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MAN-MADE CELLULOSIC FIBERS FROM *EUCALYPTUS GLOBULUS* – A BRIDGE TO A SUSTAINABLE FUTURE

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SUMMARY

Textile industry has the challenge to increase its production to meet the growing needs of consumer market and simultaneously answer the global pressure for more ecological and sustainable processes. In this scenario, the production of man-made cellulosic fibers (MMCFs) from wood pulp has gained prominence not only as a solution for the so-called cotton gap, but mainly as a biodegradable and sustainable alternative to synthetic fibers. Currently, the Portuguese economy has traditional and high-quality industries for textile, and pulp and paper production, resulting in an intermediate gap that corresponds to the transformation of pulp into MMCFs. This gap is fulfilled with external production, reducing the sustainability of textile production, since it requires higher fossil fuels consumption due to logistics, and increases the country´s dependence on foreign economies. The advances achieved by the consortium formed by Caima (Portuguese pulp producer), CeNTI (multi-sectoral oriented technology and innovation centre), CITEVE (textile and clothing technological research institute), and University of Aveiro (research group in the field of wood chemistry), to produce 100 % MMCFs on a laboratory pilot scale from optimized Portuguese *Eucalyptus globulus* dissolving pulps will be discussed, as well as the efforts on the incorporation of functionalities, to meet more demanding technical and performance requirements.

Keywords: dissolving wood pulp, Eucalyptus globulus, lyocell, man-made cellulosic fibers, regenerated fibers

INTRODUCTION

The global need for textiles is forcing the fibers market to grow. In accordance with market reports, each year a new record in fiber production is reached; global fiber production has almost doubled in the last 20 years and it is expected that by 2030 the annual production reaches 149 million tonnes.[1,2] Since more than 60 % of production comprises fossil-based synthetic fibers, the pressure on textile market to become more sustainable and environmentally friendly has increased over the years.[2] In response to these questions, investments have been made in the production of fibers manufactured by cellulose-based and recycled materials. The so-called man-made cellulosic fibers (MMCFs) are synthetic fibers obtained from wood or other plant-based fibers.[3] Having a biological and renewable source, the MMCFs are potentially a more sustainable alternative. However, this would be true when the raw materials come from forests or crops managed in a responsible way.[4]

Portugal has a strong tradition in textile and fashion markets and is also a producer of dissolving wood

pulp (DWP), the raw material for MMCFs. Therefore, the Portuguese economy has both ends of textile value chain, forcing the intermediary process of MMCFs manufacture to be carried out abroad, reducing the sustainability of textile production, since it requires higher fossil fuel consumption due to logistics, and increasing the country´s dependence on foreign economies. To fulfil this economic gap, and in accordance with political initiatives to strengthen the European production chain, Caima, from Altri Group (leading Portuguese eucalyptus pulp producer with high efficiency), together with CeNTI (multi-sectoral oriented technology and innovation centre focused on advanced materials), CITEVE (technological institute providing technical support and services to companies acting in the textile & clothing business), joined with University of Aveiro (experienced research group in the field of wood chemistry) to form a consortium to boost the knowledge of Portuguese industry and scientific community on MMCFs production, thereby further strengthening Portugal's textile wood-based economy.

Caima´s DWP is produced from certified and sustainable forests of *Eucalyptus globulus*, through a magnesium-based acid sulfite method. The combination of raw material and production method gives Caima´s pulp advantages over competing materials, since the type of wood used, hardwood, has a higher cellulose content than softwood, characteristic of northern Europe and America, which increases the yield of the pulping process. The advances achieved by the consortium to produce 100 % MMCFs on a laboratory pilot scale from an optimized *Eucalyptus globulus* Caima´s DWP will be discussed, as well as the efforts to produce functionalized MMCFs by incorporation of additives with antimicrobial, flame-resistance, and phosphor/fluorescent response, on the dissolution step.

EXPERIMENTAL

Pulp

The dissolving wood pulp from *Eucalyptus globulus* was produced by Caima through an acidic sulfite cooking process. The cooking stage was done in discontinuous digesters, under pressure, and with a temperature range between 140 and 145 ºC. The bleaching stages comprised four independent steps using sodium hydroxide, oxygen, hydrogen peroxide, and sulfuric acid, each applied in a specific sequence. The DWP obtained was characterized by the methods described in Table 1.

Table 1. Methods of pulp characterization

Property	Methods
Intrinsic viscosity	ISO 5351:2010
Kappa Index	UNE 57034
Brightness	ISO 2470

Preparation of cellulose/NMMO.H_2O solution

Lyocell dope with 10 % wt of cellulose was prepared on a Sigma kneader mixer machine (1000 mL total volume) containing an oil heating bath (Julabo, CORIO CD-B5) and a vacuum diaphragm pump (VWR, Autovac VP10). In a typical dissolution, DWP (40.2 g) was swelled overnight in water solution NMMO 50 % wt (500 mL) containing propyl gallate (0.5 % wt dry cellulose-based) as a stabilizer. The swelled pulp was manually disaggregated, and the obtained mash was transferred to the kneader mixer preheated to 90 ºC. The mixture was stirred under a vacuum at 90 ºC to remove the water excess until the cellulose dissolution condition was reached (NMMO.H_2O), about 3 h. When the mixture was transparent and uniform, the water content was determined by measuring the refractive index at 60 ºC (Krüss, AR4)[5] and the presence of undissolved particles was evaluated by observation under an optical microscope with polarized light (Leica, DM750), and a magnification of 10 x. The spinning dope (cellulose:NMMO:H_2O 10:78:12 % wt) was considered finished when the water content was around 9-12 % and few or no undissolved cellulose particles were present. The obtained dope was characterized

by its rheological properties using a rheometer (TA Instruments, HR10) with a cone-plate geometry (2º, ϕ 50 mm) at 85 ºC.

Preparation of Lyocell fibers

The cellulosic dope obtained as described above was spun using a dry-jet wet spinning process. The cellulosic dope heated at 90-105 ºC was filtered in a three-layer metal screen (400/200/50 Mesh) and pumped to the spinneret with 100 orifices (each orifice with 100 µm in diameter) by a gear pump with a throughput of 0.6 cc/rev. (Mahr, S-14). Then, it was sprayed out through the spinneret micro-holes, and the dope filaments passed through a 20 mm air gap before entering the pure water coagulation bath kept at room temperature. The cellulosic fibers were washed in water (60 ºC) and dried at 80 ºC.

Preparation of functional fibers

Functional fibers with antimicrobial, flame-retardant, and phosphor/fluorescent properties were prepared by dry-jet wet spinning of modified cellulosic dopes. The functionalized dopes were prepared as previously described, adding specific additives (Table 2) to the pulp/NMMO water solution prior to the swelling step. The spinnability of functionalized dopes was evaluated in a laboratory spinning line (Dienes, LabLine COMPACT SERIES) containing a gear pump (Pomtava, 1610-1-1) with a capacity of 0.05 cc/rev, and spinnerets of 30 orifices (each orifice with 200 µm in diameter). The dope solution at 90 ºC was spun through an air gap of around 20 mm before entering the pure water coagulation bath kept at room temperature. The fibers were washed with pure water overnight at room temperature and air-dried for 2 days. The presence of the functional compounds in the fibers was confirmed by analytical tests or visual analyse as detailed in Table 2.

Table 2. Additives for the functional fibers and method for identification

Property	Compound	Verification method
Antimicrobial	Biopolymer Modified Biopolymer	Acid orange test – the pigment acid orange has an affinity to a specific moiety of biopolymer. The presence of the polymer in fiber improves the removal of acid orange from an aqueous solution. The pigment concentration in the solution is accessed by spectrophotometry[6]
Flamme-retardant	Clay	Thermal analysis – the presence of flame-retardant in materials decreases the T_{onset} and increases the residue mass[7]
Phosphor/fluorescence	Commercial inorganic pigments	Visual analyse under UV light ($\lambda_{max.}$ 365 nm)
Fluorescence	Fluorescent polymer	Visual analyse under UV light ($\lambda_{max.}$ 365 nm)

RESULTS AND DISCUSSION

The production of MMCFs through wet spinning processes requires the use of pulp with a high-quality degree of purity, narrow molecular weight distribution, low degree of aggregation, and high porosity, which is reflected in high accessibility for solvents and reagents. These properties are in DWP, that differs from common paper pulps due to their high cellulose content (90-96 % wt) and low concentration of hemicellulose, lignin, and other extractives. These characteristics are determined by the conditions used in cooking and bleaching stages, which were optimized by Caima, resulting in an adequate Lyocell´s DWP with the properties shown in Table 3.

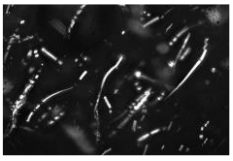
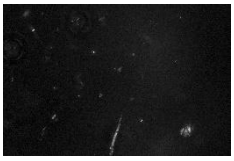
Table 3. Properties of DWP for Lyocell process

Property	Index
Viscosity (mL/g)	400-600

Kappa Number	< 1.0
Brightness (%)	> 91.0

The optimized Caima´s DWP was dissolved in NMMO to obtain the spinning dopes. The influence of the temperature gradient controlled by a heating bath on cellulose dissolution was evaluated, and the dope characterization results are displayed in Table 4. The increasing of heating bath temperature decreased the time needed to completely dissolve the pulp and the number of insoluble cellulose particles indicating that the heating bath temperature of 150 ºC is more adequate to prepare the dope. The water content and rheological properties of dope prepared at this temperature were in accordance with the desired values, 9-12 % of water and zero shear viscosity around 3000 Pa.s.

Table 4. Influence of temperature on Lyocell´s dope properties

Parameters	Heating bath temperature (ºC)		
	120	140	150
Time for complete dissolution (h)	6.05	3.33	3.28
Water content (% wt)	10.31 ± 0.04	10.19 ± 0.60	10.81 ± 0.04
Presence of undissolved particles			
Zero shear viscosity @ 85 ºC (Pa.s)	2985.35	4603.01	4545.89

The Lyocell´s dope was spun into fibers using a dry-jet wet spinning approach confirming that Caima´s DWP is suitable for the Lyocell process and allowed the production of the first 100 % Portuguese Lyocell fibers (Figure 1).

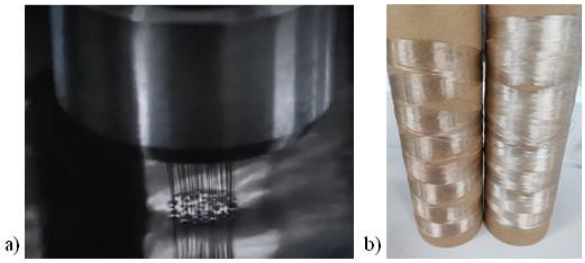


Figure 1. Dry-jet wet spinning of Caima´s DWP: a) detail of the filaments being formed in the spinneret; b) first 100 % Portuguese Lyocell´s fibers.

The spinning process displayed some instabilities mainly due to the presence of air bubbles inside the dope. This drawback has limited the increase of the draw ratio (speed ratio between the spinning and take-up) resulting in fibers with high title. The degassing process and the spinning parameters will be optimized in the future to obtain fibers with a title of 1.5-1.7 dtex.

Biopolymer, clay, and phosphor/fluorescent pigments were, separately, incorporated in Lyocell dope with the objective of obtaining fibers with antimicrobial, flame-resistance, and phosphor/fluorescent response, respectively. In this first approach, the technical performance of fibers was not tested, being evaluated the compatibility between the additive and the dope, the dope spinnability, and the confirmation of additive presence in fiber, as summarized in Table 5.

Table 5. Evaluation of additives incorporation into dope and fibers

Property	Antimicrobial		Flame-resistance			Phosphor/fluorescence	
Compound	Biopolymer	Modified biopolymer		Clay		Commercial pigment	Fluorescent polymer
Concentration (% wt) [(a)]	5	5	5	10	15	1-5	0.1-1
Compatibility with the dope	Yes	Yes	Yes	Yes	No[(b)]	Yes	No[(b)]
Lab spinnability	No[(c)]	Yes	Yes	Yes	-	Yes	-
Additive presence in fibers	Yes	Yes	No[(c)]	Yes	-	Yes	-

(a) Concentration based on dry cellulose weight.
(b) Heterogeneous dispersion.
(c) The thermogravimetric curve did not display variation in T_{onset} and residue mass to confirm the presence of the clay.

To achieve the antimicrobial property, it was used a biopolymer that showed a good dispersion in the dope. However, the dope could only be spun into fibers when the biopolymer was modified to avoid the spinneret blocking. The presence of modified biopolymer in fibers was evaluated by acid orange test. The absorbance of the pigment solution, after 90 min. in contact with a 100 % cellulosic Lyocell fiber and a 5 % additivated cellulosic fiber, was 1.50 and 0.27, respectively, confirming the presence of modified biopolymer in the second set of fibers. Pictures of the fibers used in the acid orange test [6] are presented in Figure 2, showing that the fibers containing modified biopolymer have a stronger orange colour due to the preferential interaction of the additive with the dye.

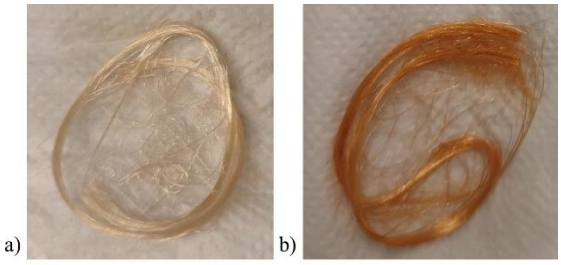


Figure 2. Lyocell fibers after 90 min in contact with acid orange water solution: a) 100 % cellulosic fiber, and b) 5 % antimicrobial additivated cellulosic fiber.

The flame-resistance additive (clay) was homogeneously dispersed in the Lyocell dope only in a concentration ≤ 10 % wt, as depicted in Figure 3. When a 15 % wt of additive was added to the dope, a completely heterogeneous mixture was obtained being considered unsuitable for the spinning process. In Table 6, the parameters of thermogravimetric curve of 100 % cellulosic fibers are compared with that of clay functionalized fibers. The lowering of decomposition temperature and increasing of residual mass, a typical behaviour of flame-resistance functionalization, was only observed for fibers containing 10 % of additive. These results confirm the incorporation of additive into the fibers and indicate that the effect of 5 % is out of the technique sensibility.

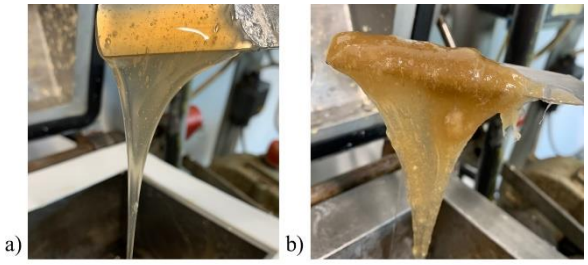


Figure 3. Addition of clay into Lyocell´s dope: a) homogeneous dispersion of 10 % wt additive; b) heterogeneous dispersion of 15 % wt additive.

Table 6. Thermogravimetry curve parameters for clay functionalized fibers

Parameters[(a)]	Cellulosic fiber		
	100 %	5 % Clay	10 % Clay
T_{onset} (ºC)	309.7	309.6	299.0
Residual mass content (%)	0.44	2.87	13.71

(a) Thermogravimetric curves obtained in the temperature range of 20-700 ºC , increased with a speed of 20 ºC/min under air atmosphere.

Commercial inorganic pigments with phosphoresce and fluorescence properties could be homogeneously incorporated in cellulosic dopes with the concentration range of 1 to 5 % wt. The spinnability of functionalized fibers was confirmed when the pigment particle size was smaller than the spinneret orifices. The incorporation of pigments on fibers was confirmed by visual analyse under UV light as depicted in Figure 4 and did not change the colour of fibers under white light (Figure 4a & c).

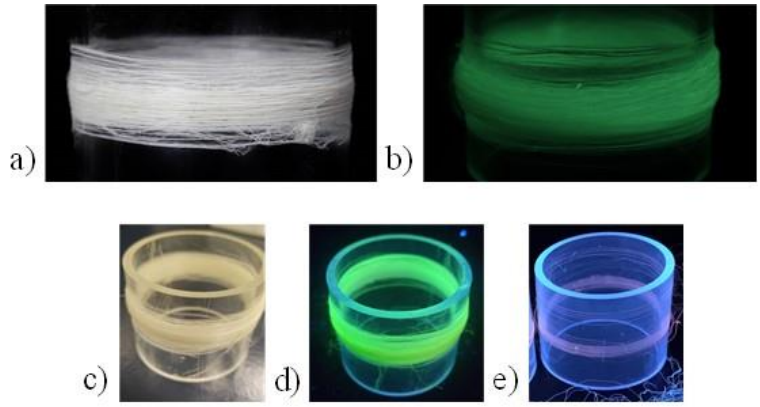


Figure 4. Phosphorescent fibers: a) under white light, and b) under UV light. Fluorescent fibers: c) under white light; d) under UV light showing green emission; and e) under UV light showing orange emission.

A fluorescent polymer was tested as an organic pigment. For the incorporation into the dope, the polymer was solubilized in THF and added as a solution to the dope before water distillation as proposed in the literature.[8] When in contact with NMMO water solution, the polymer precipitated and resulted in a heterogenous dispersion, indicating that it was not possible to functionalize the dope with this organic fluorescent pigment.

CONCLUSIONS

The set of results presented shows that the optimizations carried out by Caima in its production process,

allowed obtaining a dissolving *Eucalyptus globulus* pulp suitable to produce MMCFs through Lyocell process, as well as obtaining functionalized fibers potentially suitable for technical applications.

In addition to the technical results, it is worth highlighting the importance of the partnership between industrial companies and scientific and technological system entities, as research centres and universities such the one presented here. The union of efforts of these entities drives the development and transfer of knowledge and strengthens the local economy of the country.

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