

# Thermochemical properties of cellulose acetate blends with acetosolv and sawdust lignin: A comparative study



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## ABSTRACT

Sawdust (SD) and cotton-lignin blends (CLB) were acetylated and the effect of lignin type and content on thermoplastic properties of the acetate produced was studied. The lignin in samples did not significantly affect the degree of acetylation. An increase in acetyl groups of 1–3% was observed in acetylated SD (ASD) unlike acetylated CLB (ACLB). Thermogravimetric analysis showed two thermal degradation zones; one at 190–200 °C and the other at 330–370 °C. The early degradation in ASD corresponds to galactoglucomannans while that in ACLB corresponds to the low-molecular-weight lignin. The second degradation is due to decomposition of cellulose acetate and high-molecular-weight lignin. DSC analysis showed homogeneous behaviour in ASD with only one glass transition temperature ( $T_g$ ) at 170–180 °C, unlike ACLB that showed two  $T_g$ s at 170–180 °C. Sawdust acetylation, taking advantage of its residual lignin, showed higher reactivity and miscibility as compared to the same material produced by adding previously extracted lignin on cotton.

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## 1. Introduction

Cellulose acetate (CA) is a thermoplastic material with diverse applications. Industrially, it is produced from high-purity cellulose, which implies a high production cost [1]. This has led to the study of various lignocellulosic alternatives to reduce the cost of its production. Possible alternatives include the use of wheat straw [2–4], sugarcane bagasse [5,6], Kraft pulp [7] and rice husk [8]. In contrast to currently used raw materials, these are characterised by high content of hemicellulose and residual lignin.

Pine sawdust is a cheap and widely available by-product of forest industry with potential to be acetylated for CA production. It is composed of cellulose (40–44%), hemicellulose (30–32%) and lignin (25–32%). The main hemicelluloses are galactoglucomannans and glucuronoxylans and the predominant lignin is of the guaiacyl type [9]. Although its use in thermoplastics production could increase

its value, it is mainly used for power generation [10,11]. These considerations highlight the need for a study of thermochemical properties of acetylated sawdust components, especially the role of hemicellulose and lignin, which account for about 60% of this raw material.

The role of hemicellulose in cellulose acetylation has been analysed in several studies, and the consensus seems to be that their presence does not significantly influence the degree of acetylation [12,13]. Regarding thermal properties, cellulose shows high compatibility as it presents only one glass transition, characteristic of homogeneous samples [14]. The degradation temperatures are similar, 220–270 °C for non-isolated and 250–290 °C for isolated hemicellulose esters, these being more stable than non-esterified hemicelluloses whose degradation begins in the range 180–210 °C [3,15].

In contrast to hemicellulose, lignin changes its thermochemical properties once isolated. Native lignin possesses a complex amorphous structure and high degree of polymerization [16], resulting in slow degradation at 250–500 °C [17]; glass transition temperatures vary between 100 and 250 °C, depending on the type of lignin [18,19]. Isolated lignin changes its chemical structure and depolymerizes; such decrease in molecular weight causes rapid thermal degradation [20,21]. These characteristics define the thermoplastic behaviour of the materials and influence to the processing and mixing of polymers.

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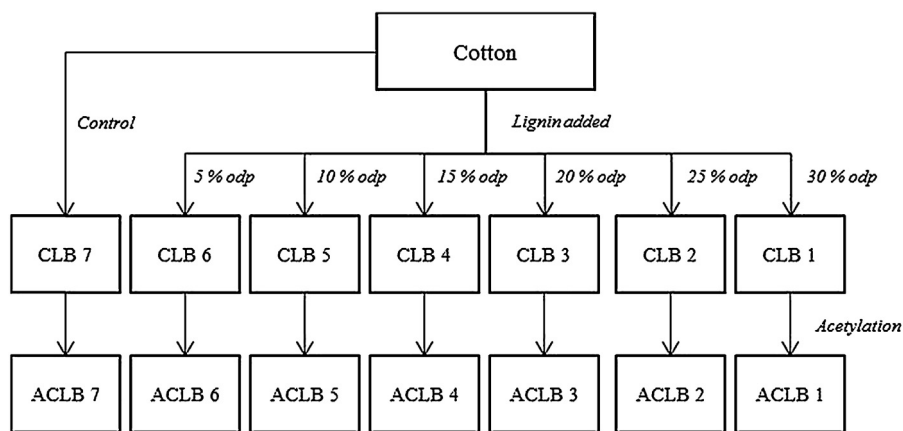


Fig. 1. Summary of treatments carried out on cotton lignin blend (CLB). (\* odp: on dry pulp).

There is very little information on the effect of lignin in CA blends. The majority of published studies deal with their isolation and subsequent esterification for use in different thermoplastic matrices. Thus, for example, Manjarrez et al. [22] showed that lignin, with or without acetylation, improves the mechanical properties, when incorporated into a cellulose triacetate matrix. More recently, Kim et al. [23] studied the blends of esterified lignin with alkyl chains to increase compatibility with polylactic acid (PLA); they reported that the degree of affinity of the components influences the thermal and mechanical properties of the blend. At the same time, Rowell et al. [24] found that the order of reactivity of the wood components in acetylation is lignin > hemicellulose > cellulose, cellulose practically unreactive under the applied conditions; they also demonstrated an ability to being modified and use lignin in different thermoplastic matrices, which not only improves thermal and mechanical properties but provides resistance against biological attacks. In all these studies, lignin should first be isolated and then blended with a thermoplastic matrix. This implies an additional cost that may complicate the application of these products at commercial level. Obtaining a thermoplastic material by acetylation of sawdust without lignin removal and avoiding its modification may thus be an economical alternative for the production of CA-based thermoplastics. If necessary a partial extraction of lignin, the most suitable method from this point of view, would be the use of acetic acid as solvent (Acetosolv method), allowing subsequent acetylation of the ligno-cellulosic material without changing the solvent. Lignin obtained by these extractions could be used directly in processes of acetylation with cellulose. Therefore, the use of Acetosolv lignin in cellulose acetate blends is of interest in this investigation.

To understand the role of the lignin content and lignin type in acetylation and thermochemical properties, here we investigate the esterification of lignocellulosic material its effects on using two different approaches: a “composite model” of cotton-lignin blends (CLB) with different lignin content, and sawdust delignified to different extents, which maintains the original lignin structure. Acetosolv lignin was used in CLB samples, which is immersed in acetic acid, hence the esterification could be performed in one step. This allowed us to make a comparative evaluation of performance of native and isolated lignin in a thermoplastic CA matrix.

## 2. Materials and methods

### 2.1. Materials

Pine sawdust (SD) was donated by local sawmills (Concepción, Chile). The sawdust was dried at 45 °C for 18 h to achieve moisture

<5%. Commercial high-purity cotton (98%  $\alpha$ -cellulose) was used. The acetosolv lignin was extracted in liquor obtained by delignification of sawdust in acetic acid at 150 °C for 2 h; it was subsequently precipitated with water and dried at 40 °C. High purity reagents were used: sulphuric acid (98%), glacial acetic acid (99.9%), acetic anhydride (99.9%), and sodium chlorite (99%) all provided by Merck Company.

### 2.2. Preparation of samples

Acetosolv lignin was dissolved in 10 mL of acetic acid and mixed in different proportions with cotton (Fig. 1). Various SD samples with different lignin contents were prepared by the Wise method modified [25]: extraction of 3 g of SD with sodium hypochlorite solution (14.4 g) in acetic acid/water (1:2.5 v/v) at 90 °C. This process was repeated for 0, 8, 10, 30, 60, 90 and 120 min to obtain different residual lignin content (Fig. 2).

### 2.3. Acetylation procedure

The acetylation procedure applied to SD and CLB samples has been adapted from Sato et al. [26]. Ten grams of each sample were impregnated with 200 mL of 99.9% acetic acid for 18 h, 120 mL of which was later removed from the mixture. Subsequently, 0.5 mL of  $H_2SO_4$  in 20 mL of glacial acetic acid was added to the sample prior to adding 25 mL of acetic anhydride, with continuous stirring, to achieve a homogeneous mixture. The mixture was reacted at 40 °C for 30 min. Twenty five mL of acetic anhydride was then added to the mixture with continued stirring for 2 h. The reaction was stopped by adding 400 mL of water at room temperature and stirring for 1 min. The system was filtered and then washed to remove excess acid from the mixture. Finally, the acetylated material was oven-dried at 40 °C to achieve a final moisture content below 2% before being ground and sieved.

### 2.4. Sample characterization

#### 2.4.1. Determination of carbohydrates and lignin

The SD, ASD and ACLB samples were subjected to hydrolysis with 72% sulphuric acid at 30 °C for 1 h and subsequent hydrolysis with 3% dilute  $H_2SO_4$  for 1 h at 121 °C to determine the carbohydrate content. Monosaccharide distribution in the material was determined by HPLC analysis of the hydrolyzed liquid phase separated in a column (Aminex HPX-87H) coupled to an IR detector (9170 Young Lin YL) using deionized water as the mobile phase. The calibration was performed with standard solutions of L-arabinose, D-xylose, D-mannose, D-galactose and glucuronic

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