Universidade do Minho
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Development of cosmetics formulations to change the shape of hair

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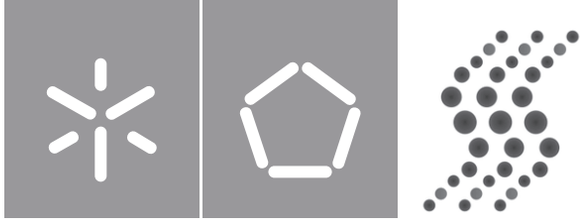

Universidade do Minho
Escola de Engenharia

José Pedro Da Silva Gonçalves Carvalho

Development of cosmetics formulations to change the shape of hair

Master's Dissertation
Master Program in Biotechnology

Work developed under the supervision of
Professor Doctor Artur Cavaco-Paulo
Doctor Madalena Martins

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To my family. To my parents for being there during this journey, even with all the difficulties, and for making all this possible from the beginning.

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Abstract

Development of cosmetics formulations to change de shape of the hair

Current hair styling cosmetic products cause irreversible damage to the hair fiber and the environment. The objective of this dissertation is to develop formulations that change the shape of hair from carbohydrate polymers, cellulose and chitosan, and benign solvents that are friendly to human health and the environment. Cellulose and chitosan have solubility limitations in water and organic solvents. Then, ionic liquids (ILs) based on imidazolium and serum were tested, along with several types of cellulose (Hydroxyethyl cellulose (HEC), Carboxymethylcellulose (CMC), Microcrystalline Cellulose (MCC)) and different types of chitosan. The stability of the formulations was evaluated through prolonged storage, thermal stress, physical stress, organoleptic properties, and pH, at different temperatures. The formulations were applied to Asian hair using different methodologies where the curling efficiency was evaluated after application and washing. The formulations with 3% and 0.5% of HEC and CMC showed the best result after washing (±10%). The pre-treatment chosen was with serum, discarding ILs. The formulations with chitosan did not show satisfactory results. The application of the DTAF dye on the cellulose, later applied to the hair, enabled the investigation of the cellulose effect through fluorescence microscopy. The labeled cellulose was absorbed by the capillary keratin fiber, adhering to the coating layer on the surface of the capillary fiber. SEM images revealed that the treated hair fiber preserved structural integrity, especially for the 3% CMC formulation. The thermal analysis of virgin and treated hair fiber was also evidenced by DSC, where formulations containing 3% and 0.5% CMC and 3% HEC demonstrated greater stability to thermal processing. It was also shown that hair fiber treated with 0.5% CMC performed well in mechanical wear resistance by calculating the percentage of mass loss. An ATR-FTIR was performed, demonstrating compliance in the spectra of the formulations, with emphasis on the 3% HEC formulation. The formulation of cellulose in serum combined with a pre-treatment based on urea proved to be a promising alternative to cosmetic products, with slightly curling effect.

Keywords: Cellulose, Ionic Liquids, Hydroxyethyl cellulose, Carboxymethylcellulose, Serum, Urea, Cosmetic Hair, Hair Shape

Resumo

Desenvolvimento de formulações cosméticas para alteração da forma do cabelo

Os produtos cosméticos atuais para modelar o cabelo causam danos irreversíveis à fibra capilar e ao meio ambiente. O objetivo desta dissertação é desenvolver formulações que alterem a forma do cabelo a partir de polímeros de carbohidratos, celulose e quitosano, e solventes benignos que são amigos da saúde humana e do meio ambiente. A celulose e a quitosano têm limitações de solubilidade em água e em solventes orgânicos. Então, líquidos iónicos (ILs) à base de imidazólio e sérum foram testados, juntamente com vários tipos de celulose (Hydroxyethyl cellulose (HEC), Carboxymethylcellulose (CMC), Microcrystalline Cellulose (MCC)) e diferentes tipos de quitosano. A estabilidade das formulações foi avaliada através de armazenamento prolongado, stresse térmico, stresse físico, propriedades organoléticas e pH, a diferentes temperaturas. As formulações foram aplicadas em cabelo asiático utilizando diferentes metodologias onde a eficiência de ondulação foi avaliada após aplicação e lavagem. As formulações com 3% e 0,5% de HEC e CMC apresentaram o melhor resultado após a lavagem (±10%). O pré-tratamento baseou-se em sérum, descartando os ILs. O quitosano não apresentou resultados satisfatórios. A aplicação do corante DTAF na celulose, posteriormente aplicado no cabelo, possibilitou a investigação do efeito da celulose através de microscopia de fluorescência. A celulose marcada foi absorvida pela fibra de queratina capilar, aderindo à camada de revestimento na superfície da fibra capilar. Imagens de MEV revelaram que a fibra capilar tratada preservou a integridade estrutural, principalmente para a formulação 3% CMC. A análise térmica da fibra capilar virgem e tratada foi evidenciada por DSC, onde as formulações contendo 3% e 0,5% CMC e 3% HEC demonstraram maior estabilidade ao processamento térmico. Foi demonstrado que a fibra capilar tratada com 3% CMC apresentou bom desempenho na resistência ao desgaste mecânico pelo cálculo da percentagem de perda de massa. Foi realizado um ATR-FTIR, demonstrando conformidade nos espectros das formulações, destacando a formulação de 3% HEC. A formulação de celulose em sérum combinada com um pré-tratamento à base de ureia mostrou-se uma alternativa promissora aos produtos cosméticos, com um ligeiro efeito de encaracolamento.

Palavras-chave: Celulose, Líquidos Iónicos, Hydroxyethyl cellulose, Carboxymethylcellulose, Sérum, Ureia, Cosméticos para Cabelo, Forma do cabelo.

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List of Abbreviations, Acronyms and Symbols

ORS	Sheath of outer root
IRS	Inner root sheath
µm	Micrometer
CMC	Cell membrane complex
KAPs	Keratin-associated proteins
nm	Nanometer
kDa	Kilodalton
µM	Micromolar
g	Gram
cm	Centimeters
ILs	Ionic liquid
RTILs	Room temperature ionic liquids
TSILs	Task specific ionic liquids
PILs	Polyionic liquids
SILMs	Membrane ionic liquids
[EMIM] Cl	1-Ethyl-3-Methylimidazolium Chloride
[EMIM] Ac	1-Ethyl-3-Methylimidazolium Acetate
[EMIM] DEP	1-Ethyl-3-Methylimidazolium Diethyl Phosphate
[EMIM] Br	1-Ethyl-3-methyl-imidazolium-bromide
C	Carbon
H	Hydrogen
MC	Methyl
HEC	Hydroxyethyl cellulose
EC	Ethyl
CMC	Carboxymethyl cellulose
MCC	Microcrystalline cellulose
HPC	Hydroxypropyl cellulose
FCS	Chitosan from crab shells
HM	Chitosan high molecular weight
LM	Chitosan low molecular weight
RT	Room temperature
P	Pleasant fragrance
L	Liquid
T	Transparent
FJ	Fluid jelly
Y	Without changes
W	Change pH to 6
Z	Change color to yellowish
J	Jelly
DSC	Differential Scanning Calorimetry
J/g	Joule/gram
Li	Length of the hair before treatment
Lf	Length of the hair after treatment
Hi	Initial amount of hair
Hf	Final amount of hair
SEM	Scanning electron microscope
h	Hour
ºC	Degrees Celsius
mL	Milliliters
rpm	Rotations per minute
PEP	Peptide
DTAF	5-([4,6-Dichlorotriazin-2-yl]amino)fluorescein hydrochloride

ATR-FTIR	Total attenuated reflectance Fourier transform infrared spectroscopy
IRE	Internal reflection element
C.F.	Curl formation
s	Serum
u	Urea
A.A.	Acetic Acid
Mins	Minutes
M	Molar
L	Liter
µL	Microliter
λ_{ex}	Excitation wavelength
λ_{em}	Emission wavelength
wt%	Weight percent
NaCl	Sodium chloride
CH_3OH	Methanol
CH_3OCH_3	Dimethyl ether
C_2H_5OH	Ethanol
$C_2H_5OC_2H_5$	Ethyl ether
CH_2OHCH_2OH	Glycol
$OH\text{-}CH_2\text{-}COOH$	Glycolic Acid
OH	Hydroxyl
CH_2OH	Hydroxymethyl
CH_3	Methyl
CH_3CO^-	Acetyl
H2O	Water
CaCl2	Calcium chloride
H	Hydrogen
N	Nitrogen
S	Sulfur

State of Art

1. Hair

Hair has a direct impact on human life. Hair is considered an important factor for physical appearance, being linked to significant psychological and social impacts. Incessant tendency to modify the physical characteristics of the hair feeds a vast cosmetic industry that tries to innovate and respond to consumer's wishes. Given this importance, several ways have been found to modify physical characteristics of the hair such as the length, color, or shape.

Human hair consists of a natural fiber yarn formed by α-keratin molecules, where two molecules coil together to form an α-helix structure. It comprises of three layers called cuticle, cortex and medulla, forming a rigid structure that provides resistance and flexibility to the yarn (Leite & Maia Campos, 2017).

Over the years, it has been possible to group hair into three primary groups such as African, Asian, and Caucasian hair. Different characteristics are taken into account about the hair fiber including diameter, ellipticity and curvature. These characteristics control most of the cosmetic and physical behavior of human hair (Célia F. Cruz et al., 2016).

Hair is a complex integrated system that contains several morphological components that act as a whole. The part of the hair that is seen above the skin is called the hair fiber. Within the skin, the hair follicle is the living part from which the hair grows and where the hair fiber is generated (Miranda-Vilela *et al.*, 2014).

1.1. Hair Morphogenesis

The human being is born with a fixed number of follicles (Chuong *et al.*, 2007). These follicles are invaginations from the epidermis to the dermis, between the 8th and 12th week of gestation of the human embryo (Uyttendaele *et al.*, 2004). When the distribution of the follicles is established, molecular events occur in the follicle to define the phenotype of each hair (Paus & Cotsarelis, 1999).

During embryogenesis, hair follicles develop and differentiate (**Figure 1**). This occurs thanks to specific molecular interactions that allow to define three main phases,

among them are induction, organogenesis and cytodifferentiation or maturation. In the first phase, induction, mesenchymal cells are transduced through Wnt-mediated signal transduction, which are signaling pathways for signal transduction, which mediate the formation of a placode. Then it occurs to organogenesis. Epithelial cells direct the underlying dermal cells to proliferate and form a dermal condensate, which in turn signals epithelial cells to proliferate and grow downward in the dermis. Finally, cytodifferentiation, where the dermal condensate is surrounded by follicular epithelial cells. There is the creation of a distinct dermal papilla, which instructs the ectoderm to shape the entire hair follicle through the action of morphogens and growth factors (Rishikaysh *et al.*, 2014; Schneider *et al*., 2009).

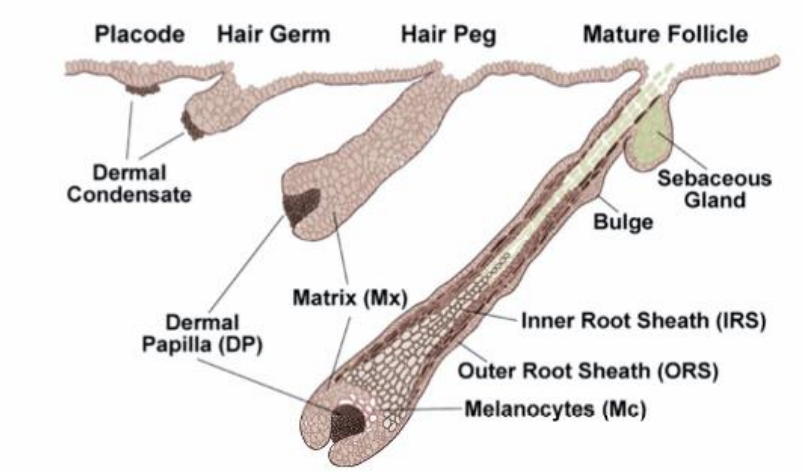


Figure 1: Embryonic stages of the human hair follicle morphogenesis (Célia F. Cruz *et al.*, 2016).

1.2. Hair Follicle Anatomy

Hair follicles are the essential structures for hair growth. At the base of each follicle, cells proliferate and, as they rise, the complex processes of protein synthesis, structural alignment and keratinization transform the cytoplasm into the fibrous material known as hair (Wolfram, 2003).

The follicle is a complex epithelial structure surrounded by a sheath of outer root (ORS) that supports hair growth and through an inner root sheath (IRS) (**Figure 2**) (Lai-Cheong & McGrath, 2013).

In addition to the ORS and IRS layers, the follicle is composed of distinct epidermal layers, such as medulla (in some cases), cortex and cuticle. It also has two dermal tissues: dermal papilla and dermal sheath (Z. Yu et al., 2009).

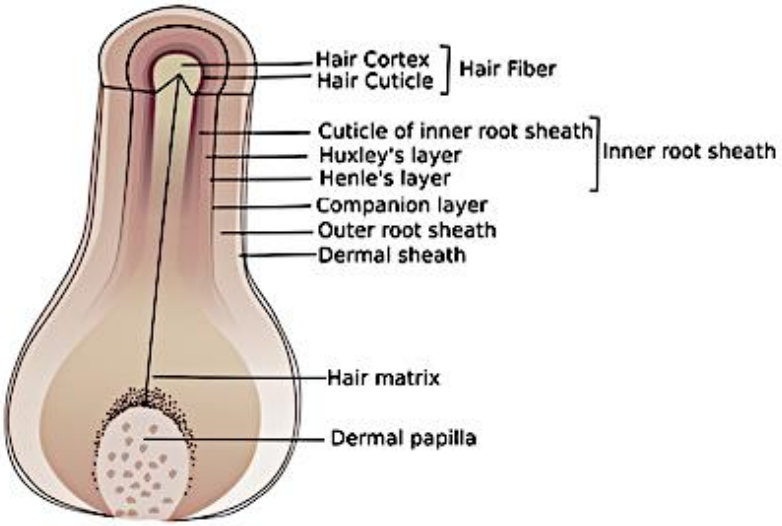


Figure 2: Schematic cross-section of a hair follicle (Célia F. Cruz *et al.*, 2016).

The follicle is located inside the skin, in a region called the hair bulb. This structure is formed by cells in active growth. In hair bulbs, there are keratinocytes, responsible for the highest proliferation rate in the human body, and there are also very specialized cells, melanocytes, capable of producing the pigment that gives color to the hair, melanin (Célia F. Cruz et al., 2016).

1.3. Hair Fiber Structure

The hair fiber has a length between 50 to 100 µm in diameter and has protective and cosmetic functions (Célia F. Cruz et al., 2016).

1.3.1. Cuticle

The cuticle has an amorphous character, its reticular structure depending on the amount of cystine present. Its main function is to serve as a “shield” for the lower layer, the cortex, protecting it from external aggressions.

It is formed by 4 subunits, where all have different chemical compositions and reactivities. The first layer together with the exocuticle, contain higher levels of cystine and an excellent hydrophobic character. Subsequently, the endocuticle has a lower cystine content and has greater solubility in water. Finally, the epicuticle is a thin hydrophobic layer that completely covers the cuticle. It is mainly composed of 18-methylenicosanoic acid, which is attached to a protolipidic membrane, which is rich in cystine (Smith & Swift, 2002).

It should be noted that between the cuticles there is the cell membrane complex (CMC). It is believed that the CMC together with the endocuticle are the main diffusion pathways in human hair (DE CÁSSIA COMIS WAGNER *et al.,* 2007).

1.3.2. Cortex

The cortex is a morphological component of the hair composed of cortical cells and the cell membrane complex (CMC) (Célia F. Cruz et al., 2016).

The cortical cell contains macrofibrils oriented longitudinally to the axis of the capillary fiber and responsible for defining hair color. They constitute 50 to 60% of the cortex mass and present two types of packaging: paracortex and orthocortex. These macrofibrils have microfibrils and keratin-associated proteins (KAPs). Microfibrils are elongated, interconnected and spindle cells also called very well-organized helical proteins, with a diameter of about 7 nm (Célia F. Cruz et al., 2016; Wolfram, 2003).

There are three types of cortical cells in the hair fiber - orthocortical, paracortical and mesocortical. What distinguishes them is the level of cystine present and the matrix level between the intermediate filaments. In view of this, orthocorticals are the ones with less cystine (3% and lower matrix level. Then, paracorticals with a high cystine content (5%) and with an acceptable level of matrix emerge. Finally, mesocorticals have an intermediate level of cystine (Bryson *et al.*, 2009).

1.3.3. Medulla

The hair fibers do not all have the same diameter. With its increase, the cord can be found in the center of the hair fiber. This consists of hollow and spherical vacuoles, packed along with the fiber and joined by a CMC-like structure. When the cord is present, it can be continuous or discontinuous. As there is still not much discovery about this constituent, it is believed that it contributes to the mechanical properties of hair fibers (Bhushan, 2008).

1.4. Hair Fiber Chemical Composition

1.4.1. Hair Proteins

The hair has several components in its constitution. Of all, the most important are keratin proteins. These belong to the family of fibrous structural proteins and are complex natural compounds with heterogeneous morphological structures. Keratin is found inside the hair cells and will give rise to the hair fiber. It has an acid isoelectric

point and is normally negatively charged to the surface of the hair. Its molecular weight varies between 40 and 70 kDa. They are a highly organized material providing significant resistance to numerous environmental (Bouillon & Wilkinson, 2005; Plowman, 2007).

Keratin is divided into two types: alpha-keratin and beta-keratin. Alpha keratin is found in the hair, nails and claws of mammals including humans. This can be further divided into type I and type II. The difference between them is that type I has a molecular weight between 44 and 46 kDa and an acid isoelectric point while type II has a size between 50 and 60 KDa and a neutral isoelectric point. Beta-keratin is present in reptiles and birds, in fabrics such as claws, shells, feathers and beaks. Table 1 lists the results of oxidative solubilization and fractionation of hair of different ethnic origins. It is evident that the fractionation pattern of the different hair types is similar and that there is no indication of significant differences in the filament and matrix texture of keratins (Wolfram, 2003).

Table 1: Keratoses fractions of solubilized hair (wt %)(Wolfram, 2003).

	Keratoses Fraction (%)	
Hair Type	**Alpha**	**Beta**
Asian	42	14
Caucasian	43	15
African	43	15

The amino acid constitution of keratins in human hair (**Table 2**) is different from other keratins. This translates into a greater amount of disulfide bonds in human hair, strengthening the hair structure and providing good mechanical, thermal and chemical resistance. It should be noted that these characteristics come from a greater amount of the cysteine residue (7.6% in keratin in human hair and 2.9% in keratin in the stratum corneum) (Dawber, 1996; J. Yu *et al*., 1993).

Table 2: Some amino acid composition of human hair of various ethnic origins (μM/g)(Wolfram, 2003).

	Hair Type		
Amino Acid	**African** (μM/g)	**Caucasian** (μM/g)	**Asian** (μM/g)
Alanine	370-509	345-475	370-415
Arginine	482-540	466-534	492-510

Aspartic acid	436-452	407-455	456-500
Glutamic acid	915-1017	868-1053	1026-1082
Glycine	467-542	450-544	454-498
Threonine	580-618	542-654	568-593
Proline	642-697	588-753	615-683
Serine	672-1130	851-1076	986-1101

Another type of protein present in hair is KAPs. These have a less defined organization than keratin, however, they have a very significant molecular weight (50-75 kDa). Sulfur-rich with a total of 20% cysteine residues. KAPs are responsible for maintaining the structure of the capillary fiber solid, that is, they are responsible for internal cohesion (Bouillon & Wilkinson, 2005).

1.4.2. Hair Lipids

Depending on ethnicity, sex and age, the lipid content present in the hair may be different (Dawber, 1996).

In hair, the lipids are distributed by the hair fiber where they make up 4% of its weight. They are divided into two groups: external and internal, which can be free or belong to the CMC (Robbins, 2012).

One of the main components of exogenous lipids or external lipids is 18-MEA, which is strongly linked to the outermost layer of the cuticle. This makes the fiber surface more hydrophobic, delaying water penetration. It acts as a lubricator, reducing capillary friction, leading to its absence to the appearance of dry hair or difficulty in combing (Tanamachi *et al.*, 2010).

1.4.3. Hair Water

Humidity is a parameter studied taking into account the advantages that good water absorption brings to the hair, which is hygroscopic (Bouillon & Wilkinson, 2005). It has been proven that parameters such as the stability of the hair protein structure, as well as its physical and cosmetic properties are related to the relative humidity. This humidity is conditioned by the relative humidity in the air (Bouillon & Wilkinson, 2005). With water absorption, the hair increases its weight from 12 to 18% (Dawber, 1996).

Water is able to slightly distort the microfibril structure, increasing the volume of the hair fiber. There are numerous water binding sites in keratin, for example, peptide

bonds and acidic and basic side chains. It is known that water permeates the hair, but the bonds within the molecular structure of the cortex are equally selective. It should be noted that the absorption of water is related to the amount of lipids as well as the pH level (Bouillon & Wilkinson, 2005).

1.5. Classification and differences between Ethnic Hair Fiber

Hair can be classified as straight, curly, or wavy. This classification is based on parameters such as the diameter of the hair curve, the curl index and the number of waves present in the hair (Loussouarn *et al.*, 2007; Mettrie *et al.*, 2007).

Each ethnic group has different characteristics regarding the constitution of hair. Variables such as growth rate, hair size and shape are differentiated from individual to individual, although they are of the same ethnicity (Hearle, 2000; Matsunaga *et al.*, 2013). In view of this, the hair is divided into three groups: Caucasian, African and Asian.

Caucasian hair has a shape that can be smooth or wavy, however, the diameter and shape of the section are intermediate. Regarding African hair, it has a curly character due to the shape of the follicle. It has a twisted, flat oval fiber with random reversals in direction. Finally, Asian hair has an invariably straight character, and its fiber has a diameter with circular geometry. The hair cuticle has a number of scales ranging from 6 to 10 in Asian hair, being less present in Caucasian hair and even less in African hair. As for the mechanical properties, these are better for Asian hair, with the weakest hair being African hair (Seshadri & Bhushan, 2008). As for humidity, African hair absorbs less water (Franbourg *et al*., 2003; Robbins, 2012; Rodney *et al*., 2013).

It should be noted that despite these huge differences between hair types, the amino acid composition of protein is identical in all. However, other constituents are still the subject of study and there is still no general consensus, for example, regarding the amount of lipids present (Saint Olive Baque *et al.*, 2012).

2. Impact of Cosmetics Treatment in Hair

2.1. Chemical Hair Cosmetics Procedures to Modulate Hair Fiber

The hair can be curly or smooth. Techniques have been developed to promote these shape changes. To ensure straight hair, techniques such as simple straightening or permanent straightening can be used. A simple straightening, called temporary, it

requires the use of physical-chemical processes such as the use of a hairdryer or a straightening board. This process has a reduced duration, for example, until the next wash. The same is true if the temporary curling technique is used, the physical-chemical processes being the same as in straightening. The change in the shape of the hair occurs in these techniques, because with heating there is a breakdown of the hydrogen bonds of the keratin allowing a temporary opening of its original structure (Miranda-Vilela *et al.*, 2014; Wolfram, 2003).

When permanent straightening or curling effect is desired, internal hair changes occur. This is due to the disulfide bonds that are essential for keratin stabilization. Two adjacent cysteines and linked, generating cystine, forming a bridge between two chains or two portions of the same chain. The susceptibility of these bonds to reduction and oxidation is the basis of most chemical hair modifications (Wolfram, 2003). The conventional chemical treatment called as permanent curly hair consists in the use of reducing agents, which break the disulfide bonds, followed by the oxidation step which reorganizes the disulfide bonds reaffirming a new form of the hair (Harrison & Sinclair, 2003) (**Figure 3**).

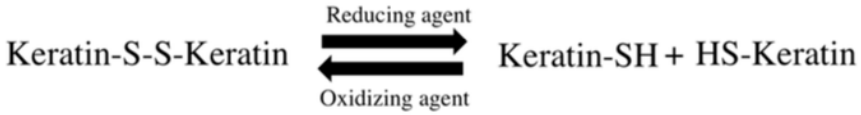


Figure 3: Chemical reaction of hair keratin fiber in the presence of reducing and oxidizing agents during treatment (Célia F. Cruz *et al.*, 2016)

An example of a formulation described and capable of being used in the permanent hair curling process is described in table 3.

Table 3:Possible formulation of a product for permanent curly effect (Maria & Fernandes, 2013)

Compound	Quantity (%)
Thioglycolic Acid (99%)	8.0%
Aqueous ammonia solution (25%)	8.6%
Distilled Water	7.,2%
Oxyethylene Lanolin (PEG 75)	2.0%
Phosphoric Acid	0.2%
Fragrance	0.4%
Noloxynol-14	1.6%

For permanent straightening, the formulation used involves an alkaline phase (sodium hydroxide, lithium hydroxide or guanidine hydroxide), an oil phase and an aqueous phase. A possible procedure for this technique would be the application of the formulation in the hair to occur its penetration in the cortex and subsequent breaking of the disulfide bridges. Upon breaking, smoothing occurs and then the formulation is removed, resulting in the formation of new disulfide bridges. These new bridges will allow the hair to maintain its straightened shape (Harrison & Sinclair, 2003).

2.2. Health and Hair Hazards of Hair Shape Modification

The procedures used to change the shape of the hair cause problems for the hair fiber. A very common damage is the removal of the monomolecular layer of fatty acids covalently linked to the cuticle, rearrangement of the disulfide bonds. This will lead to the elimination of lipid 18-MEA and consequently the hair will be drier, decrease the shine, making it more susceptible to static electricity and moisture-induced frizz, as well as to increased hydrophobicity (Dawber, 1996; Miranda-Vilela *et al*., 2014).

For example, the formulations used to straighten the hair are quite alkaline (high pH), enhancing a reduction in resistance and increasing susceptibility to friction. This can lead to cracking of the endocuticle and CMC (Gavazzoni Dias, 2015).

The use of excessive and repetitive heat treatments deeply contributes to hair damages. Excess heat produces a decomposition of tryptophan residues in oxidation products of the kynurenine type. The consequences are the yellowing of white hair and the darkening of bleached hair. After heat treatment with the addition of lipid products, hair can appear easier to comb. However, after washing and removing the lipids, the hair dries out exposing the damage caused by the excess of heat (Gavazzoni Dias, 2015). Although the use of a blow dryer causes more damage to the hair surface than natural drying, a study by Lee et al concluded that using a hair dryer at a distance of 15 cm with continuous movement causes less damage than drying the hair naturally. However, when a hot plate is applied to the surface of the hair, usually 15 to 20 times in the same place where the product was spread, it will be considered a much more aggressive method for the integrity of hair fiber proteins (Kim *et al*., 2010; Lee *et al*., 2011).

The malignant effect of changes in hair shape comes, not only from the constituents of the formulations, but also from the number of times that this type of

treatment is applied. This excessive use can provoke hair thinning, discoloration, irritation of the scalp, skin burns or even allergic reactions to chemicals presented in the formulations (Kaur *et al.*, 2002).

A problem that is being increasingly debated and has concerned the professionals and users, is the use of chemical agents in the formulations to change the shape of the hair. There is an incessant need to find viable solutions to replace these agents so that the effectiveness of the formulation is equally good. The use of chemicals such as formaldehyde, glutaraldehyde, are real examples of what these chemical agents do to the hair and the human looking for this type of scalp shape change. Serious damage to the upper respiratory tract tissue, skin and mucosal irritations, as well as carcinogenic and teratogenic potential, are some of the harmful effects of the chemical agents present in the formulations to alter the shape of the hair (Galli *et al.*, 2015; Maneli *et al.*, 2014; Miranda-Vilela *et al*., 2014).

3. Ionic Liquids

3.1 Definition and properties

Ionic liquids (ILs) are organic salts with an organic cation and with an inorganic or organic anion (**Figure 4**). For that, is possible to select the cation and the anion carefully, or add several functional groups, with an enormous capacity to adjust their properties for different applications (X.-M. Liu et al., 2009). ILs are normally composed of ions with melting point below 100 ºC.

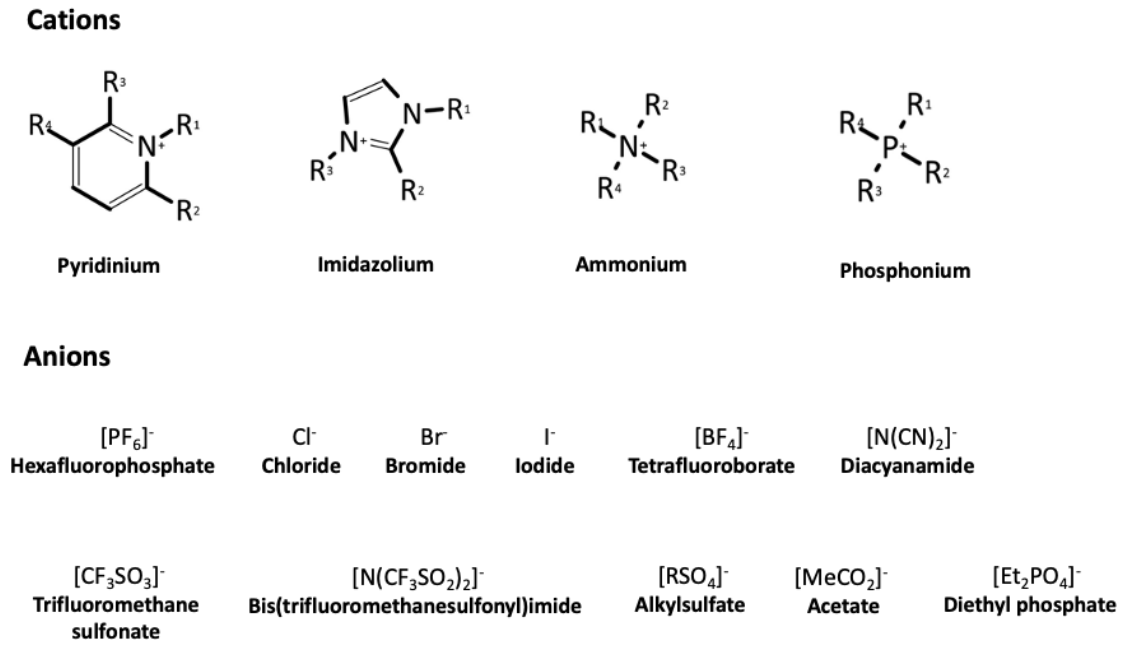


Figure 4: Structure of some cations and anions in ionic liquids.

The use of ionic liquids as new solvents in the industry is also due to the fact that they are considered relatively green chemicals and are good substitutes for volatile organic solvents due to their low vapor pressure (Keskin *et al*., 2007).

An important fact of ILs is the constitution of their side chain in both the cation and the anion. This depends on factors such as melting point, viscosity, density and miscibility in water. ILs have been reported to reach a liquid crystalline phase when they consist of an alkyl chain with more than 12 carbon atoms in the cation's imidazolic ring. When this chain was smaller than 12 carbon atoms, ILs were liquid at room temperature (Gordon *et al*., 1998; Keskin *et al*., 2007). It should be noted that the IL cations are responsible for the low melting point, since they are bulky and have a low degree of symmetry, thus reducing the network energy of the crystalline form of the salt (Muhammad *et al.*, 2015).

ILs have captivating characteristics such as chemical and thermal stability, non-flammability and low vapor pressure, high polarity, excellent acidity and basicity, recyclability and high miscibility with polar substances (Keskin *et al.*, 2007; Marsh *et al.*, 2004).

The organic-ionic hybrid nature of ILs and the resulting intermolecular interactions give rise to a complex set of phenomena, creating an area of study that is quite fascinating and challenging.

This study emerged on fields such as chemical engineering, organic chemistry, environmental science, and even on materials science. Over the years, ILs have been divided into room temperature ILs (RTILs), task specific ILs (TSILs), polyionic liquids (PILs) and membranes (SILMs). In order to better understand the usefulness of ILs, they were tested in catalysis, separations, ionogels, super-capacitors, carbonizations and lubrications. Zhang, Song and Han provided a comprehensive review of the catalytic conversion of cellulose, hemicellulose, lignin and lignocellulosic biomass into chemicals and value-added fuels, in which ILs act as solvents or as catalysts. The use of ILs in chemical engineering has facilitated enough separation processes, solving problems in critical stages of the processes. The fact that ionic liquids are considered green solvents has aroused new interest, being considered highly efficient and viable catalysts (Lei *et al*., 2017).

3.2 Potential and drawbacks of ionic liquids in industrial processes

The use of ILs in industrial processes is increasingly a point of interest, being explored mainly their properties as solvents and the electrochemical and catalysis potential they provide, as well as their application in the pharmaceutical and medical fields (**Figure 5**) (Gomes *et al.,* 2019).

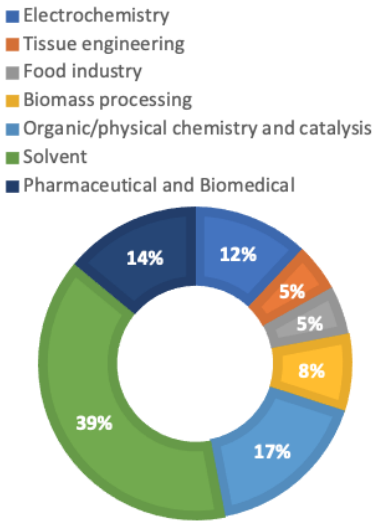


Figure 5: Schematic representation of research intensity regarding using ILs. Based on (Gomes *et al.*, 2019)

Because of their distinctive characteristics, ILs have been widely studied as solvents or catalytic agents for biomass processing. The ability to break intermolecular hydrogen bonds, and interact with hydroxyl groups in composite structures, combined with their low toxicity, makes them attractive when related to poorly soluble

biopolymers (Idris *et al*., 2013; Petkovic *et al.*, 2010). Accordingly, some ILs belonging to the alkenoate family have shown high efficiency in dissolving suberin from cork, which is insoluble in many solvents. They are also directly linked to the de-crystallization of cellulose, functioning as a cationic polymer, which is an important process in the industry, namely in the removal of acid dyes from aqueous effluents from the textile industry (Abbott et al., 2006; Q. Zhang et al., 2012).

The dissolution of keratin from feathers, as well as the dissolution of lignin from biomass, was also successfully achieved, without using any other product as an additive. In the latter case, the dissolution of the lignin allows the cellulose to be left behind, which can be digested with enzymes releasing fermentable sugars (Gomes *et al*., 2019). Recently it has been demonstrated that it is possible to develop integrated processes for the production of biodiesel through the aforementioned dissolution, presenting reduced costs and decreasing the complexity of the processes (Sun *et al*., 2016, 2017; To *et al*., 2018).

ILs have also been widely used as additives to provide some materials with enhanced and desired properties. For example, the fact that ILs form strong hydrogen bonds, makes them an attractive non-volatile plasticizer for natural biopolymers, ensuring they are economically and ecologically profitable (Colomines *et al.*, 2016).

In the pharmaceutical and biomedical fields, ILs are used as stabilizing agents for biomolecules, as solvents or as part of drug transport systems, such as API-IL (Gomes *et al.*, 2019). As an example, Banerjee *et al.* developed an effective oral insulin formulation through the use of ILs. This formulation showed high long-term stability and very good biocompatibility, with ILs being considered a viable alternative for the development of oral administration vehicles (Banerjee *et al*., 2018; Pernak *et al*., 2007). Given the ability of ILs to promote the stability of biomolecules, they are being seriously studied and tested as portable diagnostic devices. The ideal for these devices is their ability to be degraded in a controlled and non-harmful way, at the same time they can influence biological processes in a controlled way (Curto *et al.*, 2014; Jia *et al.*, 2017; Reslan & Kayser, 2018). The intense research in this area has led scientists to consider using IL-based bio-responsive systems as artificial muscles, organs or even as transient implantable medical bionics (Jia *et al*., 2017).

3.2.1 Role of Ionic Liquids in the dissolution of Cellulose

Ionic liquids have gained significant interest in the dissolution of carbohydrates and other biopolymers (Fort *et al*., 2007). ILs have been widely used in the dissolution of cellulose once it structure is linear and highly ordered generating solid intramolecular and intermolecular hydrogen bonds (Muhammad *et al*., 2015). Cellulosic materials have limited solubility in water and in many organic solvents, and ILs have attracted attention for their ability to dissolve them (**Table 4**). Until now, processing cellulose materials on an industrial scale has required aggressive solvents such as sodium hydroxide/carbon disulfide and sulfuric acid, and these processes are undesirable from an environmental and safety point of view (Johnson & Snow, 2017). This is due to the phenomenon of weak interactions between cellulose and most polymers causing agglomeration of the cellulose particles and intensive stress concentration in the resulting composites. The presence of hydroxyl groups in the cellulose structure decreases its tendency to hydrophobic polymers and solvents (Koochaki *et al*., 2020).

Table 4: Solubility of Cellulose in some ILs. Based on (Uto *et al.*, 2018).

Ionic Liquid	Cellulose solubility (wt %)	Temperature (ºC)
1-Allyl-3-methyl imidazolium Chloride (AMIMCl)	18.0	96.85
1-Ethyl-3-methyl imidazolium Chloride (EMIMCl)	12.3	96.85
1-Butyl-3-methyl imidazolium acetate (BMIMOAc)	10.7	96.85
1-Butyl-3-methyl imidazolium Chloride (BMIMCl)	9.1	96.85
1-Ethyl-3-methyl imidazolium Acetate (EMIMOAc)	7,4	96.85
1-Butyl-3-methyl imidazolium Bromide (BMIMBr)	2.0	96.85
1-Ethyl-3-methyl imidazolium Bromide (EMIMBr)	1.0	96.85

The study of the dissolution of cellulose in ionic liquids began in 1934. A key factor in cellulose dissolution is the breakdown of the intramolecular and intermolecular hydrogen bonds network. ILs are promising non-derivatizing solvents for dissolving cellulose, as they break the hydrogen bonds between the cellulose filaments and reform the hydrogen bonds with the cellulose. Numerous ionic liquids were tested and proved to be highly effective. The most used ones have a particularity in common, the presence of an imidazolic cation (Muhammad *et al.*, 2015).

Given the fact that ILs have cations and anions in their constitution, they will play a very important role in the ability to dissolve cellulose. After many studies, it was found

that ILs with large anions had more difficulty in showing high efficiency in cellulose dissolution compared to smaller anions. Both, cation, and anion need to be small enough to reach the hydroxyl groups of the cellulose to form the donor-acceptor electron complex.

The acetate anion, for example present in 1-ethyl-3-methylimidazolium Acetate, and the phosphate anion are the most effective although the acetate anion has a higher hydrogen bond basicity than phosphate. However, the dissolution of cellulose can give rise to a very viscous solution and to overcome this problem the use of 1-ethyl-3-methylimidazolium diethyl phosphate may be a good alternative since it has an excellent basic hydrogen bond since it has a phosphate anion and still has a low viscosity (Muhammad *et al*., 2015; Zavrel *et al.*, 2009).

The fact that an IL can have a cation helps in solubility as mentioned above. The principle is the same as for anions - a small cation has greater solubility efficiency than a large cation. Note that the ability to form hydrogen bonds, which is decreasing with the increase of the cation, is due to the steric impediment (H. Zhao et al., 2008).

Erdmenger et al. came to demonstrate through his study that the length of the alkyl side chain linked to the imidazolic ring also affects the dissolution of cellulose in ILs. His work shows that an odd number of carbon atoms in the alkyl chain is more efficient than an even number, with this chain having up to 6 carbon atoms (Erdmenger *et al.*, 2007). In another study, it was shown that if the alkyl chain increases the length from C2 to C4 (two carbons) it has a positive effect, however if it increases from C6 to C8, the effect is the opposite. Several positive and negative aspects were discovered when the increase in cation chains was tested (Muhammad *et al.*, 2015).

4. **Carbohydrates Polymers**

Carbohydrates are a large family of biomolecules that have highly diverse structures. They consist of monosaccharides, disaccharides, oligosaccharides, and polysaccharides, and are the most abundant biomolecules in nature. Carbohydrates are often found on the surface of cells as plant cell wall polysaccharides and as oligosaccharides that decorate the surfaces of animal cells that are involved in molecular trafficking, protein folding and biological recognition (Galermo *et al.*, 2019).

Polysaccharides are synthesized through plants, animals, and humans. The most abundant polysaccharide are chitin, glycogen, and cellulose. There is a growing desire to develop new cellulosic materials given that cellulose is a renewable resource, although many of the technologies currently used in pulp processing are classified as non-green. (Swatloski *et al*., 2002).

Cellulose is one of the most abundant bio renewable and biodegradable polymers, with a wide range of applications in membrane, paper, film and coating separations. It consists of linear polymeric glucose chains that form intermolecular and intramolecular hydrogen bonds. This structure presents a huge hurdle when you want to dissolve cellulose in water and common organic solvents. Until now, processing cellulose materials on an industrial scale has required aggressive solvents such as sodium hydroxide, carbon disulfide and sulfuric acid. These types of processes are not desirable because they have consequences for the environment. Over the years and with the need to make the best use of this resource and in a more sustainable way, several alternative solvent systems have been developed to dissolve and process pulp and improve performance in the production of pulp additives (Zheng *et al.*, 2019).

Glucose is the best-known monosaccharide and has probably been investigated more deeply than any other organic compound. The structure of glucose and several other monosaccharides, including fructose, galactose and mannose, was established by the brilliant work of the German chemist Emil Fischer, who thus laid the foundation for the chemistry of carbohydrates. They are found in the form of various derivatives, from which they can be released by hydrolysis with aqueous mineral acids or enzymes. The most abundant of the derivative are polysaccharides (**Table 5**), which are composed units of sugar formed in giant molecules that can consist of up to 26.000 monosaccharides. One of the most abundant carbohydrate is chitin, a polymer of acetylglucosamine. It is considered the main organic component of the exoskeleton of arthropods, such as insects, crabs and lobsters, which constitute the largest class of organisms, comprising about 900.000 species (Lloyd-Price *et al*., 2017).

Table 5: Most abundant polysaccharides (Vollhardt, 2013).

Polysaccharides	Source	Structure
Cellulose	Plants	Long chain polymer formed by only one monomer.

Amide	Reserve organs and plants	Mixture of two polysaccharides, amylose, and amylopectin
Chitin	Fungi and the exoskeleton of arthropods	A long chain polymer of N-acetylglucosamine
Glycogen	Animal cells and bacteria	Large aggregates or granules, which are highly hydrated

The study of carbohydrates has been enriched the chemistry, giving rise to their use of them as raw material in industries of great economic importance, such as in the paper industry, textile, pharmaceutical, food and cosmetic industries. In the cosmetic industry, carbohydrates have been an important part (Pomin, VH. e Mourão, 2006). For example, the action of amino acids and proteins is of high relevance and importance because it helps in preserving the integrity of the hair fiber, in the alignment of cuticles and hair follicles, in preventing hair loss, in smoothness, shine, elasticity, hydration, conditioning and regulation moisture. In fact, they are constituents of many hair products such as capillary resistance masks, shampoos, and conditioners.

4.1. Cellulose

Cellulose is a bio-renewable and biodegradable polymer that is quite abundant in nature. This comes from wood, which is the main source of cellulose used in the paper, fiber, ink, membrane and polymer industries (Fort *et al.*, 2007). Cellulose consists of linear polymeric chains of glucose that form intramolecular and intermolecular hydrogen bonds (**Figure 6**).

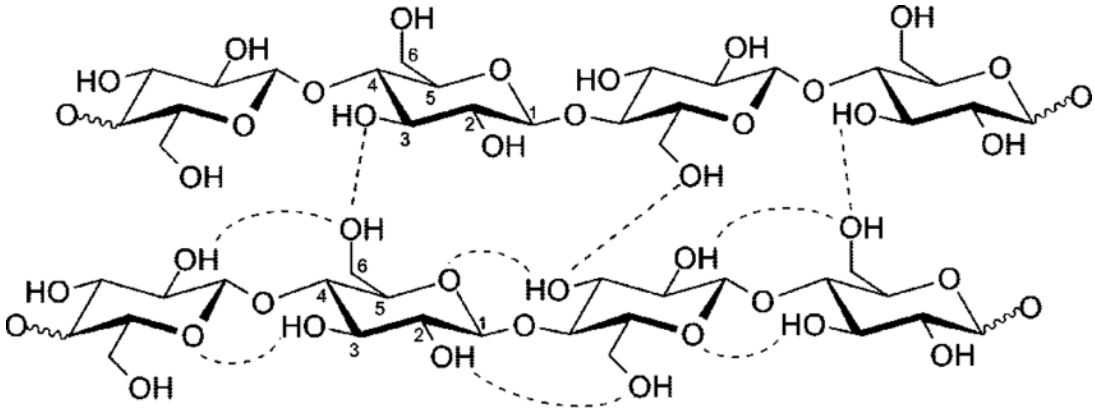


Figure 6: Intra and intermolecular hydrogen bond in structure of cellulose (Pinkert *et al.*, 2009).

The typical modifications of cellulose are esterification and etherification at the hydroxyl groups of cellulose (**Table 6**). Most water-soluble and organic solvent soluble cellulose derivatives are prepared by these substitution reactions, and drastic changes

in the original properties of cellulose can usually be achieved by these chemical modifications.

Table 6: Some of etherifying agents, co-products, and by-products from the production of cellulose ether. Based on (Kamel *et al*., 2008).

Cellulose Ether	Etherifying Agent	Co-product	By-product
			Name and formula
Methyl (MC)	Methyl Chloride	NaCl	Methanol dimethyl ether (CH_3OH/ CH_3OCH_3)
Ethyl (EC)	Ethyl Chloride	NaCl	Ethanol diethyl ether (C_2H_5OH/$C_2H_5OC_2H_5$)
Hydroxyethyl (HEC)	Ethylene Oxide	None	Ethylene glycol and polymers thereof (CH_2OHCH_2OH)
Hydroxypropyl (HPC)	Propylene Oxide	None	Propylene glycol and polymers thereof ($CH_3CH_2OHCH_2OH$)
Carboxymethyl (CMC)	Chloroacetic Acid	NaCl	Glycolic acid (HO-CH_2-COOH)

Other modifications can be ionic and radical grafting, acetylation, deoxyalogenation and oxidation. Figure 7 shows the schematic representation of the position in the cellulose structure for chemical modifications (Kamel *et al*., 2008).

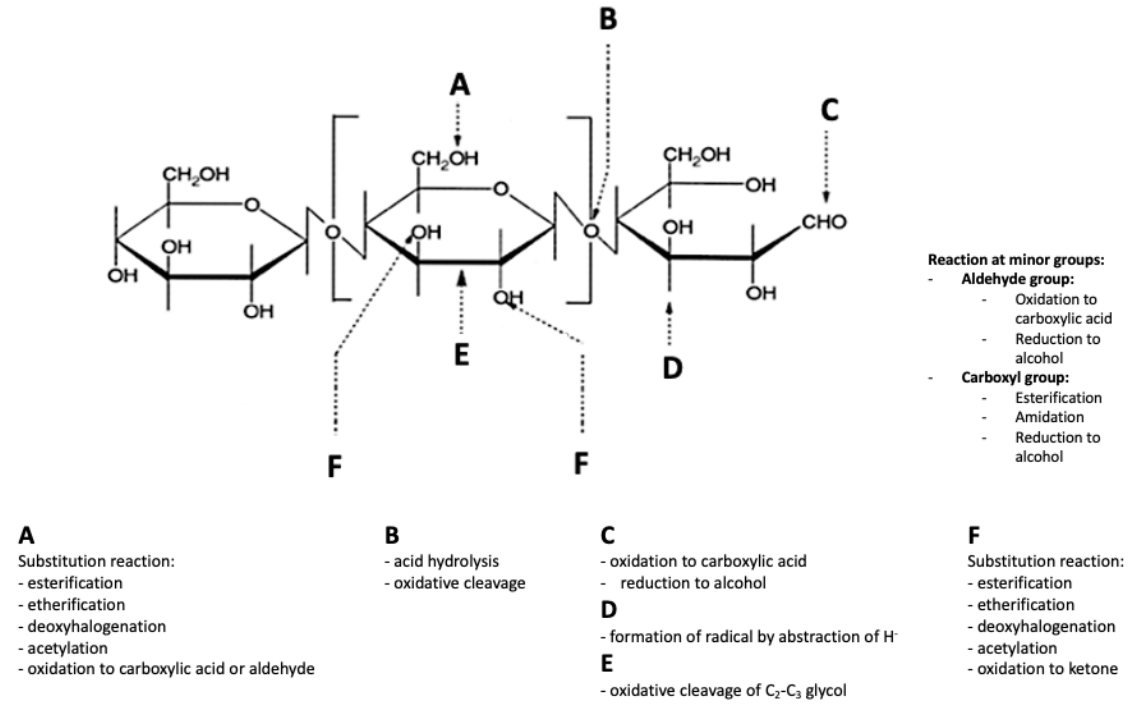


Figure 7: Position in cellulose structure for chemical modifications. Based on Kamel *et al.*, 2008).

The structure results in inter and intra-hydrogen network bonds, making it difficult to dissolve in water or organic solvents (ENTWISTLE & ROWE, 1979; Maftoonazad & Ramaswamy, 2005). Several alternative solvent systems have been developed in order to promote the dissolution of cellulose and to improve performance in the production of additives from cellulose. However, these systems presented disadvantages that did not make them profitable and viable (Basta & El-Saied, 2008; Saalwächter *et al.*, 2000).

Recently, several experiments have been showing that the use of ionic liquids (ILs), as a new class of solvents, can be an effective alternative to the cellulose dissolution. The use of ILs have enormous advantages, such as chemical and thermal stability, non-flammability and low pressure vapor (Zheng *et al*., 2019).

4.1.1. Microcrystalline Cellulose

Microcrystalline cellulose (**Figure 8**) is a derivative of micro crystallization of cellulose. Cellulose is partially depolarized and microcrystalline cellulose is obtained.

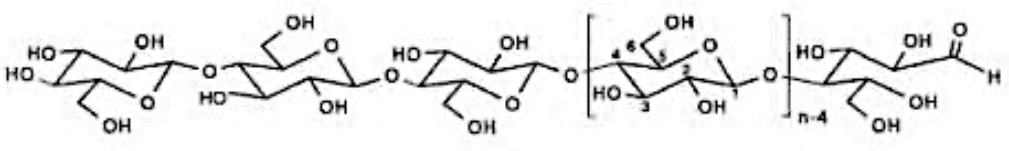
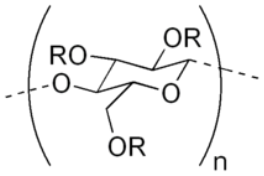


Figure 8: Structure of Microcrystalline Cellulose (Nsor-Atindana *et al*., 2017).

This cellulose was introduced in the 1960s, offering great advantages in the pharmaceutical and cosmetic area such as active role in stabilization of emulsions, anti-glomerating agent and viscosity regulator (Garba *et al.*, 2020).However, it presented some limitations such as, for example, the apparently low density, moderate fluidity, loss of thickness with increased humidity and sensitivity to lubricants. In the field of cosmetics, microcrystalline cellulose can be used to guarantee the non-formation of granules in the formulations in which it is found, to minimiz the pH change of a solution if an acid or a base is added, to allow the union of the formulation if mixed with oils or liquids, it helps other substances to flow more easily and smoothly, with no chemical reactions occurring and it also increases the thickness of an aqueous solution (Guo & Augsburger, 2003).

4.1.2. Carboxymethyl Cellulose

Carboxymethyl cellulose (**Figure 9**) is an anionic polymer derived from cellulose. It has the particularity of being very soluble in water, both cold and hot. It has a viscosity that can be controlled by pH and temperature.



R = H or CH_2CO_2H

Figure 9: Structure of Carboxymethyl Cellulose (Pushpamalar *et al.*, 2006).

Solutions containing this type of cellulose present a final gelling result. It has excellent properties as a food additive, but it also has advantages in the pharmaceutical or cosmetic industry. Its viscosity allows it to form useful gels for cosmetic products, for example, shampoos and also offers a protective film to the hair when spread evenly (Sadeghi *et al.*, 2020).

4.1.3. Hydroxyethyl Cellulose

Hydroxyethyl cellulose (HEC) (**Figure 10**) is a derivative of native cellulose, by the action of an etherifying agent, ethylene oxide.

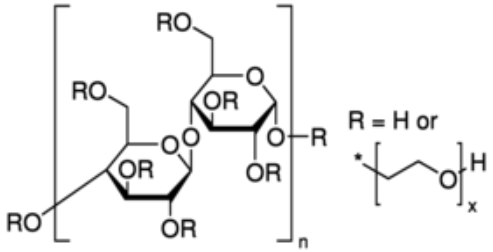


Figure 10: Structure of Hydroxyethyl cellulose (Holtzapple, 2003).

The fact that this cellulose is commercially produced through a chemical reaction, it becomes composed of glucopyranose units randomly substituted by hydroxyethyl groups in position 2, 3 or 6, whose side chains can be monomers, dimers, or trimers (Adden *et al*., 2006). Due to its high-water solubility, HEC has numerous applications, for example, in the development of polymer and copolymer networks, gelling agents and thickeners including personal care products, pharmaceutical formulations, construction materials, adhesives, among others, and as stabilizer for liquid soaps (Arai & Shikata, 2020a).

In the area of hair cosmetics, it is presented in hair creams, hair sprays, shampoos, and hair styling gels. HEC polymer is a water-binder and a thickener agent which allows to improve the texture, the appearance, the shelf-life, and the firmness of the products. When spread on hair, it forms a thin protective layer, making hair smooth and soft without flaking (Drovetskaya *et al*., 2007; Omidian & Park, 2017)

4.2. Chitosan

Chitosan is a polysaccharide derived from a substance in the marine environment. After cellulose, it is the second most abundant polymer in nature. Due to its lower cost and the easy suitability for mass production, the production of chitosan through a chemical process is industrially preferred. This process consists of an alkaline deacetylation of chitin, formed by the units D-glucosamine and N-acetyl-D-glucosamine (Muxika *et al.*, 2017).These are linked by 1,4-glycosidic bonds (**Figure 11**).

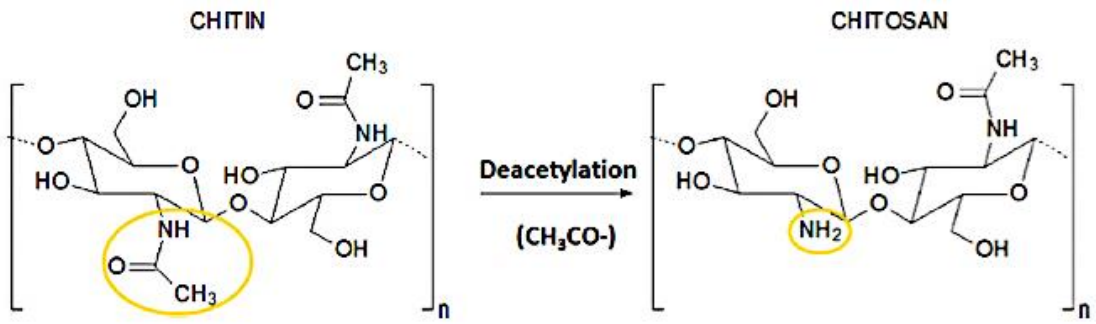


Figure 11: Chemical structures of chitin and chitosan (Muxika *et al.*, 2017).

An important fact about chitosan is that the ratio between the two units of glucosamine will determine the degree of deacetylation. When reaching 50%, the chitosan becomes soluble in an aqueous acid medium. When chitosan is dissolved in an acidic medium, the amino groups present in the chain protonate and, in the polymer, become cationic, allowing their interaction with several types of molecules. The fact that the polymer is cationic may be related to its antimicrobial activity, through the interaction with the negatively charged cell membranes of the microorganisms (Muxika *et al.,* 2017).

Chitosan has been used in a wide variety of industrial fields such as biomedicine, cosmetology, papermaking, wastewater treatment, agriculture, or pharmaceutical applications, among others. Bearing in mind that chitosan is derived from a substance from the marine environment, it has several biomedical applications as it has antibacterial and antioxidant characteristics. Its solubility is also a very important aspect, as it offers numerous opportunities to produce films, nanofibers, hydrogels or pastes (Ahmed & Ikram, 2016).

Among the natural antimicrobial compounds of marine origin, chitosan is widely used in cosmetics (Corinaldesi *et al.*, 2017). Morsy *et al.* and Wongkom and Jimtaisong carried out studies where they included chitosan as a form of treatment for skin problems (Morsy *et al.*, 2017; Wongkom & Jimtaisong, 2017). Great results were obtained, and it was deduced that chitosan promotes a defense against multi-resistant bacteria, being considered viable for substances such as antimicrobial sunscreen or as an additive for organic cosmetic sunscreen for the care of infected skin. Chitosan has also been used to encapsulate active ingredients in cosmetic products. This type of use of chitosan has shown excellent results in studies done providing a very good final hydration of the skin (Chaouat *et al.*, 2017; Libio *et al.*, 2016).

The use of chitosan in hair care products has gained greater attention as they can help in the treatment of damaged hair. Chitosan and its derivatives have been included in a wide variety of hair products, such as shampoos, rinses, permanent wave agents, hair dyes, styling lotions, sprays and hair tonics (Abugoch *et al.*, 2011). Due to its ability to interact with keratin, transparent and elastic films are formed on the hair fibers. These films increase the softness and strength of the hair and prevent damage to the hair. In addition to the filmogenic capacity of chitosan, it has a gelling capacity that allows its application in gels (Abugoch *et al.*, 2011; Brigham, 2017). The use of chitosan in salts is also a viable alternative, being used in lotions, conditioners and shampoos (Aranaz *et al.*, 2018). Chitosan is also involved in the treatment of scalp disease, androgenetic alopecia. Not being directly related to the solution of the disease, chitosan is used to ensure the solubility of minoxidil sulfate, an important part of the treatment. This is possible due to the ease that chitosan has in dissolving substances (Gelfuso *et al.*, 2011; Matos *et al.*, 2015).

Materials and Methods

5. Materials

Three types of cellulose used in this work: Microcrystalline cellulose, Carboxymethyl cellulose and Hydroxyethyl cellulose, were purchased from MerckSigma. The ionic compounds used were 1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium diethyl phosphate and 1-ethyl-3-methylimidazolium acetate were provided from Tokyo Chemical Industry- TCI chemicals. Three types of chitosan: chitosan from crab shells, chitosan high MW and chitosan low MW, urea acetic acid and benzyl alcohol were supplied from MerckSigma. Commercial serum was used as received.

6. Methods

To modify the shape of the hair, formulations were developed and tested with different types of cellulose, solvent, and application methods. Each application method had as main objective to change the shape of the hair. The formulations tested were based on benign compounds. The main objective to develop benign methodologies is the reduction of harsh chemicals agents incorporated into compounds currently used to change the shape of hair.

6.1. Development of the formulations

To circumvent the problems associated with chemicals used in cosmetic products, formulations based on carbohydrates were developed and tested their curly efficiency in Asian hair tresses. The cellulose was solubilized in distilled water and in ionic liquids, under separately experiments. Chitosan was dissolved in water under acidic pH and in ionic liquids for further application.

Various methods of application on hair of those formulations were tested at different temperatures and different times of incubation. For this purpose, was also used a commercial serum (containing benzylic acid, propylene glycol and denaturated alcohol) was also used to dissolve our carbohydrates. It was also tested a pre-treatment using a polar solvent (e.g urea) incorporated into the serum formulation.

6.2. Application method of the formulations in hair tresses

The modification of the hair shape is a process that involves several steps. The perming process is one of the most used techniques to change the shape of the hair from straight to curly. Five methods were developed in this experimental work.

The developed methods were tested from several variables such as the incubation period of the formulations on hair, the use of wet-dry cycles, tools, and equipment to dry the hair at different temperatures. These variables helped to optimize the methodologies implemented until achieve a promised result by simulating an easy and efficient application of those formulations.

The hair selected for this investigation study was the Asian hair type, taking into account that this is the most resistant hair compared to African and Caucasian (Célia F. Cruz et al., 2016).

To evaluate the curly efficiency of the formulations in each hair sample, it was measuring the length of the hair after and before treatment. The formula used to calculate the curl efficiency was in percentage (**Equation 1**).

$$\text{Curl formation (\%)}: \left(\frac{Li-Lf}{Li}\right)\times 100 \quad (1)$$

where Li is the length of the hair before treatment and Lf is length of the hair after treatment.

6.3. Formulation characterization

The formulations were evaluated in terms of physical stress, thermal stress, organoleptic properties, and storage at different temperatures. General stability of a cosmetic product in real time or in accelerated conditions should guarantee the stability and physical integrity providing its correct effect when applied.

The stability of a cosmetic product it is dependent of its capacity to manage physical variations, ideally until the end of the expiration date. To analyze and evaluate the physical stability of our formulations, the samples were subjected to a gravitational

centrifugation at 3000 rpm during 5h at room temperature. At the final of the centrifugation the formulations were examined visually.

Thermal stress was performed exposing the formulations samples at extreme temperatures, cycles at 4ºC and at room temperature. Each cycle corresponds to the exposure of the samples at 4ºC for 24h followed more 24h at room temperature. At the end of each cycle the samples were examined.

Preliminary and accelerated stability was performed to evaluate organoleptic characteristics including odor, color, and aspect. These samples were analyzed visually, for a long period of storage (12 weeks) at different temperatures (25ºC, 37ºC, 4ºC).

6.4. Morphological characterization of hair samples

Morphological evaluation of treated and untreated hair fiber was performed. Scanning electron microscopy (SEM) allowed observe the bulk structure of keratin hair fiber, using an electron microscope model Phenon-World Bv, Netherlands at 1000× magnification (**Figure 12**). Hair samples were coated with a thin layer of gold to improve samples electrical conductivity (Ribeiro *et al.*, 2021).

Figure 12: Scanning electron microscopy (SEM).

6.5. Mechanical wear resistance of hair

The mechanical properties of the hair fiber were evaluated by the percentage of mass loss resistance. Hair's resistance to mechanical wear was carried out on treated and untreated hair fiber fragments. The protocol (**Figure 13**) consists on determination of the degradation degree of hair samples to the friction between the hardened steel balls and hair fragments (Ribeiro *et al.*, 2021).

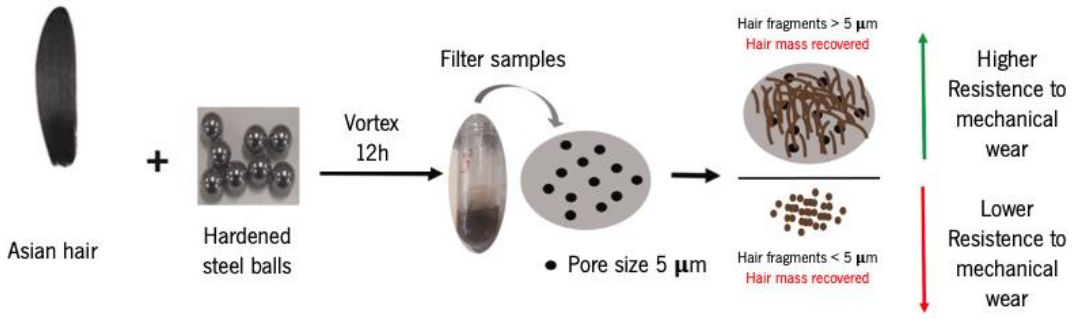


Figure 13: Process for evaluating the mechanical wear resistance of hair (Ribeiro *et al*., 2021).

Briefly, the hair resistance to mechanical wear consists of incubate 10 mg of the hair fragments (0.5 cm of length) with five hardened steel balls and 700 µL of water for 2 mL Eppendorf tubes. The samples were subjected to frictional forces by vortex agitation cycles at 2500 rpm for 12 hours. The reaction mixture of each sample was filtered (polycarbonate membrane filter, 5.0 µm) and the Eppendorf tubes were washed five times with the same volume of water used in the test. The membranes with the hair fragments material were dried at 37ºC for 24h and were properly weighted. The percentage of hair mass loss was calculated by equation 2:

$$\text{Hair mass lost (\%)} = \left(\frac{\text{Hi}-\text{Hf}}{\text{Hi}}\right) \times 100 \quad (2)$$

where Hi corresponds to the initial amount of hair and Hf to the final amount of hair present in the polycarbonate membrane filter.

6.6. Fluorescence microscopy

Transversal cuts of the hair fiber samples were analyzed by fluorescence microscopy. Firstly, hair fibers were embedded into an epoxy resin followed by transversal cuts of the fibers (16 µm width) using a microtome (Microtome Leitz). Fiber cross sections were analyzed using a LEICA DM 5000B fluorescence microscope (Leica) at a magnification of 10x (**Figure 14**). All fluorescence microscopy images were recorded using identical filter, exposure time, brightness intensity and gain settings. Hair samples were labelled with DTAF and observed with FITC spectra settings depicted as green (λ_{ex}=496 nm; λ_{em}=515 nm). The image collected was the representative of three independent experiments.

Figure 14: LEICA DM 5000B fluorescence microscope (Leica).

6.7. ATR-FTIR spectroscopy

Total reflection attenuated Fourier transform infrared spectroscopy (ATR-FTIR) is one of the powerful tools for a single human hair characterization and hair surface characterization. It was developed to acquire a spectrum from the surface of the sample (hair) by means of the total reflected radiation at the interface between the internal reflection element (IRE) and the sample. The shallow penetration depth of the evanescent wave makes ATR-FTIR spectroscopy a sensitive surface technique (Feughelman *et al.*, 2002). Furthermore, it is a non-destructive method of analyzing small sample sizes without any complicated sample preparation.

The spectra of virgin and treated hair samples were acquired using a FTIR spectrometer Alpha II (Bruker, German). The spectra were recorded at a wavelength from 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1} and 24 scans.

6.8. Statistical analysis

Statistical comparisons were performed using one-way analysis of variance (ANOVA) with post-hoc Turkey's method to identify significant differences between the results. Differences were considered statically significant at p-value < 0.05.

7. Results and Discussion

7.1. Preparation of the formulations and selection of the solvent

To develop alternatives for a viable modification of the hair shape, formulations containing cellulose, and chitosan were tested in ionic liquids, water, and serum.

The carbohydrates selected were solubilized in different solvents at different concentrations. Firstly, was tested their solubility at determined pH, temperature, and time.

First, three solutions were made. Each cellulose was dissolved in water (**Table 7**).

Table 7: Dissolution of cellulose in water. (Microcrystalline cellulose – MCC; Carboxymethyl cellulose – CMC; Hydroxyethyl cellulose - HEC).

Solvent	Cellulose	Concentration of Cellulose % (w/v)	$CaCl_2$	Temperature	Time	Physical Aspect	pH
H_2O	MCC	3%	0.8%	25 ºC	80 mins	Liquid	5
	CMC	3%	0.8%	25 ºC	180 mins	Fluid Jelly	7
	HEC	3%	0.8%	25 ºC	80 mins	Jelly	7

In each solution, water was used as a solvent in a total volume of 10 mL. A concentration of 0.8% Calcium Chloride and 3% cellulose was added. The addition of calcium chloride aims to help the dissolution of cellulose in water (Kostag *et al*., 2018). The dissolution in the presence of salts solutions is enhanced due to the ionic effects of the Hofmeister series altering the hydrogen bonding network of water. The chaotropic anion (Cl^-) in aqueous solutions is responsible for this change. The higher the Cl^- molar ratio, the easier it is for cellulose to dissolve in the aqueous solution (Z. Liu *et al*., 2016). Table 1 presents the dissolution of the three solutions which were carried out at room temperature resulting in an easier way to dissolve microcrystalline cellulose and hydroxyethyl cellulose. In the MCC sample solution, the cellulose was dispersed in the water and not solubilized, resulting in two phases (Kostag *et al.*, 2018).

The dissolution of these three types of cellulose was also tested in different ionic liquids (1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium diethyl phosphate, 1-ethyl-3 -methylimidazolium acetate) (**Table 8**).

Table 8: Dissolution of cellulose in ionic liquid. Cellulose: Microcrystalline Cellulose - MCC; Carboxymethyl Cellulose - CMC; Hydroxyethyl Cellulose – HEC. Ionic liquids: 1-ethyl-3-methylimidazolium chloride - [EMIM] Cl; 1-ethyl-3-methylimidazolium diethyl phosphate - [EMIM] DEP; 1-ethyl-3 -methylimidazolium acetate - [EMIM] Ac).

Solvent	Cellulose	Concentration of Cellulose % (w/v)	Temperature	Time	Physical Aspect	pH
[EMIM] Cl	MCC	3%	± 80 ºC	90 mins	Jelly	6
	CMC	3%	± 80 ºC	49 mins	Jelly	7
	HEC	3%	± 80 ºC	44 mins	Jelly	7
[EMIM] DEP	MCC	3%	± 80 ºC	225 mins	Jelly	6
	CMC	3%	± 80 ºC	225 mins	Jelly	6
	HEC	3%	± 80 ºC	225 mins	Jelly	6
[EMIM] Ac	MCC	3%	± 80 ºC	180 mins	Fluid Jelly	9
	CMC	11.4%	± 80 ºC	180 mins	Jelly	9
	HEC	3%	± 80 ºC	180 mins	Jelly	9

Dissolution of polysaccharides in ionic liquids involves the donor-acceptor interactions, promoting dissolution through hydrogen bonds from the hydroxyl group to the solvent anions (Swatloski *et al.*, 2002).

The preparation method to produce these solutions encompassed the variation of temperature and time of agitation. Temperature around 80ºC promotes greater efficiency in the dissolution of cellulose, varying the time of dissolution for each cellulose samples (H. Zhang *et al*., 2017).

It is well reported that the dissolution of cellulose in mixtures systems of imidazolium ionic liquids is more competent due to the high concentration of chloride, which efficiently breaks cellulose's hydrogen bond network (Fort *et al*., 2007; Zheng *et al*., 2019). Basically, dissolution of cellulose can be achieved in some hydrophilic ionic liquids including 1-butyl-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium

chloride and 1-ethyl-3-methylimidazolium (Zheng *et al.*, 2019). Recent studies have revealed that 1-ethyl-3-methylimidazolium acetate is one of the most promising ionic liquids for the dissolution of cellulose (Queirós *et al.*, 2020).

Here, was explored ionic liquids (1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium diethyl phosphate and 1-ethyl-3-methylimidazolium acetate) to dissolve the different types of cellulose (microcrystalline cellulose, carboxymethyl cellulose and hydroxyethyl cellulose). The use of those formulations on hair cosmetics field constitutes new progresses in the hair care application.

In was explorer different solvents to dissolve cellulose, and serum formulation was the selected solvent to incorporate the cellulose. Serum is an aqueous compound, which fulfills certain requirements to be a viable solvent. It has low viscosity and toxicity, is recyclable and has high thermal stability. The time and temperature at which dissolution occurs are also important factors. In addition to being a viable compound for cellulose dissolution, it has benefits for the hair, such as protecting it from daily external aggressions (sun, wind, humidity, pollution and impurities), and also prevents the hair fiber from losing water and nutrients to the external environment.

The serum was combined with two types of cellulose, in separately experiments, and with urea, a scalp moisturizer. The effectiveness of dissolving cellulose in the serum was very evident, as shown in table 9. It should be noted that in all solutions the pH remained constant (pH 7) (Cai & Zhang, 2005).

Table 9: Commercial serum solution with cellulose and urea. (Carboxymethyl cellulose - CMC; Hydroxyethyl cellulose - HEC).

Solvent	Cellulose	Urea	Peptide	Temperature	Time	Physical Aspect	pH	Volume
Serum	____	3%	0.02%	25 ºC	22 mins	Liquid	7	5 mL
	HEC (3%)	3%	0.02%	25 ºC	30 mins	Jelly	7	5 mL
	HEC (3%)	____	____	25 ºC	30 mins	Jelly	7	5 mL
	CMC (3%)	____	____	25 ºC	180 mins	Jelly	7	5 mL
	CMC (0.5%)	____	____	25 ºC	180 mins	Fluid Jelly	7	5 mL

	____	3%	____	25 ºC	15 mins	Liquid	7	5 mL

The objective of the urea incorporation into the serum, as a pre- treatment, was to promote the swelling of the hair fiber for a better diffusion of the other components. This formulation-based urea will be used as a first step in the process application followed the application of the cellulose formulation.

Dissolution of chitosan was performed, which is also used in many cosmetic products, producing a beneficial effect on hair in terms of softness and hair strength. It prevents possible damage to the hair, promotes wound healing, rapid dermis regeneration and wound healing (Sionkowska *et al.*, 2017). Considering its properties, solutions were prepared with chitosan to investigate the effect on the hair when modification of the shape of the hair is required.

Dissolution was performed in aqueous solution with acetic acid at pH around 3-5. However, the smell of these formulations was not pleasant.

First, solutions were made to dissolve chitosan in aqueous solution with acetic acid at pH around 3-5 (Furuike *et al*., 2017). The acetic acid, which is present in cosmetic products, help to decrease the viscosity of chitosan (**Table 10**).

Table 10: Chitosan dissolution in acetic acid.

Chitosan	Mass	Acetic Acid (1M)	Temperature	Time	Physical Aspect	pH
From crab shells	35 mg	3.5 mL	25 ºC	24 mins	Jelly	5
	65 mg	3.5 mL	25 ºC	50 mins	Jelly	3
MW 100000-300000	35 mg	3.5 mL	25 ºC	45 mins	Jelly	5
	65 mg	3.5 mL	25 ºC	60 mins	Jelly	3
Low MW	35 mg	3.5 mL	25 ºC	58 mins	Jelly	5
	65 mg	3.5 mL	25 ºC	75 mins	Jelly	3

Subsequently, the solubility of chitosan was tested in ionic liquids (**Table 11**). The dissolution process with 1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium diethyl phosphate and 1-ethyl-3-methylimidazolium acetate allowed to obtain solutions at a pH between 6-9.

The dissolution of chitosan in ILs has already been studied with the aim of forming gels. This was because ILs have different physicochemical characteristics because they only consist of ions and water is not needed to dissolve the chitosan (Santos-López *et al.*, 2017).

Table 11: Dissolution of chitosan in ionic liquid. (1-Ethyl-3-methylimidazolium chloride - [EMIM] Cl; 1-ethyl-3-methylimidazolium diethyl phosphate - [EMIM] DEP; 1-ethyl-3-methylimidazolium acetate - [EMIM] Ac).

Chitosan	Concentration of Chitosan % (w/v)	Ionic Liquid	Volume	Temperature	Time	Physical Aspect	pH
From crab shells	1%	[EMIM] Cl	3.5 mL	80 ºC	230 mins	After 8h turn crystal	7
	1%	[EMIM] DEP	3.5 mL	80 ºC	92 mins	Jelly	6
	1%	[EMIM] Ac	3.5 mL	80 ºC	90 mins	Jelly	8
MW 100000-300000	1%	[EMIM] Cl	3.5 mL	80 ºC	230 mins	After 8h turn crystal	7
	1%	[EMIM] DEP	3.5 mL	80 ºC	45 mins	Jelly	6
	1%	[EMIM] Ac	3.5 mL	80 ºC	40 mins	Jelly	9
Low MW	1%	[EMIM] Cl	3.5 mL	80 ºC	162 mins	After 8h turn crystal	8
	1%	[EMIM] DEP	3.5 mL	80 ºC	45 mins	Jelly	6
	1%	[EMIM] Ac	3.5 mL	80 ºC	42 mins	Jelly	9

7.2. Formulations application method on hair tresses

In this section is presented the type of methodologies developed with separately illustrations, the curly efficiency obtained in each one is presented in section 2.3.

The first method applied (**Figure 15**), consisted of the application of the formulation on the hair tress, until it is well covered. Followed by an incubation period of 30 minutes, and finally the hair was dried with a diffuser. After drying, was made two cycles of wet-dry conditions consisting in a wet spraying of water followed by drying with diffuser. After 24h, the hair was washed with shampoo and dried at room temperature.

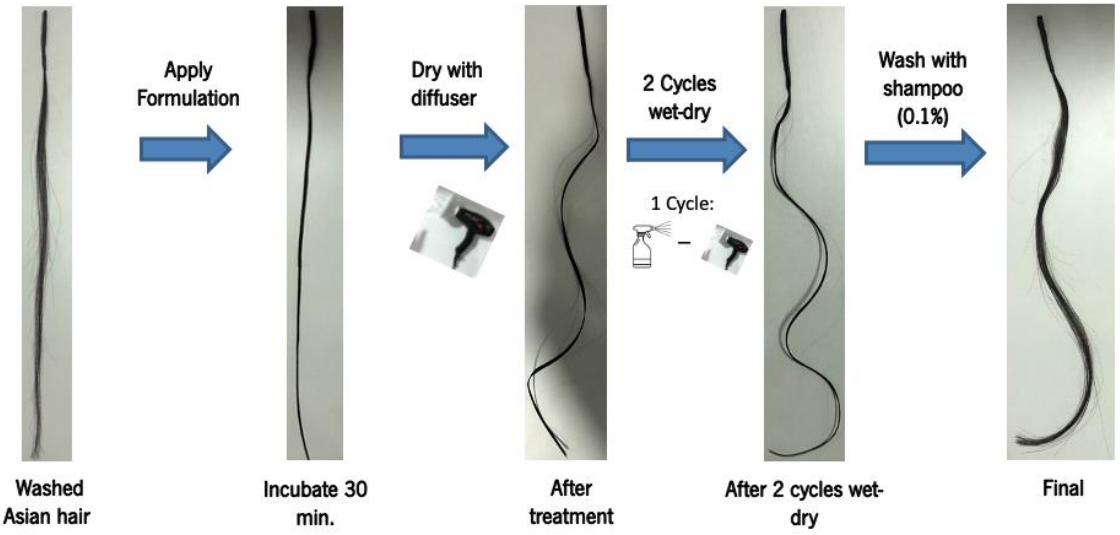


Figure 15: Schematic representation of application method number 1.

The second method (**Figure 16**) consist in spreading the formulation (ionic liquid plus cellulose and water plus cellulose) as a first step. Then, the hair was rolled in a glass rod and incubate for 15 minutes. Hair is blow-dried after 15 minutes on the glass rod. Then, the same two wetting and drying cycles were carried out, and finally the hair was washed with shampoo and dried at room temperature.

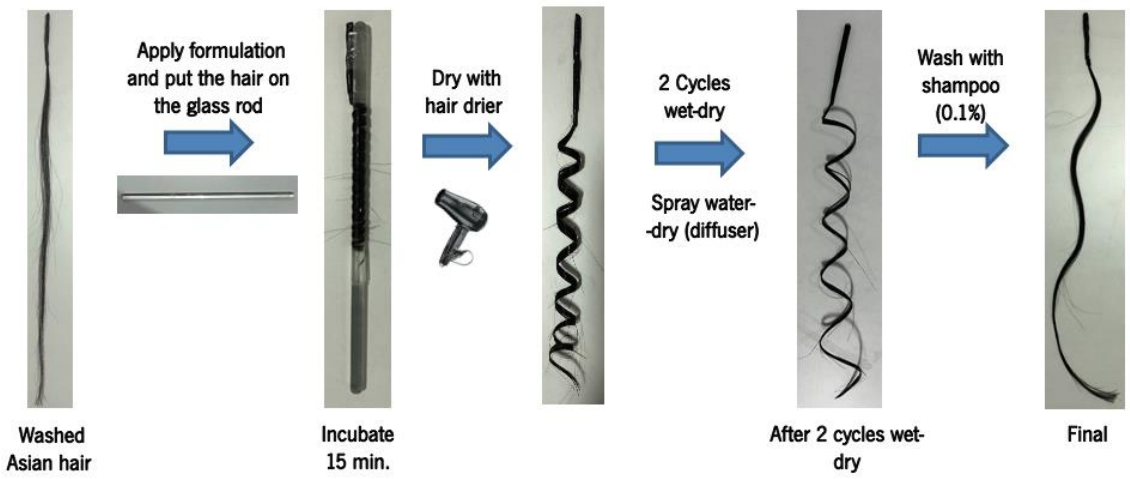


Figure 16: Schematic representation of application method number 2.

The third method (**Figure 17**) consist in the application of formulation U (3% of urea in serum formulation) during 30 minutes followed by application of formulation S (1% and 3% of cellulose in serum formulation) for 10 minutes. Then, the hair was dried with diffuser, and two cycles of wet-dry conditions were performed. In the final, the hair samples were washed with shampoo and dried at room temperature.

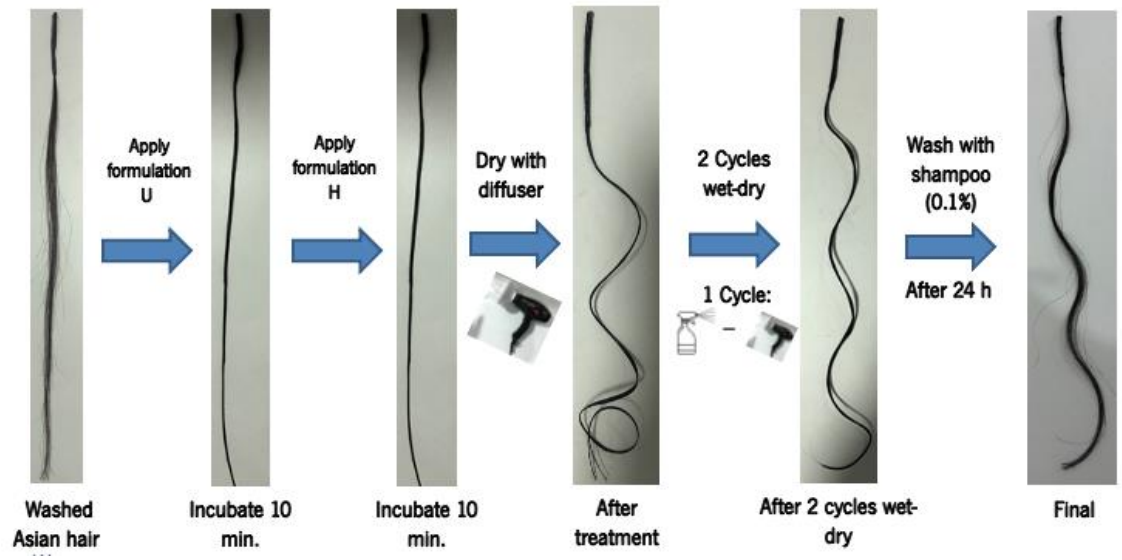


Figure 17: Schematic representation of application method number 3.

The fourth method (**Figure 18**) is identical to the third method, excepted the cycles at wet-dry conditions.

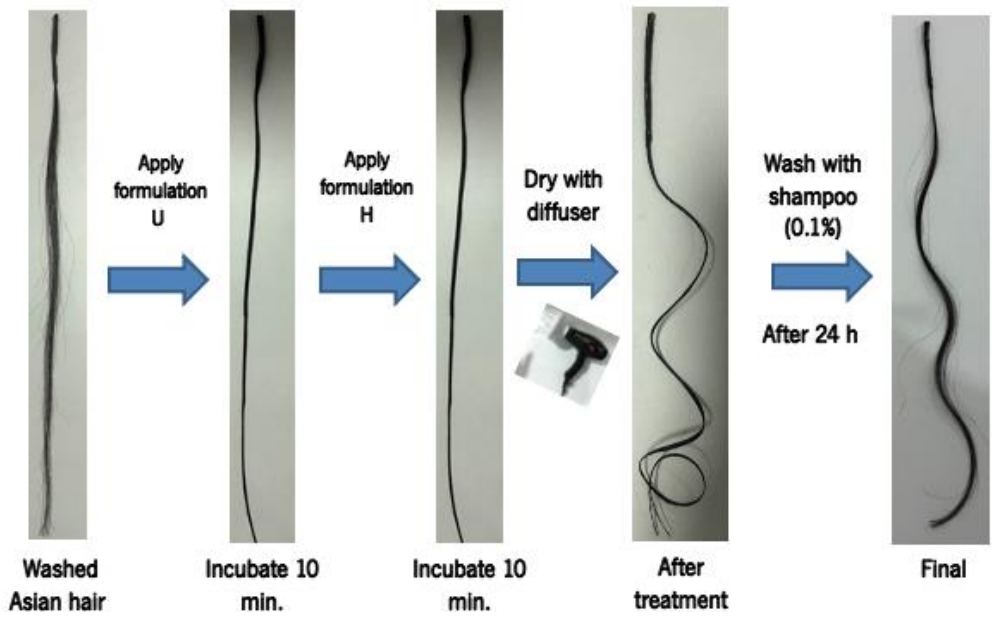


Figure 18: Schematic representation of the method number 4.

Finally, a fifth method (**Figure 19**) was performed using blow drier after 10 minutes of incubations with the formulation U as well as with the formulation H. The final stage was the washing steep with commercial shampoo.

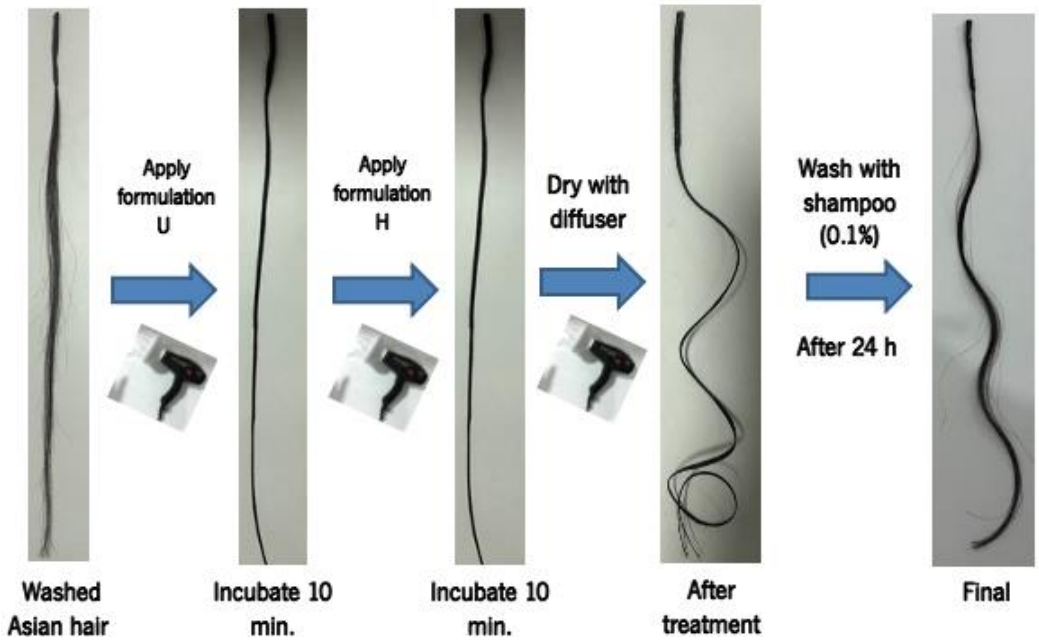


Figure 19: Schematic representation of method 5.

7.3. Efficiency evaluation of treated hair

The curly efficiency of hair samples treated with method 1 are presented in figure 20, and showed the curly efficiency after treatment, after two cycles wet-dry and after wash with shampoo. It was observed that after two cycles of wetting and drying

conditions the curly efficiency obtained was highly improved comparatively to the after treatment. Although after washing with shampoo the efficiency decreased.

Cellulose on the surface of the hair fiber promoted a change in the dimensional stability of the hair fiber. This allowed it to acquire different affinities with water in relation to the internal fiber, which led to dimensional changes in fiber length, triggered by the presence of moisture.

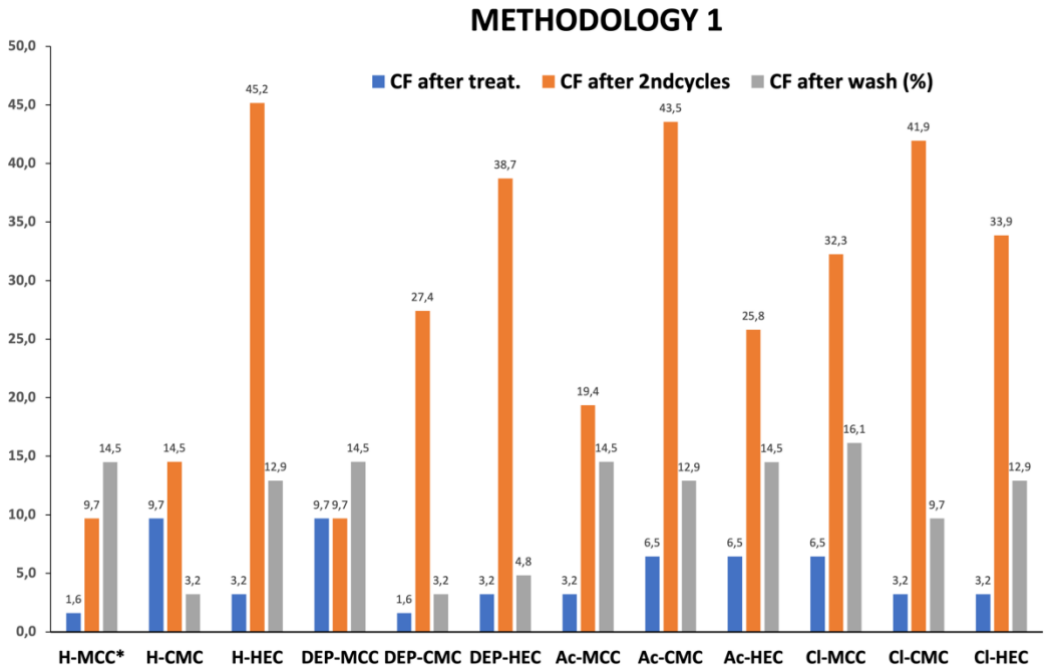


Figure 20: Comparison of the percentage of curls on hair after treatment, after two cycles wet-dry and after washing, with cellulose (MCC - Microcrystalline cellulose; CMC - Carboxymethyl cellulose; HEC - Hydroxyethyl cellulose) formulations in water (H – water) and cellulose formulations in ILs (DEP - 1-ethyl-3-methylimidazolium diethyl phosphate, Ac – 1-ethyl-3-methylimidazolium acetate and Cl - 1-ethyl-3-methylimidazolium chloride). The formulation H-MCC* forms two phases with deposit. Each value represented in the graph corresponds to a representative value of each condition tested.

In the second method, the formulations of cellulose dissolved in water were not established as they presented low results in method 1, with exception for the H-HEC formulation. This formulation exhibited a very satisfactory result in terms of waves after the cycles and after washing. This formulation was explored in the second method as well as the use of ionic liquids in the dissolution of the three types of cellulose selected (MCC, CMC, HEC) (**Figure 21**).

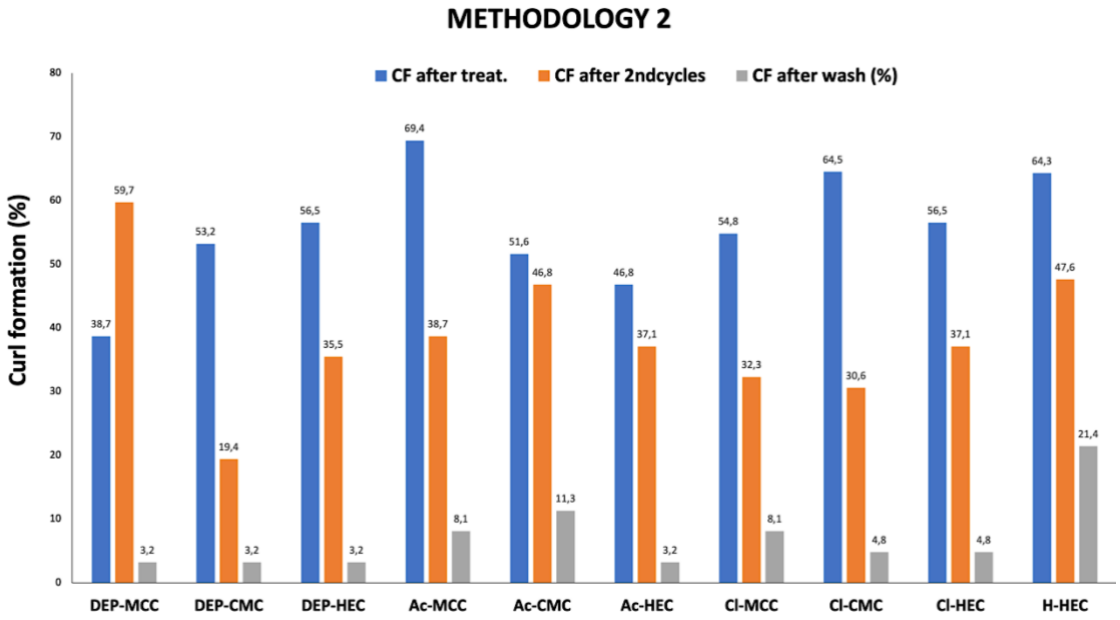


Figure 21: Comparison of the percentage of curls on hair, after treatment, after cycles and after washing, with cellulose formulations in ionic liquids and the best result of cellulose, previously formulated in water Microcrystalline cellulose - MCC; Carboxymethyl cellulose - CMC; Hydroxyethyl cellulose – HEC. Ionic liquids: 1-ethyl-3-methylimidazolium chloride - Cl; 1-ethyl-3-methylimidazolium diethyl phosphate - DEP; 1-ethyl-3 -methylimidazolium acetate - Ac). Each value represented in the graph corresponds to a representative value of each condition tested.

From Figure 21, was shown that the H-HEC formulation presented good profile of curl formation. This HEC cellulose formulation exhibited consistent results curls formation after treatment and after cycles at wet-dry conditions. HEC is the hydroxyethyl ether of cellulose which is a water binder and thickener in various cosmetic formulations. It is easily dissolved in water giving translucent solutions with a variety of viscosities depending on the concentration of HEC. Due to its high water solubility, HEC is widely used for a variety of applications such as cosmetics, building materials, film-forming materials and pharmaceutical productions (Arai & Shikata, 2020b).

Comparing both methods, we can verify that the ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIM Ac) induced highest curl efficiency. Although the application of the dissolved HEC cellulose in water on the hair achieved a curl formation quite similar or even better after washing than the application with ionic liquids (**Figure 22**). An important aspect is the viscosity of the solutions. The solution must have a captivating look, leaving the hair after application with a squeezable appearance. All formulations had a viscous appearance except for the 1-ethyl-3-methylimidazolium

chloride formulation with carboxymethyl cellulose and hydroxyethyl cellulose which had a solid appearance.

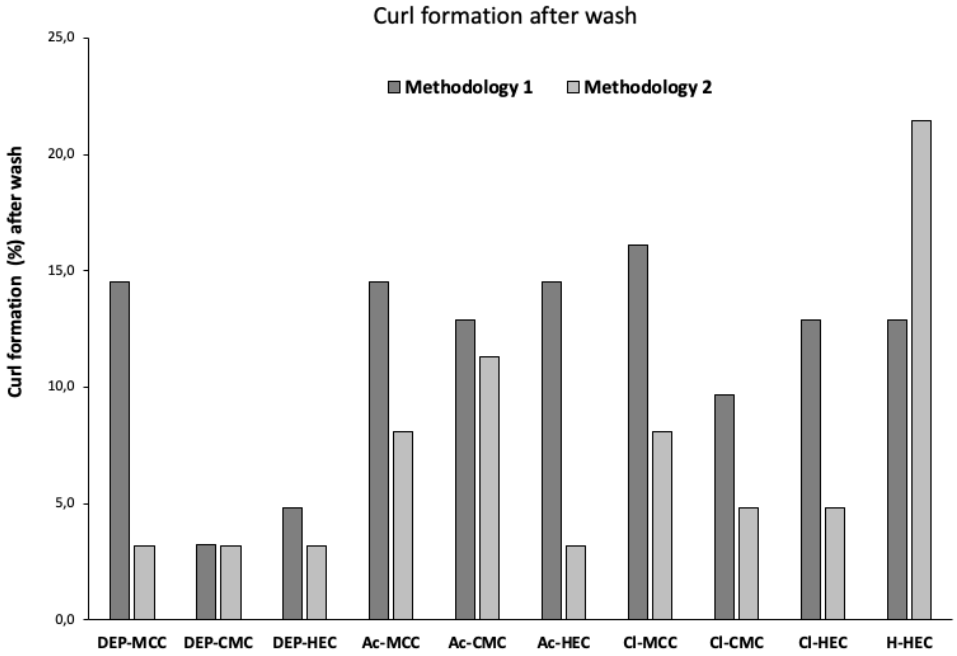


Figure 22: Comparison of the final results of curl formation after wash, obtained applying method 1 and 2 on Asian hair. Each value represented in the graph corresponds to a representative value of each condition tested.

Further experiments were carried out analyzing the effect of the pre-treatment, as a first step, with urea dissolved into the serum formulation based on polyethylene glycol, benzylic acid, and ethanol (3% urea, designated as Formulation U). This pre-treatment allowed to obtain a better swelling of the hair fiber through the use of a polar solvent, as urea (Jiang *et al.*, 2018). This methodology was intitled as method 3 including two steps applications. The second step is the application of Formulation S, where cellulose is dissolved in ionic liquid or in water/serum. Here, was used the formulations which attained better results using methods 1 and 2 previously obtained (**Figure 23**).

Figure 23: Visual curl formation on Asian hair using the methodology referenced as number 3 (after wash), including a first step pre-treatment with urea followed a second step with treatment containing cellulose in ionic liquid and in water.

From figure 23 and 24, Asian hair referenced as number 4, in figure 23, achieved the best result in terms of waves/curls on the Asian hair. This is in line with a previously data, cellulose dissolved in water reached good curly formation. The results showed that the formulation based on serum with propylene glycol, benzyl alcohol, and ethanol attained a better result than the formulation based only on benzyl alcohol.

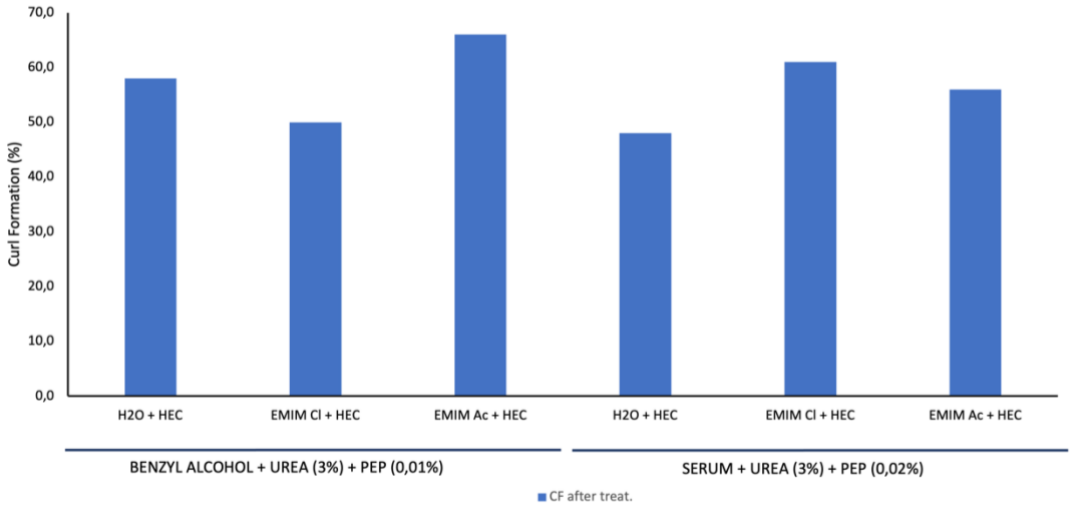


Figure 24: Curl formation (%) of the hair samples after treatment using methodology 3. Each value represented in the graph corresponds to a representative value of each condition tested.

To test the resistance to wash were performed four washes after each treatment. The results are shown in figure 24. All samples preserved their curly waves, which indicates that the formulations were absorbed and were effective in the modification of the shape of the hair fiber. After two wet-dry cycles and 4 washes, the

percentage of curl formation was deeply reduced when compared with curl formation after treatment (**Figure 25**). This behavior was expected considering that with washings, the formulation could dissipate from the hair, returning to its natural shape.

The treated hair samples with higher percentage of curl formation obtained after 4 washes was with formulation of HEC dissolved in water and in [EMIM] Ac, using both the pre-treatment of serum, urea, and peptide. The formulation of 3% HEC in water with the formulation of benzyl alcohol, PEP (0.01%) and urea (3%) was, alongside the formulation of [EMIM] Ac with 3% HEC cellulose together with the formulation of serum, urea (3%) and PEP (0.02%), which showed better efficiency. These data led us to observe that both solutions have potential for future optimization since maintained the modified hair shape for 4 washes (**Figure 25**).

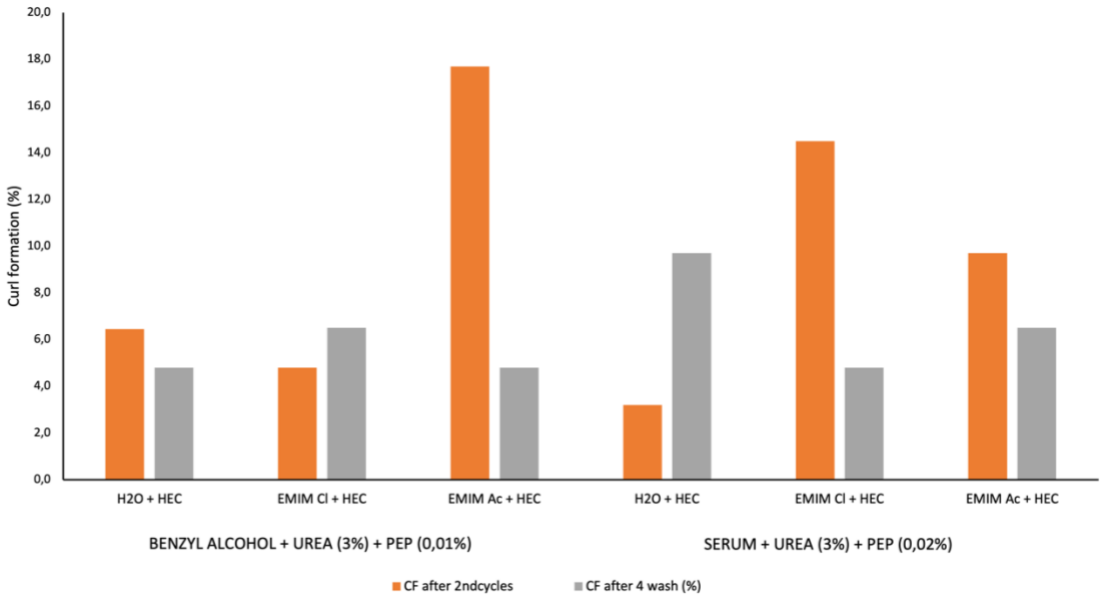


Figure 25: Curl formation (%) of the hair samples after the two cycles and 4 washes using the methodology 3. Each value represented in the graph corresponds to a representative value of each condition tested.

It was also tested the curly efficiency with formulations at alkaline pH, in order to achieve better swelling of the fiber. However, the results showed that at neutral pH the efficiency was higher, which is in accordance with previous results since the decapeptide based on keratin also presents higher performance at neutral conditions (C. F. Cruz *et al*., 2017). This peptide it is incorporated into the serum formulation. Our research group have developed this keratin-based peptide for application on relaxed damaged hair with proven characteristics of recovering mechanical properties of over-bleached damaged hair (C. F. Cruz *et al.*, 2017). Products with this peptide penetrate

easily in the hair fiber and recreate disulfide bonds that have been broken or damaged through bleaching, coloring, perming, or straightening. Once inside the hair, peptide attaches to the hair protein replacing the broken bonds adding strength and elasticity.

Additionally, was added urea to promote better swelling properties to the fiber. It has an enormous power of binding to water, which gives it the characteristic of hygroscopicity. Furthermore, it hydrates the keratin as it is a protein denaturant (X. Zhao *et al*., 2020).

This formulation was applied as a pre-treatment on the hair followed by the application of the formulation based on cellulose into ionic liquid (methylimidazolium diethyl phosphate) or in the serum formulation (**Figure 26**).

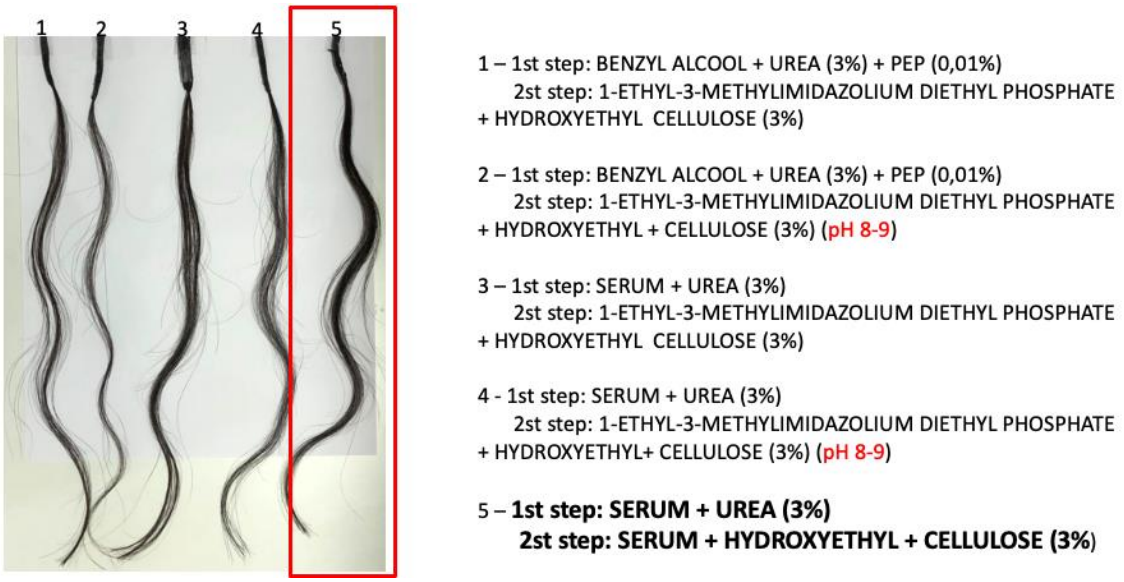


Figure 26: Comparison of the results of formulations with different pH (formulation 1: pH=7; formulation 2: pH=8-9; formulation 3: pH=7; formulation 4: pH=8-9 and formulation 5: pH=7).

The distilled water together with the calcium chloride, was replaced by the commercial serum formulation. Formulations based on serum, in both steps' application, have proved to be the most effective, as showed in figure 26 by the sample numbered as five.

Table 12: Comparison of the effect of the cellulose formulation at different concentrations on coated hair fiber. (s: serum; u: urea; HEC: Hydroxyethyl cellulose; CMC: Carboxymethyl cellulose).

Formulations	Visual Results (After treatment)	Visual Results (After wash)	Curl Formation (after wash)	Curl Formation (After 2nd Wash)	Curl Formation (After 3rd wash)

1st step: serum 2nd step: serum (control)			3.2%	3.2%	3.2%
1st step: s + u (3%) 2nd step: s + HEC (3%)			9.7%	6.5%	6.5%
1st step: s + u (3%) 2nd step: s + HEC (1%)			6.5%	6.5%	4.3%
1st step: s + u (3%) 2nd step: s + HEC (0.5%)			9.7%	6.4%	4.9%
1st step: s + u (3%) 2nd step: s + CMC (3%)			8.1%	8.1%	8%
1st step: s + u (3%) 2nd step: s + CMC (0.5%)			11.3%	6.9%	6.5%

To make cellulose profitable, its concentration was reduced from 3% to 1% and 0.5%, respectively. This concentration reduction allowed to obtain a less viscous solutions which were easier to apply on the hair tresses. A comparison between formulations is provided in table 12.

After application, the formulation containing 1% of HEC obtained similar result in terms of curl efficiency that with the formulation HEC 3%. Being the HEC a thickener agent (Omidian & Park, 2017) using lower concentration the formulation is more fluidic which facilitates it use, constituting the formulation of HEC with 0.5% a good option for future applications. Combined with better fluidity, the 0.5% HEC cellulose formulation

showed better curl formation results. In view of this, the formulation with 1% HEC cellulose was discarded.

Above was demonstrated that HEC and CMC cellulose was the promised options for our formulations since were obtained better results in terms of curl efficiency.

The result obtained for the formulation of 0.5% CMC was very interesting since visually and quantitatively the curl efficiency was evident. This is a good indicator since the formulation allows to change the shape of the hair keratin fiber with a formulation with fluid solution.

The formulations more promised were grouped and compared in figure 27.

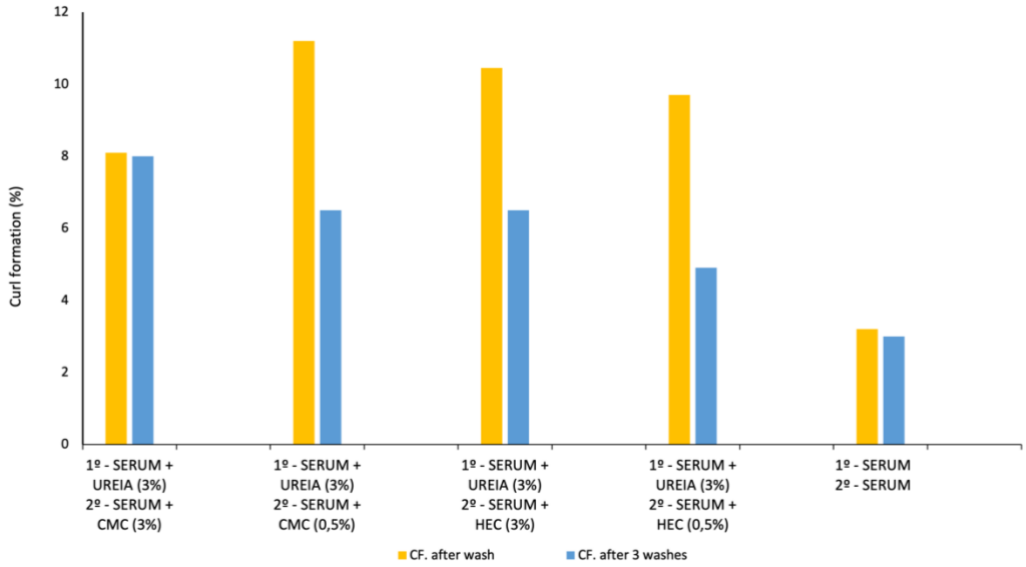


Figure 27: Comparison of the best formulations with the control formulation (Carboxymethyl cellulose – CMC; Hydroxyethyl cellulose - HEC). Each value represented in the graph corresponds to a representative value of each condition tested.

All formulations presented percentages of curls, corroborating those changes in the shape of the coated hair fiber occur with the developed formulations. The formulation with 3% HEC cellulose, as well as 0.5% and 3% CMC, were the formulations showed the best results in curl formation indicating the curly efficiency of coated hair fiber.

The other formulations showed a satisfactory result, being the modification of the hair shape also observable. However, after washing, the percentage of curl formation decreased in the formulations with 3% of cellulose.

In fact, the two formulations that showed the best results can be a viable solution in hair cosmetics, since aggressive chemical products were avoided, preventing serious

damages to the hair fiber and to the environment. It is important to note that the best performing formulations were those with lowest percentage of cellulose, which contributes to an economical and profitable formulation.

Chitosan was other carbohydrate explored in this study. Formulations with chitosan were based on acetic acid, as well as in ionic liquids. Chitosan is a beneficial polymer for biomedical applications due to its biocompatibility, biodegradability, and low toxicity. However, it has the disadvantage of not being soluble in common solvents, for example in water. This has led to less attention being paid to chitosan. For cosmetic applications, organic acids are generally suitable solvents. Chitosan is the only natural cationic gum that becomes sticky when neutralized with acid. These materials are used in permanent curling lotions, lotions and creams due to the power of chitosan to increase hair softness, hair strength and prevent hair damage (Aranaz *et al*., 2018). Formulations with three types of chitosan were tested. This was solubilized first in solutions containing 1% and 3% of acetic acid and then with two types of ILs at only 1% (**Figure 28**).

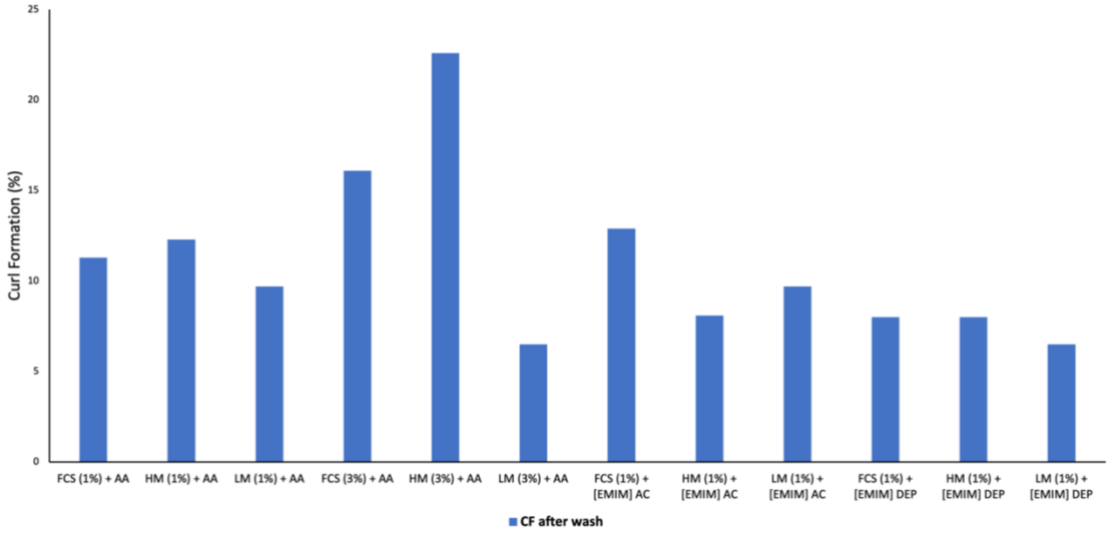


Figure 28: Comparison of the results of formulations with chitosan. The first formulation (pre-treatment) consists of serum and PEP (peptide). (Acetic Acid – AA; Chitosan from crab shells – FCS; Chitosan high MW – HM; Chitosan low MW – LM; 1-ethyl-3-methylimidazolium diethyl phosphate - [EMIM] DEP; 1-ethyl-3-methylimidazolium acetate - [EMIM] Ac). Each value represented in the graph corresponds to a representative value of each condition tested.

After treatment, the hair samples were washed, and was clearly demonstrated that the formulations were not strong enough to bind in the hair fiber and preserve the curls formed. Despite the chitosan being at the ideal pH of action on the fiber (pH=3/5), the results were not satisfactory. The appearance obtained with this formulation was a

quite pasty shape on the fiber, besides the odor was not pleasant since the pH was adjusted with acetic acid. Due to the low efficiency of curling, chitosan was discarded.

7.4. Evaluation of organoleptic properties of the formulations, pH value and stability under thermal and physical stress

Organoleptic properties and pH value control is a simple and effective method to evaluate the preparation quality of a cosmetic product and detect eventual alterations during manipulation, time, or the incorporation of some additional component. The stability study of the cosmetic formulations is crucial to guarantee the quality, security, and efficacy of the product. These studies contributed to the development of formulations, establishing the validity and motorization of the physical and chemical characteristics (Friedrich *et al*., 2007).

The developed formulations were subjected to accelerated stability evaluation to guarantee their cosmetic characteristics for long period of time. For that, was performed thermal stress at extreme temperatures and physical stress for the formulations of interest, to analyze if occurs some instability of their solutions. The main objective is to simulate daily and annual alterations of temperatures which cosmetics products are subjected.

For this, six formulations (serum (control), serum with 3% urea, serum with cellulose HEC at 3%, serum with cellulose HEC at 0.5%, serum with cellulose CMC at 3% and serum with cellulose CMC at 0.5%) were tested. Parameters such as odor, color, appearance, and pH were evaluated. These were evaluated before, during and after each test. For 12 weeks, the formulations were stored at room temperature, 4°C and 37°C.

As it is possible to see in table 13, the 3% HEC cellulose serum formulation degraded when subjected to a higher temperature (37°C). This underwent a change in color, starting to have a yellowish color and there was also a change in pH (from 7 to 6). The formulation of serum with 3% CMC cellulose also changed. However, it also suffered degradation but only changed its color from transparent to yellowish.

Table 13: Organoleptic properties and pH value of the formulations after 12 weeks. Evaluation provided of the formulations conditioned at different temperatures 4ºC, 37ºC and room temperature. (Legend: P – pleasant

fragrance; T – transparent; L – liquid; J – jelly; FJ – fluid jelly; RT – room temperature; Y: without changes; W: change pH to 6; Z: Change color to yellowish)

Formulation	Odor	Color	Aspect	pH	After 12 weeks (RT)	After 12 weeks (4ºC)	After 12 weeks (37ºC)
Serum (control)	P	T	L	7	Y	Y	Y
Serum + Urea (3%)	P	T	L	7	Y	Y	Y
Serum + HEC (3%)	P	T	J	7	Y	Y	W and Z
Serum + HEC (0.5%)	P	T	FJ	7	Y	Y	Y
Serum + CMC (3%)	P	T	J	7	Y	Y	Z
Serum + CMC (0.5%)	P	T	L	7	Y	Y	Y

The formulations that were submitted to the storage test were also submitted to the thermal stress test. Each formulation was subjected to 7 cycles, ranging from 4ºC (24h) to room temperature (24h). Every 48h, the parameters were measured. Considering that this type of test is intended to assess the stability of the formulations, they revealed great stability, with no important changes occurring in the physical and organoleptic characteristics of the formulations (**Table 14**).

Table 14: Organoleptic properties and pH value of the formulations after thermal stress. Formulations were evaluated after 7 cycles of exposure at 4ºC (24h) followed by 24h at room temperature. (Legend: P – pleasant fragrance; T – transparent; L – liquid; J – jelly; FJ – fluid jelly; RT – room temperature; Y: without changes)

Formulation	Odor	Color	Aspect	pH	After 7 cycles (4 ºC and RT, 24 each)
Serum (control)	P	T	L	7	Y

Serum + Urea (3%)	P	T	L	7	Y
Serum + HEC (3%)	P	T	J	7	Y
Serum + HEC (0.5%)	P	T	FJ	7	Y
Serum + CMC (3%)	P	T	J	7	Y
Serum + CMC (0.5%)	P	T	L	7	Y

The physical stress test provides information about formulation instability, such as flocculation, which can progress to coalescence. After performing 10 cycles at 3000 rpm for 30 minutes each cycle, no differences were observed in the formulations. This result allowed us to conclude that the formulations did not form two phases and did not show instabilities preserving their homogeneous aspect (**Table 15**).

Table 15: Organoleptic properties of formulations and pH value. Formulations were evaluated after 10 cycles of centrifugation at 3000 rpm. (Legend: P – pleasant fragrance; T – transparent; L – liquid; J – jelly; FJ – fluid jelly; RT – room temperature; Y: without changes)

Formulation	Odor	Color	Aspect	pH	After 7 cycles (3000 rpm for 30 mins, each cycle)
Serum (control)	P	T	L	7	Y
Serum + Urea (3%)	P	T	L	7	Y
Serum + HEC (3%)	P	T	J	7	Y
Serum + HEC (0.5%)	P	T	FJ	7	Y
Serum + CMC (3%)	P	T	J	7	Y

Serum + CMC (0.5%)	P	T	L	7	Y

7.5. Evaluation of properties of hair tresses

Hair mechanical properties such as resistance to mechanical wear and thermal protection are currently used as primary indicators of hair integrity and provide insight into the effect of a formulation/compound on the hair fiber. To study the feasibility of the chosen formulations, several tests were carried out studying the behavior of the coated hair fiber.

7.5.1. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) data is increasingly used to substantiate hair repair product claims. Therefore, the DSC is essential in the characterization of keratin fibers. These measurements use standard aluminum crucibles, opened, or perforated for easy removal of gases produced during heating by the flowing draft of a protective gas.

The behavior of the four best formulations tested on hair, was analyzed by DSC (**Figure 29**).

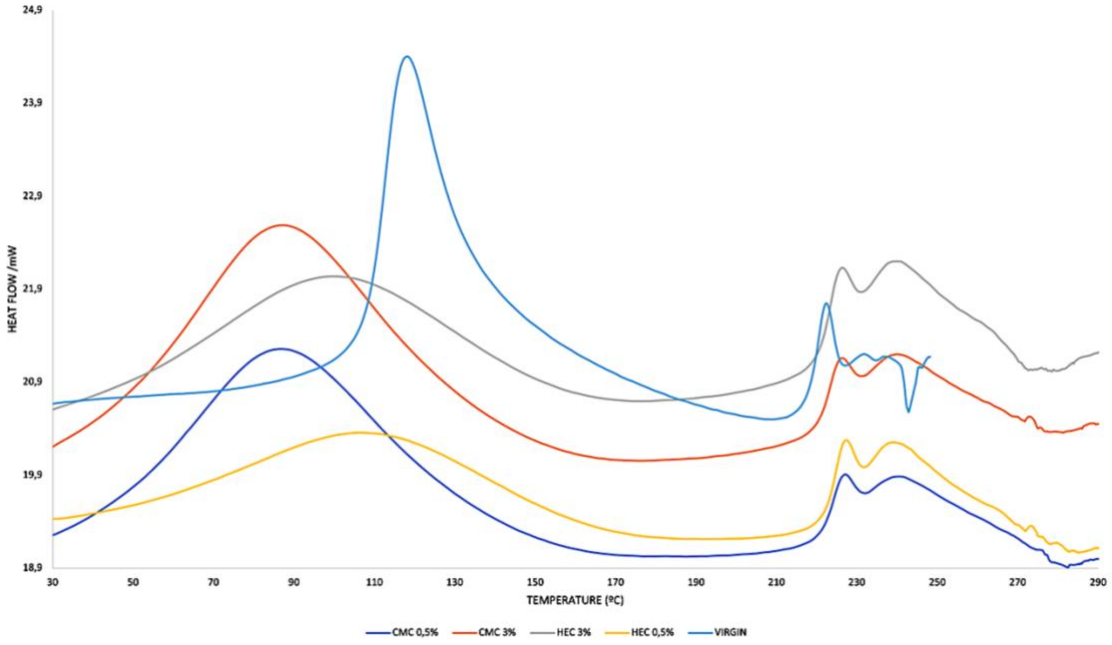


Figure 29: DSC thermograms of virgin and coated hair samples. Each curve is representative from three replicas for each condition.

Table 16: Enthalpy and temperature values of endothermic peaks of virgin and coated hair samples. Each value is representative of three replicas.

Sample	1st Enthalpy (J/g)	1st Temperature (ºC)	2nd Enthalpy (J/g)	2nd Temperature (ºC)
Virgin	121.1	118.21	17.0	223.2
HEC 3%	131.3	100.14	57.3	226.9
HEC 0.5%	125.7	107.25	30.2	227.9
CMC 3%	285.9	89.34	53.7	227.1
CMC 0.5%	221.8	86.54	42.0	227.5

Thermal analysis of virgin and coated hair fiber was evaluated using DSC (**Figure 29**). The DSC thermograms indicate an endothermic peak at around 88-120 ºC which is related to the evaporation of water content of the hair samples. The virgin hair sample is more susceptible to degradation than treated hair samples, since the curve of virgin hair sows a peak at around 223 ºC and coated hair fibers at around 227°C. This peak corresponds to keratin decomposition and alpha-helix disordering (Idris *et al.*, 2014), and therefore the temperature decomposition of keratin on coated samples were above the decomposition threshold exhibiting improved thermal stability (Popescu & Gummer, 2016).

The enthalpy values were taken in consideration to determine the keratin alpha-helix denaturation enthalpies and the value of each condition treatment is represented on table 16. Analyzing the results, it was verified that coated hair fiber was able to increase the keratin denaturation enthalpy demonstrating that the cellulose coating, HEC at 3% and CMC at 3% and 0.5%, has ability to protect the hair against thermal damage. This could be explained by the fact that the increase of denaturation enthalpy means that more energy is needed to indorse keratin fibers degradation.

7.5.2. Fluorescence microscopy (DTAF linkage to cellulose)

Labeled cellulose was performed to investigate the effect of cellulose on the surface of hair fiber. For that, HEC cellulose was dyed in a solution with a batch ratio of 1:50. As can be seen in figure 30, in the first step 0.2 wt% DTAF dye was dissolved in distilled water solution for 15 minutes at 50ºC, then HEC cellulose (0.5 g) was added to the solution for more 10 minutes. In the third step the sodium sulphate (20 g/L) was

added, and after 30 minutes sodium carbonate (15 g/L) was added maintaining at temperature of 50 ºC for 35 minutes.

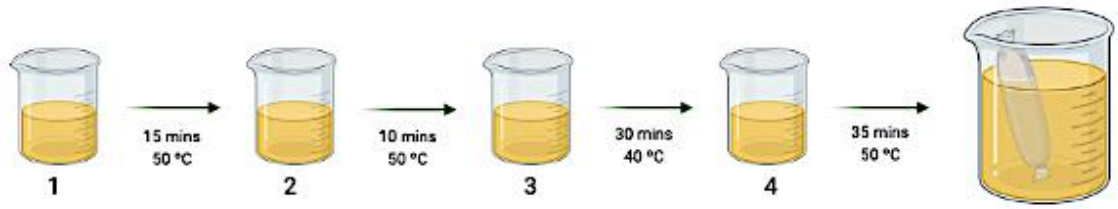


Figure 30: Illustration of the dyeing process of HEC cellulose powder using DTAF dye.

After dyeing process, to remove the free dye from the solution was performed a dialysis procedure. Then, HEC labeled in the interior of the membrane was measured spectroscopically (**Figure 31**). Fresh dye solution was also measured to compare the behavior of the sample.

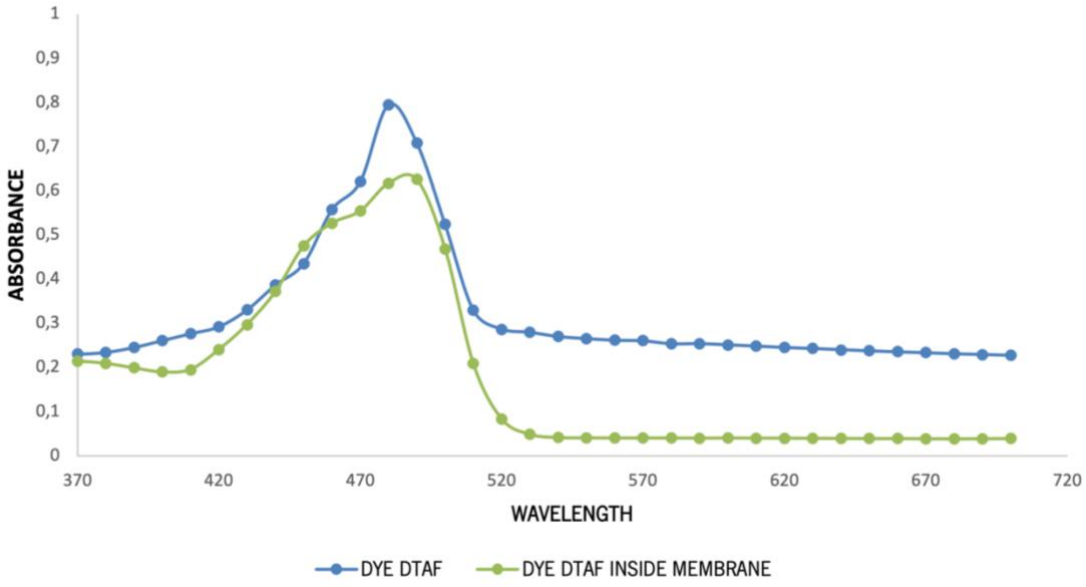


Figure 31: DSC curve of DTAF dye and DTAF dye labeled HEC.

The HEC labelled with DTAF inside the membrane has similar behavior curve spectrum at absorbance measurement. The result obtained showed that most of the dye had successfully bound to cellulose.

The rest of the intramembrane content that was not used to measure absorbance was lyophilized and later applied to a section of hair. The application on the hair was divided into two musts, one at 3% and the other at 0.5% of cellulose. The hair was observed using a fluorescence microscope and images of the cellulose attached to the hair fiber were obtained as expected (**Figure 32**). The cross-sectional images

obtained by fluorescent microscope showed the green layer of the labelled cellulose homogenously deposited on the surface of the hair fiber.

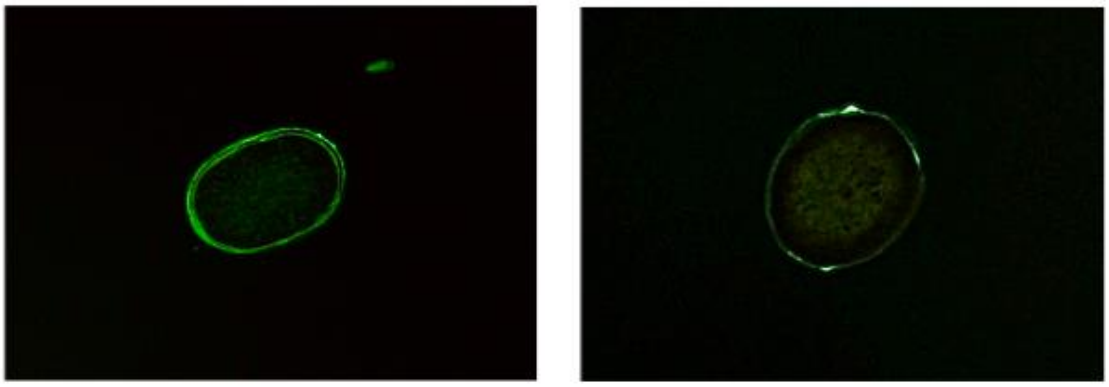


Figure 32: DTAF dye labeled HEC cellulose attached to the hairline. Images captured with a fluorescence microscope.

7.5.3. Hair resistance to mechanical wear

Six formulations were applied to Asian hair to test their mechanical strength. For each formulation, two tests were performed. The hairs were weighed and placed inside Eppendorf's. Then metal spheres and distilled water were added. The samples were left for 12h in the vortex. Hardened steel balls, when in contact with capillary fragments during vortexing, will compromise the integrity of the capillary fibers. After 24h, the samples were filtered and left in the oven for 24h. They were later weighed. Due to the variation and complex biological diversity of hair, it is important to establish how each type of hair fiber responds in terms of mechanical strength. After the procedure was completed, the resistance of each sample was calculated (**Figure 33**).

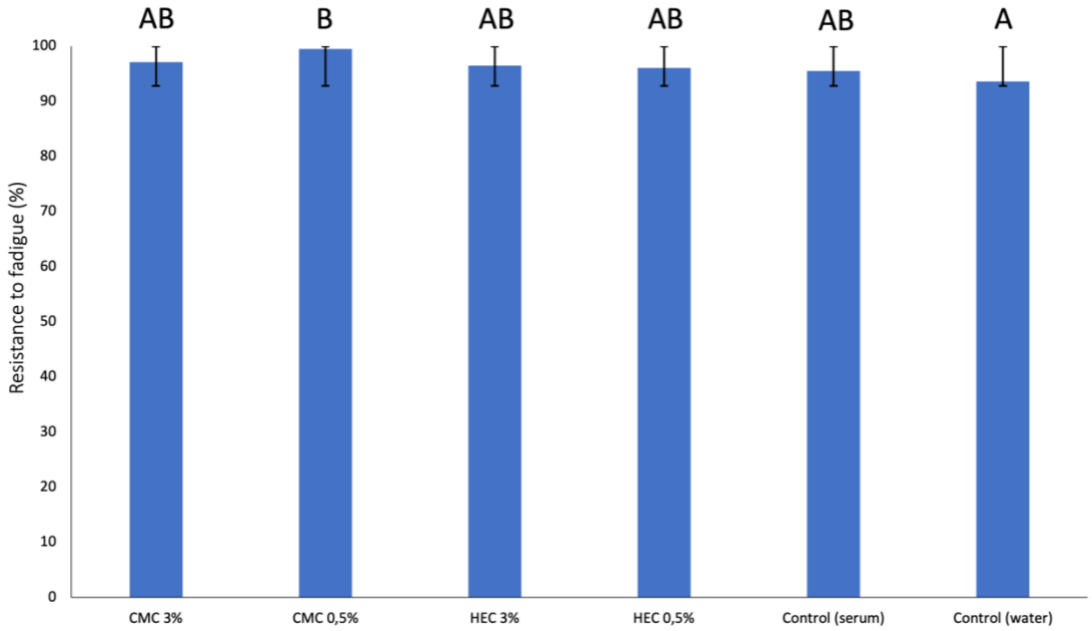


Figure 33: Effect of cellulose (CMC and HEC) dissolved in serum formulation on the resistance to mechanical wear of coated hair fiber. Grouping information using Tuckey test with 95% of confidence meaning that do not share a letter are significant different.

Although in general all formulations had good resistance compared to control formulations. It is possible to state that, that statistically, the 0.5% CMC formulation obtained better resistance to fatigue than controls. This formulation presented significant difference, did not share a letter, compared to the control formulation (water). This indicates that the cellulose used promoted resistance to mechanical wear to the hair fiber presenting lower weight mass loss during the fatigue test. The mass loss obtained after treatment is related with the degradation degree to hair's resistance to mechanical wear. Lower degradation rates of the coated hair samples reflect higher resistance to mechanical wear and lower damages on the surface cuticle layer. To corroborate this result, coated hair samples were evaluated by SEM analysis.

Before the analysis, the sample were covered with 20 Å of gold. The microscopy result is shown in the figure 34.

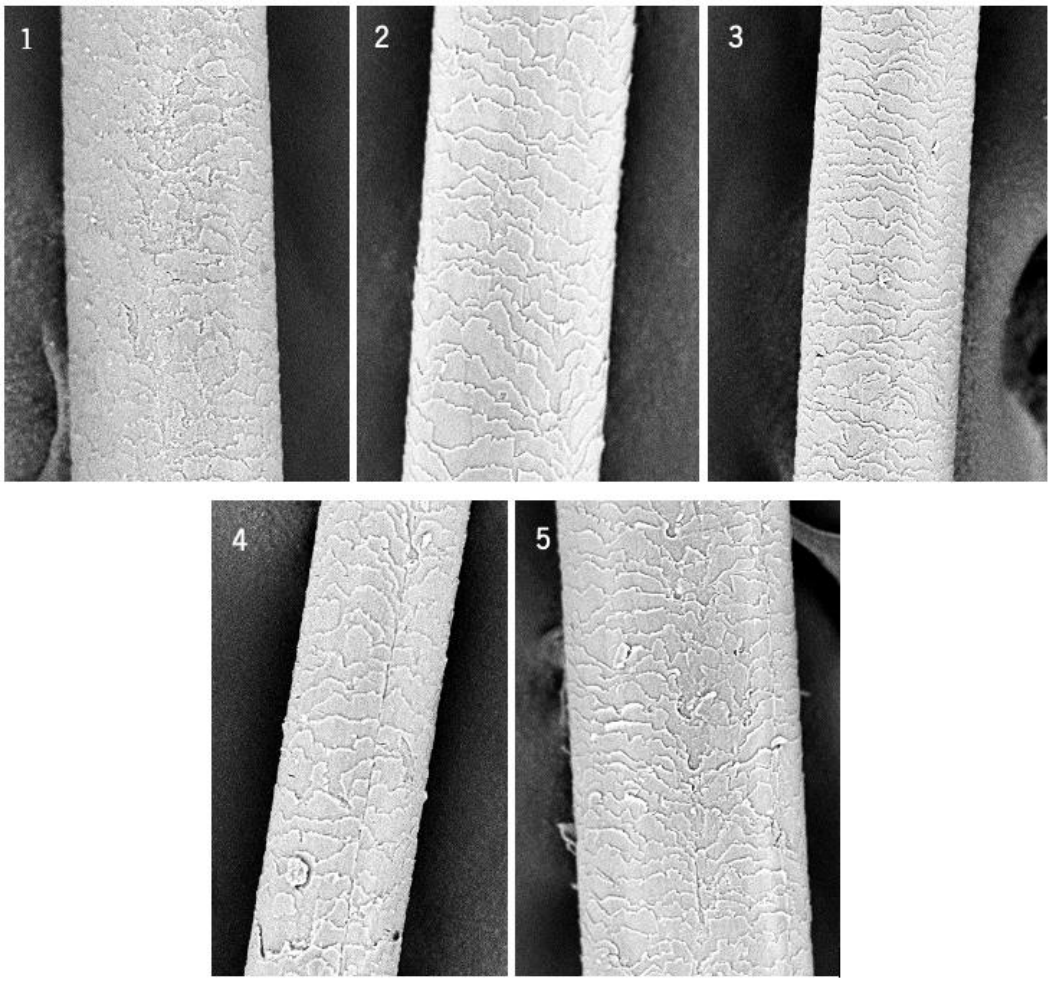


Figure 34: SEM imagens of the hair samples treated and untreated: 1-virgin Asian hair (control), 2-Asian hair treated with 3% CMC, 3-Asian hair treated with 0.5% CMC, 4-Asian Hair treated with 3% HEC, 5-Asian hair treated with 0.5% HEC.

From figure 34 it is possible to observe that the coated hair samples exhibited low patterns of damages corroborating the results attained in the fatigue resistance. The treated hair sample with 3% CMC exhibited flat cuticle cells superimposed on the surface, maintaining a smoother and more intact appearance. This may indicate that these formulation with 3% CMC increase the elongation capacity under mechanical stress decreasing the damage that can arise from the application of frictional forces. This cellulose may have a treatment effect on the general properties of the hair fiber, and not necessarily a possible mechanism underlying mechanical wear resistance.

The remaining samples (0.5% CMC and 3% and 0.5% HEC) showed a greater visible decomposition in the irregular surface, and in the smaller space between the cuticles, which may be related to a lower resistance to mechanical wear, therefore. of

its lesser ability to stretch under mechanical stress, resulting in greater damage during application of friction.

7.5.4. ATR-FTIR spectroscopy

The coated hair samples were evaluated by FTIR microscopy to analyze changes in the chemical structure of the hair fibers surface. A compilation of the spectra of all evaluated formulations was carried out (**Figure 35**). As shown in figure 35, all the treated hair samples showed the typical peaks at around 1640 cm-^{1} related to amide I, 1525 cm^{-1} attributed to amide II and 1240 cm^{-1} to amide III.

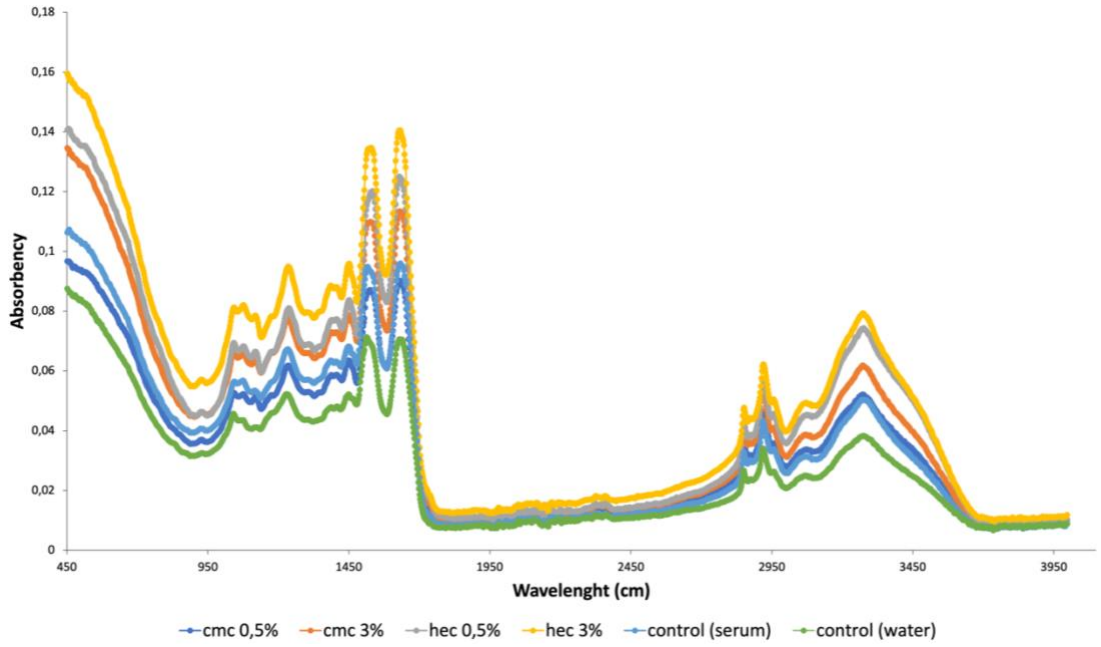


Figure 35: The ATR-FTIR spectra of hair fibers treated with different types of cellulose and with water and serum. Each value represented in the graph corresponds to a representative value of each condition tested.

The Amide I peak corresponds to the C=O elongation and a small contribution from the N-H vibration. The Amide II peak corresponds to two components, the C-N elongation, and the N-H oscillation vibrations, while the N-H torsional vibration plus the C-N elongation vibration and the contribution of the O=C-N bending vibration correspond to the Amide III.

The absorption bands recorded between 2850 cm^{-1} were attributed to C-H stretching vibration, whereas bands at around 1400 cm^{-1} correspond to C-H bending strain vibration. The broad band appeared at around 3280 cm^{-1} correspond to the stretching vibrations of -OH and -NH groups. Coated hair samples present a broader peak at 3280 cm^{-1} than control hair samples which is related with intermolecular hydrogen bonding of the coated cellulose on the hair fiber (Pienpinijtham *et al.*, 2018).

Conclusions & Future perspectives

8. Conclusion and Future Perspective

The main objective of this dissertation to develop new formulations to modify the shape of the hair was achieved. Here, was developed a methodology for application of dissolved cellulose on the surface of the hair fiber to modify the shape of fiber. From a general point of view, the results showed an effective modification of the shape of coated hair fiber presenting slightly dimensional variations in length and in the formation of curls.

Formulations were based on cellulose dissolved in ionic liquids and in serum formulations were studied. All celluloses used hydroxyethyl cellulose (HEC), carboxymethyl cellulose (CMC), microcrystalline cellulose (MCC) were soluble in ionic liquids (1-ethyl-3-methylimidazolium chloride, 1-ethyl-3-methylimidazolium diethyl phosphate, 1-ethyl-3-methylimidazolium acetate), as well as in water and in the serum formulation, with exception of MCC which formed two phases in water solution. From dissolution evaluation, the cellulose HEC and CMC exhibited homogeneous solutions in water and in ILs. From a cosmetic point of view, the formulation based on water as the serum formulation (75% is water) was the selected solvent for cellulose dissolution.

The developed formulations were subjected to accelerated stability and storage stability evaluation to guarantee their cosmetic characteristics for 12 months.
The formulation of serum with 0.5% CMC cellulose no changes and degradation were observed when subjected to different temperatures (4ºC, 37ºC and room temperature). The parameters of odor, color and appearance maintained their initial characteristics after 12 months. The same was observed in pH value (constant, pH 7). Accelerated stability at thermal stress, 7 cycles at 4ºC during 24h followed by more 24h at room temperature, of the formulations revealed great stability with no significant changes in the physical and organoleptic characteristics. Physical stress, after centrifugation cycles, formulations preserved their homogenous aspect.

Formulations with HEC and CMC at 3% and 0.5% dissolved in Serum formulation presented curls formations around 12%. The resistance to washes was preserved for 4 washes with shampoo.

The deposition of dissolved cellulose on the surface of hair fiber revealed the successful adhesion of the coating layer on the hair fiber. This was observed by fluorescence microscopy and the integrity of the structure of the fibers was confirmed by SEM morphology images. Thermal properties of the treated hair samples were improved by the covering of cellulose on the surface of hair fiber. The covered hair fibers achieved improved resistance to wear corroborated with thermal stability results. The developed methodology constitutes an important data in hair cosmetics area since the slightly formation of curls in hair fiber using cheap compounds and with reduced side effects could constitute a high value breakthrough in the hair care.

The presented treatment is cleaner and consumer-friendly for environment and humans than common oxidative hair treatments. It is also important to notice that the application process of the methodology presented with satisfactory results is around 10 minutes which is not time consuming.

Due to the hight potential of these formulations to change the shape of the hair fibre, the developed methodology in this study could constitute the basis for future new material science.

In short, it should be noted that formulations with serum and cellulose have many advantages and combat problems that current cosmetic products have. Unfortunately, the curl percentage is not as good as that obtained with existing cosmetic chemicals.

As future work, there are three points to explore.

Pre-treatment could be explored using other polar compounds combined with natural reducing agents to prepare the keratin fiber for the shape change process.

The type of cellulose used can also be explored to possibly develop some chemical modification in the structure of the cellulose.

The method of applying the treatment to the hair must also be studied as well as the drying process. It's an innovative process, but it needs more research.

In short, this dissertation is a good starting point for a greener and healthier future.

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