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(54) **BIODEGRADABLE FIBRE AND ITS PROCESS OF MANUFACTURE**

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(57) **ABSTRACT**

The present invention concerns a biodegradable fibre comprising composite filaments of cellulose and cellulose acetate, and a process for making such a fibre comprising providing a solution dope comprising a blend of cellulose and cellulose acetate in an ionic liquid or in N-methylmorphilone-N-oxide (NMMO), and spinning casting the blend into a protic solvent to generate fibres. The invention also concerns materials made from such a fibre, and garments or soft furnishings made from such a material.

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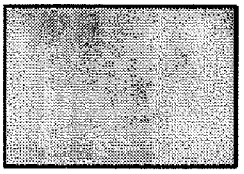

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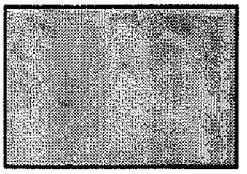

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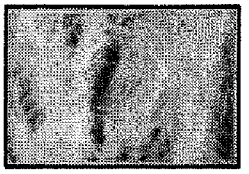

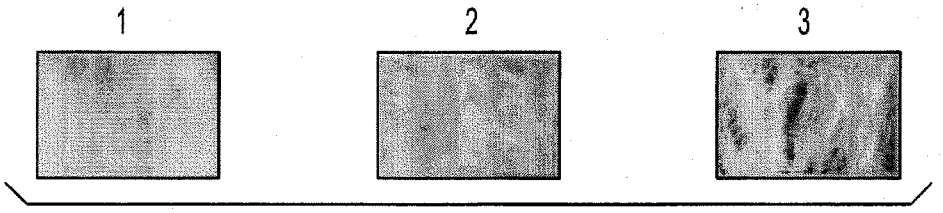

FIG. 1

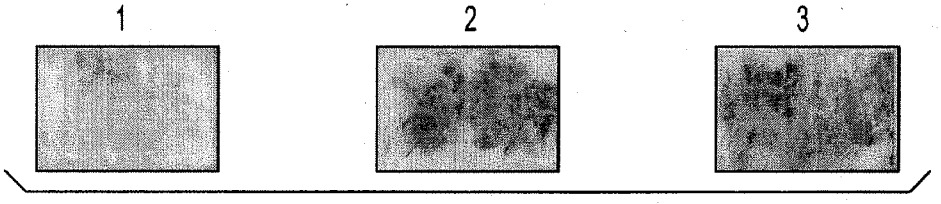

FIG. 2

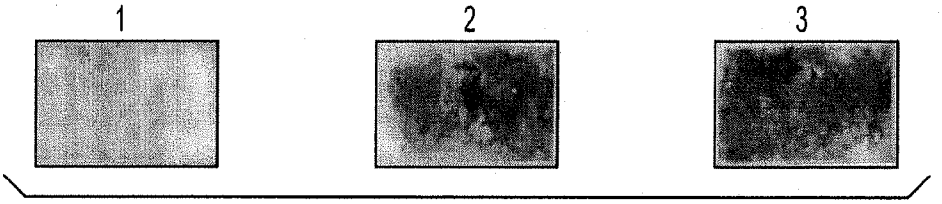

FIG. 3

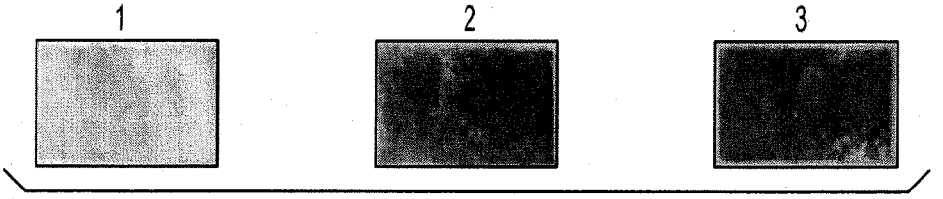

FIG. 4

BIODEGRADABLE FIBRE AND ITS PROCESS OF MANUFACTURE

[0001] This application claims priority to International Patent Application No. PCT/GB2010/051771, filed Oct. 21, 2010, which claims priority to Great Britain Patent Application No. 0918633.9, filed Oct. 23, 2009. The entirety of all of the aforementioned applications is incorporated herein by reference.

FIELD

[0002] The present invention concerns biodegradable composite fibres.

BACKGROUND

[0003] One of the most pressing issues for manufacturers of fibres is the rate at which the fibres biodegrade. Cellulose acetate fibres can take between one month and three years to biodegrade, dependant on environmental conditions.

[0004] A range of approaches to the preparation of biodegradable fibres, particularly for use in the manufacture of cigarette filter tows, have been suggested and include the use of composites of cellulose acetate with other biodegradable polymers, additives for increasing the rate of degradation of cellulose acetate, cellulose acetate with a low degree of substitution (DS) for increased biodegradability, and biodegradable polymers such as PHB/PVB and starches as the filter tow or fibre raw material.

[0005] However, to date no satisfactory commercial solution has been found for producing consumer-acceptable fibres that degrade sufficiently quickly

[0006] The present invention seeks to address these problems.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] The invention will now be more particularly described in the following drawings:

[0008] FIG. **1** shows three slides showing fibres of i) cellulose acetate; ii) cellulose; and iii) a blend of cellulose and cellulose acetate in accordance with the invention.

[0009] FIG. **2** shows the slides of FIG. **1** after 2 weeks biodegradation under anaerobic conditions.

[0010] FIG. **3** shows the slides of FIG. **1** after 4 weeks biodegradation under anaerobic conditions.

[0011] FIG. **4** shows the slides of FIG. **1** after 6 weeks biodegradation under anaerobic conditions.

DETAILED DESCRIPTION

[0012] According to the present invention there is provided a biodegradable fibre comprising composite filaments of cellulose and cellulose acetate.

[0013] Cellulose and cellulose acetate are typically cast in the form of fibres or films. In one of its aspects, this invention concerns fibres. Preferred fibres in accordance with the invention comprise fibres spun from a coagulated solution of cellulose and cellulose acetate.

[0014] Reference herein to composite filaments of cellulose/cellulose acetate shall be understood to mean filaments spun from a dope comprising cellulose and cellulose acetate.

[0015] We have found that composite filaments of cellulose/cellulose acetate have significantly greater biodegradability than equivalent filaments comprising only cellulose or cellulose acetate. Without wishing to be bound by any such theory, we believe that the presence of acetate in the composite may disrupt the crystallinity of the cellulose, causing it to biodegrade more rapidly than cellulose itself.

[0016] Conventionally, cellulose is cast or spun from viscose, and it is difficult or impossible to cast or spin cellulose acetate from the same blend because of the likelihood of hydrolysis of the cellulose acetate under such conditions. Conversely, cellulose acetate is conventionally cast or spun from acetone and it is difficult or impossible to cast or spin cellulose from the same blend because of the limited solubility of cellulose in acetone.

[0017] However, we have found that by casting or spinning cellulose and cellulose acetate from an ionic liquid (IL) or from N-methylmorphilone-N-oxide (NMMO), it is possible to form spun fibres and cast films comprising a composite blend of these materials. The enhanced biodegradability of such composites and their suitability for use in fibre manufacture has not previously been recognised.

[0018] Consequently, the fibre of the invention is preferably formed from fibres of cellulose and cellulose acetate spun or cast as a blend from an ionic liquid (IL) or from N-methylmorphilone-N-oxide (NMMO).

[0019] The use of ILs and NMMO for dissolving cellulose and other polymers has been well documented, for example in US20050288484 and US 20070006774 of the University of Alabama, US20080188636 of the North Carolina State University and WO2005098546 of Holbrey et al. A wide range of ionic liquids, including those disclosed in the aforesaid publications, are suitable for dissolving cellulose and cellulose acetate and for casting as blends fibres or films therefrom. General types of suitable IL include those based on imidazole, pyrrole, thiazole or pyrazole cations in combination with halogen, phosphate, carboxylate or metal chloride anions. Particularly preferred ILs include 1-butyl-3-methylimidazolium chloride (BMIM-Cl) 1-butyl-3-methylimidazolium acetate (BMIM-Ac) and 1-ethyl-3-methylimidazolium acetate (EMIM-Ac).

[0020] The solution of cellulose and cellulose acetate from which fibres are spun or cast is referred to herein as a dope. The dope may also comprise an aprotic solvent such as DMSO, DMF, THF or dioxane to aid dissolution of the cellulose and/or cellulose acetate. One particularly preferred aprotic solvent is DMSO.

[0021] The blend of cellulose acetate and cellulose in the dope may also comprise one or more further thermoplastic materials, such as polyhydroxyalkanoates such as PHB and/or PHVB which may add further functionality, such as water barrier functionality, to the fibres of the invention. Other functional additives may include triacetin, polyacrylonitrile (PAN), poly-2-hydroxyethylmethylacrylate (PHEMA), polyvinylalcohol (PVA), polyaniline and polyethylene glycol for functional purposes such as modification of absorption profile, degradation enhancement (by, for example, water-soluble materials), and processability improvement, in connection for example with wet strength.

[0022] The weight ratio of cellulose to cellulose acetate in the dope, and consequently in the fibre of the invention is from 10:90 to 90:10, for example from 20:80 to 80:20, or from 30:70 to 70:30.

[0023] Typically, the dope comprises a solids content of up to about 50% w/w, preferably up to about 40% w/w, more preferably up to about 30% w/w and most preferably up to about 20% w/w.

[0024] The fibres of the invention may additionally comprise one or more plasticisers, such as triacetin. The plasticiser may be included in the dope, or may added subsequent to spinning or casting, for example by spraying onto the surface of the formed fibre.

[0025] The fibres of the invention may additionally comprise a catalyst promoting oxidative degradation of the fibre. Suitable catalysts include iron and copper oxides and chlorides, which may be introduced into the fibre by immersing the composite filaments in an aqueous solution of a water-soluble iron or copper salt, such as sulphate or chloride, and precipitating the oxide (preferably in nano-form) onto or into the filament by treatment with sodium hydroxide or other suitable precipitating agent.

[0026] The fibres may also comprise one or more lubricants to reduce electrostatic charge. Preferred lubricants include mineral oils. For example, 1% w/w of mineral oil with an emulsifier may be applied to the composite filaments during spinning of the fibres.

[0027] Preferably the fibres of the invention comprise composite filaments of cellulose/cellulose acetate manufactured at 1, 5 or 9 denier per filament (filament thickness (denier per filament) being defined as the mass (grams) of 9000 m of a single filament).

[0028] The total fibre mass (total denier) (defined as the total mass of 9000 m of fibre, typically comprising many thousands, for example 11,000, individual fibres) will vary considerably depending on the methods employed in fibre spinning and the number of individual filaments in the fibre. One typical fibre mass would 35,000 g.

[0029] Preferably the fibres of the invention comprise fibres having a trilobal filament cross-section (optionally formed using triangular spinneret holes) to optimise surface area.

[0030] The moisture content of the fibres according to the invention is preferably at least about 2% w/w, more preferably at least about 5% w/w, even more preferably at least about 10% w/w. Moisture content has been found to be important for preventing electrical charges, but should preferably not be too high (e.g. not higher than 50% w/w) because with a very high moisture content it may be difficult for the fibre to retain a crease.

[0031] The fibres of the invention preferably comprise entangled filaments.

[0032] Also provided in accordance with the invention is a material woven or otherwise made from the fibre as hereinbefore described.

[0033] Also provided in accordance with the invention is a garment or soft furnishing made at least partly from a material as hereinbefore described.

[0034] Also provided in accordance with the invention is a process for manufacturing fibres comprising providing a solution comprising a blend of cellulose and cellulose acetate in an ionic liquid or in NMMO, and spinning or casting the blend into a protic solvent to generate fibres.

[0035] Water is the preferred protic solvent for the regenerative casting of the blend.

[0036] In the process of the invention, composite cellulose/cellulose acetate materials can be produced at any ratio by regenerating solutions in water and/or other protic solvents. The rate of coagulation in water has been found to be dependant on the cellulose acetate content of the dope, where increased levels of cellulose acetate reduce the rate of coagulation.

[0037] In another aspect, this invention provides a biodegradable film cast from a coagulated dope comprising cellulose and cellulose acetate, the resulting film being a cellulose/cellulose acetate composite material.

[0038] The invention will now be more particularly described in the Examples which follow and which make reference to the following drawings:

[0039] FIG. **1** shows three slides showing fibres of i) cellulose acetate; ii) cellulose; and iii) a blend of cellulose and cellulose acetate in accordance with the invention.

[0040] FIG. **2** shows the slides of FIG. **1** after 2 weeks biodegradation under anaerobic conditions.

[0041] FIG. **3** shows the slides of FIG. **1** after 4 weeks biodegradation under anaerobic conditions.

[0042] FIG. **4** shows the slides of FIG. **1** after 6 weeks biodegradation under anaerobic conditions.

[0043] The invention will now be more particularly described in the Examples:

EXAMPLE 1

[0044] The biodegradability of wet-spun fibres of blended cellulose/cellulose acetate was assessed in comparison with equivalent wet-spun fibres of cellulose, and equivalent wet-spun fibres of cellulose acetate.

[0045] Using standard wet-spinning equipment fibres were spun from solutions of i) cellulose (DP ~800) and ii) 1:1 cellulose: cellulose acetate (Eastman, CA-398-30), at 10% solids in EMIM-Ac: DMSO (20:80). A 40-orifice spinneret with an orifice diameter of 70 μm was used, which was submerged in a room temperature coagulation bath containing clean water. The fibres were reeled-up wet, extensively washed on the reel then dried at 50° C.

[0046] With reference to FIGS. **1** to **4**, a surprising property of these composite materials is that the rate of biodegradation under anaerobic environments exceeds that of cellulose and greatly exceeds that of cellulose acetate under the same conditions (see appendix 1). It is thought (although this theory is in no way to be considered binding) that the two components form an intimately mixed composite and that the enhanced rate of degradation arises from a reduction in the crystallinity of the cellulose. Degradation of the cellulose component of the composite is thought to lead to the cellulose acetate component being deposited on a molecular scale. We have also found that the rate of biodegradation under aerobic conditions of the fibres in accordance with the invention is similarly improved.

[0047] The application of these composite materials in the manufacture of fibres offers a route to achieving a fibrous product with both the desired versatility and comfort achieved by using cellulose acetate alone, but with greatly increased rates of biodegradation.

EXAMPLE 2

[0048] Fibre according to the invention is manufactured using a dry-spinning process. A dope is first prepared by dissolving cellulose diacetate and cellulose (1:1 blend) at 10% solids in EMIM-Ac: DMSO (20:80). TiO2 is added to give a whitened appearance. The dope is then filtered and spun into chambers, causing the filaments to solidify and become thinner. More than 10,000 filaments are spun from a series of spinning cabinets, which are combined to form a single band. A material is woven from the fibre, and a garment is made from the material.

[0049] The resulting garment is found to retain to advantageous biodegradability properties as shown in Example 1 and to have an acceptable comfort signature.

1. A biodegradable fibre comprising composite filaments of cellulose and cellulose acetate.

2. The fibre according to claim **1**, further comprising one or more further thermoplastic materials.

3. The fibre according to claim **2**, wherein the further thermoplastic material is selected from one or more of PHB, PHVB, polyacrylonitrile (PAN), poly-2-hydroxyethylmethylacrylate (PHEMA), polyvinylalcohol (PVA), polyaniline and polyethylene glycol.

4. The fibre according to claim **1**, wherein the weight ratio of cellulose to cellulose acetate is from 10:90 to 90:10.

5. The fibre according to claim **4**, wherein the ratio of cellulose to cellulose acetate is from 20:80 to 80:20.

6. The fibre according to claim **5**, wherein the ratio of cellulose to cellulose acetate is from 30:70 to 70:30.

7. The fibre according to claim **1**, further comprising one or more plasticisers.

8. The fibre according to claim **1**, further comprising a catalyst promoting oxidative degradation of the fibre.

9. The fibre according to claim **1**, further comprising one or more lubricants to reduce electrostatic charge on the fibre.

10. A material woven produced from the fibre according to claim **1**.

11. A garment or soft furnishing at least partly made from the material according to claim **10**.

12. A process for manufacturing the fibre according to claim **1**, comprising:

providing a solution dope comprising a blend of cellulose and cellulose acetate in an ionic liquid or in N-methylmorphilone-N-oxide (NMMO); and

spinning or casting the blend into a protic solvent to generate fibres.

13. The process according to claim **12**, wherein the dope further comprises an aprotic solvent to aid dissolution of the cellulose and/or cellulose acetate.

14. The process according to claim **13**, wherein the aprotic solvent comprises one or more of DMSO, DMF, THF or dioxane.

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