



**DEVELOPMENT OF NOVEL HYDROPHOBIC
FILM-FORMING POLYURETHANES
APPLICABLE TO HAIR-CARE COSMETIC
PRODUCTS**

B A C H E L O R T H E S I S

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List of abbreviations & acronyms

Abbreviation	Definition
C=O	Carbonyl
DLS	Dynamic Light Scattering
EN	Electronegativity
FT-IR	Fourier Transform Infrared Spectroscopy
H	Hydrogen
HS	Hard Segment
IC	Internal Code
MWD	Molecular Weight Distribution
-NCO	Isocyanate
PEPO	Polyester-based Polyol
PPE	Personal Protective Equipment
PU	Polyurethane
S-S	Disulphide
SEM	Scanning Electron Microscopy
SS	Soft Segment
VOC	Volatile Organic Compound
WPU	Waterborne Polyurethane Dispersion

1. Abstract

English version

The continuous demand for innovative and versatile cosmetic products drives companies to explore and experiment with new formulations. Polyurethanes, known for their diverse range of properties, are commonly utilized as film-formers in hair-care products and other cosmetic articles. This study focuses on the development of an autonomous film-forming polyurethane with exceptional hydrophobicity, aimed at enhancing water-resistance in hair. Multiple prototypes were synthesized, incorporating variations in keratin-reactive groups, polyol composition, and ionomer concentration.

The effectiveness of these prototypes was assessed through various characterization techniques, including pH analysis, solid content determination, dynamic light scattering (DLS), and water drop tests. Furthermore, synthetic hair samples were subjected to scanning electron microscopy (SEM) to evaluate the performance of the different prototypes using diverse application methods.

Versió en català

L'insistent demanda de nous productes cosmètics versàtils i innovadors ha forçat a les empreses ha emprendre en la recerca de noves formulacions. Els poliuretans, coneguts per el seu gran ventall de possibles propietats i aplicacions, son comunament presents com a agents filmejants en la composició dels productes pel cuidat del cabell, entre d'altres. Aquest estudi es centra en el desenvolupament d'un poliuretà autofilmejant d'alta hidrofobicitat que aporti resistència a l'aigua al cabell. S'han sintetitzat múltiples prototips a base de la modificació dels seus grups reactius a la queratina, la composició del polioli, o la concentració de ionòmer. Les propietats d'aquests prototips s'ha determinat mitjançant diverses tècniques de caracterització, inclosos l'anàlisi de pH, la determinació de contingut de sòlids, dispersió dinàmica de la llum (DLS), i tests de gota d'aigua.

Així mateix, l'eficàcia de cadascun dels prototips es va avaluar sobre cabell sintètic mitjançant un microscopi electrònic de rastreig, seguint diferents mètodes d'aplicació.

2. Objective

The present bachelor thesis is devoted to the synthesis and development of a film-former polyurethane based on a highly hydrophobic polyester main frame capable of producing a coating layer without the assistance of any film-forming additive. This polyurethane product is specifically designed for incorporation into "leave-on" hair-care cosmetic formulations, to provide the hair of a smooth effect, silky touch, water-resistance, and high thermal stability.

A critical aspect of this research revolves around achieving a delicate balance between the requisite high hydrophobicity of the polyurethane to be considered 'water-resistant' and its affinity to the essential biomolecules present in hair, most notably keratin.

3. Introduction

3.1 Polyurethane chemistry

Polyurethanes are macromolecules constituted by the repetitive combination of polyols, isocyanates, and amines, through polycondensation reactions. The term 'polyurethane' (abbreviated as PU) refers to those polymers containing a majority of urethane groups in their molecular backbone, even if they also contain other moieties (such as esters, ethers, amides, ureas, aliphatic hydrocarbons, etc.). PUs are considered 'block copolymers' given that they are composed by two discernible regions of different chemistry, such domains are the so-called 'soft segments' and 'hard segments', as it is visually represented in *Fig. 1*.

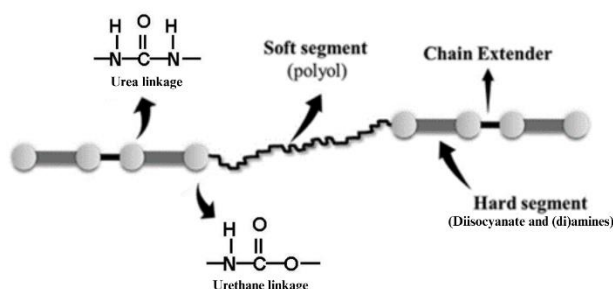


Figure 1 – Schematic polyurethane structure.¹

The *soft segments (SS)* are domains composed of polyols, compounds containing multiple reactive hydroxyl groups, such as polyesters, polyethers, polyacrylates, polycarbonates, etc. Polyols constitute a major part of the PU backbone, which is why they possess a vast effect on the final polymer's properties, e.g., polyester-based polyols² (abbreviated as PEPOs) bring susceptibility against weathering to the final PU; the gradual hydrolysis the ester groups suffer under the continuous exposure to moisture deteriorates the mechanical properties of the material, however, PEPOs provide excellent oil resistance.

Isocyanates are highly reactive derivatives of isocyanic acid³ (H-N=C=O) that constitute the most part of the *hard segments (HSs)*. The high electrophilicity of such functional group entails readily and fast reactions with all kinds of nucleophiles across its carbon-nitrogen double bond. Such electrophilicity is defined by the electron density that is held in the carbon, which varies according to the electron-withdrawing or donating nature of its substituents. E.g., aromatic isocyanates are remarkably more reactive than aliphatic given the extremely withdrawing nature of the conjugate system of the ring. The HS is also commonly constituted of chain-extenders, cross-linkers, or capping reagents³ – di-, poly- or mono-amines respectively – which are widely used to strategically control the molecular weight of the polymer, and thus, modifying its mechanical properties. Chain-extenders are normally applied to coatings, adhesives, or sealants to provide them with elasticity.

3.1.1 Properties of polyurethanes

The properties of polyurethanes are not defined by the discrete properties of their components but an average according to their presence within the polymer, the different linkages that are formed, and the intermolecular interactions that can be established. The *functionality* of the monomer is determined by the reactive points within their structure that are able to form a new bond. It is a decisive factor to the final spatial architecture of the polymer, and so, its rheologic properties: difunctional species lead to linear and flexible PUs, whereas polyfunctional monomers involve branching or even cross-linking, which stiffen the chains.

Hard segments are composed of polar functional groups that arise from the polycondensation reaction with alcohols or amines: urethane and urea linkages, respectively. The lone pair of electrons at the carbonyl of these functional groups – as well as the esters', ethers', etc. – tend to be attracted to the partial positive charge that is formed on the hydrogen from the nearest N-H group due to the high electronegativity (EN) of the nitrogen atom (*Figure 2*).² These intermolecular attractions result on the restrain of the free movement of the chains forcing their folding, which derives into an improvement on the packing, and so, the crystallinity. The lack of motion of the chains demands higher energy to allow rotation, hence the glass (T_g) and melting temperatures (T_m) rise. The excess of urea within the PU sharply increases the extent of *hydrogen interactions* that can be established given that two protons are present per urea linkage.²

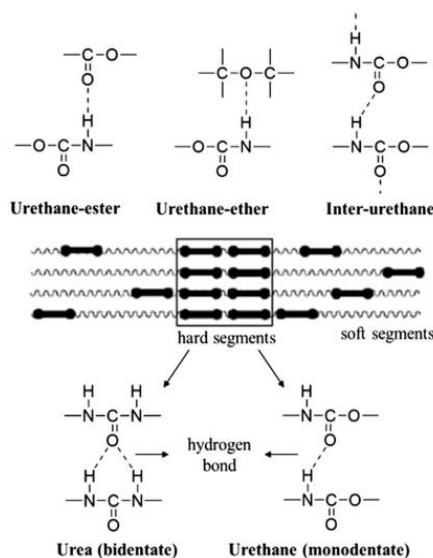


Figure 2 - Intermolecular hydrogen interactions.¹

Whilst the hard domains of the PU provide a physical reinforcement to the backbone through the hydrogen interactions, the soft domains act as a filling offering elasticity.⁴ The relative concentration between these segments is described by the *NCO/OH ratio*, a useful interrelation that is normally exploited to approximately set the physicochemical properties of the polymer. An increase of the NCO/OH ratio reduces the *weight average molecular weight* (M_w), the statistical molecular weight of the polymer according to the longest and heaviest chains. The reason behind that relies on the excess of NCO, which does not allow the elongation of the chains, rather enhances the proliferation of new ones. The *viscosity* of the polymer is tightly linked with its M_w and so, the NCO/OH. A large molecule (M_w), granted by a specific NCO/OH, confers them a greater resistance against flowing, meaning greater viscosity.

3.1.2 Polyurethane synthesis

Polyurethanes as well as polyureas or polycaprolactams are known as '*polycondensation polymers*'³ now their polymerization results from the reaction between two functional groups. These condensation polymerizations follow a step-growth mechanism that consists in repetitive propagation reactions between monomers and oligomers producing chains of different nature. The synthesis of polyurethanes revolves around the chemistry of the isocyanates. These reactions normally proceed without catalysis, in such case, the polyol acts autocatalytically.⁵ However, organometallic catalysts (based on tin, bismuth, etc.) are sometimes used to speed the rate of the reaction up.² The optimal reactive temperatures vary according to the reagent's nature, nonetheless, all polyols usually require mid hot temperatures, around 50 to ~120°C to proceed.

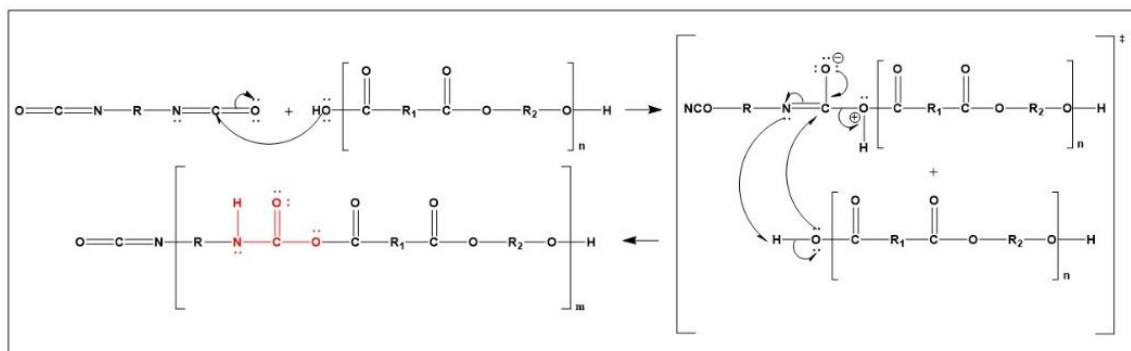


Figure 3 - Mechanism of the reaction between the PEPO SS and HS leading to the formation of urethane bonds.

The reaction that binds both segments together consists in the nucleophilic addition of the polyol to the electrophilic carbon of the diisocyanate (*Fig. 3*). The high EN of both oxygen and nitrogen atoms shifts the electron density away from the carbon atom increasing its electrophilicity. Simultaneously, the polyol catalytically attacks the electron-demanding site forming an intermediate complex that interacts with another polyol to finally yield the urethane product, most commonly named '*pre-polymer*'.

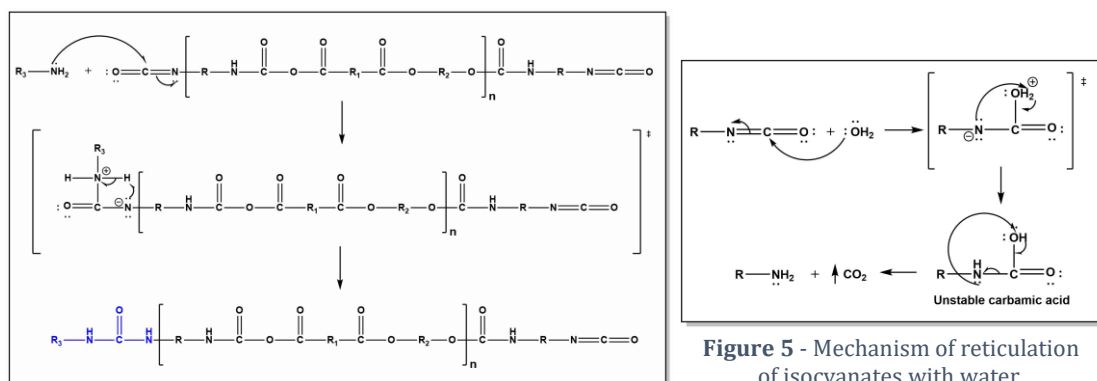


Figure 4 - Capping reaction mechanism.

The extension or capping of the NCO-terminated pre-polymer, normally pursued with (di)amines, results in the formation of urea linkages (*Fig. 4*). These reactions take place

vigorously at low temperatures, around 18°C to 25°C, due to their strong nucleophilicity. At higher temperatures, above 140°C, amines undergo secondary cross-linking reactions that yield other ureic and urethane-related functional groups: allophanates, biurets, etc.³ The reaction follows the same mechanism (Fig. 4) that polyols' (Fig. 3). The synthesis of PUs is drastically sensitive to water given the isocyanates' extremely high reactivity towards nucleophiles at environmental conditions. In fact, isocyanates spontaneously react with the water in moisture (Fig. 5) producing an unstable carbamic acid intermediate⁴ that cannot be stabilized through proton transfer, and so, spontaneously dissociates into an amine and carbon dioxide. For this reason, working with isocyanates requires strict hermetic reaction conditions, otherwise, such uncontrolled secondary condensations may lead to the irreversible blocking of the isocyanates altering the properties of the PU.

3.2 Waterborne polyurethane dispersions

Waterborne polyurethane dispersions (or WPUs) are binary systems containing PU solid particles dispersed in a continuous aqueous phase. Generally, polymers are not soluble in water due to their few hydrophilic segments and vast hydrophobic character of their chains.

Polyurethanes are structurally modified with surfactants to increase the hydrophilicity of the polymer backbone enough to be dispersible in water. This emulsifier, the so-called *ionomer*, provides the PU of cationic, anionic, or hydrophilic functional groups that are able to interact with the dispersing media through ion-dipole or dipole-dipole interactions (Fig. 6). These ionomers are usually introduced in the backbone through polyols containing such hydrophilic groups (sulfonic, carboxylic, phosphoric, etc.), however, they may also be added by the hydrogen-substitution at the urethane linkages.⁶ The difference in hydrophilicity between the HS and SS induces the formation of micelles, in cationic PUs, the surface of these micelles are positively charged forming a solvation layer by the interaction with water, whereas in anionic PUs, the dispersion is stabilised through the repulsion between particles.²

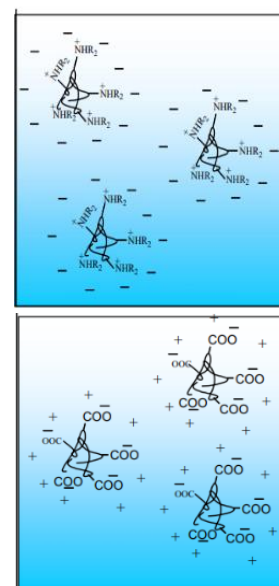


Figure 6 - Representation of a cationic (above) and anionic (below) PU micelle.²

3.2.1 Production of WPUs

The production of WPUs does not follow the conventional synthetic methods of PUs given the high reactivity of isocyanate groups towards water, instead, several synthetic alternatives have been developed. Nowadays, the production of WPUs is based on different

processes, each of them confers unique advantages. E.g., the *pre-polymer mixing process* is used to produce low-viscous pre-polymers, such low viscosity provides free diffusion of the particles removing the need of a co-solvent. This thesis focuses on the *acetone process*. The acetone process¹ consists in the synthesis of a pre-polymer with a polyol and an excess of diisocyanate in solution with a low-boiling-point solvent (e.g., acetone, THF, etc.) to mitigate the increase in the viscosity when the chain extenders (or cross-linkers) are added. The ionomer is incorporated to the polymer backbone to provide hydrophilicity, and get the PU dispersed in water. The emulsion step^{6,7} consists in a phase-inversion process where the system transitions from an organic continuous phase (the PU) phase to the aqueous continuous phase. Initially, water solvates the ionic centres of the ionomer reducing the ionic interactions between neighbouring molecules, this sharply reduces viscosity, increasing the amount of water, the hydrophobic segments precipitate, rising the viscosity. Finally, with the extended addition of water the dispersion changes into a biphasic system where the PU particles get dissolved by the co-solvent reducing the viscosity once again. The last step of the process is the removal of such co-solvent through vacuum distillation, obtaining a free-VOC (volatile organic compounds) product.

3.2.2 Applications of WPU: film formers

Considering the versatility of properties polyurethane may comprise, there is a wide-open possibility of applications where they can be extremely useful. Water-based PUs offer unique advantages such as non-toxicity, due to the absence of VOCs, good adhesion, flexibility, etc., which is why they are extendedly used as adhesives or coatings. Given the high strength of WPU and their chemistry, these organic coatings^{1,2} act both as a physical and chemical barrier, which isolate the substrate from the environment. WPU are specifically applied as coatings because of the easiness of their film formation process (*Fig. 7*), based on the coalescence of the PU particles throughout the loss of water by evaporation.³ High-solid content WPU have recently caught the eye of product developers given their short film-forming time, nevertheless, such polymers are not easy to apply considering their inherent high viscosity.⁸

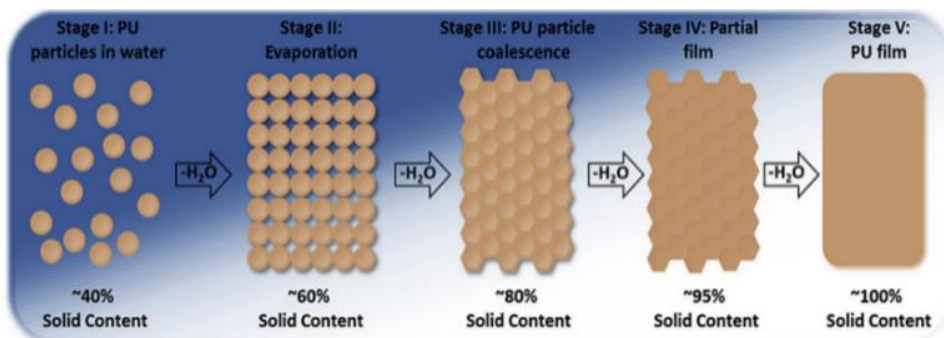


Figure 7 - Film-forming process of WPU.¹

4. Experimental part

The research on this new highly hydrophobic WPU capable of binding to keratin resulted in the optimization of three different prototypes, each of them being the continued improvement of the previous. In the next pages, the first two prototypes will be mentioned according to their new commercial name: prototype I as 'ELYSAN HR W' and prototype II as 'ECOFIXER', whilst the reagents are named according to their internal codes (IC) in the company's database.

4.1 Materials and hazards

4.1.1 ELYSAN HR W

All prototypes' soft segments are constituted by a polyester. Specifically, in ELYSAN HR W, the SS is totally composed of a lineal saturated aliphatic polyester (IC: P-089-B) containing a few pendant groups. Using the polyester as the hydroxyl source provides flexibility as well as high hydrophobicity to the main frame. The polyester does not present any hazard, no special precautions are required. However, at room temperatures P-089-B is normally solidified, it needs to be totally melted (at max. 80°C) before use.

The employed diisocyanate (IC: I-92) is cyclic and contain several pendant groups; unlike the polyol, diisocyanates require the strict use of several PPEs (personal protective equipment), including a gas-mask, now they are extremely toxic, a health and environmental hazard. In addition to that, all dispensable laboratory equipment (e.g., Pasteur pipettes) in contact with any mixture containing free NCO must be neutralized before being disposed away.

The first prototype is extended with a branched and cyclic diamine (IC: AM-75). The direct contact must be avoided at all costs, amines are extremely hazardous, in this case, they do not only present a health and environmental hazard, but also an irritant and corrosive behaviour: gloves, goggles, and a gas-mask must be worn. Another linear amine (IC: AM-84) is present within its HS, it contains an anionic functionality, a sulfonic group. The AM-84 not only extends the polymer with the N-H group, but also acts as an ionomer thanks to its anionic group. As an amine, it must be handled with gloves given its corrosivity.

4.1.2 ECOFIXER

ECOFIXER shares the same polyester (IC: P-089-B) and diisocyanate (IC: I-92) with the previous prototype. Notwithstanding, the composition of both SS and HS are not equal, ECOFIXER is actually composed of two polyols: the P-0589-B polyester, which provides the hydrophobicity and flexibility that is sought for the polymer, and a linear polyether (IC: P-

079), which provides the pre-polymer of sufficient hydrophilicity to be self-emulsifying and prescind of ionomers.

In order to increase the affinity to keratin, a thiol-containing reagent (SIL-78) is incorporated at the HS. SIL-78 is polyfunctional and extremely reactive, however, it presents no hazards. Nevertheless, such high functionality may lead to cross-linking reactions, which is why a monofunctional amine (AM-66) is added: to cap some of the NCO groups and control the MW. Since AM-66 is a waxy solid at room temperatures, it requires of melting before prior use. In addition to that, as it is an amine, it must be handled with all PPEs to avoid its irritant, corrosive and health hazardous nature.

4.1.3 Prototype III

The last prototype is contemplated as a correction of ELYSAN HR W given they both share the exact same reagents except for a small addition, another polyol (P-085). P-085 is a glycol composed of an easily reducible disulphide bridge that will act as a binding point towards keratin.

4.2 Synthesis

Despite all prototypes are prepared from different reagents, the synthetic processes are all based on the acetone process (3.2.1.), so they can be generally described with the procedure below. However, the variations and their reasoning are remarked in the 5. *Results* section.

I. DRYING OF THE DIOLS

The hygroscopic nature of polyesters, among other type of polyols, sometimes causes the loss of control on the molecular weight of the prepolymer if the reaction environment is not maintained hermetically closed. The moisture in air may get absorbed by the polyols during their manipulation (e.g., weighing, loading, etc.); the presence of this water later provokes secondary reactions spending NCO groups and so, reducing their availability for the formation of prepolymer. For this reason, diols are dried under vacuum at mid-high temperatures (~90°C) until the mixture stops bubbling.

II. INERT ATMOSPHERE

The reaction environment must be completely inert to avoid undesired side-reactions, therefore, an inert atmosphere is generated inside the reactor (*Fig. 8*). Moisture cannot only leak into the vessel absorbed in the polyols but also whilst taking samples or loading other

reagents inside. In order to maintain the inert atmosphere throughout the process, nitrogen is continuously supplied through a balloon, which deflates in case of breaching.

III. FORMATION OF THE PREPOLYMER

The heat is lowered down to mid temperatures before the addition of the diisocyanate in order to avoid secondary crosslinking reactions. The reaction is tracked by means of IR (4.3.1) until all polyols have reacted. Once the prepolymer had been totally formed, the solvent is loaded in the reactor to ease the increasing viscosity of the mixture, taking into account the low-boiling point nature of the solvent, the temperature may need to be decreased again beforehand.

IV. ADDITION OF THE IONOMER

This step is different in all the three prototypes, while in ECOFIXER does not exist, in PROTOTYPE III and ELYSAN HR W is performed at different stages during the process. In case of these last two prototypes, AM-84 is loaded well dissolved in water just before the emulsion.

V. EMULSION

The following is the key step of the synthesis, an impeccable phase-transition is crucial to yield a dispersion with a narrow molecular weight distribution, and so, consistent properties. Even if the dispersion heavily depends on the prepolymer formation as well, the emulsion is the final test to corroborate the efficiency of the process. Water is introduced in the reactor drop-by-drop, an efficient organic-to-aqueous phase-transition requires time and high revolutions to let all its steps take place (*explained in 3.2.2*).

VI. CHAIN EXTENSION OR CAPPING

Even if during the emulsion, most part of the unreacted diisocyanate had been spent, there is a minor part that is left free among the dispersion. The high toxicity of these compounds forbids the possibility of leaving some traces in the products, all the more reason in cosmetics. The addition of amines fulfils this purpose, besides having the opportunity to increase

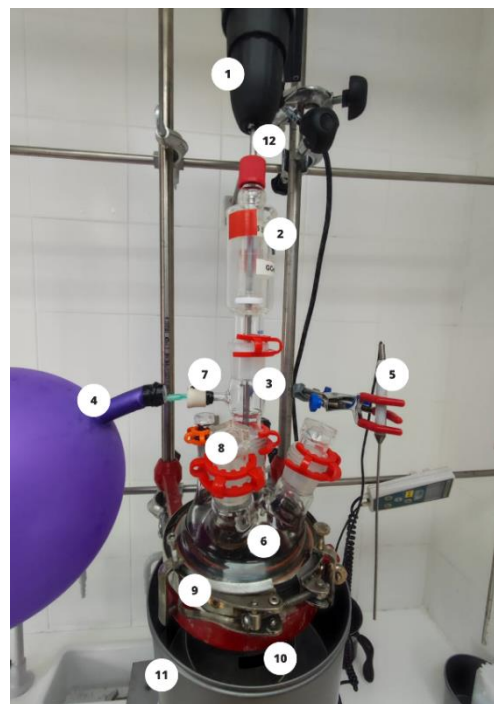


Figure 8 - Assemble for a WPU synthesis.
(1) Motor (2) Superior & central guide (3) Inferior guide (4) N₂ balloon (5) Thermostat (6) 5-necked cover (7) Septum (8) Glass plug (9) Clamp (10) Round-reaction flask (11) Oil bath (12) Spatula

the molecular weight of the prepolymer or, on the other side, avoiding its proliferation. The capping/chain-extension reaction is tracked by IR.

VII. DISTILLATION

The last step of the process is the obtention of the WPU from the mixture through the evaporation of the solvent. Considering that low-boiling point solvents are used, the temperature of this extraction process is not required to be very high. Sometimes, the high revolution the dispersion is being stirred at, its volume, temperature, or the vacuum itself might make the dispersion defoam and leak into the condenser; if such defoaming is threatening, a few drops of an anti-defoaming additive can be added to avoid the loss of product. The distillation process is continued until there is no further accumulation of condensate in the collector. The solid content of the dispersion is determined and checked to be in the range of 30-33%. Otherwise, the distillation may be continued some extra time; however, it is not recommended now water might be lost as well. The vacuum distillation setup is showed in *Fig. 9, 10* below.

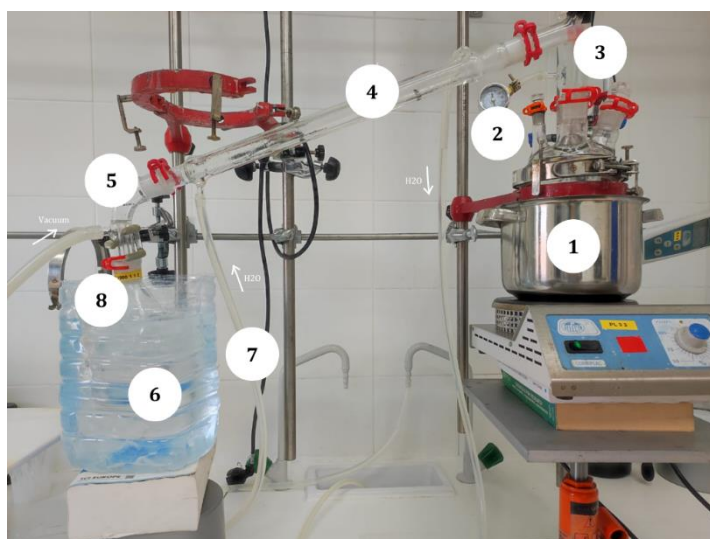


Figure 9 - Vacuum distillation set-up.
(1) Oil-bath (2) Manometer (3) Distillation head (4) Liebig condenser (5) Vacuum adapter (6) Ice-bath (7) Rubber tube (8) Collector



Figure 10 - Vacuum circuit.
(9) Vacuum manifold (10) Pressure regulator (11) Diaphragm pump

4.3 Reaction monitoring

Keeping a good track of the on-going reactions is decisive on the success of the synthesis; unreacted polyols, or the excess of diisocyanate throughout the process widens the molecular weight distribution (MWD), causing a significant variance between the molecular weights of the different chains within the dispersion. An overage widening of the MWD risks losing the exact properties the product was intended to possess, for this reason, the following quantitative techniques are employed.

4.3.1 Infrared spectroscopy

Infrared spectroscopy (FT-IR) is a spectroscopic technique that measures the vibrational energy involved in the different movements and motions of the chemical bonds. Depending on their chemical environment, the bonds will require more or less energy to move. Applying infrared radiation, the different functional groups will absorb energy of a particular wavelength. This distinctive physical feature provides information of the structural nature of the polymer throughout the reaction.

Wavelengths of Absorption Bands				
-N=C=O (diisocyanate)	2275 cm ⁻¹	2250 cm ⁻¹	1350 cm ⁻¹	
-NH-COO-(urethane)	1640 cm ⁻¹	1610 cm ⁻¹	1650 cm ⁻¹	1680 cm ⁻¹
C=C (in benzene)	800 cm ⁻¹	1610 cm ⁻¹	1500 cm ⁻¹	
Aromatics	3030 cm ⁻¹	1600 cm ⁻¹	1500 cm ⁻¹	
-OH (hydroxyl)	3200 cm ⁻¹	3400 cm ⁻¹		
C-O-C (ether)	1150 cm ⁻¹	1070 cm ⁻¹		
ArNH ₂ (aromatic amine)	1350 cm ⁻¹	1250 cm ⁻¹		
AlNH ₂ (aliphatic amine)	1280 cm ⁻¹	1180 cm ⁻¹		

Figure 11 – Wavelengths of important absorption bands in FT-IR.³

In Fig.11 there are listed the most relevant absorption bands and their corresponding wavelengths, nevertheless, the tracking is focused on the different absorption bands of the carbonyl (-C=O) moiety as it conforms all the functional groups of concern and it shows the most distinctive bands: $\bar{\nu}_{\text{NCO}, (\text{C}=\text{O})} \approx 2275\text{cm}^{-1}$, $\bar{\nu}_{\text{-NH-COO-}, (\text{C}=\text{O})} \approx 1686\text{cm}^{-1}$ and $\bar{\nu}_{\text{-NH-CO-NH-}, (\text{C}=\text{O})} \approx 1650\text{cm}^{-1}$. The other parameter of interest is the intensity of the bands, which according to the *Lambert-Beer law*, it is associated with the concentration of the corresponding functional group: “the absorbance of a moiety is proportionally related with its absorptivity and concentration within the sample.”

Considering that the synthesis of polyurethanes is based on the chemistry of isocyanate with the other reagents, the monitoring of the reactions is mainly centred on the presence of the -NCO moiety in the spectrum. Even though, the presence of urethane and urea bands are extremely useful in determining whether the diisocyanate is spent in desired reactions or it is being consumed in secondary-reactions. In order to carry out an accurate monitoring, the sampling is done every 30 min to 1 h until the NCO band is either extinct or does not decrease. The obtention of a reliable spectrum mainly depends on the sampling and the tidiness of the spectrometer (ThermoFisher Scientific), as well as the speed of the measuring: the NCO in the sample reacts with the humid air as it was transported into the spectrometer, even more without solvent, a slow measuring may yield inaccurate results. In case that the sample contains solvent, it must be either left to dry or flushed out with N₂ to remove the diluent, otherwise, the bands may be deformed or shadowed by the solvent's peaks. The blank must be recorded before any measurement, even if the sample is the same.

4.3.2 Back-titration

Back-titration or indirect titration is a quantitative volumetric technique that is applied during the prepolymer formation reaction to estimate the percentage of free NCO that is present in the mixture once, presumably, all the polyols have reacted. It defines the real available amount of diisocyanate to react with the amines. The difference between the theoretical %NCO and the experimental is contemplated as the amount of diisocyanate that has been wasted throughout the reaction-time in undesired reactions.

The back-titration is executed once the last IR spectrum shows no decrease of the diisocyanate band nor an increase of the urethane moiety with respect to the previous, meaning that the main reaction has finished. If the corresponding NCO band slightly decreases but the urethane's do not increase, the titration must be carried out straightaway since undesired reactions are probably spending the NCO left. After the sampling, the titration glass is covered with a watch glass to avoid the contact of the prepolymer with the air, both are immediately weighed in the analytical balance to know the amount of sample that is going to be titrated. Besides that, the sampling pipette is also weighed, in a beaker, to be able to consider the most accurately the amount of prepolymer that has been lost during the whole titration process in the calculations. After that, the prepolymer is diluted in cyclohexanone to diminish its viscosity and ease the titration, sometimes it requires some heating to totally melt and dissolve. Then, a standard solution of N-butylamine is added to the mixture in excess according to the sample weight, the amine reacts with the available NCO in the sample. Once the sample is homogeneous, the dilution is titrated with hydrochloric acid using an automatic titrator, as it is shown in *Figure 12* (TitraLab AT1000 Series, HACH). This technique quantifies the concentration of NCO in the sample based on the excess of N-butylamine that is left from their reaction to interact with the titrant.

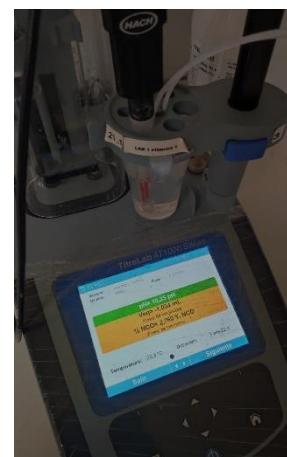


Figure 12 - Results of a finished back-titration.

4.4 Characterization

The determination of the physical and chemical properties of the different tests has been a fundamental decisive factor to conclude whether the synthesis had been successful or not, they provide a brief preview on the polymer behaviour during the applications. The characterization of the products is a demonstrable approach of considering the reproducibility of a synthetic procedure, similar results ensure the reliability of the process, which are mandatory for the validation of the product.

4.4.1 pH measurement

The acidity is quite a sensitive property of the product since it is intended to be applied in the formulations of hair cosmetic products. The pH of these kind of cosmetics affect their performance⁹: the hair pH goes around 3.67, the difference with the product's may increase or decrease the repulsion between hair strands producing a smoothing or a voluminous effect. However, the pH must also be balanced taking into account the natural human scalp pH (4.5-5.5), which is skin, after all. Even if the WPU is found at low concentrations within the product, its pH value must fit within the aforementioned range. The pH is measured with a pHmeter (Accsen pH 7).

4.4.2 Solid content

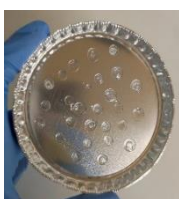


Figure 14 - Dried sample.



Figure 13 - Halogen heater.

The solid content of the final WPU refers to the actual amount of polyurethane that is dispersed in water. As it has been mentioned in 3.2.3, the film forming process consists in the slow drying of the dispersant phase leading to the coalescence of the polymer molecules. The high heat of evaporation of water¹⁰ makes the product's application time-consuming and impractical, for this reason, WPUs with a high solid content and so, lower amount of water, are preferred. However, an excessive low content of water brings poor spreadability and, overall, bad features. For this reason, all products are optimized up to a balanced concentration, around 30 to 35%.

The determination of the solid content is conducted in a halogen heater (Ohaus MB25, *Fig. 13*), where a sample of 1.0 – 1.5g is placed and heated up to 160°C. The moisture balance dries the dispersion (*Fig. 14*) and weighs the remaining mass over the total that had been sampled.

4.4.3 Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS)¹¹ is a spectroscopic technique that is based on the relation between the scattering of a polarized electromagnetic radiation and its translational diffusion through a solution. The instrument (Malvern Panalytical ZETASIZER PRO) measures the change in the scattering intensity over time, the average value is considered to be proportional to the diameter of the chains. DLS is then a perfect sensitive and qualitative technique of measuring the size of the PU particles, which is responsible of most the thermal and mechanical properties of the polymer. The sample is analysed in a dilution of 0.05% of solid content to avoid noise in the signal (or shadowing smaller particles) in a quartz cu-

vette. DLS is extremely sensitive to the analysis environment, the minimal interference does not yield reproducible data, for this reason, the working material must be impeccable: the cuvette must be thoroughly cleaned with isopropanol and dried with N₂ to avoid stains or yellowing, it also needs to be covered to prevent the evaporation of the water and the entering of dust, etc.

4.4.4 Hydrophobicity

One of the aspirations of this thesis is the obtention of a hydrophobic film-former, therefore, the validation and measurement of the degree of repulsion towards water of the different prototypes is vital. The hydrophobicity of the different products were determined by means of *water drop tests*, which consisted in dripping a droplet of water on the layer of the polymer and observe whether the drop spread over the surface of the product or kept its round shape. As the hydrophilicity of the coating increases, the stronger the attractive interaction towards water results to be, therefore, the contact angle between the drop surface and the polymer layer is lower. Hydrophobic coatings do not possess enough surface tension to interact with the droplet, in fact, a repulsion force is created between them increasing the contact angle, as it is sketched in *Figure 15*.

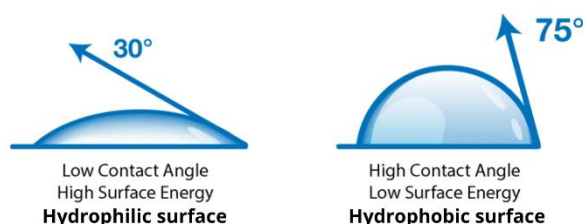


Figure 15 - Contact angle variation according to the hydrophilicity of the surface.¹²

All prototypes were first characterized at a concentration of 5% of solid content, then, several extra tests containing additives (preservatives, film-forming agents, etc.) at different concentrations were performed to check the possible alteration of the hydrophilicity of the product. Mixtures between prototypes as well as comparative qualitative tests between other products of the company were conducted. Every water drop test was carried out in a qualitative and comparative manner; the contact angle was not measured.

4.5 Application

The final and decisive test to check the compliance of the proposed objectives – the affinity to keratin and film forming ability – is but by their direct application in hair. Hair is a protein filament mainly composed of keratin (α -keratin) fibres; extended polypeptide chains rich in sulphur due to their high cysteine¹³ amino acid content. These amino acids tend to engage

intermolecular crosslinking interactions between their sulphur atoms. These resulting disulphide bridges provide hair of strength, structure, and permanent shape. Hair-care products, like the one that is being pursued in this thesis, are devoted to repairing the hair filaments by reconstructing the broken disulphide bonds or strengthen them.

All prototypes were tested in synthetic hair at different solid concentrations according to the actual content range (3% to 10%)¹⁴ in shampoo and conditioner formulations. Locks of hair were prepared with adhesive tape at the bottom, then washed and stirred by hand in the polymer solution for 2 minutes straight. Finally, the samples were left to dry overnight.

4.5.1 Activation of the disulphide bridge

Unlike ELYSAN HR W and ECOFIXER, Prototype III contain a disulphide bridge in its polymeric structure that requires an activation step to be reactive towards the hair. This so-called 'activation' consists in the reduction of the S-S linkages into thiol groups with a bio-compatible reducing reagent, as it is represented in *Figure 16*. This reducer is dissolved in a buffer solution of pH 6 to keep the activation-reaction environment of an acidity range between 5 to 8 to ensure that the reducer is present in its reduced form. The pH of the buffer solution is monitored with the pHmeter throughout the preparation of the activation media.

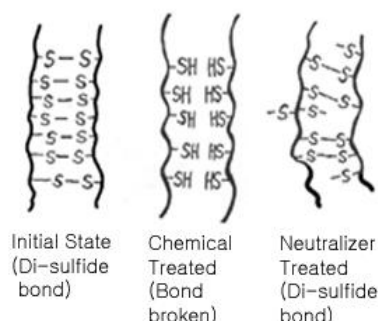


Figure 16 - Representation of the breaking and formation of S-S between hair fibres through reduction and oxidative process respectively.¹⁵

Notwithstanding, this activation may be either directly applied to the disulphide bridges of keratin in hair or, on the other hand, to the product's. Since the success of the product is also tied to its employment, both application methods are put to the test. For the activation of the product, the polyurethane dispersion is directly dissolved in the buffer solution yielding a solution of 5% of solid content. Once the solution is completely homogeneous, showing a translucent white appearance, the hair lock is wetted and stirred in it for 2 minutes straight. To activate the S-S bridges of keratin, the locks of hair are directly submerged in the buffer solution containing the reducer for 5 minutes. Meanwhile, a sample of 5 mL Prototype III is diluted down to 5% of solids with distilled water. As soon as the 5 min-wait has finished, the lock of hair is washed with the product's dilution for 2 minutes.

4.5.2 Scanning electron microscopy (SEM)

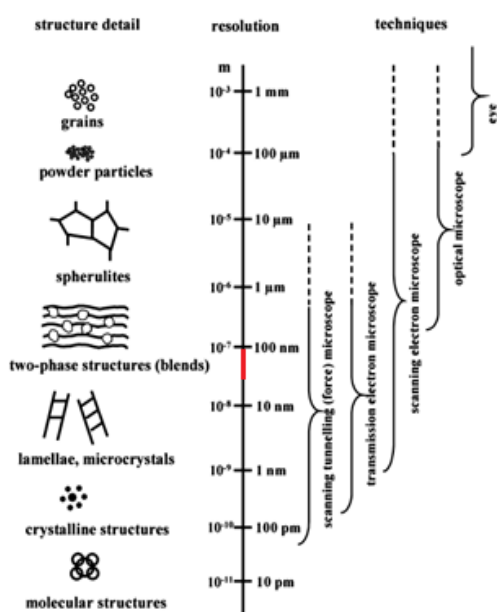


Figure 17 - The size-reach of the different microscopic techniques.¹⁶

As previously discussed, the structure of hair is a crosslinked net of keratin fibres, making the interaction with the product hard to occur. The S-S bridges tend to be shielded by the long chains of the proteins, to avoid this physical blockage, the polyurethane product is designed to fit within the nanoscale. In order to study the film-forming ability and affinity of the applied products, it is required a microscopic technique capable of attaining such small dimensions. As it is represented in *Figure 17*, a perfectly suitable option is *scanning electron microscopy (SEM)* since it provides enough resolution to capture the polymer nano-particles (highlighted in red).

SEM allows the recording of the surface of all kinds of samples down to a nano-level. The SE microscope (SU1510 HITACHI) detects the electronic interactions, X-rays, or/and possible scattered electrons of the sample's surface caused by the irradiation of a highly energetic electron beam. The signal is then electronically detected and displayed as a gradient of brightness¹⁷. Just like all polymers, polyurethanes are non-conductive materials whose surface tends to accumulate all the electron density that is irradiated. The poor conductivity of the product produce burnt images and restricts the possibility of its examination. In such cases, a previous metallization step is required: the sample is coated with a thin layer of a conductive material (such as gold, silver, platinum, etc.)¹⁸ in the metallizer.

The dried recovered lock samples are trimmed on top of a double-sided sticker. With the help of tweezers, this trimmed hair is spread over the sticky surface to avoid the shadowing of the fibres. Carefully of not fold nor stain the sticker, it is stuck on a metallic support and placed in the metallizer (Q150R S Quorum) at 90 seg/20mA. During the metallization, the SEM is started up to stop the vacuum that is left from the previous analysis. Once the sample is metallized and the microscope is in atmospheric conditions, the support is placed inside the machine and the vacuum is generated again to avoid the contamination of the sample and the scattering of the electrons of the beam due to the presence of air.

5. Results and discussion

ELYSAN HR W

Table 1 - Characterization results of all ELYSAN HR W tests.

	T-01	T-02	T-03	T-04	T-05
Reticulation (%)	0	3.87	9.54	5.00	6.84
pH	-	7.36	7.06	7.38	6.83
Solid content (%)	-	33.83	31.53	29.61	29.47
Number mean (nm)	-	70.71 ± 0.26	71.62 ± 5.65	75.65 ± 6.78	71.09 ± 8.35

▪ Test 01

The synthesis of the first ELYSAN HR W test was designed based on another similar product of the company. The nature of the polyol and chain-extenders were changed to meet the hydrophobicity requirements that the thesis demanded. Since the compounds had changed, the IR spectra that were recorded during the monitoring of the prepolymer formation – as well as the ones of the chain-extender reaction – could not be compared to the spectra of the product the T-01 was based on. Different monomers imply different reactivities (despite sharing functionalities), and so different reaction rates, as well as a different chemical environment of the urethane groups ending in the obtention of dissimilar spectra.

As its detailed in the first row in *Table 1*, the prepolymer formation reaction was monitored and proceeded with the extreme accuracy to consider that no diisocyanate was lost in secondary reactions. This monitoring is represented in *Figure 18* in the form of an increase and decrease of the bands corresponding to the functionalities involved in the reaction. The marked ($\bar{\nu} \approx 2270 \text{cm}^{-1}$) and zoomed peak located at the left-side of the spectrum corresponds to the carbonyl bond of the NCO moiety; as the reaction proceeds, the concentration of diisocyanate diminishes in the sample and so it is represented in the spectrum by a diminish of the intensity of the band. At the same time the NCO is spent, a new functionality is being formed: the urethane. This urethane group provokes a change in the chemical environment on the compound, and so, the spectra evolves accordingly. The carbonyl that conforms the urethane group displays a strong and sharp signal around $\sim 1700 \text{cm}^{-1}$ which change is barely perceptible throughout the reaction. For this reason, the formation of urethane is tracked with other less-intense bands, corresponding to bending vibrational modes of N-H and stretching of C-N, marked at $\sim 1550 \text{cm}^{-1}$. There is a great change in the last spectrum (illustrated in purple) with respect to the previous: the sharp stretching signal of urethane widens at the base indicating that a few urethane groups within the polymer vibrate at

lower frequencies. The fact that some of the urethane groups vibrate less frequently than others implies an extra force that strengthens their carbonyl bond; this strain is most likely caused by the hydrogen interactions powered by the increasing presence of new urethane groups (explained in 3.1.1). The expenditure of NCO right until that point as well as the widening of the urethane's signal indicates the formation of enough urethane to assume that the reaction has finished.

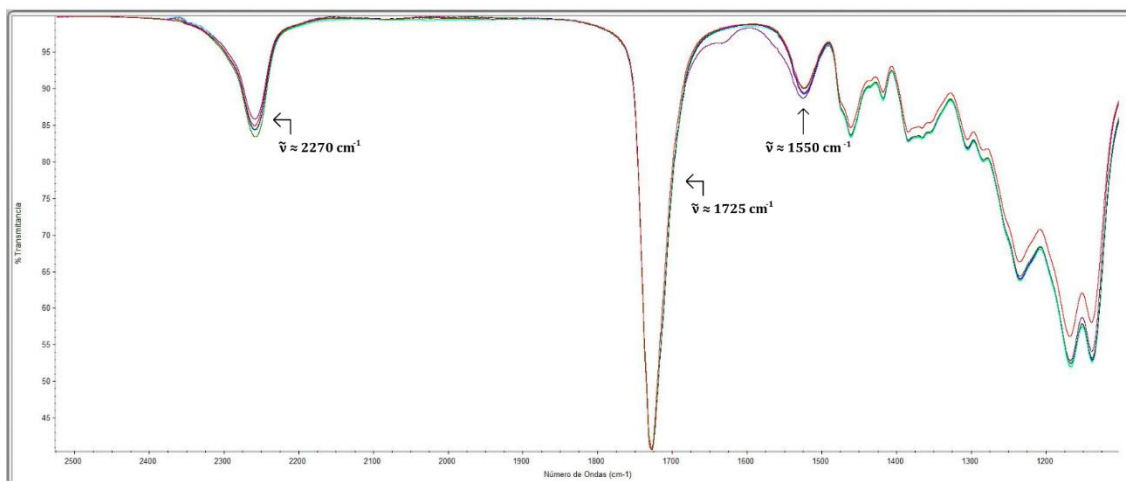


Figure 18 - Prepolymer formation FT-IR spectra of T-01 (zoomed in).

The titration indicated an experimental %NCO of 3.04. Considering that the theoretical concentration of NCO was 2.94%, the presumed ending of the reaction was then refuted. The possibility of reticulation at that point was contemplated as zero now the reaction had not already finished. However, the difference between the stabilization value (the theoretical) and the experimental is almost negligible for this reason, the synthesis was continued. It is worth mentioning that the process of performing the back-titration lasts approximately 30 minutes, therefore, it could be assumed that the NCO was spent within that lapse.

According to the synthesis design of the product ELYSAN HR W was based on, the ionomer and chain-extender were both added altogether in an aqueous solution. However, both compounds resulted to not be miscible even though both of them are amines. The first hypothesis attributed this immiscibility to the elevated basicity of the chain-extender, which form an insoluble salt with the sulfonic group of the ionomer. The pH was checked with a pH test strip. The paper turned dark blue, indicating a highly basic pH of 10 or 11, which disproved the idea of salt formation now it implies the reduction of the pH. In spite of everything, the species were loaded to the reactor resulting in the formation of solid traces and a turbid solution. Some acetone was added to try to homogenize the solution, but some of the traces remained precipitated. The synthesis was then stopped.

The most plausible hypothesis associated the formation of precipitate to the high hydrophobicity of the chain-extender and prepolymer. This hydrophobicity made the prepolymer insoluble to acetone, a polar solvent.

▪ Test 02

The procedure was modified to pursue the synthesis despite the hydrophobicity of the reagents: the chain-extender was added after the emulsion, once the dispersion was formed, to elongate the chain without risking the success of the phase change. Unlike the previous test, some NCO was lost during the prepolymer formation in secondary reactions; however, this loss did not have any effect on the properties nor completion of the synthesis, the reticulation is very low (<20%). As it is illustrated in *Figure 19*, the synthesis prevailed without the precipitation of the product.

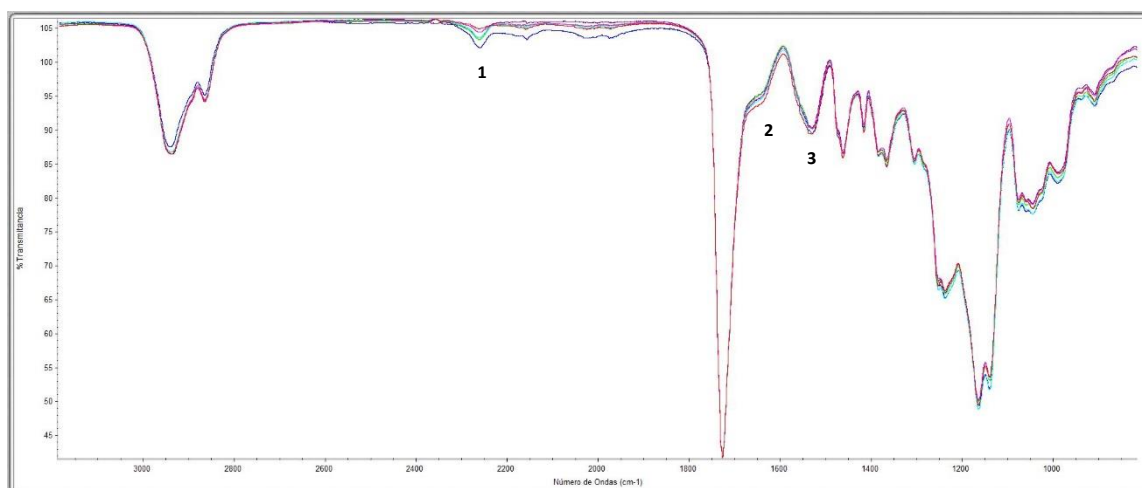


Figure 19 - Chain-extension reaction FT-IR spectra of T-02.

The combination of spectra above summarises the last reactive stage of the synthesis: the chain-extension reaction. It is observed the increase in the concentration of urea linkages at peaks 2 ($\sim 1680\text{cm}^{-1}$) and 3 ($\sim 1580\text{cm}^{-1}$): the intensity of the widened C=O stretching band (2) increases considerably given the growing engagement of hydrogen interactions due to the formation of ureas. Moreover, the carbonyl vicinity of these ureas differs from the urethanes: the nitrogen electronegativity that replaces the oxygen atom in the ureas changes the electronic distribution within the functional group, and so, it also changes the vibrational frequency of the C=O stretching. The formation of ureas entails the presence of more N-H and C-N bonds (since two nitrogen atoms are present per linkage), and then the intensity of their bending and stretching bands increase (3). The reduction of the diisocyanate's C=O band right to its extinction, the flat red spectrum, in 1 describes the course of the elongation reaction. Once the band is completely flattened, there is no reaction whatsoever taking place in the reactor now there is no NCO left.

The pH of the product is neutral, within the preestablished acceptable boundaries (pH= 6.5 to 8). The lack of ionizable and polar functional groups of the different monomers confers the final polymer of high hydrophobicity. Moreover, the resultant urethane and urea linkages tend to remain uncharged at neutral pHs – such as in distilled water – now their respective nitrogen and oxygen atoms are not basic nor acidic enough, respectively, to gain or lose any proton. Therefore, it is conceivable that the products' pH achieves this value considering its hydrophobicity.

The accuracy with which the synthesis had been performed yielded a homogeneous product with particles of the same nano-size. It can be observed by the naked-eye that the particle size distribution is not extremely wide now the dispersion does not precipitate into two phases. The polydispersity of the particles, expressed as the standard deviation and uncertainty of the particle size, is almost negligible. Both graphs (20 and 21) are monomodal, a single peak is detected, indicating that all the particles possess a similar size. The particle size value is enclosed within the peak area. The fact that both types of DLS spectra show a single peak at the same values indicates the accuracy of the measurement and precision towards the actual value. The difference between the two spectra will be discussed in further tests where there are noticeable changes.

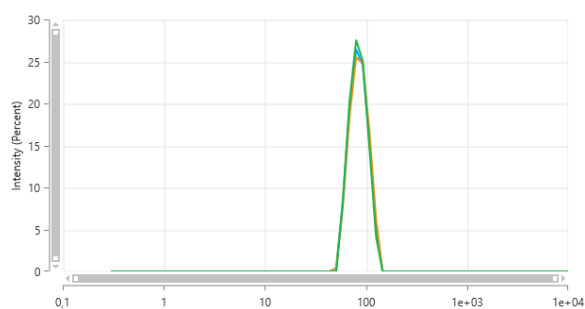


Figure 20 - DLS graph in intensity of T-02.

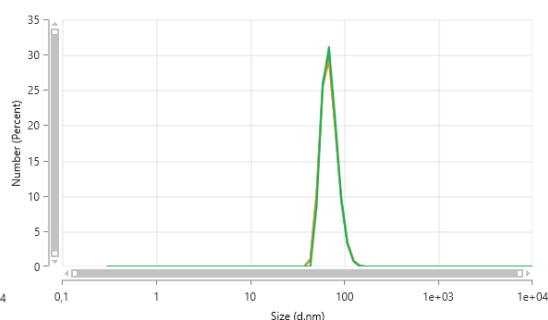


Figure 21 - DLS graph in number of T-02.

The hydrophobicity of the product was put to the test against other products. In *Figure 22* is perceptible how the round-shaped droplet remains on the layer of ELYSAN HR W (left), the contact angle appears to be greater than 65° indicating poor reactivity with water. The application on the right corresponds to a dispersion of T-02 with PVP, the most used film-forming agent in hair-care cosmetic industry, at 10% of solids. The addition of a film-forming agent, which is inherently hydrophilic, reduces quite a bit the hydrophobicity, even at low concentrations: the right droplet is able to spread further over the product leaving a lower contact angle. Since this technique was merely applied qualitatively to confirm the hydrophobicity of the product, the exact contact angle value was not measured accordingly. Although, if the quantification of the hydrophobicity had been necessary, other more

accurate methods would have been followed. Nevertheless, for that matter more precise instruments are required, normally, an optical tensiometer.¹²



Figure 22 - Water Drop Test T-02 (ELYSAN HR W on the left, ELYSAN HR W + PVP on the right).

The application and further observation of the T-02 through SEM proved that the product does not meet the expectations: it does not interact with the keratin and therefore cannot form a film covering the hair fibre. Through SEM, keratin can be appreciated in natural (and good-quality synthetic hair) as scales; an ideal film-former would cover those scales so no external chemical nor physical agent would get to the internal protein structure. As it could be perceived via SEM (*Figure 23*), almost no product attached to hair; the traces that did clustered on top of the surface of the fibres.

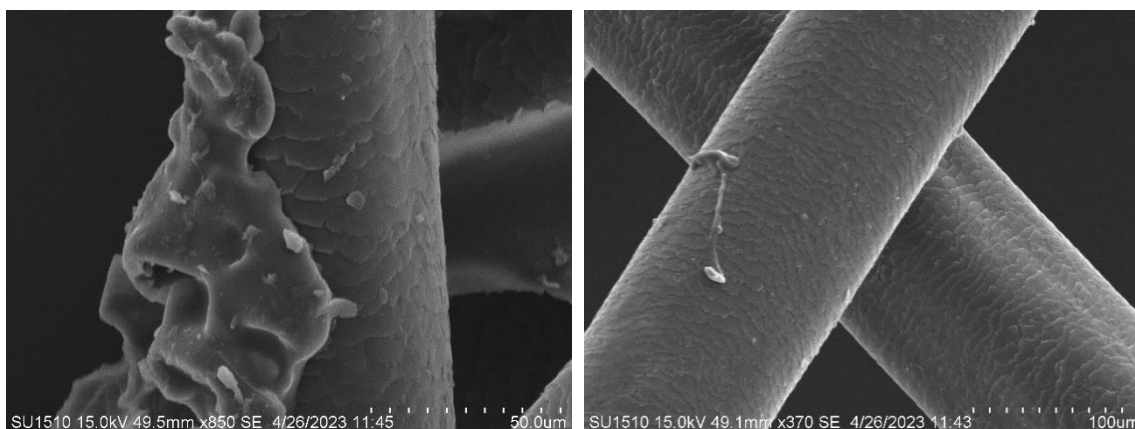


Figure 23 - T-02 applications on synthetic hair SEM images at 50 and 100 μm .

▪ Tests 03 – 05

Even though ELYSAN HR W did not accomplish the proposed goals of the thesis, its synthetic process was optimized and repeated thrice to prove the obtained T-02 results. As it is noted in *Table 1*, the results did not differ from T-02's. The repetition and success of three tests is not only a requirement to consider them a prototype, but it also provides veracity to the resultant values.[†]

[†]IR and DLS spectra of T-03, T-04, and T-05 are included in the *Annex* for those interested. However, it should be noted that the differences between these graphs and those included in T-02 are negligible, and so, they will not be further discussed.

ECOFIXER

The second prototype was designed to address the limited affinity of ELYSAN HR W to keratin by enhancing the reactivity of the polymer. To achieve this, a polythiol-containing reagent (SIL-78) was introduced into the PU formulation. However, it was crucial to carefully consider the impact on the hydrophobicity and stability of the product. The addition of this reactive and hydrophilic reagent to the mainframe would reduce the product's hydrophobic characteristics and compromise the desired water-resistant effect, potentially making the coating susceptible to chemical degradation. To achieve a balanced hydrophilicity of the polymer resulting from the thiol-containing reagent, the NCO concentration is reduced by half through the use of a capping monofunctional amine. This reduction in diisocyanate content results in the disposal of the corresponding amount of SIL-78, allowing only half of its thiol groups to react with the hard segment, while the remaining half is left to interact with the keratin.

The inclusion of the AM-84 ionomer was also called into question, given the need for an aqueous dilution. The presence of water before the incorporation of SIL-78 would further decrease the available NCO, resulting in a reduction of thiol content in the final product and, consequently, its hydrophilicity. However, the absence of a surfactant could put the emulsion's stability at risk, in consequence, the polyol is modified accordingly (4.1.2) to facilitate autonomous emulsification.

In summary, the new synthetic design consists of the introduction of a new polyol to ensure a successful phase change, the use of a capping monoamine, the addition of a thiol-reagent, and the final emulsion to get the phase change as well as consuming any remaining NCO.

Table 2 - Characterization results of all ECOFIXER tests.

	T-01	T-02	T-03	T-04	T-05	T-06
Reticulation (%)	955.75	25.93	73.29	41.16	13.25	19.23
pH	-	5.35	-	-	5.26	6.09
Solid content (%)	-	35.61	-	-	33.33	42.86
Number mean (nm)	-	23.83 ± 1.98	-	-	26.46 ± 4.89	26.49 ± 0.93
		101.90 ± 32.74			142.40 ± 4.98	154.50 ± 11.40

▪ Test 01

The monitoring of the prepolymer reaction revealed concerning results. In *Figure 24*, where it is illustrated the evolution of the prepolymer formation reaction, an irregular and excessive consumption of NCO – as indicated by the green spectrum representing the initial NCO

concentration and the red spectrum representing the excess – can be observed, with peak 1 decreasing by more than half of its height. Since the comparison between spectra from different prototypes is not feasible due to variations in polymer composition, such diminution was not a cause for alarm at that point. Nonetheless, it is noticeable the inconsistent great decrease of the diisocyanate compared to the disproportional formation of urethane groups, represented as the increased intensity of peak 2 (C=O stretching band).

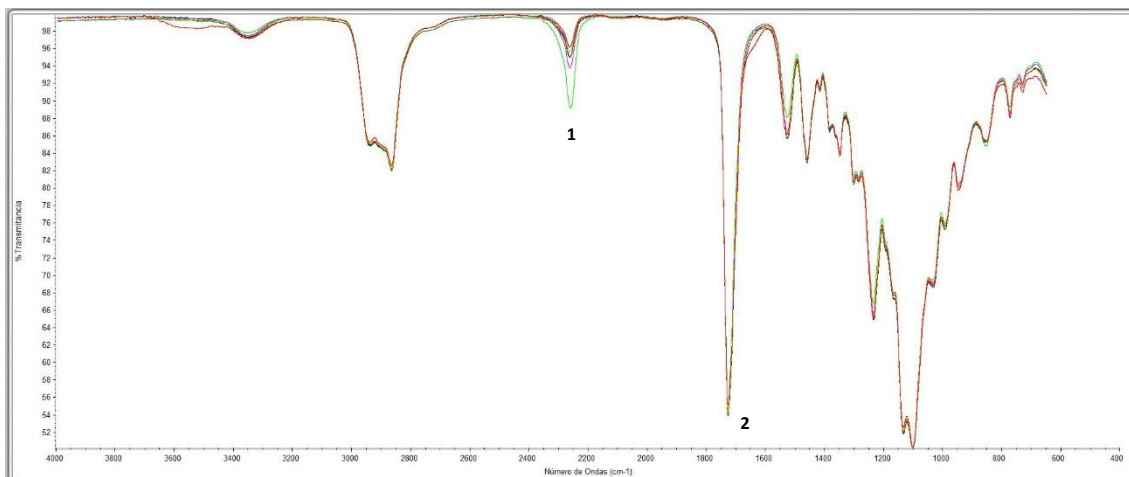


Figure 24 - Prepolymer formation FT-IR spectra of T-01

The result of the back-titration (detailed in *Table 2*) confirmed that an error was committed during the synthesis or its design. The final experimental %NCO, provided by the titrator, is calculated with the expression below (*Eq. 1*). The anomaly must come from any of the variables the %NCO_{exp.} depend on.

$$\%NCO_{\text{exp.}} = \frac{(\text{eq. NCO} - \text{eq. OH}) \cdot MW_{\text{NCO}}}{\text{total g}} \cdot 100$$

Equation 1 – Experimental %NCO, where: eq. stands for ‘equivalent’, representing the mol of a certain functionality; MW_{NCO}, the molecular weight of the diisocyanate; and ‘total mol’, the total mass of the sample.

Upon reviewing the loaded amounts of each reagent matched the theoretical in order to corroborate that the mistake was not due to over or underweighting, an error was discovered within the calculations: the equivalents of hydroxyl were calculated based solely on the new polyether as the hydroxyl source, overlooking the fact that the SS was a mixture of polyether and polyester. Consequently, the equivalents of diisocyanate were added in excess, assuming they would be consumed solely by the polyether, however, the presence of polyester consumed part of the excess of the NCO. For this reason, the reticulation (*Eq. 2*) results to be exceptionally high, this loss of the excess of NCO is considered to occur through ‘undesired reactions’.

$$\%reticulation = \frac{(\%NCO_{\text{theor.}} - \%NCO_{\text{exp.}})}{\%NCO_{\text{exp.}}} \cdot 100$$

Equation 2 – %reticulation expression.

The synthesis was called off and the calculations rectified for the following tests.

▪ Test 02

The new tracking results of T-02 proved that the error and cause behind the high reticulation was indeed the calculation of the hydroxyl equivalents. The improvement is clearly illustrated in *Figure 25*, the stabilization of the formation reaction results in a slight decrease on the intensity of the C=O stretching band of NCO (peak 1). The height difference between the peaks 1 of *Figure 25* and 24 corroborates how much excess of NCO was consumed in the prior test because of the miscalculation. Despite the minor decrease of the NCO band, peak 2 indicates that the reaction is certainly taking place since it corresponds to the stretching vibration of carbonyl double bond in the formed urethanes.

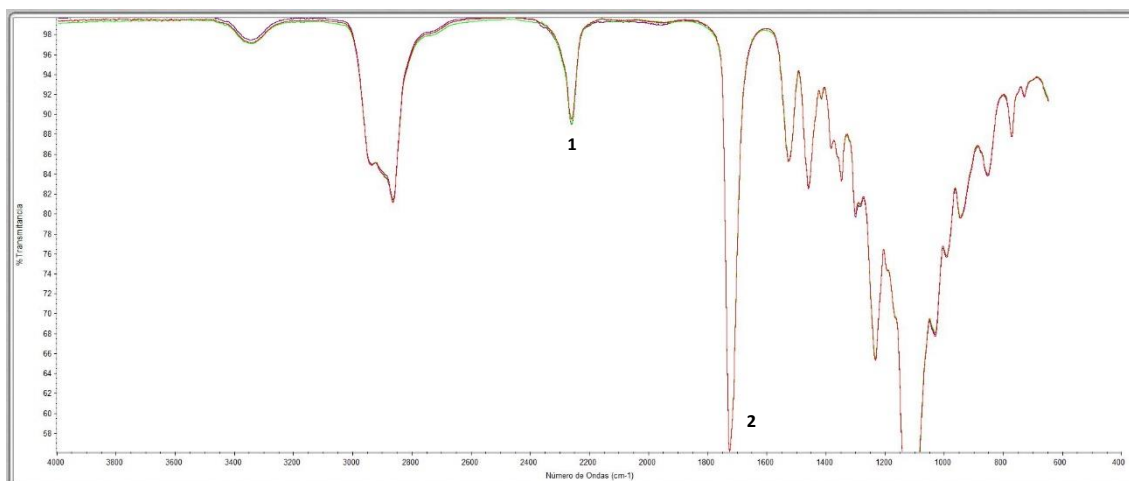


Figure 25 - Prepolymer formation FT-IR spectra of T-02.

The reticulation suffered a substantial decrease from the last test demonstrating that the NCO that had been lost during the reaction was, in fact, spent in secondary reactions. Even though the reticulation is not notably as high as the previous test, it is quite elevated (>20%) given the correction in the results. However, the reaction was left overnight leaving a considerably deflated balloon, some air might have leaked inside causing this reticulation.

The pH value of ECOFIXER is significantly lower than ELYSAN HR W. This increase on the acidity of this new product can be attributed to the incorporation of thiol groups into the PU structure. Thiols (-SH) are classified as weakly acidic ($pK_a \approx 8.8$) functional groups according to the relatively weakness of the bond between their sulphur and the hydrogen atom: the large size of sulphur provides an effective stabilization of the electronic density displacing the electron cloud away from the proton, making it slightly acidic. While thiols alone may not exhibit enough acidity to cause a substantial reduction in pH with respect to the last prototype, it is rather their concentration within the mainframe which provokes such

change. Since SIL-78 contains multiple thiol groups per molecule and is added in a quantity intended to react with the remaining NCO groups, it is plausible that the pH value is lowered to that extent.

The solid content of the dispersion surpassed the preestablished acceptable boundaries, therefore, it was corrected down to a 30% with the addition of the corresponding distilled water. The obtention of a high-solid content is sometimes caused by a prolonged distillation. Even though the boiling point of water (just like any other compound) is increased when mixed with other species, some degree of evaporation is inevitable, especially under vacuum conditions. If the volatile solvent is completely removed and the vacuum nor the temperature are stopped, the evaporation of water grows more probable.

Unlike the previous prototype, the characterization of the particle size of ECOFIXER generated an intensity and number spectra nothing alike. For this reason, in this case, both graphs is commented individually.

Dynamic light scattering provides information about the particle size distribution in different modes. In *Figure 26*, the size distribution is represented according to the intensity of the scattered light recorded over time. This relationship between particle size and light scattering intensity can be explained as follows: when a particle is larger in size, it offers a larger surface area for interacting with incident light; the increased contact area allows for a wider range of radiation of different wavelengths to be scattered, leading to a greater amount of scattered light reaching the detector. The intensity corresponds to the measured quantity of scattered light that is detected. Furthermore, larger particles exhibit slower diffusion rates, meaning that the intensity of their light scattering persists for a longer time producing pronounced and sustained peaks in the scattering spectrum.

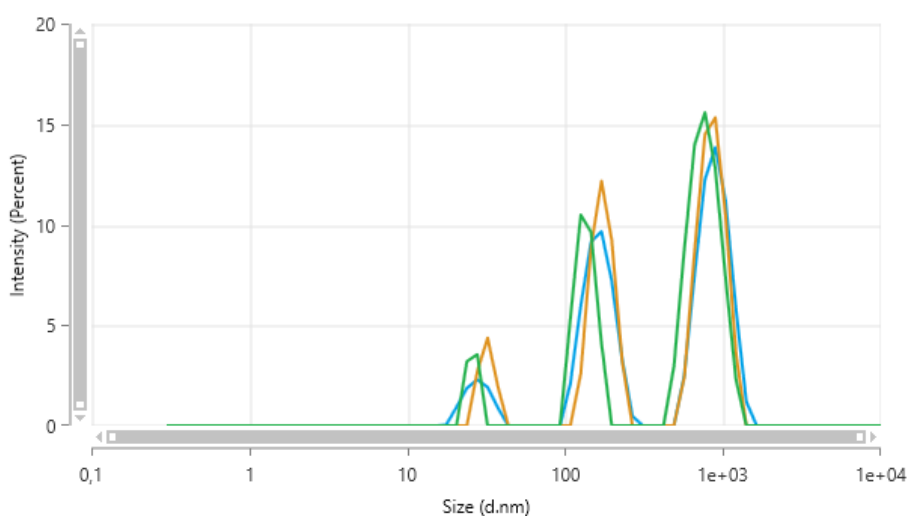


Figure 26 – DLS graph in intensity of T-02.

The scattering spectrum of T-02 is trimodal, meaning that three distinct peaks of different intensities and particle sizes are detected. According to this graph, the dispersion contains PU chains of these different sizes, however, the product looks homogeneous. The reason behind the great difference between particle sizes and the homogeneity of the dispersion lies on the concentration of the different-sized chains.

The quantification of the size of nanoparticles is usually studied according to the number size distribution (*Figure 27*), which represents the different particle sizes according to their relative concentration within the sample. The intensity distribution may sometimes be misleading now it may not accurately detect particles with less intense scattering signals, especially in the presence of larger particles, regardless of their concentration within the sample. For this reason, in the cases when both intensity and number spectra do not match, the number spectra will be prioritized.

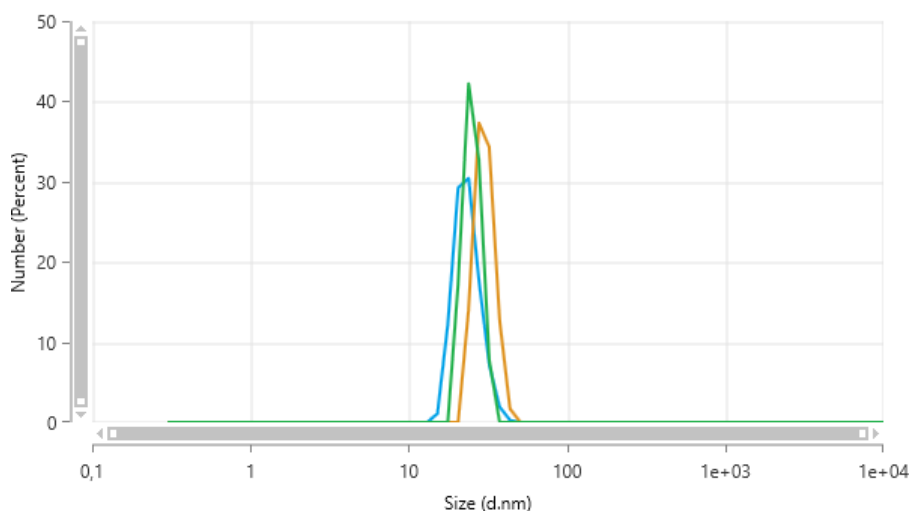


Figure 27 – DLS graph in number of T-02.

A great difference is observed in *Figure 27*, the monomodality of the spectrum entails that the concentration of the particles of 100 and 1000 nm that are represented as the second and third peak in *Figure 26* is completely scarce. In fact, according to the number particle size distribution, only a 0.05% of the polymer chains measured 101.90 (± 32.74) nm while the rest, a 99.95% had a diameter of 23.83 (± 1.98) nm as it is described in *Table 2*. The concentration of the largest molecules, represented by the third peak in *Figure 26*, is so low (<0.01%) that they were not even detected.

According to the data provided by the different modes of distribution, the particle size of the PU can be determined to be of 23.83 ± 1.98 nm.

The water drop test of Ecofixer yielded positive results, the hydrophobicity of the polymer was maintained regardless of the great thiol content of the HS. In *Figure 28* it is observed that the droplet in the left, applied on the layer of dried Ecofixer, forms a contact angle of approximately 85° . This high contact angle assures the hydrophobicity of the product. The loss of hydrophobicity was also tested for ECOFIXER with an application of the product with the 10% of the same external reagent as the last test. The hydrophobicity was again considerably reduced, the contact angle decreased proportionally.

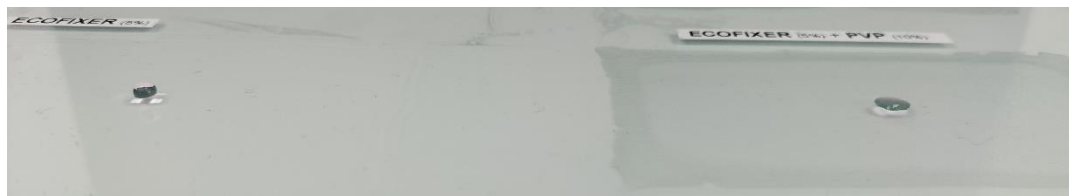


Figure 28 - Water Drop Test T-02 (ECOFIXER on the left, Ecofixer + PVP on the right).

The application of Ecofixer on hair at a concentration of 5% in solids can be observed in *Figure 29* below. Despite the incorporation of thiols in the PU synthesis, the polymer exhibits minimal affinity for keratin, resulting in the absence of barely any trace of polymer, as it can be observed in the hair fibres captured through SEM.

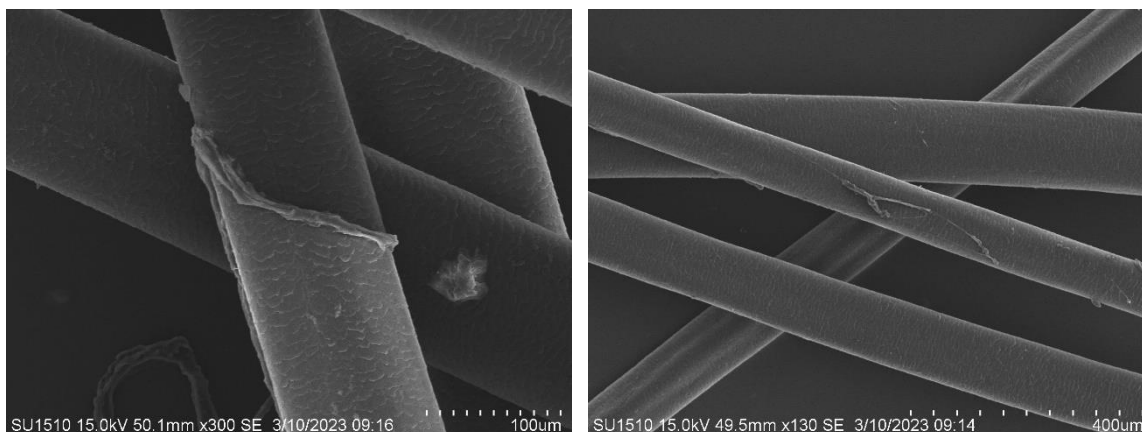


Figure 29 - T-02 applications on synthetic hair SEM images at 100 and 400 μm .

The most plausible reasoning behind the ineffectiveness of the introduced thiol-containing reagent is the persistent inherent hydrophobicity of most part of the chain fragment. These large hydrophobic regions provoke repulsive forces towards the hydrophilic hair surface shadowing, at the same time, the few hydrophilic attracting forces created by the thiol groups. The few polymer particles that remained on top of the hair attract each other by means of the aforementioned hydrophobic forces and agglomerate as it is observed in *Figure 29*, without forming any film. The hydrophobic nature of the polyester, which is the major polyol in the mixture, in addition to the lack of emulsifier provoke that the overall

hydrophobicity of the product resembles the ELYSAN HR W's. Therefore, the product fails to adhere to keratin and form any coating layer just as the first prototype.

▪ Test 03

The failure of the previous test can be entirely attributed to the high hydrophobic character of the polymer. By decreasing this repulsive hydrophobic character, the reactive hydrophilic points of the HS would be exposed binding the polyurethane to the protein filaments effortlessly. In the next synthesis, the weight composition of the SS is adjusted accordingly while keeping the total equivalents of hydroxyl constant to avoid any changes in the HS. The concentration of polyester is reduced by half whilst the remaining hydroxyl equivalents are provided by the polyether. With this new polyol composition, it is expected to significantly reduce the hydrophobicity of the product.

In *Figure 30* is detailed the evolution of the structure of the polymer throughout the reaction[‡]. The green spectrum indicates the stabilization of the %NCO_{exp} manifesting the ending of the prepolymer reaction formation. However, an additional IR was conducted 15 minutes later to ensure the completion of the process: the yellow spectra illustrates a small but clear decrease of the concentration of diisocyanate (peak 1) whereas there is not any perceivable increase on the concentration of the urethane's band (peak 2). Consequently, a back-titration was successively performed to determine the loss of NCO that is illustrated in the decrease of the peak 1 between the green and yellow spectra. The resulting %NCO_{exp} was significantly lower than expected indicating an excessive reticulation of the polymer (%reticulation >> 20). The decrease of the peak 1 between the yellow and green spectra is not that extremely pronounced to produce such a loss of diisocyanate. However, the intensity of both bands are noticeably lower than T-02 (*Figure 25*) resembling more to the NCO band of T-01 (*Figure 24*), even though they cannot be compared due to the difference in their polyol composition.

Regardless, the synthesis is continued as it is illustrated in *Figure 30*: the blue spectrum describes the amount of NCO that is capped by the monofunctional amine, whilst the red spectrum is obtained after the reaction of the remaining diisocyanate with the thiol-containing reagent, which completely consumes it, as evidenced by the disappearance of peak 1. The height of the C=O stretching bands (peak 2) appears to decrease as the synthesis progresses, given that the blue spectrum shows a shorter peak than the red spectrum. However, this decrease in height is not due to a reduction in their concentration within the

[‡] Although a significant larger number of IR spectra were recorded during the synthesis, they have not been included in *Figure 30* to facilitate the appreciation of the progressive changes in the bands.

polymer, but rather because their relative concentration is overshadowed by the more intense bands produced by the thiol-containing reagent. Another proof that support this 'shadowing' is the widening of the C=O stretching band basis of the urethane signal, which as it was explained before, take place due to the increasing hydrogen interactions. This widening is present in the shortest spectra once the thiol-containing reagent has already been added and all the urethane linkages had been formed but absent in the highest peaks.

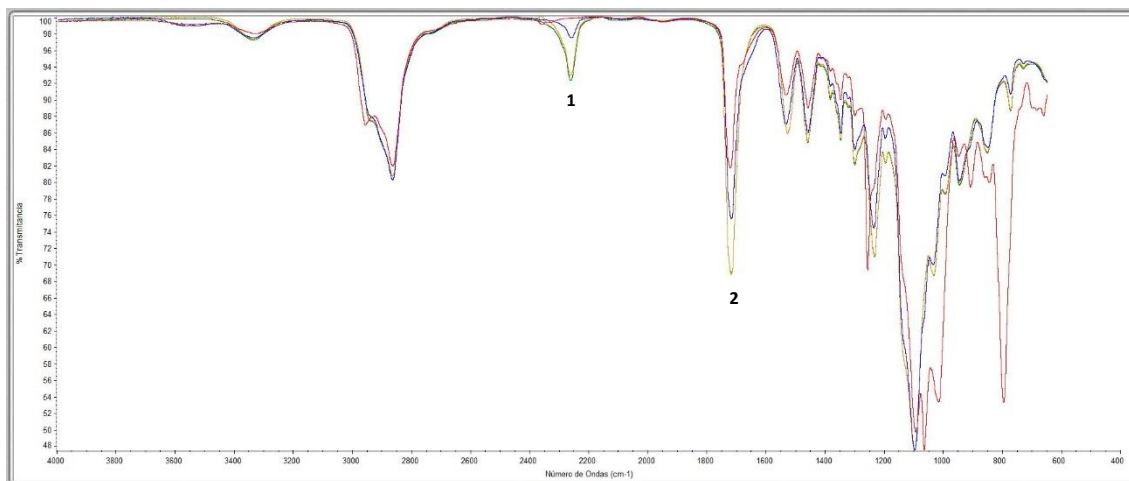


Figure 30 – FT-IR spectra of the complete synthesis of T-03.

The thiol-containing reagent was added to the reaction mixture and left to react for two days at room temperature with slow stirring. This reaction yielded a highly viscous polymer, which partially precipitated leaving some gelatinous traces on the walls of the reactor. Despite more solvent was loaded to mitigate the viscosity of the product, the viscosity remained unchanged throughout the emulsion process, which usually varies between its stages. The emulsion yielded a turbid dispersion with white polymer traces in suspension, which indicated an unsuccessful change of phase.



Figure 31 – DLS sample of T-03.

A sample of the undistilled "dispersion" was diluted in water in order to determine an approximate particle size distribution. However, the floating traces of polymer were not diluted even under stirring (Figure 31). Consequently, the dispersion was discarded.

▪ Test 04

Upon reviewing the calculations and finding no miscalculations or errors in the expressions including the starting reagents, it is reasonable to exclude mathematical errors as a possible cause now the lack of NCO is observed since the beginning of the process. In this case, the

presence of another systematic error or blunder should be considered. Therefore, the synthesis design was kept unchanged and repeated with caution.

The following *Figure 32* and *33* demonstrate that the error is apparently persistent despite meticulously weighing the starting reagents, monitoring the temperature and the reaction more often, drying the polyols thoroughly, etc. The possibility of being an instrumental systematic error was also rejected since the instruments were lately calibrated as well as they were being used and showed a normal response.

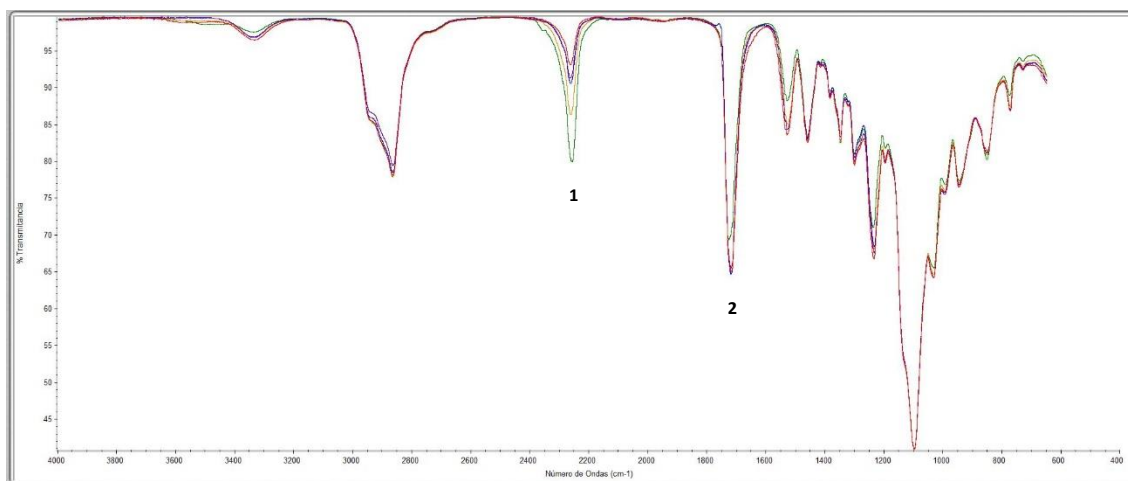


Figure 32 – Prepolymer formation FT-IR of T-04.

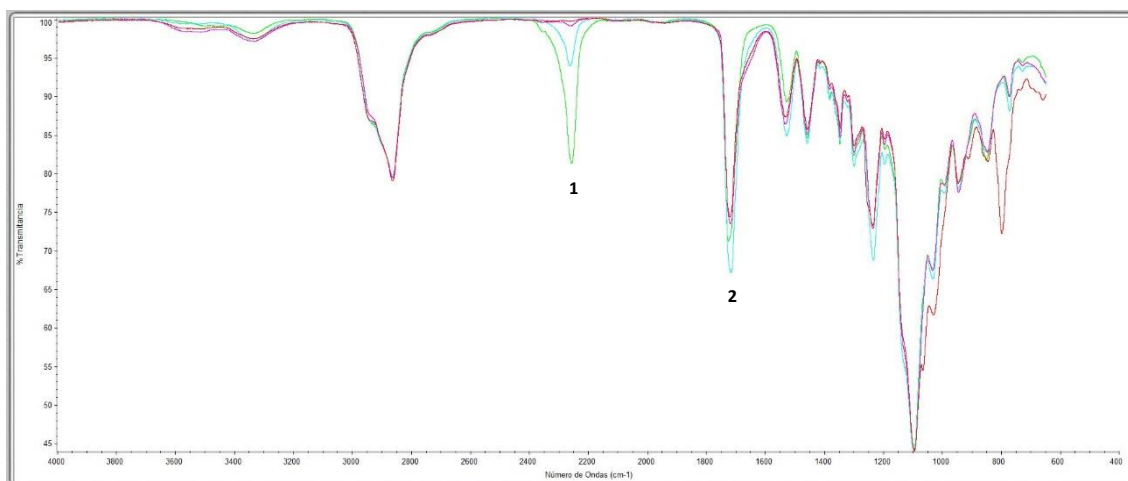


Figure 33 – FT-IR of complete synthesis of T-04.

The same extensive loss of NCO as in T-03 is observed in both *Figure 32* and *33* at the first peak. The C=O stretching band of NCO shows a decrease of more than half its height between the initial stages of the prepolymer formation (displayed in green in *Figure 32*) and the stabilised band, displayed in a red colour (*Figure 32*). In this case, both spectra are comparable to those recorded in T-03 now both products shared the same polyol composition.

Therefore, upon re-examining *Figure 30* it is expectable to obtain a high reticulation value given how much the NCO band in T-04 has decreased compared to T-03.

The overshadowing effect of the bands also observed in *Figure 33* becomes noticeable in the final stages of the synthesis: the pink and red spectra corresponding to the addition of the capping monoamine and the thiol-containing reagent, respectively, show an increase of the C=O urethane stretching band suggesting that the concentration of this linkage increased over time. Nevertheless, in *Figure 32*, which is dedicated to the early stages of the synthesis – the prepolymer formation reaction – the overshadowing is not observed. In fact, it is evident that the presence of urethane groups within the polymer increases over time, the green spectrum (in *Figure 32*) is clearly shorter than the last red and purple spectra, which are the same height indicating the end of the reaction. The difference in behaviour of peaks 2 is related to the presence or absence of the thiol-containing reagent, as mentioned in the discussion of *Figure 30* above.

The obtained degree of reticulation, as indicated in *Table 2*, confirms the presence of a systematic error. Even though the loss of NCO is almost the half of the previous test, it is still too high (%reticulation $\gg 20$) to achieve a successful phase-transition. The synthesis is continued, and the emulsion is attempted; the resultant dispersion contain gelatinous traces, once again. Consequently, the distillation is cancelled.

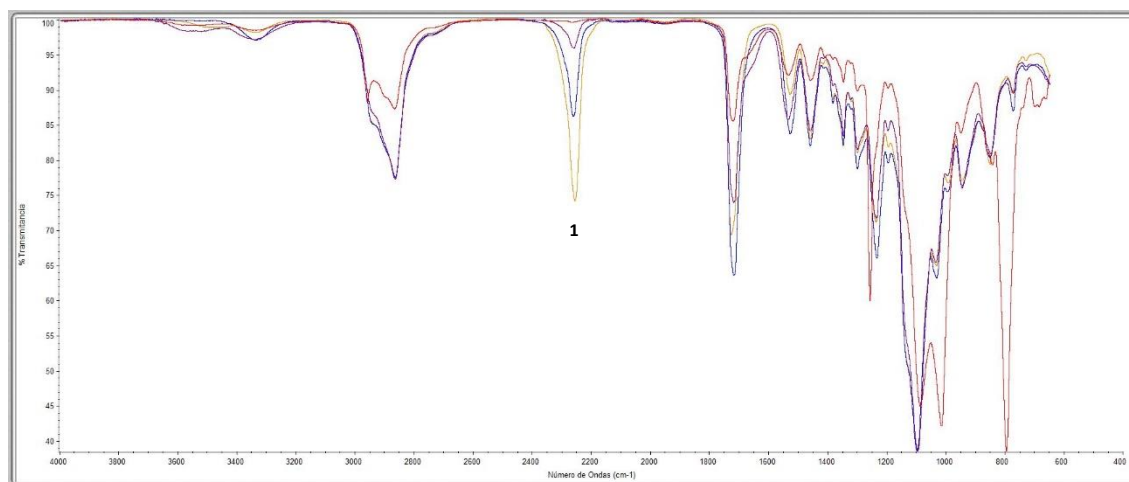
During the synthesis of the product, the polymer physical aspect was thoroughly monitored the whole time to detect any irregularities. During the addition of diisocyanate, the addition funnel was accidentally touching the stirring spatula due to the small dimensions of the reactor (500 mL) and the same spatula. The high revolutions of the spatula in contact with the funnel adding the diisocyanate provoked that the loaded reagent spilled and splashed the walls of the reactor. Even though this NCO was not lost in secondary reactions, it was not available to react with the prepolymer at the bottom of the reactor, therefore it was considered to be lost. To prevent such losses in the future, the rubber dripping tip of the funnel was trimmed.

▪ **Test 05**

After identifying and addressing the causes of the systematic errors, the synthetic design was, once again, adjusted to improve the final properties of the product. Even if the polyol composition had already been tuned to reduce the hydrophobicity of the chain, the NCO/OH ratio was increased. One of main goals of the product is not only to be attracted to hair, or at least not repelled, but to actively interact with it. To achieve this, the proportion of HSS

within the product was increased to multiply the amount of thiol groups per chain and, consequently, rise the reactivity towards keratin.

It is worth mentioning how much NCO is saved with the correction of the systematic errors, even though the IR spectra (*Figure 34*) cannot be compared to the previous due to the change in the new test composition. The reticulation of the test is higher than the expected (*Table 2*), however, it was an acceptable value that did not entail any difficulties in the phase change.



Spectrum 34 – FT-IR of the complete synthesis of T-05.

The other characterization results summarised in *Table 2* followed the trend of those of T-02 despite their differences on the polyol and HS/SS composition. The conservation of certain chemical and physical properties whilst only changing the compromising ones ease the development of the desired product.

The scattering intensity graph of T-05 (*Figure 35*) exhibits a bimodal distribution whilst the *Figure 26* is trimodal. This change in the modality of the dispersion is caused by the increase of the NCO/OH ratio between the two tests. By increasing the amount of diisocyanate equivalents relative to the hydroxyl equivalents, which is to say, increasing the excess of diisocyanate in the process provokes a narrowing in the molecular weight distribution which is directly reflected in the particle size distribution recorded through DLS. When an excess of NCO is added to the prepolymer reaction, because of their relative concentration, it is likely that the polyols react with individual diisocyanate monomers instead of reacting with growing chains. This results on the shortening of the length of the chains leading to smaller particles. In *Figure 35* is noticed the absence of the third peak that appeared in *Figure 26*, such intense peak corresponded to the largest particles within the dispersion; in T-05 the largest particles are comprised within the second peak. The resemblance of *Figure 27* and *36* proves

that the most common particle size has not been modified along the hydrophobicity and affinity of the polymer.

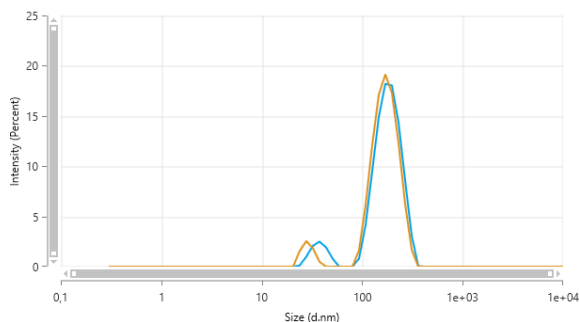


Figure 35 - DLS graph in intensity of T-05.

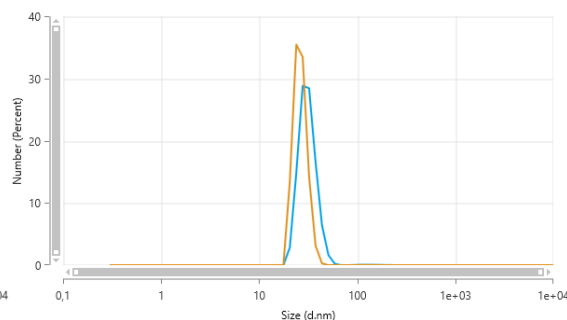


Figure 36 - DLS graph in number of T-05

The water drop test conducted on T-05, as shown in *Figure 37*, highlights a decrease in the hydrophobicity of the product compared to the previous test (T-02). In the left part of *Figure 28*, it is observed a perfectly round droplet whereas in the right part of *Figure 37*, also pertaining to the application of the pure polymer dispersion, the droplet loses its round shape and spreads more over the application. The alteration in the contact angle between the tests is feasible now the hydrophilicity of the products have changed.



Figure 37 – Water Drop Test T-05 (ECOFIXER + PVP + preservative agent on the left, ECOFIXER on the right)

It is worth mentioning that the hydrophilicity of T-05 does not surpass the hydrophilicity achieved in the altered T-02 application with a film-forming agent, the contact angle of T-05 falls somewhere in between. If the film-forming agent is added to the hydrophilic T-05, its hydrophobicity will be further reduced, almost removing its water-resistant character, as it is illustrated in the left of *Figure 37* where the water drop is nearly flattened.

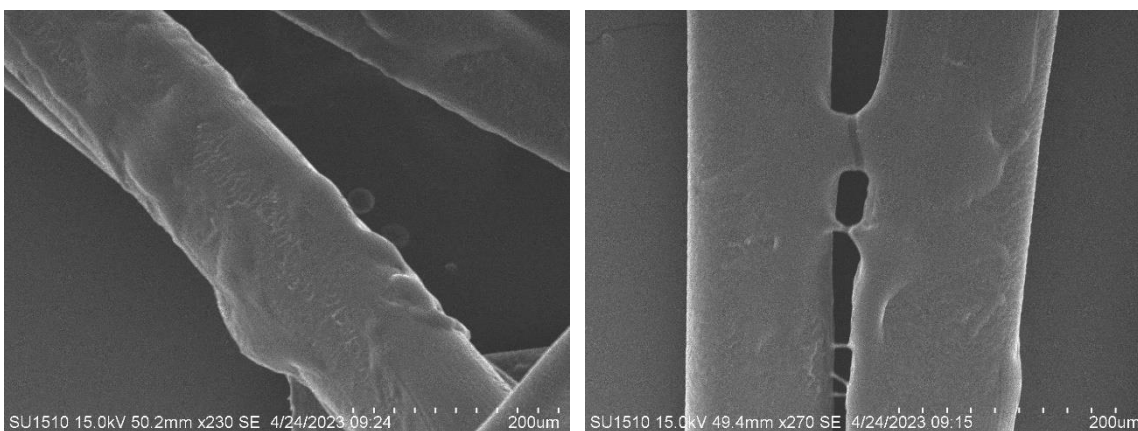


Figure 38 - T-05 applications on synthetic hair SEM images at 200 µm.

The SEM images revealed that ECOFIXER could indeed attach to keratin as it is evidenced in *Figure 38*, where the hair fibres filled with the PU covering part of the keratin scales.

Nevertheless, it is observed that the polyurethane coating does not uniformly cover the entire hair fibre. Instead, it forms polymer patches. Even though part of the hydrophobicity of the PU was sacrificed in favour of the film-forming ability, the results were not satisfactory enough. For this reason, a new PU formulation able to form a uniform and homogeneous covering is sought without losing hydrophobicity.

▪ **Test 06**

Even though ECOFIXER did not accomplish the proposed goals of the thesis, its synthetic process was optimized and repeated thrice to prove the obtained T-05 results. As it is noted in Table 2, the results did not differ from T-05's. All the IR and DLS spectra of this test is included in the *Annex* for those interested. Nevertheless, these graphs will not be discussed due to their resemblance to the T-05's.

PROTOTYPE III

The last prototype was developed to address the limited affinity of ELYSAN HR W to keratin employing a different approach than ECOFIXER. The second prototype relied the reactivity of the product on the concentration of thiol groups within the hard segment, which could demote the water-resistance capacity of the product if increased too much. In the synthesis of ECOFIXER only one feature could be enhanced at a time: the hydrophobicity or the affinity, now they depended on the concentration of thiols. PROTOTYPE III takes a novel perspective, it incorporates potentially reactive groups within its structure which do not alter the hydrophobicity of the chain until their activation, nonetheless, once applied to hair, it recovers its hydrophobic character back as the reactive groups have reacted with keratin. *(Detailed information in 4.5.1)*

Table 3 - Characterization results of all PROTOTYPE III tests.

	T-01	T-02	T-03	T-04
Reticulation (%)	0	0	8.23	0
pH	7.74	7.29	7.15	7.40
Solid content (%)	32.84	33.17	34.30	30.35
Number mean (nm)	45.69 ± 9.12	50.07 ± 1.29	58.31 ± 11.34	64.70 ± 15.14
	166.80 ± 64.95	268.3 ± 3.69	349.70 ± 1.85	558.40 ± 288.40

▪ **Test 01 and 02**

The synthesis of PROTOTYPE III, as it explained in 4.1.3, is based on the improvement of the reactivity of the ELYSAN HR W product. As previously discussed regarding the variations

between ECOFIXER tests, any modifications to the parameters of the polyurethane must be approached with caution to avoid unintended alterations of certain properties. In the case of PROTOTYPE III, it is crucial to maintain the chemical and physical characterization properties, including the hydrophobicity, at levels similar to that of ELYSAN HR W. The primary objective of PROTOTYPE III is to specifically modify its reactivity towards keratin, while preserving the other desired properties, in order to achieve this, the concentration of disulphide-containing polyol is adjusted.

Comparing the characterization results of ELYSAN HR W (*Table 1*) and the PROTOTYPE III, it can be concluded that maintenance of the properties was successful despite the change in the SS nature: the pH remained neutral indicating that the modification of the polyol source did not significantly affect the acidity (S-S bridges do not contain any proton to donate nor any delocalised lone pair to accept protons), the solid content fitted the boundaries, and there was no substantial loss of NCO throughout the prepolymer formation. Nevertheless, the resulting particle size has undergone a substantial increase, reaching twice the size of ELYSAN HR W.



Figure 41 - Phase separation of T-01.

The scattering graph of T-01 (*Figure 39*) shows trimodality, indicating the presence of particles with approximately three distinct sizes within the dispersion. The dimensions of these different chains vary from 45.69 ± 9.12 to 166.80 ± 64.95 nm (as it is tabulated in *Table 3*) to, even, a peak of ~ 1310 nm. The last value is not included in the table because no standard deviation was provided by the program, meaning that it was only detected in a single run, therefore its actual presence on the dispersion is not ensured. *Figure 40* reveals that the concentration of polymer particles measuring approximately 167 nm is approximately 0.38%, while the remaining 99.60% of particles measure approximately 48 nm. The presence of such a small proportion of larger particles is sufficient to induce their precipitation, as it is slightly appreciable in *Fig 41*.

In order to mitigate polydispersity in T-02, the concentration of ionomer is increased to enhance the intramolecular interactions between the hard segments and so, promote their folding and reducing the particle size. Considering that the ionomer is a difunctional amine which not only provides an ionic group but also acts as a chain-extender the precise adjustment of its concentration becomes crucial to enhance intramolecular interactions while avoiding excessive polymer chain elongation. Despite the increase on the ionomer concentration pursued in T-02 did not yield noticeable changes in the particle size now it was

detected particles of both 50.07 ± 1.29 and 268.30 ± 3.69 nm. Even if the numerical value appear to be different from the T-01, it is important to note that the uncertainty associated with these results is significantly larger. Taking into account the standard deviation of the results, the particle size can get to match the ones of the previous test.

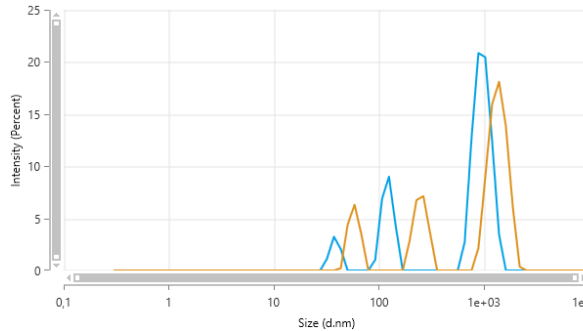


Figure 39 - DLS graph in intensity of T-01.

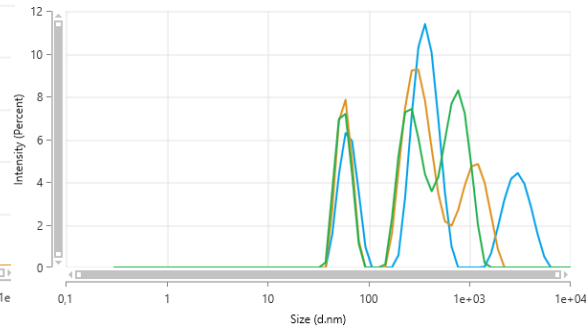


Figure 41 - DLS graph in intensity of T-02.

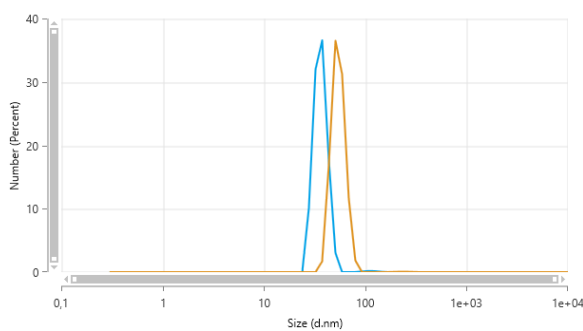


Figure 40 - DLS graph in number of T-01.

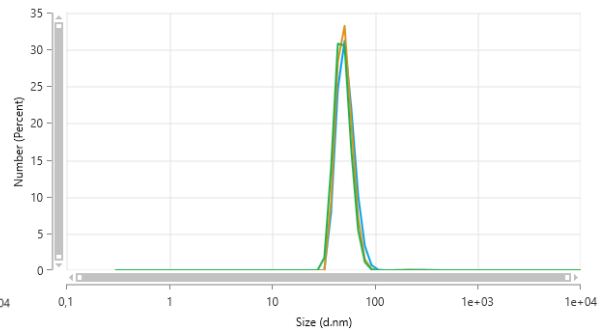


Figure 42 - DLS graph in number of T-02.

Figure 41 appear to be trimodal, nevertheless, the last two peaks' bases merged. The instrument detected them as a single signal (*Figure 42*), for this reason, only two size values are provided in *Table 3*. Not only the change of the particle size was not successful, but the final dispersion also contained enough particles of different sizes to be separated through precipitation. Nevertheless, according to *Graph 42*, which provided the relative concentration of the different peaks, the amount of large particles did decrease regarding to T-01 (0.18%) with the rise of ionomer content.

▪ Test 03

For the third test, the concentration of ionomer was increased 1% its concentration with respect to the first. The different characterization techniques verified that all the properties mentioned in *Table 3* were not modified excessively, including the particle size.

Contrary to the previous tests, *Figure 43* exhibits a clear bimodal distribution, indicating the presence of particles with a diameter of 58.31 ± 11.34 and 349.70 ± 1.85 nm. The first peak value is consistent with the other particle sized obtained in the other tests, however, the

second and most intense peak describes a particle size 100nm larger than those observed in both T-01 and T-02. The reason behind such difference may be attributed to the distribution of the ionomer molecules among the chains: some chains might have introduced sufficient amount of ionomer molecules, enabling them to fold down to a size of ~58 nm, while a few chains may have undergone excessive interaction with ionomer molecules, leading to chain elongation and the formation of larger particles measuring 350 nm.

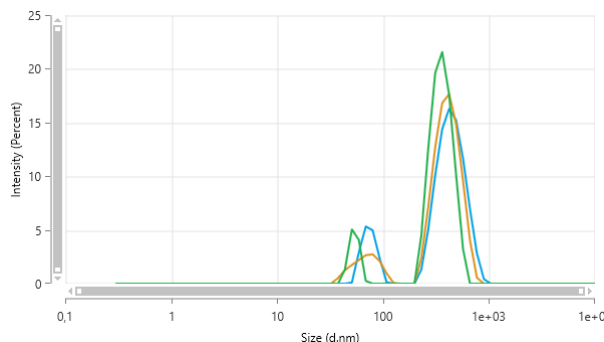


Figure 43- DLS graph in intensity of T-03.

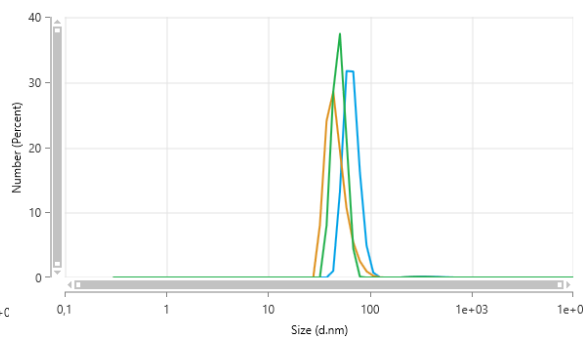


Figure 44 - DLS graph in number of T-03.

Despite the particles with a ~350nm diameter comprise a 0.46% (*Figure 44*) of the total polymer chains, which is quite high, the dispersion is not precipitated. A possible explanation may be the excessive concentration of ionomer within their structure, which increases its hydrophilicity enough to be able to be dispersible through the continuous aqueous phase without precipitating.

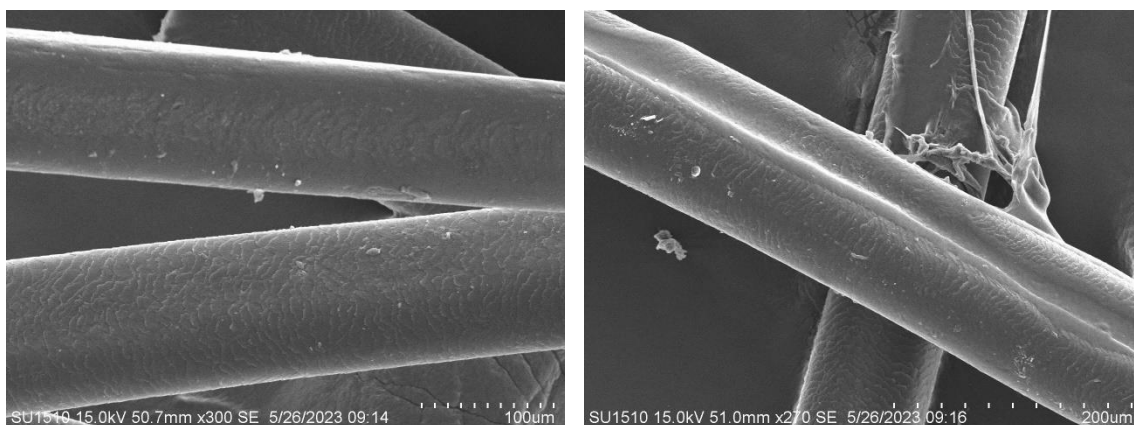
The characterization of the homogeneous and single-phased T-03 dispersion was carried on. PROTOTYPE III demonstrated a hydrophobicity comparable to ELYSAN HR W. The increase of the ionomer concentration did not reduce the water-resistant character of the product yielding great contact angle as it can be observed in *Figure 45*.



Figure 45 - Water Drop Test T-03.

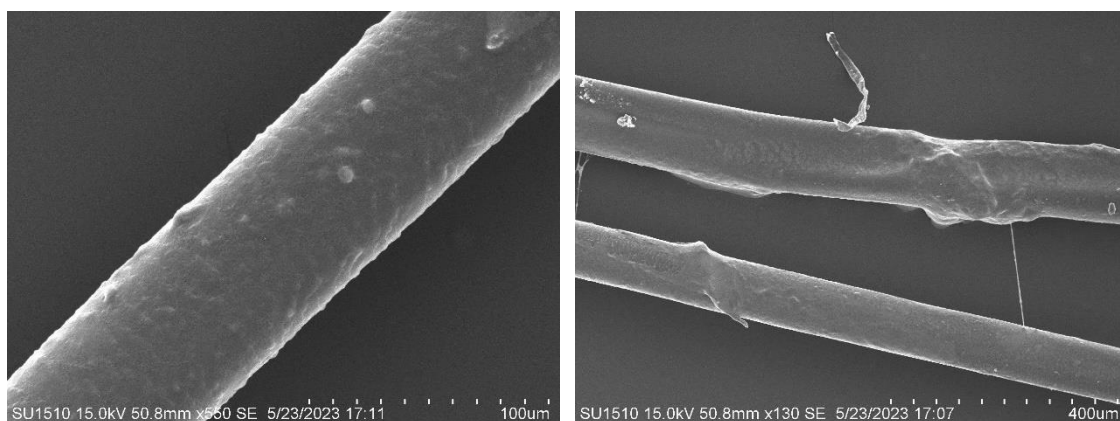
The affinity and film-forming capacity of this last prototype was analysed following two different application methods (explained in 4.5.1). The effectiveness of the methods are verified through SEM: the first pictures (*Figure 46*) illustrate how the hair fibres end up after the application of PROTOTYPE III in which the same hair fibres had previously been reduced. Based on the attached captures, when the product is directly applied to hair that has undergone prior reduction of their inherent S-S bridges in keratin, the polymer can hardly be attached to hair. Although certain regions of some hair fibres exhibit partial coverage, as

showed in the left capture (right on the top fibre), a continuous and uniform coating is not achieved. Consequently, the activation of hair does not prove to be an effective method for achieving optimal film formation.



**Figure 46 - T-03 applications on synthetic hair SEM images at 100 and 200 µm.
ACTIVATION OF THE HAIR APPLICATION METHOD**

Even if the reducing agent is added in excess, the concentration of disulphide bridges in keratin exceeds the stoichiometric amount of thiol groups provided by the reducer. As a result, the reducer is completely consumed in breaking the keratin S-S bridges. The result of this activation is the formation of new S-S bridges between the keratin and the reducer, unopened keratin S-S bridges, and a limited number of unreacted thiol groups. It is these residual thiol groups that enable partial binding and coverage of the product on the hair fibres. However, due to their low abundance, the polymer exhibits minimal attachment to the hair, resulting in limited coverage.



**Figure 47 - T-03 applications on synthetic hair SEM images at 100 and 400 µm
ACTIVATION OF THE PRODUCT APPLICATION METHOD**

On the other hand, the prior activation of the polyurethane product enhances the reduction of the disulphide bridges present in the polyol to thiol groups. Since the reducer is added in excess, some product's sulphur ends are lost forming new S-S bridges. However, since the functionality, and so, the equivalents of the S-S that are contained in the polyol are known,

the reducer concentration can be adjusted accordingly in excess leaving some unreacted thiol groups. These remaining thiol groups are available to furtherly react with the S-S bridges of keratin forming a homogeneous and continuous coating around the fibres, as it is illustrated in *Figure 47*.

▪ **Test 04**

Given that the last prototype test successfully accomplished the proposed goals of the thesis, its synthetic process was optimized and intended to be repeated thrice to corroborate the characterization results. Only one extra test could be done, as it is noted in *Table 3*, the results did not differ from T-03's.

6. Conclusions

English version

In conclusion, this bachelor thesis has effectively accomplished the synthesis and optimization of three distinct potential prototypes. Among them, a single product proved to gather the three preestablished properties detailed in the research objectives. PROTOTYPE III, still unnamed, achieved a high degree of hydrophobicity due to the lack of hydrophilicity provided by both its PEPO main composition, and hydrophobic chain-extender. The synthesis of PROTOTYPE III exhibited successful dispersion in water, facilitated by the presence of ionomers within its structural composition regardless of the hydrophobicity of the main-frame. Furthermore, the product displayed remarkable affinity to keratin, effectively facilitated by the presence of potentially reducible S-S bridges. Upon the cleavage of these S-S bonds, the film-former functioned autonomously creating a continuous and homogeneous coating around the hair fibres. The film-forming capacity appeared to rely solely on the S-S activation mechanism.

Future research could focus on refining the synthesis process, investigating the long-term durability of the coating layer, exploring potential modifications to enhance specific properties such as thermal stability or washing resistance. Additionally, investigating the interaction of these polyurethanes with other ingredients commonly used in hair-care products could provide valuable insights for formulation development.

Versió en català

En conclusió, la recerca durant aquesta tesi ha permès aconseguir sintetitzar i optimitzar tres potencials prototips amb eficàcia. S'ha pogut provar que, d'entre tots ells, només un reuneix totes tres propietats descrites als objectius la recerca. El tercer prototip, encara sense nom comercial, consta d'una alta d'hidrofobicitat gràcies a la poca hidrofilitat d'ambdós poliols i allargador. La síntesis del tercer prototip s'ha dispersat fàcilment, tot i la hidrofobicitat de l'estructura, en aigua degut a la presència de ionòmer als segments durs. No només això, el producte ha demostrat la seva gran afinitat amb la queratina, facilitada pels grups disulfur. Mitjançant la reducció d'aquests ponts disulfur, el producte ha sigut capaç de filmejar homogènia i contínuament de manera autònoma sobre el cabell. La capacitat de filmejar sembla dependre únicament del mètode d'activació del disulfur.

La possible futura recerca es podria centrar tant en refinar el procés de síntesis, determinar la durabilitat del recobriment, com investigar possibles modificacions del producte per millorar certes propietats (estabilitat tèrmica, resistència a rentats, etc.). A més a més, es podria estudiar l'estabilitat i interacció d'aquest producte amb altres components que normalment solen estar presents en les formulacions de productes pel cabell.

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Annex

I. ADDITIONAL IR SPECTRA

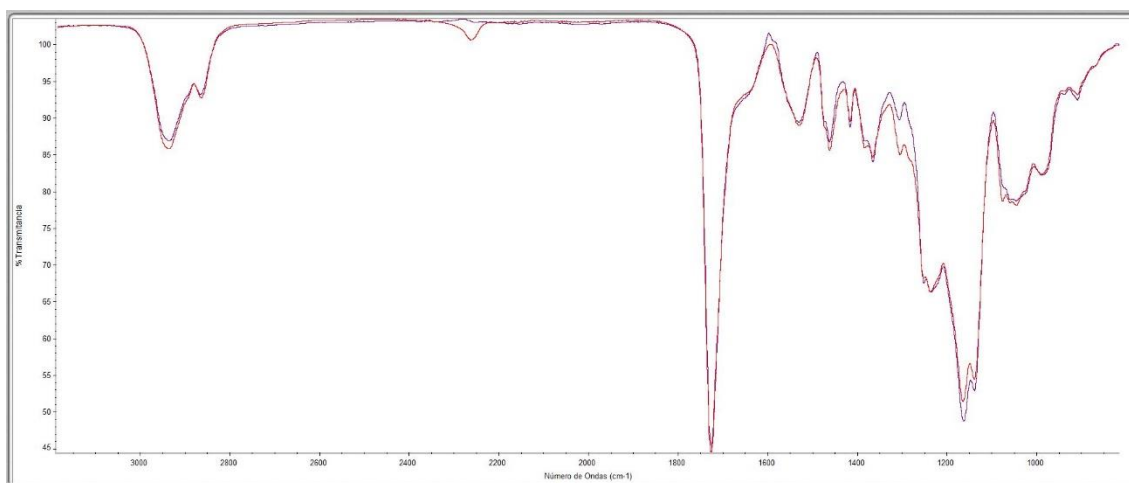


Figure S1 - Chain-extension reaction FT-IR spectra of ELYSAN HR W (T-03)

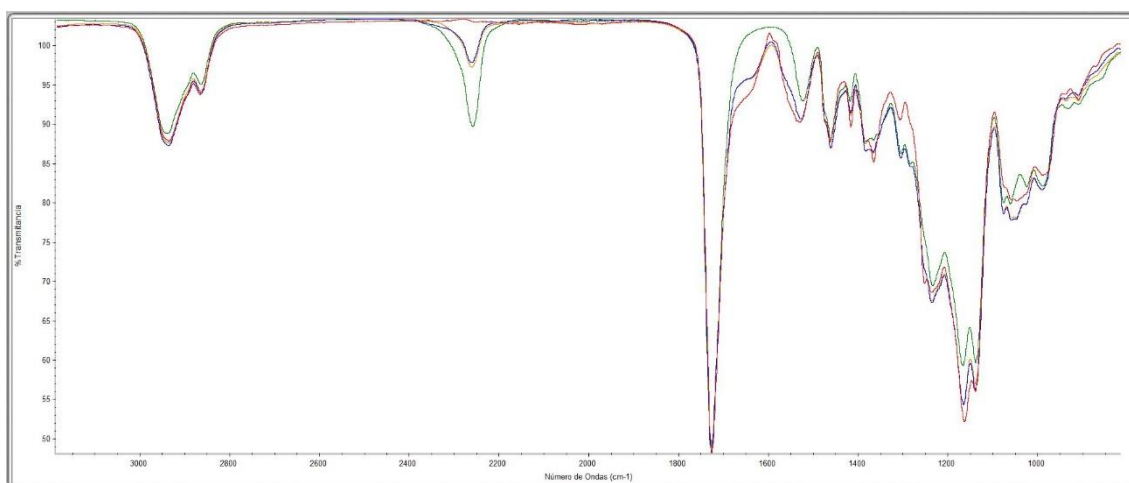


Figure S2 - FT-IR spectra of the complete synthesis of ELYSAN HR W (T-03)

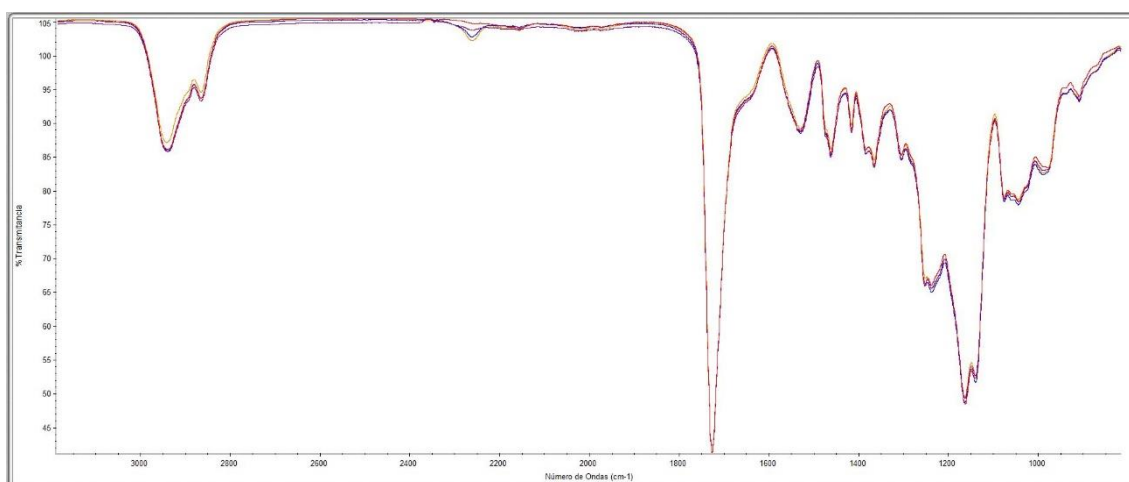


Figure S3 - Chain-extension reaction FT-IR spectra of ELYSAN HR W (T-04)

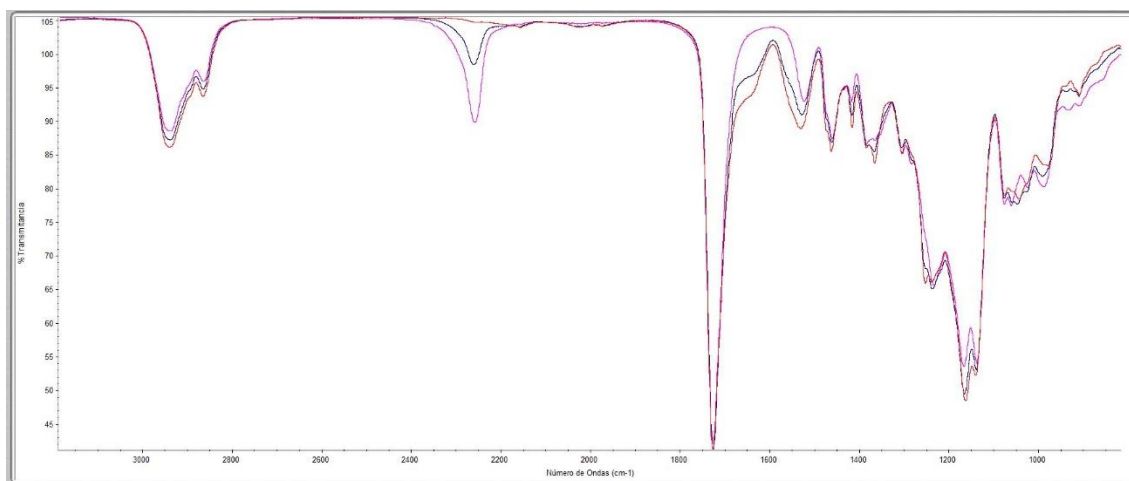


Figure S4 - FT-IR spectra of the complete synthesis of ELYSAH HR W (T-04)

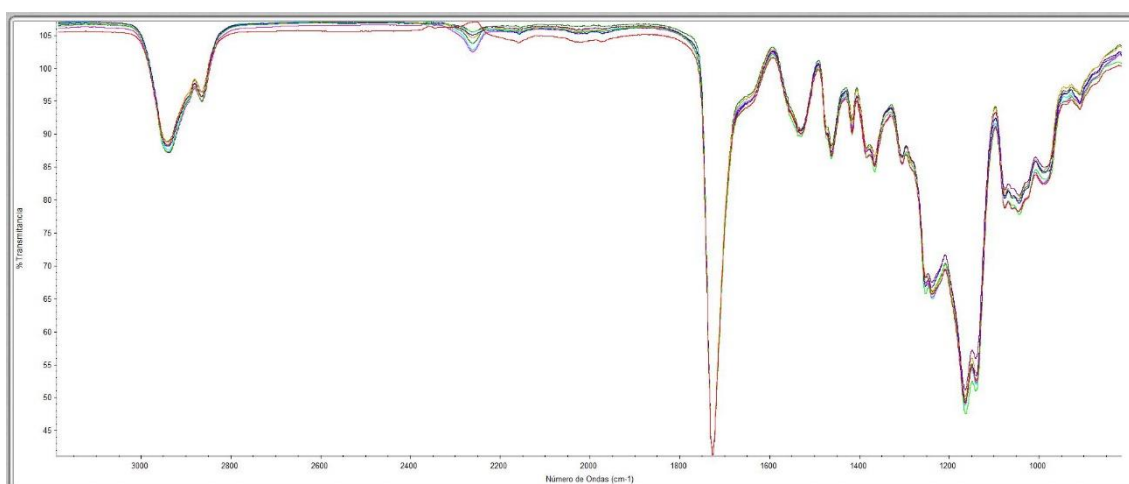


Figure S5 - Chain-extension reaction FT-IR spectra of ELYSAN HR W (T-05)

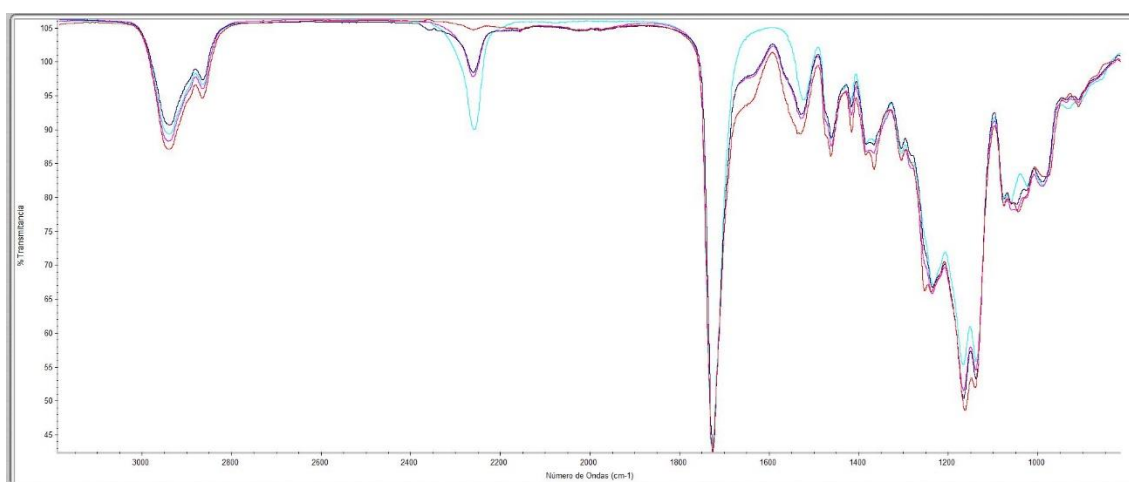


Figure S6 - FT-IR spectra of the complete synthesis of ELYSAH HR W (T-05)

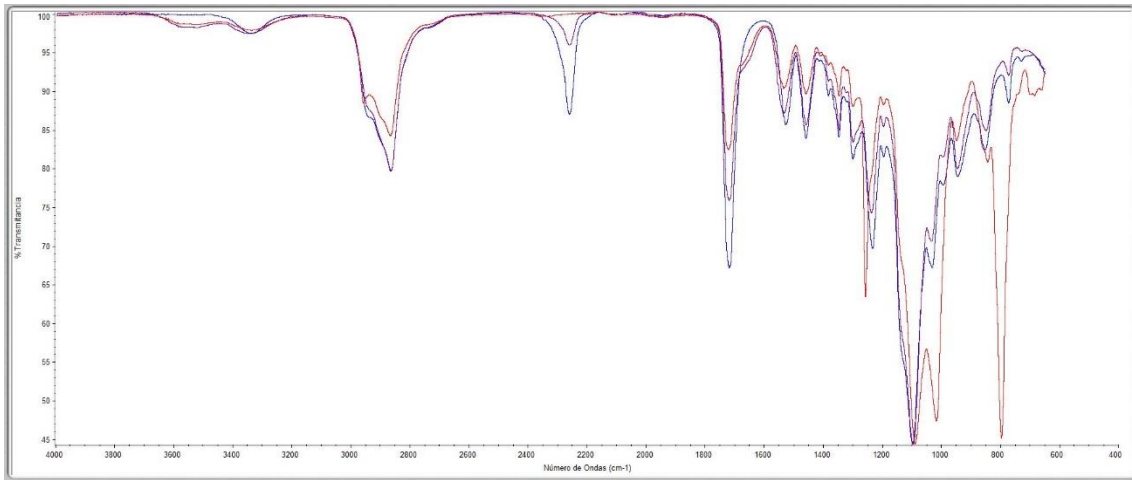


Figure S7 – FT-IR spectra of the complete synthesis of ECOFIXER (T-06)

II. ADDITIONAL SCATTERING GRAPHS (DLS)

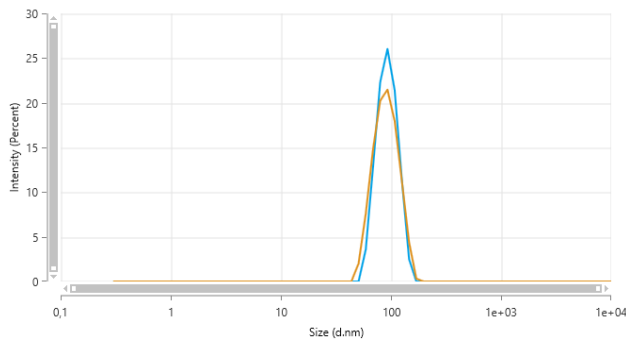


Figure S8 - DLS graph in intensity of ELYSAN HR W (T-03)

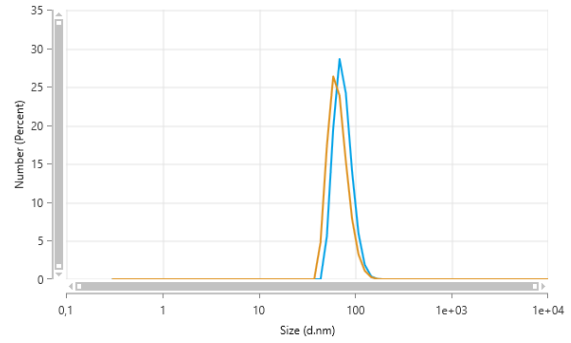


Figure S9 - DLS graph in number of ELYSAN HR W (T-03)

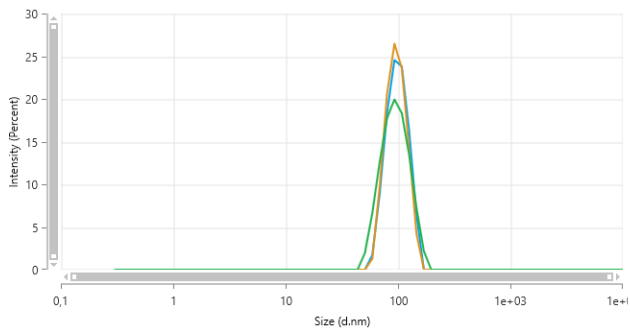


Figure S10 - DLS graph in intensity of ELYSAN HR W (T-04)

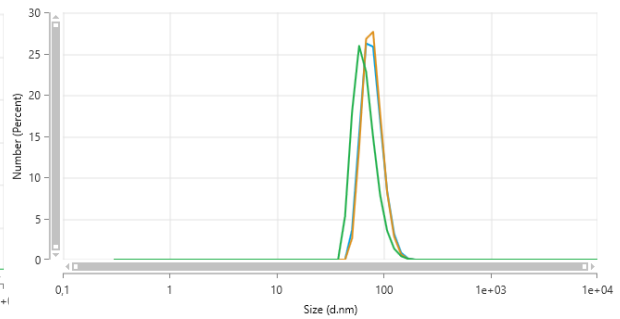


Figure S11 - DLS graph in number of ELYSAN HR W (T-04)

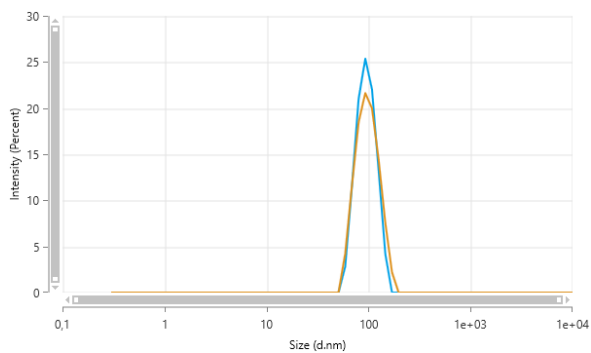


Figure S12 - DLS graph in intensity of ELYSAN HR W (T-05)

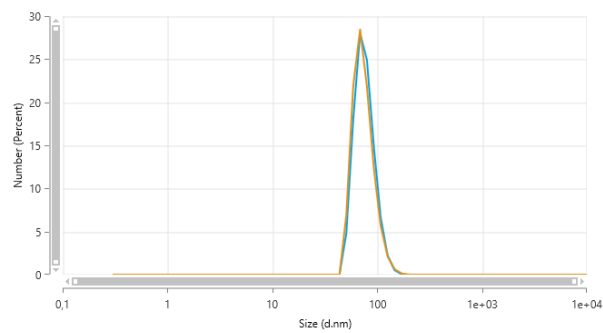


Figure S13- DLS graph in number of ELYSAN HR W (T-05)

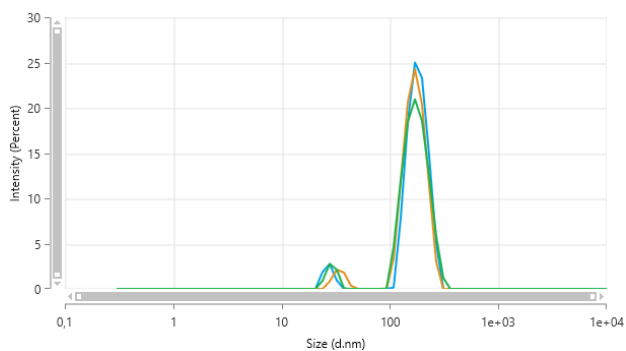


Figure S14 - DLS graph in intensity of ECOFIXER (T-06)

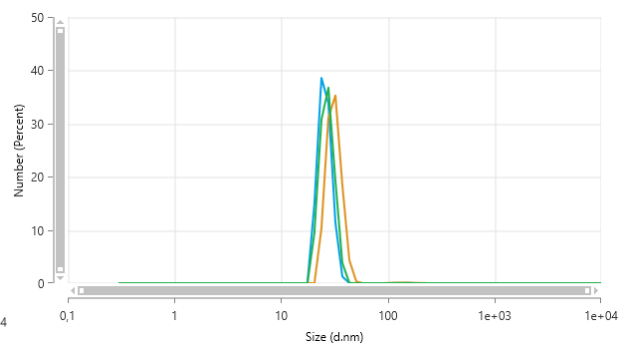


Figure S15 - DLS graph in number of ECOFIXER (T-06)