Book Chapter

Polyelectrolytes from Modified Natural Polysaccharides

Ana Moral\(^1\)*, Roberto Aguado\(^1\), Andrea Pipió\(^1\), Antonio Tijero\(^2\) and Menta Ballesteros\(^1\)

\(^1\)ECOWAL Group, Molecular Biology and Biochemical Engineering Department, Pablo de Olavide University, Spain
\(^2\)ECOWAL Group, Chemical Engineering Department, Complutense University of Madrid, Spain

*Corresponding Author: Ana Moral, ECOWAL Group, Molecular Biology and Biochemical Engineering Department, Pablo de Olavide University, Seville, Spain

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In the chapter, authors want to simplify article conclusions to make a didactic explanation. The objective is to facilitate the knowing of the fundamental relationships between cellulose modifications and the most influential variables.


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**Introduction**

Paper manufacturing processes need toxic retention agents to minimize water pollution (compacting pulps and/or increase flocculation) such as aluminum compounds, ferric sulfate, ferric chloride, quicklime or polyamines [1]. The use of cationic polysaccharides is an efficient and less contaminant alternative to produce big, dense, compact and stronger flocs, which allows better sedimentation conditions [2].

Cellulose is an interesting homopolymer of β-D-glucose because of its chirality, hydrophilicity and formation of semi-crystalline derivatives [3]. Native cellulose (essentially cellulose I) treated with NaOH (mercerization) changes its crystalline structure [4]. Fengel, D., Jakob, H. and Strobel, C. (1995), showed that with a higher percentage of NaOH, the degree of crystallization decreases until stability is achieved [5]. In this point, cellulose changes to a more stable polymorphism than native cellulose, which five different structures. Fibrous orientation and the considerable degree of crystallinity explain the more α-cellulose stability [6].

Stability of α-cellulose and its derivatives make it versatile in paper and textile industries. Furthermore, it could use to biomedical investigation (separation membranes), construction (drilling fluids), food (stabilizer and texturizer), and pharmaceutical or cosmetic industries [3].

Cationic modification of cellulose commonly goes by the etherification with a 2-hydroxy-3-(trimethylammonium) group, which can be obtained by the reaction of 2,3-epoxypropyltrimethylammonium chloride (EPTAC) and biopolymer. EPTAC is toxic, unstable and not use in industrial applications. An alternative is the use of 3-chloro-2-hydroxypropytrimethylammonium chloride (CHPTAC), which has been studied [7]. Flocculation efficiencies for the resulting
products are similar at the classical commercial polyacrylamides [8].

CHPTAC-cellulose reaction has three steps: 1. CHPTAC chlorohydrin is converted into EPTAC epoxide, 2. a hydroxyl group of cellulose reacts with a base, becoming an alkoxide, 3. cellulose alkoxide reacts with EPTAC resulting in cationized cellulose. In this point, we must avoid a secondary reaction between water and EPTAC, because this would increase the costs of the process, due to the diol that would form could not react with cellulose, involving extra treatment [9,10]. The addition of base (NaOH) is necessary to the formation of EPTAC and to weaken the hydrogen bonds present between the molecules, thus making more cellulose accessible [11].

The aim of this work is to develop a cationic polymer for papermaking purposes based on α-cellulose due to its stability and applications. Kinetics were discussed to find the optimal concentrations of reagents. Use of modified natural polysaccharides is currently regarded as a sustainable alternative to synthetic polymers and hence as desirable with a view to developing new improved products.

**Experimental**

**Alkalization**

Raw material was commercial α-cellulose (AldrichC8002). Cellulose was mixed with an aqueous NaOH solution (10–30% w/w). Fibers were separated by passage through a Whatman Glass Microfiber Binder Free Grade GF/D filter (2.7μm) and washed with demineralized water.

**Cationization**

The agent was 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) at 60% (w/w) from Aldrich. The process was carried out in two steps: 1. epoxypropyltrimethylammonium chloride formation (EPTAC) 2. nucleophilic substitution of the hydroxyl group bonded to C6 in the anhydroglucose unit (AGU). Fibers were separated by passage through a Whatman Glass
Microfiber Binder Free Grade GF/D filter (2.7\(\mu\)m) and washed with demineralized water.

**Characterization of Samples**

Carbon and Nitrogen contents were determined by LECO CNS-2000I elemental macro-analyser. The results could be processed to evaluate the kinetics models.

**Results and Discussion**

Table 1 is a measure of the Nitrogen percentage, degree of substitution and kinetic constant for times of 90 minutes. The concentrations of Nitrogen have determined by elemental analysis. The degree of Nitrogen substitution (DNS) of the cellulose was calculated from the Nitrogen content (%N) and the molecular weight of the anhydroglucose unit (AGU), 162.15.

Table 1: Parameters of pseudo-second-order kinetic.

<table>
<thead>
<tr>
<th></th>
<th>[NaOH]\textsubscript{1}</th>
<th>[NaOH]\textsubscript{2}</th>
<th>[NaOH]\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%N, N_{eq})</td>
<td>0.17</td>
<td>0.19</td>
<td>1.79</td>
</tr>
<tr>
<td>DNS\textsubscript{eq}</td>
<td>0.02</td>
<td>0.02</td>
<td>0.26</td>
</tr>
<tr>
<td>K(%Nmin)\textsuperscript{-1}</td>
<td>3.54</td>
<td>2.87</td>
<td>0.07</td>
</tr>
</tbody>
</table>

1:10% 2:20% 3:30%

Results were processed with various kinetic models and a pseudo-second-order rate equation was found to provide the best fit. Pseudo-second-order kinetic model proposed by Blanchard et al. is typically applied to adsorption phenomena occurring in solution [12]. These kinetic expressions have been applied to a variety of systems [13]. The theoretical background has been examined by Azizian [14]. The kinetic constants of pseudo-second-order model show combinations of the initial solute concentration and the adsorption and desorption parameters. If the assumption of a pseudo-second-order model is fulfilled, then the intercept of the curve will represent the highest proportion of elemental nitrogen incorporated by effect of the reaction of EPTAC, previously formed in the reaction between CHPTAC
and NaOH, with alkali activated sites of the hydroxyl group on C6 in the anhydroglucose unit (AGU).

**Conclusions**

The proportion of nitrogen at equilibrium in cationized cellulose increases linearly with increasing content of amorphous cellulose in the starting material.

The overall cationization reaction fits a pseudo-second-order kinetic equation. To obtain cationic cellulose with a high substitution degree, it is advisable to have a previously performed alkalization stage under severe conditions.

**References**

7. Prado HJ, Matulewicz MC. Cationization of polysaccharides: a path to greener derivatives with many


