Dissolving Pulp From Eucalyptus Sawdust For Regenerated Cellulose Products

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Abstract

This study assesses the possibility of obtaining regenerated cellulose products (beads and films) from eucalyptus sawdust dissolving pulps produced by non-conventional processes, compared with a commercial dissolving pulp as a reference. Eucalyptus sawdust dissolving pulps were obtained by soda pulping followed by two different TCF sequential bleaching processes OOpZ and OOp (where O is oxygen, Op is oxygen reinforced with hydrogen peroxide, and Z is ozone), followed by a cold soda extraction. The characterization of dissolving pulps involved alpha-, beta- and gamma-cellulose content, alkali solubility with 10 wt% (S₁₀), and 18 wt% NaOH (S₁₈) aqueous solutions, and degree of polymerization. Fock's method was used to measure cellulose reactivity and the alkali solubility in a 9 wt% NaOH aqueous solution at -5 °C to evaluate the pulps dissolving capacity. Dissolving pulps presented high cellulose content (> 93 %, expressed as α-cellulose) and good reactivity (almost 84 %). The dissolving pulps were adequate raw materials for regenerated cellulose products (beads and films) from two cellulose dissolution methods: direct dissolution in NaOH/urea and cellulose carbamate solution. The sequence OOpE (where E is an alkaline extraction) was determined to be a more economically feasible and straightforward process to produce dissolving pulp than OOpZE. The experimental pulps showed the expected characteristics of the dissolving pulp to obtain regenerated cellulose products. However, it is necessary to deepen the study of producing regenerated cellulose films with enhanced mechanical properties from experimental dissolving pulps, solvents, coagulation, and regeneration conditions.

Introduction

The pulp and paper industry is going through a transition to developing new products and markets to improve its competitiveness. The main strength of this industry is its capacity to produce high-value products along with conventional products from lignocellulosic biomass.

Cellulose and its derivatives are potential alternatives to petroleum-based polymers for flexible and rigid packaging, composites, and films, among others. The most critical segment in cellulose processing corresponds to regenerated cellulose products, primarily fibers (rayon), films, membranes, and sponges. These derivatives are obtained from the dissolving grade pulps (Gindl and Keckes 2005; Yousefi et al. 2011; Ghaderi et al. 2014). Yield, residual lignin content, brightness, and strength properties are the main characteristics of papermaking chemical pulp grade (unbleached and bleached). The most relevant requirements when it comes to dissolving pulp are high content of α-cellulose (90–99 %), low content of non-cellulosic compounds (lignin, hemicelluloses, extractives, and ash), good reactivity to derivatizing chemicals, and specified cellulose molar mass and its distribution (Gavrilescu 2013). The use of raw material with relatively low hemicellulose content, such as eucalyptus, is ideal as it produces dissolving pulp with a significantly low xylans content and high yield. Currently, the primary efforts in dissolving pulp production are focused on selective removal of hemicelluloses and increasing reactivity (Kumar and Christopher 2017).

Conventional dissolving pulp is obtained from cotton linter or wood by soda, kraft, or sulfite pulping. The main advantage of lignocellulosic waste (i.e., bagasse, straw, sawdust, others) as raw material instead of cotton linter or commercial wood pulp is the decrease in water and (or) land use.

However, industrial products from lignocellulosic wastes can only compete with those obtained from conventional raw materials, such as petroleum, if they are optimally exploited. This trend catalyzed the development of novel and integrated processes based on biorefinery concepts.

Dissolving pulps require low hemicelluloses, lignin, and extractives contents, so their production in biorefineries has considerable potential (Kumar and Christopher 2017). Traditional pulp mills can be biorefinery platforms due to the

raw materials characteristics, infrastructure, processes know-how, and sustainability (renewable feedstock, integrated production, as well as heat and power generation) (Popa 2013).

Dissolving pulp is mainly used to produce viscose, but it is also a raw material for other cellulose derivatives, such as cellulose acetate, cellophane, carboxymethyl cellulose, and other high-value-added cellulose products (Chen et al. 2019). In the last years, regenerated cellulose production caused a significant growth of the dissolving pulps market (Sixta et al. 2013). Between 2016 and 2017, the global production of dissolving pulp was 8 million tons, approximately (Kumar and Christopher 2017; Chen et al. 2019). Its price is affected by the price of bleached chemical pulp, which usually is 150–300 USD more expensive than bleached chemical pulp. The United States, Canada, Brazil, and Europe produce around 60 % of global dissolving pulp production from wood (Chen et al. 2019). Currently, Asia–Pacific regions are the principal producers of viscose (80 % of the global production) due to lower labor costs and softer environmental regulations compared to Europe and the United States. Within the region, China is the largest global producer of viscose (62 % of the total), and it also imports other regenerated cellulosic fibers such as Lyocell and modal. Overcoming the cost and environmental burden of the transportation of dissolving pulps from wood sources could enhance the development of the local textile industry in various regions (Rana et al. 2014).

The challenges of dissolving cellulose demand improved processes and technology to overcome the limitations for larger-scale use and application of cellulose-based green products. The supramolecular structure of cellulose causes it to be insoluble in most common organic solvents. The dissolution of cellulose involves the disruption of a strong hydrogen bonding network, both inter- and intramolecular and different dissolution alternatives exist. While direct cellulose dissolution using non-derivatizing solvents breaks the hydrogen bonds and avoids their re-conformation, derivatizing solvents modify the –OH groups, thus avoiding the hydrogen bonding formation.

The viscose process is the most used to dissolve and mold cellulose. In this process, the cellulosic pulp is treated with CS₂ to obtain cellulose xanthate - a metastable intermediate - solubilized in dilute aqueous alkali to form the viscose solution. For the molded products, the substituents are removed from the viscose solution, and then regenerated into highly pure cellulose. This process is highly efficient and fully known but it poses great environmental concerns. The use of CS₂ causes sulfur products to be released during the cellulose regeneration, creating contamination at both atmospheric and aqueous levels, which are very expensive and difficult to remove (Vo et al. 2010; Chen et al. 2016). These economic and environmental reasons have driven the manufacturers of regenerated cellulose products to continuously search for alternative manufacturing practices more environmentally friendly processes (Liu et al. 2016). NaOH and urea mixtures at low temperatures have been heavily investigated in the last years, showing improved performance than in the case of dissolving cellulose using pure NaOH. This process causes the fast dissolution of native cellulose with the additional advantage of alkali recovery, avoiding contaminants generation (Chen et al. 2016; Liu et al. 2016).

The conventional cellulose dissolution method involves the following stages: (i) cellulose activation, (ii) formation of intermediates, (iii) processing and shaping, and (iv) regeneration (Gericke et al. 2013). The most commonly used solvents for the direct dissolution of cellulose are LiCl/DMAc, NMMO, NaOH, and BmimCl (Gindl and Keckes 2005; Shibata et al. 2013). However, not all of these apply to industrial scales due to their low dissolution rates, toxicity, and inability to be recycled.

Cellulose carbamate is a cellulose derivative produced by the reaction of cellulose with urea (CO(NH₂)₂). The cellulose carbamate process is an environmentally friendly alternative to the viscose processes with great potential. However, its industrial application is at an early stage and it requires more research and technological developments (Pinnow et al. 2008; Zhang et al. 2019). Obtaining regenerated cellulose through the carbamate process involves several steps: (i)

cellulose and urea react at high temperatures to form cellulose carbamate, (ii) cellulose carbamate is dissolved in NaOH solution, and (iii) the products are formed in a regenerating bath using diluted sulfuric acid and sodium sulfate as co-solvent media. The preparation of cellulose carbamate solution is the more critical stage of this process (Fu et al. 2014c) due to required conditions in the synthesis step (catalyst, solvents, reaction time, and temperature).

In this study, we assess the possibility of obtaining regenerated cellulose products (beads and films) from eucalyptus sawdust dissolving pulps (EPs) produced by non-conventional processes. The performance of the products was compared with a commercially available dissolving pulp. EPs were obtained by soda pulping followed by a sequential oxidative treatment (oxygen and ozone), followed by alkaline extraction. Beads and films were produced prepared by coagulating and regenerating processes. Beads were characterized by average diameter and porosity, and films by tensile strength.

Materials And Methods

2.1 Materials

Eucalyptus sp. sawdust was collected from a local sawmill carpentry (Misiones, Argentina). Commercial dissolving eucalyptus pulp (CP) Solucell® provided by Bahia Specialty Cellulose S.A. (Camacari, Brazil).

2.2 Eucalyptus sawdust dissolving pulp production

The chemical characterization of eucalyptus sawdust was performed and reported in previous work (Rangel et al. 2016). Briefly, the chemical composition was 41.8 % of glucans, 10.7 % of xylans, 0.38 % of arabinans, 1.41 % of acetyl groups, 31.3 % of lignin, 7.86 % of extractives, and 0.59 % of ashes; % based on oven-dry sawdust.

2.3 Pulps characterization

The characterization of the pulps involved the following analytical techniques: alpha-, beta-, and gamma-cellulose content (TAPPI T203 cm-99); alkali solubility with 10 wt% and 18 wt% NaOH aqueous solutions, called S₁₀ and S₁₈ respectively (TAPPI T235 cm-00); and intrinsic viscosity and viscosimetric average degree of polymerization (DP_V) in cupriethylenediamine (CUEN) (Marx-Figini 1987). Fock's method was used to measure the cellulose reactivity (Fock 1959), and the solubility in alkali allowed to determine the soluble material of pulp in 9 wt% NaOH at -5°C (Rahkamo et al. 1998).

2.4 Mechanical and enzymatic pretreatment of the dissolving pulps

The refining mechanical pretreatment was carried out in a PFI mill under standard conditions (T 248 sp-00) with 6,000 rpm. Subsequently, the enzymatic treatment was carried out with a cellulase preparation (Celluclast 1.5L – Novozymes A/S Denmark), at 5 % consistency, 9 % enzyme dosage on dry fiber, at 40 °C and pH 5.4 for 60 min.

2.5 Direct dissolution of cellulose in NaOH/Urea

The direct dissolution of mechanical and enzymatically treated pulp was carried out in a cryo-bath at -5°C, in a mixture of 7 wt% NaOH and 12 wt% urea, under constant agitation for 30 minutes. Then the solution was centrifuged for 15 minutes at 12,000 rpm to remove the undissolved cellulose. The undissolved material was neutralized with 3 % H₂SO₄ and washed with abundant distilled water. Finally, it was filtered using a porous glass filter and dried at 105°C for 24 hours to quantify the dry residue. The cellulose solution was stored at low temperatures in closed containers. The processing steps and conditions used for direct dissolution are shown in Fig. 2.

Solubility was determined as the dissolved cellulose weight (the difference between the initial weight and the undissolved residue) concerning the initial weight of cellulose.

2.6 Production of cellulose carbamate (CC) solution

The cellulose carbamate was prepared from dissolving pulp suspension (4 % consistency) by activation and impregnation treatments with 6 wt/v% NaOH and 30 w/v% urea solution at 25°C under continuous stirring for 120 minutes. Then, the excess solution was removed by pressing to an impregnated cellulose/pulp ratio of 4.25:1. The impregnated cellulose was disintegrated and dried in an oven at 60°C for 20 hours. The cellulose esterification reaction of the dried mixture was carried out by heating in a microwave oven at 160 W for 15 minutes. After the reaction, the CC was washed with abundant water until neutrality, separated from the by-products (urea and residual alkali), dried at 60°C, and ground in a Wiley mill to a particle size of approximately 40 mesh.

The nitrogen content (N%) was determined by CHONS organic elemental content analysis of powered CC by dry combustion based on the Dumas principle using a CHONS Elemental Analyzer (LECO® CHN628). The degree of substitution (DS) of cellulose carbamate was calculated from its nitrogen content as described elsewhere (Klemm et al. 1998), corresponding to the number of carbamate groups for each anhydroglucose unit (UAG). The intrinsic viscosity and viscosimetric average degree of polymerization (DP_v) in cupriethylenediamine were determined following the method described by Marx-Figini (Marx-Figini 1987).

The CC solution was prepared by dissolving the ground CC in 8 wt/v% NaOH and 0.6 wt/v% ZnO solution at 0°C under stirring at 800 rpm for 15 minutes. The CC solution was centrifuged at 9,000 rpm at 0°C for 15 minutes. The undissolved material was neutralized with 3 % H_2SO_4 and washed with abundant distilled water. Finally, it was filtered using a porous glass filter and dried at 105°C for 24 hours to quantify the dry residue. The cellulose solution was stored at low temperatures in a closed container.

CC solubility was determined as the dissolved cellulose weight (the difference between the initial weight and the undissolved residue) concerning the initial weight of cellulose carbamate. The processing scheme and conditions used to obtain CC are shown in Fig. 3.

2.7 Regenerated cellulose beads preparation

Cellulose solutions were taken and extruded through a syringe pump with a flow rate of 30 mL/h. The cellulose beads were prepared by coagulating and regenerating in a mixture of 5 % H_2SO_4 and 5 % anhydrous Na_2SO_4 . Coagulated beads were washed and stored in a refrigerator for further use. The average size and shape of the beads were assessed from images of beads dried on tissue paper (wet weight). Then they were dried in an oven at 105 °C overnight (dry weight). The particle diameter was measured from optical microphotographs, calculating the mean, standard deviation, and coefficient of variation. Total porosity was calculated from the wet and dry weights of the beads, using 1.5 g/cm^3 for bulk cellulose (Ettenauer et al. 2011).

2.8 Cellulose regenerated films preparation and characterization

The cellulose solution was spread over a glass plate in the form of a gel sheet with a thickness of approximately 0.04 mm, and then immediately immersed in a coagulating and regenerating bath (5 % H_2SO_4 and 5 % anhydrous Na_2SO_4) for 10 minutes. The films were washed and stored in a refrigerator for further use.

The tensile strength (σ) and elongation at break (ϵ) of the films conditioned at 23°C and 50 % relative humidity were measured with a universal testing machine (INSTRON 3344) according to ISO 527-3 at a speed of 2 mm/min.

Results And Discussion

3.1 Eucalyptus sawdust dissolving pulp production

The yields, kappa number, and viscosity obtained in the sequential treatment of the eucalyptus sawdust by soda pulping and OOp bleaching stage are presented in Table 1.

Table 1
Yields, kappa number, and viscosity in the different stages to obtain experimental OOp eucalyptus sawdust pulps.

Stage	Yield (%)	Kappa number	Viscosity (mL/g)
Soda pulping	49.0	29.9	n.d.
O	95.6	13.1	761
Op	97.1	8.20	552
n.d. = not determined; O = oxygen and Op = oxygen reinforced with hydrogen peroxide			

Both sequential treatments (soda pulping + TCF bleaching) applied to the eucalyptus sawdust followed by an alkaline extraction produced the required purity of cellulose to be considered a dissolving pulp (low hemicelluloses content (< 6%), and lignin and other impurities traces) (Sixta 2006). In the OOpE sequence, the OOp pulp contained 18.8 % of xylans, 0.3 % of residual lignin, and 1.1 % of ash, expressed as dry pulp base. The kappa number of the OOp pulp was 8.2, and the corrected Kappa number was 2.3 (on free hexenuronic acids pulp). The viscosity of the OOpE pulp was determined at 487 mL/g. In the OOpZE sequence, the Z bleaching stage (yield: 98.0 %) allowed to extract 12.2 % of residual lignin (kappa 7.9), and the viscosity of the OOpZE pulp was 509 mL/g. Both E stages allowed the hemicelluloses extraction with yields of 84.9 % and 85.4 % for EP-1 y EP-2, respectively.

3.2 Chemical characterization of the dissolving pulps

The chemical characterization of the commercial pulp (CP) and the eucalyptus sawdust pulps (EP-1 and EP-2) are shown in Table 2. The α -cellulose content represents the cellulose purity degree. The α -cellulose is the non-degraded fraction of the pulp with a high degree of polymerization, which is resistant to the sequential extraction by the 17.5 wt% NaOH and 9.45 wt% NaOH solutions. The β -cellulose is the soluble fraction with a low degree of polymerization, which can be re-precipitated by acidification. Finally, γ -cellulose is the remaining material in the solution, consisting mainly of hemicelluloses. CP and EP pulps have high and similar cellulose content, high cellulose molecular weight (expressed as α -cellulose), and low β -cellulose and γ -cellulose contents.

Dissolving pulps are classified in different grades by their intrinsic viscosity. The intrinsic viscosity of CP and EP pulps is in the range of 250 and 600 mL/g, allowing its use for most applications (Manhaes and Ferreira Lima 2001). NaOH solutions extract low molecular weight carbohydrates, degraded cellulose, and hemicelluloses (S_{10} y S_{18}). Solubility values of both CP and EP pulps are within the specified range for the different dissolving pulps grades. S_{18} also indicates the purity degree -the lower S_{18} , the higher the purity of the pulp- while a higher S_{18} value is detrimental to derivatization yield and derivatives quality. Typical S_{18} ranges between 4 and 2 % for cellophane, rayon, and other derivatives such as acetates. Table 2 shows low S_{10} and S_{18} values for both pulps, even though EP-2 pulp showed higher values due to its higher γ -cellulose content (mainly hemicelluloses).

Table 2
Chemical characteristics of the dissolving pulps from eucalyptus sawdust and commercial pulps

Dissolving pulp	S ₁₀ (%)	S ₁₈ (%)	α -cellulose (%)	β -cellulose (%)	γ -cellulose (%)	DPv	Intrinsic viscosity (mL/g)	Fock' Reactivity (%)	NaOH 9% solubility (%)
EP-1	2.8	2.3	96.7	3.0	0.3	1385	559	69.4	18.9
EP-2	8.6	4.3	93.7	1.6	4.7	1156	487	83.9	20.9
CP	6.4	2.9	95.3	3.8	1.0	993	428	68.4	34.2
EP: eucalyptus sawdust pulps, CP: commercial pulp									

The solubility in alkali allows to determine the soluble material in 9 wt% NaOH at -5°C and to evaluate the incidence of the pretreatments on the pulp accessibility (Rahkamo et al. 1998). Using the Fock test allows determining the reactivity of dissolving pulp for the viscose process. The results are expressed as a percentage of regenerated cellulose yield (Fock 1959). Considering the pulps chemical characteristics in Table 2, EP-1 and CP showed similar reactivity (about 69 % of Fock's reactivity). Solubility was higher in the commercial pulp, but EP-2 pulp presented the highest Fock's reactivity (83.9 %), probably due to its higher γ -cellulose content (highly reactive hemicelluloses fraction).

3.3 Mechanical and enzymatic pretreatments

The mechanical and enzymatic pretreatments applied to the dissolving pulp improve the accessibility and, consequently, the reactivity of these pulps (Table 2). Additionally, the DPv was reduced to values lower than 700 (about 200–300 mL/g of intrinsic viscosity) which has been shown to facilitate the solubility of cellulose in a simple solvent system (Lue and Zhang 2010). In general, pulps with lower DPv values present a higher cellulose dissolution (Isogai and Atalla 1998; Zhou et al. 2002; Wang et al. 2006, 2008; Wang 2008). The mechanical and enzymatic sequential pretreatment showed a favorable decrease in the degree of polymerization of the pulps, 50 % for EP-1, 58 % for EP-2, and 35 % for CP (Table 3).

Table 3
Degree polymerization and viscosity of pretreated dissolving pulps.

	EP-1	EP-2	CP
Degree polymerization (DPv)	690	481	635
Intrinsic viscosity (mL/g)	290	202	267

3.4 Direct dissolution of cellulose (DD)

Using NaOH/urea as a direct solvent, a high cellulose amount from all dissolving pulps (> 70 %) was effectively dissolved. EP-1 and EP-2 reached a solubility of 74 % and 75 % for EP-1 and EP-2, respectively, and 80 % for CP. The commercial pulp achieved the highest solubility with an intermediate viscosity value (consider that the intrinsic viscosity is an average molar mass distribution of the dissolved polysaccharides in the solvent). The OOp and OOpZ bleaching steps generate pulps with different chemical and physical characteristics, reflected in their behavior in the DD treatment. As mentioned, CP presented the highest soluble material amount in 9 wt% NaOH at -5°C, which shows high accessibility of CP attributable to the production process (Rahkamo et al. 1998). The molar mass distribution curves obtained by size-exclusion chromatography (SEC) before and after the combined treatment could clarify EP-1 and EP-2 behavior in the direct dissolution of cellulose.

3.5 Production of cellulose carbamate (CC) and its dissolution

As well reported in the literature, the introduction of carbamate groups on the cellulose backbones leads to an increase in its solubility (Fu et al. 2015). Previous reports revealed that a high degree of substitution ($DS \geq 0.25$, $N\% \geq 2\%$) is beneficial for the dissolution of CC in NaOH solution. However, Fu *et al.* found that CCs with $N\%$ as low as 0.5 % can be well dissolved in NaOH solution by adding a small amount of ZnO (0.4 – 2.0 wt%) (Fu et al. 2015). In our study, cellulose carbamate (CC) was obtained from experimental and commercial dissolving pulps by activation and impregnation with NaOH/urea, based on previous studies (Lanieri 2017). The cellulose esterification reaction was carried out by microwave heating at 160 W for 15 min. Table 4 shows that the commercial pulp has the highest N content ($DS = 0.2$), whereas that of the EP pulps is similar ($DS = 0.17$).

The CC dissolution was carried out in NaOH: ZnO aqueous solution (ratio 8:0.6 wt/v%) at a relatively low temperature (0°C). The solubility of cellulose carbamates from EP-2 and CP were similar and higher (73 % and 74 %, respectively) than that of EP-1 (63 %). However, the low levels of solubility achieved lead to regenerated products with low cellulose content. An optimization of solubility and CC dissolution temperature is planned for future work.

Table 4
Viscosity, degree of polymerization, $N\%$, and degree of substitution of cellulose carbamate (CC).

	EP-1	EP-2	CP
Viscosity (mL/g)	272	202	201
DPv	647	481	477
$N\%$	1.39	1.44	1.62
DS	0.17	0.17	0.20

3.6 Regenerated cellulose products

Regenerated products were prepared by direct dissolution (DD) with NaOH/Urea and cellulose carbamate (CC). The cellulose derivative intrinsic viscosity is a critical parameter of this process, the average DP of the cellulose will have a direct impact on the final mechanical properties of the regenerated cellulose product. According to the literature, it is well known that lower DP values produce a higher dissolution rate of cellulose (Isogai and Atalla 1998; Zhou et al. 2002; Wang 2008). As an example, the viscose process requires intrinsic viscosity values of cellulose between 200–300 mL/g. These values are in the range of intrinsic viscosity of the mechanically and enzymatically pretreated pulps (Table 3) in the case of both DD and CC methods (Table 4), Another study reported intrinsic viscosity values of CC between 100–150 mL/g with 1–2 $N\%$ ($DS = 0.11–0.25$) to produce regenerated cellulose products (Fu et al. 2014a, b).

3.6.1 Regenerated cellulose beads

Table 5 shows the average diameters and porosity of the beads obtained (Fig. 4) by the drip technique (4.0 % cellulose solution). CC bead diameters were slightly higher (2.53–2.78 mm) than DD beads (2.47–2.73 mm). Both methods produced CP beads with similar diameters and porosity. However, the porosity and diameters of EP-1 and EP-2 beads varied depending on the dissolution method. CC beads from CP, EP-1, and EP-2 presented similar porosity.

The coefficients of variation for the diameters of the beads were below 10 %, indicating that the diameters distribution of the cellulose beads was homogeneous in both cases.

Table 5
Characterization of cellulose beads obtained from eucalyptus sawdust and commercial dissolved pulps

Dissolution method	Beads	Diameter (mm) ^a			CV (%) ^b	Total porosity (%) ^c
NaOH/Urea (DD)	EP-1	2.47	±	0.04	5.87	90
	EP-2	2.59	±	0.04	7.01	95
	CP	2.73	±	0.03	5.57	94
Cellulose carbamate (CC)	EP-1	2.53	±	0.02	3.90	92
	EP-2	2.78	±	0.03	4.38	91
	CP	2.77	±	0.02	3.87	93

EP: Eucalyptus sawdust pulps, CP: commercial pulp ^a average value plus-minus the confidence interval. ^b coefficient of percentage variation. ^c relationship between the volume of water contained in the beads and the total volume.

3.6.2 Regenerated cellulose films

The aspect feature of regenerated cellulose films from the cellulose carbamate method (CC) and direct dissolution method (DD) is showed in Fig. 5.

The stress (σ) - strain (ϵ) curves of the regenerated cellulose films from direct dissolution and cellulose carbamate dissolution from experimental and commercial pulps conditioned at 23 °C and 50 % relative humidity are shown in Fig. 6.

The different dissolution methods have a clear impact on the mechanical performance of the films as observed in the stress-strain curves (Fig. 6). The tensile behavior of cellulose regenerated films obtained from EP-1 and CP pulps by DD were similar, with maximums of 35.7 and 48.5 MPa, respectively (Fig. 6.a). On the other hand, regenerated cellulose films from EP-2 showed lower tensile strength with a maximum of 21.2 MPa and elongation capacity similar to the commercial pulp. These differences in DD films could be explained by the lower solubility achieved by the experimental pulp when compared to the commercial pulp.

Films produced using the CC solution from EP-2 and CP pulps showed similar tensile strength, reaching maximums values of 41.3 and 40.4 MPa, respectively. On the other hand, the maximum tension value of the film prepared with EP-1 was 28.2 MPa (Fig. 6.b). The elongation capacity was approximately 10 % higher for EP-2 (2.5 %) and CP (2.6 %) compared to EP-1 (2.3 %).

The properties of the regenerated products are related to the cellulose solubility (% dissolved) and DP of the sample. The films from CP, with the highest solubility and intermediate DP, presented the highest tensile strength. Intrinsic viscosity and DP determined by viscometry are average values of the dissolved cellulose sample.

On the other hand, CC samples reached relatively lower solubility values under the conditions of this study. The results obtained in this study indicated that low freezing temperatures are vital to achieving optimal CC dissolution. Fu *et al.* showed that adding a small amount of ZnO (0.4 – 2.0 wt%) significantly improves the solubility of CC in the NaOH solution (Fu et al. 2014c). Furthermore, the solubility of CC rapidly increased as the temperature decreased from – 5°C to – 23°C.

In another study, Fu *et al.* analyzed the structure and properties of regenerated cellulose membranes produced from aqueous CC solution in NaOH/ZnO by coagulation in dilute sulfuric acid (Fu et al. 2014a). CC was obtained from cotton linters dissolving pulps with the content of α -cellulose of 93 % by impregnation in urea solution and heating with microwaves at 425 W for 15 min. They obtained two cellulose carbamate samples with different N content (1.22 and 1.04 N%) and DP (540 and 400). The membranes coagulated in a 3 wt% H₂SO₄ solution at 10°C for 10–15 min exhibited good tensile strength and elongation at break (120 MPa and 15 % respectively). Fu *et al.* showed that both the coagulant concentration and the temperature influence their strength properties (Fu et al. 2014a).

While we still need to optimize the dissolution conditions in the mixing stage of simple solvents (NaOH/urea with or without ZnO addition) as well as in the derivatization stage to cellulose carbamate with subsequent dissolution in NaOH/ZnO solution, overall, our eucalyptus sawdust bleached dissolving pulps (EP-2) obtained by soda pulping and two different short TCF sequences (OOp) followed by a cold soda extraction steps showed the desired characteristics of purity, α -cellulose, intrinsic viscosity, reactivity, and solubility of dissolving pulps to obtain regenerated cellulose products.

Conclusions

This study showed the feasibility of using sawdust as a source of high-quality dissolving pulps as evidenced by the experimental values of purity, α -cellulose, intrinsic viscosity, reactivity, and solubility. Eucalyptus sawdust bleached dissolving pulps (EP-2) obtained by soda pulping and two different short TCF sequences (OOp) followed by a cold soda extraction produces dissolving pulps and regenerated products by cellulose carbamate dissolution with quality comparable to a commercial one.

Both experimental dissolving pulps presented high and similar cellulose content and high molecular weights when compared to CP. S₁₀ and S₁₈ values of CP and EP pulps were within the range specified for the different grades of dissolving pulps. Both pulps showed very similar reactivity, being slightly higher in CP. The sequential mechanical and enzymatic pretreatment applied to the pulps favored the decrease of the degree of polymerization.

The direct dissolution method produced a high dissolved cellulose amount from all dissolving pulps studied. The solubility of cellulose carbamate from experimental and commercial pulps was slightly lower than in the direct dissolution method. The solubility of cellulose carbamate from EP-2 was similar to commercial dissolving pulp, whereas EP-1 was lower than both pulps (almost 10 %).

The beads obtained with the commercial pulp had higher average diameters and total porosity than those obtained from the sawdust pulp. The distribution of diameters of the cellulose beads was homogeneous in both cases.

The films obtained by both dissolution methods showed different stress-strain curves.

This study showed that dissolving pulps and regenerated cellulose products (beads and films) can be produced from eucalyptus sawdust by non-conventional processes. The OOpE sequence could be a more economical and straightforward process to produce dissolving pulp than the OOpZE sequence by the cellulose carbamate method. However, if the objective is obtaining regenerated cellulose films from experimental dissolving pulps with high mechanical properties, the solvent, coagulation, and regeneration conditions should be optimized.

Declarations

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Figures

Figure 1

Schematic process to obtain dissolving pulps from eucalyptus sawdust (O: oxygen, Op: oxygen reinforced with hydrogen peroxide, Z: ozone, E: alkaline extraction).

Figure 2

Schematic process used to obtain cellulose solution by direct dissolution of dissolving pulp in NaOH/Urea.

Figure 3

Schematic process used to obtain cellulose solution by cellulose carbamate method.

Cellulose regenerated beds – CC method

Cellulose regenerated beads – DD method

Figure 4

Regenerated cellulose beads from cellulose carbamate method (CC) and direct dissolution method (DD).

Cellulose regenerated products – CC method

Cellulose regenerated products – DD method

Figure 5

Photography of the aspect of regenerated cellulose films from cellulose carbamate method (CC) and direct dissolution method (DD).

Figure 6

Stress-strain curves of the regenerated cellulose films obtained from the eucalyptus sawdust (EP-1 and EP-2) and the commercial (CP) dissolved pulps by (a) direct dissolution method and (b) cellulose carbamate method.