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From waste to an ecological material: a new way to value the waste paper

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ABSTRACT: We propose an alternative solution to plastic from petrochemical origin, with biodegradable and compostable plastic, which comes from waste paper. We present a new method of recovering waste paper to obtain cellulose acetate. The composition of papers is more than 80% of cellulose. Our objective is the recovery of cellulose by synthesizing a derivative that is cellulose acetate derivative with high degree of substitution via direct acetylation using acetic anhydride. So the optimization of experimental parameters influencing the acetylation reaction (temperature, reaction time, report (acetic acid / cellulose anhydride) were conducted. The cellulose of waste paper was treated with acetic anhydride and catalytic amount of sulfuric acid to obtain cellulose acetate. The results confirmed the identity with literature.

KEYWORDS: Recovery; paper; waste; cellulose acetate; acetic anhydride; X-ray diffraction.

1 INTRODUCTION

The demand for environmentally friendly materials has significantly increased. Therefore, the interest in materials based on renewable resources has grown tremendously. Consequently, in recent years, many researchers have been devoted to the use of natural materials in manufacturing such as woods, straws, corn and starch, as raw materials for produces biofuel or biodegradable plastics. Cellulose acetate, invented in 1865, is a plastic material of vegetable origin. Known by its shock resistance property, the ease of modeling, brilliance and transparency and especially its biodegradability and compostability, cellulose acetate has had many uses, such as base films in photography, varnish, enamel false or as electrical insulator [1].

Moreover, thousands of tons of paper waste represent an average of 40% collected annually. The recycling of waste paper can be sorted into three different categories. There is energy recovery through incineration for the production of heat and electricity, production of methane by anaerobic fermentation mixed with other organic waste, and recycling of paper and cardboard [2].

The goal of this work is based on the implementation of a new method of recycling paper waste, by the extraction of the cellulose which forms the paper in order to transform it into biodegradable plastic. Indeed our study is related to the acetylating of cellulose derived from recycled paper.

What has been known in the arts such as acetylation of cellulose fibers has existed for decades, while for processes that are use of native cellulose, such as cotton, wood pulp, flax or the like. Cellulose is the most abundant polymer on earth [3]. Indeed, this glucose polymer constitutes the main structure of many plants. It is the main component of the cell walls of plants and wood. The content varies depending on the plant species, about 40% in wood and 95-99% in cotton fibers. Cellulose is a macromolecule to very long chain stereoregular and belongs to the family of β-D-glucans. It is composed exclusively of β-D-glucose units linked together by I type bonds (1->4). The repeating unit composed of the combination of two glucoses, is called cellobiose. Figure.1 shows presents the cellulose chain.

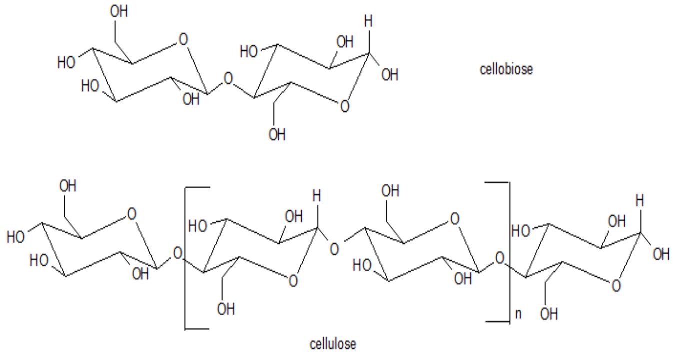

Fig. 1. *Cellulose chain*

The crystal structure of cellulose is very complex and there are different crystalline organizations called I, II, III, IV, or Iα, Iβ, IIII, IIIII, IVI and IVII (Fig. 2). In its natural state, cellulose is a crystalline configuration I. After numerous studies, it was found dimorphism of cellulose I. In fact, the cellulose I is constituted of two different structures, celluloses Iα and Iβ. It was until the appearance of the 13C NMR by "cross-polarization - magic angle spinning" (CPMAS) to describe these two native cellulose states. The Iα cellulose is composed of a single phase triclinic chain while the Iβ cellulose is composed of a monoclinic phase to two parallel chains. The Iα cellulose prevails in the cellulose produced by bacteria and algae as the Iβ cellulose is more common in the cellulose produced by plants. Cellulose I to cellulose II becomes after treatment with concentrated sodium hydroxide at 18%(mercerization). This treatment induces a change in hydrogen bonds amending polymorphism cellulose.

The process of mercerization produces a mechanical reinforcement of the cellulose fibers and the cellulose II can also capture a greater quantity of water [4]. Other polymorphic forms of cellulose have two configurations: parallel (IIII and IIA) and antiparallel (IIIII and IVII). The transition from one polymorph to another is not always reversible. The possibilities and methods for obtaining them are summarized in Figure.2.

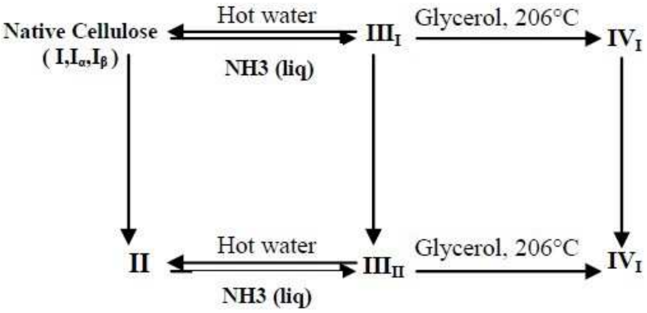

Fig. 2. *Interconversions between different types of cellulose*

2 RECYCLING AND OBTAINING THE PAPER PULP

Pulp is the raw material for papermaking. It is also re-acquired through recycling paper [5]. The usual recycling process consists of two main steps: the transformation of waste paper pulp and pollution-cleaning and refining the paste. The basic process of recycling is presented as follows:

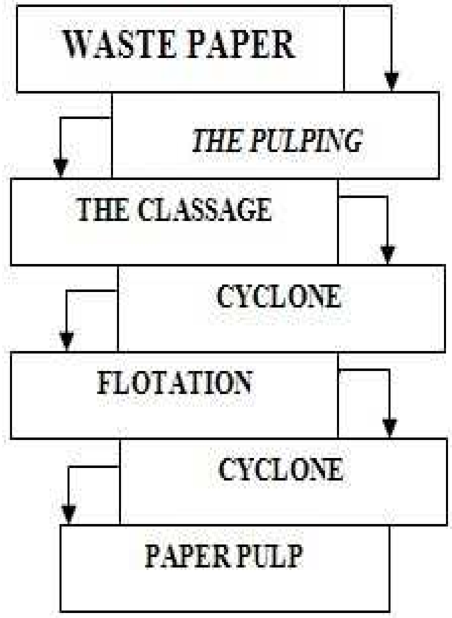

Fig. 3. Steps for obtaining paper pulp

2.1 THE PULPING

Also called industrial logs, the principle of this step is to break the bonds joining the cellulose fibers together and to separate the main pollutants (plastics, metals, etc.).

The operation takes place in a pulper. Waste paper is mixed with water and additives and crushed. The goal is to separate the fibers, taking care however not to split the impurities in the following stages. The pulp used to separate impurities according to their size. Hydrocyclones are used to separate items based on their density. With the cyclone, the pulp is brought into rapid rotation where the densest elements are placed in the periphery and the least dense in the center. The pulp is thus free of impurities [6].

2.2 THE DEINKING

To remove the ink particles from the paper pulp, the principle of flotation was used. Adding a surfactant (soap) to the pulp, the air bubbles pass through the pulp in which was sticking ink particulate matters and rise to the surface. The foam thus created containing the ink particles is removed by overflow or aspiration. Once pressed and dehydrated, these foams become deinking sludge.

2.3 THE BLEACHING

The pulp bleaching is obtained either by dilution with a paste of improved whiteness (e.g. virgin pulp or the result of old high-quality paper) or through chemical bleaching by adding hydrogen peroxide.

3 ACETYLATION CELLULOSE

In any transformation, cellulose must be pre- treated or activated, because of the large number of hydrogen bonds. Acetylation of cellulose with acetic acid or acetic anhydride has been known for a long time. Acetic anhydride by itself is unable to acetylate cellulose. It needs a pre-activation step that weakens the intermolecular interactions within it. Thus cellulose pulp is treated with certain reagents which cause a rupture or weakening of its intermolecular bonds. For that the cellulose pulp must be heated in the presence of sulfuric acid and acetic acid to give cellulose acetate [7].

Acetylation is accomplished by adding acetic anhydride and the acid catalyst H_2SO_4 to form a cellulose triacetate (Figure.4).

3.1 THE CLASSAGE

Complete dissolution of cellulose triacetate does not occur in the presence of a large excess of acetic anhydride, it indicates only the end of the esterification. This reaction causes two phenomena: the reaction of the hydroxyl groups of the cellulose, and the fission of cellulose chains and thus decreasing the cellulose substitution of degree. The temperature favoring the hydrolysis of cellulose, ensure its precise control, especially as this reaction is highly exothermic. Water was added to the above mixture (acetic acid solution) to allow hydrolysis of the diacetate and triacetate. This step is catalyzed by sulfuric acid. It serves primarily to modulate the synthesized derivative by degree of substitution (DS). The last step is the precipitation and purification. Once the DS of acetate was adjusted, the cellulose acetate precipitated by adding water to the solution and the precipitate is washed with water again. This purification is essential to remove traces of chemicals and recycle acetic acid [8].

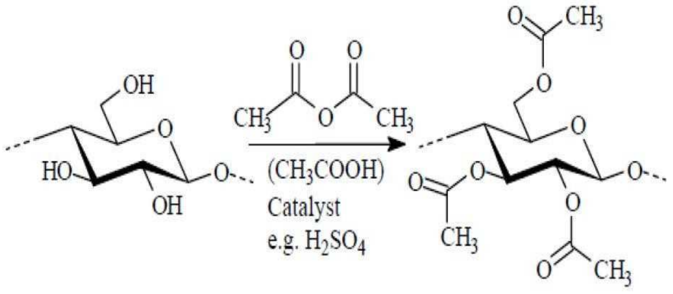

Fig. 4. Reaction of cellulose acetylation

4 MATERIALS AND METHODS

10g of paper into small balls was added 60 ml of glacial acetic acid and a few drops of 95% sulfuric acid. The mixture was adjusted to reflux, with variation of temperature between 50 and 90°C during 30 to 60 min. After cooling down, 60 ml of acetic anhydride was added and again the mixture was heated untile all the paper has completely disappeared. At the end of the reaction 12ml of acetic acid solution 20% was added and again heated at 70 °C during 10 min [9]. After cooling, the solution is poured into a 400 ml beaker and slowly with stirring. The precipitated cellulose triacetate then filtered and washed with cold water until neutral pH. The product is dried at 60 °C to a constant mass.

5 RESULTS AND DISCUSSION

Almost all cellulose acetates are manufactured through a solution process using sulfuric acid as a catalyst with acetic anhydride in acetic acid solvent, using raw material cotton.

In our study, the same process and the same chemical composition were used to prepare the cellulose acetylated but on cellulose obtained from paper waste. Using paper waste lowered production costs and gave new life to waste [10].

Yields calculated based on the amount of cellulose used and the DS acetate. For example, the cellulose will provide cellulose acetate with DS of 1.4 to 2.8 according to the experiments carried out. The calculation of average value of acetyl groups %AG is carried out in equation (1):

$$\%AG =[\,[(Vbi+Vbt)\,\mu b - Va\mu a\,]\;43\,/mca\,]*100 \qquad (1)$$

%AG = percentage of acetylated groups
Vbi = volume of NaOH added to the system Vbt = volume of NaOH lost in the titration µb = NaOH concentration
Va = volume of HCl added to the system
µa = HCl concentration
43 = molecular mass of the acetyl group mca = weight of the cellulose acetate sample

Degree of substitution (DS) is the average value of acetyl groups (AG) replacing the hydroxyl groups in the glycoside unit equation (2) present degree of substitution:

DS = (3,86 × % AG) / (102.4 - % AG) (2)

The tests are performed based on paper, varying the settings (temperature, time, volume, etc.) and other tests on cotton to confirm the results. Table.1 illustrates the results of DS made on acetates cellulose products:

Table 1. The results of DS made on acetates cellulose Products

sample	**P5**	**P3**	**P4**	**C4**
DS	2,6	2,8	1,9	2,8

The product was characterized by IR and the results was compared with literature (Figure 6

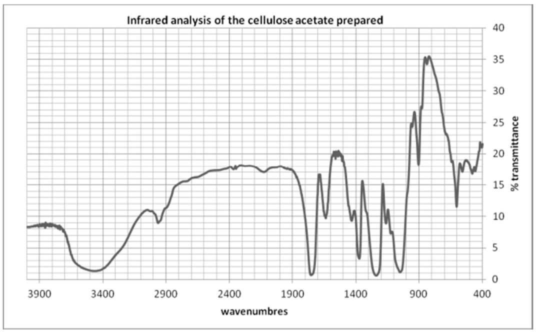

Fig. 5. IR analysis of the prepared cellulose acetate

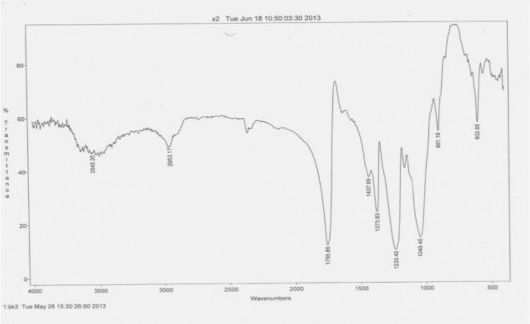

Fig. 6. Theoretical IR spectrum of cellulose acetate

Figures 5 and 6 show that experimentally and theoretical IR spectra are very close, which confirms that the desired product is obtained by esterification (Figure 7), and that hydrogen bonds are destroyed in the cellulose skeleton.

Fig. 7. Powder of cellulose acetate obtained

6 CONCLUSIONS

We focused on the chemical modification of cellulose with acetic anhydride. The method involves an esterification of cellulose of paper and waste paper, in heterogeneous phase which allowed to successfully modifying the cellulose substrate with yield of 84.12%, and a substitution degree of 2.8, which can grant to the material plastics and hydrophobic properties. Characterization methods have allowed demonstrating the chemical modification of cellulose by esterification.

Analysis by infrared verified confirmed the structure of the esters obtained. The results obtained are very similar with those of the literature. The uses of cellulose acetate are various, ranging from biodegradable plastic film to membrane to micro-filters. It will be interesting to modify cellulose of user paper. This will reduce the costs of production of cellulose acetate and contribute to sustainable development.

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