DIFFERENT STRATEGIES TO MODIFY COTTON PROPERTIES

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Abstract*:*

Cellulose is a cheap, renewable, biodegradable, and the most abundant organic raw material in the world. Nevertheless, the modification of cellulose has been widely investigated in order to improve the mechanical, physical and chemical properties.

The chemical strategies to modify the properties of cotton for a particular application are diverse and could include cross-linking reactions with bi or polyfunctional compounds, grafting processes with specific monomers, depending on the desired effect. Chemical reactions can be used as well to change the characteristics of cellulosic polymers, namely in terms of dyeability.

Independently of modification process applied, the mechanical properties of fabrics could change, not always in favorable sense.

The aim of present paper is to describe a methods to prepare cationised cotton using to different kinds of starch. The quaternary cationic agent (based on maize and potato starches modifications) was synthesized and controlled by FTIR-ATR techniques. The efficiency of cationisation was comparatively analyzed in terms of dye uptake and mechanical properties.

Dyeing process with a direct dye (CI Direct Red 80) was used to compare dyeing performance of modified and unmodified samples. The variables of process were analysed and potato starch cationic agent results in better dye exhaustion when compared with untreated cotton without salt.

Keywords: cationised cotton, cationic maize starch, cationic potato starch, cationic product, chemistry modification, CI Direct Red 80.

1. Introduction

Cellulose is a non-branched polymer of ß (1,4) glucose. The degree of polymerization (DP) depends on the nature of the vegetable species from which the cellulose is obtained and on the type of treatment applied. The mechanical properties of a cellulose – based fibre, such as tensile strength, are heavily dependent on its DP, by the cellulose crystaline structure and by the crystalline/amorphous ratio present [1,2].

In order to improve the properties of cotton, the chemical structure of cellulose can be modified by different ways [3]:

- Replacement of the hydroxyl groups: usually esterification or ether formation reactions are used. This type of treatment reduces some of the less desirable characteristics of the material such as flammability and susceptibility to microbial attack.

- Reaction with bi or polyfunctional compounds: these reactions give cross-linking products whose generally the global effect is the increase of mechanical strength of the material.
- Grafting reaction: this process binds synthetic polymers to cellulose thus improving the mechanical and dyeability properties of cellulosic materials.

Cationic starches are widely used as additives in the paper, textile, wastewater treatment or cosmetic industry processes because of their relatively low price, excellent properties and biodegradability [4-6]. Most commercial cationic starches have low DS, less than 0.2, but cationic starches with high DS have preferable properties for some particular applications [4].

Cationic starches are usually produced by etherifying reaction of starch with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHTAC) [7].

The aim of present paper is to describe a method to prepare cotton with surface cationic charges. The quaternary cationic agents (based on maize starch and potato starch modifications) were synthesized and controlled by FTIR-ATR techniques. These obtained reaction products were applied to the cotton by pad-batch process.

The modified cotton samples were characterized using FTIR-ATR techniques and comparatively analyzed in terms of dye uptake and mechanical properties.

Dyeing process with a direct dye (CI Direct Red 80; Figure 1) was used to compare dyeing performance of modified and unmodified samples.

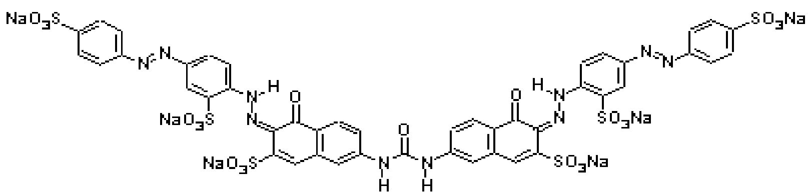

Figure 1- Molecule structure of the dye CI Direct Red 80

2. Experimental

2.1. Materials

The maize and potato starches and CHTAC were obtained from Sigma (Portugal).

A commercial sample of CI Direct Red 80 (from Dystar, Portugal) was used in this study, without further purification.

Cotton fabric desized and bleachedan was purchased from Lameirinho, Portugal.

2.2. Methods

2.2.1. Hydrolyse of maize and potato starch

Two types of starches (maize and potato) are hydrolyzed. Startch (50g) was stirring at 50 ºC for 1 hour with 250 mL of HCl (1M) solution. The liquor/starch ratio used was 5.

2.2.2. Synthesis of cationic hydrolysed starches

The hydrolyzed maize starch and potato (10g) were mixed with 60 g of CHTAC and treated with 100mL of NaOH (1,5M) at 80 ºC for 1h with stirring.

These solutions are adjusted to pH 7 using acetic acid (1M). Then the compounds were percipitate in water:etanol solution, filtered and washed with ethanol. Finally the precipitate was dried for 24 h.

2.2.3. Fourier–transform infrared spectroscopy (FTIR) spectroscopy analysis

IR spectra of synthetised products and reagents were recorded on a Fourier–transform infrared spectrophotometer Nicolet-Avatar 360 with 32 scans and 4 cm^{-1} resolution using KBr pellets.

FTIR spectra of cotton samples were obtained by attenuated total reflectance technique (ATR). Zinc selenide was the ATR correction made with OMNIC 5.2 software (Nicolet, Izasa, Portugal).

2.2.4. Modification of the cotton with the hydrolyzed maize starch and potato

The application of the cationic maize and potato starches on cotton was carried out by pad-batch process in alkaline conditions, pH 10 (pick-up 80%.)

Different amounts of starches, 0 to 0.5g, were applied in each case.

2.2.5. Dyeing procedure

The untreated and cationic cotton samples were dyed with CI Direct Red 80 (1% w.o.f), using a 30:1 liquor ratio, during 1h at 90 ºC. The samples were then rinsed in cold water for 10 minutes.

The untreated cotton fabric is dyed in normal conditions with NaCl (10 g/L) and the other samples were dyed without salt.

2.2.6. Fabric strength tests

To establish the influence of the process on the strength properties of cotton samples, tensile strength tests were performed by Hounsfield Tester, with cross head speed of 100 mm/min and sample of 200x50 mm according to ISO 13934-1.

An average of 5 tests for warp and 5 tests for weft had been reported for each analysed sample.

3. Results and discussion

3.1. Synthesis of cationic hydrolyzed maize starch and potato

The synthesis of cationic starch was carried out as described by Zhang and co-works (2007), however with some modifications in the practical procedure [7]. Starches from different sources were hydrolysed and modified by reaction with CHTAC and NaOH as catalyst (Figure 2).

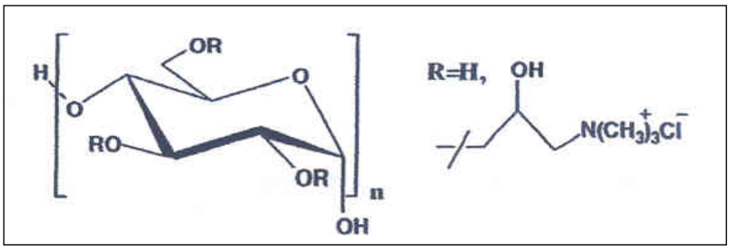

Figure 2 – Structure of cationic hydrolyzed starch.

As will be discussing below based on obtained IR spectra for modified starches, the potato starch is the only start material that allow obtain cationic derivative. The reaction yield is low manly due to the high difficulties in the reaction product purification (aprox. 10%).

3.2. Characterization of the cationic hydrolyzed maize starch and potato

The reaction was controlled by IR Spectophotometry. The Spectra of starting reagents and final product were compared to deduce the chemical changes formed.

IR spectra of modified hydrolyzed potato starch confirmed the presence of the cationic groups on molecule (Figure 3). It shows not only the characteristic starch backbone at 1152 and 577 cm^{-1}, but also the additional absorption band of the quaternary ammonium groups at 1476 cm^{-1} assigned to the CN vibration.

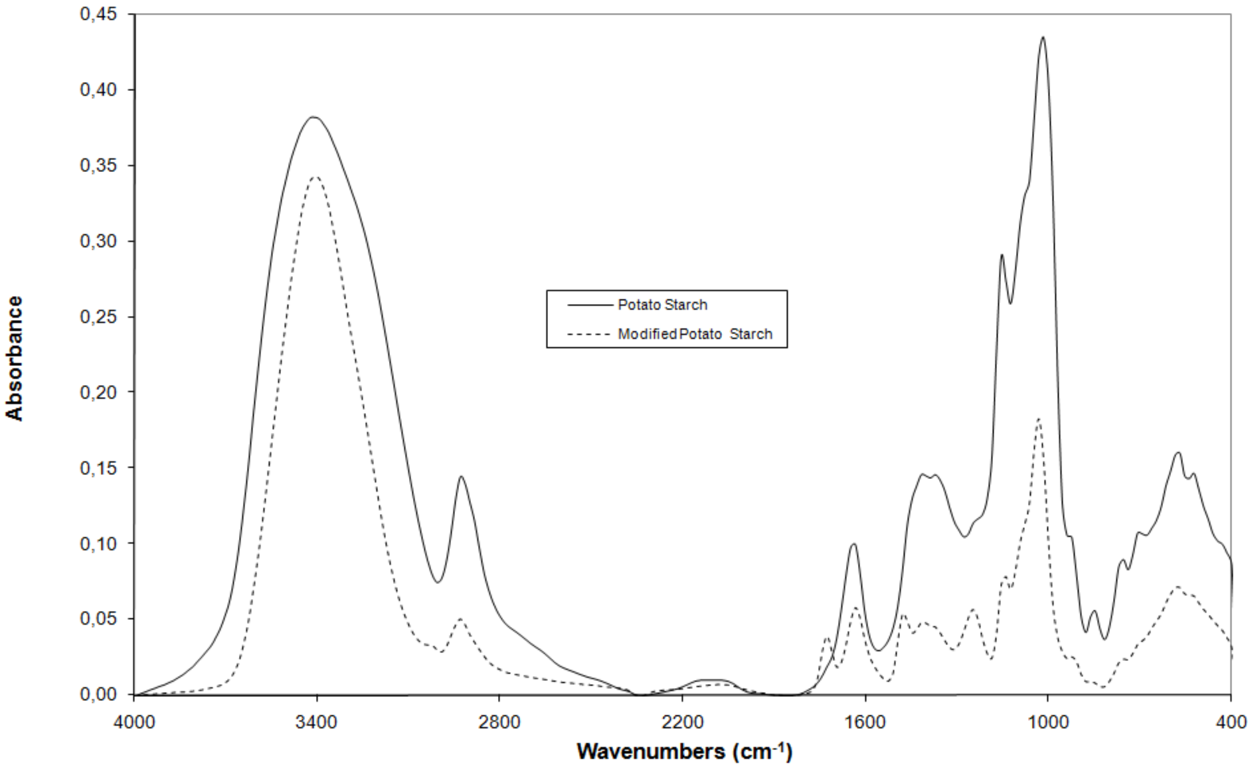

Figure 3 - FTIR spectrum of starting and modified potato starch (KBr pellets).

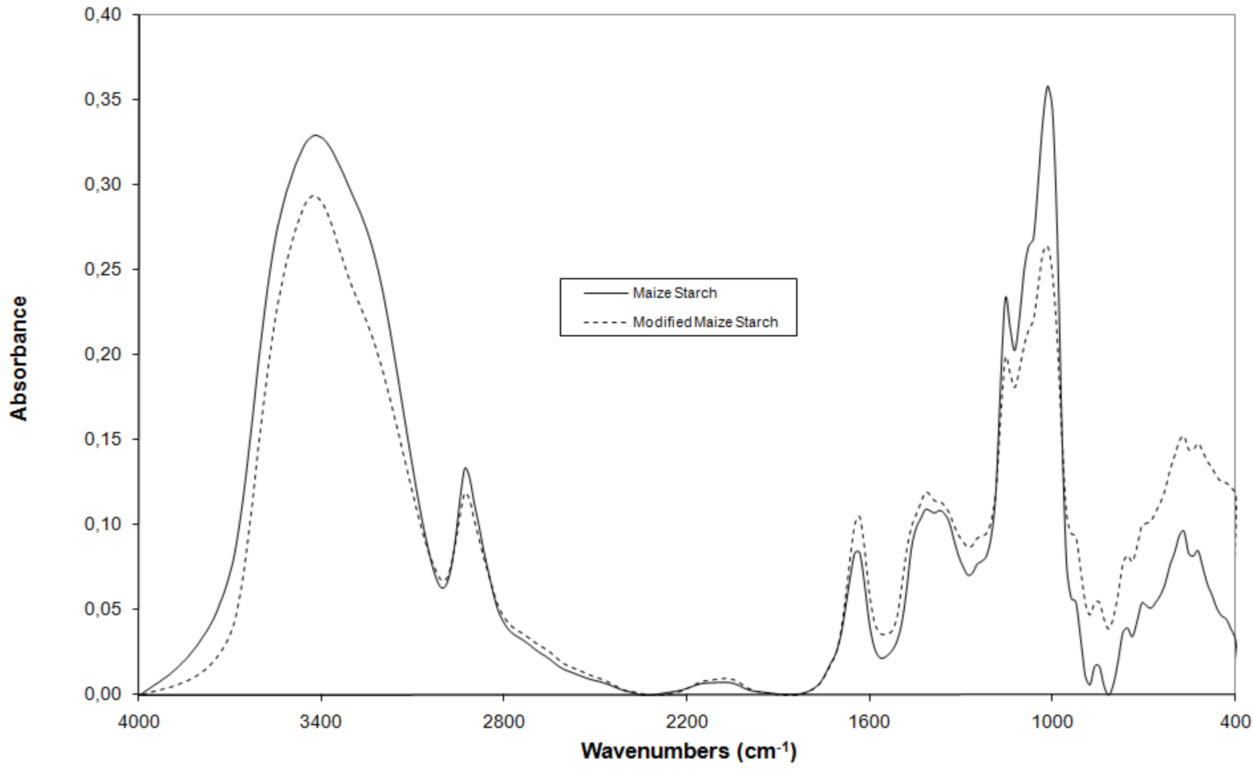

Figure 4 - FTIR spectrum of starting and modified maize starch (KBr pellets).

The FTIR spectra of original and cationic maize starches (Figure 4) don't show relevant differences among the absorption bands. The some conclusions can be applied to the analysis of the untreated and modified cotton fabrics FTIR spectra. These results allows as to supected that the starch was´nt modiffied by the described procedure. Nevertheless, the samples were impregnated with the resulting product and dyed in similar conditions to the potato starch modified samples to evalute their dyeing behaviour.

3.2. K/S values of dyed samples

Several cotton samples were modified with different type and amount of starch cationic derivatives.

Dye uptake can be deduced by the analysis of K/S values presented by the different dyed samples. Figure 5 shows the results obtained by cotton samples prepared with 0.3g of potato starch derivative, 0.3g and 3.0g of maize starch derivative. The results of untreated cotton, dyed with and without salt are analysed as well.

Only slight changes were noted by comparing the K/S results obtained for maize starch modified samples and the untreated sample, even if the amount of compound applied was 10 fold increased. These results prove that the starting maize starch was not significantly modified which the lake of spectral changes in IR spectra collected already confirmed.

Besides, the sample modified with potato starch cationic agent present better dye uptake when compared with the untreated sample and dyed in similar dyeing conditions. However, the results are not so good when compared with the obtained for the sample not treated and dyed with salt.

On the other hand, it is verified that with the increase of potato starch cationic agent concentration used the k/s value increases too (results not shown).

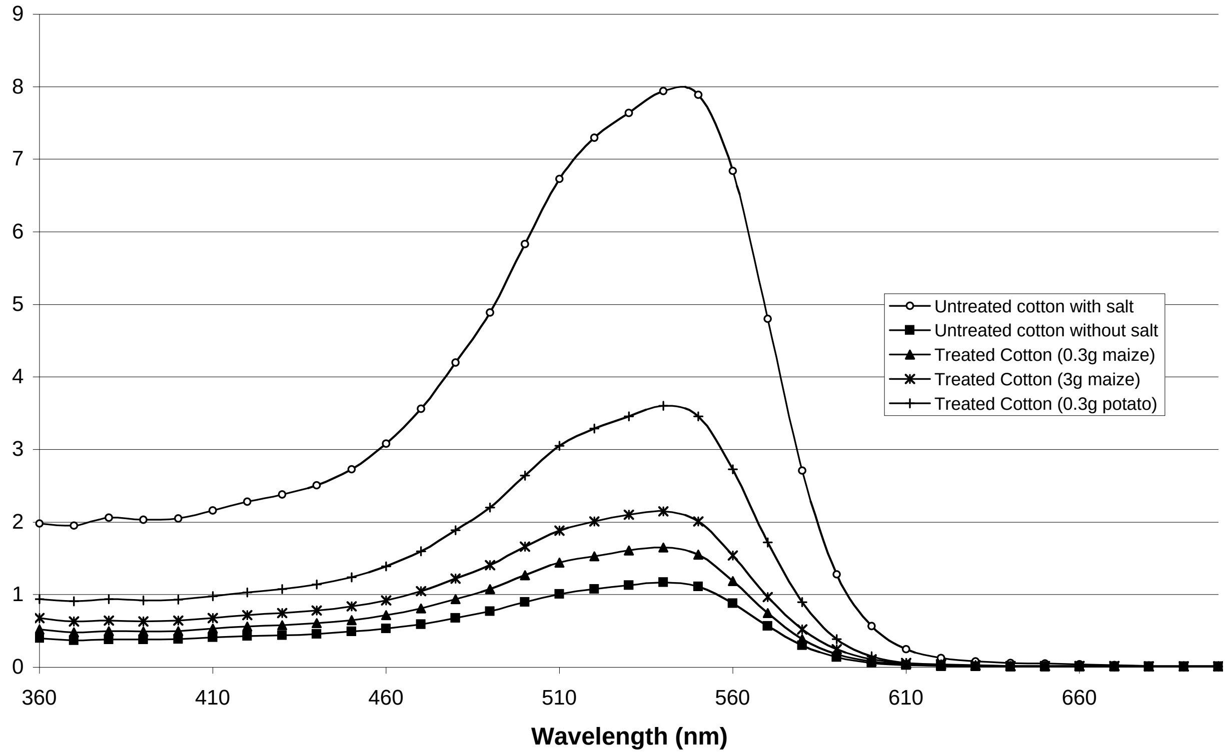

Figure 5 - K/S values presented by the different samples dyed with CI Direct Red 80

3.3. Mechanical properties of modified cotton

The mechanical properties could be changed during materials modification processes and Table 1 presents the medium values obtained for tensile strength properties evaluated according standard method ISO 13934-1. Tensile strength results of untreated and treated specimens are shown in table 1 (warp and weft directions).

Table 1 - Mechanical properties of fabrics.

Sample	Tensile strength (N)	
	Warp	Weft
Dyed cotton	291.2	351.4
Modified wih potato starch and dyed	287.6	373.0
Modified wih maize starch and dyed	276.4	347.4

It was observed that no significant changes occur in the tensile strength (warp and the weft directions) for the modified fabrics.

4. Conclusion

The work described allows us to conclude that:

The obtained results demonstrated that was possible to synthesise cationic potato starch.

This chemical modification process is ineffective in case of maize starch used and with this particular procedure.

The modified cotton with the starches derivatives can be dyed with direct dye without salt. However the best result was obtained with the cotton not treated in presence of salt, which indicates that further experiments must be carried out to improve the dyeing exhaustion behaviour of cotton samples using salt-free process.

The cotton mechanical properties, analysed in terms of tensile strength, are not significantly affect by the modification process.

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