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Escuela de Ciencias Biológicas e Ingeniería

TÍTULO: Dissolution and regeneration of cellulose from different sources in an NaOH/urea aqueous system

Trabajo de integración curricular presentado como requisito para la obtención del título de ingeniería biomédica

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Dedication

I dedicate this work to my parents, Gladis and Francisco, for their unconditional support, for showing me the way to overcoming and for having forged me as the person I am today.

To my sisters, for believing in me and for protecting me even when I no longer needed it.

To my friends and loved ones, for their support and for having made more pleasant the course of my university career.

To all of you, I hope not to disappoint you and always count on your valuable support, sincere and unconditional. I could not have done it without them.

Dedico este trabajo a mis padres, Gladis y Francisco, por su incondicional apoyo, por mostrarme el camino hacia la superación y por haberme forjado como la persona que soy hoy.

A mis hermanas, por creer en mí y por protegerme aun cuando ya no lo necesitaba.

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Nigel Francisco Haro Sisa

Resumen

La celulosa es uno de los polímeros naturales más abundantes del mundo que recientemente ha llamado la atención de investigadores ya que es renovable, biodegradable, biocompatible y no tóxico, por lo tanto, puede ser utilizado como un material sostenible para la creciente demanda de productos ecológicos. Ecuador, que tiene una gran biodiversidad vegetal, tiene una amplia variedad de plantas fibrosas de donde se puede extraer celulosa para su uso en aplicaciones como, películas de celulosa regenerada (CR) útiles para la industria, así como para el campo de la ingeniería biomédica. Debido a sus propiedades resistentes a los solventes, es difícil disolver la celulosa. Sin embargo, dentro de la variedad de solventes de celulosa; el hidróxido de sodio (NaOH) es uno de los más utilizados puesto que es un solvente simple, económico y amigable con el medio ambiente. Junto con aditivos, como la urea, puede mejorar la solubilidad de la celulosa. Este trabajo se centró en 1) la disolución de diferentes fibras de celulosa natural, así como la celulosa de tipo industrial en una solución acuosa de NaOH / urea; 2) la fabricación de películas CR. Se varió sistemáticamente las concentraciones de solvente, las concentraciones de celulosa y los diferentes medios de coagulación para optimizar el proceso de disolución con el fin de mejorar la integridad y la morfología de las películas regeneradas. Aunque no fue posible fabricar películas a partir de todas las muestras de celulosa que se estudiaron, se descubrió que las mejores películas se obtuvieron a partir de una concentración de disolvente de 14% en peso de NaOH / 24% en peso de urea, una concentración de celulosa de 5,7% en peso y la regeneración a partir de un baño de coagulación en etanol al 80% en volumen.

Palabras clave: solvente de celulosa, NaOH / urea, películas de celulosa regenerada, fibras de celulosa, biodiversidad.

Abstract

Cellulose is one of the most abundant natural polymers in the world which has recently attracted the attention of researchers due to it is renewable, biodegradable, biocompatible, nontoxic and hence it serves as a sustainable material for the increasing demand of green products. Ecuador, which has a great biodiversity of plants, has a wide variety of fibrous plants from which cellulose can be extracted for use in different applications, such as films of regenerated cellulose (RC) for industry as well in the field of biomedical engineering. Due to its solvent resistant properties, it is hard to dissolve cellulose. However, within the variety of cellulose solvents; sodium hydroxide (NaOH) is one of the most commonly used due to the fact it is a simple, inexpensive and environmentally friendly solvent. Together with additives, such as urea, it can enhance the solubility of cellulose. This work focused on 1) the dissolution of different natural cellulose fibers as well as industrial type cellulose in NaOH/urea aqueous solution and 2) the fabrication of RC films. It was systematically varied the solvent concentrations, cellulose concentrations and different coagulation media in order to optimize the dissolution process in order to improve the integrity and morphology of the regenerated films. Although it was not possible to fabricate films from all the cellulose samples that were tested, it was found that the best films were obtained from a solvent concentration of 14 wt% NaOH/ 24 wt% urea, cellulose concentration of 5.7 wt% and regeneration from a coagulation bath in 80 v% ethanol.

Keywords: Cellulose solvent, NaOH/Urea, regenerated cellulose films, cellulose fibers, biodiversity.

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Problem Statement

The growing demand for biodegradable and environmentally friendly materials has awakened interest of scientists for the use of renewable raw materials. Ecuador, is a country whose economy is based mostly in the agricultural sector (Banco central del Ecuador, 2019). According to the data from the “Instituto Nacional de Estadísticas y Censos (INEC)” in its agricultural statistics visualizer, “Encuesta de Superficie y Producción Agropecuaria Continua (ESPAC)”, Ecuador has around 5.3 million hectares dedicated to the agricultural work, from which, permanent crops represent 26.2% and transient crops represent 15.1% of the surface with agricultural work. For these reason, Ecuador is a source of a wide variety of plants from which, cellulose fibers which can be extracted from plants, fruits, as well as from the generated agroindustrial wastes which can serve as a raw material for the development of new technologies. However, this material is wasted since the residual biomass is not properly disposed after its primary extraction. This represents a problem due to the accumulation of large quantities of this solid waste as it could attract rodents and insects that cause diseases since the degradation of these materials is slow. On the other hand, although a small part of the residual biomass is used for animal feeds, most of it is burned, which produces particles and emissions into the atmosphere that contribute greatly to environmental pollution. For this reason, research is needed in the processing of these agroindustrial wastes in order to find applications and gives an added value to natural fibers which could constitute an economic contribution to the country besides generating new sources of employment.

Hypothesis and Specific Objectives

Hypothesis

Regenerated cellulose films obtained from extracted cellulose fibers are equal in morphology and resistance to those obtained from industrial type cellulose.

Specific Objectives

- Extract natural cellulose fibers from different sources of plants, fruits and agroindustrial wastes.
- Determine the concentration of solvent capable of generating a homogenous and transparent cellulose solution.
- Regenerate cellulose fibers in the form of a thin film with good optical and mechanical properties.

Chapter I

Introduction

1.1. Justification

Ecuador is one of the countries with the largest biodiversities in the world, both in flora and fauna. Within its 283 561 km², it houses around 11% of vertebrate animals and 6.4% of plants of the world (Bravo, 2014; Estrella, Manosalvas, Mariaca, & Ribadeneira, 2005). Hence, the Ecuadorian flora is immensely rich. According to the Ecuadorian Ministry of Environment (2013), it has been estimated that there are around 18 000 species of vascular plants, which are scattered in the different climatic regions of Ecuador. This vast biodiversity is due in part to the different climatic regions of Ecuador, which influences the structure, shape and properties of the plants (Kicińska-Jakubowska, Bogacz, & Zimniewska, 2012; Kozłowski & Mackiewicz-Talarczyk, 2012). For this reason, there is a potential field of natural fiber production in Ecuador because of its biological wealth since it is possible to find a wide variety of plant fibers with different structures and chemical compositions.

1.2. Background

Cellulose is the most abundant polymeric material in the biosphere, made of a long chain of linked α-1,4- D-glucose rings. Most of this inexhaustible natural polymer exist in the form of natural fibers. These fibers can be produced in Nature by plants, animals and via geological processes.

1.2.1. Natural fibers

The overall accessibility of natural fibers and other amply available agrowaste inspires the new enthusiasm for research in maintainable innovation. Around the world, tons of agricultural crops are produced daily, resulting from corn, banana, bagasse and grass. Although some of these wastes are used as livestock feed, the rest is burned, which contributes to environmental contamination (Thomas, Paul, Pothan, & Deepa, 2011). For this reason, the efforts to find applications to these wastes have been intensifying over the last few years. Some applications have already been developed, such as in packaging, building, automobile, aerospace, electronics, leisure and household (Kozłowski & Mackiewicz-Talarczyk, 2012).

Natural fibers are abundant and possess certain advantages, such as low density, high toughness, relatively high specific strength/stiffness properties, low abrasiveness, low energy consumption in fabrication, and CO_2 neutrality; these unique features have led to research in the replacement of synthetic fibers with natural fibers (Bhattacharyya, Subasinghe, & Kim, 2015). Within the vast variety of natural fibers that exists, a classification can be made based on the source, plants, animals and mineral, as shown in figure 1.1. Plant fibers, also named lignocellulose fibers, are mainly composed of cellulose fibers and lignin matrix, they are widely used as reinforcement for fiber composites. This type of fibers can be found in bast (or stem or sclerenchyma) fibers, leaf or hard fibers, seed, fruit, wood, cereal straw, and other grass fibers. (Akil et al., 2011; Bhattacharyya et al., 2015; Kozłowski & Mackiewicz-Talarczyk, 2012; Thomas et al., 2011).

On the other hand, animal fibers can be classified into two groups depending on the protein on which they are based: α-keratin fibers (hair, wool and leather) and fibroin fibers (silk and spider web). Finally, the fibers produced by mineral sources are mainly composed of asbestos and have a highly crystalline structure that differentiates them from animal and plants fibers. However, despite having great mechanical properties and being highly resistant to fire, their use has been limited as they represent a high risk to human health (Bhattacharyya et al., 2015). Nonetheless, the present work is exclusively focused on the main component of plant fibers.

1.2.2. Plant fibers

Nature, in its abundance, offers numerous fibrous plants that grow in multiple climatic zones. As a result of this, a great variety can be found in the physical and chemical morphology of these natural fibers, as well as in the growth of the cell wall, the patterns and the thickness, the dimensions and the shape of the cells, the cross-section forms, the distinctive character of the lumens, in addition to their chemical compositions (Thomas et al., 2011). This, in turn, influences the properties of each fiber, which allows the development of a wide variety of fibers of diverse structure and composition, resulting in different levels of cellulose, crystallinity, morphology and, therefore, different properties that characterize each of the fibers. In addition, the use of some plant fibers plays as a circle of renewable resources since their cultivation, extraction and processing, until the disposal of these materials; these fibers are immersed in various stages that form a life

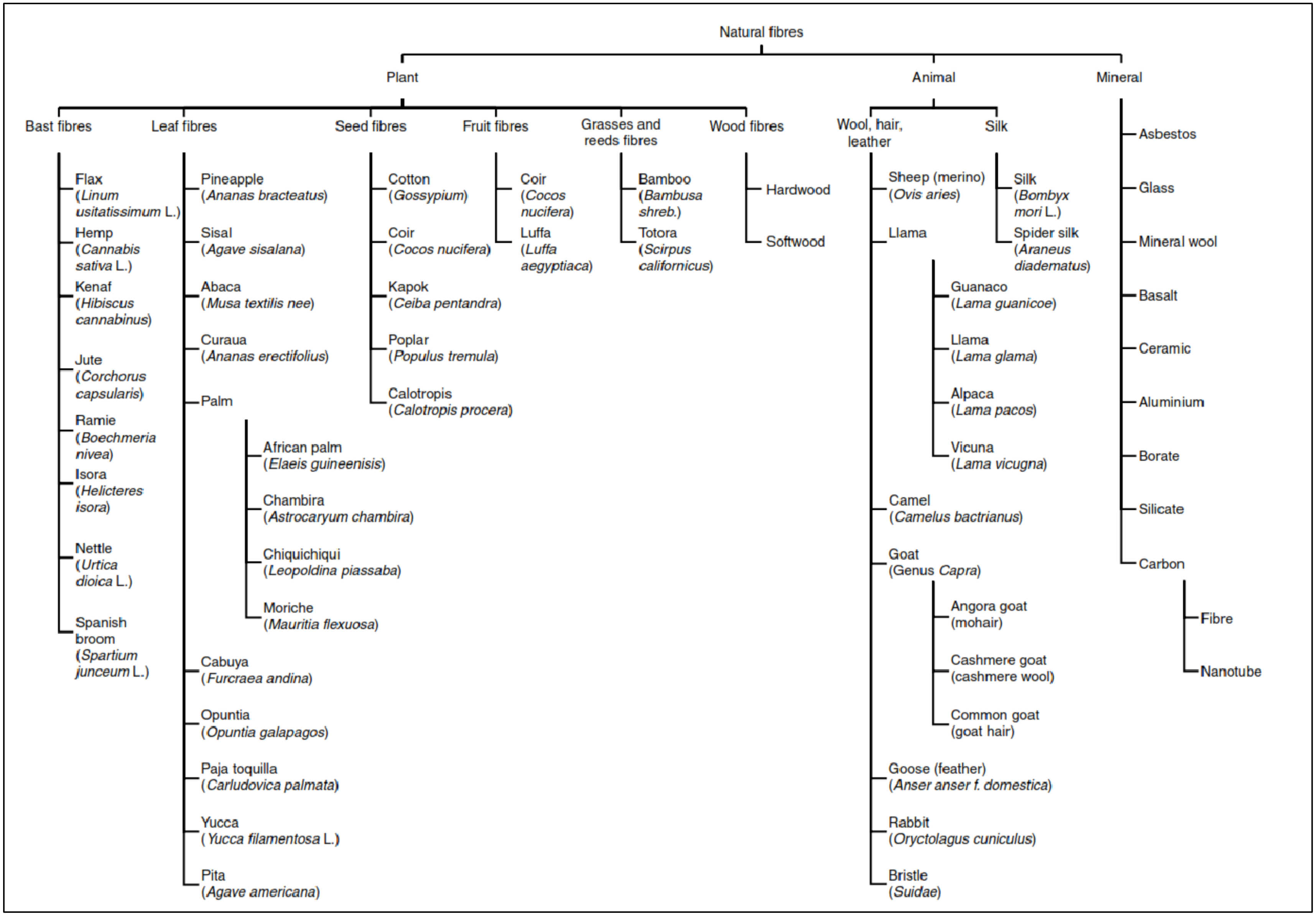

Figure 1.1 Classification of natural fibers. Image extracted from: Kozłowski R. Handbook of natural fibres. 1st ed. Oxford: Woodhead Pub.; 2012.

cycle (Fig. 1.2). This is what makes them interesting: the great biodiversity and availability of natural fibers with specific properties can be used in different applications in industry, medicine or research.

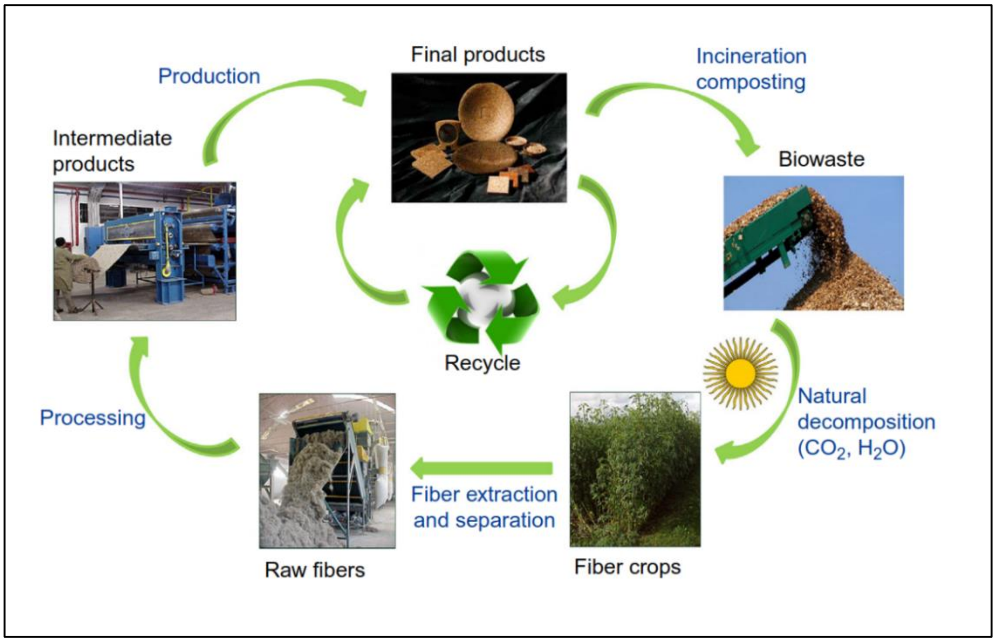

Figure 1.2 Life cycle of natural fibers. Image extracted from: Bhattacharyya D, Subasinghe A, Kim N. Natural fibers: Their composites and flammability characterizations. 2019.

1.2.2.1. Structure

The general structure of plant fibers consists of hemicellulose, lignin, pectin, and other waxy substances. The major component of plants, cellulose, is present in the cell walls (fig. 1.3) (Ahuja, 2016; Akil et al., 2011; Bhattacharyya et al., 2015; Kozłowski & Mackiewicz-Talarczyk, 2012; Thomas et al., 2011; Thygesen, Oddershede, Lilholt, Thomsen, & Ståhl, 2005). A typical plant cell is 1 to 50 mm in length and 10 to 50 µm in diameter. Several plant cells are embedded in a matrix of hemicellulose-lignin with cell walls made of semicrystalline cellulose microfibrils. These cell walls can be differentiated between the primary and secondary cell wall. They differ in their composition, the proportion among cellulose and lignin/hemicellulose, and the orientation or spiral angle of the cellulose microfibrils (Thomas et al., 2011).

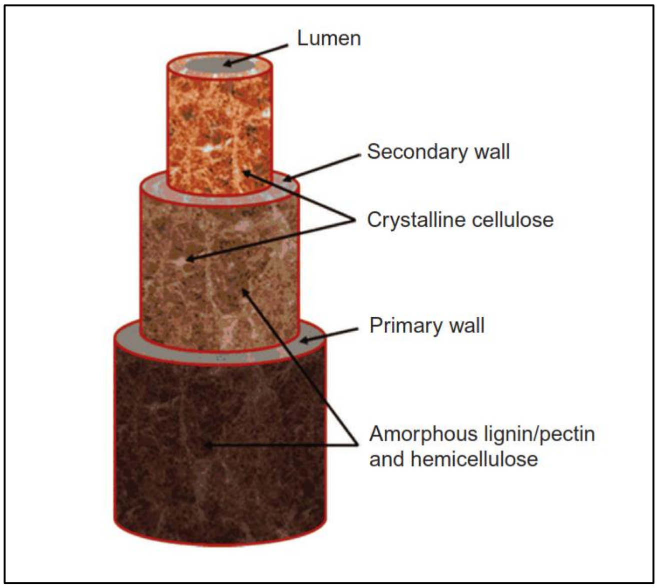

Figure 1.3 Structure of a plant fiber. Image extracted from: Thomas S, Paul S, Pothan L, Deepa B. Natural Fibres: Structure, Properties and Applications. Cellulose Fibers: Bio- and Nano-Polymer Composites. 2011:3-42.

1.2.2.2. Chemical composition

The chemical composition of natural fibers is complex due to the different environmental conditions which influence the development of plants and their fibers (Komuraiah, Kumar, & Prasad, 2014). For this reason, depending on the type of fiber, the chemical composition of these fibers varies. This is important because depending on the properties of each compound and their quantities, the overall properties of the fiber are affected (Thomas et al., 2011). The highly complex organic matrices of natural fibers are composed of three major components: cellulose, hemicellulose and lignin, along with a small percentage of smaller extractable compounds (pectin and waxes) (Bhattacharyya et al., 2015; Jones, Ormondroyd, Curling, Popescu, & Popescu, 2016; Komuraiah, Kumar, & Prasad, 2014; Kozłowski & Mackiewicz-Talarczyk, 2012; Thomas et al., 2011).

Hemicellulose is the second most abundant compound of vegetable fibers, which, despite its name, differs a lot with respect to cellulose in three aspects. First, they contain several different sugar units, whereas cellulose contains only 1,4-β-D-glucopyranose units. Second, they exhibit a considerable degree of chain branching, whereas cellulose is strictly a linear polymer. Third, the degree of polymerization of native cellulose is 10–100 times higher than that of hemicellulose. Unlike cellulose, the constituents of hemicellulose differ from one plant to another (Thomas et al., 2011).

Lignin is an organic polymer composed of phenyl-propane units, it is amorphous and hydrophobic in nature (Thomas et al., 2011). This polymer is part of the cell walls and, together with other non-cellulose substances, it provides structural support to the plant. It is important in adhesive quality and provides rigidity to plants. Although its mechanical properties do not match those of cellulose, it influences the mechanical properties of the plant (Akil et al., 2011; Jones et al., 2016; Wang, Bai, Yue, Long, & Choo-Smith, 2016).

Pectin is a mixture of acidic and neutral branched polymers which is known as heteropolysaccharides. This material is part of the cell wall and is responsible for giving flexibility to the plant. Waxes make up the rest part of fibers and are the minor constituents in plant natural fibers which consist of several alcohols.

The last component that we will described here is cellulose, the most important and abundant component of natural fibers.

1.2.3. Cellulose

Cellulose is the basic and the most important structural component in all natural fibers because it is the major component of the plant cell walls (Akil et al., 2011; Komuraiah et al., 2014). Furthermore, it can also be found in bacteria, algae, fungi and even animals (Bhattacharyya et al., 2015). It is a long chain polysaccharide consisting of cellobiose units composed of D-anhydroglucopyranose units (AGU) rotated by 180° from each other. These AGUs are connected by β-1,4-glycosidic linkages (fig. 1.4) (Akil et al., 2011; Bhattacharyya et al., 2015). From the number of repeating units, we can obtain the degree of polymerization (DP) of cellulose, which depends on the cellulose sources and the treatment methods of cellulose (Ding, 2011). DP can be useful to determine the size as well as the average molecular weight of the cellulose molecules (by the product of the DP and the molecular mass of a single AGU) (Singh et al., 2015).

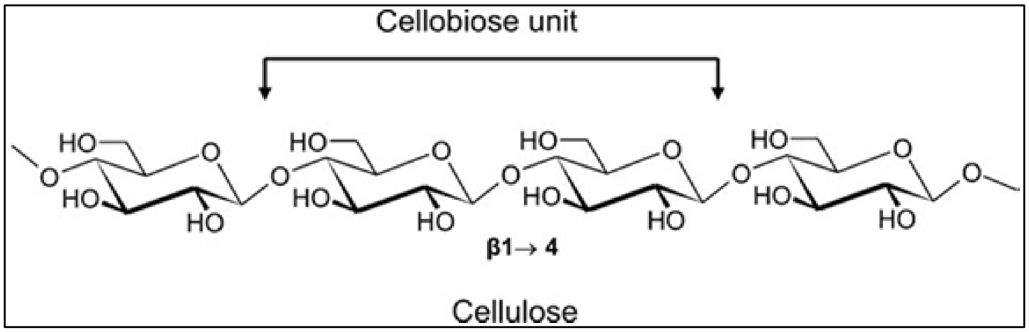

Figure 1.4 Cellulose chemical structure showing a cellobiose repeat unit composed of two anhydroglucose units joined together by β-1,4-glycosidic linkages. Image extracted from: Chhabra N. Biochemistry for Medics - Lecture Notes [Internet]. Biochemistry for Medics – Lecture Notes. 2019 [cited 9 April 2019]. Available from: http://www.namrata.co

Each AGU comprises three hydroxyl groups, causing cellulose to be hydrophilic, two primary and one secondary, without taking into account the terminal ends where a second secondary hydroxyl group is present on C1 (reducing end) and on C4 (non-reducing end) (Singh et al., 2015) (fig. 1.5). Due to the multiple hydroxyl groups in the repeating units, a large quantity of strong intra- and inter-molecular hydrogen bonds exists on the same or an adjacent chain, holding the chains firmly alongside each other (Ding, 2011; Haslinger, 2018; Singh et al., 2015; L. Zhang, Ruan, & Zhou, 2001). Thus, microcrystalline structure with regions of high order (crystalline regions) are formed. However, this natural polymer is also formed for regions of low order (amorphous regions), which also influences the properties of cellulose (Thomas et al., 2011).

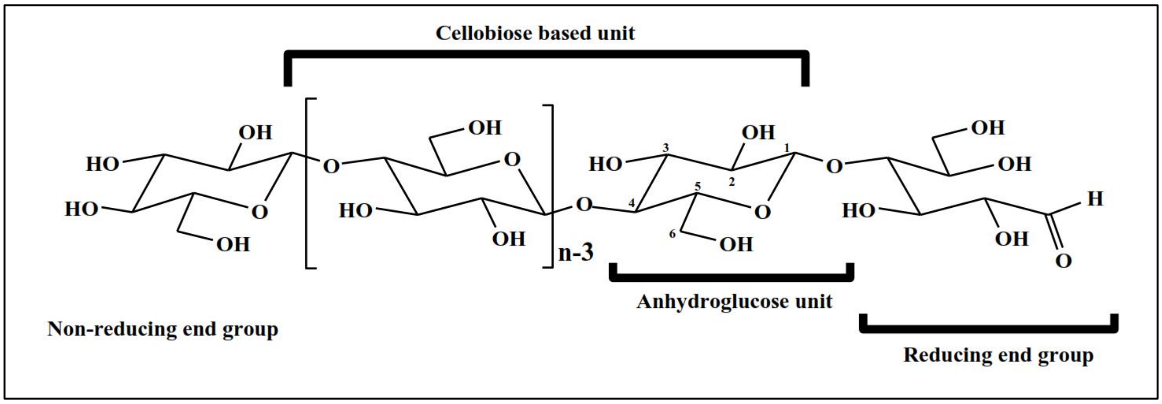

Figure 1.5 D-anhydroglucopyranose units (AGU), connected by β (1–4)-glycosidic bonds. Image extracted from [14]

1.2.4. Cellulose Dissolution

Due to the intra- and inter-molecular hydrogen bonds, cellulose has a very poor solubility in most solvents hindering the processing of this material. For this reason, there has been increased efforts in the research of different solvents in order to obtain a stable homogeneous cellulose solution. However, a limited number of solvent systems have been used to dissolve cellulose, which include, N,N-dimethylacetamide (DMAc)/LiCl, NaOH/urea, dimethyl sulfoxide (DMSO)/tetrabutylammonium fluoride, N-methylmorpholine-N-oxide (NMMO), N-methyl morpholine N-oxidewater, liquid ammonia-ammonium thiocyanate-water, LiCl-1,3-dimethyl-2-imidazolidinone (DMI) and a few others (Liu et al., 2011; Lu, 2017; Roman, 2009; Zhang et al., 2001). Nonetheless, among all the mentioned solvents, the NaOH/urea system is widely used as the processing occurs at low temperatures and allows a fast and efficient dissolution of cellulose (Li, Wang, Lu, & Zhang, 2015; Lu, 2017; Miyamoto, Yamane, Seguchi, & Okajima, 2009; Singh et al., 2015; L. Zhang et al., 2001; Zhang, Mao, Zhou, & Cai, 2005; Zhou, Zhang, Cai, & Shu, 2002). Besides, this system offers certain advantages with respect to other solvents, such as low cost, simplicity and friendly to the environment (Bhatt, 2012; Qiu et al., 2018; Roman, 2009; Yang, Miyamoto, Yamane, & Okajima, 2007). Therefore, it is possible to dissolve cellulose in order to prepare regenerated cellulose (RC) films. The importance of studying RC films/membranes resides in the fact that they have potential applications in the industry, such as microfiltration, packaging and food processing (Lu & Wu, 2008; Roman, 2009; Xu & Chen, 1994; Zhang et al., 2005) as well as in the field of biomedical engineering and medicine due to their biocompatibility, biodegradability and chemical stability for applications in dialysis, artificial kidneys, hemodialysis, drug delivery systems, organic solvent filtration, protein separation and pharmaceutical processes (Ali, 2013; Lu & Wu, 2008; Roman, 2009; Zhang et al., 2005; Zhou, Zhang, Cai, et al., 2002).

Chapter II.

Methodology

The experimental part, material preparation for natural cellulose fibers extraction and films preparation are described in this chapter.

2.1. Materials

As mentioned earlier, Ecuador has a wide biodiversity of plants. Moreover, some of these plants generate agroindustrial waste after their fruit is used or after having undergone a primary extraction. For this reason, eleven different types of sources were selected to extract cellulose fibers, including fruits (F1, F7, F17, F19, F28), agroindustrial residues (C1, BS) and plants for their content of cellulose fibers (F20, C2, FB, FS). In addition, six different types of cellulose of industrial type were used as a control group, cellulose type 20 (T20), cellulose type 50 (T50), cellulose type 101 (T101), cellulose fibers medium (TM), international cellulose (TI) and commercial cellulose (CC) from Sigma Aldrich, this last sample was used for the first experiments in order to find the best conditions for making films.

Table 2.1 Cellulose samples from different sources

Industrial type Cellulose	Cellulose fibers from fruits	Cellulose fibers from plants	Cellulose fibers from agroindustrial waste
T20	F1	F20	C1
T50	F7	C2	BS
T101	F17	FB	
TM	F19	FS	
TI	F28		
CC			

In the following sections, the corresponding label is used to refer to each type of sample.

Sodium hydroxide in pellets (NaOH) from Sigma Aldrich and urea (CH_4N_2O) from Fisher Scientific were used to prepare an aqueous solution in order to dissolve the cellulose. Ethanol

(99.9%), isopropanol (99.9%) and sulfuric acid (97%), obtained from Merck, were used as coagulants. Ethanol was diluted to 80 v% and sulfuric acid to 5 v%, isopropanol was used as received (for practical purposes its purity was rounded to 100%); Distilled water was used for the washing bath.

2.2. Methods

The first experiments were carried out with the control CC sample to find the ideal concentration of both solvent solution and cellulose, as well as the appropriate coagulant amount that would result in a homogeneous and transparent solution of cellulose, aiming to produce a transparent film of regular/smooth surface. Once the appropriate method was found, a protocol was developed and applied to the other cellulose samples (cellulose fibers and industrial type cellulose).

2.2.1. Extraction of cellulose fibers

For the extraction of the cellulose fibers, agro-industrial waste as well as plants and fruits in their maturation stage were chosen. Then, cellulose extraction was carried out using established protocols of chemical extraction followed by acid/base treatment, bleaching, and multiple washes with water to remove all the non-cellulose components, such as hemicellulose, lignin, pectin and waxes.

2.2.2. Cellulose solution

Cellulose solution and regeneration was carry out according to previously reported methods (Cai & Zhang, 2005; Fu et al., 2014; Miyamoto et al., 2009; Qi, Chang, & Zhang, 2009; Zhang et al., 2005). NaOH/urea concentrations were picked up from previous works in which it is stated that homogenous and transparent cellulose solutions were obtained from 14 wt% NaOH/24 wt% urea (14/24 wt%) (Qi et al., 2011; Tovar-Carrillo et al., 2013); 12 wt% NaOH /24 wt% urea (12/24 wt%) (Qi, 2017a); 7 wt% NaOH /12 wt% urea (7/12 wt%) (Cai et al., 2007; Fukuzumi et al., 2011; Hamilton, 1986; Qi et al., 2009); 7.5 wt% NaOH /11 wt% urea (7.5/11 wt%) (Zhang et al., 2005); 6 wt% NaOH /4 wt% urea (6/4 wt%)(Zhou, Zhang, Shu, et al., 2002); 5 wt% NaOH /6 wt% urea (5/6 wt%)(Morgado, Frollini, Castellan, Rosa, & Coma, 2011), and distilled water. The resulting aqueous solution mixture was stored in a refrigerator for precooling at 0 °C. Once the aqueous solution reached the required temperature, right amount of cellulose sample was added immediately to the pre-cooled solvent at different cellulose concentrations of 4.16 wt%; 5.7 wt%

and 10 wt%. Based on the concentration of the NaOH/urea aqueous solution, two processes were used for the dissolution of cellulose, a two-step process and a common one-step process. The two-step process was used only for 14/24 wt% solvent concentration (fig. 2.1). In this method, cellulose samples were dissolved first in NaOH 14 wt% aqueous solution pre-cooled to 0 ºC with stirring for 1 min (step 1); Then urea 24 wt% aqueous solution pre-cooled to 0 ºC was added immediately to the mixture and stirred vigorously until a homogeneous solution is obtained (Qi, 2017b; Qi et al., 2011; Tovar-Carrillo et al., 2013).

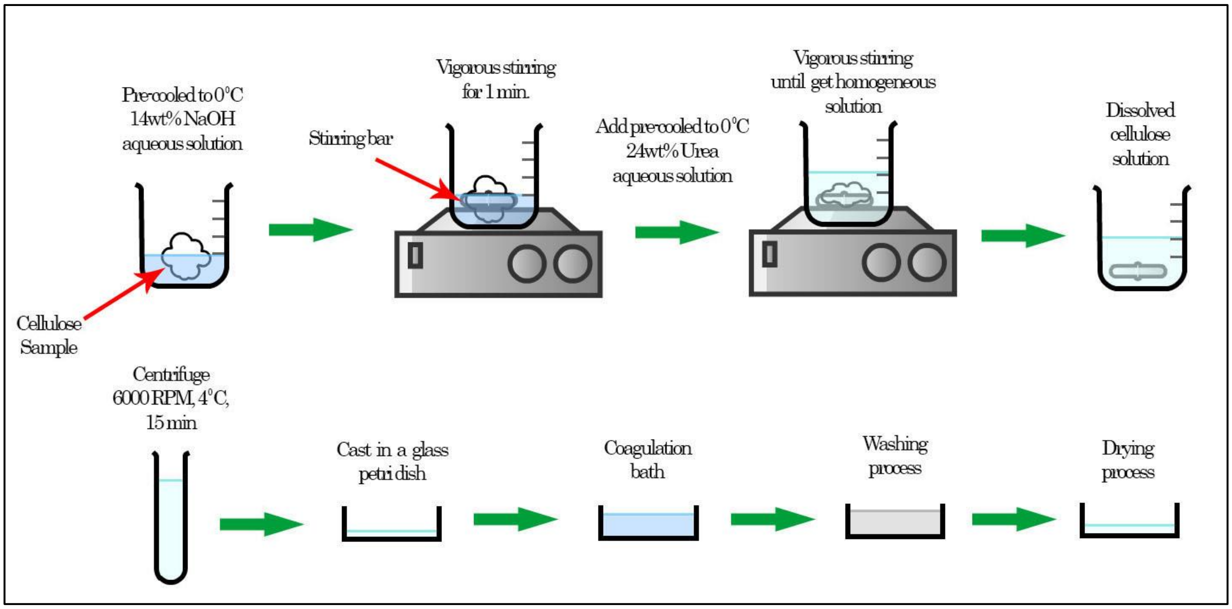

Figure 2.1 Two- step scheme for preparation of regenerated cellulose films from 14wt% NaOH / 24wt% Urea aqueous solution.

On the other hand, the one-step or direct dissolution method (fig. 2.2) was used for the rest of solvent concentrations (12/24 wt%, 7/12 wt%, 7.5/11 wt%, 6/4 wt%, 5/6 wt%); after pre-cooling the right NaOH/urea solution at 0 ºC, cellulose was added immediately, the mixture was stirred vigorously until a homogeneous solution is obtained.

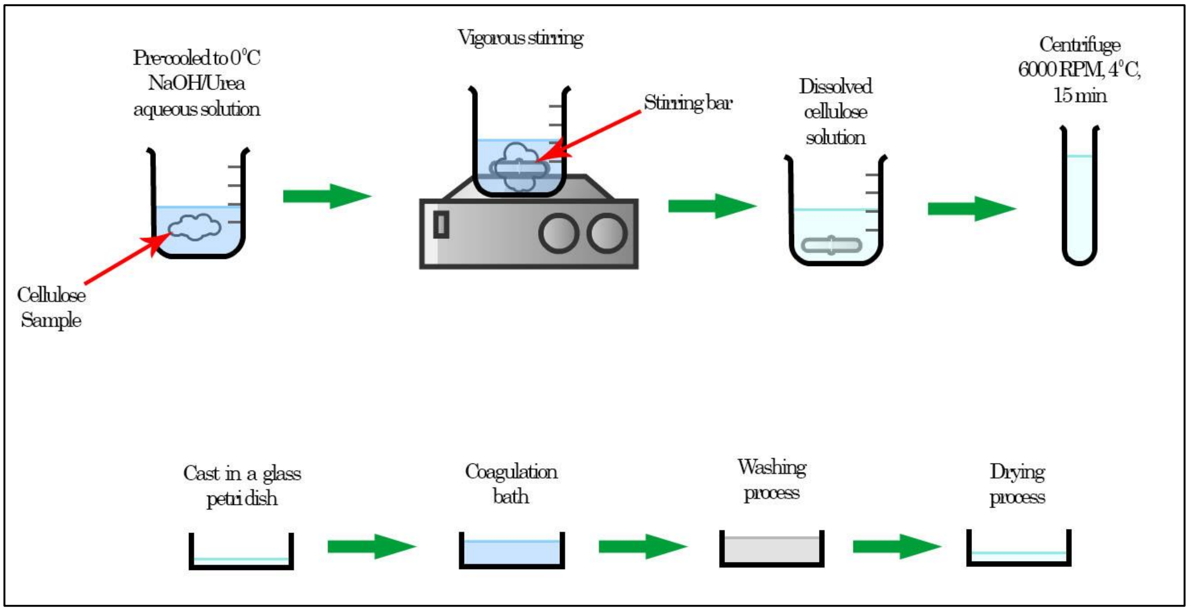

Figure 2.2 One step scheme for preparation of regenerated cellulose films from NaOH/urea aqueous solution.

2.2.3. Preparation of regenerated cellulose films

The resulting cellulose solutions were centrifuged at 6000 rpm for 15 min at a temperature of 4 ºC in order to carry out a degasification (Zhang et al., 2005; Zhou, Zhang, Shu, et al., 2002). After being centrifuged, cellulose solutions were immediately casted slowly onto a completely flat plate, avoiding bubbles as much as possible. Subsequently, the layers were immersed in a coagulation bath at room temperature for regeneration (coagulation) of film. Three coagulants were used, 80 v% ethanol, 100 v% isopropanol and 5 v% sulfuric acid. The immersion time for the coagulation bath was different for each coagulant and depended on the individual film. In general, it took, 20 min for 80 v% Ethanol, 20 min for 100 v% isopropanol and 5 min for 5 v% sulfuric acid or until a solid film is observed. Then, the resulting RC films underwent a washing process with distilled water three times. Then, the films were fixed on flat plate to prevent shrinkage and, finally, they were dried at room temperature between 24 and 48 hours, depending on the type of sample.

Chapter III

Results & Discussion

3.1. Results

3.1.1. Cellulose natural fibers

After the natural sources of cellulose were subjected to the different treatments in order to extract cellulose from them, the cellulose fibers were dried for two days by the freeze-drying method and were kept at room temperature until used.

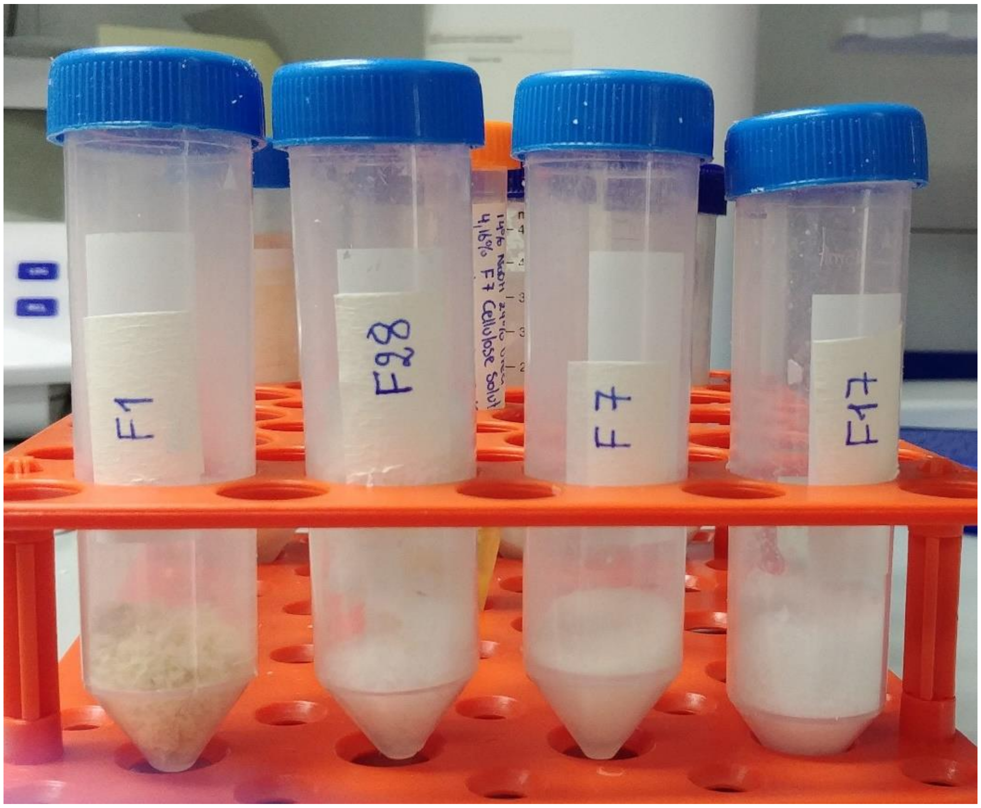

Figure 3.1 Cellulose fibers extracted from natural sources, after the purification and drying process. from left to right, cellulose fibers F1, F28, F7 and F17.

3.1.2. Influence of the solvent concentration on the quality of CC cellulose solution

It is well-known that the aqueous solution of NaOH/urea is capable of dissolving cellulose. However, the concentration of the solvent is the key factor that influences the experiment outcome that is expected; For the purposes of this work, it is necessary to obtain a homogenous and transparent cellulose solution and, therefore, the most optimal concentration of solvent was studied.

First, NaOH/urea aqueous solution concentrations of 14/24 wt%, 12/24 wt%, 7/12 wt%, 7.5/11 wt%, 6/4 wt%, 5/6 wt% were used to dissolve commercial cellulose (CC). However, not all concentrations resulted in a transparent (based on how clear is the solution that allows to see through it) and homogeneous cellulose solution (table 3.1).

As can be seen in figure 3.2, at low concentrations of solvent of 6/4 wt% (fig 3.2 a) and 7.5/11 wt% (fig 3.2 b), 5/6 wt% (fig 3.2 c), cellulose solutions are not completely transparent or homogeneous since it two phases can be slightly appreciated. However, the best results were observed at a concentration of 7/12 wt% (fig 3.2 d) that yielded a homogeneous solution. As a consequence, we decided to increase the concentration of the solvents.

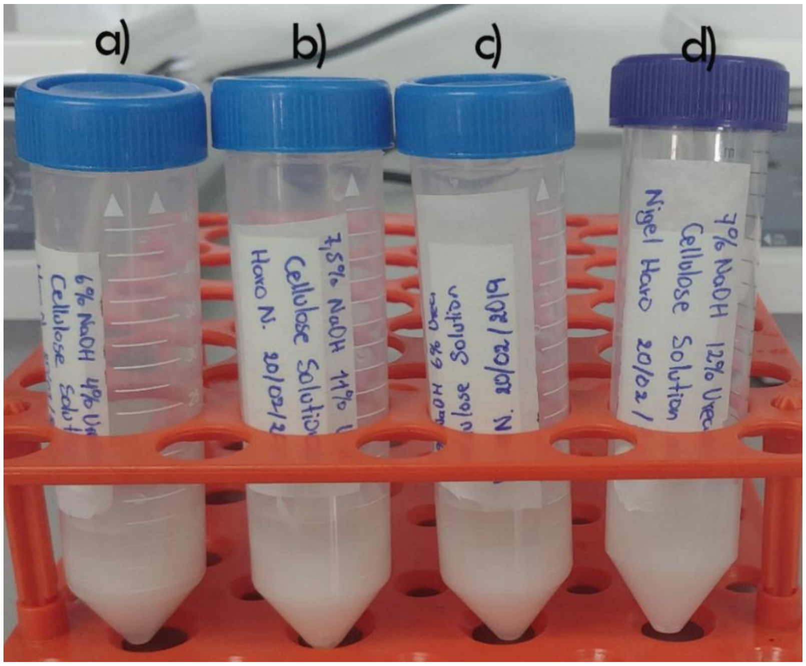

Figure 3.2 CC cellulose solution at a concentration of 4.16 wt% in low concentrations of precooled at $0\ ^{0}$C NaOH/urea aqueous solution. (a) CC cellulose solution at 6/4 wt% solvent concentration, (b) CC cellulose solution at 7.5/11 wt% solvent concentration, (c) CC cellulose solution at 5/6 wt% solvent concentration and (d) CC cellulose solution at 7/12 wt% solvent concentration

High concentrations of solvents, such as 7/12 wt% (fig 3.3 a), 12/24 wt% (fig 3.3 b) and 14/24 wt% (fig 3.3 c) could dissolve cellulose homogeneously, but only 12/24 wt% (fig 3.3 b) and 14/24 wt% (fig 3.3 c) concentrations resulted in a transparent solution, 14/24 wt% concentration being the one of greater transparency.

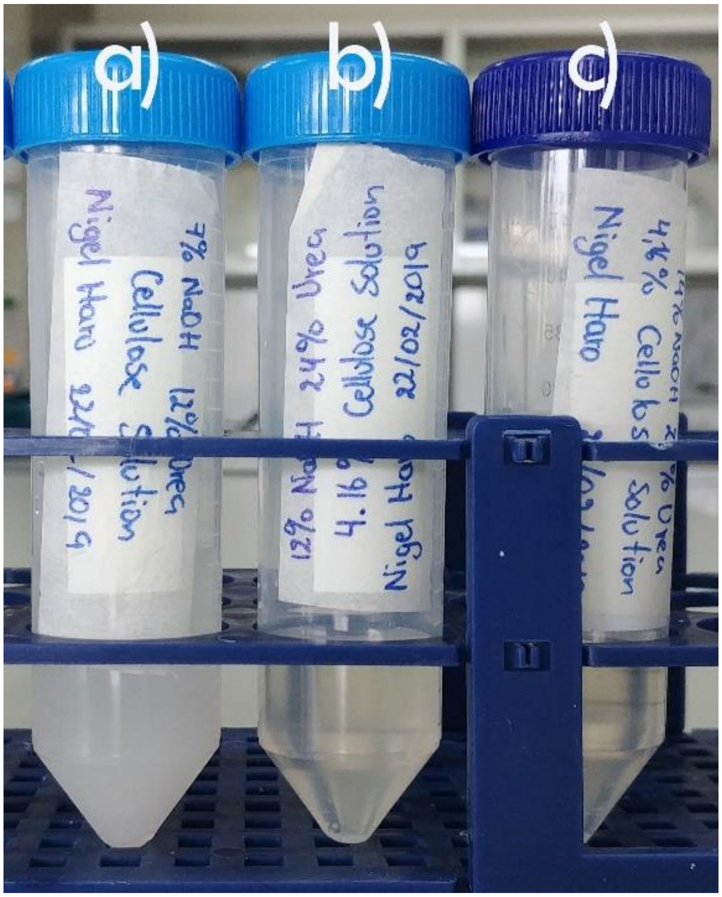

Figure 3.3 CC cellulose solution at 4.16 wt% cellulose concentration in high concentrations of NaOH/urea aqueous solution precooled at 0 ^{0}C. (a) CC cellulose solution at 7/12 wt% solvent concentration, (b) CC cellulose solution at 12/24 wt% solvent concentration and (c)CC cellulose solution at 14/24 wt% solvent concentration.

The centrifugation of the cellulose solutions allows a better visualization of the differences between the solutions at a low solvent concentration (fig. 3.4 a) and the solutions at high solvent concentration (fig. 3.4 b) in terms of both homogeneity and transparency. This suggests that low concentrations of the aqueous solution solvent do not completely dissolve CC cellulose; On the other hand, solutions of high solvent concentrations result in transparent and homogeneous CC cellulose solution. However, other factors such as the concentration of cellulose that dissolves must be considered.

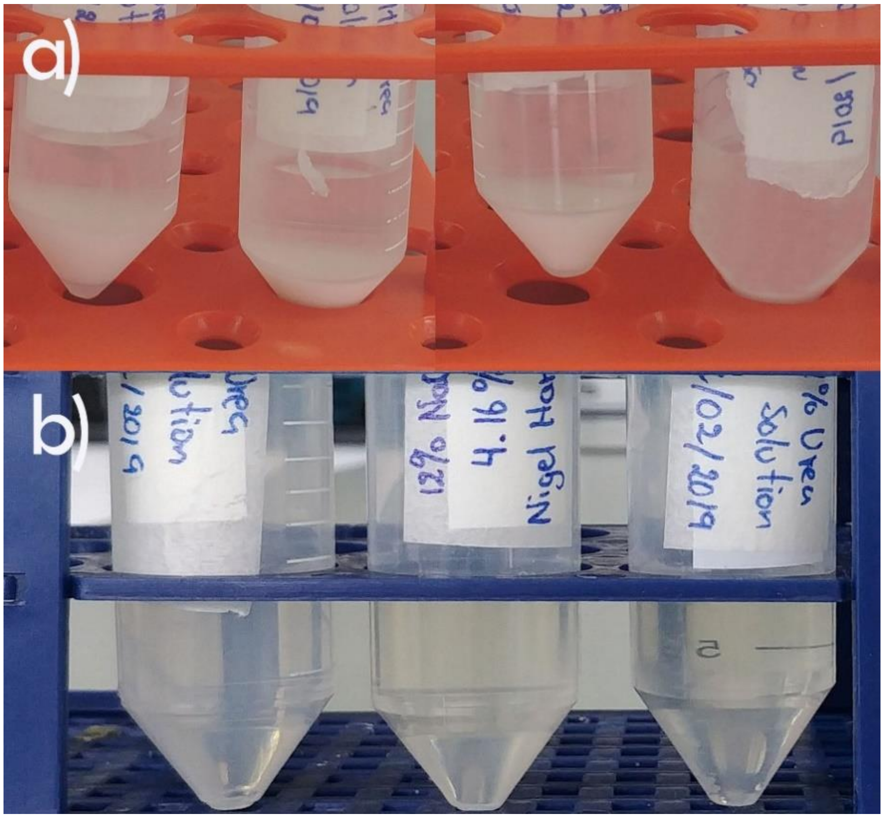

Figure 3.4 CC dissolved cellulose solutions at different cellulose solutions after centrifugation at 6000 rpm at 4 ^{0}C for 15 min. (a)From left to right: CC cellulose solutions from 6/4 wt%, 7.5/12 wt%, 5/6 wt% and 7/12 wt% NaOH/urea low concentration aqueous solution. (b) From left to right: CC cellulose solutions from 7/12 wt%, 12/24 wt% and 14/24wt% NaOH/urea low concentration aqueous solution.

Table 3.1 Quality of CC cellulose solutions from the NaOH/Urea solvent system.

Concentration of the NaOH/urea system	Cellulose dissolution	Homogeneous dissolution	Transparent dissolution
5 wt% NaOH /6 wt% urea (5/6 wt%)	YES	NO	NO
6 wt% NaOH /4 wt% urea (6/4 wt%)	YES	NO	NO
7.5 wt% NaOH /11 wt% urea (7.5/11 wt%)	YES	NO	NO
7 wt% NaOH /12 wt% urea (7/12 wt%)	YES	YES	NO
12 wt% NaOH /24 wt% urea (12/24 wt%)	YES	YES	YES

14 wt% NaOH/24 wt% urea (14/24 wt%)	YES	YES	YES

3.1.3. Influence of the cellulose concentration and coagulation bath on regenerated CC cellulose films.

The concentration of cellulose and coagulation agents are two important factors that influence the mechanical and optical properties of the films. Previous studies have determined that sulfuric acid (Fukuzumi et al., 2011; Miyamoto et al., 2009; Qi et al., 2009; Zhang et al., 2005; Zhang, Ruan, & Gao, 2002; Zhou, Zhang, Shu, et al., 2002) and alcohols, such as isopropanol and ethanol (Gao, Wang, Ma, & Zhao, 2012; Gavillon & Budtova, 2007; Y. Lu & Wu, 2008; Tovar-Carrillo et al., 2013; Urena, 2015; Xu & Chen, 1994), are cellulose coagulants that allow the regeneration of cellulose in the form of films with a smooth surface besides proving them with good mechanical properties. Therefore, the effect of each of these coagulating agents in different concentrations of both cellulose and solvent was assessed. Following the process for the manufacture of films, after having centrifuged the cellulose solutions, they were dispersed in a petri dish to later perform the coagulation bath with the appropriate agent.

Based on the results obtained from 14/24wt% NaOH/urea aqueous solution, the amount of CC cellulose was increased to monitor the differences. As can be seen in figure 3.5, as the amount of cellulose increases from 4.16 (fig. 3.5 a) to 5.7 (fig. 3.5 b) and 10 wt% (fig. 3.5 c), the solution becomes increasingly opaque and more viscous, which is a factor that influences the quality of the cellulose solution and, therefore, the quality of the RC film.

Sulfuric acid at 5 v% concentration was the first coagulant to be tested at different CC cellulose solutions from 14/24 wt% NaOH/urea aqueous solution to compare the differences between them. The regeneration with sulfuric acid of a 4.16 wt% cellulose solution (fig. 3.6 a) did not result in a resistant film of regular/smooth surface after being coagulated for 5 min, the film was fragmented during the washing and drying processes.

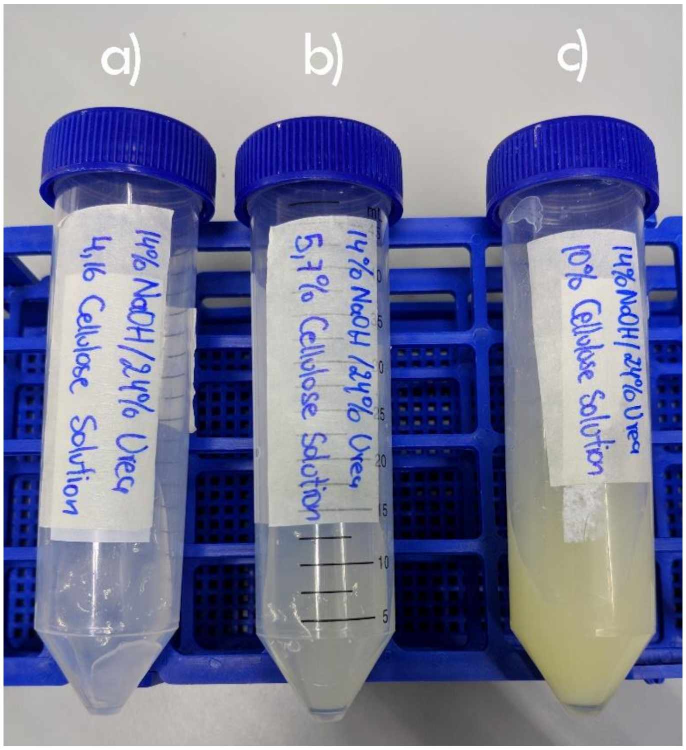

Figure 3.5 Influence of the cellulose concentration on the transparency of the CC cellulose solution from 14/24 wt% NaOH/urea aqueous solution. (a) cellulose solution at a concentration of 4.1 6wt%; (b) cellulose solution at a concentration of 5.7 wt%; and (c) cellulose solution at a concentration of 10 wt%.

From here, the regeneration of higher cellulose concentrations (5.7 and 10 wt%) was tested to overcome this problem. The regeneration of a cellulose solution at 5.7 wt% resulted in a film whose integrity was maintained after the washing process; However, the film was very thick and had a very irregular surface (fig. 3.6 b). Similar results were obtained by a regeneration of a cellulose solution at 10 wt%, the difference being that this film shows a greater thickness as well as a more irregular surface (fig. 3.6 c) in comparison with films of lower cellulose concentrations. The regeneration of films with sulfuric acid at 5 v% shows that, at lower concentrations of cellulose, a more regular surface can be obtained than at high concentrations of cellulose; however, more resistant films are obtained at higher concentrations of cellulose.

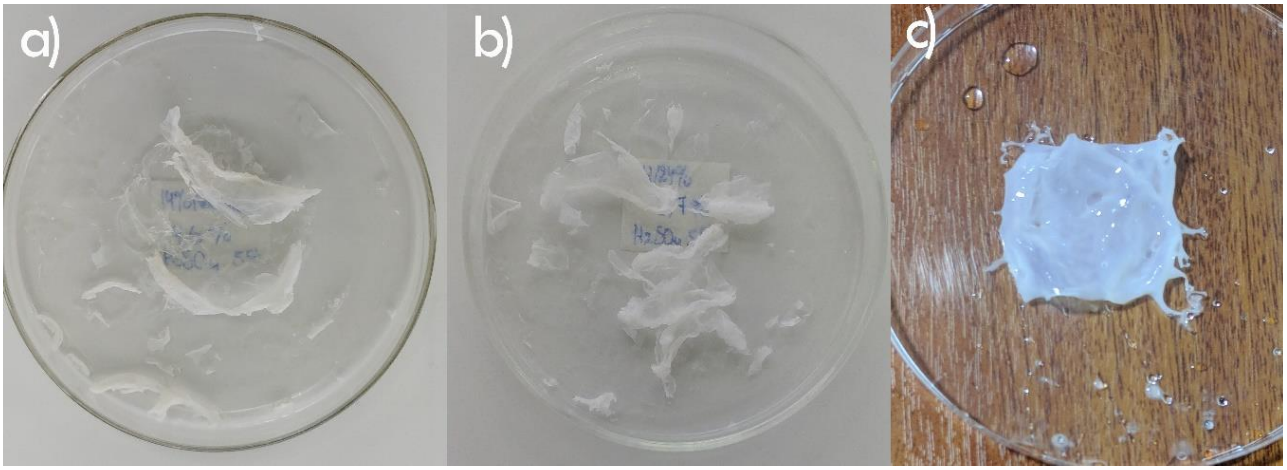

Figure 3.6 RC films obtained from coagulation with 5 v% sulfuric acid of CC cellulose solutions, 14/24 wt% NaOH/urea aqueous solution and different CC cellulose concentrations. (a) RC film obtained from 4.16 wt% cellulose solution, (b) RC film obtained from 5.7 wt% cellulose solution, (c) RC film obtained from 10 wt% cellulose solution.

Subsequently, the results obtained of the cellulose regeneration from 14/24 wt% NaOH/urea aqueous solution at different CC cellulose concentrations with 100 v% isopropanol were evaluated to observe the differences. The CC cellulose solutions were subjected to the coagulation bath for 20 min and were recovered successfully after the washing and drying processes (fig. 3.7). After the drying process, the film resulting from 4.16 wt% cellulose solution showed to be transparent with a smooth and regular surface; However, the film suffered from shrinkage besides being fragile enough not to withstand stretching (fig. 3.7 a). Similar results were obtained from the resulting films with the solutions of 5.7 wt% (fig. 3.7 b) and 10 wt% (fig. 3.7 c). Nonetheless, as the concentration of cellulose increased, the films became more resistant to shrinkage but opaquer. This effect increased with the passage of time as the films shrunk more and became opaquer and fragile. Therefore, these films could not be manipulated or used.

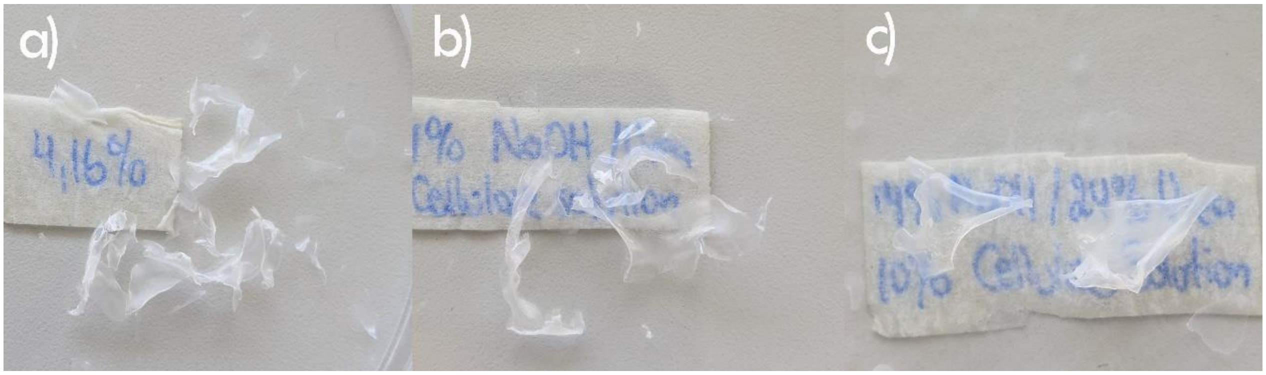

Figure 3.7 RC films obtained from 4.16wt% CC cellulose solutions, coagulation bath with 100 v% isopropanol and 14/24 wt% NaOH/urea aqueous solution (a) transparent CC film after 1 h of drying, (b) Shrinkage of CC film after3 days at room temperature.

Finally, experiments were performed with 80% ethanol to regenerate CC cellulose of different concentrations dissolved in an 14/24 wt% aqueous solution. From the regeneration of films by means of ethanol, it is possible to obtain transparent films with a smooth surface and resistant to manipulation, which could be recovered successfully after the washing and drying processes. At cellulose concentrations of 4.16 wt% (fig 3.8 a) and 5.7 wt% (fig 3.8 b), transparent films were obtained, unlike the 10 wt% film (fig 3.8 c), which turned out to be opaque. On the other hand, regenerated films with ethanol also showed shrinkage; However, as the cellulose concentration increased, this effect became less and less noticeable.

Figure 3.8 RC films obtained from 14/24 wt% NaOH/urea aqueous solution at different CC cellulose concentrations, regenerated with 80 v% ethanol. (a) Film obtained from a cellulose concentration of 4.16 wt%, (b) film obtained from a cellulose concentration of 5.7 wt%, (c) film obtained from a cellulose concentration of 10 wt%.

The results obtained through experiments with CC sample show that the best films are obtained from a coagulation bath with 80 v% ethanol and a cellulose concentration from 4.16 wt% to 5.7 wt% because, at these conditions, it is possible to obtain transparent, resistant films that do not suffer from a pronounced shrinkage.

3.1.4. Regenerated cellulose films from cellulose fibers and industrial type cellulose

After having determined the optimal coagulant agent and both solvent and cellulose concentrations from experiments with CC cellulose sample, this information was used to prepare regenerated cellulose films from natural cellulose fibers as well as type-industrial cellulose starting from dissolution, regeneration until washing and drying processes.

The dissolution of all the cellulose samples was carried out successfully although they did not result in a homogeneous and transparent solution, even at a high concentration of solvent (14/24 wt%) and a 4.16 wt% cellulose concentration, liquid solutions were obtained instead of viscous (fig. 3.9). Although some of the cellulose fibers were of a whitish color as well as the CC cellulose, the solutions turned out to be a yellowish\orange color at the moment of dissolving them (fig. 3.9 a). None of the solutions of cellulose fibers resulted in a homogeneous and transparent solution, unlike industrial type cellulose (fig 3.9 b). However, after centrifuging and separating the cellulose solution from the pellet, some solutions of natural fibers took on a more transparent color (fig 3.9 c). This effect could be seen more in the solutions of the industrial type cellulose samples (fig 3.9 d).

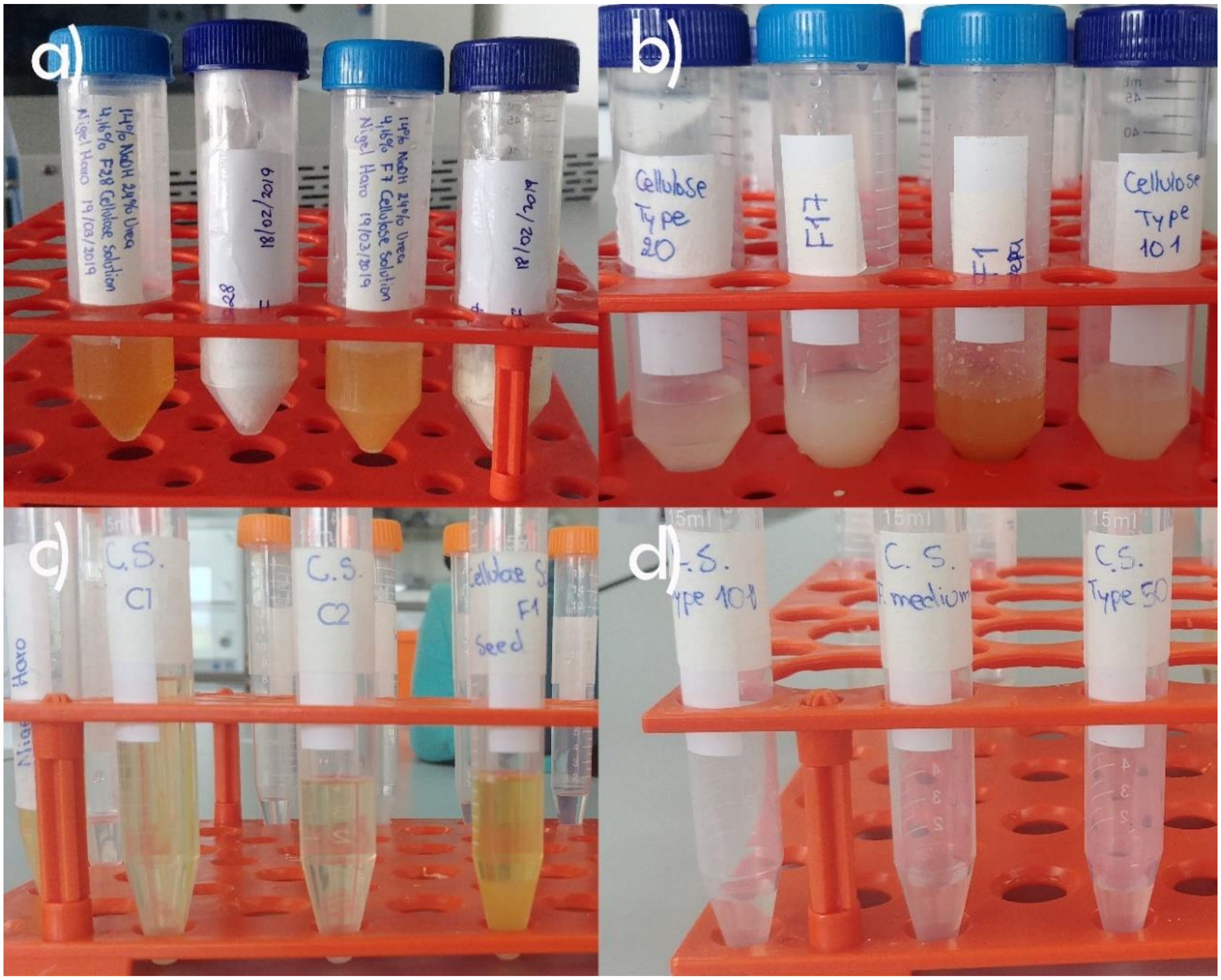

Figure 3.9 Cellulose dissolution of different sources from 14 wt% NaOH/24 wt% urea aqueous solution. (a) Cellulose fibers F28 and F7 solutions with their corresponding white cellulose fibers, (b) cellulose solution of cellulose fibers F17, F1 and industrial type cellulose T20, T101, (c) dissolution of cellulose fibers after centrifugation at 6000 rpm at 4 ºC for 15 min, (d) industrial type cellulose solutions after centrifugation at 6000 rpm at 4 ºC for 15 min.

During the stage of regeneration of the films with 80% ethanol, it was observed that, although the cellulose coagulated in the form of a smooth surface film, only the films made of industrial type cellulose could be recovered successfully (fig. 3.11 d). RC films made of cellulose fibers resulted in very thin and fragile films which, at the time of removing the coagulant, were fragmented (fig. 3.10 a). Some films were fragmented during the washing process and others, despite remaining intact for the drying process, they were very thin to be manipulated or recovered from the surface where they were casted (fig. 3.10 b). Therefore, the regeneration of films from cellulose fibers resulted in thin and fragile films that could not be recovered maybe due to the poor dissolution of cellulose fibers.

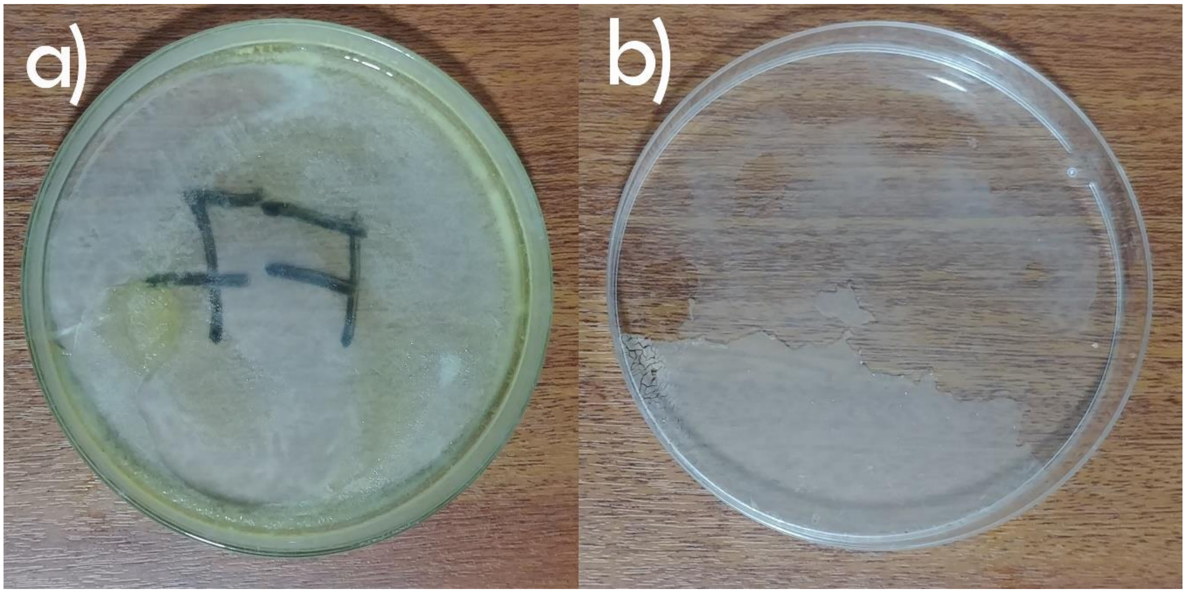

Figure 3.10 Regeneration of cellulose fiber films from 4.16 wt% cellulose solutions, 14/24 wt% NaOH/urea aqueous solution and 80 v% ethanol bath. (a) Remains of F7 film after having extracted the excess ethanol from the coagulation bath, (b) F28 film obtained after washing process and drying process at room temperature.

For these reasons, it was decided to maintain the cellulose solutions at a temperature of 0 ºC after being dissolved by 14/24 wt% NaOH/urea aqueous solution for 8 hours in order to improve the dissolution process (Morgado et al., 2011; Zhou, Zhang, Shu, et al., 2002) as well as to test with 5 v% sulfuric acid and 100 v% isopropanol to compare the differences in the process of obtaining the film. For this test, the effect of the cellulose fibers C1, C2, F1 and F17, as well as the industrial type cellulose T20, T50, T101 and TI was studied. The cellulose fibers samples regenerated with 5% sulfuric acid resulted in thin films, except for the F1 film which did not coagulate; however, it was not possible to recover the rest of the films because they did not coagulate properly and they fragmented when they were collected (fig. 3.11 a). Similar results were obtained for the coagulation of the cellulose fibers with 100% isopropanol, samples F17 and F1 did not coagulate as films, they looked with a granular appearance while C1 and C2 samples coagulated as thin films but, even so, it was not possible to recover them due to their fragility (fig. 3.11 b). The best results were achieved by coagulating the cellulose fibers with 80% ethanol as the films were a little thicker than the ones obtained with the previous methods, they were regenerated but still not enough resistance to be recovered. (fig. 3.11 c). On the other hand, industrial type cellulose samples were studied in sulfuric acid, where films resistant enough to be recovered were obtained, but with an irregular surface, while, films coagulated with ethanol resulted in recoverable films, transparent and of smooth surface (fig. 3.11 d), like the results obtained with CC cellulose. The results of this experiment confirm that regeneration from 80% ethanol gives better results than coagulation with sulfuric acid and isopropanol. However, no significant differences were observed in the maintenance of cellulose solutions at low temperatures. Accordingly, it was tested with dissolved cellulose samples at a concentration of 5.17 wt% in order to overcome the problem of the regeneration of fragile and thin films from 80% ethanol. Nonetheless, many of the films that were prepared could not be recovered due to they were very fragile and were destroyed during the washing process or when trying to collect them. Hence, two types of films were differentiated.

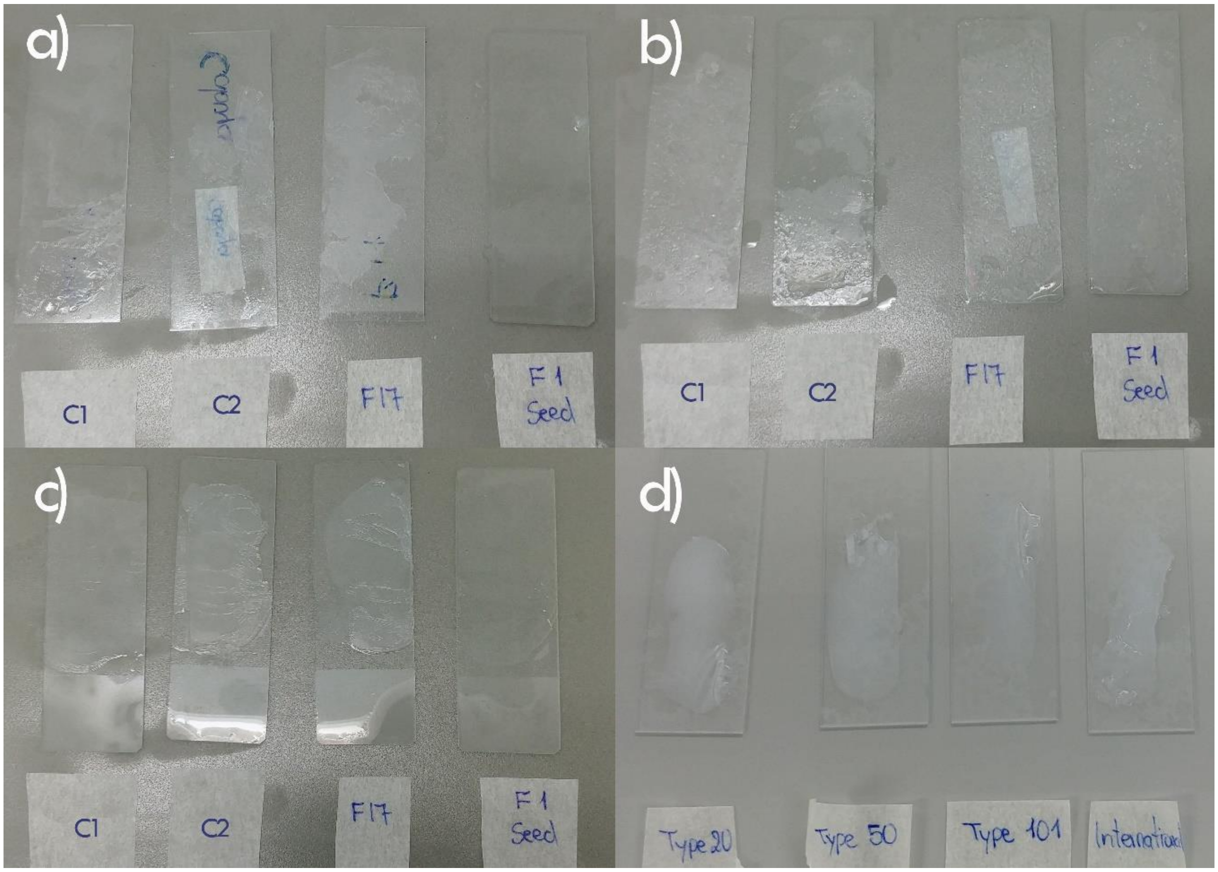

Figure 3.11 RC films of different cellulose samples obtained from 4.16% cellulose solutions, 14/24wt% NaOH/Urea aqueous solution and different coagulating agents. (a) coagulation of 4.16wt% cellulose fiber solutions (C1, C2, F17 and F1), with 5v% sulfuric acid, (b) coagulation of 4.16wt% cellulose fiber solutions (C1, C2, F17 and F1) with 100v% isopropanol, (c) coagulation of 4.16wt% cellulose fiber solutions (C1, C2, F17 and F1) with 80v% ethanol, (d) coagulation of 4.16wt% industrial type cellulose (T20, T50, T101 and TI) with 80v% ethanol.

First, samples that regenerated films but could not be collected because they were fragmented in the steps subsequent to the coagulation stage are called "recoverable" since they actually resulted in a film that could be recovered but due to their fragility they could not be collected for use (fig. 3.12). Second, the samples whose regeneration in films could be collected after the processes of coagulation, washing and drying, are called "usable", because they could be manipulated and used (fig 3.13).

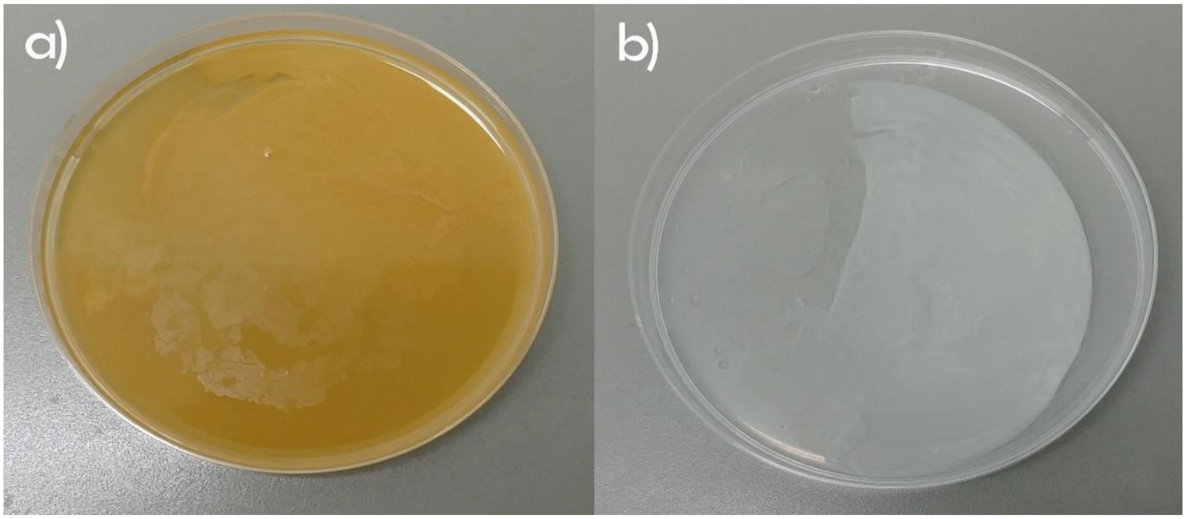

Figure 3.12 Regeneration of "recoverable" films of a 5.7 wt% cellulose fiber solution from 14/24 wt% NaOH/urea aqueous solution and 80% ethanol coagulation bath. (a) C1 film after 20 min of coagulation, (b) C2 film after 20 min of coagulation.

Finally, from the seventeen cellulose samples (11 types of cellulose fibers extracted from natural sources and 6 types of industrial type cellulose including the CC control sample) that were studied for regeneration of cellulose films, only seven samples of cellulose resulted in films that could be used, three cellulose fibers: BS, FB and FS, and four industrial type cellulose: T20, T50, Medium and CC. The rest of the cellulose samples, although they were regenerated in the form of films, could not be collected for their use because some were fragmented during the extraction of the coagulant, such as C1 and T19, some others were fragmented after the washing process to recover the films for the drying process, such as F1, F7, F17, F28; the rest, after being recovered for the drying process, did not result in usable films as they did not dried form a film, such as F20, C2, TM and TI.

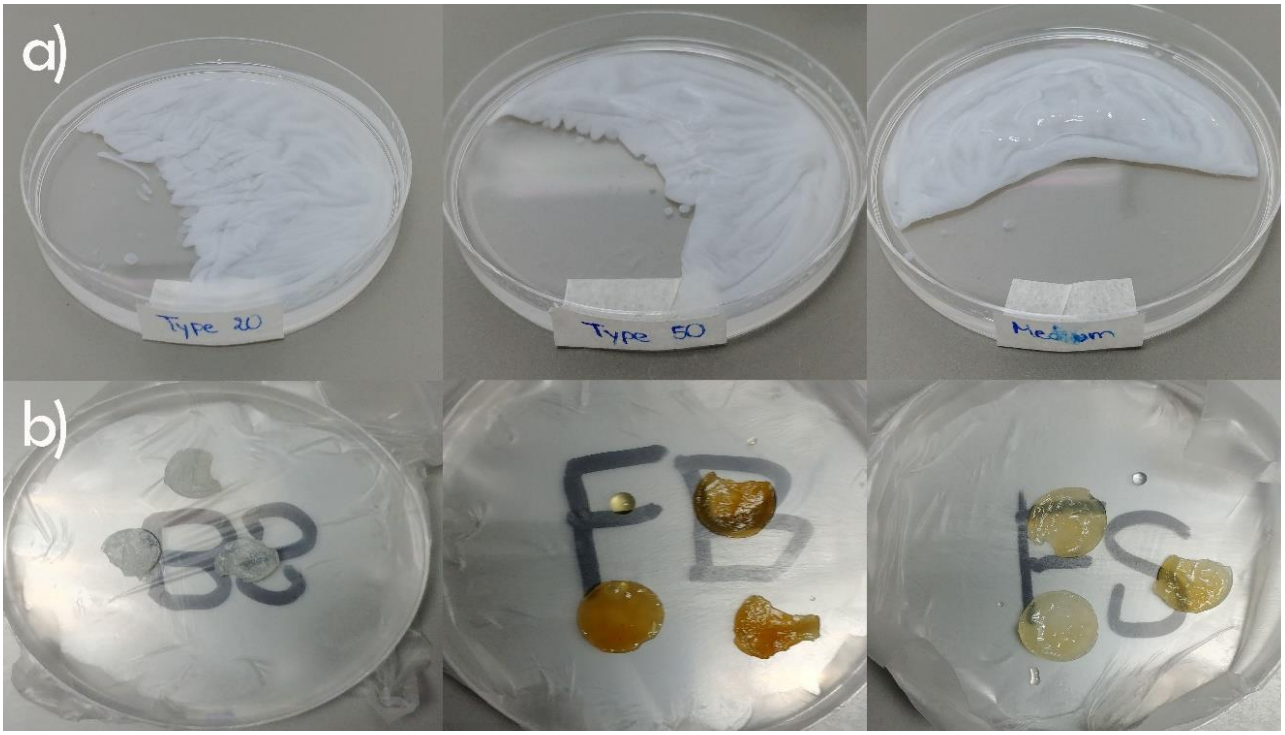

Figure 3.13 RC films usable from a cellulose concentration of 5.7wt%, 14/24wt% NaOH/urea aqueous solution and coagulation with ethanol at 80 v%. (a) From left to right: T20, T50, TM usable films obtained from industrial type cellulose, (b) From left to right: BS, FB, FS usable films obtained from natural cellulose fibers.

The tables below summarize the experiments conducted in the laboratory. Table 3.2 shows the results of coagulation of the different cellulose samples with sulfuric acid, isopropanol and ethanol while Table 3.3 summarizes the results of films based on cellulose fibers and industrial type cellulose by coagulation with 80% ethanol.

Table 3.2 Summary of the trials in the lab. √ successful; X unsuccessful; — not done.

SAMPLE	Coagulation		
	Sulfuric acid 5 v%	Isopropanol 100 v%	Ethanol 80 v%
F1	X	X	✓
F7	——	——	✓
F17	X	X	✓
F19	✓	——	✓
F20	✓	——	✓
F28	✓	✓	✓
C1	✓	✓	✓
C2	✓	✓	✓
BS	✓	——	✓
FB	✓	——	✓
FS	✓	——	✓
T20	✓	——	✓
T50	✓	——	✓
T101	✓	——	✓
TM	✓	——	✓
TI	✓	——	✓
CC	✓	✓	✓

Table 3.3 Summary of the films that could be recovered and can be used. √: YES; X: No

SAMPLE	Films	
	Recoverable	Usable
F1	✓	X
F7	✓	X
F17	✓	X
F19	✓	X
F20	✓	X
F28	✓	X
C1	✓	X
C2	✓	X
BS	✓	✓
FB	✓	✓
FS	✓	✓
T20	✓	✓
T50	✓	✓
T101	✓	X
TM	✓	✓
TI	✓	X
CC	✓	✓

3.2. Discussion

3.2.1. Dissolution of cellulose samples from NaOH/urea aqueous solution

It was observed that all NaOH/urea concentrations could dissolve CC cellulose. However, better results were obtained with certain concentrations. Cellulose was successfully dissolved because NaOH is a strong base which interacts with cellulose to form different complexes depending on NaOH concentration and temperature. The dissolution of cellulose with an aqueous solution of NaOH/urea is based on the formation of hydrates NaOH, urea hydrates and free water when the solvent was cooled; NaOH hydrates at low temperatures can form hydrogen bonds with the cellulose chain, then the urea hydrates would be added to the surface of the new hydrogen-bonded networks associated with the cellulose chain and the NaOH hydrates to create the cellulose inclusion complex (Haibo Xie Nicholas Gathergood, 2013). Therefore, the addition of urea and the low temperature play important roles in the improvement of cellulose dissolution because low temperature creates a large and stable inclusion complex associated with cellulose, NaOH, urea, and H_2O clusters through hydrogen-bonding, which destroys effectively the interchain hydrogen bonding in cellulose and bring cellulose into aqueous solution (Yu, 1995).

The dissolution of cellulose is strongly dependent on the concentration of NaOH as well as temperature. For this reason, depending on the concentration of NaOH, there are mainly three processes for the dissolution of cellulose in an aqueous system based on NaOH. (1) 6– 10 wt% NaOH for freezing–thaw at room temperature; (2) 6.5–10 wt% NaOH for direct dissolution from -10 to -12 ºC; and (3) 10–18 wt% NaOH for two-step process at 0 ºC (Qi, 2017b). However, only the cellulose solution with a concentration of 14/24 wt% was carried out following the two-step method and the appropriate temperature due to limitations in the laboratory that did not allow us to precool the aqueous solutions at temperatures of -12 ºC. As a result, the dissolution of cellulose from 14/24 wt% NaOH/urea aqueous solution was the best result obtained.

Although all cellulose samples could be dissolved in 14/24 wt% NaOH/urea aqueous solution, only industrial type cellulose samples of industrial type gave results similar to those of the cellulose control sample in terms of transparency, homogeneity and viscosity. This is due to the similarity of the samples. On the other hand, it was observed that the dissolution of natural cellulose fibers did not result in a transparent homogeneous solution from 14/24 wt% NaOH/urea aqueous solution, which were also liquid. There are several factors to consider in order to understand these results. The first factor to consider is the quality of the cellulose and their color, since the cellulose might not have been properly purified and other residues could be present not allowing therefore transparent and homogeneous dissolution of the fibers. The second factor is related to the properties of cellulose. Not all types of cellulose can be dissolved from the NaOH/urea system. There are limitations such as the degree of polymerization which, for this solvent is high, varies between DP = 500-900(Qi, 2017b). However, during chemical purification, the DP of the resultant cellulose is greatly reduced (Xu & Chen, 1994). The last factor is related to the storage of cellulose as well as the freshness of the samples prior to their use because the literature claims that cellulose should remain in a drying process until its use. Nonetheless, due to the limitations of the laboratory, the cellulose samples were kept at room temperature before use.

3.2.2. Influence of different coagulating agents on RC film

It was observed that the regeneration of cellulose was strongly influenced by the type of coagulant used. In general, the type of solvent and the coagulation agent as well their concentration are the main factors that influence the regeneration of cellulose (Y. Lu & Wu, 2008; Mukuze, Yao, Xia, & Zhang, 2014; Zhang et al., 2005). NaOH/urea is a non-derivatizing solvent which dissolve cellulose by separating the individual cellulose chains from each other as a result of the formation of a inclusion complex without chemical modification (Haslinger, 2018). The mechanism of cellulose regeneration begins when the cellulose solution comes in contact with the coagulating agent, the inclusion complex associated with cellulose, NaOH and urea is interrupted by adding a non-solvent, such as ethanol, isopropanol or sulfuric acid, which leads to the rearrangement of hydrogen bonds and therefore self-association of cellulose. Therefore, coagulation of films from NaOH/urea solvent system results from a phase separation (Medronho & Lindman, 2015; Mukuze et al., 2014). This separation of phases is based on a solvent exchange at the time of the coagulation bath which produces a change in the ratio of polymer, solvent and anti-solvent in the film formation region and, in turn, generates the separation of a dense phase rich in polymers and a poor phase almost polymer-free. After that, dense phase will cure to eventually become a film. (Cai & Zhang, 2005; Y. Lu & Wu, 2008). Therefore, the morphology of the films depends on the speed of the phase separation process and the kinetics of the curing process, which is different for each type of coagulant, in which when the phase separation process is slow and the curing process is fast, it is favorable to form a dense membrane; Otherwise, a porous membrane may prefer to form. This is corroborated by the literature; firts, in the case of the use of alcohols, it is claimed that cellulose regeneration through alcohols results in porous films (an effect that is directly related to the concentration of alcohol) (Gao et al., 2012); second, the regeneration of cellulose from sulfuric acid also results in porous structures (Haslinger, 2018). Characterization techniques like SEM and AFM are needed to study the differences.

Hence, it is possible to understand the results obtained from the experiments carried out with CC cellulose as well as with natural cellulose fibers. It is suggested that the coagulation with ethanol and isopropanol resulted in a slower curing process compared to the phase separation process, this led to the formation of a porous structure as well as allowed the formation of a regular / smooth surface. On the other hand, coagulation bath with sulfuric acid resulted in a slow phase separation process and a rapid curing process. For these reasons, the films regenerated with sulfuric acid resulted in highly irregular ones due to a higher speed of film cure that does not allow a phase separation to obtain a regular surface. This effect could also explain the reason why the coagulation bath with alcohols took longer than sulfuric acid.

On the other hand, films regenerated from natural fibers could not be collected for use as they were very thin and fragile. This could be the effect of a poor cellulose content in the solutions and, therefore, during the regeneration of the films, a sufficiently dense and polymer-rich phase was not generated during the separation phase resulting in a thicker film during the curing process.

Conclusions and recommendations

It was possible to extract cellulose from natural sources such as fruits, agroindustrial residues and fibrous plants, these fibers were used as raw material for cellulose derivatives applications.

The concentration of the solvent, cellulose and temperature strongly influence the quality of the cellulose solution from the NaOH/urea system. The dissolution of cellulose with a two-step method from 14wt% NaOH/ 24wt% urea aqueous solution precooled at 0 ºC allows the dissolution of extracted cellulose fibers samples while homogeneous and transparent solutions are obtained for industrial cellulose samples.

Cellulose solutions were successfully regenerated through a coagulation bath with sulfuric acid, isopropanol and ethanol. The morphology of regenerated cellulose films is strongly influenced by the type of coagulating agent. The regeneration of cellulose from sulfuric acid results in an irregular surface film due to the speed with which cellulose is regenerated. On the other hand, the regeneration of cellulose by alcohols results in films of regular surface. However, the coagulation bath with isopropanol results in fragile films which with, the passage of time, become opaque while the coagulation bath with ethanol allows the regeneration of transparent films of greater resistance compared to the ones obtained with isopropanol. Cellulose concentration is another factor that affects the fragility and transparency of films. Films with concentrations of 10 wt% cellulose showed to be resistant to shrinkage and stretch without breaking easily but turned out to be opaque while films at a concentration of 4.16 wt% showed to be transparent but are prone to shrink and break easily.

It was determined that the best films can be produced through a dissolution of cellulose at 5.7 wt% from 14 wt% NaOH/ 24 wt% aqueous solution precooled at 0 ºC regenerated through a coagulation bath with 80% ethanol. It was discovered that three cellulose fibers FB and FS extracted from plants and BS extracted from agroindustrial waste, resulted in usable films which provides a potential application of conversion of cellulosic waste resource into functional materials.

For future work, since the fact that it was not possible to determine the purity of the cellulose fibers as well as a detailed study of the morphology of the films to determine the porosity, the characterization of both cellulose and film by FTIR, XRD and SEM is strongly recommended. It is also recommended to study the preparation of films through other types of solvents such as N-methylmorpholine-N-oxide (NMMO) and lithium chloride/dimethylacetamide (LiCl/DMAc) solvent systems, as well as a systematic study of the influence of temperature during the drying process in order to obtain films with good mechanical and optical properties.

Annexes

Procedure for making films

This part describes the steps that were followed for the preparation of films, from the dissolution of cellulose to the regeneration of the film.

A.1 Preparation of aqueous solutions

An aqueous solution of 14 wt% NaOH and an aqueous solution of 24 wt% urea were prepared then were allowed to cool to a temperature of 0 ºC.

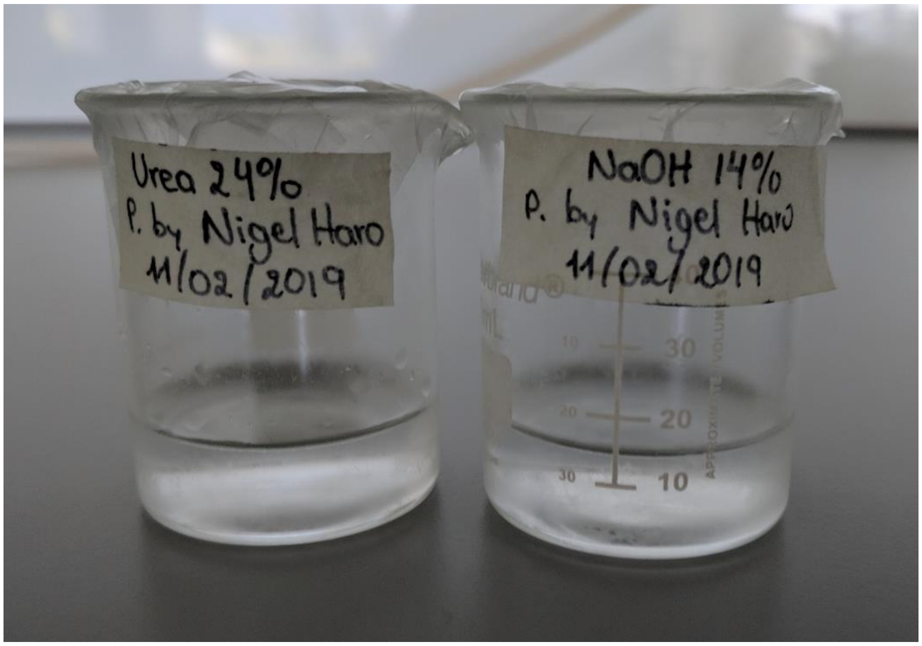

Figure A.1 Low temperature aqueous solutions. (a) 24wt% urea precooled at 0 ºC, (b)14wt% NaOH precooled at 0 ºC

A. 2 Dissolution of cellulose

The dissolution of cellulose was carried out following the two-step method.

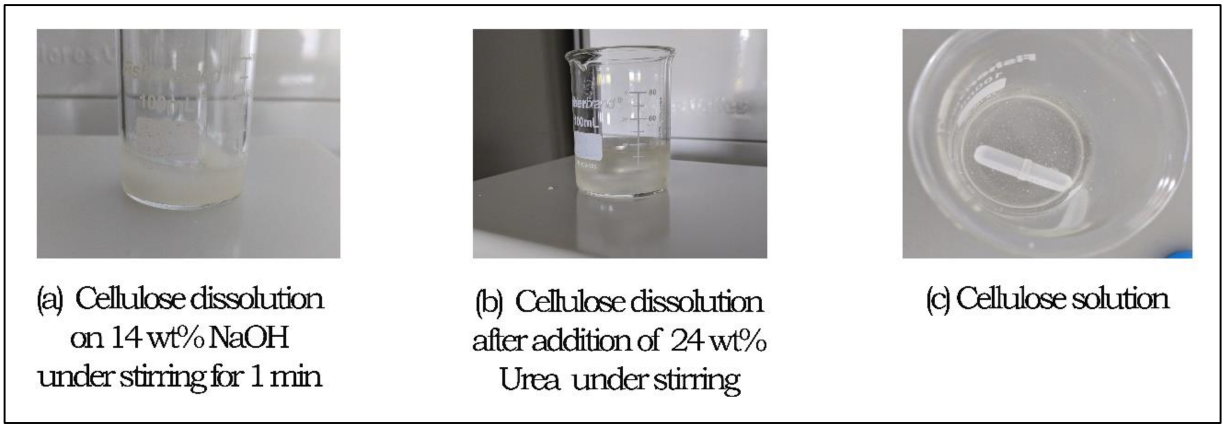

Figure A.2 Dissolution of cellulose through the two-step method under 14/24wt% solvent concentration., cellulose is dissolved first in NaOH 14 wt% aqueous solution pre-cooled to 0 ^{o}C with stirring for 1 min then urea 24 wt% aqueous solution pre-cooled to 0 ^{o}C is added immediately to the mixture under vigorous stirring until a homogeneous solution is achieved.

A. 3 Regeneration of the film

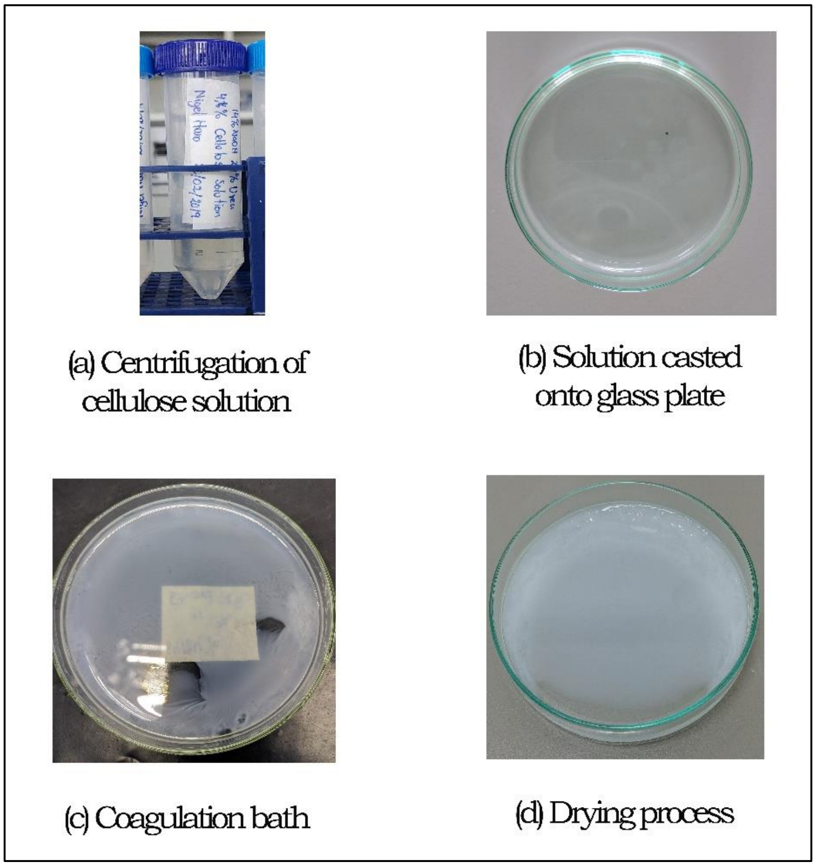

Figure A.3 Process for the regeneration of the film. (a) Centrifugation of the cellulose solution for degassing, (b) the solution is spread on a glass petri dish, (c) the solution is subjected to a coagulation bath for regeneration, (d) the regenerated film is washed with distilled water and let to dry at room temperature.

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