(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 536 832 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
11.09.2019 Bulletin 2019/37

(51) Int Cl.:
D01F 2/00 *(2006.01)*

(21) Application number: **18160141.0**

(22) Date of filing: **06.03.2018**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

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(54) LYOCELL FIBER WITH IMPROVED DISINTEGRATION PROPERTIES

(57) The present invention provides a lyocell fiber with increased disintegration properties as well as a method for producing same and products comprising same.

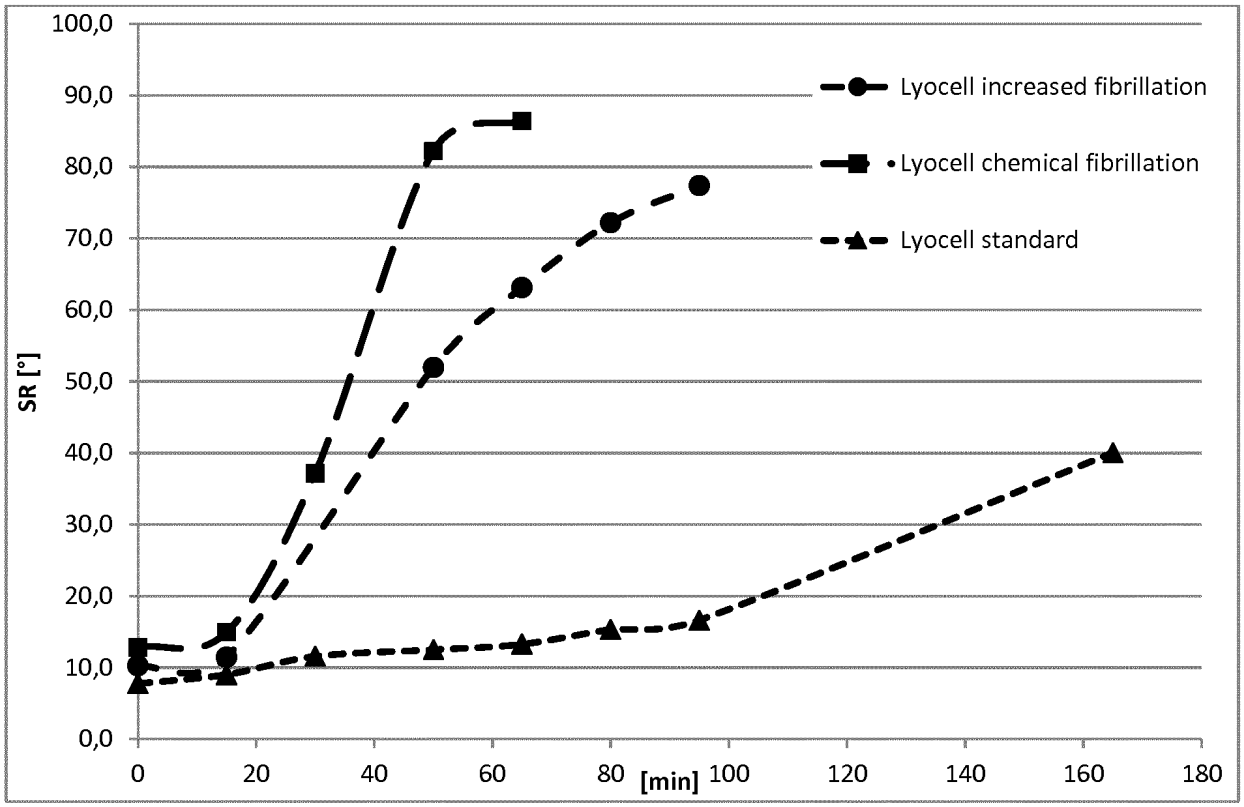

Figure 1: Fibrillation dynamics of three types of fibers.

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Description

[0001] The present invention relates to a lyocell fiber with improved disintegration properties, a method for producing same as well as to products comprising the lyocell fiber.

State of the art

[0002] The disposal of textiles or nonwovens is a severe challenge in today's environment. The most common option for textiles is the second-hand market for used clothing or conversion into substandard new products like cloths for cleaning and wiping. Incineration for energy gain is also a possibility. Composting is a way to convert organic materials into biomass, valuable in soil amendment.

Terms such as disintegration and biodegradation do have a well defined meaning in the art, such as disclosed in: http://innprobio.innovation-procurement.org/bio-based-products-services/factsheets/ on 24th of Nov. 2017, Factsheet #3. According to this disintegration is the physical breakdown of material into microscopic pieces, whereas biodegradation is the chemical breakdown of a material into carbon dioxide, methane and biomass. Biodegradation and disintegration have to occur simultaneously for a material to decompose. Biodegradation and disintegration can take place in soil, fresh water or sea water.

[0003] It is well known in literature and to experts that cellulosic fibers are biodegradable, compostable and undergo disintegration. Cellulosic fibers can either be fibers from natural origin like wool, linen, cotton, flax,... or man-made cellulosic fibers.

Ratajska et al (Reactive and Functional Polymers 1998, 38, 35-49) compare viscose and cellulose carbamate fibers, whereas the carbamate degrades (aqueous and soil) faster, the authors postulate the faster degradation can be explained by the changes in the chemical structure of the carbamate by its modification.

[0004] Warnock et al (Summ Ark Cotton Res,2009, 208-211) compare cotton, viscose and lyocell fabrics having a similar chemical composition, but different degrees of polymerization and crystallinities. Cotton shows high degrees of polymerization (6000-10000) and crystallinities (70%), whereas viscose shows lower values, with only 30% of crystallinity and decreased DP 400-700 adjusted during the production. The lyocell fiber is defined as a high crystalline fiber. Biodegradation experiments (soil burial tests) proved the influence of these properties on the rate of biodegradation - the viscose degrades rapidly, followed by a medium degradation of cotton and a slow rate for lyocell. The rate of biodegradation increases with the decreased crystallinity and decreased length of cellulose chains.

[0005] Park et al (Journal of Applied Polymer Science, 2004, 94, 248-253) evaluate the biodegradability using a soil burial test (AATCC Soil Burial Method 30-1993), an activated sewage sludge test (ASTM D 5209-92) and enzyme hydrolysis. The authors find the biodegradability of the cellulose fabrics in the following order: rayon>cotton. They state that the rate of biodegradability is dependent on the crystallinity of the fiber (the lower the crystallinity the faster the rate) and the moisture regain (hydrophilicity).

[0006] Articles and a master thesis describe the biodegradation of natural cellulosic fibers like cotton, linen or wool. F.e. Li et al (Journal of Engineered Fibers and Fabrics, 2010, 5(4), 42-53) compare the biodegradation (according to ASTM D 5988-03 standard (Standard Test Method for Determination of Aerobic Biodegradation in Soil of Plastic Materials or Residual Plastic Materials after Composting)) of cotton fabrics with 3 different finishing treatments and a PES fabric under laboratory and large-scale conditions. All cotton samples were confirmed compostable, whereas the PES fabric only showed slight initial degradation.

Arshad and Mujahid (Master Thesis, 2011, Report No. 2011.7.8) address the biodegradation of fabric samples made from cotton, jute, linen, flax, wool and a flax/PES blend. The results are similar as described above - all cellulose-based samples are biodegradable, the rate of biodegradation is dependent on specifications of the fabric. The synthetic fiber PES shows no signs of degradation. Wool shows a slow rate of biodegradation due to surface effects. Arshad et al (Tekstilec, 2014, 57(2), 118-132) compares the biodegradation of natural fabric samples (cotton, jute, linen, wool), which are all cellulose-based. They state that the mechanism for the breakdown of the fabrics in the soil is the same for all fabrics, but the velocity of biodegradation differs with the structure of the yarns - the more tightly twisted the yarn, the slower the biodegradation. In trials with PES blends, the PES fibers stayed undamaged during the experiments.

[0007] Cellulose based fibers are employed in a wide variety of applications. Due to ever increasing demands even for such fibers based on renewable resources such as wood attempts have been made to increase the variety of raw materials which may be employed for the production of such fibers. At the same time a demand exists towards a further functionalization of such fibers, targeting specific fiber properties. Another aim is to mimic properties and structure of natural fibers. Fibers based on cellulose regeneration differ in their structure from natural fibers in that they typically do not show any internal cavities/lumen. For example viscose fibers do show an oval cross section comprising a dense sheath and a sponge like core of the fiber. Lyocell fibers on the other hand do show a circular cross section with a three layered structure, comprising an outer compact skin with a thickness of 100 to 150 nm and a small pore size from 2 to 5 nm, followed by a middle layer with increasing porosity and a dense, non-porous core.

[0008] The process for preparing lyocell fibers offers only limited options to influence fiber properties and structure. However, it would be advantageous if means existed to influence fiber properties to a greater extend even in the lyocell process. During the process of preparing viscose fibers, due to the type of solvent used and the general robustness of the process, it is possible to add a broad variety of additives and additional components to adjust fiber properties. Due to the specific solvent system used for the lyocell process there are however only limited options available for the addition of additives in order to further vary the structure and/or properties of lyocell fibers.

[0009] It is for example known that chemical pre-treatment may influence fiber properties. US 6042769 shows an example of chemical treatments to enhance fibrillation tendency. It discloses chemical treatments to reduce the DP (degree of polymerization) by 200 units, thereby increasing fibrillation tendency. Chemical treatments mentioned in this patent refer to the use of bleaching reagents, such as sodium hypochlorite or mineral acids, such as hydrochloric acid, sulfuric acid or nitric acid. A commercialization of this procedure did not succeed up to now.

[0010] US 6706237discloses that meltblown fibers obtained from hemicelluloses rich pulps show a decreased or reduced tendency to fibrillate. A similar disclosure is also given in US 6440547, which again refers to meltblown fibers. For these as well as for centrifugal fibers crystallinity was determined, showing a rather insignificant decrease of crystallinity for the meltblown fibers with high hemicelluloses content as compared to standard lyocell fibers (decrease of less than 5%). US 8420004 discloses another example of meltblown fibers for producing non-woven fabrics.

[0011] For viscose fibers it has been shown (WO2014086883) that the addition of hemicelluloses enables the modification of fiber properties. However, these modifications were always accompanied by a decrease of other important fiber properties, such as tenacity. However, such modifications, due to the differences in fiber production cannot be applied without problems to lyocell fibers.

[0012] Zhang et al (Polymer Engineering and Science 2007, 47, 702-706) describe lyocell fibers with higher hemicellulose contents. The authors postulate that the fibers tend to show an enhanced fiber fibrillation resistance, lower crystallinity and better dyeability. However, the determination of crystallinity in this paper showed an only insignificant decrease (less than 5%). They also postulate that the tensile strength only decreases insignificantly and that the fiber properties could be even increased further by higher hemicelluloses concentrations in the spinning dope. Zhang et al (Journal of Applied Polymer Science 2008, 107, 636-641), Zhang et al (Polymer Materials Science and Engineering 2008, 24, 11, 99-102) disclose the same figures as the paper by Zhang (Polymer Engineering and Science 2007, 47, 702-706), while Zhang et al (China Synthetic Fiber Industry 2008, 31, 2, 24-27) describe better mechanical properties for 2.3 dtex fibers. The same authors postulate this same theory in Journal of Applied Science 2009, 113, 150-156. The fibers described in the paper by Zhang et al. (Polymer Engineering and Science 2007, 47, 702-706) are produced with lab equipment not allowing the production of lyocell fibers in commercial quality (as for example drawing ratios, equilibriums in spinning baths, production velocities and after-treatment do not reflect scale-up qualities). The fibers, not being produced in equilibrium states and with insufficient drawing therefore can be expected to show different structures and properties compared to the fibers produced at production (semi)-commercial scale. In addition no information is provided in the paper concerning the distribution of the hemicelluloses over the cross section of the lyocell fibers.

[0013] In this regard it is known for viscose fibers that an increase in hemicellulose content leads to an enrichment of the hemicelluloses content at the surface of the fiber, with a rapid decrease of the hemicelluloses content towards the core of the fiber. Similar distributions of hemicelluloses contents are known for standard lyocell fibers produced from high purity cellulose raw materials.

[0014] Wendler et al. (Fibers and textiles in Eastern Europe 2010, 18, 2 (79), 21-30) and Wendler et al (Cellulose 2011, 18, 1165-1178) describe the addition of different polysaccharides (xylans, mannans, xylan derivative,...) into lyocell dopes (NMMO, ionic liquids, NaOH) and subsequent analysis of the fibers. Disclosed are the water retention values of the fibers which show only an insignificant increase of the WRV with the addition of xylans in NMMO-based dopes. It is suspected that the fibers act differently produced by addition of polysaccharides into the dope or direct dissolution of a hemi-rich pulp. The fibers from both publications were produced with a self-made lab equipment not reflecting (semi)-commercial scale production conditions.

[0015] Schild et al (Cellulose 2014, 21, 3031-3039) describe xylan-enriched viscose fibers, wherein the xylan is added in a late step in the viscose production process. The authors investigated the distribution of the xylan over the cross-section of the fiber and detected an enrichment of the xylan in the outer layers of the fiber. Also an increased water uptake was observed. Singh et al (Cellulose 2017, 24, 3119-3130) also describe the addition of hemicelluloses to the viscose process. They postulate that the fiber properties stay unaffected by this addition. lyocell fibers are mentioned as reference fibers but no addition of xylan is described.

[0016] In the literature degradation behavior of various fibers and fabrics from different natural origins (cotton, flax, linen...) or different production techniques (viscose, lyocell, cellulose carbamate,...) were compared. It is presumed that the degradation rate is dependent on the crystallinity, moisture regain and surface area of the fiber. The higher the surface area the more points of attack for bacteria are given. Viscose fibers have a very high surface area with their lobed and rough surface. The lyocell fibers on the other hand have a smaller surface area with a very even surface and a round cross section. Therefore the lyocell fibers and fabrics show a slower rate of degradation/disintegration compared

to cotton or viscose. Lyocell fibers/fabrics also have higher crystallinities and lower water retention values (presenting the moisture regain properties).

Object of the present invention

[0017] The viscose fiber is well-established within the market, with over 100 years of experience. In the last 20 years a new technology - lyocell - found its way on the market. These lyocell fibers are presumed as "new-age" fibers produced with an environmental friendly, closed-loop, direct dissolution process. In terms of rate of biodegradability and disintegration the lyocell fibers are inferior to viscose fibers. A lyocell fiber with a higher rate of biodegradation and disintegration comparable to viscose would allow new application fields for lyocell.
The task of the present invention accordingly was to provide a new lyocell fiber with increased biodegradability and disintegration properties.

Brief description of the invention

[0018] The present inventors accordingly provide the fiber as defined in claim 1, the method for producing same as described in claim 11 as well as products containing same as defined in claim 12. Preferred embodiments are described in the respective subclaims as well as in the specification.
[0019] In particular the present invention provides the following embodiments, which are to be understood as being embodiments for which further explanations are provided below.

1.) Lyocell fibers with increased disintegration properties having a WRV value of at least 70% and a hemicelluloses content of equal to or more than 5 wt.-%.
2.) Lyocell fiber according to embodiment 1, having a titer of 6.7 dtex or less, preferreably 2.2 dtex or less, even more preferably 1.3 dtex or less
3.) Lyocell fiber according to embodiment 1, whereas increased disintegration properties mean a similar disintegration rate as viscose, preferably an almost completed disintegration after 3 weeks, determined in accordance with the procedure illustrated in the examples.
4.) Lyocell fiber according to embodiment 1 or 2, having a hemicelluloses content of 5 wt.-% or more.
5.) Lyocell fiber according to any one of embodiments 1 to 3, having a crystallinity of 40% or less, preferably 35% or less.
6.) Lyocell fiber according to any one of embodiments 1 to 4, wherein the hemicelluloses comprises C5/xylan and C6/mannan in a ratio of from 125:1 to 1:3, preferably from 25:1 to 1:2.
7.) Lyocell fiber in accordance with any one of embodiments 1 to 5, with a xylan content of 6 wt.-% or more, preferably 8 wt.-% or more and more preferably 12 wt.-% or more.
8.) Lyocell fiber in accordance with any one of embodiments 1 to 6, with a mannan content of 3 wt.-% or more, preferably 5 wt.-% or more.
9.) Lyocell fiber in accordance with any one of embodiments 1 to 7, with a mannan content of 1 wt.-% or less, preferably 0.2 wt.-% or less and more preferably 0.1 wt.-% or less.
10.) Lyocell fiber in accordance with any of the preceding embodiments, prepared froma pulp having a scan viscosity of from 300 to 440 ml/g.
11.) Method for producing a lyocell fiber according to any one of the preceding embodiments comprising the following steps:

a) Manufacture of a spinning solution containing 10 to 20 wt.-% cellulose with a hemicelluloses content of 7 wt.-% or more,
b) Extrusion of the spinning solution through extrusion nozzles to obtain filaments,
c) Initial coagulation of the filaments via a spin bath containing a coagulation liquor with a concentration of tertiary amine oxide of 20% or less;
d) Washing the filaments; and optional
e) After-treatment (f.e. washing, cutting, drying) to yield wet or dry filaments or staple/short cut fibers or other cellulosic embodiments.

12.) Product, comprising the lyocell fiber according to any one of embodiments 1 to 10, or the fiber produced according to embodiment 11.
13.) Product according to embodiment 12, selected among non-woven fabrics and textiles.
14.) Product according to embodiment 13 and/or 14, selected among tissues and wipes.

Brief description of the Figures

[0020] Figure 1 shows the fibrillation dynamics of a fiber in accordance with the present invention in comparison with a standard fiber and a standard fiber subjected to chemical fibrillation. Figures 2 and 3 show the results of an enzymatic peeling test, while Figures 4 to 6 show the results of degradation experiments in soil.

Detailed description of the invention

[0021] As defined in claim 1 the fiber in accordance with the present invention is a lyocell fiber with an increased degradation behavior. The novel fibers display properties similar to standard lyocell fibers, such as mechanical fiber properties, while other properties, such as WRV and fibrillation tendencies, as well as degradation behavior are similar to the advantageous property levels known from viscose fibers.

[0022] In embodiments the fiber of the present invention shows a novel structure of the cross section, as compared to standard lyocell fibers. While the three layer structure known from standard lyocell fibers is maintained, at least the inner core layer shows an increased porosity, as compared with standard lyocell fibers. In embodiments also the surface layer may be less thick and/or the pore size, which is typically for standard lyocell fibers in the range of from 2 to 5 nm, may be larger.

[0023] In further embodiments, which may be considered in combination with the embodiments mentioned above as well as embodiments mentioned below, the fibers in accordance with the present invention are lyocell fibers with enhanced fibrillation tendencies, which are produced without any chemical pre-treatment. The chemical pre-treatment step weakens the fiber properties (working capacity) on the one hand and adds cost to the fiber production on the other hand. Additionally the fiber in accordance with the present invention shows well-balanced fibrillation dynamics between standard lyocell fibers and fast fibrillated fibers obtained with additional chemical pre-treatments. Accordingly, in embodiments the lyocell fiber in accordance with the present invention avoids the need for chemical pre-treatment whilst achieving fast fibrillation.

[0024] Standard lyocell fibers are currently commercially produced from high quality wood pulps with high α-cellulose content and low non-cellulose contents such as hemicelluloses. Commercially available lyocell fibers such as TENCEL™ fibers produced from Lenzing AG, show excellent fiber properties for nonwovens and textile applications. As mentioned in the patents referred to above, if a high fibrillation tendency is required these lyocell fibers are chemically pre-treated using agents such as mineral acids or bleaching reagents. By this chemical treatment the fiber properties are weakened drastically and the working capacity decreases.

[0025] The lyocell process is well known in the art and relates to a direct dissolution process of cellulose wood pulp or other cellulose-based feedstock in a polar solvent (for example N-methylmorpholine N-oxide [NMMO, NMO] or ionic liquids). Commercially, the technology is used to produce a family of cellulose staple fibers (commercially available from Lenzing AG, Lenzing, Austria under the trademark TENCEL® or TENCEL™) which are widely used in the textile and nonwoven industry. Other cellulose bodies from lyocell technology have also been produced.

[0026] The fibers in accordance with the present invention were produced on a semi-commercial pilot plant (~1 kt/a) and a complete, commercial-like after-treatment of the fiber. A straightforward scale-up from this production unit to a commercial unit (>30 kt/a) is feasible and reliable.

According to this method the solution of cellulose is extruded in a so called dry-wet-spinning process by means of a forming tool and the moulded solution is guided for example over an air gap into a precipitation bath, where the moulded body is obtained by precipitation of the cellulose. The molding is washed and optionally dried after further treatment steps. Such lyocell fibers are well known in the art and the general methodology to produce and analyze same is for example disclosed in US 4,246,221 and in the BISFA (The International Bureau for the Standardization of Man-Made Fibers) publication "Terminology of Man-Made Fibres", 2009 edition. Both references are included herewith in their entirety by reference.

[0027] The term lyocell fiber as employed herein defines a fiber obtained by this process, as it has been found that fibers in accordance with the present invention differ greatly from fibers for example obtained from a meltblown process, even if using a direct dissolution process of cellulose wood pulp or other cellulose-based feedstock in a polar solvent (for example N-methylmorpholine N-oxide [NMMO, NMO] or ionic liquids) in order to produce the starting material. At the same time the fibers in accordance with the present invention also differ from other types of cellulose based fibers, such as viscose fibers.

[0028] The term hemicelluloses as employed herein refers to materials known to the skilled person which are present in wood and other cellulosic raw material such as annual plants, i.e. the raw material from which cellulose typically is obtained. Hemicelluloses are present in wood and other plants in form of branched short chain polysaccharides built up by pentoses and/or hexoses (C5 and / or C6-sugar units). The main building blocks are mannose, xylose, glucose, rhamnose and galactose. The back bone of the polysaccharides can consist of only one unit (f.e. xylan) or of two or more units (e.g. mannan). Side chains consist of arabinose groups, acetyl groups, galactose groups and O-acetyl groups as well as 4-O-methylglucuronic acid groups. The exact hemicellulose structure varies significantly within wood species.

Due to the presence of sidechains hemicelluloses show much lower crystallinity compared to cellulose. It is well known that mannan predominantly associates with cellulose and xylan with lignin. In sum, hemicelluloses influence the hydrophilicity, the accessibility and degradation behavior of the cellulose-lignin aggregate. During processing of wood and pulp, side chains are cleaved off and the degree of polymerization is decreased. The term hemicelluloses as known by the skilled person and as employed herein comprises hemicelluloses in its native state, hemicelluloses degraded by ordinary processing and hemicelluloses chemically modified by special process steps (e. g. derivatization) as well as short chain celluloses and other short chain polysaccharides with a degree of polymerization (DP) of up to 500.

[0029] The pulps preferably employed in the present invention do show as outlined herein a high content of hemicelluloses. Compared with the standard low hemicellulose content pulp employed for the preparation of standard lyocell fibers the preferred pulps employed in accordance with the present invention do show also other differences, which are outlined below.

[0030] Compared with standard pulps the pulps as employed herein display a more fluffy appearance, which results after milling (during preparation of starting materials for the formation of spinning solutions for the lyocell process), in the presence of a high proportion of larger particles. As a result the bulk density is much lower, compared with standard pulps having a low hemicellulose content. This low bulk density requires adaptions in the dosage parameters (f.e. dosage from at least 2 storage devices). In addition the pulps employed in accordance with the present invention are more difficult to impregnate with NMMO. This can be seen by evaluating the impregnating behavior according to the Cobb evaluation. While standard pulps do show a Cobb value of typically more than 2.8 g/g (determined according to DIN EN ISO 535 with the adaptation of employing an aqueous solution of 78% NMMO at 75° C with an impregnation time of 2 minutes), the pulps employed in the present invention do show Cobb values of about 2.3 g/g. This requires an adaptation during spinning solution preparation, such as increased dissolution time (f.e. explained in WO 9428214 and WO 9633934) and/or temperature and/or increased searing during dissolution (f.e. WO9633221, WO9805702 and WO 9428217). This ensures the preparation of a spinning solution enabling the use of the pulps described herein in standard lyocell spinning processes.

[0031] In one preferred embodiment of the present invention the pulp employed for the preparation of the lyocell products, preferably fibers, as described herein, has a scan viscosity in the range of from 300-440 ml/g, especially 320-420 ml/g, more preferably 320 to 400 ml/g. The scan viscosity is determined in accordance with SCAN-CM 15:99 in a cupriethylenediamine solution, a methodology which is known to the skilled person and which can be carried out on commercially available devices, such as the device Auto PulpIVA PSLRheotek available from psl-rheotek. The scan viscosity is an important parameter influencing in particular processing of the pulp to prepare spinning solutions. Even if two pulps seem to be of great similarity as raw material for the lyocell-process, different scan viscosities will lead to completely different behaviour different during processing. In a direct solvent spun process like the lyocell-process the pulp is dissolved in NMMO as such. No ripening step exists comparable to the viscose process where the degree of polymerization of the cellulose is adjusted to the needs of the process. Therefore, the specifications for the viscosity of the raw material pulp typically are within a small range. Otherwise, problems during production may arise. In accordance with the present invention it has been found to be advantageous if the pulp viscosity is as defined above. Lower viscosities compromise mechanical properties of the lyocell products. Higher viscosities in particular may lead to the viscosity of the spinning dope being higher and therefore, spinning will be slower. With a slower spinning velocity lower draw ratios will be attained, which significantly alters the fiber structure and its properties (Carbohydrate Polymers 2018, 181, 893-901; Structural analysis of loncell-F fibres from birch wood, Shirin Asaadia; Michael Hummel; Patrik Ahvenainen; Marta Gubitosic; Ulf Olsson, Herbert Sixta). This will require process adaptations and will lead to a decrease in mill capacity. Employing pulps with the viscosities as defined here enables smooth processing and production of high quality products.

[0032] As employed herein the terms lyocell process and lyocell technology relate to a direct dissolution process of cellulose wood pulp or other cellulose-based feedstock in a polar solvent (for example N-methylmorpholine N-oxide [NMMO, NMO] or ionic liquids). Commercially, the technology is used to produce a family of cellulose staple fibers (commercially available from Lenzing AG, Lenzing, Austria under the trademark TENCEL® or TENCEL™) which are widely used in the textile and nonwoven industry. Other cellulose bodies from lyocell technology have also been produced. According to this method the solution of cellulose is usually extruded in a so called dry-wet-spinning process by means of a forming tool and the moulded solution gets for example over an air gap into a precipitation bath, where the moulded body is obtained by precipitation of the cellulose. The moulding is washed and optionally dried after further treatment steps. A process for production of lyocell fibers is described, for instance, in US 4,246,221, WO 93/19230, WO95/02082 or WO97/38153. As far as the present application discusses the drawbacks associated with the prior art and the unique properties for novel products as disclosed and claimed herein in the context of using laboratory equipment (in particular in the prior art) or (semi-commercial) pilot plants and commercial fiber spinning units, the present invention is to be understood to referring to larger scale plants/units, which may be considered as follows concerning their respective production capacity:

semi-commercial pilot plant: about1 kt/a

commercial unit >30 kt/a

[0033] The task and object mentioned above was solved by lyocell fibers with the properties mentioned above, The fibers in accordance with the present invention show, in embodiments due to the specific structure, the required improved degradation properties, which in turn may also be determined for example by increased enzymatic peelability and increased WRV, decreased crystallinity, and/or increased fibrillation tendency. In other embodiments, which may be considered in combination with all embodiments mentioned herein, the WRV may be influenced by the crystallinity as well as by the structure of the fiber, in particular the porous core layer.

[0034] Standard lyocell fibers are currently commercially produced from high quality wood pulps with high α-cellulose content and low non-cellulose contents such as hemicelluloses. Commercially available Lyocell fibers such as TENCEL™ fibers produced from Lenzing AG, show excellent fiber properties for nonwovens and textile applications.

[0035] The present invention surprisingly is able to provide fibers with the unique properties as described herein by using hemicellulose-rich pulps with a hemicellulose content of at least 5 wt.-%. Contrary to the disclosure in the prior art discussed above, such high hemicellulose content surprisingly, for lyocell fibers of the present invention, gives rise to an increased degradation property. Also the WRV is increased as well as fibrillation tendencies. Accordingly the present invention surprisingly achieves the tasks as outlined above while using a cellulose based raw material with a higher hemicelluloses content, as compared for standard lyocell fibers.

[0036] As already outlined above, Zhang et al (Polym. Engin. Sci. 2007, 47, 702-706) describe fibers with high hemicellulose contents. Likewise meltblown fibers with high hemicelluloses contents are known from the prior art discussed above. However, contrary to the results as reported in the prior art the present invention provides fibers with completely different properties as outlined above. One possible explanation for these contrasting findings may be the fact that the fibers in accordance with the present invention are fibers produced using large scale production equipment employing a lyocell spinning process, while the fibers described in the prior art are either produced with lab equipment not allowing the production of lyocell fibers in commercial quality (as for example drawing ratios, production velocities, after-treatment do not reflect scale-up qualities) or produced using meltblowing techniques. The fibers, not being produced with insufficient drawing and inadequate after-treatment therefore show different structure and properties compared to the fibers produced at production scale at titers reflecting market applications.

[0037] The content of hemicelluloses in the pulps - which can also be a mixture of different pulps (as long as the essential requirements are met) - may be from 7 to 50 wt.-%, such as from 10 to 25, preferably 10 to 15 wt.-%. The hemicellulose content may be adjusted according to procedures known in the art. The hemicellulose may be the hemicelluloses originating from the wood from which the pulp is obtained, it is however also possible to add individual hemicelluloses depending on the desired fiber properties from other sources to high purity cellulose with a low original hemicellulose content. The addition of individual hemicelluloses may also be employed to adjust the composition of the hemicelluloses content, for example to adjust the ratio of hexoses to pentoses.

[0038] The hemicelluloses contained in the pulp used for preparing the fibers in accordance with the present invention may have varying compositions, in particular regarding the content of pentoses and hexoses. In embodiments the content of pentoses in the hemicellulose-rich pulp employed in the present invention is higher that the hexose content. In embodiments, the ratio of C5/xylan to C6/mannan may be in the range of from 125:1 to 1:3, preferably 25:1 to 1:2. In some embodiments, preferably in combination with a high overall hemicelluloses content of 10 wt.-% or more as defined above, including the ranges given above, the xylan content preferably is 6 wt.-% or more, more preferably 8 wt.-% or more and in embodiments even 12 wt.-% or more, with a suitable upper limit being about 20 wt.-%. The mannan content preferably, wither in isolation from or in combination with the above identified hemicelluloses content and/or xylan content, in embodiments is 3 wt.-% or more, preferably 5 wt.-% or more, with a suitable upper limit being about 10 wt.-%. In other embodiments the mannan content is low, such as 1 wt.-% or less, preferably 0.2 wt.-% or less and in embodiments 0.1 wt.-% or less, i.e. below a typical detection threshold.

As the hemicelluloses content as well as the composition in particular of xylan and mannan content and ratio is not altered much during fiber spinning the above identified ranges, contents and ratios, presented in the context of the pulp used for the preparation of the lyocell fiber are also applicable for the lyocell fibers as such.

[0039] The fibers in accordance with the present invention typically have a titer of 6.7 dtex or less, such as 2.2 dtex or less, such as 1.7 dtex, or even lower, such as 1.3 dtex or even lower, depending on the desired application. If the fiber is intended to be used in nonwoven applications a titer of from 1.5 to 1.8 dtex typically is suitable while for textile applications lower titers such as from 0.9 to 1.7 dtex are suitable. Surprisingly the present invention enables the formation of fibers with the desired titers over the whole application range, from nonwoven applications to textile applications. However, the present invention also covers fibers with much lower titers, with suitable lower limits for titers being 0.5 dtex or higher, such as 0.8 dtex or higher, and in embodiments 1.3 dtex or higher. These upper and lower values as disclosed here define ranges of from 0.5 to 9 dtex, and including all further ranges formed by combining any one of the

upper values with any one of the lower values.

[0040] The fiber in accordance with the present invention may be prepared using lyocell technology employing a solution of cellulose and a spinning process employing a precipitation bath according to standard lyocell processes, known to the skilled person

[0041] The fiber in accordance with the present invention preferably shows a reduced crystallinity, preferably of 40% or less. The fiber in accordance with the present invention preferably shows a WRV of 70% or more, more preferably 75% or more. Suitable ranges, in particular in combination with the crystallinity described herein and/or the hemicelluloses content and composition, are from72% to 90%, such as from 75% to 85%.The fiber in accordance with the present invention does not show any sulfuric smell so that olfactoric drawbacks of viscose fibers are overcome, while properties such as WRV and working capacity enable the use of the fibers of the present invention as viscose replacement fibers.

[0042] The fiber in accordance with the present invention, in isolation or in any combination with features outlined above as preferred for the claimed fiber, has a crystallinity of 40 % or less, preferably 39 % or less. In particular fibers to be employed for non woven applications do show preferably a low crystallinity of for example from 39 to 30%, such as from 38 to 33 %. The present invention however is not limited to these exemplary crystallinity values. As explained above, in comparison to standard Lyocell fibers the fibers in accordance with the present invention do show a reduced crystallinity of 40 % or less.

[0043] The fiber in accordance with the present invention shows in embodiments a novel type of distribution of the hemicelluloses over the cross section of the fiber. While for standard lyocell fibers the hemicelluloses are concentrated within the surface region of the fiber the fibers in accordance with the present invention do show an even distribution of the hemicelluloses over the entire cross section of the fiber. Such a distribution enhances the functionality of the fiber, as hemicelluloses increase for example binding properties towards other additives with a matching chemical reactivity. In addition the even distribution of the hemicelluloses may also contribute towards stabilizing the novel structure of the fibers in accordance with the present invention, comprising larger pores in the surface layer and a porous core layer. This novel structure enhances uptake as well as retention of other molecules, such as dyes and also contributes towards a faster degradation, in particular biological (enzymatic) degradation / disintegration.

[0044] The fibers in accordance with the present invention may be employed for a variety of applications, such as the production of nonwoven fabrics, but also textiles. The fibers in accordance with the present invention may by employed as the only fiber of a desired product or they may be mixed with other types of fibers. The mixing ratio can depend from the desired end use.

[0045] As far as the present application refers to parameters, such as crystallinity, scan viscosity etc., it is to be understood that same are determined as outlined herein, in the general part of the description and/or as outlined in the following examples. In this regard it is to be understood that the parameter values and ranges as defined herein in relation to fibers refer to properties determined with fibers derived from pulp and containing only additives, such as processing aids typically added to the dope as well as other additives, such as matting agents (TiO_2, which often is added in amounts of up to 0.75 wt.-%), in a total amount of up to 1 wt.-% (based on fiber weight). The unique and particular properties as reported herein are properties of the fibers as such, and not properties obtained by addition of particular additives and/or post spinning treatments (such as fibrillation improving treatments etc.).

[0046] However, it is clear to the average skilled person that the fibers as disclosed and claimed herein may comprise additives, such as inorganic fillers etc. in usual amounts as long as the presence of these additives has no detrimental effect on dope preparation and spinning operation. The type of such additives as well as the respective addition amounts are known to the skilled person.

Examples:

Example 1: Lyocell fiber production and analysis

[0047] 3 different fibers were produced using 3 different types of pulp with different hemicellulose contents (table 1). The lyocell fibers were produced according to WO93/19230 dissolving the pulps in NMMO and spinning them over an air-gap into a precipitation bath to receive fibers with titers from 1.3 dtex to 1.7 dtex, with and without matting agent (0.75% TiO_2).

Table 1: Sugar contents of the different pulps for the lyocell fiber production.

sugar [%ATS]	reference pulp	hemi-rich pulp 1	hemi-rich pulp 2
Glucan	95.5	82.2	82.3
Xylan	2.3	8.3	14
Mannan	0.2	5.7	<0.2

(continued)

sugar [%ATS]	reference pulp	hemi-rich pulp 1	hemi-rich pulp 2
Arabinan	<0.1	0.3	<0.1
Rhaman	<0.1	<0.1	<0.1
Galactan	<0.1	0.2	<0.1

[0048] The fiber properties of the lyocell fibers produced were analyzed. The results are summarized in table 2. Fiber 1 is produced from hemi-rich pulp 1 and fiber 2 from hemi-rich pulp 2. The standard lyocell (CLY) fibers are produced from the standard lyocell reference pulp. Bright indicates a textile fiber without matting agent, whereas the dull fibers contain the matting agent identified above.

Tablle 2: Fiber properties.

fiber type	Titer [dtex]	working capacity [cN/tex*%]	FFk [cN/tex]	FDk [%]
1.3 dtex / 38 mm fiber 1 bright	1.33	410	31	13.2
1.3 dtex / 38 mm CLY standard bright	1.28	491	35.7	13.8
1.7 dtex / 38 mm fiber 1 bright	1.69	380	30.4	12.5
1.7 dtex / 38 mm CLY standard bright	1.65	571	38.6	14.8
2.2 dtex / 38 mm fiber 1 bright	2.12	339	28.2	12.1
2.2 dtex / 38 mm CLY standard bright	2.14	559	41.7	13.4
1.7 dtex / 38 mm fiber 1 dull	1.67	333	28.7	11.6
1.7 dtex / 38 mm CLY standard dull	1.71	384	32.1	11.9
1.7dtex /38 mm fiber 2 dull	1.72	315	27.6	11.4

[0049] The displayed results show that the fibers in accordance with the present invention may be prepared over the commercially relevant range of fiber titers, while maintaining sufficient mechanical properties, in particular working capacity, to render these fibers suitable as viscose replacement fibers.

***Example 2*:** Crystallinity measurements

[0050] Crystallinities of the fibers of Example 1 are measured using a FT/IR with a Bruker MultiRAM FT-Raman spectrometer with a Nd-Yag-laser at 1064 nm and 500 mW. The fibers are pressed into pellets for a smooth surface. Fourfold determination with a spectral resolution of 4 cm^{-1} with 100 scans respectively. Evaluation of the measurements was done using a chemometric method (calibration with WAXS-data).

[0051] It can be seen that the crystallinities of the fibers of the present invention (fiber 1 and 2) decrease by 15 and 16% respectively compared to the standard lyocell fibers. But they are still significantly higher compared to viscose fibers.

Table 3: Crystallinities of the different lyocell fibers.

fiber type	crystallinity [%]
1.3 dtex / 38 mm CLY standard bright	44
1.3 dtex / 40 mm viscose standard bright	29
1.3 dtex / 38 mm fiber 1 bright	37
1.7 dtex / 38 mm CLY standard dull	47
1.7 dtex / 40 mm viscose standard dull	34
1.7 dtex / 38 mm fiber 1 dull	40
1.7 dtex / 38 mm fiber 2 dull	39

***Example 3*:** WRV determination

[0052] For determining the water retention value, a defined quantity of dry fibers is introduced into special centrifuge tubes (with an outlet for the water). The fibers are allowed to swell in deionized water for 5 minutes. Then it is centrifuged at 3000 rpm for 15 minutes, whereupon the moist cellulose is weighed right away. The moist cellulose is dried for 4 hours at 105 °C, whereupon the dry weight is determined. The WRV is calculated using the following formula:

$$\mathrm{WRV}[\%] = \frac{(\mathrm{mf}-\mathrm{mt})}{\mathrm{mt}*100} \qquad (\mathrm{m_f} = \text{moist mass}, \mathrm{m_t} = \text{dry mass})$$

[0053] The water retention value (WRV) is a measured value that indicates how much water of a moisture penetrated sample is retained after centrifuging. The water retention value is expressed as a percentage relative to the dry weight of the sample.

[0054] In table 4 the water retention values of the fibers of the present invention (fiber 1 and 2) compared to the reference fibers are listed and an increase of the WRV by 26% and 19% respectively can be observed.

Table 4: WRV of the different lyocell fibers.

fiber type	WRV [%]
1.7 dtex / 38mm CLY standard bright	69.6
1.3 dtex / 40 mm viscose standard bright	89.9
1.3 dtex / 38 mm fiber 1 bright	82.8
1.7 dtex / 38 mm CLY standard dull	65.3
1.7 dtex / 38 mm fiber 1 dull	82.5
1.7 dtex / 38 mm fiber 2 dull	78.0

[0055] These results prove that the fibers in accordance with the present invention display a WRV rendering these fibers suitable as viscose replacement fibers.

***Example 4*:** Fibrillations tendencies

[0056] In table 5 the CSF (analyzed according to TAPPI Standard T227 om-94) values of different fiber types are compared. The CSF values after 8 min of mixing are shown.

[0057] The CSF values show a significantly increased fibrillation tendency of the invented fibers.

Table 5: Comparison of CSF values of different fibers after 8 min of mixing time.

fiber type	CSF [ml]
1.3dtex / 38 mm CLY standard bright	405
1.3 dtex / 38 mm fiber 1 bright	276
1.7 dtex / 38 mm CLY standard dull	285
1.7 dtex / 38 mm fiber 1 dull	115

[0058] The results show a higher fibrillation tendency for the fibers of the present invention, as compared with standard lyocell fibers.

Example 5: Comparison of fibrillation dynamics

[0059] 3 different fiber types were compared:

[0060] The standard 1.7 dtex / 4 mm lyocell fibers are commercially available as TENCEL™ fibers from Lenzing AG ("lyocell standard").

[0061] Lyocell fibers subjected to a chemical pre-treatment ("lyocell chemical fibrillation") were produced as described

in AT 515693. A fiber tow with single titers of 1.7 dtex was impregnated with diluted sulfuric acid at room temperature with a liquor ratio 1:10 and afterwards pressed to -200 % moisture. After-treatment of the fiber tow in a steamer for -10 min allows application of water vapor under pressure. The fiber bundle is washed acid-free, a soft-finish is applied and the fibers are dried. The dried fiber tow is cut into 4 mm shortcut fibers subsequently ending up with 1.7 dtex / 4 mm "lyocell chemical fibrillation" fibers.

[0062] Lyocell fibers of the present invention were produced from the hemicellulose-rich pulp 1 from example 1 with a hemicelluloses content of >10%, yielding after post-spinning treatment 1.7 dtex / 4 mm fibers.

[0063] The 3 different fiber types were refined in an Andritz Laboratory plant 12-1C plate refiner (NFB, S01-218238) at a starting concentration of 6 g/l, 1400 rpm and 172 l/min flow rate. The gap was fixed at 1 mm.

[0064] The refining results are illustrated in Figure 1. It can be seen that lyocell fibers of the present invention, designated lyocell increased fibrillation and lyocell chemical fibrillation fibers fibrillate at a significant higher rate compared to Lyocell standard fiber, meaning a decrease in time- and energy effort. The lyocell increased fibrillation fiber however showed a slower increase in fibrillation. These results do show that the fiber in accordance with the present invention also displays a fibrillation dynamics rendering same suitable as lyocell replacement fiber without any chemical pre-treatment.

***Example 6*:** Enzymatic peeling

[0065] The lyocell fibers CLY standard bright and fiber 1 bright (1.3 dtex / 38 mm bright) evaluated in Example 1 were subjected to an enzymatic peeling test according to Sjöberg et al (Biomacromolecules 2005, 6, 3146-3151). A viscose fiber with an enhanced xylan content of 7.5% was chosen for comparison from the paper by Schild and Liftinger (Cellulose 2014, 21, 3031-3039). This xylan content is close to the xylan content of the new fiber with 6.8%. The test enables the generation of data concerning the hemicellulose distribution over the cross section of fibers, in particular xylan (by HPLC determination) including information relating to different densities and structures of layers (as denser layers show a slower response as well as layers with smaller pore sizes).

[0066] The standard lyocell fibers as well as the xylan enriched viscose fibers showed a slow peeling rate (fig. 2). This effect is even more pronounced for prolonged peeling times due to the denser cores. At the same time, the xylan liberation determined corresponds to fibers with high hemicellulose content at the surface of the fiber and a sharp concentration decrease towards the core (fig. 3). Contrary thereto, the fibers in accordance with the present invention show a peeling behavior corresponding to a fiber structure with an even distribution of the hemicellulose content over the entire cross section. Additionally, the peeling is much faster. This is even more astonishing and completely new as this phenomenon could not be achieved with xylan enriched viscose fibers. Due to the faster peeling rate it can be concluded that the new fibers have more porous core and surface layers with increased pore sizes and numbers and a homogenous distribution of the xylan over the whole fiber cross section.

***Example 7*:** Disintegration in soil

[0067] 3 different fiber types were used to test the different disintegration behavior - 1.7 dtex / 38 mm fiber 1 dull; 1.7 dtex / 38 mm CLY standard dull and 1.7 dtex / 40 mm viscose standard dull.
The fibers were subsequently converted into 50 gsm wipes using spunlacing-technology.

[0068] Disintegration is qualitatively evaluated during 8 weeks (the test normally lasts 12 weeks, but after the material completely disappeared after 8 weeks, the test was stopped) of composting, simulating industrial composting conditions.

[0069] The test materials were put in slide frames, mixed with biowaste and composted in a 200 liter composting bin.

[0070] The test is considered valid if the maximum temperature during the composting (industrial composition requirements) is above 60°C and below 75°C. Moreover, the daily temperature should be above 60°C during 1 week and above 40°C during at least 4 consecutive weeks.

[0071] The requirements were largely fulfilled. After start-up the temperature increased almost immediately till above 60°C and stayed below 75°C, except shortly after 5 days with a maximum value of 78.0°C. However, immediate action was undertaken when the temperature exceeded the limit and lower temperatures were established. The temperature remained above 60°C during at least 1 week. After 1.1 weeks of composting the bin was placed in an incubation room at 45°C to ensure a temperature above 40°C. Elevated temperatures during the composting process were mainly due to the turning of the content of the bin, during which air channels and fungal flocks were broken up and moisture, microbiota and substrate were divided evenly. As such optimal composting conditions were reestablished, resulting in a higher activity and a temperature increase

[0072] The mixture in the bin was regularly turned manually during which the disintegration of the test items was visually monitored. A visual presentation of the evolution of the disintegration of the test materials in slide frames during the composting process is shown in figure 4 up to figure 6. The results are summarized in table 6.

[0073] It can be clearly seen in figure 4 that fiber 1 disintegrates much faster compared to standard lyocell. The disintegration after 4 weeks is comparable with the viscose test sample, after 2 weeks large holes can be observed at

the fiber 1 sample, whereas the viscose sample shows only small tears and holes and the lyocell sample is still intact.

[0074] All examples prove that in accordance with the present invention novel lyocell fibers are obtained which do show improved degradation properties, while maintaining desired and typical lyocell fiber properties as well as achieving properties similar to favorable properties of viscose fibers.

Table 6: Overview of the visual observations during the test.

Test item	1 week	2 weeks	3 weeks	4 weeks	6 weeks	8 weeks
fiber 1	Intact - brown color	Large holes - brown color	A border of test material remained present - brown color	A few tiny pieces remained present - dark brown color	All slide frames were completely empty.	Test was stopped.
viscose	Intact - brown color	Small tears and holes - brown color -fungal growth	A small border of test material remained present - brown color	A few tiny pieces remained present-dark brown color	All slide frames were completely empty	Test was stopped
lyocell	Intact - brown color	Mainly intact - brown color	Tears and holes - brown color	A few tiny pieces remained present - dark brown color	All slide frames were completely empty	Test was stopped

Claims

1. Lyocell fibers with increased disintegration properties, having a WRV value of at least 70% and a hemicelluloses content of equal to or more than 5 wt.-%.

2. Lyocell fiber according to claim 1, having a titer of 6.7 dtex or less, preferably 2.2 dtex or less, and even more preferably 1.3 dtex or less.

3. Lyocell fiber according to claim 1 and/or 2, whereas increased disintegration properties mean a similar disintegration rate as viscose, preferably an almost completed disintegration after 3 weeks, determined in accordance with the procedure illustrated in the examples.

4. Lyocell fiber according to claim 1 or 2, having a hemicelluloses content of 5 wt.-% or more.

5. Lyocell fiber according to any one of claims 1 to 3, having a crystallinity of 40% or less, preferably 35% or less.

6. Lyocell fiber according to any one of claims 1 to 4, wherein the hemicelluloses comprises C5/xylan and C6/mannan in a ratio of from 125:1 to 1:3, preferably from 25:1 to 1:2.

7. Lyocell fiber in accordance with any one of claims 1 to 5, with a xylan content of 6 wt.-% or more, preferably 8 wt.-% or more and more preferably 12 wt.-% or more.

8. Lyocell fiber in accordance with any one of claims 1 to 6, with a mannan content of 3 wt.-% or more, preferably 5 wt.-% or more.

9. Lyocell fiber in accordance with any one of claims 1 to 6, with a mannan content of 1 wt.-% or less, preferably 0.2 wt.-% or less and more preferably 0.1 wt.-% or less.

10. Lyocell fiber in accordance with any of the preceding claims, prepared from a pulp having a scan viscosity of from 300 to 440 ml/g.

11. Method for producing a Lyocell fiber according to any one of the preceding claims comprising the following steps:

    f) Manufacture of a spinning solution containing 10 to 20 wt.-% cellulose with a hemicelluloses content of 7 wt.-% or more,
    g) Extrusion of the spinning solution through extrusion nozzles to obtain filaments,

h) Initial coagulation of the filaments via a spin bath containing a coagulation liquor with a concentration of tertiary amine oxide of 20% or less;
i) Washing the filaments; and optional
j) After-treatment (f.e. washing, cutting, drying) to yield wet or dry filaments or staple/short cut fibers or other cellulosic embodiments.

12. Product, comprising the Lyocell fiber according to any one of claims 1 to 10, or the fiber produced according to claim 11.

13. Product according to claim 12, selected among non-woven fabrics and textiles.

14. Product according to claim 12 and/or 12, selected among tissues and wipes.

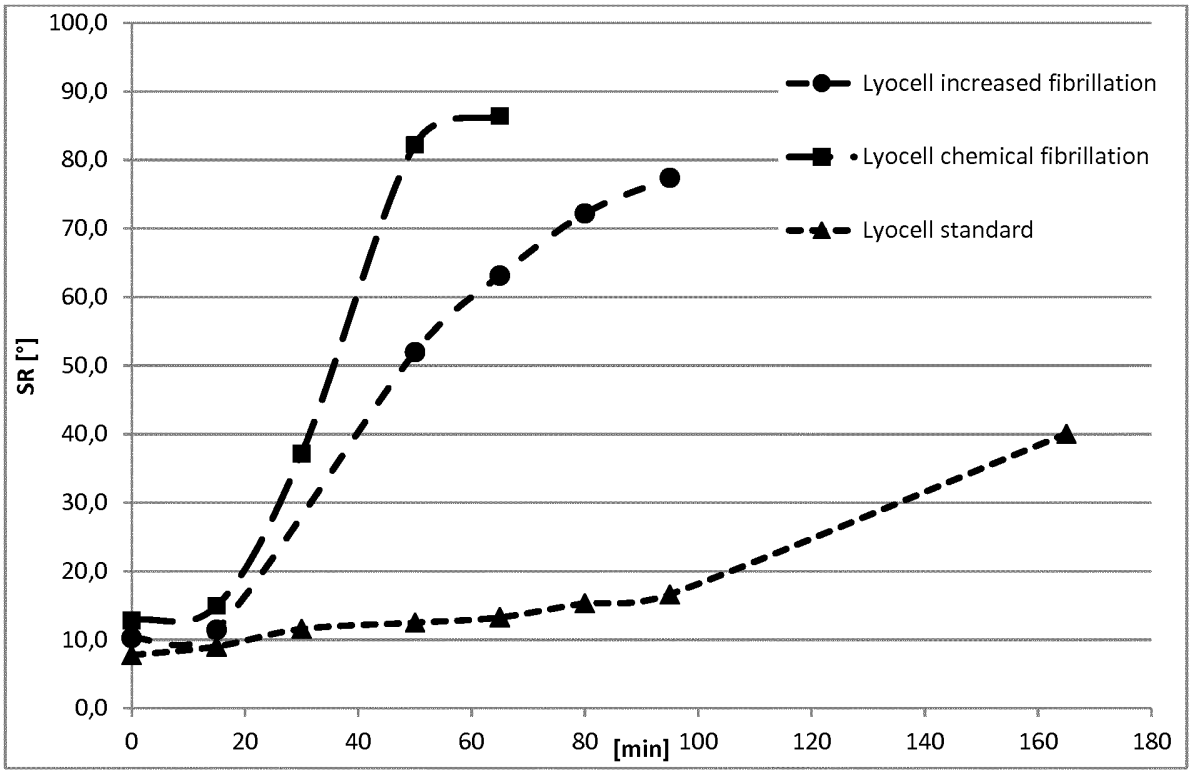

Figure 1: Fibrillation dynamics of three types of fibers.

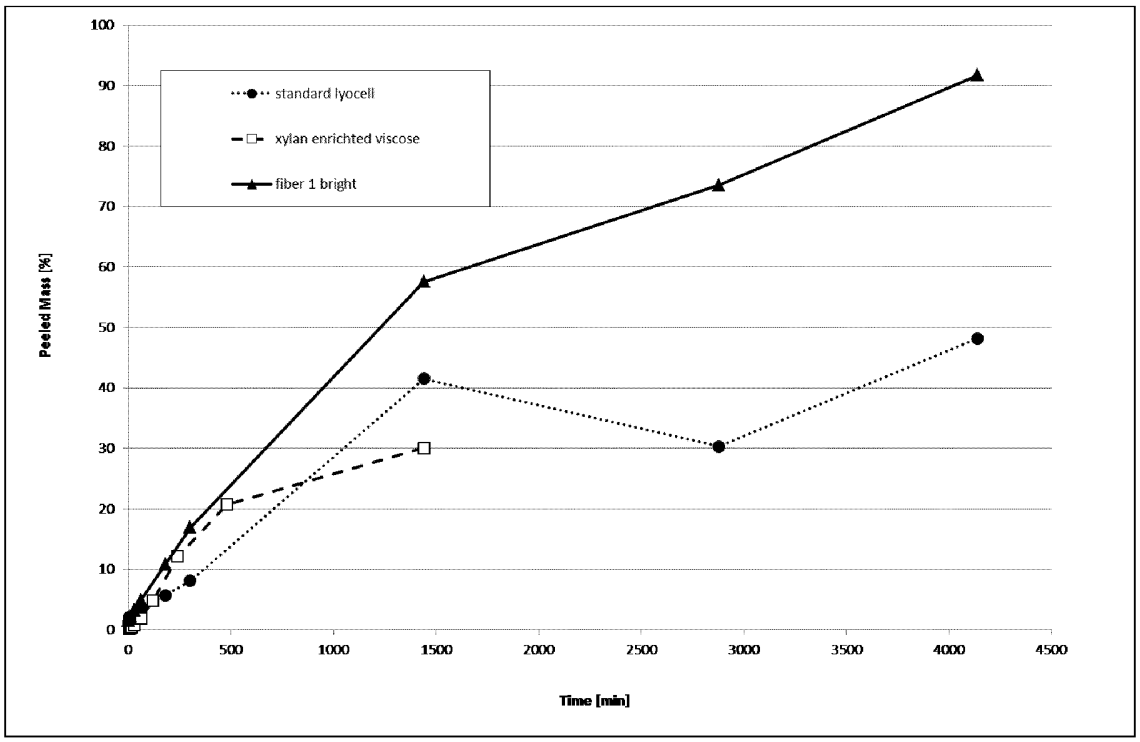

Figure 2: Velocity of enzymatic peeling for the new lyocell fiber with increased degradation behaviour compared to a standard lyocell fiber and a xylan enriched viscose fiber.

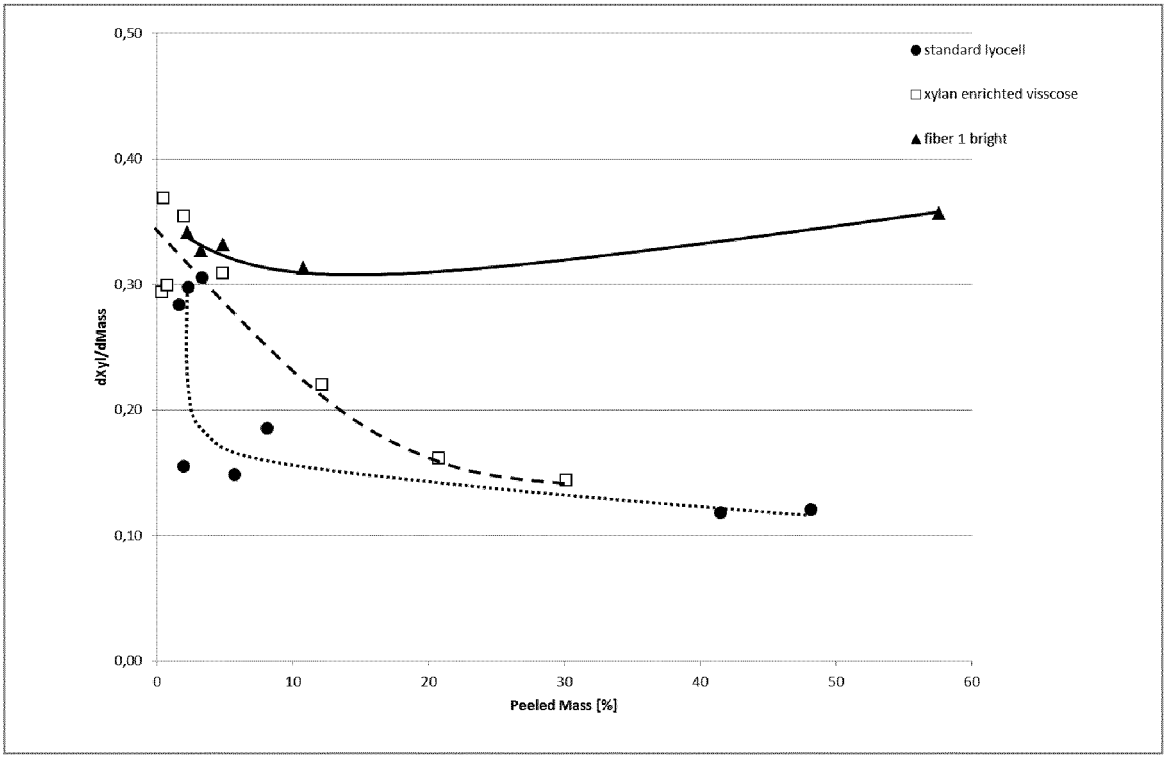

Figure 3: Xylan concentration over the fiber cross section of the new lyocell fiber with increased porosity compared to a standard lyocell fiber and a xylan enriched viscose fiber.

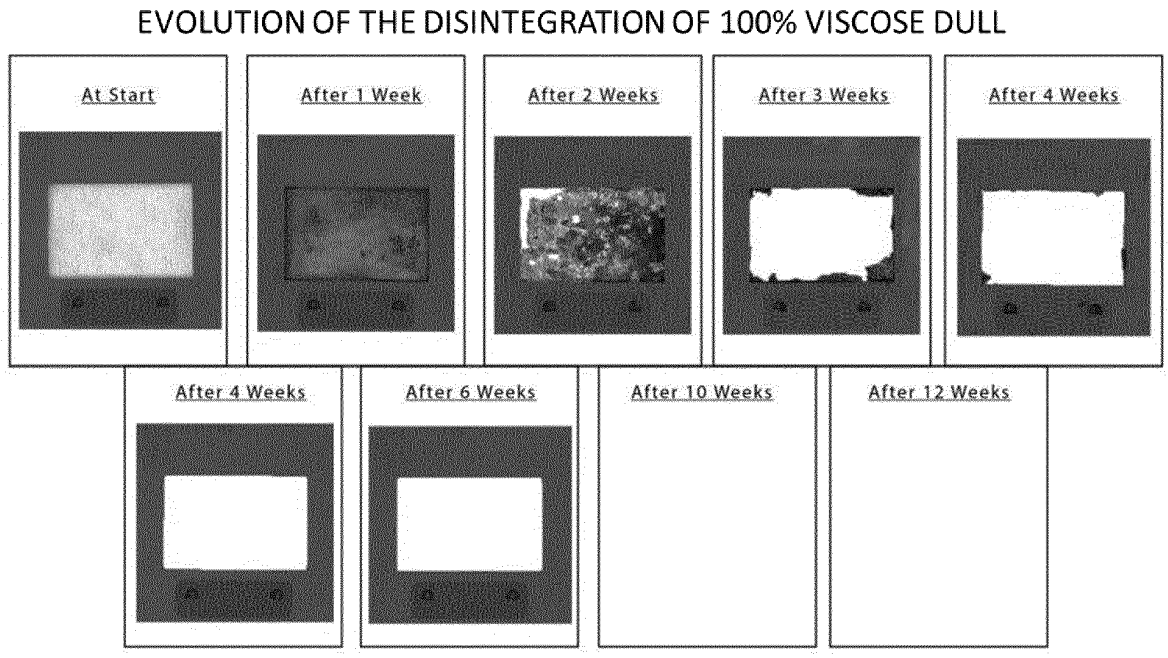

Figure 4: Visual presentation of the evolution of the disintegration of test material fiber 1 full in slide frames during the composting process.

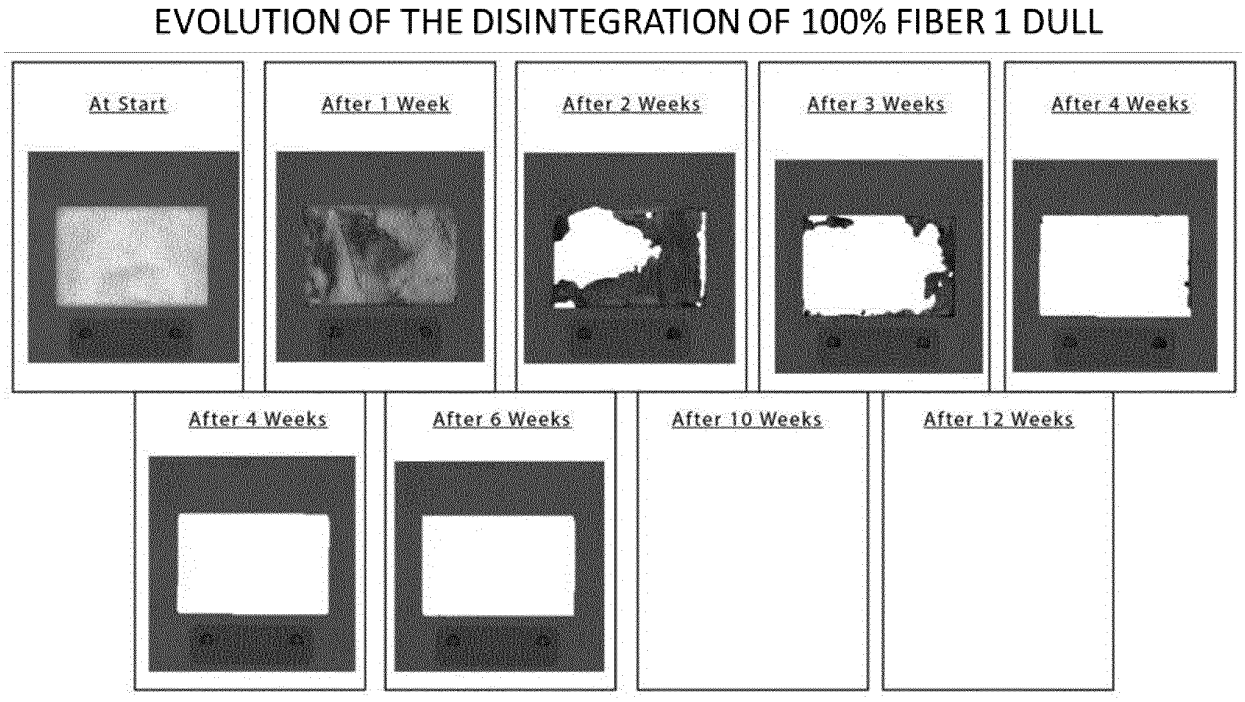

Figure 5: Visual presentation of the evolution of the disintegration of test material 100% viscose dull in slide frames during the composting process.

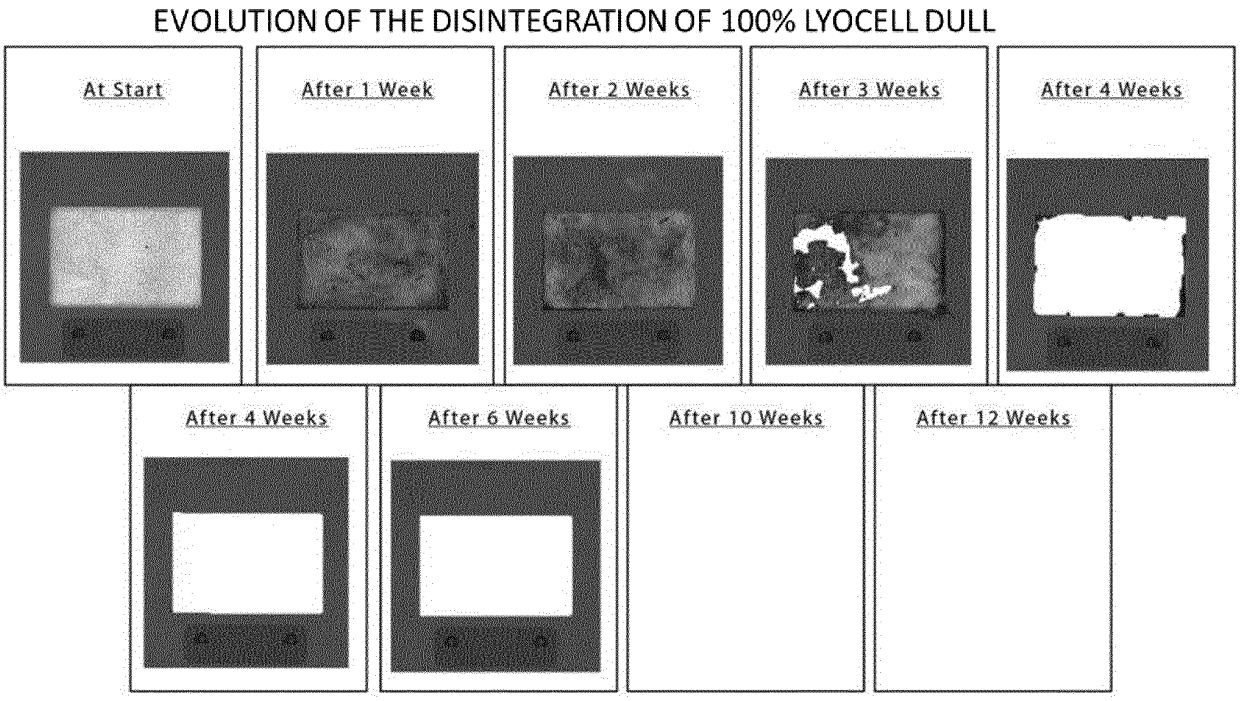

Figure 6: Visual presentation of the evolution of the disintegration of test material 100% Lyocell dull in slide frames during the composting process.

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EUROPEAN SEARCH REPORT

Application Number
EP 18 16 0141

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	16 August 2018	Verschuren, Jo

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