

CHARACTERIZATION OF ALKALICELLULOSE OF PINUS RADIATA AND EUCALYPTUS GLOBULUS BASED ON ITS MOLECULAR WEIGHT AND DEGREE OF ACCESIBILITY

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SUMMARY

The alkaline degradation of bleached kraft cellulose from *Pinus Radiata* and *Eucalyptus Globulus* in a 30% NaOH w/w solution over the time was studied. Both types of cellulose showed at the beginning, first hour, a fast drop in their molecular weight, determined by capillar viscometry, and then the decaying was more slow, reaching stabilization at the end of treatment. Besides, the degree of accesibility obtained in the cellulose at different times of treatment (1h, 8h, and 24h) was evaluated through the determination of % moisture of the alkalicellulose obtained. It was not observed any effect of the time over the degree of accesibility for both types of cellulose.

KEYWORDS: Cellulose of *Pinus radiata*, Cellulose of *Eucalyptus Globulus*, Alkalicellulose, Alkaline cellulose degradation, Cellulose accesibility

RESUMEN

Se estudió la degradación alcalina en el tiempo de celulosa blanqueada kraft proveniente de *Pino Radiata* y *Eucaliptus Globulus* en solución de NaOH al 30% p/p. Ambos tipos de celulosa mostraron al comienzo, primera hora, una rápida caída en su peso molecular, determinado por viscosimetría capilar, y luego el decaimiento fue más lento alcanzando la estabilización al final del tiempo de tratamiento. Además se evaluó el grado de accesibilidad obtenido en la celulosa a diferentes tiempos de tratamiento (1h, 8h, 24h) a través de la determinación del % de humedad del álicelulosa obtenida. No se observó un efecto del tiempo sobre el grado de accesibilidad obtenido en ambos tipos de celulosa.

PALABRAS CLAVE: Celulosa de *Pino Radiata*, Celulosa de *Eucaliptus Globulus*. Álicelulosa, Degradación alcalina de celulosa, Accesibilidad de celulosa

INTRODUCTION

The common procedures used in the preparation of cellulose ethers are based on the reaction of Williamson. In the first step of the reaction, cellulose is treated with NaOH solution to obtain alkalicellulose which is the activated specie of cellulose. Then, in the second step, the alkalicellulose is reacted with an etheryficant agent to obtain the cellulose ether (1).

The properties of the cellulose ether obtained, such as molecular weight, degree of etheryfication and distribution of substituents, depends on the source of cellulose used, treatment with NaOH and etheryfication reaction conditions (2).

The purpose of this work was to compare the properties of the alkalicellulose obtained from the two principal sources of cellulose of Chile, *Pinus radiata* and *Eucalyptus Globulus*, based on their molecular weight and degree of accesibility.

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EXPERIMENTAL

Bleached kraft cellulose from *Pinus Radiata* (α -cellulose=86.2%, β -cellulose=7.4%, γ -cellulose= 6.4%.CMPC, Chile) and bleached kraft cellulose from *Eucalyptus Globulus*(α -cellulose=89.5%, β -cellulose=7.3%, γ -cellulose= 3.2%. Forestal Santa Fe, Chile) were used as cellulose sources.

The determination of the molecular weight was done by capillar viscometry using the Mark-Houwink's constant described for the cellulose in the solvent mixture 9% of LiCl in N,N-dimethylacetamide at 30°C. $K=1.278 \cdot 10^{-4}$ ml/g and $a=1.19$ (3,4).

The alkalicellulose was prepared as following: 50 g of bleached kraft cellulose, previously milled in a hammer mill (DIAF A/S) provided with a sieve with circle openings of 1 mm, was submerged in 1000 g of 30% NaOH w/w solution by 1h, 8h, and 24 h. At each time the paste obtained was centrifuged in a basket centrifuge (Martin Christ Osterode/Harz, type UJ3), then was washed with distilled water and neutralized with 10% HCl w/w solution. Finally, the product was centrifuged in a decantation centrifuge (Sorvall RC53) at 4500 rpm and dried in a vacuum oven by 8h at 40°C. The alkalicellulose obtained was placed in a desicator provided with silica gel at room temperature.

The determination of % moisture of alkalicellulose was done by Markusson's method (5).

RESULTS AND DISCUSSION

The alkaline degradation behaviour of both types of cellulose in 30% NaOH w/w solution is shown in Figure 1. There is no significant differences for both types of cellulose in relation with their initial molecular weight (460,000 and 440,000 approximately) and in the behaviour of decaying of their molecular weight over the time. In both types of cellulose was observed a fast drop in the molecular weight during the first hour, for then going to the stabilization process of it. This behaviour can be explained based on the theory of alkaline degradation of the cellulose in which it can be distinguished two processes, called peeling reaction and occlusion reaction. The peeling reaction involves a gradual shortening of cellulose chains by the mechanism of β -elimination. The occlusion reaction has a similar mechanism of the peeling reaction, except that the elimination produce a product which stabilize the cellulose chain. The reactions of peeling and occlusion compete between them, but the peeling reaction has a faster propagation than the occlusion reaction(6). The occlusion reaction can explain the observed stabilization of the molecular weight of alkalicellulose.

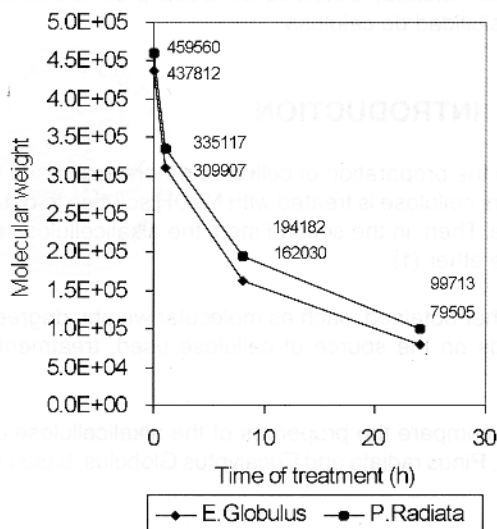


Fig.1.Alkaline depolymerization in 30% NaOH w/w solution of cellulose of P.Radiata and E. Globulus

Cellulose molecular cohesion is due to the large number of hydroxyl groups forming intramolecular hydrogen bonds between adjacent glucose units of the chain and intermolecular hydrogen bonds between different chains. These hydrogen bonds are responsible for the fibrillar and crystalline structure of cellulose. However, a considerable number of free hydroxyl groups are also present in cellulose fibers, primarily in the noncrystalline regions of cellulose. Therefore, as the capacity of cellulose for water absorption depends largely on the availability of free hydroxyl groups, it is generally considered that water absorption (equivalent to bound water) occur almost entirely in the amorphous region of cellulose, neglecting the free hydroxyl groups that may be present on the surfaces of the crystallites (7). Thus, if the alkal cellulose is dried under controlled conditions and a constant relative humidity atmosphere is maintained, the % of moisture would be measured. The % of moisture of the alkal cellulose could estimate preliminary the degree of accessibility reached by the treatment with 30% NaOH w/w solution.

The % of moisture of alkal cellulose from *Pinus Radiata* and *Eucalyptus Globulus* at different times of treatment is shown in Figure 2. There is no significant differences in the % of moisture between both types of cellulose and there is no effect of the time of treatment over the % moisture. These results pointed out that both types of cellulose, as well as the time of treatment (1h, 8h, and 24h), would not have any effect over the degree of accessibility of the cellulose. By the other hand, it can occur that the method used for the estimation of the absorbed water was not enough sensible to detect the differences between the alkal celluloses. Thus, it could be useful to try more sensible methods for this estimation by FT-IR (8) and DSC (7).

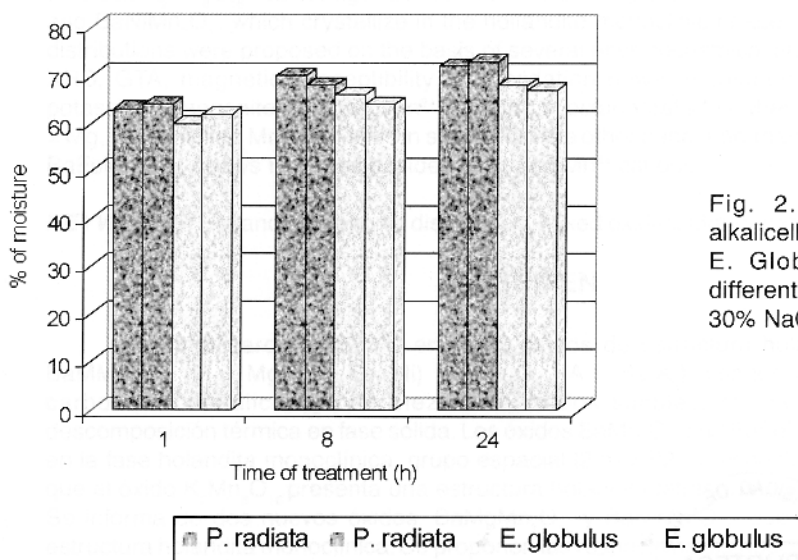


Fig. 2. % of moisture of alkal cellulose of *P. Radiata* and *E. Globulus* obtained with different times of treatment in 30% NaOH w/w solution.

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