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STUDY AND DEVELOPMENT OF COATING FORMULATIONS

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Study and development of coating formulations

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of

Pedro Miguel Sousa Martins

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held in

Tintex Textiles S.A

TINTEX NATURALLY ADVANCED

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Abstract

The textile coatings industry in Portugal is a sector that has been growing throughout the years. However, due to the formulation of a coating material usually being a process, that is mostly based on the experience of the operator, instead of the properties of the components of the coating formula, it runs the risk of becoming a stale industry. In the present work, an attempt is done to diverge from a trial and error approach, by studying the components of a discontinued coating formulation of Tintex Textiles. These components are also applied in many of Tintex products, meaning the knowledge gained from this work, will have a ripple effect on the formulation of future coatings at Tintex.

The focal point of the dissertation was to study the reactions between the crosslinker and the binder, given that understanding them is the first step to be able to optimize the formulation. That lead to performing a chemical characterization (DSC, TGA and FTIR-ATR analysis) of the binder Impranil DLN-SD (polyester-urethane dispersion), as well as the crosslinker Arkophob DAN New liq (polyurethane dispersion) of the formulation studied. Other crosslinkers such as Imprafix 2794 (polyisocyanate dispersion), and Acrafix EP 6047 (polycarbodiimide dispersion) were also characterized to assess if they are better alternatives to the crosslinker of the formulation. The evaluation of the interaction of the crosslinkers with the binder at the studied cure temperature, was done by assessing if the system dissolved when mixed with dimethylformamide (DMF). The substrate which is a knit made of 100% cotton, was analysed by itself and in conjunction with the binder and the crosslinker, to understand its importance on the system. Furthermore, it was also attempted the optimization of the coating formula (with all the components), by taking into account information obtained from the chemical characterization of the binder/crosslinker system.

The results obtained from this work, lead to the conclusion that the substrate employed was a good option for the formulation analysed, due to reacting with the crosslinker through free -OH groups, which improve the adhesion of the layers and favours the curing process. Moreover, it was assessed that the polycarbodiimide did not crosslink with the binder and neither the knit, suggesting that recurring to a binder based on an acrylic polymer (it would crosslink through carboxylic acid groups) and a substrate of polyester, would be a better system for these type of crosslinkers. Regarding Imprafix and Arkophob, both can be considered good crosslinkers for the system analysed. However, Imprafix showed the most promising results due to being able to crosslink at a lower temperature and being able to present similar results to Arkophob, which the ingredients were already optimized by the supplier, suggesting that Imprafix has potential to be the best crosslinker for the binder, once the remaining agents of the formulation were adjusted to its properties.

Keywords: coating; knit; polyurethane; isocyanate; polycarbodiimide.

Resumo

A indústria de revestimentos têxtil em Portugal é um setor que tem crescido ao longo dos anos. No entanto, devido ao processo de formular um revestimento ser usualmente baseado maioritariamente na experiência do operador, ao invés das propriedades dos componentes da fórmula de um revestimento, corre o risco de ficar estagnada. Neste trabalho tentou-se divergir de uma metodologia baseada na tentativa-erro, através do estudo dos componentes de uma formulação de revestimento descontinuada na Tintex Textiles. Estes componentes são aplicados numa porção significativa dos produtos da Tintex, o que leva a aferir que o conhecimento obtido devido à realização deste trabalho, pode ser aplicado em futuras formulações da Tintex.

Esta dissertação tem como foco principal o estudo das reações entre o reticulante e o ligante, visto que compreendê-las é o primeiro passo para ser possível otimizar a formulação. Tal levou a efetuar a caraterização química (análise de DSC, TGA e FTIR-ATR) do ligante Impranil DLN-SD (dispersão de poliéster-uretano), assim como do reticulante Arkophob DAN New liq (dispersão de poliuretano) da formulação estudada. Outros reticulantes como o Imprafix 2794 (dispersão de poliisocianato) e o Acrafix EP 6047 (dispersão de policarbodiimida) também foram caraterizados, de forma a aferir se são melhores alternativas ao reticulante da formulação. A avaliação da interação dos reticulantes com o ligante à temperatura de cura térmica, foi efetuada através da análise da possível dissolução do sistema quando misturado com dimetilformamida (DMF). O substrato corresponde a uma malha constituída por 100% algodão e foi analisado isoladamente e conjuntamente com o ligante e o reticulante de forma a compreender a sua importância no sistema. Para além do referido, também se efetuou a otimização da fórmula do revestimento (com todos os componentes), tendo em consideração a informação obtida na caraterização química do sistema ligante/reticulante.

Os resultados obtidos, levam a concluir que o substrato utilizado é uma boa opção para a formulação analisada, devido a reagir com o reticulante através de grupos -OH livres, favorecendo o processo de reticulação e a adesão entre camadas. Também foi aferido que o Acrafix não reticula com o ligante, nem com a malha, sugerindo que recorrendo a um ligante baseado num polímero acrílico (reticula através de grupos de ácidos carboxílicos) e utilizando um substrato de poliéster, seria o sistema ideal para o Acrafix. Relativamente ao Imprafix e ao Arkophob, ambos podem ser considerados bons reticulantes para o sistema estudado. No entanto, o Imprafix apresenta os resultados mais promissores devido a ser capaz de reticular a temperaturas mais baixas e apresentar resultados semelhantes ao Arkophob, cujos ingredientes já se encontravam otimizados pelo fornecedor, sugerindo que o Imprafix tem o potencial de ser o melhor reticulante para o ligante, após uma otimização dos restantes agentes da formulação, que tem em consideração as propriedades do Imprafix.

Palavras chave: revestimento; malha; poliuretano; isocianato; policarbodiimida.

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions are indicated and due reference is given to the author and source.

Pedro Martins

The 1st of September 2020

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Notation and Glossary

Greek Letters

μ	Dynamic viscosity
σ	Standard deviation

List of Acronyms

ATR	Attenuated Total Reflectance
COVID-19	Corona Virus Disease of 2019
CV	Coefficient of Variation
DLaTGS	Deuterated L-alanine Doped Triglycene Sulphate
DMA	Dynamic Mechanical Analysis
DMF	Dimethylformamide
DMP	Dimethylpyrazole
DSC	Differential Scanning Calorimetry
FEUP	Faculty of Engineering of the University of Porto
FTIR	Fourier Transform Infrared Spectroscopy
FTIR-ATR	Fourier Transform Infrared Spectroscopy working in the mode of Attenuated Total Reflectance
HDI	Hexamethylene diisocyanate
HEUR	Hydrophobically Modified Ethoxylated Urethanes
HMDI	Hydrogenated Version of Methylene Diphenyl Diisocyanate
IPDI	Isophorone Diisocyanate
MDI	Methylene Diphenyl Diisocyanate
MEKO	Methyl Ethyl ketoxime
R&D	Research and Development
RPM	Rotations Per Minute
SEM	Scanning Electron Microscopy
SG	Savitzky-Golay
STA	Simultaneous Thermal Analysis
TDI	Toluene Diisocyanate
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
UV	Ultraviolet
VOC	Volatile Organic Compounds

1 Introduction

1.1 Framing and presentation of the work

The textile coatings industry in Portugal features a great deal of potential. Despite that, it is necessary to reformulate the way of thinking, to fulfil all its potential. Nowadays, optimizing a coating based on a trial and error approach, is a standard method of formulating a coating material. An operator tries to adapt an established formulation (provided by the supplier), by changing the conditions of operation, or the amount of each ingredient. After several experiments, an approximation of the desired handle, flexibility and gloss of the coating is usually achieved, however, the whole process is time-consuming. As a result, understanding each component role in the formulation, and all the chemical reactions involved is crucial. It leads to a curtailment of the attempts needed, to achieve optimal conditions of operation.

In the framework of this dissertation, a discontinued coating formulation from Tintex Textiles S.A will be studied, giving special attention to the relations between the binder and the crosslinker, where most of the chemical reactions occur. Therefore, different crosslinkers were studied in conjunction with the binder, by recurring to chemical characterization equipment, to infer which systems crosslink, the type of reaction mechanisms occurring, as well as the importance of temperature on those reactions. It is also emphasized the relations between the coating and the surface, in which its inserted. The final step of this work was to optimize the coating formulation and the conditions of operation.

1.2 Presentation of the company

Tintex Textiles S.A, was founded in the Porto region, in 1998. They are renowned for dyeing and finishing textiles. In 2015, the company created a textile coating department, which has been growing significantly since its genesis. Nonetheless, there is still much space for improvement, and the main goals are to increase the level of production and to dominate all the facets of this field. Their slogan is “naturally advanced”, which emphasizes the need for Tintex to always be in the frontlines of innovation and sustainability.

Regarding Tintex processes, they are continuously improving due to a considerable investment (over 26 million euros) in highly advanced machinery, ground-breaking dyeing, coating and finishing technologies, as well as research and development (R&D). Their products mainly serve as a basis for the products of other companies or entities, such as designers, R&D centres and famous clothing brands. Some of the most productive segments for Tintex Textiles are contemporary fashion, sports, and lingerie.

1.3 Contribution of the author to the work

This project allowed Tintex to better understand on a fundamental level, how a coating system should be developed. Moreover, it was also possible to obtain an in-depth knowledge of common coating components, utilized by the company. Some of the knowledge gained from the analysis of the components of the coating system will lead to Tintex producing better coatings by altering some of the conditions or components of their systems, based on actual evidence, instead of only the experience of the operator. This work can also lead to Tintex applying some tweaks on the method they employ to produce their coatings.

The preparation of the samples and the experiments performed related to the chemical characterization (DSC, TGA, FTIR-ATR) equipment were performed by the author of the dissertation. However, the recording of the samples on the spectrometer was accompanied by Dr. Diana Paiva, due to time constraints, as well as limited access to this equipment. The experiments related to dimethylformamide (DMF), which allowed to evaluate the interactions between the crosslinker and the binder at the studied temperature, and the experiments associated with the optimization of the coating formulation and conditions of operation done at Tintex Textiles, were all performed by the author of this work.

1.4 Organization of the thesis

In order to facilitate the reading of the work developed, the dissertation is divided into six chapters (including the present chapter).

Chapter 2 corresponds to “Context and State of the Art”. Its purpose is to explain the importance of textile coatings and describing all the content related to the formulation of the coating material, taking into consideration the processes and products of Tintex Textiles.

Chapter 3 entitled “Materials and Methods”, summarily describes all the products and equipment utilized during the dissertation. The methods associated with the equipment are also described.

Chapter 4 is named “Results and discussion” and presents an analysis of the relevant results obtained throughout this project. These results are mostly related to the chemical characterization techniques performed at FEUP, and the coating samples produced at Tintex.

Chapter 5 is called “Conclusions”. The main purpose of the chapter is to explain the usefulness of the results obtained.

Chapter 6 is designated “Assessment of the work done”. It explains the objectives of the work that were fulfilled, and which aspects of the work can be further studied or improved.

2 Context and State of the art

2.1 Introduction to textile coatings

A textile coating is a continuous overlay or film of a polymer, which is inserted on a textile surface to improve their characteristics (e.g. mechanical, chemical, and physical properties).[1,2]

Global demand for textile coatings is continuously increasing and is expected to be worth close to 4.13 thousand million euros by 2025. The Asia-Pacific region accounts the highest demand (in terms of volume), however, Europe and North America dominate revenue-wise. This growth is justified by the increasing significance of textile coatings in industries such as automotive, footwear and apparels, medical devices, and protective clothing.[3] Furthermore, biopolymers are becoming more important than synthetic petroleum-based raw materials in textile coatings, due to their sustainable character.[4] Tintex Textiles is an apologist of biopolymers, starting recurring to them for their coatings in 2020.

Coatings present a vast array of functions however, sometimes it goes unnoticed their utility. They are not useful products by themselves, therefore a coating can be considered an enabling material, increasing the value of other products significantly.[4] The ability to protect the covered surface and improve its aesthetic, are some of the most useful and standard functions of the coating material.[5]

Functional textile coatings have additional roles, beyond passive decoration and protection. They enable the textiles to present increased functionalities, like being wrinkle-free and flame retardant. Moreover, there are also active textile coatings that detect changes in the conditions of the environment surrounding it, responding to those changes predictably and conspicuously. These coatings contain memory materials, phase-change and chromic materials, among others. The most usual functions of active and functional textile coatings are presented in Table 1.[2]

Table 1 *– Common functions of active and functional textile coatings. Adapted from [2].*

Categories	Functional coatings	Active coatings
Aesthetic	Wrinkle-free; flat appearance; dimensional stability; anti-stain; water or oil repellent; colour resistance.	Colour change; self-cleaning.
Comfort	Windproof; thermal resistance; water resistance; moisture management.	Thermal adjustability; breathability.
Protection	Humidity resistance; flame retardant; ultraviolet protection; antistatic; reflective; chemical resistance; blood resistance; anticorrosion; safety airbag; thermal insulating; ageing resistance.	Antibacterial; wearable electronics for biomedical use; self-healing.

2.2 Coating system

Textile coatings are commonly applied as multi-layered systems that are composed of a primer and a topcoat.[6] A usual configuration of a coating is a three-layer system, which is illustrated in Figure 1.[7]

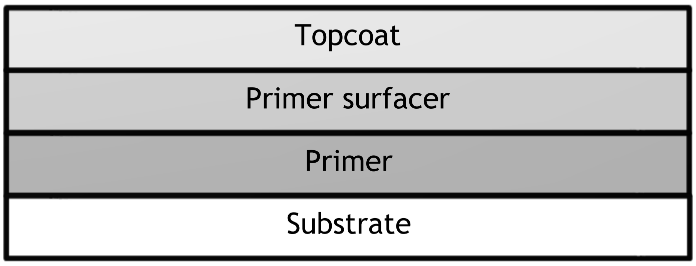


Figure 1 *- Three-layer coating system. Adapted from [7].*

The primer main tasks are sealing the substrate from the environment, as well as improving its adhesion to the coating. The primer surfacer (intermediate layer) improves the barrier effect of the primer, and facilitates the adhesion to the top layer, levelling the substrate roughness. The top layer confers long-lasting protection to weatherability (e.g. ultraviolet radiation, rain or humidity), chemical resistance (e.g. bird droppings) and resistance to solvents (e.g. petrol). It is also the layer responsible for providing the coating visual properties, like gloss and colour.[5,7]

Tintex usually employs a system consisting of a topcoat and a textile substrate that was subjected to different types of finishes, such as hydrophilic/softening agents, mercerization and laminating (Annex A), which can considerably improve the properties of the final product.

2.3 Coating formulation

The development of any coating material must fulfil specific requirements, demanded by the customer (such as properties of the coating and the substrate, application, and environmental legislation). A skilled chemist accommodates all these different requests, usually utilizing a reference recipe as a starting point. An appropriate raw materials selection, and the ratio of the components in a formulation, are crucial factors when developing coating formulas. A calculation recipe is formulated to yield one hundred parts by weight and is listed in order, in which the ingredients are added. It should include specific manufacturing directions, warnings of safety hazards, information about individual ingredients, quality control tests, and cautions against potential manufacturing pitfalls (e.g. cracking).[7]

The main components of a coating recipe are the binders, the crosslinkers, solvents, pigments, and multi-purpose additives.[5] Tintex divides the formulations into three classes: paste, stable foam, and unstable foam. The main differences between those types of coating applications are presented in Table 2.[8]

Table 2 *- Key differences in coating applications. Adapted from [8].*

Unstable foam	Stable foam	Paste
Viscosity (μ) – 1-8 dPa·s. **Handfeel** – dry and harsh. **Applications** – e.g. velour and automotive back coatings, imitation suede. The formulation does not contain foaming agents. 	**Viscosity (μ)** – 8-35 dPa·s. **Handfeel** – delicate or rough. **Applications** – e.g. roller blinds, breathable coatings for anoraks and rainwear. The formulation contains foaming agents. 	**Viscosity (μ)** – superior to 35 dPa·s. **Handfeel** – plasticized, continuous. **Applications** – e.g. skiwear, umbrellas, pressure-sensitive coatings (medical). The formulation contains defoaming agents. 

2.3.1 Binders

Polyurethanes are essential polymers in the coatings industry, being adopted by Tintex Textiles for a significant amount of their coating components (including binders). They combine numerous desirable properties, such as durability, toughness, flexibility, high resistance to abrasion, excellent chemical resistance, and also provide formulation flexibility.[9]

Polyurethanes are polyaddition products (Figure 2) of a di- or polyisocyanate with a di- or polyfunctional alcohol (polyol). There are two methods of reaction control, which are the "one-shot" technique and the prepolymer process.[10]

In the "one-shot" technique, a polyol blend is created by simultaneously mixing polyol, diisocyanate, a chain extender, surfactants and catalysts. The mixture is then mixed with an isocyanate phase, creating an emulsion that is then placed in a vessel, where the foaming reaction carries on.[10] The prepolymer process is divided into two stages. The first one consists of a reaction between a diisocyanate and polyol, resulting in a prepolymer of molecular weight of about 20,000 g·mol^{-1}. Depending on the stoichiometry of the polyol and the diisocyanate, the prepolymer is terminated by isocyanate or hydroxyl groups. The prepolymer, then reacts with a chain extender yielding the finished product, either by a polyfunctional alcohol or an amine. Hydrophilic polyurethanes are all made via this method.[10-11]

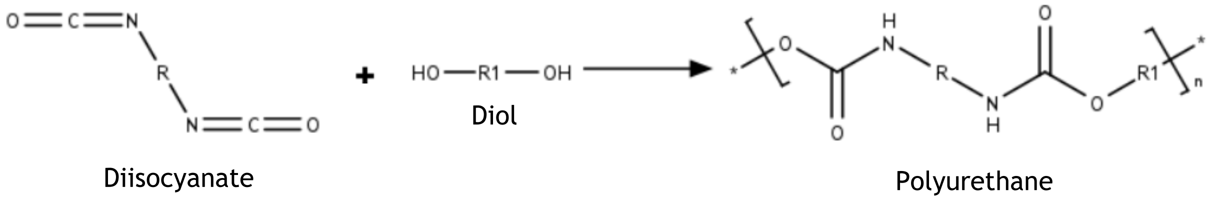


Figure 2 *– Formation of polyurethane. Adapted from [10].*

Regarding isocyanates, which correspond to one of the building blocks of polyurethane, their most chemically relevant attribute is being extremely reactive with groups containing one active hydrogen. This reaction (Figure 3) occurs by the nucleophilic addition across the N=C bond.[9,12]

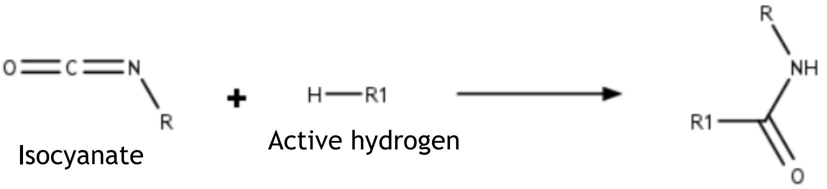


Figure 3 *- Reaction of isocyanates with an active hydrogen compound. Adapted from [12].*

Concerning the reactivity of isocyanates, it is important to point out that aromatic isocyanates tend to be more reactive than aliphatic isocyanates. The presence of electron-withdrawing substituents on the aromatic ring structures increases reactivity, whereas electron donors diminish it.[12] Moreover, aromatic isocyanates are also generally less expensive, which makes them a better value proposition than aliphatic isocyanates. The most produced isocyanate is methylene diphenyl diisocyanate (MDI), and is followed by toluene diisocyanate (TDI). Pertaining aliphatic isocyanates, even though they are less popular, the vast majority is utilized for coatings, due to reduced weather-induced colouring of aliphatic-based urethanes when compared to aromatic-based urethanes. The aliphatic isocyanates market is dominated by hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and the hydrogenated version of MDI (HMDI).[9]

A limitation of the reactivity of the isocyanates is their reaction with moisture (Figure 4) either from the atmosphere or water, causing premature gelation and evolution of carbon dioxide gas.[13-14]

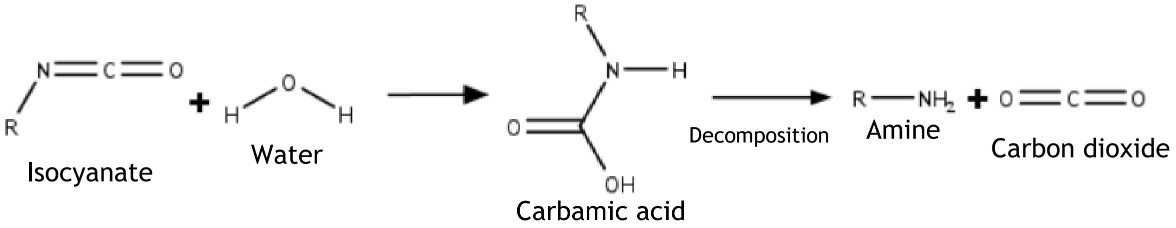


Figure 4 *- Isocyanate reaction with moisture. Adapted from [14].*

It is, however, possible to prevent the reaction between isocyanates and polyols by masking the isocyanate groups, thus preventing the reaction at room temperature, as well as the isocyanate reaction with moisture, only allowing it to take place at elevated temperatures. This is achieved by carrying out a reaction between the isocyanate and a blocking agent (Figure 5) forming a thermally labile bond before mixing with the polyol (frequently -OH terminated polyesters).[10,13,15] On heating, the bond dissociates to regenerate the isocyanate group.[10] The unblocking of the isocyanate can lead to the reaction of the N=C=O groups with polyols, to form the urethane polymer. The released blocking agent, either stays in the coating or is removed by evaporation.[13]

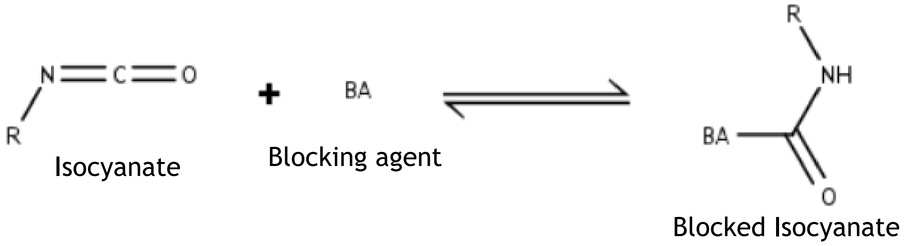


Figure 5 *- Reaction of the blocking of isocyanate. Adapted from [13].*

In addition to the isocyanates, the other important building block of polyurethanes are polyols. These are reactive substances, containing at least two isocyanate-reacting groups connected to a single molecule.[12]

There are four main classes of polyols:

Polyethers – these materials are the product of the reaction between an initiator such as ethylene glycol, propylene glycol, glycerin, pentaerythritol, with a cyclic ether such as ethylene oxide, propylene oxide, a mixture of both or tetrahydrofuran (THF). They are the most commonly used polyols and produce very high-quality polyurethane foams and elastomers.[12,16]

Amine-terminated polyethers - they are based on polyether polyols, in which primary or secondary amino functionalities, replace the terminal groups -OH.[12]

Polyesters – these are polyalkylene glycol esters, such as polybutylene terephthalate, adipate or caprolactone polyesters. The condensation reaction is controlled, to ensure that these polyols contain terminal hydroxyl groups. These compounds are used less frequently than polyether polyols, due to being more costly to produce, and more viscous than polyethers with comparable chain lengths. The most common acids used in the production of polyesters are adipic, glutaric, and azeloic acids. [12,16]

Polycarbonates – this class is prepared by condensation of phosgene or alkylene glycol carbonates (e.g. dimethyl carbonate), with alkylene glycols, such as 1,6-hexanediol. Similarly to polyester polyols, the chemistry is manipulated to ensure that these compounds contain terminal hydroxyl groups.[12]

In textile coating, binders are mostly organic polymers, whose main purpose is forming the film of the coating. This coating component is primarily responsible for determining the permeability, mechanical properties, chemical resistance, ultraviolet (UV) resistance of the coating and needs to promote good adhesion between the layers of the coating system.[10,17-18]

Several criteria must be considered when selecting the appropriate binder, namely:[5]

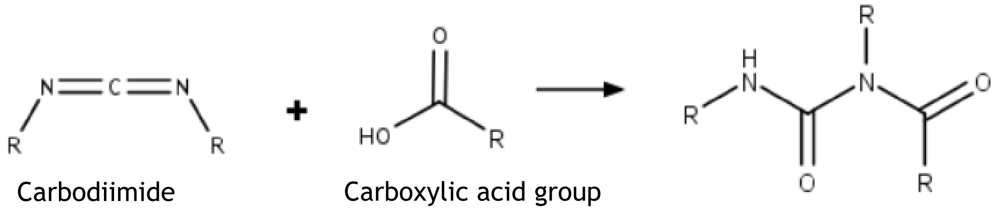
- Type of use: indoor or outdoor. Exterior coatings should not degrade when exposed to UV radiation, or rainwater. In interior coatings, those requirements are not a priority;
- Type of layer: primer, intermediate coat and topcoat;
- The binder's adhesion is dependent on the type of substrate: metal, wood, glass, fabric, among others;
- Requirements of the target property, including gloss, hardness, colour, solvent resistance and corrosion protection;
- Application method: brushing, spray drying, dip-coating, among others;
- Environmental and health considerations (regulations, protocols, norms);
- Price (the coating needs to be sold at an attractive price point).

2.3.2 Crosslinkers

A significant amount of coatings, especially water-based coatings, obtain their integrity (form a continuous film) by drying, which is merely solvent evaporation. Meanwhile, others can only achieve their integrity, after producing a covalently bonded network insensitive to hydrolysing agents (washing liquors, body sweat, industrial atmospheres).[2,6,19] This process is designated as curing or crosslinking and is usually done with a thermal treatment. For ease of handling and spreading, most polymer coatings are applied as a liquid.[5] They are transformed from this thermoplastic phase into the final thermoset state (especially water-borne coatings), immediately after being applied on a substrate by crosslinking.[5,19] Curing improves the adhesion to the substrate and the coating performance, including wear, abrasion, chemical resistance, and toughness.[19]

Frequently, it is added a crosslinking agent to the formulation, which consists of a small molecule that can react with an active group of the binder, so that a polymeric network is created. Binders and crosslinkers are only compatible, when they have in common structural parts of similar polarity or solubility.[5,6] Water-based systems are typically cured by blocked dispersions of polyisocyanates and polyurethanes, as well as dispersions of polyaziridines and polycarbodiimides.

Regarding polycarbodiimides and polyaziridines, they react with the binder through carboxylic acid groups, resulting in a crosslinked network. Due to the toxicity profile of polyaziridines, they are becoming less prominent in the coating industry. Meanwhile, polycarbodiimides are a very interesting prospect given they are VOC (volatile organic compounds) free, easy to use and present a very high crosslinking performance and chemical resistance when compared to polyisocyanates. The crosslinking reaction of carbodiimides is presented in Figure 6.[20,21]



Carbodiimide

Carboxylic acid group

N-acryl urea

Figure 6 *- Crosslinking reaction of carbodiimides. Adapted from [20].*

2.3.3 Pigments and fillers

Pigments can be defined as coloured, black, white, fluorescent or non-coloured particulate compounds, which are added to coatings, and need to be insoluble and physically and chemically unaffected in solvents, as well as in the medium where they will be applied. [5,17,22] They confer the aesthetic appeal required for the coating (colour, opacity, gloss). Pigment colour is dependent, mainly, on its chemical structure. Selective absorption and the reflection of several wavelengths of light that are imposed in the pigmented surface, define its hue. A desirable pigment also requires good tinctorial strength, dispersibility, flocculation resistance, chemical and heat stability. These properties are affected by the pigment's state of dispersion and its crystalline structure. The shape and size of the particle are also critical parameters. Another recurring function of pigments is protecting the system against corrosion (utilizing, e.g. sacrificial or conductive components).[5,22]

The most general classification of the different types of pigments is the following:

- Inorganic pigments - these can be coloured or white. A white pigment typically uses oxides like titanium dioxide, zinc oxide, or sulfides such as zinc sulphide. Regarding coloured pigments, normally they are based on carbon black, mixed oxides or metallic flakes.[5]
- Organic pigments - these are often constituted by coloured pigments, being the azo-containing compounds (RN=NR) the most common, which are then followed by phthalocyanines.[5]

These coating components can also be called fillers, when they increase the volume of the coating through the incorporation of low-cost materials such as chalk or wood, sometimes providing structural reinforcement within the film. They may also improve properties like resistance to abrasion, permeability to water and can alter the stiffness of the coating material. Talc and mica are used extensively as fillers (extenders).[5,17]

2.3.4 Solvents

The main purpose of solvents is to control the viscosity of the coating components, enabling their homogeneous mixing.[17] They are inherently volatile compounds, which evaporate after application and affect the processability, film formation and appearance of the coating.[5,6]

Coatings are one of the primary sources of VOC pollutants, which are responsible for the excess of ozone in the air.[7] As a result of, water-borne coatings accomplishing similar levels of performance when compared to solvent-borne coatings, and being able to fulfil all legislation related to VOC, their importance is increasing.[23,24] One of Tintex Textiles main mottos is being as sustainable as possible, so water-borne coatings are the only type of coatings they produce.

2.3.5 Additives

Modern coatings are complicated systems, where a diverse array of organic and inorganic materials with very different molecular weights and properties, need to behave as a homogeneous mixture. Additives are added in small quantities and affect the system greatly by modifying properties of the coated material during manufacture, storage and application.[5]

There are several types of coatings additives, which can be classified according to their function. The most common additives in the coatings industry are the thickeners, wetting agents, coalescing agents (promoters of the film formation of polymer dispersions), emulsifiers, foaming and defoaming agents, as well as flame retardants.

Catalysts also fit well in the additive class, being generally used in high-performance coatings, which can be characterized by their excellent chemical and weatherability resistance, and their low content of VOC. They serve as increasers of the reaction rate, namely in crosslinking reactions, enabling the decrease of the temperature needed for the reaction to occur.[25] It will be discussed in further detail, some of the most typical additives utilized by Tintex Textiles.

A foaming agent is a reducer of surface tension, being crucial for converting a liquid into a foam. It can be considered a surfactant, designated as a foam stabilizer or a blowing agent, and sometimes it can perform both roles.[26]

A foam stabilizer allows the settling of the foam or even avoids its collapse. When gas bubbles reach the liquid surface, their behaviour differs if there is a foam stabilizer incorporated in the blend. Without it, the bubbles tear apart, and the imprisoned gas escapes flowing with the liquid. On the other hand, utilizing a foam stabilizer, which concentrates in the lamella at the gas-liquid interface, means the bubbles do not collapse when reaching the surface.[25,27] The electrostatic repulsion provided by the ionic groups of the surfactant, as the lamella drains and the inner and outer surfaces come together, stabilize the foam. Both scenarios can be observed in Figure 7.[28]

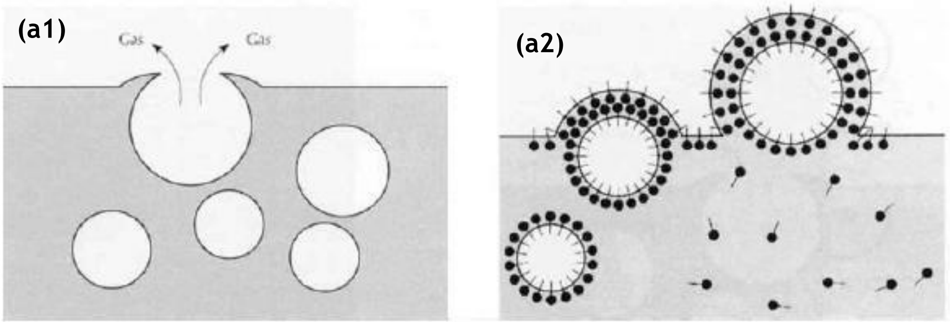


Figure 7 - Ascension and stabilization of air bubbles in liquids, which are free of foam stabilizers (a1) and liquids which contain foam stabilizers (a2). Adapted from [25].

Blowing agents can be defined as a substance able to produce a cellular structure in the matrix, through a foaming process, of a polymer that succumbs to hardening or a phase change. This agent helps the expansion of foam cells, incrementing their volume, forming a light foam. The original material density is decreased, and its thermal and acoustic insulation as well as its relative stiffness increases.[19,29]

A defoamer is a low surface tension liquid that has controllable solubility with the liquid medium. After entering the foam lamella, the agent spreads over the interface and interacts with the surfactant. The lamella becomes less cohesive as the surface tension decreases, which will lead to rupture and collapse of the foam. Defoaming agents are either mineral oil or based on silicone and fluorinated materials.[28]

Wetting agents are surfactants, which consist of amphiphilic molecules, that facilitate the dispersion or the adhesion process in the coating formulation, by increasing the speed at which the liquid phase wets the pigment surface.[25,30] This process is influenced by the polarities of the pigment surface and the binder solution, the viscosity of the liquid phase, as well as the geometry of the pores within the pigment agglomerates.[31]

Thickeners are utilized in coating materials, in order for the system to achieve the desired rheological properties. This type of additives can be divided into two classes: conventional and associative thickeners.[25,32]

In conventional thickeners, the hydrophilic polymer backbone tends to associate with the water molecules by hydrogen bonding, increasing the hydrodynamic volume of the polymer itself. Consequently, there is less available space for the particles to move freely, therefore the viscosity increases. The most common conventional thickeners are cellulose ethers.[32]

Associative thickeners correspond to hydrophobically modified water-soluble polymers, which can act by either thickening the water phase or by association with other formulation ingredients. The hydrophobic groups connect with emulsion particles through surface adsorption. The most widely used associative thickeners in water-borne coatings are hydrophobically modified ethoxylated urethanes (HEUR). These thickeners provide unique properties, including improved flow and levelling, to the coating materials.[28,32]

An emulsion is a stable mixture of two or more immiscible liquids, which are held in suspension. The blend is stabilized by emulsifiers, which reduce the surface tension at the interface of the suspended particles.[28]

2.4 The substrate

The primer layer is one of the main solutions to improve adhesion between the textile substrate and the coating material. Nonetheless, the finishing of a textile can sometimes be enough to ensure good adhesion and dimensional stability. Several parameters of chemical finishing (processes that alter the chemical composition of the textile) must be considered, such as the type of textile (fibre and construction of the yarns) being treated, which affects the sedimentation and accommodation of the coating layer, as well as the performance requirements of the finish (extent of effect and durability). These factors directly affect the deposition profile of the coating in the substrate.[33]

Concerning the fibres, they are divided as natural, man-made, synthetic polymers, metal fibres or ceramic fibres. Natural fibres can be subdivided into animal (protein) fibres (e.g. wool and silk) or cellulose-based vegetable fibres. Tintex utilizes fibres, such as cotton, wool, recycled synthetic polyester and lyocell, which for the same coating formulation, lead to a completely different final product.[34]

Pertaining to the textile substrate, it is responsible to promote adhesion and fixation of the coating. The three main classes of a textile substrate can be considered to be a knit, a woven or non-woven material.[10,35]

Knitting is a process whereby fabrics are formed by the interlacing of threads, utilizing yarn loops forming techniques. These are the base element of a thread, being obtained by the deflection of a yarn. There are two types of knitted structures: weft and warp.[10,36] The weft knitting process is the method of developing a fabric by the interlocking of loops in a weftwise or crosswise direction. In weft knits, a loop is composed of a head and two legs, and the section of yarn linking two adjacent loops is known as a sinker. The fundamental weft knitted structures are the jersey, the rib, and the purl. All the other structures are derived from these three. A big portion of Tintex Textiles products is jersey and rib structures. Regarding the jersey arrangement, the vertical component of the loops appears only on the face side. On the other hand, the horizontal components of the loops are seen on the reverse side of the fabric. In a rib structure, both directions have the same appearance.[10,36-37] The interlock arrangement is a rib derivative, utilized regularly by Tintex, where yarns are knitted on two sets of needles aligned opposite to each other. This positioning allows the loops on the front and the back to be intertwined or interlocked.[38]

In warp knitting, each yarn is knitted by one needle. The needle bar that carries the needle moves sideways, as well as up and down, allowing the yarns being carried vertically and slightly diagonally. The fabric is formed by the intermeshing of parallel warp yarns, that are fed from a warp beam.[35] Concerning the loop of this structure, it is divided into overlap and underlap, as it can be seen in Figure 8.[36]

A woven material possesses a cohesive surface and is created by the perpendicular interlacing of two or more sets of yarns.[35,38] The interlacing pattern of the warp and the weft is called the weave and affects the handfeel of the coating. The basic structures, from which any weave can be derived, are the plain, twill and sateen weaves. Pertaining to plain weaves, which are the simplest and most widespread arrangement, warp yarns interlace alternately with weft yarns. [10,38] In Figure 8, it is shown an example of a woven material, as well as knitted structures.

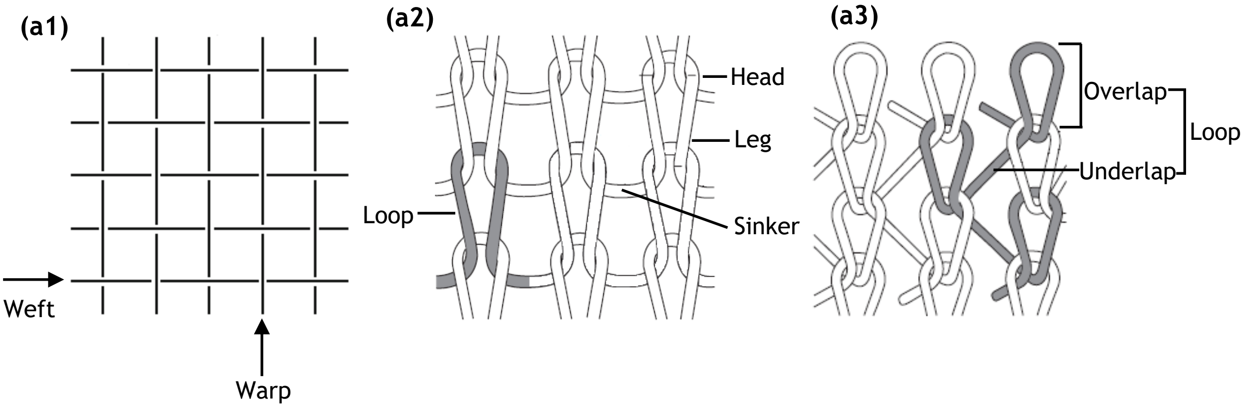


***Figure 8** - Substrate structures. (a1) woven material; (a2) weft knit; (a3) warp knit.*
Adapted from [35-36].

Textile fabrics can also be produced directly from webs of fibres by bonding, fusing or interlocking to make non-woven fabrics, but their physical properties tend to restrict their potential end-usage.[37] They can be classified according to the type of fibre used, method of web formation, nature of bonding and type of reinforcements used.[10] The two main non-woven manufacturing systems are the melt-blown and the spunlace process. The melt-blown is a one-step process that converts polymers into low diameter fibre non-woven webs. Spunlace or hydroentangling corresponds to needling a non-woven fabric, recurring to high-pressure water jets.[39]

2.5 Coating methods and processes

Coating a layer of polymeric material on a textile sheet, provides new properties to the base fabric. There are several coating methods, which are the following:[10]

For fluid coatings (coating material in the form of paste, solution, or latexes):

- Knife coaters: Wire wound bars, round bars, among others. These are post-metering equipment.
- Roll coaters: Reverse roll coaters, kiss coaters, gravure coaters, dip coaters, among others. These are pre-metered devices.
- Impregnators: The material to be coated is dipped in the fluid, and the excess is

eliminated by a squeeze roll or doctor blades.

- Spray coaters: The material is sprayed onto a web or a roll for transfer.

For dry coatings, such as solid powder or a film, the procedures can be: melt coating (extrusion coating, powder coating, and so forth), calendering and lamination.

After the substrate is formed, Tintex dyes the textile, improving the solidity of the colour and employs several other processes, which stabilize chemically and physically the substrate. In Annex A, it is presented a more in-depth analysis of those processes.

The deposition of the coating in the textile is performed either by knife coating or rotary screen-printing. The last step of the process is the finishing of the coating, which can utilize both calendering and embossing equipment. For each production batch, Tintex normally only requires one of those machines, to fulfil the client's demands.

Before a full-blown production of the coating material, Tintex must produce several coating samples, to achieve the desired coating properties. This process of finetuning is also done during the production phase, given that even though the techniques employed in both phases are the same, the required equipment is vastly different. Some issues, such as cracking and blistering of the textile coating are more predominant, during the production stage.

The coating processes of Tintex Textiles will be discussed in more detail below.

2.5.1 Rotary screen coating

The rotary screen-printing method is utilized mainly for the coating and printing of textiles. Tintex can only resort to this technique, when the coating thickness is equal or below 0.5 mm, the viscosity of the blend is quite low, and the diameter of the particles is in conformity with the mesh number of the screen. If those requirements are fulfilled, this method is the best option for Tintex, given that it leads to more freedom to apply different aesthetic patterns to the coating material, and also improves the handle of the material.

Regarding the screen, it is a seamless nickel cylinder with perforations. As it can be seen in Figure 9, a squeegee is mounted in the screen, serving as the supply and distribution pipe of the coating paste. The fabric moves at the same speed as the rotation of the screen, which means there is no frictional contact between the two. The squeegee blade and centrifugal force push the paste out through screen perforations in the form of dots, on to the surface of the fabric. Then, the resin in the dots flows and merges in order to form a continuous coating. In some instances, when a continuous system is not achieved, it is used a whisper blade to assist the coalescing of the dots, in order to form a smooth and compact coating material. The amount of coating applied is mainly dependent on the mesh number of the screen, the squeegee pressure (i.e. the angle between the blade and the screen), and the viscosity of the coating.[10,40-41]

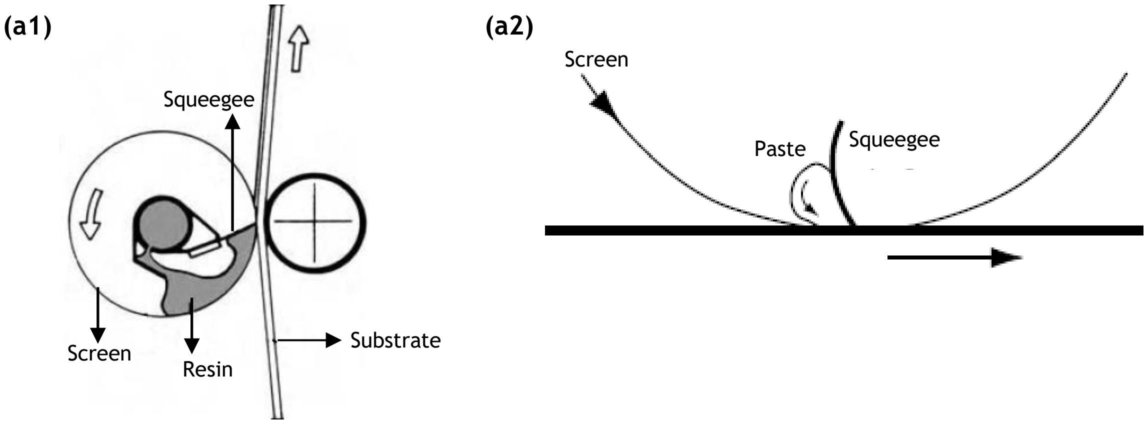


Figure 9 *– (a1) Rotary screen application. (a2) Ampliation of the interface substrate-paste in rotary screen coating. Adapted from [40-41].*

2.5.2 Knife coating

In knife coating, a small piece of a smooth fabric is fed over the roll under a knife, also known as a doctor blade. The coating material is then poured in front of the blade by a dipper over the entire width of the substrate.[10]

There are three distinct arrangements of knife coating: knife on-air, knife on blanket, and knife over roll. The knife over roll (Figure 10), which is the system Tintex opts to use, is the most widely used technique, thanks to its simplicity and much higher accuracy. In this configuration, a suitable doctor blade is suspended over a high-precision roller.[10,42]

The knife does not touch the substrate directly, meaning there is always an opening between the substrate and the bottom of the blade, controlling the coating thickness. However, variations in substrate thickness lead to non-uniform coatings.[10,18,43]

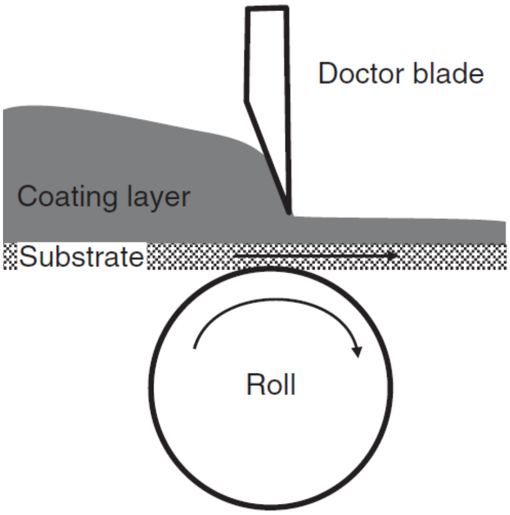


Figure 10 *- Knife over roll configuration. Extracted from [18].*

2.5.3 Calendering

After the coating is embedded in the substrate, Tintex frequently utilizes a calender to finish the coating material, altering properties such as colour and gloss and changing the handle of their product, according to their costumer's needs.

In a doctor blade application, a liquid coating is used, which hardens in a drying process (gelling). In the case of calendering, a solid coating material is heated.[35] A fabric calendering machine is constructed with multiple rollers mostly made of hard metal, arranged in a specific order, usually vertically above one another. The fabric is placed in contact with the polished surface of a hot roll, which then contacts with the compliant roll made of materials, such as polyester, polyimide and rubber. The nip area, as shown in Figure 11, is the physical contact area between the two rolls. Optimizing the distance between the rolls, nip pressure and the heat applied to the fabric, results in an improvement of the coating properties.[35,41,44]

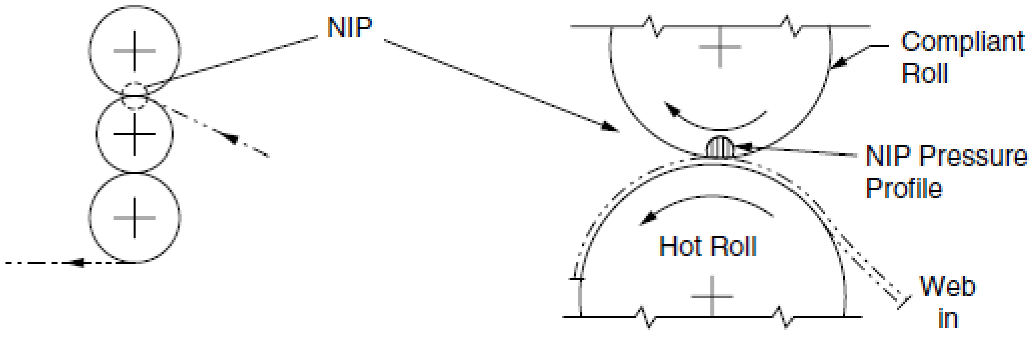


Figure 11 *- Nip definition. Extracted from [41].*

2.5.4 Embossing

In the embossing process, a coated paper is heated through a metal-engraved roll, allowing to impart the pattern of the paper onto the coated fabric. Pressure, temperature and pressing time are the most critical factors for achieving lasting and good embossments. As a result of the pressing time being significantly higher than when using a calender, the coating material will look starkly different.[10,35]

3 Materials and Methods

3.1 Materials

All the coating components, utilized throughout this dissertation, were provided by Tintex Textiles. Table 3 includes the suppliers of each ingredient contained in the original coating formula, as well the additional crosslinkers that were tested, and a small description of each component. Besides these compounds, dimethylformamide (DMF), which was supplied by José Manuel Gomes dos Santos, LDA was needed to infer the occurrence of crosslinking between the binder and the crosslinkers evaluated.

***Table 3** – Chemical basis and suppliers of the coating components.*

Name	Chemical basis	Supplier
Impranil DLN-SD	Aliphatic polyester-urethane dispersion	Covestro
Tubicoat SHM	Aqueous solution of ammonium stearate	CHT
Arkophob DAN New liq	Aqueous dispersion of polyurethane	Archroma
Imprafix 2794	Aqueous dispersion of polyisocyanate	Covestro
Acrafix EP 6047	Aqueous dispersion of polycarbodiimide	Tanatex chemicals
Hostapur SAS 30	Secondary n-alkane sulphonate. Sodium salt	Archroma
Afilan A01 liq.	Aqueous dispersion of amines, C_{12-18}, alkyldimethyl, n-oxides	Archroma
Appretan Thickener 2710 liq	Polyacrylic acid derivative	Archroma

The substrate employed for the formula analysed was a jersey knit made of 100% cotton. The same knit was tested without being treated with a hydrophilic softener named Hydroperm RPU New liq c, supplied by Clariant (Annex A). In Figure 12, it can be observed the treated and non-treated knit.

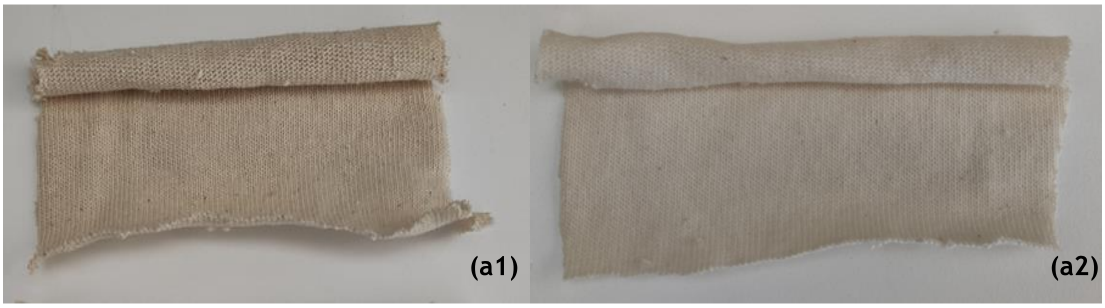


***Figure 12** – Substrate made of 100% cotton not treated (a1) and (a2) treated with Hydroperm RPU new liq c.*

3.2 Methods

3.2.1 Production of coating samples

One of the main tasks proposed for this project is to optimize a coating formula, which was discontinued by the company. All the steps necessary to produce a coating material in Tintex Textiles will be discussed further below. An illustration of most equipment utilized in Tintex Textiles is displayed in Appendix A.

Firstly, each ingredient is weighted in a scale (Metler Toledo) and then added to a beaker. The thickener is usually the last ingredient to be added to the blend. The homogenization of the mixture is done in a mechanical agitator (IKA EUROSTAR 20 digital). During this homogenization, the thickener is added to the blend. Considering the amount needed to obtain the required viscosity is not specified in the formulation, the preferred way to obtain the required rheological properties, specified for the coating blend, is to add a small volume of thickener, and then to visually analyse the presence of air bubbles, agglomerates or lumps in the mixture. If any of these problems are observed, then the operation speed in the agitator is reduced to ensure that poor foaming of the coating does not occur. After not observing, either issue, it is slightly increased the rotational speed. This process ends, when it is visually identifiable, that the blend is within the range of viscosity needed for the product.

The viscosity is then measured in the Viscotester VT02. The first step of the measurement is to choose rotor one (measuring range between 3 and 150 dPa·s). In case it is needed to evaluate the viscosity of the mixture, before employing the thickener, rotor three is employed (measuring range between 0.3 and 13 dPa·s). Then, the measuring system is locked with a clamp and connected to the rotor. After calibrating the equipment, the rotor is immersed into the liquid of the container, preferably up to the dip mark on the shaft. After a few seconds, the viscosity of the substance is displayed in the equipment. All viscosity measurements were performed at approximately 25 °C.

In case the viscosity of the mixture is within an acceptable range (usually suggested by the supplier), then the formulation is ready to be agitated with a Becken mixer. After a certain time, it is visually identifiable the formation of the foam, which means the mixture is ready to be inserted on the substrate.

3.2.2 Knife coating, drying and crosslinking

The Mathis Labcoater type LTE-S is the equipment adopted by Tintex Textiles, which accommodates all types of knife coating configurations. It is a hybrid equipment, given that it is a combination of a dryer and a laboratory coating table. The settings that can be toggled during the use of the equipment, which affect the final product are the dwell time (has to be at least 5 seconds and can go up to 1000 minutes), the fan speed (which was always 1000 RPM for every experiment) and the circulation air temperature, which can go up to 300°C, covering most drying and crosslinking temperatures of any coating formulation.

After the substrate is settled in the machine it is necessary to set the thickness of the coating material. To measure the thickness of the coating, Tintex utilizes a Teng F21 feeler gauge set that supports thickness between 0.05 mm to 1 mm, containing 20 pieces. Firstly, it is selected the piece closer to the thickness needed, and then that piece goes through the gap between the bottom of the blade and the substrate. If the piece is too loose or too tight when passing through the gap, the height of the opening is adjusted by recurring to the handwheel and dial gauge of the equipment. The coating is now ready to be applied evenly in the substrate. After applying the material onto the equipment, the coating is dried by inputting the dwell time, temperature and the rotational aeration speed. Before crosslinking the polymer blend with the Mattis lab coater, the coated textile can be finished, in either the embossing machine or a Monti calender.

3.2.3 Foam density

In the coating industry, the foam density ($g{\cdot}L^{-1}$) is a parameter that characterizes the formulation. An approximation of that value is achieved by filling a beaker with the coating, after being mixed on the Becken equipment. Given that it was known the volume (L) and mass (g) of the beaker utilized, it was possible to have a reasonable idea of the foam density, by recurring to Equation 1.

$$Foam\ density = \frac{Mass_{cup+mixture} - Mass_{cup}}{Volume_{cup}} \tag{1}$$

3.2.4 Evaluation of interaction between the crosslinkers and the binder

In order to evaluate the occurrence of crosslinking with the binder at the studied cure temperature, 2 mL of the binder or 2 mL of a mixture containing the binder and one of the crosslinkers evaluated, at the same mass ratio of the complete formulation (3% of the crosslinker and 97% of the binder), were inserted on a teflon circular plaque (Figure 13), and then heated at 170 °C for 30 minutes on the Scientific series 9000. The film formed was then removed from the teflon plaque and mixed with 9 mL of DMF (polar solvent), with a magnetic stirrer for 30 minutes.

Figure 13 *– Film of the binder or crosslinker/binder system on teflon circular plaques.*

3.2.5 Chemical characterization

One of the main goals of the dissertation is to understand the chemical reactions (especially the unblocking of the crosslinker and the cure reaction) associated with the binder, the crosslinker and the knit. FTIR-ATR (Fourier Transform Infrared – Attenuated Total Reflectance), DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric analysis) are the techniques that help to accomplish that objective. Illustrative photos of the equipment needed to perform these methods are displayed in Appendix A.

The substances analysed in both the STA and DSC equipment were prepared on a vacuum oven (Vacucel) at 40 °C and 0.1 bar for 40 hours. Concerning the FTIR-ATR equipment, some of the samples evaluated, instead of being in the vacuum oven, were heated at 120 °C, 170 °C or 245 °C for 30 minutes in a non-vacuum oven (Wtc binder or Scientific series 9000). Regarding the type of samples, some corresponded to the substance applied in a glass plaque, meaning the dispersion was analysed by itself. On the other hand, some samples were analysed by being applied on the substrate (knit). When a substance was a mixture of two coating components, before the application, they were mixed in a magnetic stirrer for 30 minutes. To simulate the application of the material by knife coating, a film applicator was employed (elcometer model 3540) which lead to a film thickness of 200 µm. An example of both types of samples analysed is shown in Figure 14 and an illustration of the application with the elcometer is displayed in Figure 15.

Differential scanning calorimetry was performed using a DSC 214 Polyma (NETZSCH) calorimeter. The samples utilized for the DSC analysis were weighed in an aluminium concave pan, which was then sealed. To allow the evaporation of the compounds, the lid was pierced. This configuration of the pan avoided the overfilling of any liquid substances during heating, meaning the base of the cell of the DSC equipment would not be contaminated. Regarding the DSC measurements, they were carried out at heating rates of 10 $°C·min^{-1}$. The temperatures, in which the coating components were evaluated, ranged from -10 °C up to 500 °C. The involved atmosphere consisted of nitrogen, which was pumped at around 40 $mL·min^{-1}$. To improve the accuracy of the analysis, the weight of the sample was always between 5 mg and 15 mg.

The TGA curves were obtained using the STA 449 F3 Jupiter (NETZSCH) equipment. In the case of this equipment, to obtain the best possible results the sample should not correspond to more than half of the size of the concave open aluminium pan (mass of the sample was usually between 20 mg and 25 mg). The test was performed on an inert atmosphere of nitrogen with a flow rate of 30 $mL·min^{-1}$. Pertaining to the temperature, the sample was heated from a temperature of 30 °C up to 500 °C at a rate of 10 $°C·min^{-1}$.

The infrared spectra were recorded using a VERTEX 70 FTIR spectrometer (BRUKER) in transmittance mode with a high sensitivity DLaTGS detector at room temperature. Samples were measured in ATR mode, with a A225/Q PLATINUM ATR diamond crystal. The spectra were subjected to 64 scans and recorded from 4000 to 500 cm^{-1}, with a resolution of 4 cm^{-1}. Each sample was examined three times, in different zones of the sample, to ensure the intensities of transmittance yielded by the equipment, were consistent. The conversion to absorbance, normalization of the spectra, as well as the second derivative spectroscopy of the spectra was executed in the Essential FTIR v3.50.196 software. All the graphs related to the normalized spectra are presented on a semi-log scale, to facilitate the visualization of the intensity of the peaks, especially in the region between 1000-1800 cm^{-1}. The normalized second-order derivative of the spectra was employed, by selecting 17 smoothing points and choosing the Savitzky–Golay (SG) quadratic/cubic numerical algorithm as the smoothing method.

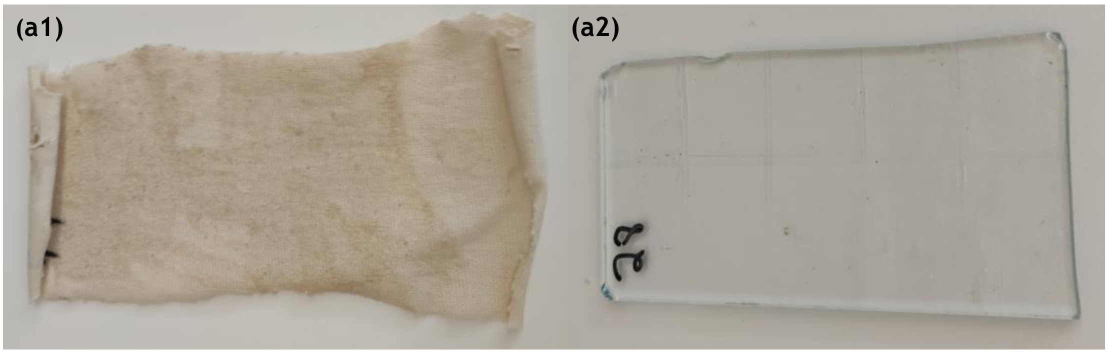


Figure 14 - *Sample prepared in the knit (a1) and the glass plaque (a2), after being heated in the laboratory oven for 30 minutes (Wtc binder).*

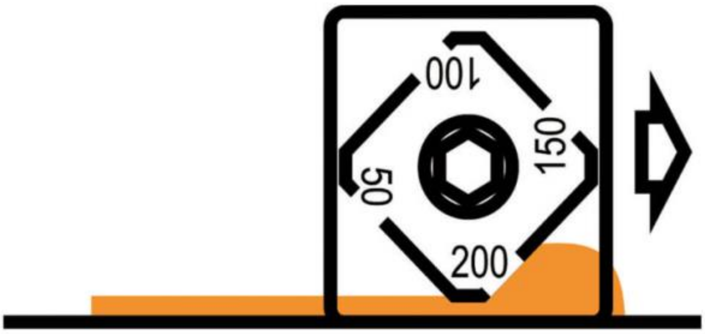


Figure 15 - *Application of the film on the knit or the glass plaque, by recurring to a film applicator.*

4 Results and discussion

4.1 Coating formulation

The coating studied during the course of this dissertation is a stable foam, with a foam density between 350-400 g·L^{-1}. Its thickness is 0.65 mm and the viscosity of the blend at 25 °C is between 30-35 dPa·s. This coating material was discontinued by the company, due to cracking of the coating in the production/post-processing phase. The main reason Tintex suggested the study of this formula was due to the components of the formulation being present in a considerable number of products of the company. The mass fraction and function of each component of the formula, is presented in Table 4.

Table 4 *- Coating components mass fraction and their function in the formulation.*

Name	Mass fraction / %	Function
Impranil DLN-SD	89.87	Binder
Tubicoat SHM	4.50	Foam stabilizer
Arkophob DAN New liq	2.70	Crosslinker
Hostapur SAS 30	1.20	Foaming and wetting agent
Afilan A01 liq.	1.20	Foaming and wetting agent
Appretan Thickener 2710 liq	0.53	Thickener

Regarding the temperatures of operation, the supplier recommends drying the coating for 3 minutes at 120 °C and to cure the polymer at 170 °C for 4 minutes. In order to improve the performance of the coating studied it was analysed the knit, the binder, several crosslinkers that could be applied in the formulation, and the relations between these components of the coating system.

4.2 The substrate – knit

The substrate corresponds to a knit made of 100% cotton, which means the main component of the material is cellulose (Figure 16).[45]

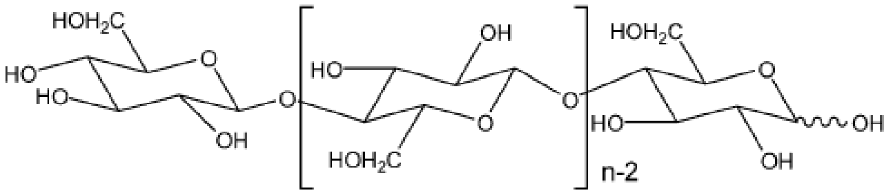


Figure 16 *- Cellulose - main component of the knit. Adapted from [45].*

4.2.1 FTIR-ATR analysis

Given the knit is cured with a non-ionic thermo-reactive polyurethane softener (Annex A), at 150 °C for 4 min, it was compared with a virgin knit (at room temperature), to assess any substantial changes in composition (Figure 17).

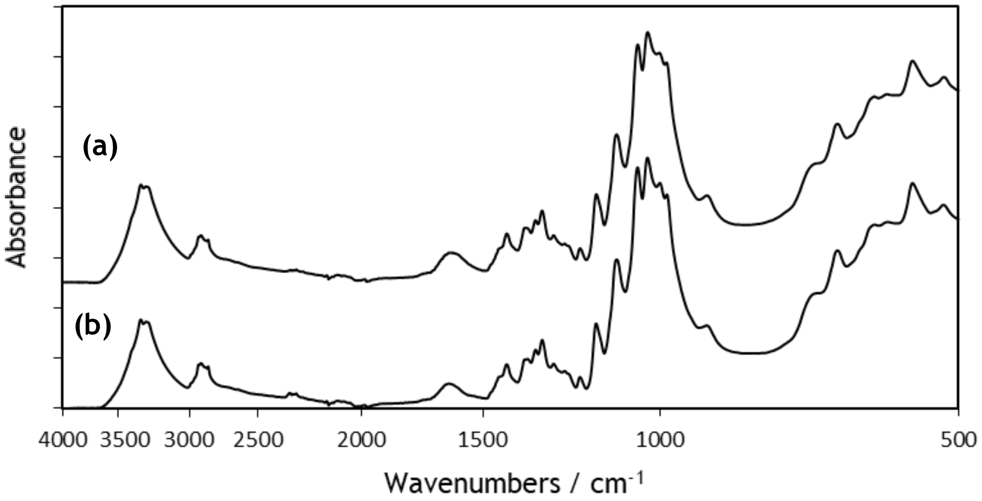


Figure 17 *- Normalized FTIR - ATR spectrum of a (a) virgin knit and a (b) knit treated with a softener.*

In either the treated and non-treated knit, its only identifiable cellulose related peaks, like CH_2 antisymmetric and symmetric stretching at 2899 cm^{-1} and 2850 cm^{-1}, respectively, and C-O stretching of C-O-H/C-O-C in the region between 1000-1204 cm^{-1}. Furthermore, at around 3293-3332 cm^{-1}, -OH stretching occurs and between 1620-1635 cm^{-1} it appears a peak related to H_2O adsorbed molecules, which are at a lower intensity in the treated knit, due to some water being removed from the knit at 150 °C.[45]

4.3 The binder – Impranil DLN-SD

Impranil DLN-SD is an anionic aliphatic polyester-urethane dispersion formed by a hexane or neopentyl adipate polyester and HDI. A proposed structure of the polymer chain can be seen in Figure 18.[46-47]

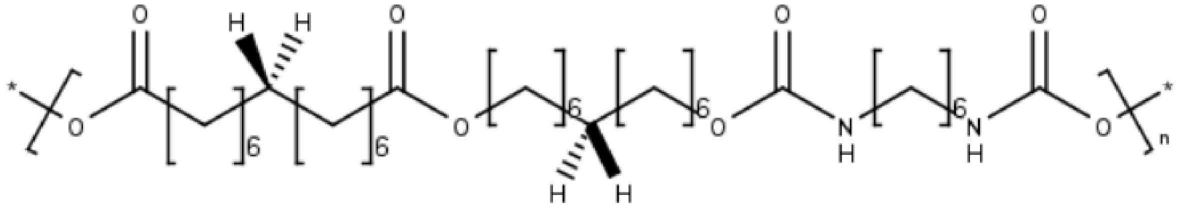


Figure 18 *- Proposed structure of Impranil DLN-SD. Adapted from [46].*

4.3.1 Thermal analysis

To assess the occurrence of hydrolysis and that no other major reactions occur at the studied temperatures in Impranil by itself and coated on the knit, after being 40 hours at 40 °C and 0.1 bar (vacuum), a DSC analysis was performed (Figure 19).

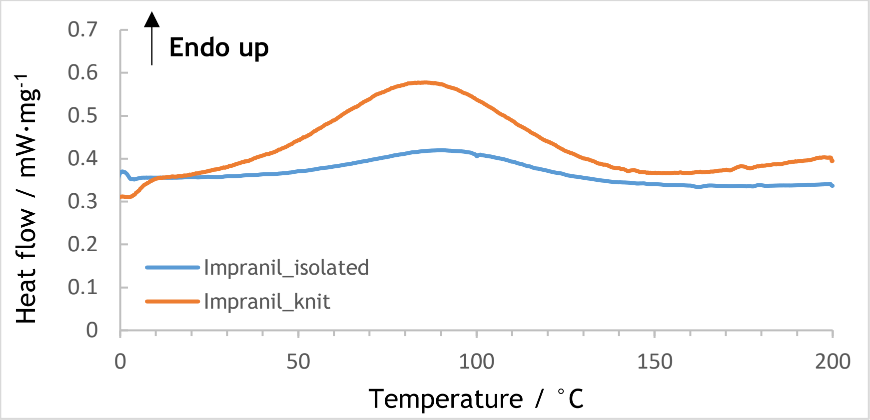


Figure 19 *- DSC curve of Impranil by itself and applied on the knit.*

It was observed an endothermic peak in Impranil adhered to the knit and in the binder by itself, at about 85 °C and 90 °C, respectively. This broad peak corroborates the fact, that both samples still contained water, however, the amount of water was significantly higher in the coated sample (higher and broader endothermic peak), due to the loss of water molecules bonded to the hydroxyl groups in the cellulose polymer. At 130-140 °C, the peak ends, and thus water is completely removed in both cases. No other peaks are seen at the range analysed in the DSC curve (between 0 °C and 200 °C), which leads to believe that Impranil DLN does not undergo chemical changes at these temperatures. A TGA curve of Impranil DLN-SD by itself is present in Appendix B and it shows a slight decrease of the mass (1.3%) until 140 °C, suggesting the evaporation of water residues. Moreover, the curve has a step between 250 °C and 500 °C, which can be associated with thermal degradation of Impranil DLN.

4.3.2 FTIR-ATR analysis

The spectrum of Impranil DLN at 40 °C under vacuum, 120 °C (drying temperature) and 170 °C (cure temperature) is shown in Figure 20.

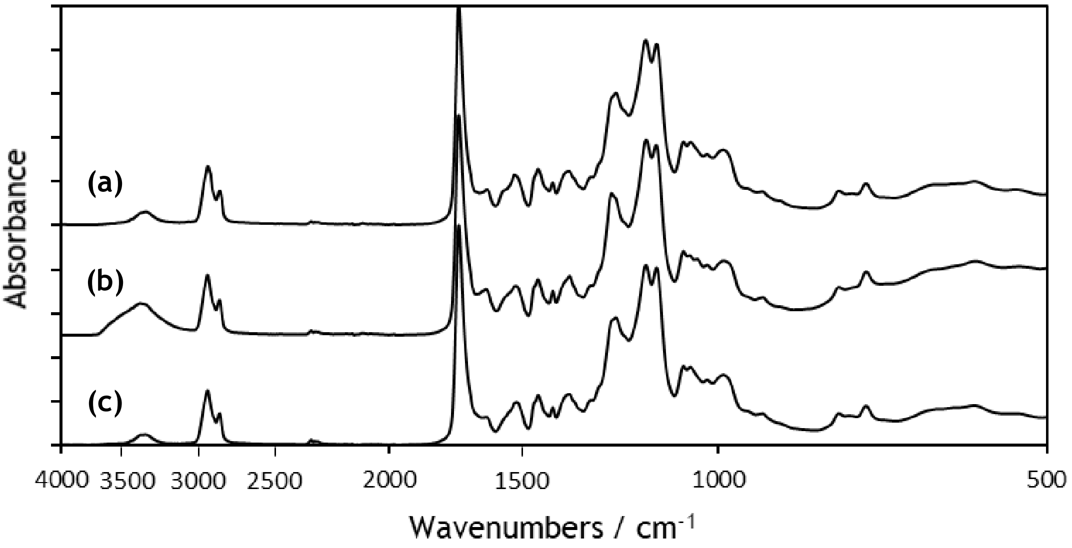


Figure 20 *- Normalized FTIR-ATR spectrum of Impranil DLN-SD isolated at (a) 40°C under vacuum, (b) 120 °C and (c) 170 °C.*

In Impranil isolated at 40 °C under vacuum, it can be seen N-H stretching (3345 cm^{-1}), CH_2 antisymmetric stretching (2934 cm^{-1}) and a peak associated with -CH_2 symmetric stretching (2862 cm^{-1}). Between 2300-2400 cm^{-1} there is a doublet of bands, which correspond to small traces of atmospheric carbon dioxide (CO_2), detected by the equipment. This signal appears in most spectra analysed. In the region of around 2200-2300 cm^{-1}, no free isocyanate peak is seen, meaning all N=C=O groups reacted. The peak at 1725 cm^{-1}, corresponds to the C=O of ester and urethane functionalities, which overlap each other. Moreover, urethane C-N-H bending appears at 1535 cm^{-1}. The peaks seen at 1170 cm^{-1} and 1070 cm^{-1} can be related to asymmetric and symmetric stretching vibration of S=O groups (corroborating the anionic character of the binder), respectively.[48-49] The N-H stretching peak at 120 ˚C, shifts to 3384 cm^{-1} and becomes broader and more intense suggesting that -OH groups are overlapping with N-H groups. This can be attributed to water molecules being adsorbed in Impranil at 120 ˚C and the reaction rate of hydrolysis increasing with the heat applied on the blend, leading to the presence of -OH groups formed by hydrolysis of the polyester component of Impranil, which happens at the weak carboxylic ester bonds.[50] At 170 °C, that peak being similar to the one at 40 ˚C, can be due to no water molecules being adsorbed in the blend at that temperature. In the scenario of Impranil applied on the knit (Figure C-1), the band above 3000 cm^{-1} is similar at any of the studied temperatures, due to the equipment mostly detecting the -OH groups of the knit (cellulose), which do not change considerably in intensity with the increase of temperature.

4.4 The crosslinkers

The crosslinker of the formulation analysed is Arkophob. It is an aliphatic non-ionic polyurethane dispersion blocked with methyl ethyl ketoxime (MEKO).[51,52] The blocking reaction is shown in Figure 21.

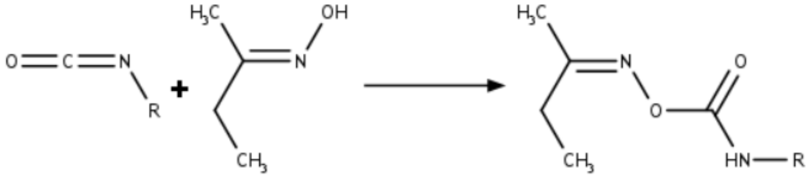


Figure 21 *- Blocking reaction of isocyanate groups with MEKO. Adapted from [52].*

Other crosslinkers analysed, include Imprafix 2794 which is an ionic polyisocyanate dispersion based on HDI, that is blocked with 3,5-dimethylpyrazole (3,5-DMP). A proposed blocking reaction of the compound is presented in Figure 22.[53]

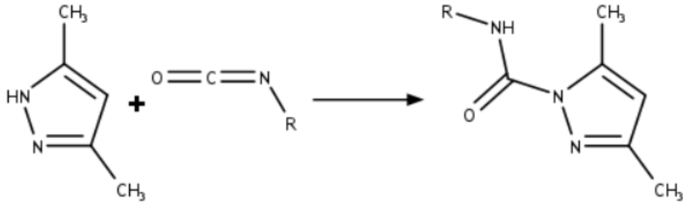


Figure 22 *– Proposed blocking reaction of Imprafix 2794. Adapted from [53].*

The type of deblocking reactions of these crosslinkers can be an elimination followed by an addition reaction (Figure 23). In this scenario, a blocked isocyanate deblocks at a high temperature (elimination step), and then reacts with a nucleophilic group (addition step). In the case of an addition-elimination reaction (Figure 24) there is an addition of a Nu-H group, that is present in the mixture, to the blocked isocyanate, followed by elimination of the blocker.[53]

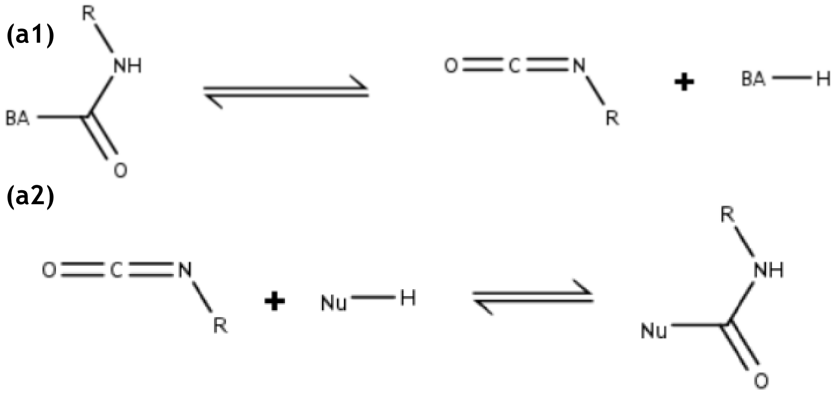


Figure 23 *– Elimination (a1) - addition (a2) reaction. Adapted from [53].*

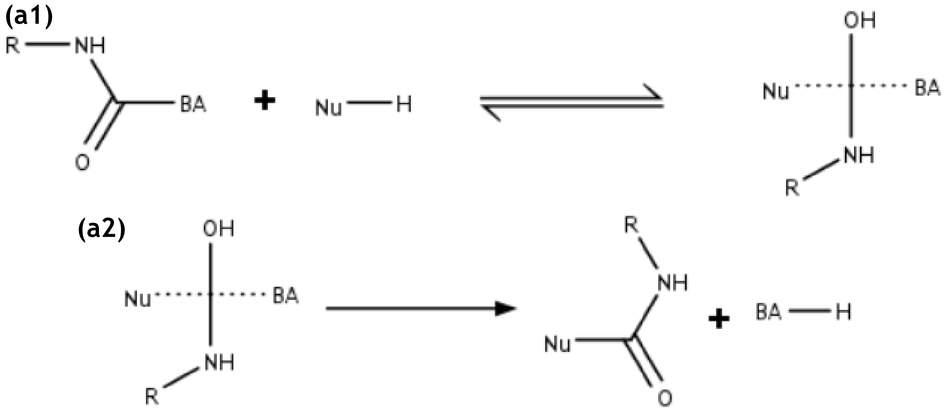


Figure 24 *– Addition (a1) - elimination (a2) reaction. Adapted from [53].*

Moreover, the cure of these crosslinkers can occur through N-H groups of the urethane component of the binder, leading to the formation of an allophanate bond (Figure 25).[54]

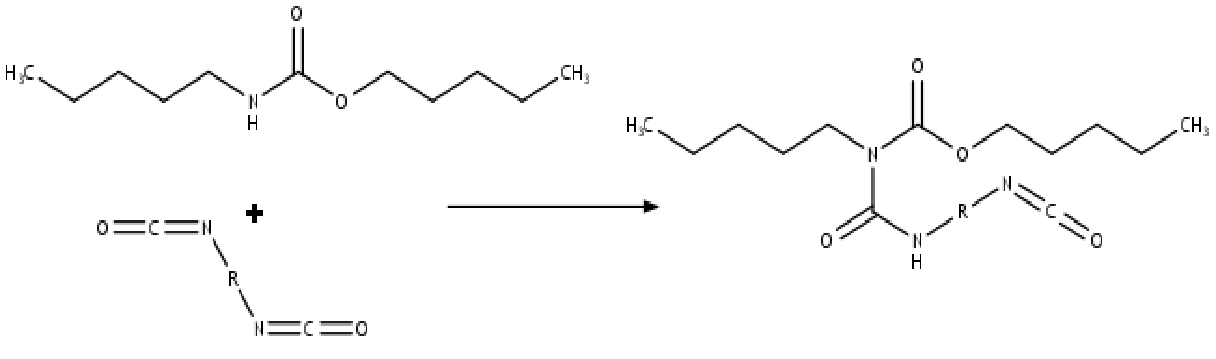


Figure 25 *- Formation of allophanate bond by crossliking through N-H groups. Adapted from [54].*

In the case, crosslinking happens through -OH groups, then it could be formed a urethane or an allophanate bond (Figure 26). The formation of allophanate only occurs under conditions of elevated temperature and due to the presence of excess isocyanate in the immediate vicinity of the urethane linkage. If water molecules are still present in the system after the unblocking reaction occurred, the allophanate bond formed in both scenarios, turns into a urea bond (all the steps of the reaction are shown in Figure D-1).[54-55]

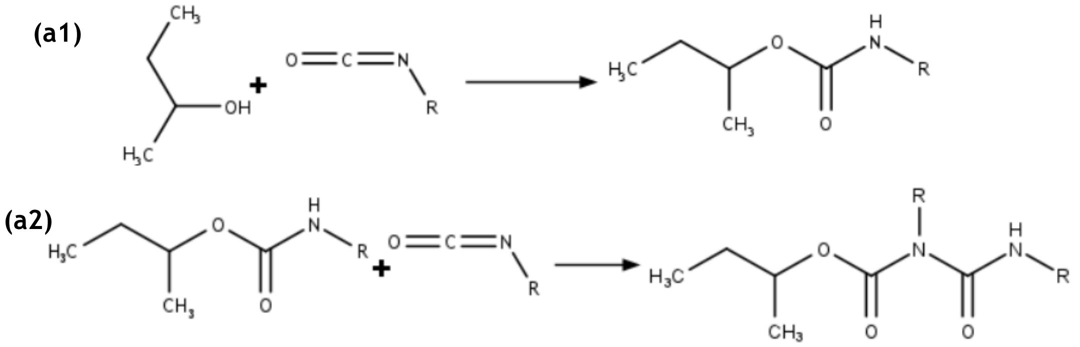


Figure 26 *- Formation of urethane bond through -OH groups (a1) or (a2) an allophanate bond by reaction of the urethane component with excess isocyanate. Adapted from [55].*

Concerning the other crosslinker analysed (Acrafix EP 6047), it is an ionic polycarbodiimide dispersion fully co-solvent free, that can crosslink with polyurethane dispersions through carboxylic acid residues (Figure 6), which can be produced through a hydrolysis reaction of the dispersion.[21]

4.4.1 Evaluation of interaction between the crosslinkers and the binder

In crosslinked polyurethanes, the polymer chains are covalently tied together meaning they are not able to dissolve in polar solvents, such as tetrahydrofuran (THF) and dimethylformamide (DMF). The polymer instead swells, as a result of penetration of a solvent into the polymer network, leading to a visible change in volume.[56]

By exposing Impranil to the cure temperature (170 °C) for 30 minutes, a film is created, which is then mixed with DMF, followed by stirring for 30 minutes (magnetic stirrer), and then rested at room temperature for 2 hours. As it can be seen in Figure 27-a2, the non-crosslinked binder completely dissolved in DMF, producing a transparent solution. By confirming that the non-crosslinked Impranil was soluble with DMF, it is then possible to evaluate whether crosslinking takes place with the binder, i.e. whether crosslinkers react with Impranil, instead of just reacting with themselves or the knit. The system binder/crosslinker was applied in the same proportion of the original formulation, and the same conditions of the reference test of the mixture of Impranil and DMF (Figure 27).

As it can be seen in Figure 27b-2 and 27c-2, the mixture of Arkophob and Imprafix 2794 swelled, forming a gel. Thus, it can be inferred that both systems are crosslinked and that these crosslinkers can crosslink through the N-H groups of the urethane component of Impranil DLN-

SD. Pertaining to the system of Impranil DLN and Acrafix EP 6047, it completely dissolved in DMF (Figure 27d-2), confirming the crosslinking reaction does not occur at 170 °C.

Concerning the yellowing of the mixtures, it can be seen in Figure 27b-1, 27c-1, 27d-1 that Imprafix is the crosslinker, that in conjunction with the binder possesses a less intense yellowish colour. In a mass ratio of 33/67 (crosslinker/binder), the mixture of Imprafix is the only one capable to prevent the appearance of the yellow colour on the blend, after heating at 170 °C for 30 minutes (Figure E-1).

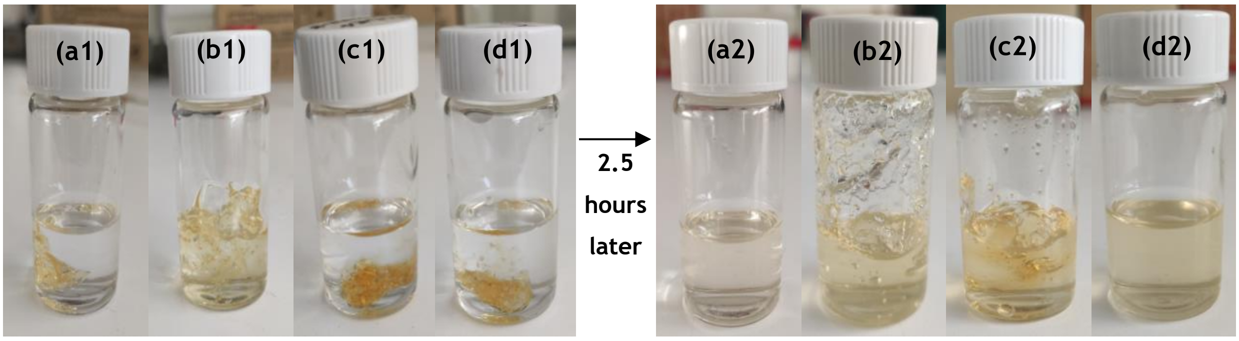


Figure 27 *- Impranil DLN with DMF (a1) immediately after mixing and (a2) after 2.5 hours. Mixture of Imprafix 2794 (b1) immediately after mixing and (b2) after 2.5 hours. Mixture of Arkophob DAN New liq (c1) immediately after mixing and (c2) after 2.5 hours. Mixture of Acrafix EP 6047 (d1) immediately after mixing and (d2) after 2.5 hours.*

4.4.2 Thermal analysis

The DSC and TGA curves were obtained for all crosslinkers, to evaluate the occurrence of a deblocking reaction and thermal degradation. In Figure 28 and 29, it is presented the DSC and TGA curves of Arkophob, respectively. Even though there is no information in the literature about the unblocking of Arkophob, it can be inferred through the DSC curve of Arkophob, that the unblocking reaction initiates at around 150 °C (the heat flow starts to increase). Furthermore, the boiling point of MEKO is 152 °C at 1 bar, meaning that when the blocking agent is not covalently bonded to the polyurethane, due to the unblocking reaction, it will evaporate.[57] In the TGA curve, its also observed a slight loss of mass between 100-150 °C that can be related to the evaporation of water residues. Regarding the broad endotherm observed between 150 °C and 245 °C, it indicates a slow and controlled release of the blocking agent and that 245 °C could be related to the end of the unblocking reaction. Furthermore at 185 °C, the increase of heat flow is slightly higher, meaning that the rate of the unblocking reaction is increasing. The TGA curve is congruent with the DSC curve, given that the decrease of mass is more evident at 185 °C. Moreover, the heat flow increases considerably at 280-290 °C, coinciding with the boiling point of isotridecanol ethoxylated (290 °C at 1 bar), which is a compound present in small amounts in the dispersion.[58] The mass loss observed in the TGA curve between 245 °C and the boiling point of isotridecanol ethoxylated (290 °C at 1 bar), can be associated with the evaporation of residues of the blocking agent and the beginning of the thermal degradation of Arkophob. At temperatures above 290 °C, it is observed the last step of the TGA curve, which suggests a significant increase on the rate of thermal degradation of Arkophob.

The most likely pathway of degradation is the urethane linkage being broken into the initial reagents (isocyanate and alcohol). The evaporation of these compounds can be one of the main reasons, for a 16% decrease in mass, between 300-400 °C. After 400 °C, other degradations pathways start to become more favourable, like the dissociation of the urethane bond into small molecules such as carbon dioxide, primary and secondary amines, eventually with olefin formation.[53] The significant reduction of mass from 59% at 400 °C, to 5% at 500 °C, supports this possibility.

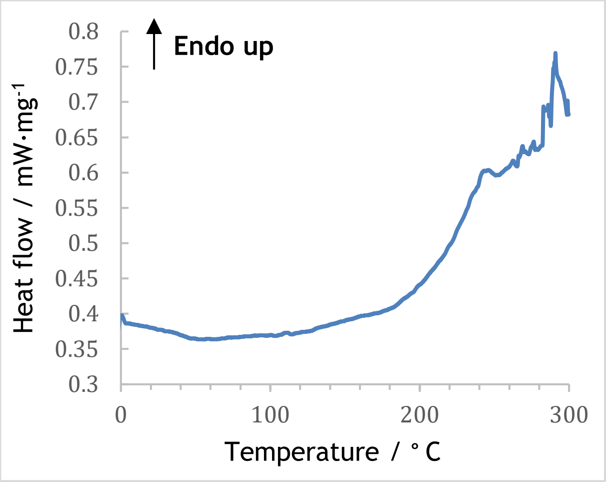


Figure 28 *- DSC curve of an Arkophob sample.*

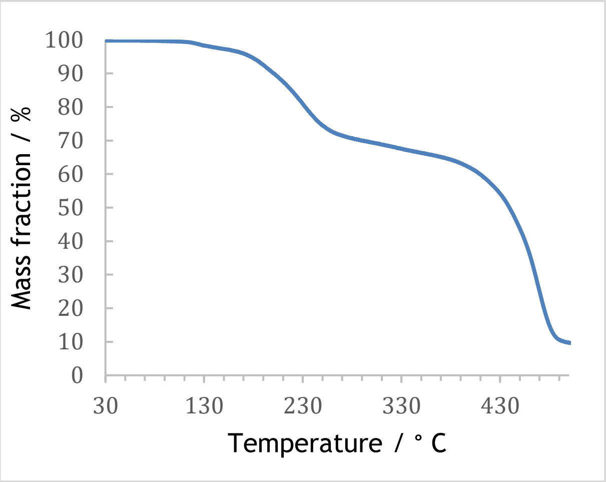


Figure 29 *- TGA curve of an Arkophob sample.*

Concerning the thermal analysis of Imprafix 2794, the DSC and the TGA curve of this compound, can be observed in Figure 30 and 31, respectively.

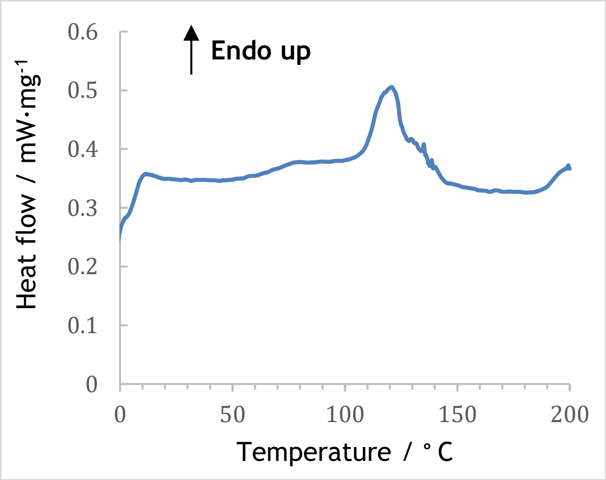


Figure 30 *- DSC curve of an Imprafix sample.*

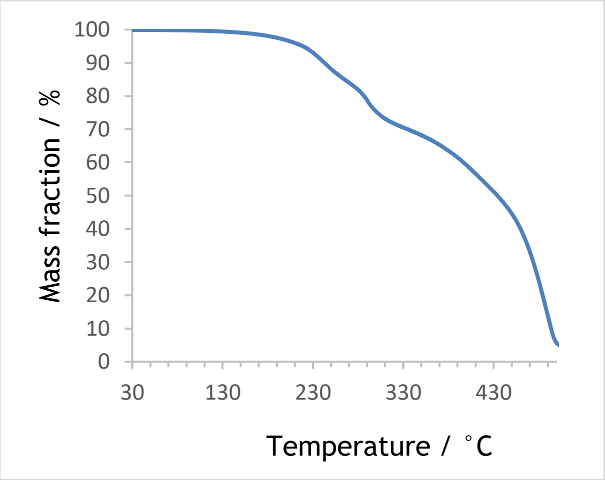


Figure 31 *- TGA curve of an Imprafix sample.*

In the STA equipment, all experiments are done in an open pan, meaning the evaporation of the blocking agent will drive the reaction toward free isocyanate formation. In the case of Imprafix, the blocking agent 3,5-DMP has a higher boiling point (218 °C at 1 bar) than the temperature of the deblocking reaction reported in the literature (120 °C), leading to imprecisions in the deblocking range, observed in tests done thermogravimetrically.[53,59-60]

The DSC test of Imprafix 2794 presented in Figure 30, shows a temperature peak of about 121 °C (peak range of 110-125 °C), which is close to the one reported in the literature. Meanwhile, in the STA-DSC test illustrated in Figure B-1, the peak appears at around 126 °C (peak range of 110-145 °C). After the unblocking temperature, it can be observed the peak rising until it drops down to an exothermic peak at 495 °C (STA-DSC test). The reason for this peak appearing at that temperature, could be associated with an exothermic thermal decomposition reaction of the substance. In the TGA curve, the unblocking region is between 110-150 °C, which corresponds to the first step of the graph. The second step corresponds to a range of 150-270 °C. In this zone, it occurs thermal degradation of the polyisocyanate based on HDI. The third step goes on until the end of the range evaluated, in which the decline of mass becomes more pronounced at around 400 °C, suggesting a big increase on the rate of degradation of the polyisocyanate.

Acrafix EP 6047, the polycarbodiimide crosslinker, DSC and TGA curves can be seen in Figure 32 and Figure 33, respectively.

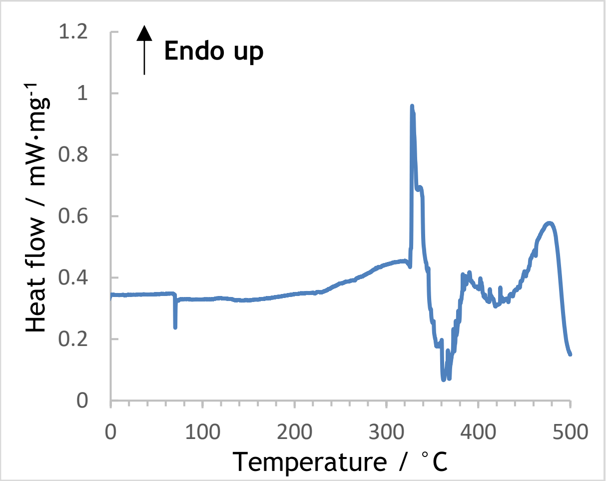


***Figure 32** - DSC curve of an Acrafix sample.*

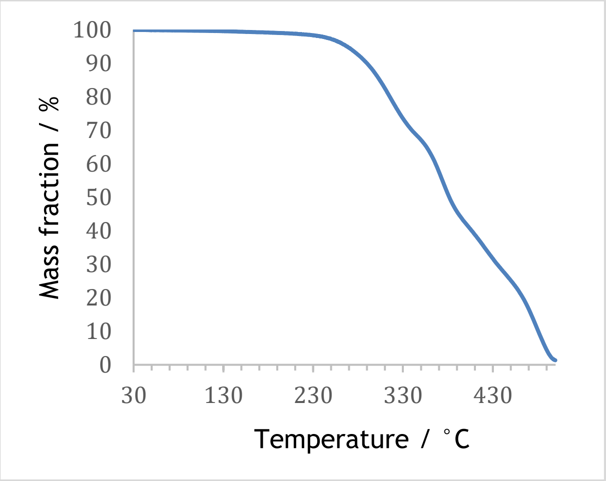


***Figure 33** - TGA curve of an Acrafix sample.*

By analysis of Figure 32, it is observed a very small exothermic peak at 70 °C that can be considered an artefact, and then very small variations are observed until 230 °C. At 230 °C, the peak starts rising, culminating on a maximum value (endothermic peak) at 330 °C. In the range between 230 °C and 330 °C, the slight increase of the heat flow indicates evaporation of an unknown product present in the dispersion. The fact that carbodiimide decomposes into isocyanate at a temperature around 320 °C, explains the huge spike of heat flow at 330 °C.[61] At 372 °C, it is found the minimum value of the graph corresponding to an exothermic peak, leading to the conclusion that an exothermic reaction of degradation is favourable in the range between 350 °C and 400 °C. The same thought process can be applied to the endothermic peak found at 475 °C. The TGA curve of the compound is in agreement with the DSC curve, meaning a significant loss of weight starts at 230 °C and ends at the maximum temperature analysed (1.5% of the original mass of the crosslinker). The loss of mass after 230 °C is almost linear, with exceptions of the zones coinciding with the peaks of degradation, observed in Figure 33.

4.4.3 FTIR-ATR analysis

All crosslinkers were analysed by FTIR-ATR, with the purpose of understanding which are the groups these substances have an affinity to crosslink, the effect of the temperature and the substrate, in either the system or the crosslinker by itself. The mass ratio of the mixtures was always 33/67 (crosslinker/binder) instead of 3/97, to ensure the equipment detected the peaks related to the binder, as well as the crosslinker.

- **Arkophob DAN New Liq**

Firstly, it was analysed Arkophob by itself at different temperatures (Figure 34).

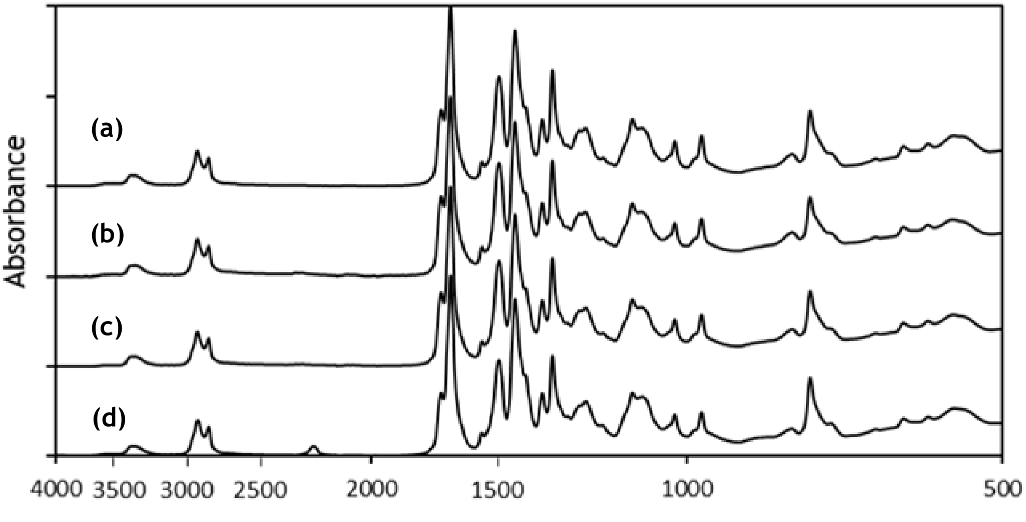


Figure 34 *- Normalized FTIR-ATR spectrum of Arkophob DAN New liq isolated at (a) 40 °C under vacuum, (b) 120 °C, (c) 170 °C and (d) 245 °C.*

At 40 °C under vacuum, it can be seen N-H stretching at 3356-3385 cm^{-1}, sharp peaks at 2929 cm^{-1}, corresponding to the $-CH_2$ antisymmetric stretching and at 2859 cm^{-1}, related to the $-CH_2$ symmetric stretching. The band of isocyanate (between 2200-2300 cm^{-1}) does not appear due to the isocyanate being blocked. The C=O band at 1716 cm^{-1} is from carbonyl stretching vibrations of the urethane functionality in nonbonded form. On the other hand, the band at 1681 cm^{-1} is related to carbonyl stretching vibrations of the urethane in associated form and also to the C=N stretch in the blocking agent MEKO. Other peaks related to Arkophob are N-H deformation overlapping with C=O stretching at 1511 cm^{-1}, and CH_2 bending vibration found in aliphatic compounds at 1458 cm^{-1}. [62] Concerning the drying and crosslinking temperatures, it is not seen a significant difference on the peaks and their intensity, when compared to 40 °C under vacuum, suggesting that adsorbed water molecules are present in very small amounts on the sample at both temperatures (band above 3000 cm^{-1} remains narrow indicating that is mostly related to N-H groups). Moreover, the isocyanate band (between 2200-2300 cm^{-1}) not appearing at 170 °C, lead to testing the sample at 245 °C, which can be considered the end of the range of unblocking in the DSC curve of Arkophob (Figure 28). At this temperature, the peak of isocyanate appears at around 2270 cm^{-1}, confirming the deblocking reaction by an elimination-addition mechanism, given that the elimination reaction leads to free isocyanate groups (Figure 23a-1). Furthermore, the peak not appearing at 170 °C is evidence that the unblocking rate is still very low at that temperature. The fact that no other visible peaks appear or disappear at the temperature of 245 °C, or even considerably change in intensity is also further evidence, that the range of 170 °C and 245 °C is only related to the unblocking reaction (secondary or degradation reactions will only occur at higher temperatures).

Concerning Arkophob coated on the knit (Figure 35) compared to the sample by itself (Figure 34), the main difference of the spectra corresponds to the intensity of the bands that are partially attributed to the cellulose (-OH groups of cellulose between 3000-3600 cm^{-1} and C-O stretching between 1000-1200 cm^{-1}) being higher on the knit. Pertaining to the peaks related to the H_2O adsorbed molecules found on the knit by itself (1620-1635 cm^{-1}), they are masked by the groups of Arkophob. These alterations of peak intensities associated with the cellulose of the knit, always occur when comparing the crosslinker by itself and coated on the knit.

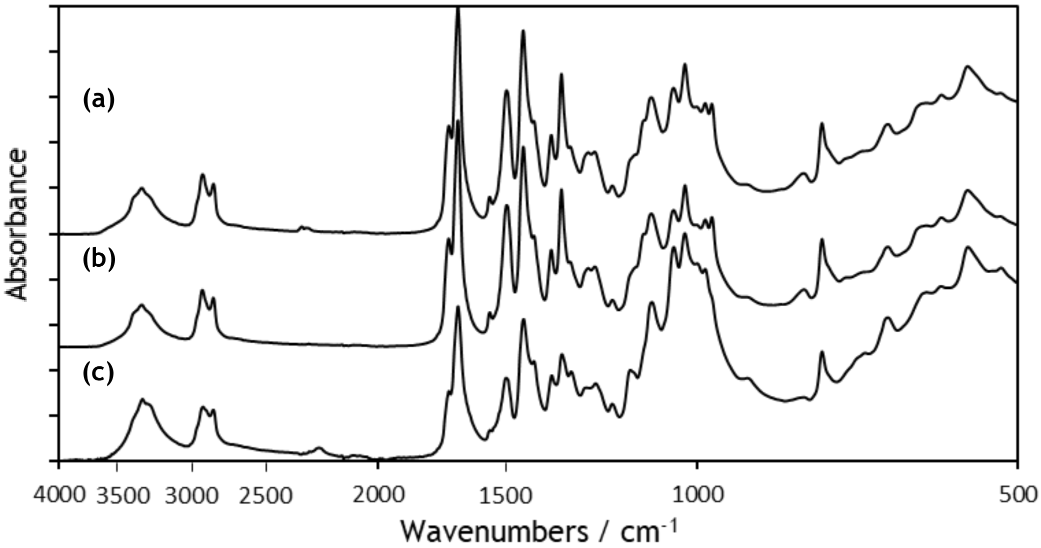


Figure 35 *- Normalized FTIR-ATR spectrum of Arkophob DAN New liq applied on the knit at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

Regarding the spectrum of Arkophob applied on the knit at the different temperatures, the main differences were found at 170 °C, where a peak appears at 2273 cm^{-1} (free isocyanate group), leading to the conclusion that the rate of the deblocking reaction is favoured by the crosslinker being inserted on the knit. Moreover, the cellulose related bands (3000-3600 cm^{-1} and 1000-1200 cm^{-1}) are considerably more intense when compared to 40 °C under vacuum and

120 °C, suggesting that at this temperature the detection of the compounds present on the knit was higher, due to Arkophob being more impregnated on the knit. Regarding the peaks of C=N of the blocking agent (1683 cm^{-1}), N-H (1512 cm^{-1}) and the C=O groups (1721 cm^{-1}, 1683 cm^{-1} and 1512 cm^{-1}) of Arkophob, the differences observed with the increase of temperature are not very clear, so an intensity (height) peak ratio analysis of the second derivative of the spectrum (Figure C-2) was performed. To compare the intensities of the peaks, the -CH_2 antisymmetric stretching peak (2920-2940 cm^{-1}) should be used as a reference, due to being a very stable band that must present approximately the same height at the studied temperatures. As it can be seen in Table 5, the ratio of the peaks (height of the peak at 120 °C or 170 °C divided by the height of the peak at 40 °C under vacuum) remains fairly similar, regardless of which ratio was analysed. At 120 °C, the ratio ranges between 1.02 and 1.05, and at 170 °C between 0.51 and 0.46, implying only very small amounts of free isocyanate groups react with -OH groups of cellulose at 170 °C, given the deblocking reaction is still starting.

Table 5 *- Intensity peak ratios (normalized second derivative absorbance) of the spectrum related to Arkophob on the knit.*

	Temperature (T) / °C	$\frac{I\_T_{CH_2}}{I\_40\,°C_{CH_2}}$	$\frac{I\_T_{C=O}}{I\_40\,°C_{C=O}}$	$\frac{I\_T_{C=O+C=N}}{I\_40\,°C_{C=O+C=N}}$	$\frac{I\_T_{N-H+C=O}}{I\_40\,°C_{N-H+C=O}}$
Arkophob on the knit	120	1.04	1.05	1.04	1.02
	170	0.49	0.51	0.50	0.46

The mixture of Arkophob DAN with the binder isolated, at different temperatures, is shown in Figure 36.

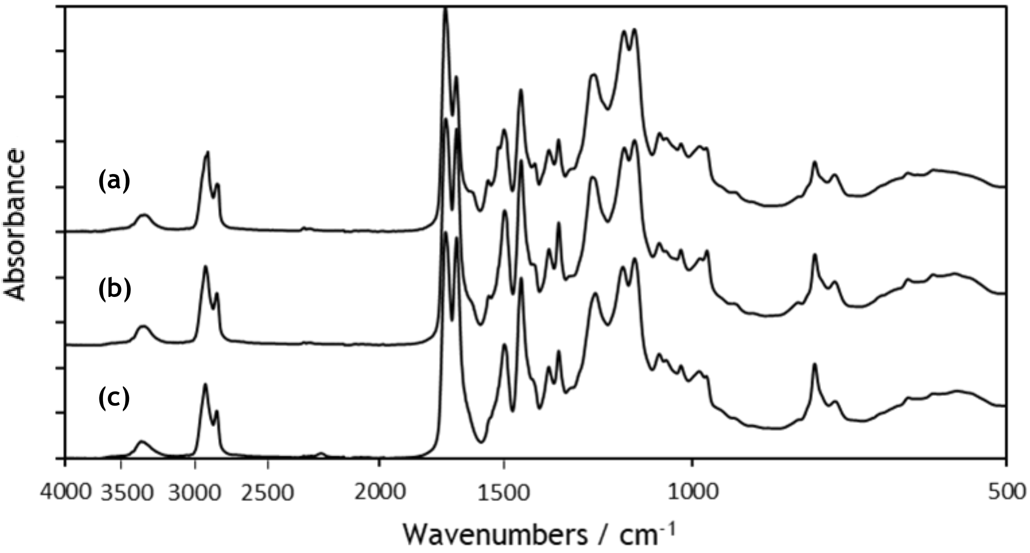


Figure 36 *- Normalized FTIR-ATR spectrum of the mixture of Arkophob DAN New liq with Impranil DLN isolated at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

In this scenario, a small isocyanate peak appears at 170 °C, suggesting Arkophob being mixed with Impranil increases the rate of unblocking, when comparing with Arkophob isolated. Furthermore, the N-H of the urethane component of the mixture is not overlapping with the C=O group. Instead, at around 1540 cm^{-1} the N-H peak appears and close to 1520 cm^{-1} it is seen the C=O peak (ampliation of the spectrum is presented in Figure C-4). The significant decrease of the intensity of N-H (1540 cm^{-1}) at the cure temperature is observed, corroborating that crosslinking is happening through those groups (Figure 25).

Regarding the mixture applied on the knit (Figure 37), at 120°C, a small peak of isocyanate appears (ampliation of the second derivative absorbance spectrum is seen in Figure C-3), and at 170 °C the band appeared at a higher intensity than the blend of Arkophob isolated (Figure 36), meaning the unblocking/crosslinking is favoured by applying the mixture on the knit. This can be explained by the fact that as a general rule, the relative reactivity of a primary hydroxyl against isocyanate is much higher than the N-H groups of the urethane component of Impranil. In the knit, crosslinking was mostly done through -OH groups, leading to allophanate/urea formation (Figure 26 a-2 and Figure D-1). In the case of the polymer mixture by itself (Figure 36), -OH groups can only be found in very small quantities (related to hydrolysis products), meaning that most of the reaction is performed through -NH groups, which also implies the formation of urea/allophanate bonds (Figure 25 and Figure D-1).[53] Furthermore, carbonyl stretching vibrations of the urethane functionality in nonbonded form overlap with C=O groups of Impranil DLN (1725-1730 cm^{-1}). Meanwhile, carbonyl stretching vibrations of the urethane functionality in associated form (1681 cm^{-1}) overlap with C=N of MEKO, and increase significantly in height at the drying temperature and then slightly increase at the crosslinking temperature, corroborating allophanate/urea formation. Concerning the peak of N-H stretching of Impranil in the band between 1515-1520 cm^{-1}, it is clearly smaller at 170 °C, which indicates that crosslinking is occurring through the N-H groups of the urethane component of the binder, proving that even on the knit this crosslinker has a high affinity to these groups.

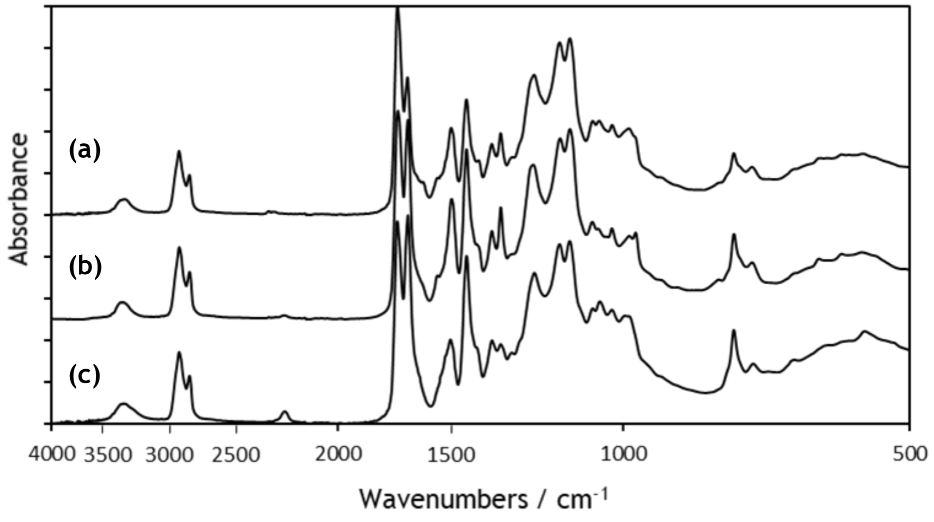


Figure 37 *- Normalized FTIR-ATR spectrum of the mixture of Arkophob DAN New liq with Impranil DLN applied on the knit at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

- **Imprafix 2794**

Regarding Imprafix 2794, in Figure 38, it is illustrated the spectrum at different temperatures of the crosslinker by itself.

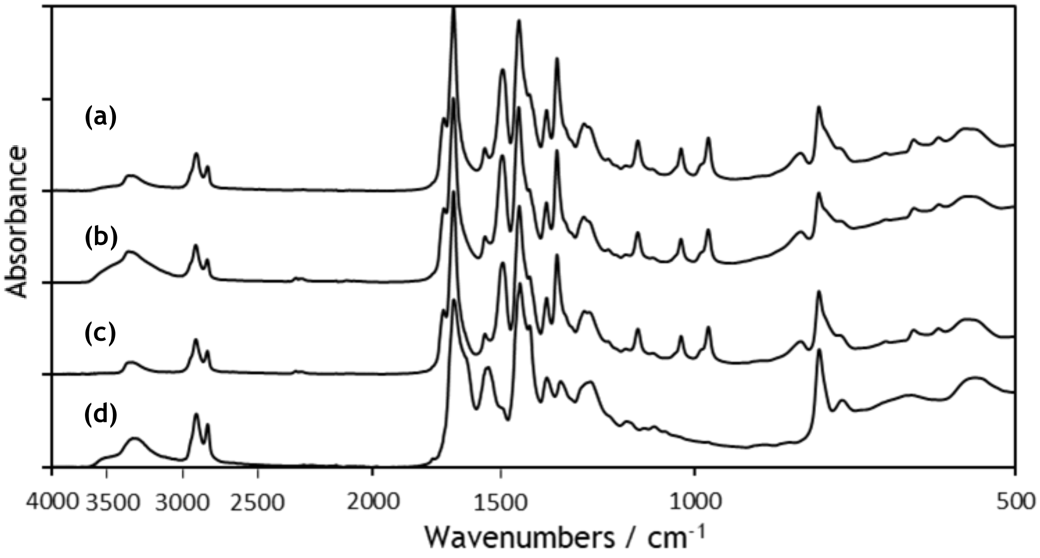


Figure 38*- Normalized FTIR-ATR spectrum of Imprafix 2794 isolated at (a) 40 °C under vacuum, (b) 120 °C, (c) 170 °C and (d) 245 °C.*

At 40 °C under vacuum, it is seen N-H stretching at 3356-3385 cm^{-1}, peaks at 2927 cm^{-1} and at 2857 cm^{-1}, related with -CH$_2$ antisymmetric stretching and -CH$_2$ symmetric stretching, respectively. The isocyanate band does not appear at any of the studied temperatures, so the sample was also tested at 245 °C, which is significantly above the boiling point of the blocking agent (218 °C at 1 bar). Even at that temperature, the peak did not appear, suggesting an addition-elimination mechanism is prevailing (Figure 24). The nucleophilic group, that will react with Imprafix, for the addition reaction to occur, can be associated with free -OH groups of the hydrolysis products, given that at 120 °C, the band above 3000 cm^{-1} is much broader than the one at 40 °C under vacuum or at 170 °C (-OH groups overlapping with N-H groups). At 245 °C, that band also being broad, could be due to poor baseline correction of the spectrum. Most of the other peaks observed at 245 °C are considerably smaller or disappear, which suggests thermal degradation of the polyisocyanate. Regarding the peak at 1716 cm^{-1}, it can be related to the C=N/C=C stretching of 3,5-DMP due to the peak being approximately constant at all temperatures, except at 245 °C, in which the peak disappears, implying the compound completely evaporated (at that temperature 3,5-DMP surpassed its boiling point). The peak at 1681 cm^{-1}, is related to the C=O of an amide (Figure 22). Pertaining to the peak seen at 1510 cm^{-1}, it could be associated with N-H deformation overlapping with C-N stretching, and it remains similar at the studied temperatures, except at 245 °C, where it vanishes, due to thermal degradation of Imprafix.[63,64] Regarding the spectrum of the crosslinker inserted on the knit (Figure C-5), it is congruent with the analysis done to the spectrum of Imprafix by itself.

The spectrum of the mixture of Impranil and Imprafix isolated is seen in Figure 39.

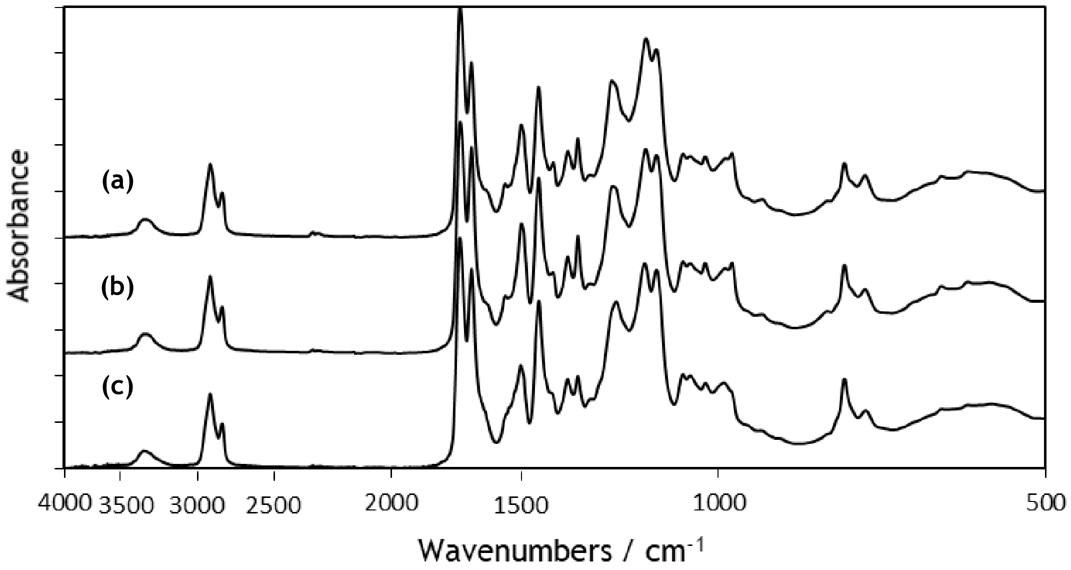


Figure 39 *- Normalized FTIR-ATR spectrum of the mixture of Imprafix 2794 with Impranil DLN by itself at 40 °C under vacuum, 120 °C, and 170 °C.*

As it can be seen in Figure 39, the peak of isocyanate did not appear, implying the occurrence of the addition-elimination mechanism. The peak at 1728 cm^{-1}, is related to the C=O of ester and urethane of Impranil, as well as the C=N/C=C of 3,5-DMP and it is not observed a major variation of intensity with the increase of temperature. The curing process is corroborated by the increase of the intensity (from 40°C to 120 °C) of the peak at 1686 cm^{-1} (formation of urea/allophanate), and the decrease of intensity at 170 °C of the peak related to N-H deformation (at around 1510 cm^{-1}), indicating crosslinking through N-H groups of the urethane component of Impranil. The same change of intensities of those peaks also occurs on the mixture applied on the knit (Figure C-6), however, at 120 °C and 170 °C very small traces of the isocyanate peak appear by assessing the normalized second derivative of the spectrum in that region (Figure 40). In this scenario, the addition-elimination mechanism is still prevailing, however, the elimination-addition reaction also occurs, at a low reaction rate.

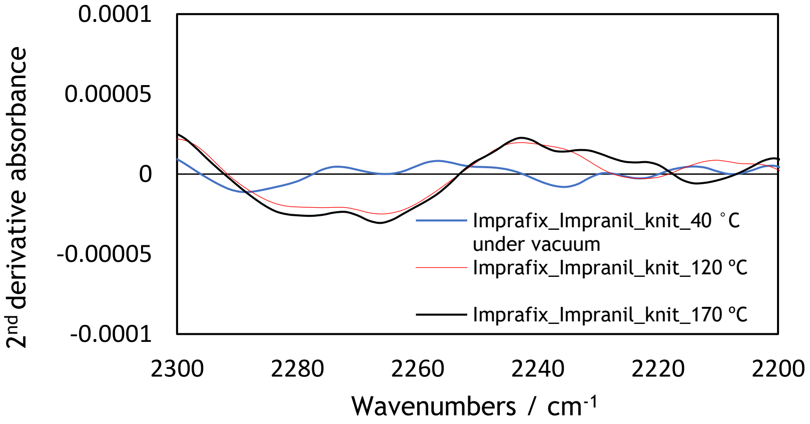


Figure 40 *- Normalized FTIR-ATR spectrum of the mixture of Imprafix 2794 with Impranil DLN applied on the knit at 40 °C under vacuum, 120 °C, and 170 °C.*

- **Acrafix EP 6047**

Concerning the polycarbodiimide dispersion (Acrafix EP 6047), the spectrum of the polymer by itself, at different temperatures can be observed in Figure 41.

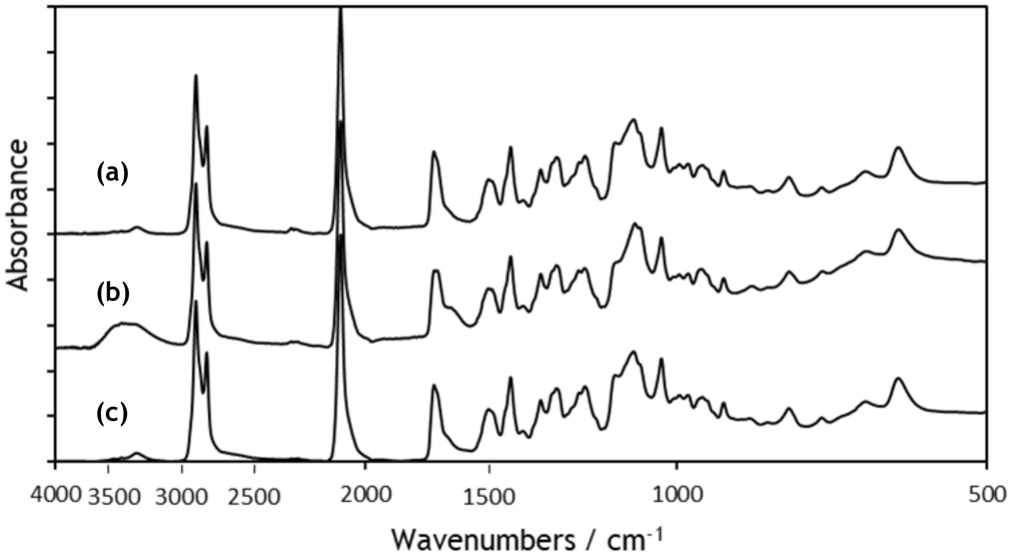


Figure 41 *- Normalized FTIR-ATR spectrum of Acrafix EP 6047 by itself at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

At 40 °C under vacuum, it is found a small N-H stretching band at 3332 cm^{-1}, when compared to the same band found in the other crosslinking agents. That band could be related to an R-group of the dispersion. At 120 °C, that band is broader and more intense, which could be related to hydrolysis products due to water molecules being adsorbed in the mixture. Furthermore, the shift of the peak to around 3450 cm^{-1} at the drying temperature, indicates that the hydrolysis products would only be related to -OH groups (carboxylic acid stretch should be centred at 3000 cm^{-1}). The very intense N=C=N peak of the polycarbodiimide (2114 cm^{-1}) can be found at all temperatures, proving there is no blocking agent associated with the crosslinker. Other peaks found in the spectrum are at a relatively low intensity when compared to the other crosslinkers evaluated, such as the C=O stretching vibration (1717 cm^{-1}) of an R-group of Acrafix EP 6047. On the region of 1300-1520 cm^{-1}, those peaks could be attributed to C-H stretching found in aliphatic compounds, however, it cannot be confirmed this compound is aliphatic, especially considering the fact that a peak appears at 608 cm^{-1}, which could be related to aromatic compounds. In the case of the sample on the knit (Figure C-7), the same observations are made, however, the band height of the peak at around 3335 cm^{-1} is similar across all temperatures, due to the -OH peaks of cellulose overshadowing any potential hydrolysis products that could have happened at 120 °C.

The experiment made with the mixture of Acrafix and DMF (Figure 27d-2) proved that at 170 °C, no crosslinking occurred. The main question is if crosslinking happens at 120 °C. In the spectrum of the mixture of the crosslinker with Impranil by itself (Figure 42) and applied on the knit (Figure 43), it is not possible to assess the change of the intensities of the peaks, given that the CH_2 reference peak (2920-2925 cm^{-1}) height varies considerably when changing the temperature of analysis. The intensity of the CH_2 band should be similar at any of the studied temperatures, given that the amount of CH_2 groups does not change with the increase of temperature. As it can be seen in Table 6, a ratio analysis was done (second derivative spectra of the mixtures are seen in Figure C-8 and Figure C-9) between the N=C=N peak (1116 cm^{-1}) and the reference CH_2 peak. In all cases, the ratio regarding the N=C=N group is similar to the ratio concerning the CH_2 peak, indicating no cure reaction occurred (no evidence of consumption of free carbodiimide groups at 120 °C). The slight differences of the peak height ratio (when comparing the CH_2 peak ratio with the N=C=N peak ratio), can be attributed to slight variations of the mixing ratio of the blend. To occur crosslinking, the carbodiimide peak intensity would have to decrease significantly at 120 °C, so it can be concluded Acrafix EP 6047 does not crosslink with Impranil. Moreover, the absence of crosslinking corroborates the conclusion obtained from the analysis of Figure 41, that the potential formation of hydrolysis products at 120 °C, would only be related to -OH groups (instead of -COOH groups).

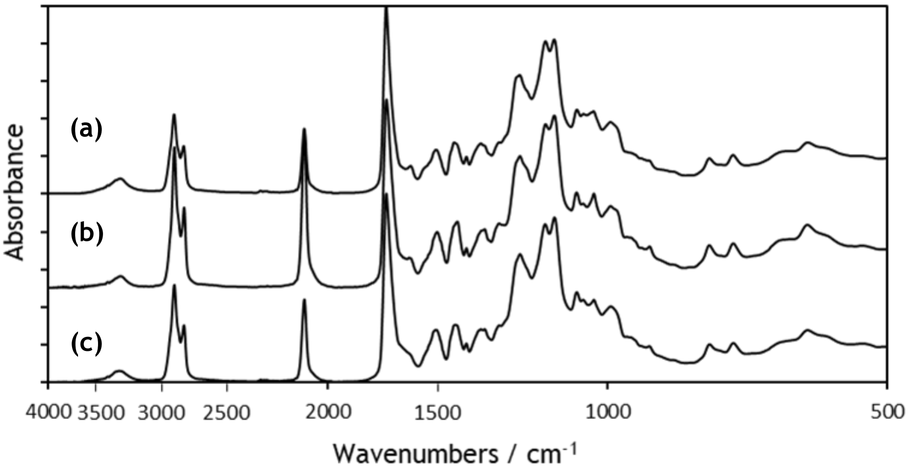


Figure 42 *- Normalized FTIR-ATR spectrum of the mixture of Acrafix EP 6047 by itself at (a) 40 °C under vacuum, (b) 120 °C and (c) 170 °C.*

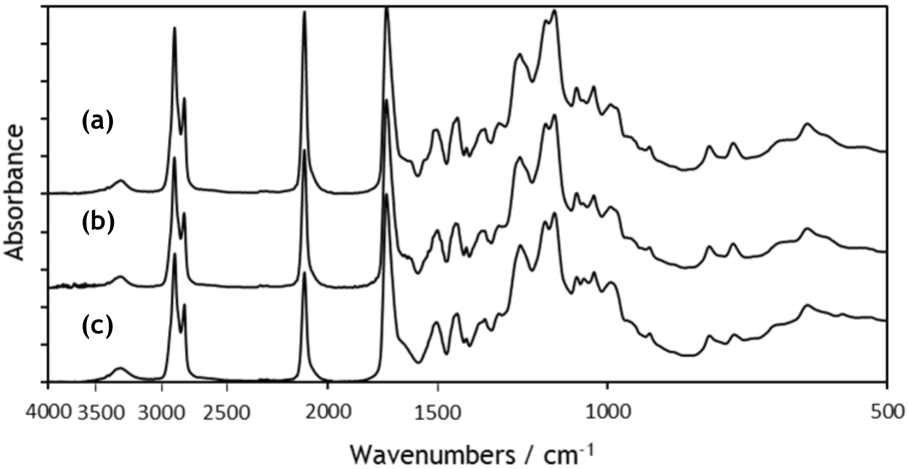


Figure 43 *- Normalized FTIR-ATR spectrum of the mixture of Acrafix EP 6047 applied on the knit at (a) 40 °C under vacuum, (b) 120 °C and (c) 170 °C.*

Table 6 *- Intensity peak ratios of the normalized second derivative spectra related to the mixture of Acrafix EP 6047 and Impranil DLN-SD.*

	Temperature (T) / °C	$\frac{I\_T_{N=C=N}}{I\_40\ °C_{N=C=N}}$	$\frac{I\_T_{CH_2}}{I\_40\ °C_{CH_2}}$
Mixture of Acrafix EP 6047 with Impranil DLN by itself	120	1.72	1.75
	170	0.93	0.97
Mixture of Acrafix EP 6047 with Impranil DLN applied on the knit	120	0.75	0.70
	170	0.60	0.65

4.5 Coating formulation and operation conditions optimization

The results obtained from the experiments performed at FEUP made it clear that Acrafix EP 6047, was not a suitable crosslinker for the coating formula, so the only crosslinkers tested at Tintex were Imprafix 2794 and Arkophob DAN New liq. Before optimizing the complete formulation, several tests were employed with the binder, thickener, and crosslinker, which are analysed in Appendix F.

The supplier does not specify the amount needed of thickener to achieve the requested viscosity for a coating application. In order to know the necessary amount, it was added a small amount of thickener to the blend. In case it was not visually identifiable after a few minutes that the desired viscosity was achieved, the process was repeated until the viscosity of the blend achieved was between 30-35 dPa·s. After knowing the necessary amount of thickener, it was then needed to produce the sample with constant time and velocity of agitation of the mixture before and after adding the thickener, in which the blend was being stirred. This last step is essential to ensure the reproducibility of the results and is a method that Tintex can apply in future formulations. After several attempts, the conditions of operation optimized were 5 minutes at 300 RPM before adding the thickener to the blend and 13 minutes at 450 RPM after adding it. The parameters evaluated to ensure those conditions are optimal can be seen in Table 7.

Considering that in all trials, the values of the foam density as well as the viscosity after adding the thickener are within the range recommended (30-35 dPa·s) and the coefficient of variation (CV), which is the standard deviation (σ) divided by the arithmetic mean of the results, is significantly below 30% for any of the measurements, these conditions of operation are appropriate.[65]

The formula was then studied with Imprafix, instead of Arkophob, which lead to tweaking the mass fraction of each component (Table F-2), due to being needed a slightly higher amount of thickener (0.57% instead of 0.53%) to achieve a blend with the desired viscosity. Moreover, the conditions of operation remained the same before employing the thickener, however, they were changed to 15 minutes at 450 RPM, given that a higher amount of thickener, results in the lumps present in the blend taking more time of stirring to completely disappear from the mixture. In Table 8, there are also presented the values for each trial of the parameters studied as well as the coefficient of variation, and given they obey the criteria applied to Arkophob these conditions are also valid.

Table 7 *– Parameters evaluated of the formula containing Arkophob.*

Trial	**Foam density / g·L^{-1}**	**Viscosity of the blend / dPa·s**	
		Before adding the thickener	**After adding the thickener**
1	362	1.15	32.5
2	380	1.23	31.8
3	378	1.25	30.2
CV / %	2.16	3.57	3.06

Table 8 *- Parameters evaluated of the formula containing Imprafix.*

Trial	**Foam density / g·L^{-1}**	**Viscosity of the blend / dPa·s**	
		Before adding the thickener	**After adding the thickener**
4	363	0.64	33.4
5	371	0.69	34.9
6	390	0.59	30.1
CV / %	3.02	6.38	6.11

In Figure 44, it is illustrated a sample of the original formulation after 1 week and 3 months of being applied, as well as a sample after 1 week of being applied, where the crosslinker was Imprafix. Due to time constraints, and not being possible to use the required equipment to perform a complete analysis of the coating system, it was only performed a superficial analysis that is somewhat similar to what is done at Tintex for rapid evaluation, on which is the best coating to iterate upon. The fingernail test, which is one of the parameters evaluated, is a simple way to evaluate the fingernail deformation of the material, in which the nail is applied to the coating, and it is observed how fast can the material recover its original form. Regarding the colour of the material analysed it remained white, in all scenarios (as it can be seen in Figure 44, only variations on the tone of the colours are observed).

Regarding the samples that contain Arkophob, it is observed that the one exposed to ambient moisture levels for a long time presented the worst results. By slightly applying force with the nail on the coating the recovery time, was instantaneous on the newer sample and considerably longer in the coating analysed after 3 months of being produced. Increasing the force applied, resulted in the older coating being the only one not able to recover its form.

The sample, in which the crosslinker of the formulation is Imprafix, presents a lower recovery time than the older sample containing Arkophob, and a higher recovery time than the newer sample of Arkophob. By applying higher intensity (with the fingernail), on the coating, the sample recovered its original form. Regarding the handfeel of the coating, it is a subjective matter, so it would be needed to perform an extensive statistical analysis with different subjects to properly characterize the coating. Nonetheless, it can be said that all samples presented a soft handling.

In order to improve the coating material, it was also attempted to optimize the drying and crosslinking temperature of operation, and respective times of operation. In both scenarios, the drying temperature was changed to 90 °C and the time increased to 4 minutes.

Concerning the cure temperature of the blend of Arkophob it was increased the temperature, due to the crosslinking range seen in the DSC test (Figure 28) going up to 245 °C. It can be observed in Figure 45a-2, that performing a temperature ramp that started at 150 °C and ended at 210 °C after 6 minutes of heating, resulted in the yellowing of the mixture and a reduction of the mass of the coating (noticeable decrease of the coating thickness). Changing the conditions to 3 minutes of heating that start at 170 °C and end at 195 °C, prevented the yellowing (Figure 45a-3), however, the loss of mass still happened. The occurrence of degradation or secondary reactions at higher temperatures than 170 °C, as well as evaporation of compounds (including the foaming agents, the foam stabilizer and the thickener) of the mixture, limit the options of optimizing the cure temperature. Concerning the handfeel of the coating, it was rough (especially in the sample heated up to 210 °C), instead of the soft and delicate touch of the other samples analysed (Figure 44).

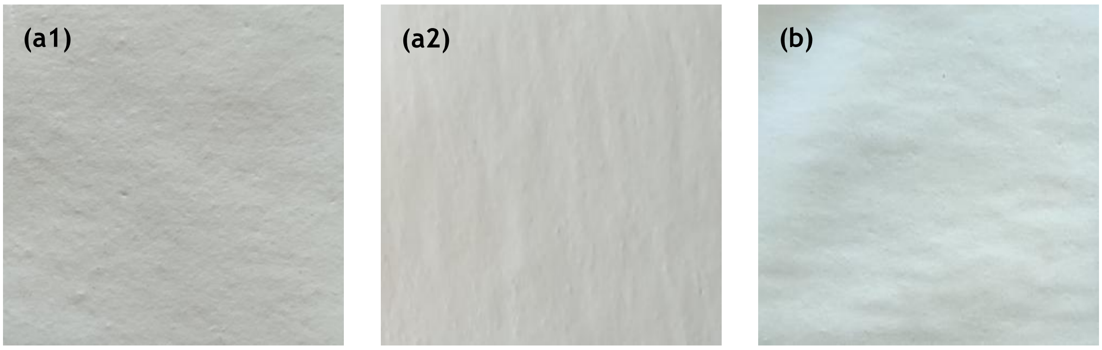


Figure 44 *– Sample of the complete formulation containing Arkophob after (a1) 3 months of application and (a2) 1 week of application. (b) Sample of the complete formulation containing Imprafix after 1 week of application.*

Regarding the cure temperature of the mixture with Imprafix, it was obtained a sample (Figure 46a-2) by performing a temperature ramp from 125 °C to 150 °C and the time of operation was 10 minutes. The rate of heating in the Mathis Labcoater is not constant, so it can only be affirmed that it took 140 seconds for the temperature to reach 150 °C. The decrease of the maximum temperature from 170 °C to 150 °C and increase of time of heating lead to an improvement of the fingernail deformation when compared to the original conditions (faster recovery time at low intensity of application, and recovered its form at higher intensity), however the material did not recover its properties as fast as the experiment related to the newer sample of Arkophob, in the original conditions. Nonetheless, the fact that a formulation that was designed with Arkophob in mind, lead to very similar results, when changing the crosslinker to Imprafix, it is a clear indicator that adjusting the type or the quantities of the foaming and stabilizing agents of the formulation to take into account the change of crosslinker, will undoubtedly improve the final product.

The preliminary tests done at Tintex (Appendix F) also corroborate this conclusion, due to the fact that it was required a slightly higher mass percentage of thickener to achieve the desired viscosity (30-35 dPa·s) in the case of the complete formulation with Imprafix, even though the viscosity of the mixture binder/crosslinker/thickener, in the same proportion, was considerably higher when Arkophob was the crosslinker (63.3 dPa·s), instead of Imprafix (45.7 dPa·s). The interference of the additives in the viscosity of the mixture is noteworthy, suggesting an optimization of these agents to the properties of Imprafix, would yield the best coating system.

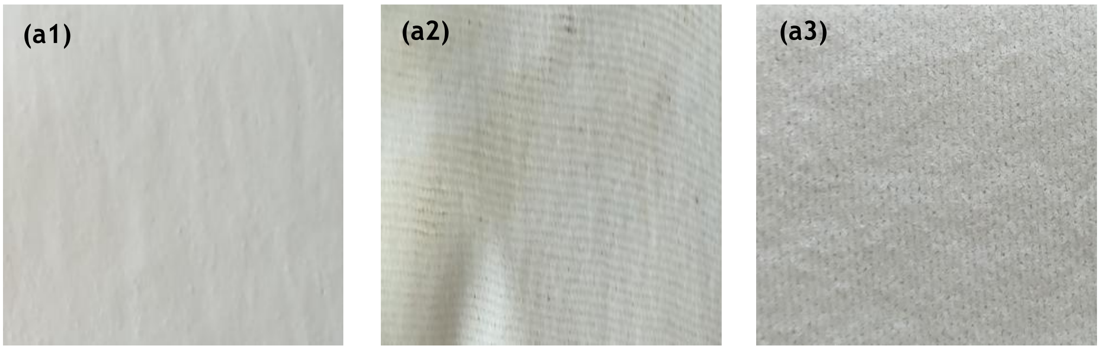


Figure 45 *– Sample containing Arkophob after 1 week of application at different drying and crosslinking conditions. (a1) - 120 °C (3 min) and 170 °C (4 min). (a2) - 90 °C (4 min) and 150 °C up to 210 °C (6 min). (a3) - 90 °C (4 min) and 170 °C up to 195 °C (3 min).*

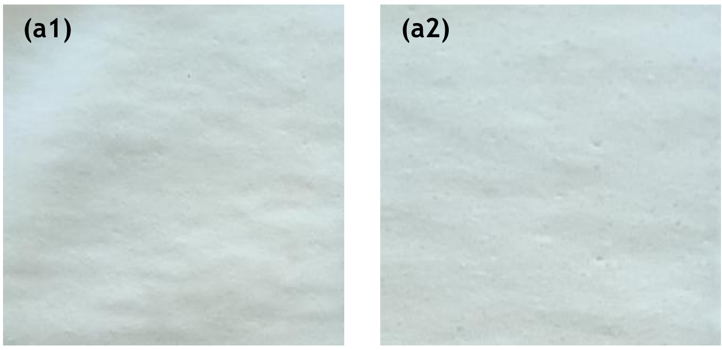


Figure 46 *- Sample of the formulation containing Imprafix after 1 week of application, at different drying and crosslinking conditions. (a1) - 120 °C (3 min) and 170 °C (4 min). (a2) - 90 °C (4 min) and 125 °C up to 150 °C (10 min).*

5 Conclusion

This project was divided in two phases. The first one consisted on characterizing the components of a model textile coating system, namely the binder, several crosslinkers that could crosslink with the binder, and the substrate, as well as studying the relations between them by performing several characterization techniques (DSC, TGA, FTIR-ATR analysis and evaluation of crosslinking at 170 °C with the binder, by recurring to DMF). The second phase of this work was related to optimizing the whole system (with all the components) at Tintex, by evaluating the velocity and time of stirring of the blend before and after adding the thickener, the drying and crosslinking temperature of operation (and respective times). An analysis of the properties of the coatings yielded, allowed the assessment of the best coating system.

Concerning the first phase of the dissertation, it was concluded that Acrafix was the only crosslinker not able to crosslink with the binder. Imprafix and Arkophob both are able to crosslink through the N-H groups of the urethane component of Impranil, however, they also react with the -OH groups of the knit, meaning that both unblocking and crosslinking reactions were favoured by the knit employed, and the adhesion between the layers is improved, suggesting this substrate is a good option for the system analysed. However, if the system studied was Acrafix with a binder able to crosslink with it through carboxyl acid groups (e.g. acrylic polymer), then the substrate studied would not be a good option, due to not reacting with Acrafix. In this scenario, choosing a substrate containing carboxyl acid groups, such as synthetic polyester would be a better alternative. Furthermore, it was also uncovered that Imprafix unblocks at a temperature around 120 °C through an addition-elimination mechanism. Meanwhile, Arkophob unblocks by an elimination-addition mechanism at higher temperatures, with a broad temperature range around 150-245 °C.

The second phase of the project, allowed to infer that Imprafix is a valid alternative to Arkophob, given that after optimizing the temperature and times of drying and crosslinking it was able to present similar characteristics to a formula, which was designed with Arkophob in mind. Furthermore, the higher temperature of unblocking of Arkophob does not allow much freedom in the optimization of the cure temperature, given that higher temperatures than the one suggested by the supplier, lead to a decrease of mass the coating, a change of the handfeel of the coating, and yellowing of the blend. Imprafix has a lower temperature of unblocking, meaning that the problems observed at higher temperatures are less likely to occur, which could potentially prove that it would be easier to develop a coating formula from scratch with this crosslinker, instead of Arkophob.

6 Assessment of the work done

6.1 Objectives Achieved

The focus of this dissertation was to understand the relations between the binder and the crosslinker, as well as the knit and the coating of a discontinued coating formula of Tintex Textiles, leading to an optimization of the coating components, not based on trial and error.

These objectives were achieved, however, there is still plenty of work that can be done in future dissertations at Tintex. In order to obtain the ideal coating, it is needed to optimize the additives of the studied formula. By performing a SEM (Scanning Electron Microscopy) analysis, it would be possible to infer how the thickening mechanism, as well as the foaming process, differs when changing the crosslinkers of the formula, which could result in a change of the type of additive and the quantities employed of each additive. Regarding the knit made of 100% cotton, it was possible to infer its function in the system, however, it was not tested other types of substrates that Tintex utilizes in their coatings, such as synthetic polyester. The study by FTIR-ATR, of the system analysed (binder/crosslinker), applied on the non-treated knit, could also be important to understand if the softener employed by Tintex, on their cotton knits, is improving the hydrophilicity of the knit, as well as its adhesion to the coating.

Furthermore, the optimization of the coatings applied at Tintex Textiles could be improved by performing a dynamic mechanical analysis (DMA), resistance to abrasion, rubbing and adhesion tests to the system analysed. Moreover, the analysis of other binder/crosslinker systems, available at Tintex Textiles, should also be a major component of the work of future dissertations at the company. For instance, the combination of the polycarbodiimide dispersion (Acrafix EP 6047) with other types of binders can turn this crosslinker into a staple of Tintex Textiles.

6.2 Final Assessment

This dissertation was the first one done at Tintex Textiles, that was related to chemical engineering. This fact associated with the ongoing pandemic, made it very hard to set a clear path of the work to be done, leading to weekly assessments of the current situation of the dissertation. The restrictions of access to the equipment (due to COVID-19) that were presented in FEUP and Tintex, lead to a considerably less amount of time to achieve the desired experiments. Nonetheless, I believe this work was a success, given that this dissertation set the groundwork for future dissertations at the company, and can redefine the future of coating development at Tintex Textiles. On a personal level, this dissertation improved my approach to any type of adversity that stands on my way.

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8 Annex A – Tintex Textiles processes

There are several processes that Tintex employs in their substrate (e.g. cotton fabric), before the coating is inserted into it. Firstly, the company prepares a fabric to be dyed, that will adhere well with the coating material. The preparation consists on folding and whitening the fabric (bleaching), which usually presents the colour beige.

8.1 Dyeing

Dyeing consists of providing colour to the substrate as uniformly as possible. The colour of the textile is matched with a pre-selected colour, that should resemble the reference utilized, and not present variation in the shade over the textile. Several methods can be employed to achieve the desired aesthetic, such as exhaust dyeing (technique adopted by Tintex), continuous dyeing and printing.[66]

In exhaust dyeing (batch), auxiliaries can be used that enhance the uniformity of the textile. After inserting them into the dyebath, a certain amount of time is needed for them to spread evenly in the substrate surface. Then, it is added the dye, which is allowed time to circulate, before the temperature is raised to ensure the dye uptake is consistent throughout the textile. The process in due course will achieve equilibrium, and, hence, the dye concentration in the fibre and the dyebath will barely change. When the concentration of the dye in the dyebath is low, it is expected that the adsorbed dye has diffused uniformly along the textile. If any anomaly is observed, like not achieving the desired shade, small amounts of dye are added. Tintex employs this technique by recurring to pressurized jet dyeing machines, where the dyebath is inserted into the textile. A typical dyeing profile is shown in Figure AN-1.[66]

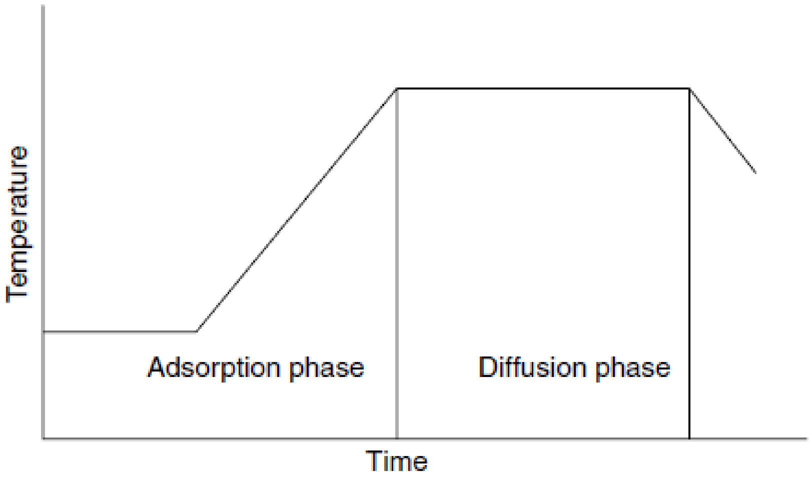

Figure AN-1 *- Typical dyeing profile. Extracted from [66].*

As the name implies, in continuous dyeing, providing the desired shade of colour to the textile, and fixating the dye is done continuously and simultaneously. The dye can either be printed onto the substrate or the textile is immersed in the dyebath. Excesses are removed by squeeze rollers (padding).[66]

Concerning the printing of textiles, ink-jet printing is becoming more popular than rotary screen printing, due to no problems being found when printing with soluble dyes for substrates such as cotton, nylon and wool. Direct-printing is the most employed method, whereby the dyes are applied as a paste containing thickeners and auxiliaries.[66]

8.2 Anti-pilling

A major problem of fabrics, especially the ones formed from spun yarns is pilling. Pills correspond to chunks of tangled fibres that are seen on the fabric surfaces during wear or laundering. They lead to poor handfeel and appearance of the textile.

This issue is widely found in cotton fabrics, which means Tintex must prevent pills accumulation on the textile surface, recurring to a bio finish. Due to enzymes being able to boost certain chemical reactions of organic materials, this chemical finish is able to ensure a decrease of the fibre strength, which provokes the pills to fall off from the fabrics, immediately after being formed. Cellulases, hemicellulases and pectinases are common catalyzing agents, that make possible the detachment of all the fibres that are not tight in the yarns.[67]

8.3 Drying

Tintex requires drying in their textile finishing operations, due to the need to remove water from the dyed textile. That water is then converted to vapour, which must be relocated, in order to not affect the textile properties. The process of drying directly impacts the quality of the final product and is costly, due to demanding a significant amount of energy.[68]

The first stage of this method is aimed at removing the water content mechanically attached to the fibres, by employing hydro-extraction. This is the cheapest method because it is a non-thermal process, meaning no heating costs are involved. Several methods are available like squeezing, centrifugation and steam pressure (jet force). Tintex opts to squeeze the textile, utilizing a padding machine through two or three rollers involved with a rubbery material.[69]

Meanwhile, in the second step, the fabric should be completely dry. A stenter machine is employed for this stage. In this equipment, the fabric is conveyed through the machine in open width (with precise control). A hot current of air is blown along the textile, resulting in the evaporation of the water. Besides the drying of the textile, stenters are also useful for the application of several types of finish, which alter the aesthetic and handle of the fabric.[68]

8.4 Finishes

Chemical softeners are now widely utilized on textiles to make them supple, pliant, sleek and fluffy. The textiles also become easier to process, and present improved wearability. Even though the softness of the textile is quite a subjective matter, there are physical parameters that help quantify it, such as elasticity, compressibility and smoothness of the material.[33,70]

Tintex most usual softener is Hydroperm RPU New liq c, which consists of a non-ionic thermo-reactive polyurethane resin. Besides being a softening agent, this substance is also responsible for producing hydrophilic finishing effects on the substrate, which is the main reason Tintex utilizes this compound. The physical arrangement of the softener on the textile depends on its ionic character, as well as the relative hydrophobicity of the fibre surface. Given this substance is non-ionic, its orientation varies with the type of the fibre employed, meaning the hydrophilic portion of the softener is attracted to hydrophilic surfaces and the hydrophobic segment prefers hydrophobic surfaces. A scheme of the orientation of a non-ionic softener is displayed in Figure AN-2.[33]

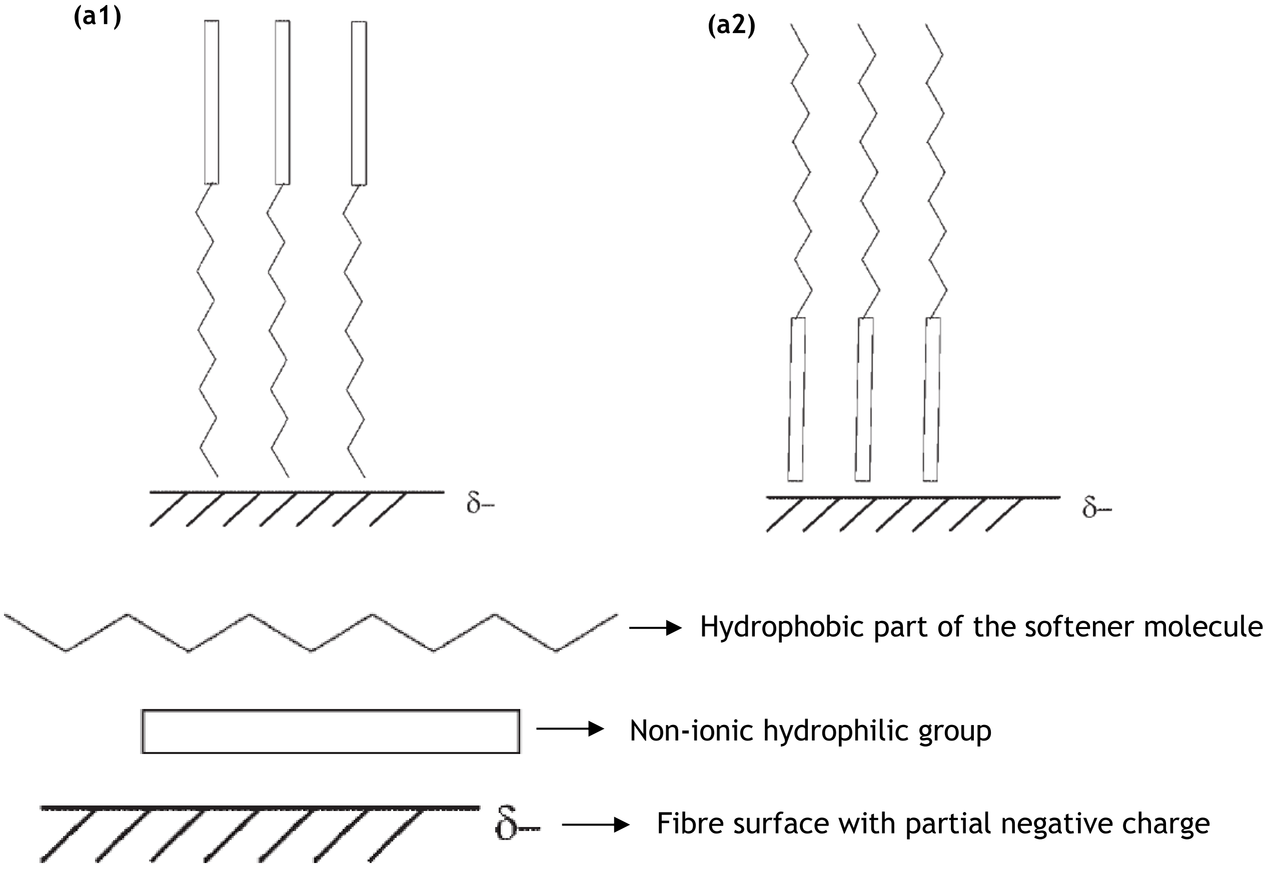

Figure AN-2 *- Schematic orientation of non-ionic softener at a hydrophobic (a1) and a hydrophilic (a2) fibre surface. Adapted from [33].*

Other types of finishes that are employed by Tintex on the substrate, are lamination and mercerization.

Concerning mercerization, it is regarded as a pretreatment for wet processing steps like durable press finishing and enzyme treatments. This technique is utilized for treating cotton yarns, by means of a caustic soda solution. The fibre swells, leading to increased lustre, tensile strength, dimensional stability and dyeability (in terms of uniformity and colour yield).[33]

Regarding laminating, this method consists of applying an adhesive coating to the surface of the main substrate, bringing the secondary substrate together with an adhesive layer. This three-layer system is heated at an appropriate pressure, forming the final laminate.[33]

9 Appendix A - Illustrative photos of the equipment employed

In this Appendix, it is presented most of the equipment needed to perform all the experiments related to this dissertation.

9.1 Producing of coating samples

In Figure AP-1 is presented the scale utilized in Tintex, the stirrer (IKA EUROSTAR 20 digital) needed to mix all the ingredients, and the device used to measure viscosity (Viscotester VT02), with rotor one employed. Figure AP-2 illustrates the feeler gauge set used, to adjust the coating thickness. The dryer and laboratory coating table is shown in Figure AP-3.

Figure AP-1 *– (a1) Scale used to weight the coating ingredients, (a2) stirrer utilized to mix them, and (a3) viscotester employed to measure the viscosity of the blend.*

Figure AP-2 *- Feeler gauge set employed to measure coating thickness.*

Figure AP-3 *- Mathis Labcoater type LTE-S.*

9.2 Preparation of samples at FEUP

Regarding the experiments associated with chemical characterization, in Figure AP-4 is shown the film applicator utilized to prepare the samples, in different perspectives. Figure AP-5 shows the vacuum laboratory oven, whereas Figure AP-6 presents both ovens that were not operated in low vacuum.

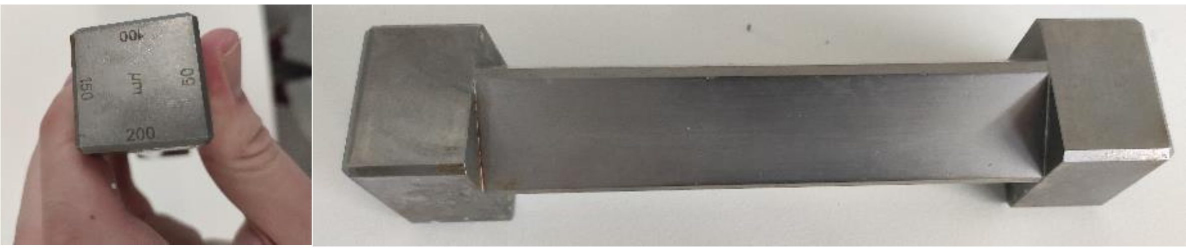

Figure AP-4 *- Different views of the film applicator employed.*

Figure AP-5 *- Vacucell oven.*

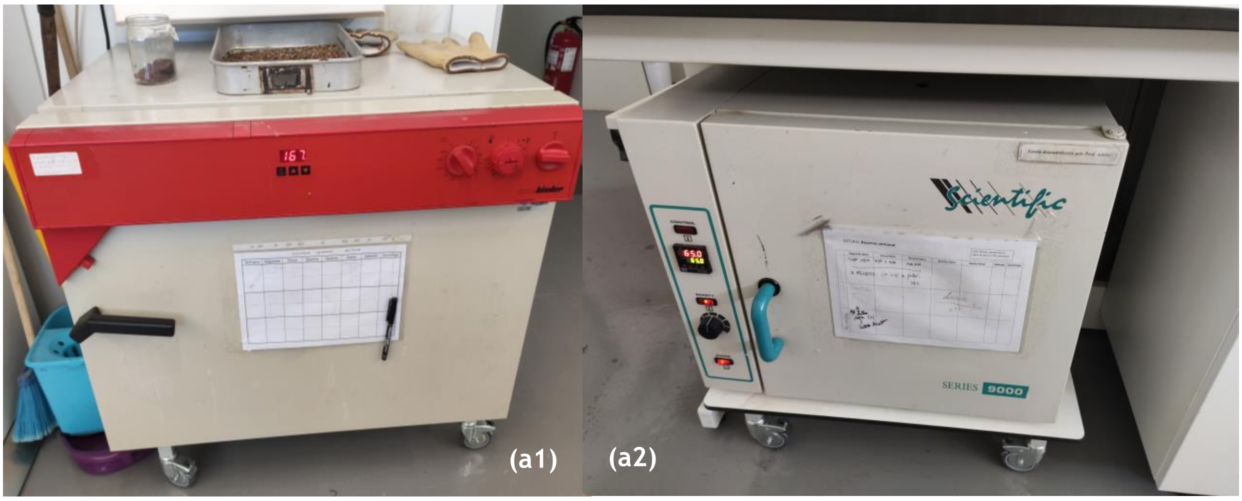

Figure AP-6 - Laboratory ovens. (a1) Wtc binder. (a2) Scientific series 9000.

9.3 Chemical characterization equipment

Figure AP-7 displays the DSC equipment employed in the experiments, as well the device needed to create a hole in the pan utilized, allowing the evaporation of compounds. The STA equipment needed to obtain a TGA curve of the substances analysed, and a less precise STA-DSC curve is shown in Figure AP-8. The spectrometer utilized during the dissertation is presented in Figure AP-9.

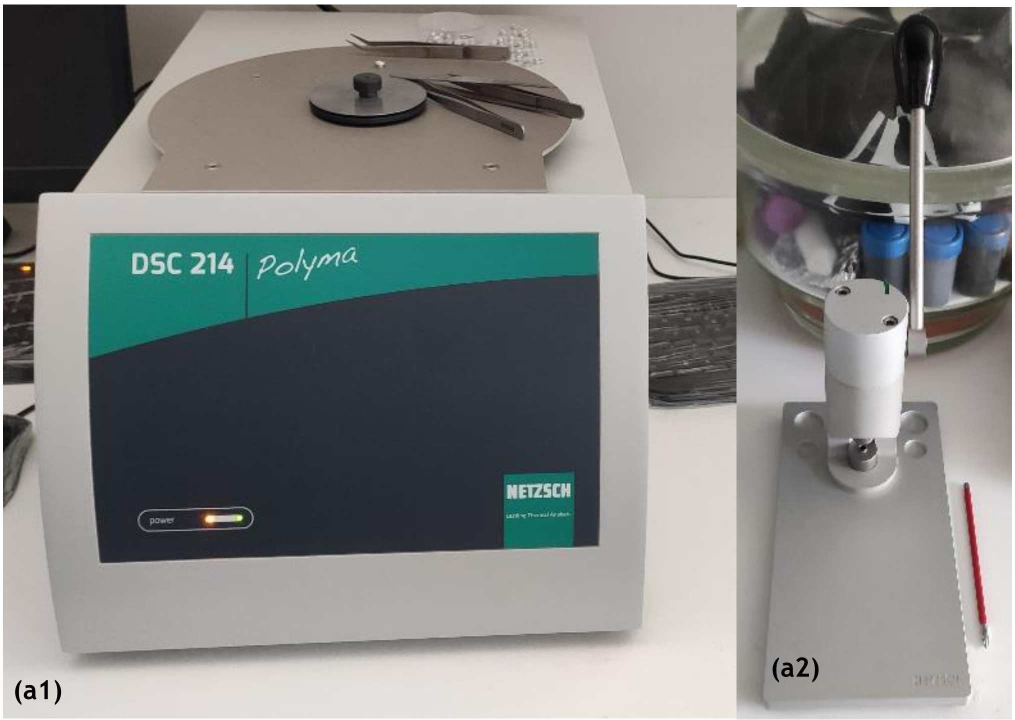

Figure AP-7 *– (a1) DSC 214 Polyma (NETZSCH) calorimeter. (a2) Device employed to create a hole on the pan.*

Figure AP-8 *- STA 449 F3 Jupiter (NETZSCH) equipment.*

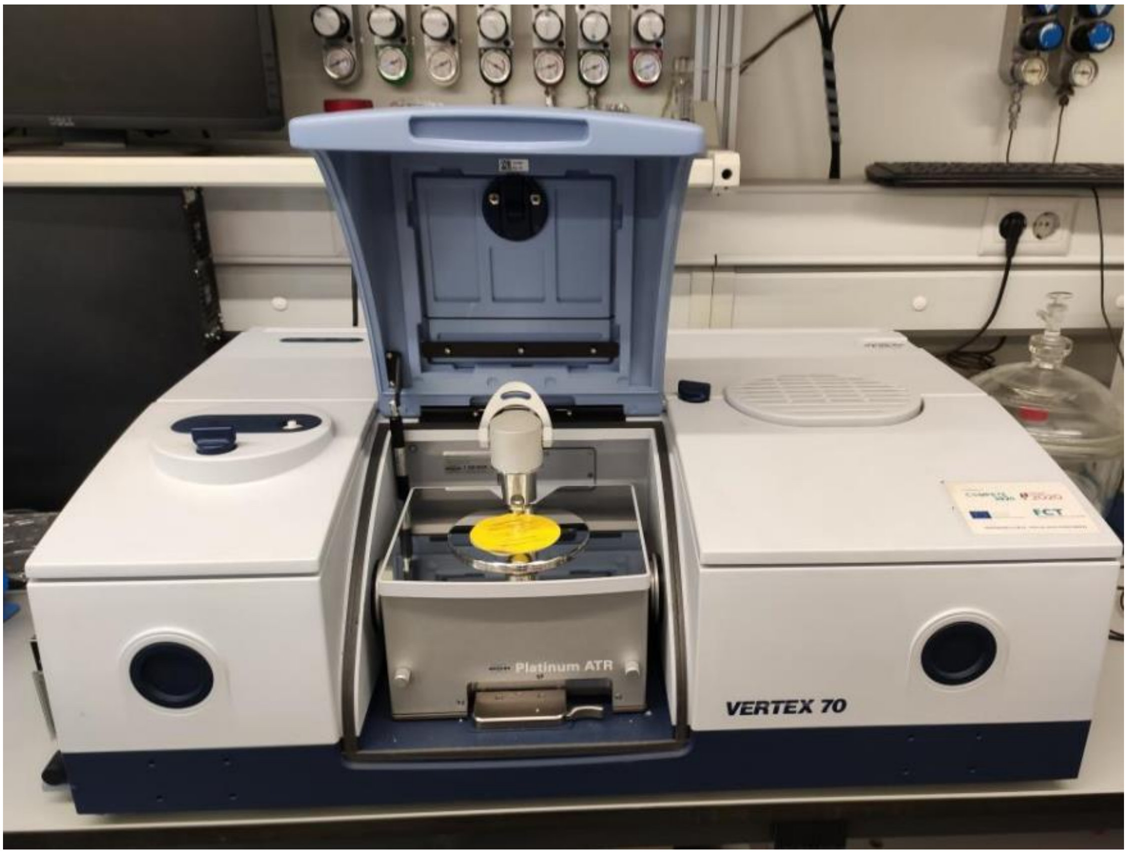

Figure AP-9 *- VERTEX 70 FTIR spectrometer (BRUKER).*

10 Appendix B - Thermal analysis

The DSC curve of Imprafix 2794 done in the STA equipment is illustrated in Figure B-1.

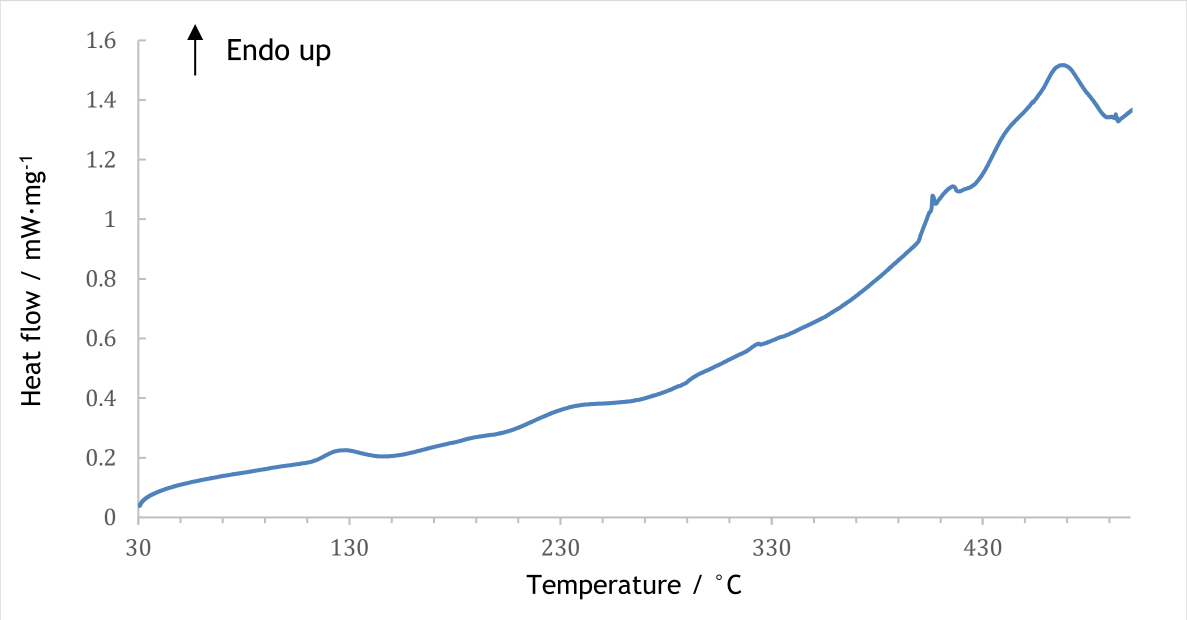

Figure B-1 *- DSC curve of Imprafix 2794 measured in the STA equipment.*

The TGA curve of Impranil DLN-SD performed in the STA equipment is illustrated in Figure B-2.

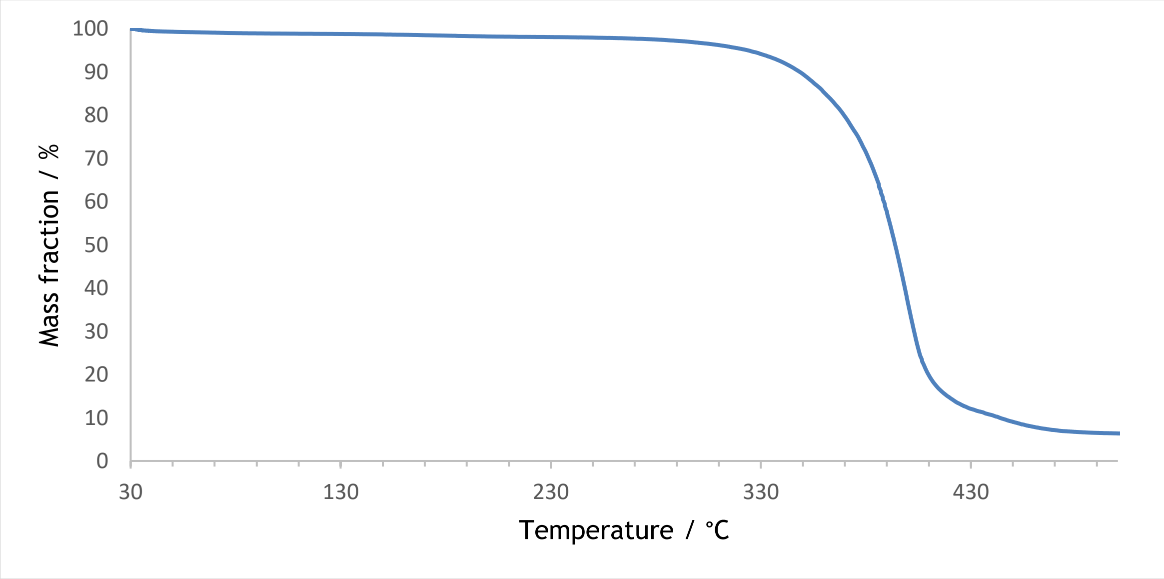

Figure B-2*- TGA curve of Impranil DLN-SD.*

11 Appendix C - FTIR-ATR spectra

Figure C-1 presents the spectrum of Impranil coated on the knit, at different temperatures.

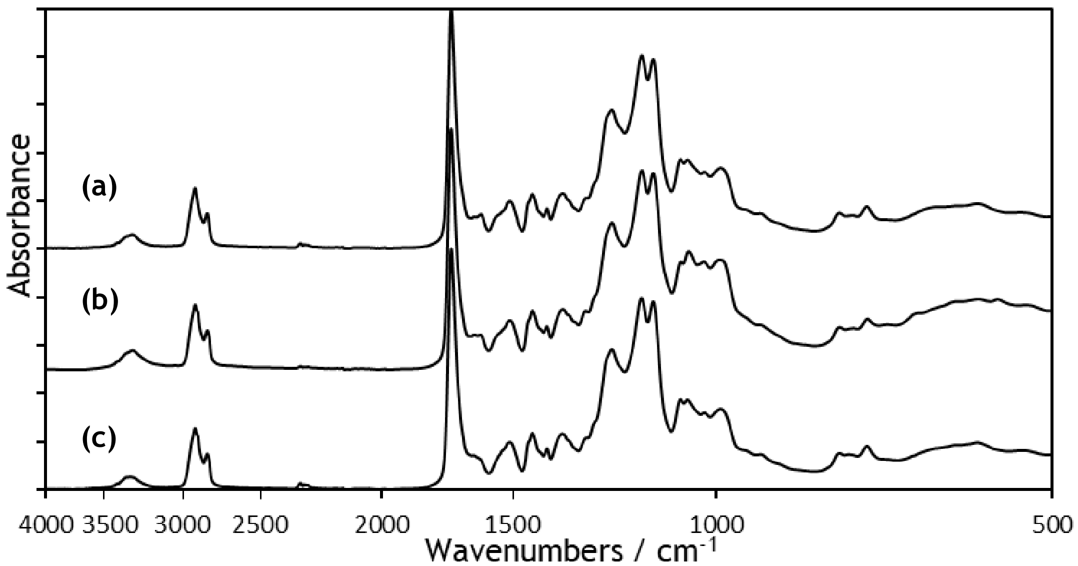

Figure C-1 *- Normalized FTIR-ATR spectrum of Impranil DLN applied on the knit at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

In Figure C-2, it is presented the spectrum of the second derivative of Arkophob (on the region between 1000 cm^{-1} and 3500 cm^{-1}), applied on the knit at different temperatures.

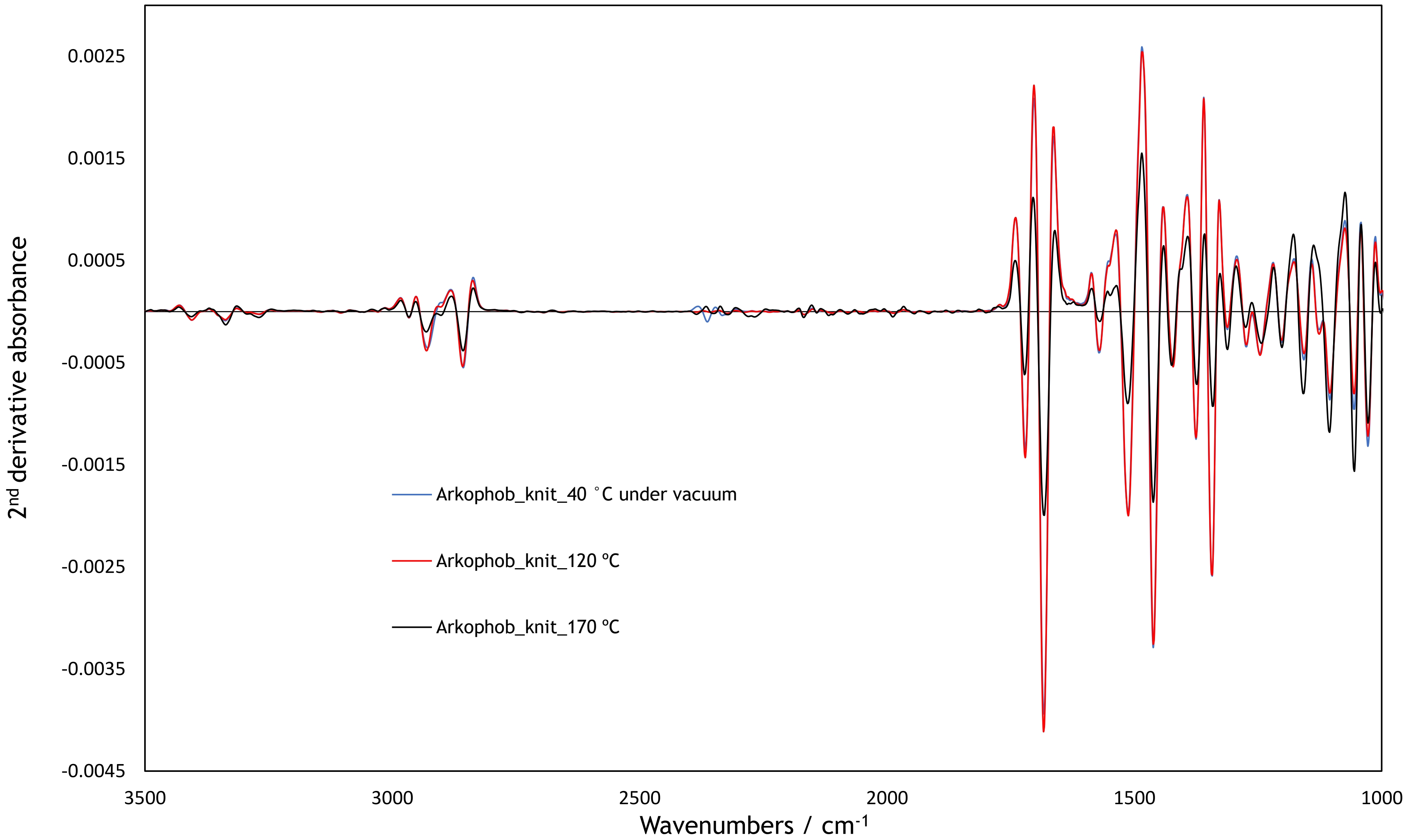

Figure C-2 *- Normalized second derivative spectrum of Arkophob applied on the knit at 40 °C under vacuum, 120 °C, and 170 °C.*

In Figure C-3, it can be seen the spectrum of the second derivative of the mixture of Arkophob, on the knit at different temperatures, in the region of the isocyanate band (2200-2300 cm^{-1}).

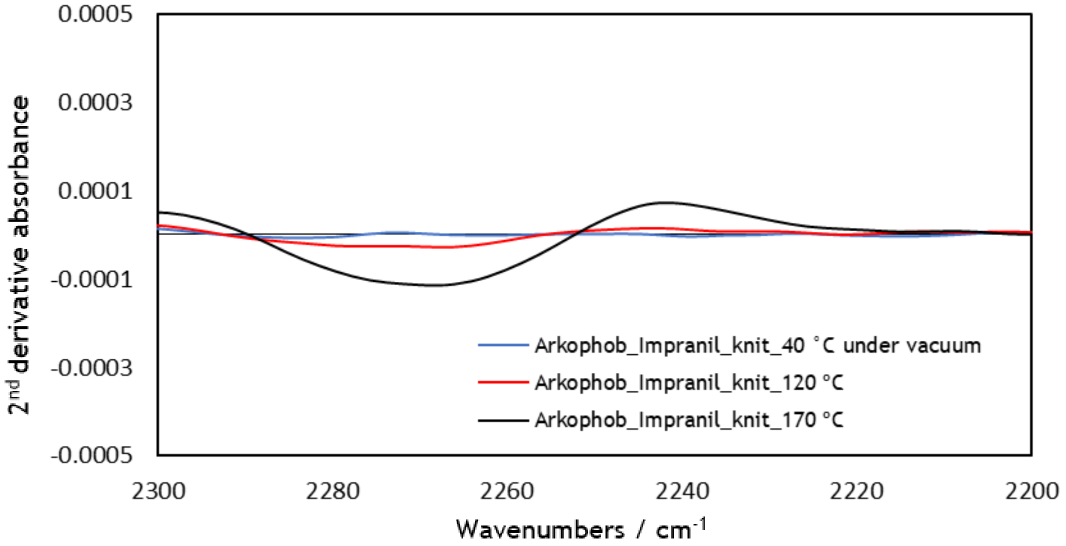

Figure C-3 *- Normalized second derivative spectrum of the mixture of Arkophob applied on the knit at 40 °C under vacuum, 120 °C, and 170 °C.*

An ampliation of the spectrum (without being in semi-log scale) of the mixture of Arkophob DAN New liq with Impranil DLN by itself, at different temperatures, on the region of 1400-1600 cm^{-1} is displayed in Figure C-4.

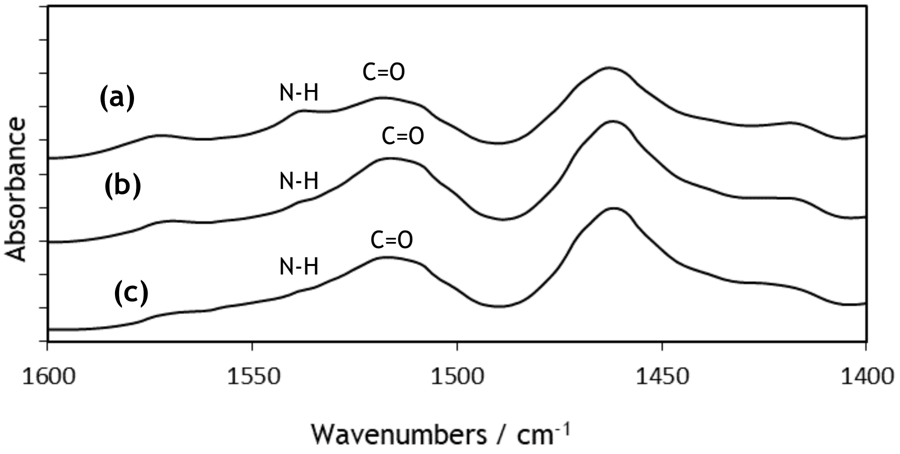

Figure C-4 *– Ampliation of the normalized FTIR-ATR spectrum of the mixture of Arkophob DAN New liq with Impranil DLN by itself at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

In Figure C-5, it is displayed the spectrum of Imprafix coated on the knit, at different temperatures. Given that Imprafix was extremely impregnated on the knit, some of the peaks observed are mostly related to the peaks of the knit. With the increase of the temperature, it was more noticeable that the peaks of the knit were overshadowing some of the peaks of the crosslinker.

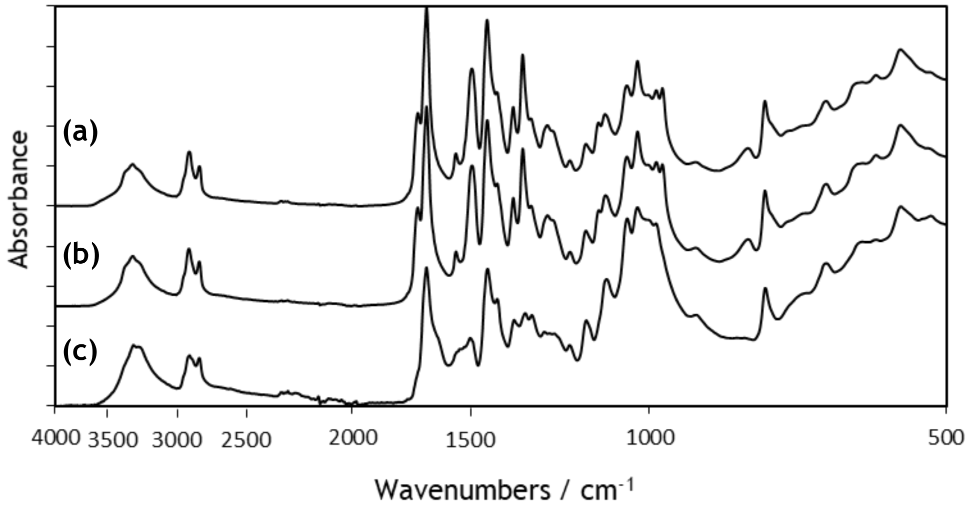

Figure C-5 *- Normalized FTIR-ATR spectrum of Imprafix applied on the knit at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

In Figure C-6, it is illustrated the spectrum of the mixture of Imprafix coated on the knit, at different temperatures.

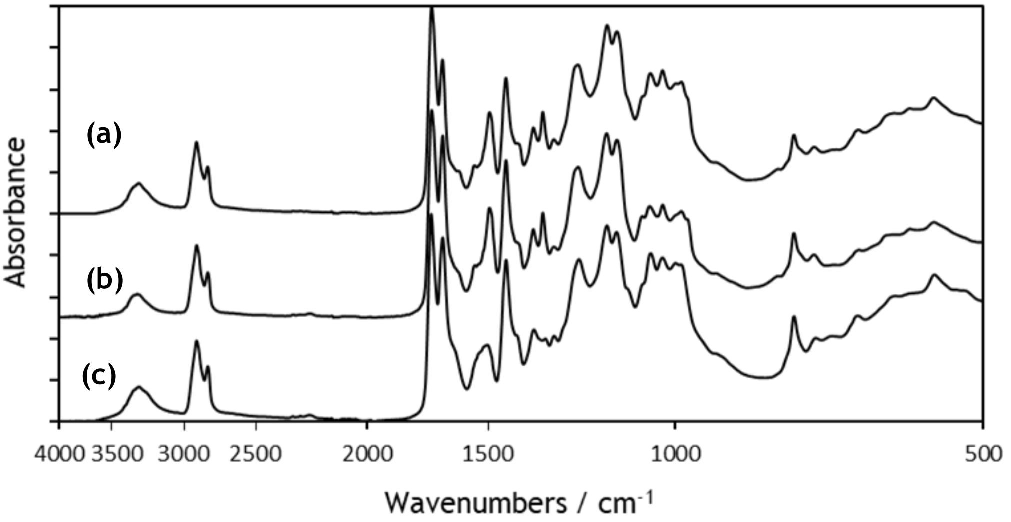

Figure C-6 *- Normalized FTIR-ATR spectrum of the mixture of Imprafix applied on the knit at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

In Figure C-7, it can be observed the spectrum of Acrafix coated on the knit, at different temperatures.

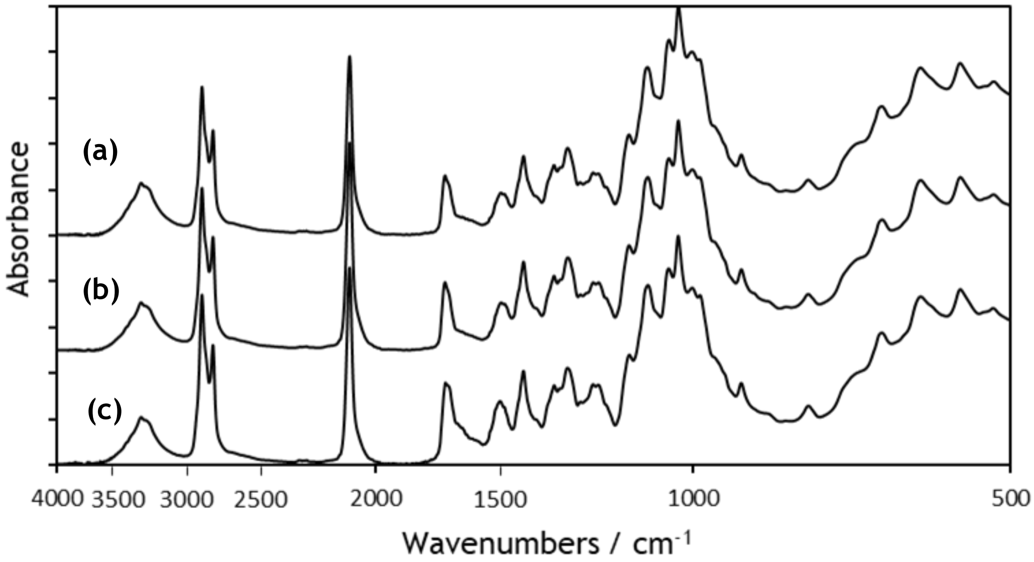

Figure C-7 *-Normalized FTIR-ATR spectrum of Acrafix applied on the knit at (a) 40 °C under vacuum, (b) 120 °C, and (c) 170 °C.*

Regarding the normalized second derivative spectrum of the mixture of Acrafix by itself, and coated on the knit, they are shown in Figure C-8 and Figure C-9, respectively, at different temperatures, in the region containing the CH_2 reference peak and the carbodiimide group (2000-3000 cm^{-1}).

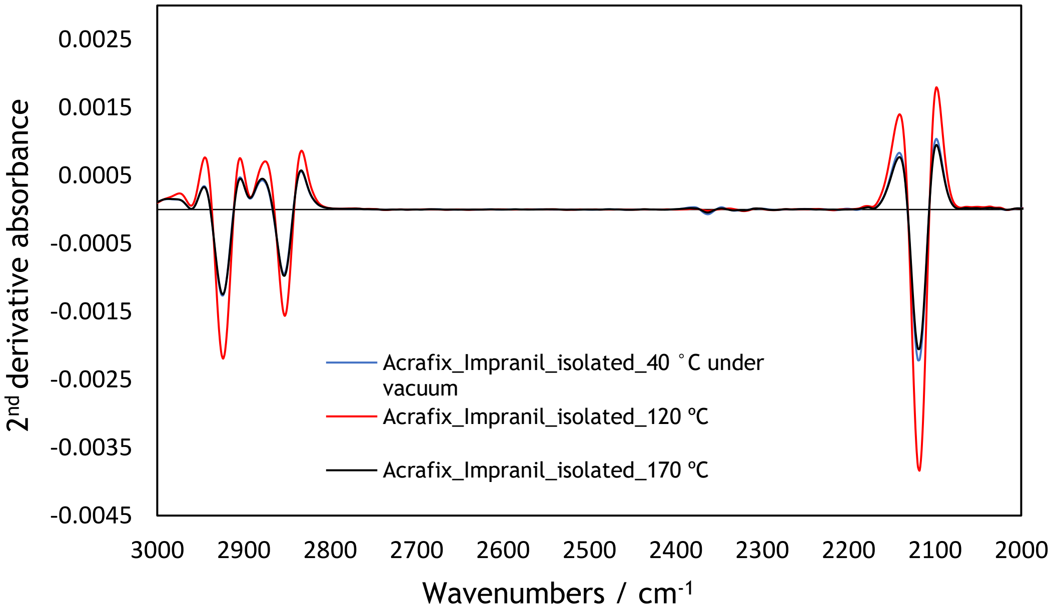

Figure C-8 - *Normalized second derivative spectrum of the mixture of Acrafix by itself at 40 °C under vacuum, 120 °C, and 170 °C.*

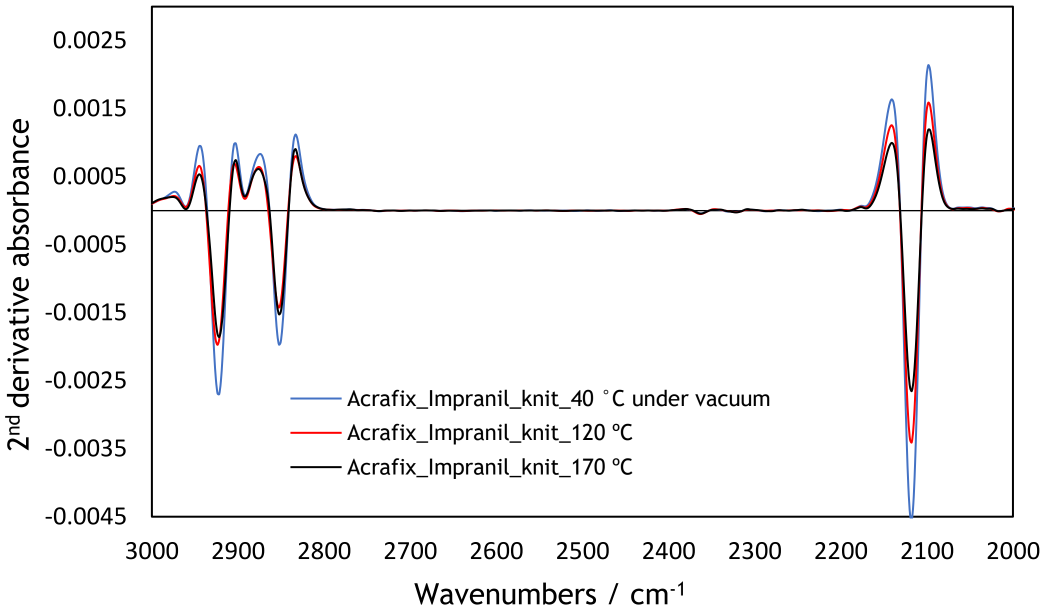

Figure C-9 *- Normalized second derivative spectrum of the mixture of Acrafix applied on the knit at 40 °C under vacuum, 120 °C, and 170 °C.*

12 Appendix D – Formation of the urea bond

In Figure D-1, it is presented all the steps of the reaction of the allophanate bond with water molecules, that lead to the formation of the urea bond.[54]

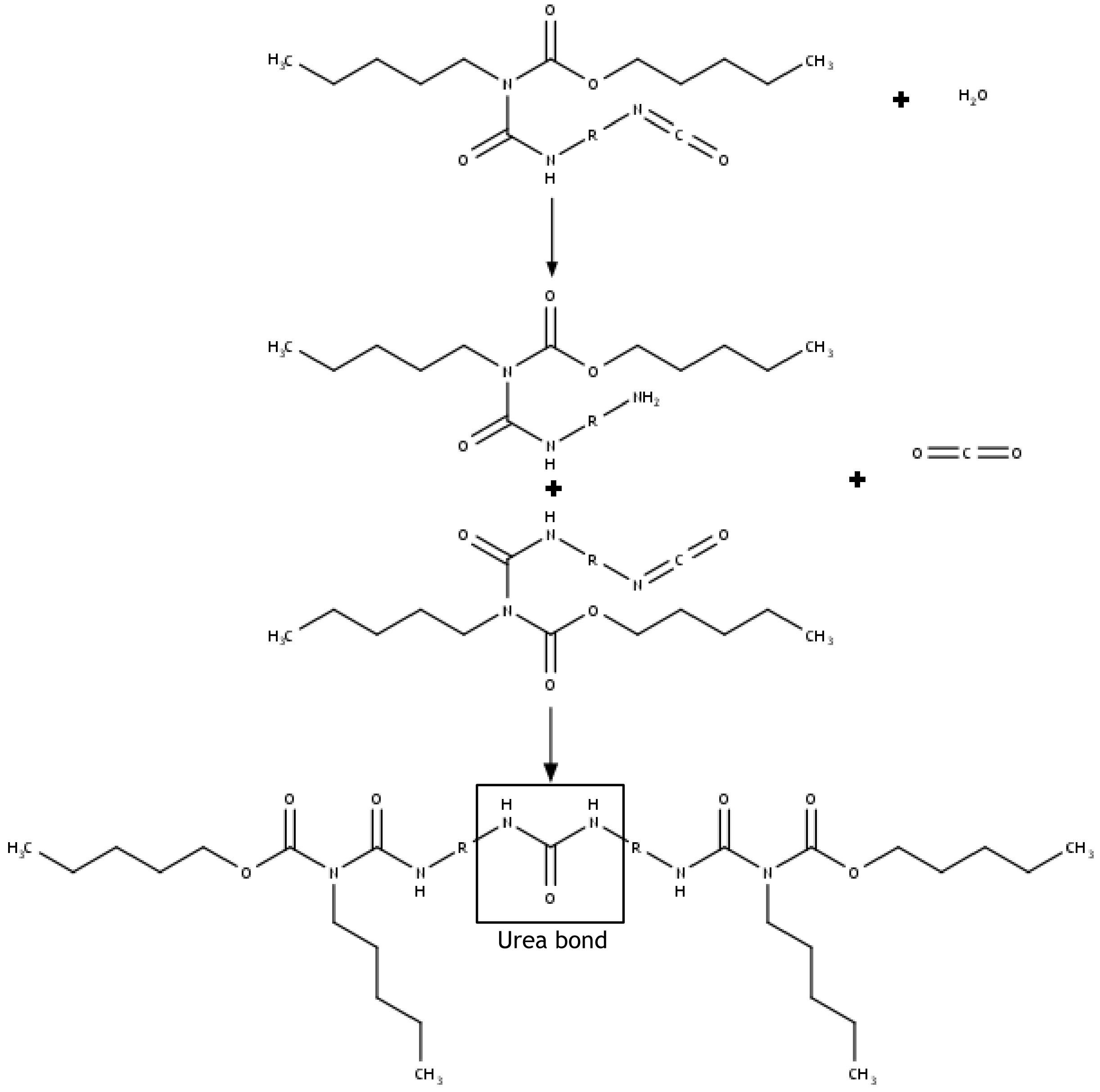

Figure D-1 *– Formation of the urea bond through the reaction of the allophanate bond with water molecules. Adapted from [54].*

13 Appendix E – Yellowing of the mixtures

In Figure E-1, it can be seen that Imprafix provides less yellowing of the mixture with Impranil (at a 33/67 crosslinker/binder mass ratio) compared to the other crosslinkers, and the binder itself, after being heated at 170 °C for 30 minutes. The polymer film becomes translucid, in contrast to the yellow colour observed in Figures 28b, 28c and 28d.

Figure E-1 *- Mixture of Impranil DLN-SD with (a) Imprafix 2794, (b) Acrafix EP 6047, (c) Arkophob DAN New liq at a 33/67 mass ratio. (d) Impranil DLN-SD by itself.*

14 Appendix F - Tintex textiles experiments

The first set of tests performed at Tintex correspond to the binder, the mixture of the crosslinker and the binder as well as the mixture of the binder, the crosslinker and the thickener Appretan 2710 liq (Table F-1). Regarding the mass percentage of the thickener in the mixture is the same of the whole formulation (0.53%). The temperatures and times of operation were the ones recommended by the supplier for the original formulation. As it can be seen in Table F-1, it cannot be correlated that higher viscosity before adding the thickener will result in a mixture (including the thickener) with a higher viscosity. Moreover, the importance of the crosslinkers can also be associated with the viscosity of the blend, given that the blend of Impranil mixed with the thickener has a higher viscosity than the ones that include the crosslinkers. In the case of the blend that includes Arkophob and the thickener, it has a higher viscosity than the one with Imprafix, however, in the complete formulation, it was needed a higher amount of thickener than Arkophob to accomplish the desired viscosity. This evidence further suggests that if the formulation was optimized with Imprafix in mind, then a lower amount of thickener would be needed.

Table F-1 *- Viscosity of a set of trials involving the binder, the crosslinker and the thickener.*

Mass fraction / %	Viscosity / dPa·s
100% Impranil	0.80
99.47% Impranil + 0.53% Aprettan	78.10
97% Impranil + 3% Arkophob	0.93
96.55% Impranil + 2.92% Arkophob + 0.53% Appretan	63.31
97% Impranil + 3% Imprafix	0.59
96.55% Impranil + 2.92% Imprafix + 0.53% Appretan	45.68

The mass fraction of each component of the formulation that contains Imprafix is presented in Table F-2.

Table F-2 *- Coating ingredients mass fraction and their function in the formulation containing Imprafix.*

Name	Mass fraction / %	Function
Impranil DLN-SD	89.83	Binder
Tubicoat SHM	4.50	Foam stabilizer
Imprafix 2794	2.70	Crosslinker
Hostapur SAS 30	1.20	Foaming and wetting agent
Afilan A01 liq.	1.20	Foaming and wetting agent
Appretan Thickener 2710 liq	0.57	Thickener