found that pick-up of the chitosan added to the slurry by the sheet after sheet making was substantially complete. The composite sheets were subjected to the treatment with stearic acid in the same manner as in Example 1. The breaking lengths in wet of these composite sheets are shown in Table 3 below, from which it is understood that chitosan should desirably have a degree of deacetylation of at least 40% in order to exhibit a practical reinforcing effect on the sheet of cellulose fibres although the use of chitosan having a degree of deacetylation lower than 40% was not ineffective in increasing the wet strength of the sheet as compared with a similar sheet prepared without addition of chitosan which had a wet strength of 0.3 km.

Table 3

Degree of deacetylation, %	32	40	51	65	84	92	99
Breaking length, wet, km	0.9	1.9	2.0	2.0	2.2	2.3	2.4

Example 4.

Several composite sheets of cellulose fibres and chitosan were prepared in the same manner as in Example 1 and subjected to a treatment with a higher fatty acid also in the same manner as in Example 1 excepting the use of various higher fatty acids having 6 to 18 carbon atoms in a molecule dissolved in methyl alcohol each in a concentration of 0.5% by weight. The composite sheets thus prepared contained 0.59% by weight of the higher fatty acid based on the cellulose fibres. The amounts of water in % by weight absorbed by these composite sheets kept overnight in water are shown graphically in the figure of the accompanying drawing as a function of the number of carbon atoms in a molecule of the fatty acids. As is shown by the graph, the amount of water absorption was very significantly decreased when the fatty acid was lauric acid or a higher one.

Further, the composite sheets of cellulose fibres and chitosan were treated with a methyl alcohol solution of stearic acid in varied concentrations of 0.1 to 1 .0% by weight and the amount of water absorption of the thus treated sheets was determined to find that the degree of hydrophobicity imparted to the composite sheet remained unchanged when the concentration of the stearic acid solution was increased over 0.5% by weight despite the rapid increase of the amount of stearic acid picked up by the composite sheets. This fact led to a conclusion that the treatment with a higher fatty acid should be performed by using a solution of the fatty acid in a concentration not exceeding 0.5% by weight.

Claims

1. A composite material which comprises:
(a) cellulose fibres shaped in the form of a sheet;
(b) chitosan in an amount in the range of from 1% to 99% by weight based on the amount of cellulose fibres; and
(c) a higher fatty acid in an amount in the range of from 0.05% to 1.0% by weight based on the amount of the cellulose fibres.

2. A composite material as claimed in Claim 1 wherein the chitosan has a degree of deacetylation of at least 40%.

3. A composite material as claimed in Claim 1 or Claim 2 wherein the chitosan has an average molecular weight in the range of from 2,000 to 500,000.

4. A composite material as claimed in any one of the preceding claims wherein the higher fatty acid is a saturated aliphatic carboxylic acid containing from 12 to 18 carbon atoms.

5. A method for the preparation of a composite material as calimed in Claim 1 which comprises the steps of:

(1) preparing a sheet composed of cellulose fibres impregnated with chitosan;
(2) soaking the sheet with a solution of a higher fatty acid in an organic solvent; and
(3) drying the thus soaked sheet.

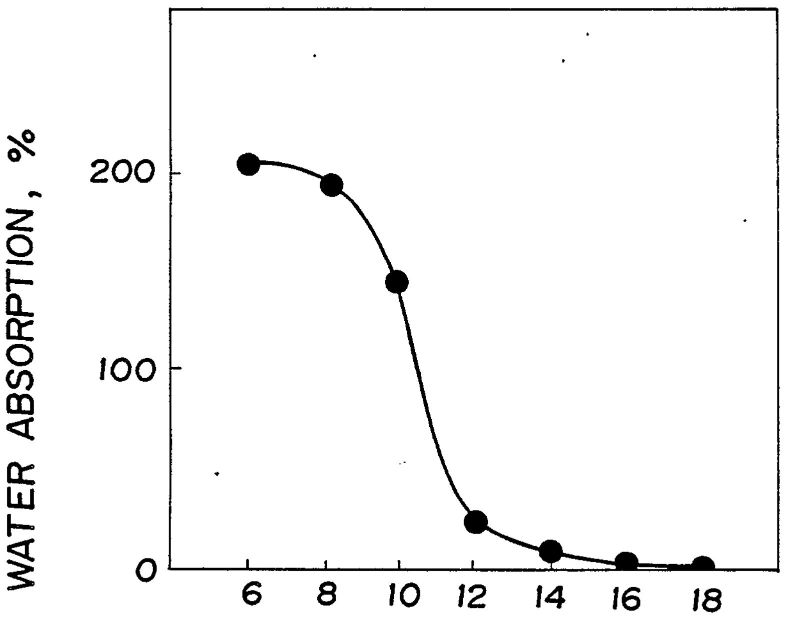
6. A method as claimed in Claim 5 wherein the solution of the higher fatty acid has a concentration in the range of from 0.1% to 0.5% by weight of the fatty acid.

7. A method as claimed in Claim 5 or Claim 6 wherein the organic solvent is methyl alcohol.

8. A method as claimed in any one of Claims 5 to 7 wherein the sheet composed of cellulose fibres impregnated with chitosan is prepared by soaking a sheet of cellulose fibres with an acidic solution of chitosan and drying the sheet.

9. A method as claimed in any one of Claims 5 to 8 wherein the amount of chitosan impregnating the sheet of cellulose fibres is in the range of from 1% to 99% by weight based on the amount of cellulose fibres.

10. A method as claimed in any one of Claims 5 to 9 wherein the chitosan has an average molecular weight in the range of from 2,000 to 500,000.



NUMBER OF CARBON ATOMS IN FATTY ACID MOLECULE