Cellulose acetate films from chemo-enzymatic dissolving pulps

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ABSTRACT

The purpose of this work is to obtain dissolving cellulose fibers that are suitable for the manufacturing of cellulose derivatives. Therefore, the combination of enzymatic and chemical treatments during the bleaching stage (lignin removal) and purification stage (hemicellulose removal) is proposed. The obtained dissolving cellulose was submitted to acetylation reactions, and then acetate films were prepared as an example of end product. Assessing the quality of acetate films, it was concluded that dissolving cellulose fibers had good properties and fulfilled the quality requirements. These satisfactory results were compared with acetate films obtained under same acetylation conditions, but the dissolving cellulose fibers used as a raw material came from a conventional and industrial process.

Keywords: *Dissolving pulp, acetylation, acetate films, endoglucanase*

INTRODUCTION

Dissolving-grade pulp is a highly pure pulp that exhibits high α-cellulose content (over 90%) and low levels of hemicelluloses (<4%), lignin and extractives. Dissolving grade-pulp is used as a raw material to produce a wide range of products such as cellulose nitrate, cellulose ethers, regenerated cellulose, lyocell fibers, among other products.

The biomass source that is found in the nature that has high cellulose content (>90%) is cotton. Unfortunately, cotton production cannot cover the current huge demand of dissolving fibers, and therefore dissolving fibers obtained from wood source are used. Importantly, in the coming years the forecast of dissolving fibers production will be increasing even more. This growth is attributed to different factors: an expanding market for textiles products due to an increasing demand in China and other Asian countries, changes in fashion against oil-based textile materials and environmental concerns related to cotton cultivation since it requires huge quantities of land, water, fertilizers and pesticides.

The present work studied the conversion of unbleached sulfite fibers to biobleached dissolving cellulose fibers by means of chemo-enzymatic treatments. Then, the obtained biobleached dissolving fibers were investigated as far as their suitability to synthesize acetylated cellulose, a kind of specialty cellulose product. Acetylation is a common chemical modification in which acetyl groups (CH_3CO^-) react with the surface hydroxyl groups (-OH) of cellulose, making its surface less hydrophilic. The acetylation process depends on the fiber accessibility and the susceptibility of -OH groups in the crystalline and less crystalline domains of cellulose. This work, therefore, aims at determining if chemo-enzymatic dissolving fibers are suitable for the synthesis of cellulose acetate film via homogeneous acetylation. So, samples obtained by homogeneous acetylation were used to prepare transparent films via solvent casting technique.

EXPERIMENTAL

As starting material, unbleached sulfite pulp was bleached at the laboratory scale with a laccase–violuric acid system and then complemented with a pressurized hydrogen peroxide stage ($L_{VA}PO$) (Quintana et al., 2013). Afterwards, the resulting biobleached fibers, denoted here as *L*, for simplicity, were subjected to a cold caustic extraction treatment *(C)* followed by endoglucanase treatment *(E)* (resulting in fibers that are denoted thereafter as L_{CE}). The purpose of introducing an endoglucanase treatment was to improve fiber reactivity. By its side, cold caustic extraction was a purification stage where hemicelluloses were removed and, as a result, fiber quality was improved (Quintana et al., 2015). Finally, the chemo-enzymatic dissolving fibers were subjected to homogenous acetylation and the samples obtained were used to prepare transparent films via solvent casting (Quintana et al., 2018).

In Figure 1 is shown the experimental plan followed in this study.

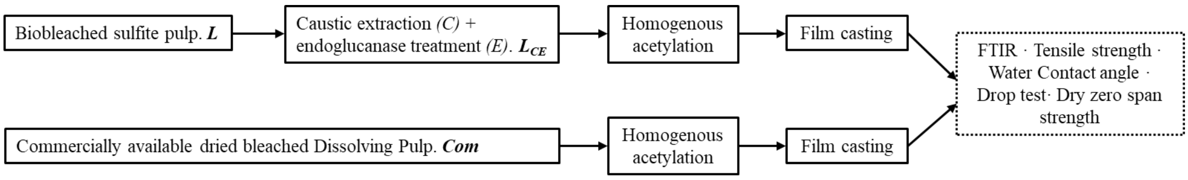

Figure 1. Outline of experimental procedures and samples studied. Bleached commercial dissolving pulps (Com) were used as a reference, and same homogeneous acetylation reactions were performed on such reference fibers.

RESULTS AND DISCUSSION

As shown in Table 1, the chemo-enzymatic treatments applied at the bleaching and purification stages let to obtain dissolving fibers comparable to available conventional commercial dissolving fibers with the advantage that a green technology was applied.

Then, the effect of homogeneous acetylation on the quality of the systems obtained from L_{CE} and *Com* was evaluated (Table 2 and Figure 2).

Table 1. Main characteristics (mean ± SD) of L_{CE} and *Com* reference

	L_{CE}	*Com*	*Dissolving cellulose specifications*
Kappa number	<0.5 ± 0	<0.5	<1
ISO brightness (%)	83.7 ± 1.5	90.3 ± 0.1	>90
Viscosity (mL/g)	447 ± 18	476 ± 1	<500
Fock solubility (%)	71.5 ± 2.3	67.3 ± 2.1	> 67
Hemicellulose (%)	6.3	4.3	<10

FTIR spectroscopy confirmed that acetylation reactions were substantial, as indicated by the fingerprint peak at 1730 cm^{-1}, since native cellulose does not have this functional group (Figure 2). The quantification of the degree of substitution by titration confirmed that the acetylation reaction was successfully achieved and similar acetylation degrees for all studied fibers were found. Values between ~33 and ~36 % of acetyl substituted groups were found (Table 2), indicating a high level of acetylation comparable to commercial available cellulose acetate (from Sigma-Aldrich ~ 39 %). The excellent degree of acetylation (i.e. acetyl group content) displayed by L_{CE} sample was in agreement with the good reactivity data (~72 %). Therefore, it is suggested that the chemo-enzymatic treatment was able to improve the accessibility of hydroxyl groups and as a result greater dissolution behavior of fibers was obtained.

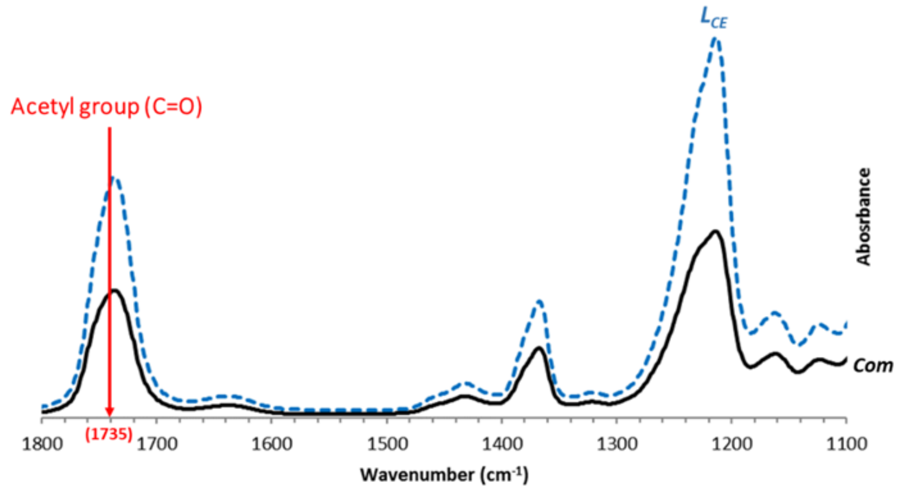

Figure 2 FTIR spectra for acetylated cellulose from L_{CE} and *Com* films

Fibers obtained after acetylation were freeze-dried, then dissolved in acetone and the resulting viscous solution was used to prepare films via solvent casting. As shown in Table 2, despite the fact that a similar acetyl content was measured for all samples, *Com* films presented a tensile strength three times higher than those measured for the samples acetylated after chemo-enzymatic treatment (L_{CE}), this can be explained by the differences in fiber morphology of precursor fibers prior to acetylation. In terms of dry zero-span tensile strength, *Com* and *chemo-enzymatic acetylated fibers* showed values in the same range. As expected, the presence of acetyl groups reduced the hydrophilic character, giving a contact angle between 67º and 76º.

Although high hydrophobicity was not achieved (contact angle <90º), water drops remained long time on the surface until complete absorption as WDT assay showed. Overall, cellulose acetate fibers with new functional groups and high strength-related properties were achieved.

Table 2. Acetyl group % determined by the titration method and dry tensile strength index of films produced by solvent casting of L_{CE} and *Com* samples after homogenous acetylation reaction

	Acetyl groups (%)	Dry tensile strength index (N·m/g)	Dry zero-span tensile strength (kN/cm)	Water drop test (s)	Contact angle (º)
L_{CE}	35.5 ± 3.9	22 ± 11	0.07 ± 0.01	5435 ± 293	67 ± 4
Com	33.3 ± 4.4	67 ± 28	0.05 ± 0.006	5445 ± 507	67 ± 7

CONCLUSIONS

A homogeneous phase acetylation reaction was studied from a commercial dissolving fiber grade (Com) and from a newly introduced fiber obtained by chemo-enzymatic treatment of sulfite fibers (L_{CE}). The enzymatically treated pulps displayed properties comparable to those of commercial dissolving pulps. In particular, they exhibited good solubility in acetone and produced transparent films (via solvent casting) with enhanced dry strength, less hydrophilic character and longtime absorption resistance. From these results, it is concluded that chemo-enzymatic dissolving fibers are suitable to manufacture a particular kind of specialty cellulose product with the advantage that green technologies were used during the upgrading process.

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