



Preparation and Characterization of Cellulose Acetate and Cellulose Nitrate Prepared from Cellulose Extracted from *Calamagrostis intermedia*

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The main purpose of this research work is to prepare and characterize cellulose nitrate and cellulose acetate from cellulose extracted from *Calamagrostis intermedia*. Cellulose nitrate was prepared by nitration with a sulfonitric mixture, while cellulose acetate was prepared with acid and acetic anhydride. In both cases, an FTIR analysis was performed. Optical microscopy was applied to the prepared semi-synthetic compounds, showing crystalline networks corresponding to well-defined polymeric chains. Finally, the cellulose acetate was subjected to viscometry in order to determine the molecular weight of the prepared polymer, tending a value of 220.34×10^3 g/mol. The results highlighted the feasibility of preparation of such polymers from a non-conventional source and the strategies for characterization and preparation at laboratory level.

Keywords: *Calamagrostis intermedia*, Cellulose acetate, Cellulose nitrate, FTIR analysis, Semi-synthetic polymers.

INTRODUCTION

An increase in environmental pollution results in part from the excessive use of polymers worldwide has reached dangerous levels. Polymers produced from the petroleum resources are not biodegradable [1], since they defy microbial degradation, they end up in landfills and pollute the environment. This problem causes oil prices to fluctuate according to market requirements [2]. Thus, the study of new natural sources for the preparation of polymers is the result of two main problems (i) the environmental impact and (ii) the use of finite oil resources [3]. Polymers are broadly classified into two main categories *viz.* natural and synthetic, although under some doctrines there is a perception of semi-synthetic polymers, in the latter the monomeric chains come from extracts of natural origin, but the polymers obtained are given by radical substitution in the polymerization reactions [4].

Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources [5]. Biodegradation of polymers occurs mainly due to the breaking of bonds by hydrolysis or enzymatic action leading to erosion of the polymer

[6]. Biodegradable polymers, such as starch and cellulose, have gained a lot of space in secondary polymer synthesis by modifying and improving their processes, for example, the production of green polyethylene, polyvinyl chloride and other green plastics [7].

The species *Calamagrostis intermedia* is a perennial herb, endemic to the Andean highlands that forms dense clumps, groups of 10 to 100 cm in height. The stems are erect rhizomes, herbaceous, round and short with absent stipules. It has a single leaf; ligule 7-11 mm long; linear, completely involute, usually as long as sugar cane that supports the inflorescence so that it is hard, erect and hairless with inconspicuous parallel veins [8].

Within the cellulosic family, cellulose acetate is prepared by mixing cellulose with acetic anhydride and a solution of acetic acid and sulfuric acid as a catalyst. The sulfuric acid reacts with the acetic anhydride to form acetylsulfuric acid [9]. During the acetylation process, both sulfuric acid and acetylsulfuric acid react with cellulose to form an acid ester of cellulose sulfate [10]. Most of the sulfate groups are replaced by acetyl groups during the acetylation process. This mixture is left to react until the three hydroxyl groups have been substituted

by the acetyl groups. In next step, the hydrolysis is carried out to remove the acetyl and sulfate groups under controlled conditions of time, temperature and acidity [11]. This helps to improve the physical properties of cellulose acetate. The hydrolysis process also removes the combined acid sulfate ester and thus improves thermal stability [12]. In addition, the cellulose can be pre-treated with water or acetic acid to obtain a faster and more uniform ester [13]. This pretreatment swells the fiber and thus reduces intramolecular hydrogen bonds. The acetylation rate of pre-swollen cellulose is about three times higher than that of unswollen cellulose. It also makes them accessible to the esterifying mixture and thus increases their reactivity. The cellulose acetate obtained is generally used in films and sheets [14,15].

On the other hand, cellulose nitrate is produced by preparing a sulfonitric mixture with concentrated sulfuric and nitric acid, this nitrifying mixture allows the substitution of hydroxyl groups by nitro groups in the natural polymer [16]. The nitro-cellulose can take various physical forms, from white fibers to thin sheets and thick liquids. Nitrocellulose can also be a white, yellow or transparent plastic. Its rigidity varies from brittle to flexible [17]. The unique properties allow nitrocellulose to now be used in a wide variety of products. The variability in physical properties comes from the nitrogen content and determines the use. The hydroxyl group of the glucose units reacts to form membranes and nitrocellulose chains. Therefore, nitrocellulose is a solid fibrous polymer consisting of cellulose ester of nitric acid [18].

Products using nitrocellulose range from a strong, tough plastic to a class B (highly flammable, explosive when confined) unstable explosive material. Major products include smokeless gunpowder, waterproof fuses in pyrotechnics, inks, adhesives, varnishes, resins, lacquer coatings, embedding sections in microscopy, photography and plastics [19]. In this way, the present research work demonstrates the feasibility of synthesis of the semi-synthetic compounds and their characterization based on infrared spectroscopy (FTIR), viscosimetry and optical microscopy, to generate the scientific knowledge for the sake of the environmental problems caused by the use and production of polymers, thus providing a new renewable source for the synthesis of these compounds [20].

EXPERIMENTAL

Cellulose extraction: An alkaline method was used for the extraction, because it does not require prior degreasing, so 100 g of sample were collected in the Condor Chamana sector of Urbina parish, belonging to the Guano canton in the province of Chimborazo, Ecuador, at an altitude of 4140 m at coordinates 1°28'13.225"S, 78°45'1.001"W. The collected sample was sent to QAP Herbarium of the Central University of Ecuador for the botanical identification while the sample collection was performed following the guidelines for sampling and analysis of plant matter reported by the National Institute of Forestry, Agricultural and Livestock Research, belonging to the Federal Government of Mexico [21]. For the experimental part, three replicates were performed to confirm the validity of the experimental data, thus in 500 mL of 10% NaOH solution. The beaker

with the glass-rod containing solution was placed on a heating plate, the heating was stabilized when the first boiling bubble appeared and a boiling was carried out for 10 min at 90 °C. It was left to cool for 20 min at room temperature. It was washed and filtered with sufficient distilled water until reaching a pH of 7. The washed sample was dried at 65 °C until the weight become constant. Sufficient amount of 4% sulfuric acid solution was added to cover the dried sample and then boil the solution on a hot plate at a constant temperature for 1 h, after which time the mixture was allowed to cool to room temperature. It was washed and filtered again with sufficient distilled water until reaching a pH of 7.

The washed sample was immersed in a 3.5% solution of sodium chlorite and left for untouched for 3 h, then it was placed on a water bath at 95 °C for 40 min. It was allowed to cool, washed and filtered with distilled water until the solution become pH of 7. The washed sample was dissolved in a minimum amount of 20% NaOH solution and placed on a magnetic stirrer with constant agitation for 1 h. The washed sample was washed and filtered with sufficient distilled water to pH 7. The washed sample was dissolved in 0.5% sodium chlorite solution, placed on a magnetic stirrer with constant agitation for 1 h. It was then washed and filtered with distilled water to a pH of 7. The washed sample was dried at 65 °C until the weight was constant. Finally, the weight of the extracted dry cellulose was recorded.

Preparation of cellulose acetate: Cellulose (2 g) were placed in 100 mL of glacial acetic acid and acetic anhydride (4:6) and then 0.5 mL of 95% sulfuric acid was added. The mixture was subjected to constant stirring at medium speed on a magnetic stirrer for 15 min and then the mixture was placed in a microwave for 10 s and stirred slowly, repeating this step until 2 min, then allowed to cool to room temperature followed by the addition of 100 mL of ice-cold distilled water was added. The mixture was then filtered and the precipitate was washed with distilled water to pH 7. The washed and filtered precipitate was dried at 60 °C to a constant mass.

Characterization of cellulose acetate

Molecular weight determination: The determination of the molecular weight was carried out by viscosimetry using an Ostwald viscometer, in brief, 0.035 g of cellulose acetate was placed in a 50 mL volumetric balloon, enough acetone was added to prepare solutions with concentrations of 0.1; 0.3; 0.5; 0.7 g/L. To calibrate the equipment, 15 mL of acetone standard for the Ostwald viscometer was placed maintaining at 30 °C, then 15 mL of solution prepared separately in the Ostwald viscometer maintaining the same temperature and the time it takes to travel through the capillary of the equipment was recorded.

Preparation of cellulose nitrate: In a beaker 50 mL of concentrated nitric acid was placed in an ice bath, until reaching 8 °C at this point was added dropwise with agitation 40 mL of conc. sulfuric acid. The mixture was left untouched at room temperature until reaching 18 °C, to this mixture was added 1 g of cellulose and placed in a stirring plate at medium speed during 2 h at 40 °C, then it is left in rest until reaching room

temperature. Addition of 100 mL of distilled water results in the generation of a precipitate, which was filtered and washed until reaching pH 7 and finally dried at 60 °C until obtaining a constant mass.

Optical microscopy: Cellulose acetate/nitrate (1 g) and acetone (1 mL) were mixed to form a solution at a cellulose acetate-acetone interface, which was dried at room temperature until all the contained acetone evaporates, then placed a drop of the residual on a plate covered by a cover slip and analyzed by optical microscopy in 20, 40 and 80 X lenses.

FTIR analysis: Cellulose acetate/nitrate (2 g) was placed in a mortar and ground to a homogeneous particle size, the solid sample was placed in a JASCO FT/IR-4100 typeA IR spectrophotometer and analyzed in the range 4000 to 600 cm^{-1} . The spectral lines were reported in the Spectral Manager software.

RESULTS AND DISCUSSION

The cellulose extracted from the plant species containing hydroxyl (OH) groups, which results in the formation of hydrogen bonds between the cellulose molecules, making the cellulose unable to soft with heat or dissolve with solvents without causing the chemical decomposition. However, after treatment with nitric acid in presence of sulfuric acid as a catalyst and water, the -OH groups are replaced by nitro groups (-NO₂) (Fig. 1). The degree of nitration determines the solubility and flammability of the final product, hence the importance of FTIR analysis as part of the characterization, since it will show the level of substitution in the original polymer chain.

Fig. 2 shows the synthesis of cellulose acetate began with the activation of regenerated cellulose by glacial acetic acid. During the activation process, the cellulose structure swelled and thus the intermolecular hydrogen bonds decreased. Therefore, cellulose reacted more easily and attached acetyl groups during the acetylation process. When acetic anhydride and sulfuric acid were added as catalyst, acetylation occurs to form acetyl sulfate, then reacts with the cellulose to produce cellulose acetate in the solid phase.

Molecular weight: Table-1 shows the different concentrations of cellulose acetate, considering that the first is the solvent standard with the calibrated equipment, in this way it is possible to calculate based on the time and the standard the different viscosities. Fig. 3 shows the approximation of the concentration and the reduced viscosity when the concentration tends to zero. Therefore, a value has been determined $[\eta] = 385$, now the value of K is $16 \times 10^{-3} \text{ g/mL}$ and a value α of 0.82 [15] at 30 °C, for such a molecular weight of $220.34 \times 10^3 \text{ g/mol}$ weight that is consistent with the reported value [22].

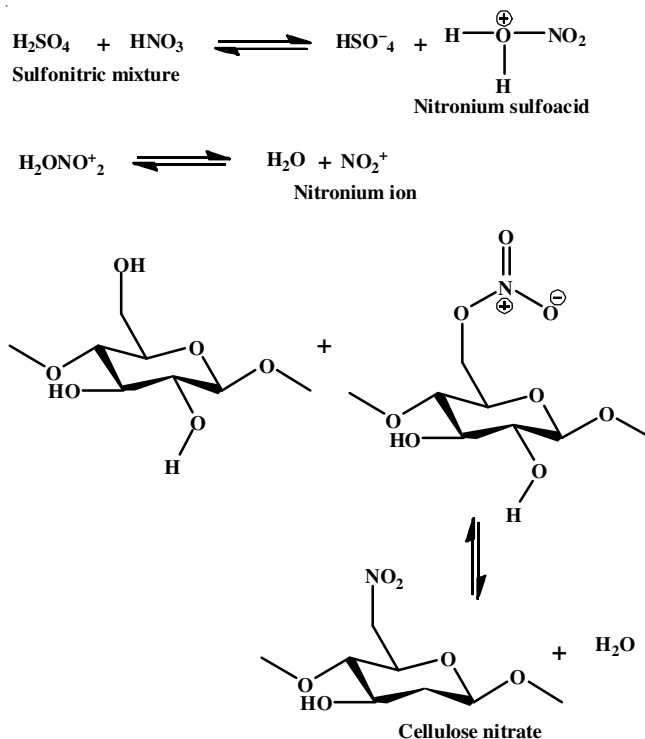


Fig. 1. Synthetic route of cellulose nitrate

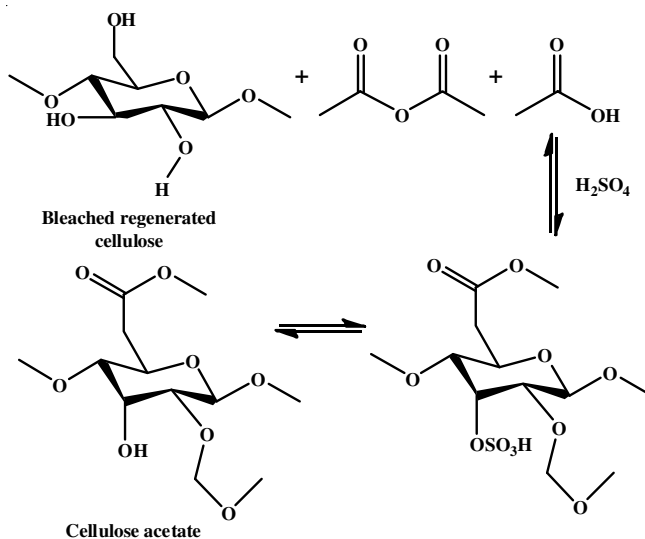


Fig. 2. Synthetic route of cellulose acetate

Optical microscopy: Fig. 4 shows scattered crystalline regions in the sample and polymeric formation of said networks, as well as an amorphous structure dispersed throughout the sample area, which is almost similar to the earlier reports [23-25].

TABLE-1
DETERMINATION OF VISCOSITIES FOR CELLULOSE ACETATE

Test	Concentration (mol/L)	Time (s)	Relative viscosity (t/t_0)	Specific viscosity ($\eta_{\text{rel}}-1$)	Reduced viscosity ($\eta_{\text{sp}}/\text{concentration}$)
1	0	8	x	x	x
2	0.00202	14	1.75	0.75	371.287129
3	0.00606	24	3.00	2.00	330.033003
4	0.01012	32	4.00	3.00	296.442688
5	0.01420	36	4.50	3.50	246.478873

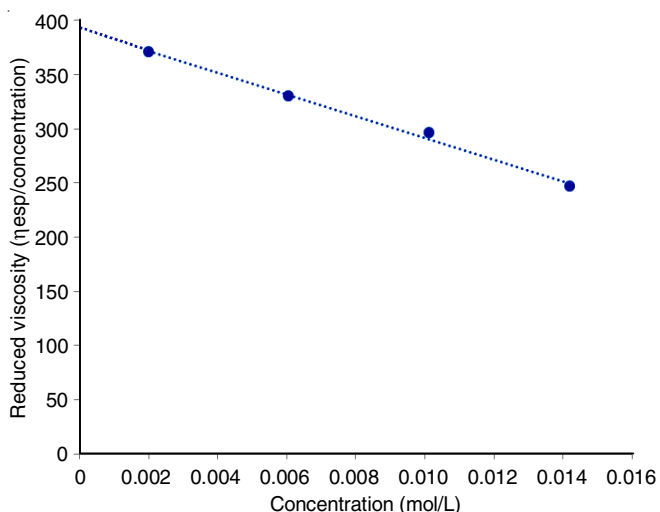


Fig. 3. Determination of reduced viscosity for cellulose acetate

Yield of the products: Table-2 shows the values of the masses corresponding to the extracted cellulose used for the synthesis of cellulose acetate/nitrate, as well as the masses after washing, pH regularization and the corresponding drying at constant temperature until obtain a variable weight, in this way the weight yield obtained for the synthesis corresponds

to the ratio between the mass of starting cellulose and the dry mass in a ratio of 100 parts. While a value of 74.62% was obtained for cellulose nitrate, which is interpreted as an increase in mass in the sample due to the addition of synthetic functional groups of the nitro group and polymerization of the cellulose chains. Analogously in cellulose acetate 68.49% yield was obtained, it should be considered that the difference between the yield percentages in the synthesis of nitrate and cellulose acetate are due to the use of volatile compounds such as acetic acid and acetic anhydride.

FTIR studies: Based on the similarity of wavenumbers, it was possible to determine that the analyzed sample corresponds to cellulose acetate/nitrate. Fig. 5 shows the characteristic vibrations of each functional group which confirmed the formation of the cellulose acetate/nitrate and the wavenumbers of the peaks are compared with those reported in a similar study (Table-3) [9,26-28].

Optical studies: The optical microscopic images of the prepared cellulose nitrate are shown in Fig. 6, where a semi-uniform film with an amorphous texture is observed using the 20X magnification. However in 60X magnification, the arrangement of microparticles in the film is observed due to the formation of a crystalline network transparent or whitish, which is similar to the earlier report [19].

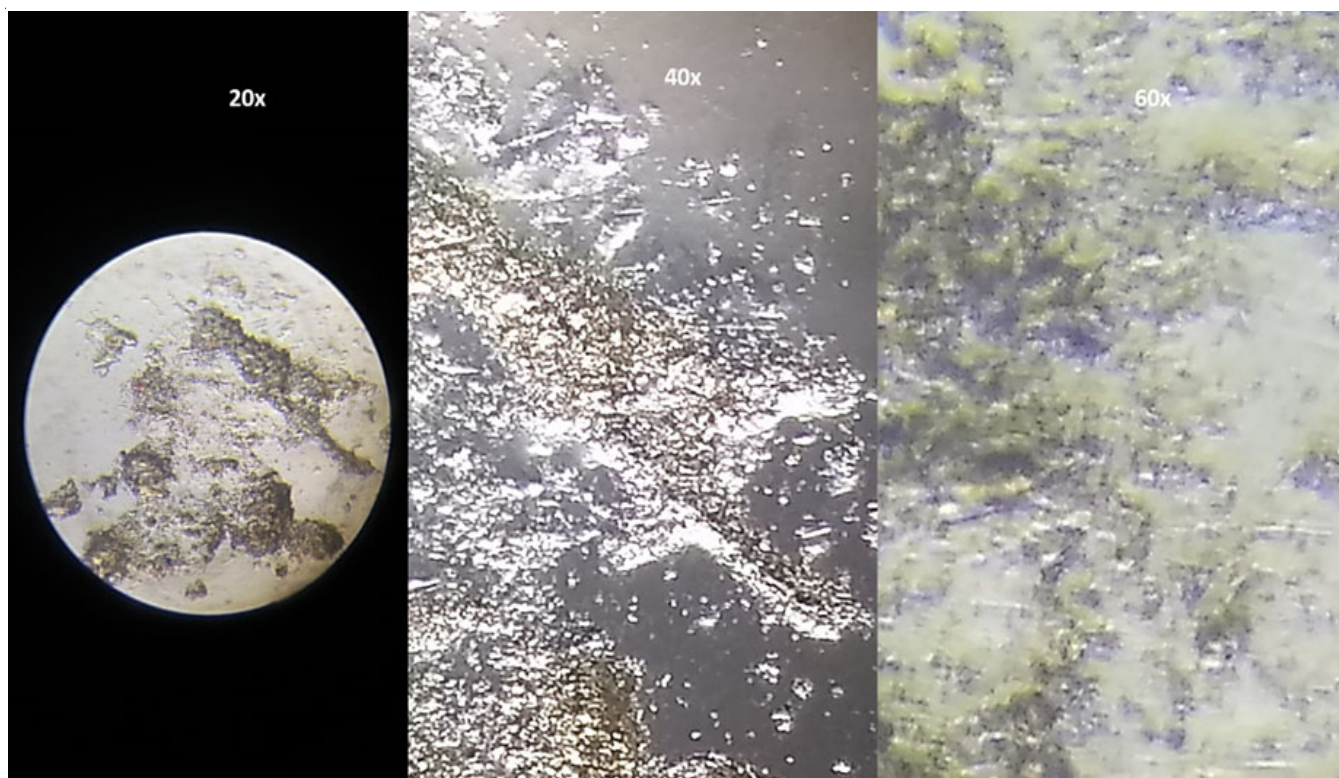


Fig. 4. Light microscopy of cellulose acetate

TABLE-2
MASS YIELD OF SYNTHESIS REACTIONS

	Cellulose mass before synthesis (g)	Sample mass after washing (g)	Sample mass after drying (g)	Mass difference due to drying (g)	Weight yield (%)
Cellulose nitrate	1	3.12	1.34	1.78	74.62
Cellulose acetate	2	4.81	2.92	1.89	68.49

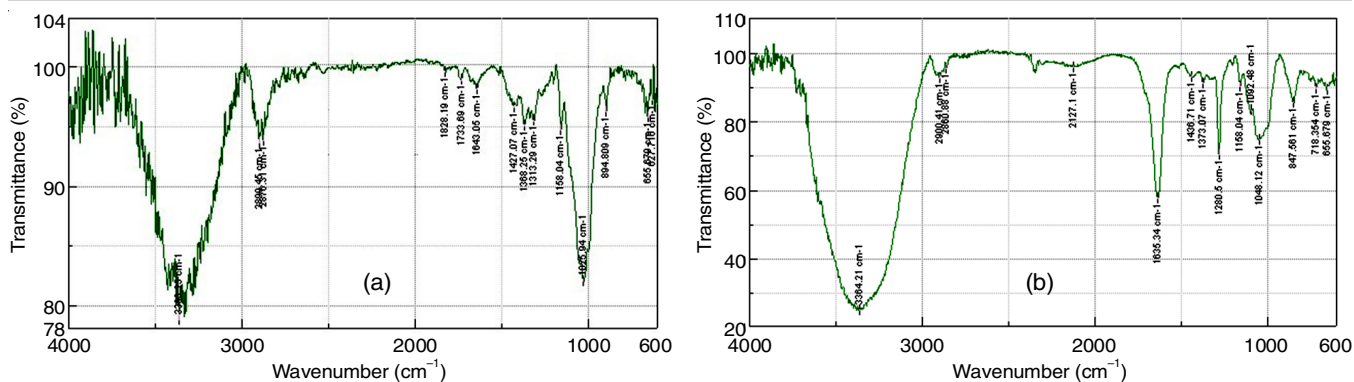


Fig. 5. FTIR analysis of (a) cellulose acetate and (b) cellulose nitrate

TABLE-3
INTERPRETATION OF FTIR RESULTS CELLULOSE NITRATE AND CELLULOSE ACETATE

Cellulose nitrate				Cellulose acetate			
Observed wavenumbers (cm ⁻¹)	Peak assignment	Functional group and vibration	Reported wavenumbers (cm ⁻¹) [20]	Observed wavenumbers (cm ⁻¹)	Peak assignment	Functional group and vibration	Reported wavenumbers (cm ⁻¹) [26]
3364.21	OH	Hydroxyl Stretch	3480	3363.25	OH	Hydroxyl Vibration	3376
2900.41	C-H	Anti symmetrical stretch CH in CH, in the cellulosic backbone	2905	2899.45	C-H	CH vibration in cellulosic backbone	2902
2860.88	C-H	Anti symmetrical stretch CH in CH, of ethoxy groups	2870	1733.69	C=O	Cellulose acetate functional group stretching, carbonyl ester	1753
1635.34	NO ₂	Antisymmetric stretch nitro groups	1650	1643.05	C=C	Anti symmetric and peak stretch C=C	1631
1436.71	CH ₂	Deformation CH, in the cellulosic backbone	1460	1427.07	CH ₂	Vibration CH ₂	1428
1373.07	C-H	Deformation CH in the cellulosic backbone	1375	1025.94	C-O	Vibration C-O	1041
1280.5	NO ₂	Stretch nitro groups	1280	627.716	O-.C-C	C-O stretching of the acetyl group	607
1158.04	C ₅ OCOC ₄	Acetal structure of polysaccharides	1160				
847.561	NO	Stretch nitro groups	897				
718.354	NO ₂	Deformation nitro groups	750				
655.679	NO ₂	Deformation nitro groups	690				



Fig. 6. Light microscopy of cellulose nitrate

Conclusion

The semi-synthetic compounds cellulose acetate and nitrate were prepared from the cellulose extracted from the *Calamagrostis intermedia* and characterized by FTIR analysis. The optical microscopy exhibited the uniform crystalline regions, a polymeric formation of said networks and the arrangement of microparticles in the film forming a transparent or whitish crystalline network, as well as an amorphous structure dispersed throughout the sample area. The molecular weight of cellulose acetate (220.34×10^3 g/mol) was obtained using viscosimetry considering the fact that it is not possible to determine the cellulose nitrate derivatives using viscosimetry analysis, since no constant values are yet reported using Mark-Houwink equation. A yield of 74.62% and 68.49% by weight was determined for the synthesized cellulose nitrate and cellulose acetate, respectively. The results show the efficiency of the applied methodology and revealed the feasibility of using a cellulosic species which does not come from wood or trees, thus contributing to the mitigation of the environmental impact caused by deforestation.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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