Master in Chemical Engineering

# *Development of a flexible epoxy coating for tribological applications*

## A Master's dissertation

of

**Catarina Peixoto Marques**

**Developed within the course of dissertation**

held in

**Tribochem**

Supervisor at FEUP: **Prof. Margarida Bastos**

Supervisor at Tribochem: **Eng. Judith Pedroso**

**Departamento de Engenharia Química**

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# Abstract

In order to develop a flexible epoxy formulation for tribological applications, three main objectives were determined: Obtain a flexible binder with good adhesion to the substrate, incorporate additives to provide tribological properties and study the tribological properties of the final coatings.

Three epoxy resins were considered as candidates: two bisphenol A/F based and one Novolac. A polyether polyamine (PEPA) and a cycloaliphatic polyamine (CAPA) were chosen as curing agents. The curing agents were blended in different equivalent molar proportion (PEPA:CAPA) and combined with each resin. First, the curing cycle for the binders was researched. Then, the binders were analysed according to flexibility, hardness and adhesion. Finally, PTFE was incorporated in order to confer tribological properties.

The results showed that the higher the quantity of polyether polyamine in the binders, the lower the glass transition temperature and less heat is necessary to completely cure the system. Also, higher quantities of polyether polyamine, confer higher flexibility, and lower hardness. Regarding adhesion, every binder presented excellent results. Binders with a good balance between hardness and flexibility were selected for the incorporation of PTFE. The incorporation of PTFE was not effective since the resultant coatings had agglomerates. Regarding mechanical properties of the coatings with PTFE, the adhesion and the flexibility were not affected. The hardness decreased in every sample, concluding that the PTFE has a substantial impact on the surface properties.

The best tribological result obtained was from the sample N3PTFE (Novolac resin with 50:50 curing agents equivalent molar proportion and PTFE), with a COF of 0.112. The worst result was from sample BB2PTFE (2BPA/F resin, 75:25 curing agents equivalent molar proportion and PTFE), showing a COF of 0.166. The COF obtained demonstrate that softer coatings tend to result in poor tribological properties. Despite the need for improvements, the best coating to pursue the optimization is N3PTFE, since it showed the best tribological results, balancing hardness and flexibility. However, longer tribological tests should be performed in order to understand better the behaviour of the coating in terms of wear. Lastly, the PTFE incorporation should be optimised in order to eliminate defects.

Keywords: epoxy resins; flexibility; tribology; coating

# Sumário

De maneira a desenvolver uma formulação epoxídica flexível para aplicações tribológicas, foram determinados três objetivos principais: obter um ligante flexível com boa adesão ao substrato, incorporar aditivos para fornecer propriedades tribológicas e estudar as propriedades tribológicas dos revestimentos finais.

Três resinas epoxídicas foram consideradas: duas à base de bisfenol A/F e uma Novolac. Uma poliéter poliamina (PEPA) e uma poliamina cicloalifática (CAPA) foram escolhidas como agentes de cura. Os agentes de cura foram misturados em diferentes proporções molares de equivalentes (PEPA:CAPA) e combinados com cada resina. Primeiramente, foi estudado o ciclo de cura dos ligantes. Em seguida, os ligantes foram analisados quanto à flexibilidade, dureza e adesão. Por fim, politetrafluoroetileno (PTFE) foi incorporado para conferir propriedades tribológicas.

Os resultados mostraram que quanto maior a quantidade de poliéter poliamina nos ligantes, menor a temperatura de transição vítrea e menor o calor necessário para curar completamente o sistema. Além disso, maiores quantidades de poliéter poliamina, conferem maior flexibilidade e menor dureza. Em relação à adesão, cada ligante apresentou excelentes resultados. Os ligantes com bom equilíbrio entre dureza e flexibilidade foram selecionados para a incorporação de PTFE. A incorporação de PTFE não foi eficaz, pois os revestimentos resultantes apresentaram aglomerados. Em relação às propriedades mecânicas dos revestimentos com PTFE, a adesão e a flexibilidade não foram afetadas. A dureza diminuiu em todas as amostras, concluindo que o PTFE tem um impacto substancial nas propriedades de superfície.

O melhor resultado tribológico obtido foi da amostra $N3_{PTFE}$ (resina de Novolac com 50:50 agentes de cura equivalentes à proporção molar e PTFE), com um coeficiente de atrito de 0,112. O pior resultado foi da amostra $BB2_{PTFE}$ (resina 2BPA/F, 75:25 agentes de cura equivalentes em proporção molar e PTFE), com um coeficiente de atrito de 0,166. O coeficiente de atrito obtido demonstra que revestimentos mais duros tendem a ser melhores para aplicações tribológicas. Apesar da necessidade de melhorias, o melhor revestimento para é o $N3_{PTFE}$, pois apresentou os melhores resultados tribológicos, equilibrando dureza e flexibilidade. No entanto, ensaios tribológicos mais longos devem ser realizados de maneira a compreender melhor o comportamento do revestimento em termos de desgaste. Por último, a incorporação de PTFE deve ser otimizada para eliminar defeitos.

# Declaration

I hereby declare, on my word of honour, that this work is original and that all non-original contributions were properly referenced with source identification.

*1st of July 2019~*

Catarina Peixoto Marques

*Catarina Peixoto Marques*

# Index

# Notation and Glossary

| | | |
|---|---|---|
| *Tg* | Glass transition temperature | ˚C |

*List of Acronyms*

| | |
|---|---|
| AHEW | Amine Hydrogen Equivalent Weight |
| CAPA | Cycloaliphatic Polyamine |
| COF | Coefficient of friction |
| DGEBA | Diglycidyl ether of bisphenol-A |
| DMA | Dynamic mechanical analysis |
| DSC | Differential scanning calorimetry |
| EEW | Epoxy Equivalent Weight |
| FTIR | Fourier transform infrared spectroscopy |
| PA | Phthalic anhydrides |
| PEPA | Polyether Polyamine |
| PTFE | Polytetrafluoroethylene |
| SEM | Scanning Electron Microscopy |
| TGAP | Trifunctional triglycidyl ether of p-Aminophenol |
| TGMDA | Tetrafunctional Tetraglycidyl Methylenedianiline |
| THPA | Tetrahydrophthalic Anhydride |
| UV | Ultraviolet Radiation |

# 1 Introduction

## 1.1 Framing and presentation of the work

Tribology is the science of friction, wear, and lubrication. This study field is essential in applications as rolling or sliding components, where is mattering to modify and control friction and wear [1]. Historically, these goals have been achieved by design changes or lubricants. The concept of tribological coatings emerges as a better way of altering the tribological characteristics of the materials. The applicability of tribological coatings extends in many fields. In industries, for example, the decrease of friction and wear of bearings or gears results in the improvement of the efficiency of production machines, leading to cost reductions [2]. Also, in bioengineering research, tribology is used in biological systems such as human hip and knee joints [3]. Fundamentally, every moving piece against others can benefit from tribological improvements, and new possible applications emerge with the rise of new products on the market. New products tend to bring new requests. Developing tribological coatings for different shapes, materials and physical demands can be challenging.

As proposed by the company, this present work had the purpose to develop a customized tribological coating for a mechanical system that requires, besides tribological properties, other properties such as flexibility, to be feasible. Apart from these requirements, the coating must be epoxy based. Inside the company's portfolio of available raw materials and polymers, epoxy resins show to be the less costly option as well as chemically versatile, being strategically interest to explore this possibility.

Epoxy resins are commonly used as a thermoset material [4]. Their main application is in the coating industry as protective coatings due to their ability to establish highly cross-linked systems. These systems usually lead to stiff coatings that tend to be brittle, resulting in poor toughness and flexibility [5]. As tribological coatings, epoxy resins demand suitable fillers to contribute to a low coefficient of friction and high wear life [6, 7]. Although the company already has developed epoxy-based tribological coatings, the providence of flexibility is still an unexplored field, since the result of the combination of flexible epoxy systems with tribology is still unknown.

## 1.2 Presentation of the company

Tribochem is a research and development startup company based in UPTEC Asprela II. Their main focus lies in the development of coatings for tribological applications. They formulate and tailor the coatings according to the needs of the application, creating unique and customized solutions.

## 1.3 Contributions of the Work

With my work, I contributed to the development of a flexible epoxy coating with tribological properties. Despite the need for optimization, the concept was proved, showing it is possible to have the flexibility and low coefficient of friction with an epoxy-based coating. However, the coating was not tested in the final application. This project was a positive starting point for a possible solution to the problem presented by the company.

## 1.4 Organization of the thesis

This thesis is organized in six main chapters: Introduction, State of the art, Materials, and Methods, Results and discussion, Conclusions and Assessments of the work done.

The Introduction chapter presents the problem, explaining the scope of this thesis.

In the State of the Art, the main theoretical concepts needed to better understand the project are explored.

The Materials and methods consist of an overview of the methodology of the experimental assays performed and the materials and equipment used for that effect.

The Results and discussion chapter explore the followed path to achieve the main goal of the project, as well as the results obtained. In this chapter, the results are analysed and discussed.

In Conclusion, a summary of the main results obtained along with critiques is presented. It enhances the achievements and the failures of the project.

The Assessments of the work done chapter discusses the strengths and weaknesses of the work done, as well as suggestions for improvements.

# 2 Context and State of the art

## 2.1 Epoxy Resins

The word “epoxy” is the combination of the Greek prefix “ep”, meaning between, and the word “oxy”, the combining form of oxygen [5]. Epoxy resins, by strict definition, consist of uncrosslinked monomers or oligomers containing epoxide groups - a ring-shaped structure with oxygen bonded to two other atoms, as shown in the Fig. 1 [4].

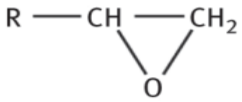


*Fig. 1) Molecular structure of an epoxide group.*

Further, in order to yield high-performance thermosetting polymers, epoxy resins are cured usually by the addition of a crosslinking promoter, as known as a curing agent or hardener. Therefore, the concept of epoxy resin is also used to define a final crosslinked structure resultant of the curing process, although after curing all epoxide groups may have reacted [4].

Cured resins are known for having outstanding properties like high adhesion strength or good mechanical and chemical resistance. These properties vary depending on the resin, the curing agent and the curing process. Therefore, resins have been used in a wide range of applications like protective coatings, electronic materials, adhesives, binders for composites, among others [4, 8].

### 2.1.1 Historical Context

The first epoxy resin was produced during the 30s, using bisphenol-A and epichlorohydrin [9]. Since this discovery, new developments and technologies on the field started to appear, making epoxy resins flourish on the market in the 60s [10].

The market’s desire for a better polymer with an improved resistance induced the development of multifunctional resins in the early 60s, being these used in aerospace composites and corrosion-resistant coatings [4, 5].

The same decade witnessed the commercialization of cycloaliphatic epoxy resins, characterized by good thermal and UV stability [5, 11].

In the 80s, the rise of the electronic and computer industry opened, even more, the spectrum of possible applications. Aiming for the creation of encapsulants for semiconductors, the need for thermal stability and resistance to moisture promoted the development of high performing and high purity epoxy resins [5, 10].

Lately, due to the arising of environmental awareness and regulations, epoxy powder coatings started to gain popularity [5]. Even more recently, the growing need of creating sustainable technology using renewable resources brought to us bio-based epoxy resins, resins synthesized using biomass like vegetable oils or lignin [12].

Nowadays, a wide range of different epoxy resins exists on the market, with countless different characteristics and applications. That said, there is a lot more to explore regarding epoxy resin development and future applications.

### 2.1.2 Types of Epoxy Resins

A lot of different types of resins exist, being difficult to categorize them all. Nevertheless, the main groups of epoxy resins are presented next.

**DGEBA**

The first epoxy resin created, based on bisphenol A and epichlorohydrin, is named diglycidyl ether of bisphenol-A (DGEBA) and its synthesis, described in Fig. 2, is still used nowadays [4, 13].

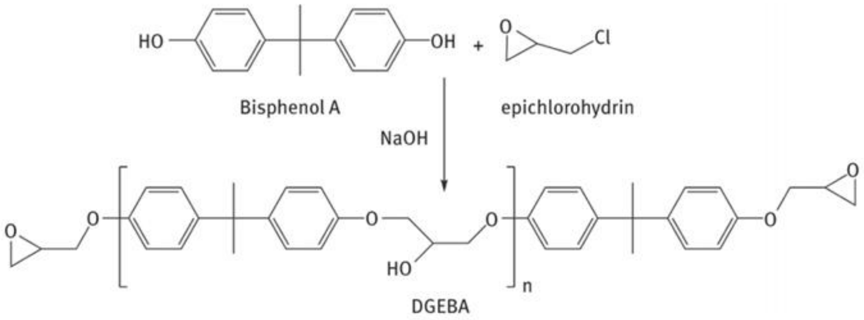


*Fig. 2) DGEBA synthesis from bisphenol A and epichlorohydrin [13].*

The DGEBA resin is based on the reaction of bisphenol-A with epichlorohydrin in the presence of a strong base, such as NaOH. The resulting molecular weight can be refined through the relation between the reagents. Liquid, waxy or solid DGEBA resins can be obtained according to the different molecular weights [5, 13].

**Multifunctional Epoxy Resins**

Functionality is the number of functional reactive groups on a molecule [4]. Multifunctional epoxy resins are known for having higher functionality (higher than 2) than DGEBA resins, providing a higher crosslinking density. This leads to increased chemical and thermal resistance [5].

Novolac epoxy resins, based on phenolic formaldehyde novolacs, are one of the main multifunctional epoxy resins. Phenol novolac resins are specially used in elevated temperature environments and cresol novolac resins in the semiconductor industry [5].

Aromatic glycidyl amine epoxy resins also play an important role in the multifunctional world of epoxies. These epoxies have a tertiary amine, which confers a higher reactivity. The trifunctional triglycidyl ether of p-aminophenol (TGAP) and the tetrafunctional tetraglycidyl methylenedianiline (TGMDA) are examples of important glycidyl amines on the market [5, 8]. The molecules referred are presented in the Fig. 3.

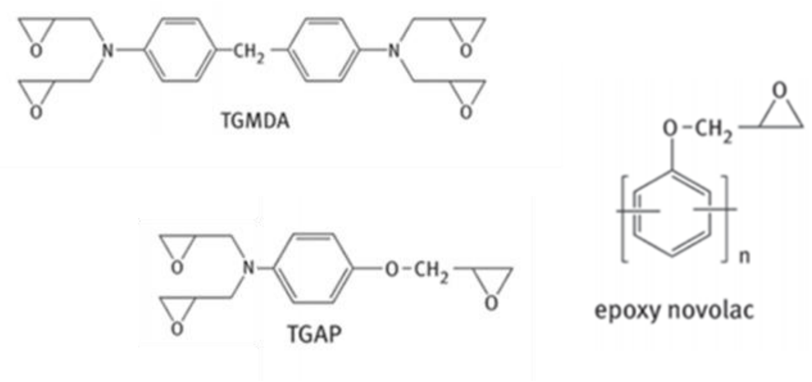


*Fig. 3) Chemical structure of multifunctional epoxy resins [13].*

**Cycloaliphatic Epoxy Resins**

Cycloaliphatic epoxies have an aliphatic backbone and a fully saturated molecular structure (Fig. 4) [8]. These are based on diepoxides of cycloaliphatic dienes, resulting in a low viscosity, good wheaterability and in excellent electrical properties. Therefore, they are mainly used in electrical insulation [5, 8].

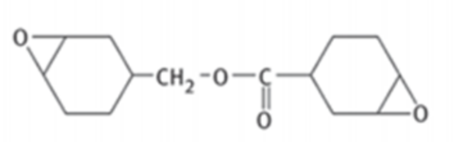


*Fig. 4) Molecule of a cycloaliphatic epoxy resin*

**Flexible Epoxy Resins**

In order to overcome the lack of physical and chemical properties of standard epoxy resins, specialty epoxy resins have been developed. One of the main efforts has been increasing the toughness and flexibility of epoxy systems. A way of achieving that is the incorporation of rubber particles in the epoxy resin, existing nowadays on the market what it's known as elastomer-modified epoxy resins [5]. In these materials, an elastomeric phase is dispersed in the resin. This phase separates from the epoxy binder in the curing process, changing the material structure and stress state in the region around rubber particles. This method is proved to increase toughness and fracture resistance [14-17]. However, undesirable reduction in strength and elastic modulus is reported as a downside [14, 18, 19]. An approach to overcome that is by chemical modification. By the incorporation of flexible elements into the epoxy resin backbone, it is possible to create a more flexible backbone structure and improve the elastic modulus of the resin [14]. Nowadays, the incorporation of rubber particles and the change of epoxy backbone are made in the same product, existing many options of flexible epoxies on the market. [17]

## 2.2 Curing Agents

In order to give to epoxy resins the characteristics of a thermoset polymer, it is necessary to address to a curing agent. A curing agent is the promoter of the curing reaction [4]. The curing agent can be a catalyst, which promotes the reaction of the epoxy resin with itself, or a coreactive curing agent, which binds with the resin. In both cases, it is created a three-dimensional cross-linked structure [20, 21]. Usually, catalytic agents are mixed in small quantities with the epoxy resin, while others may need a stoichiometric calculation to achieve optimum properties [20].

The most used type of curing agents is amine curing agents, followed by anhydrides. Both integrate the final structure of the thermoset, being the choice of the hardener as important as the choice of the resin to achieve a good result after curing [4, 22].

### 2.2.1 Amine Curing Agents

Primary and secondary amines react well with the epoxide group [4, 22]. The reaction held is described by the Fig. 5.

Amines can be aliphatic, cycloaliphatic or aromatic, each one leading to different chemical structures [8]. Aliphatic long chains tend to give more flexibility, aromatic groups provide more chemical and thermal stability and cycloaliphatic amines provide better thermal stability than the aliphatic and better flexibility than aromatic ones [5].

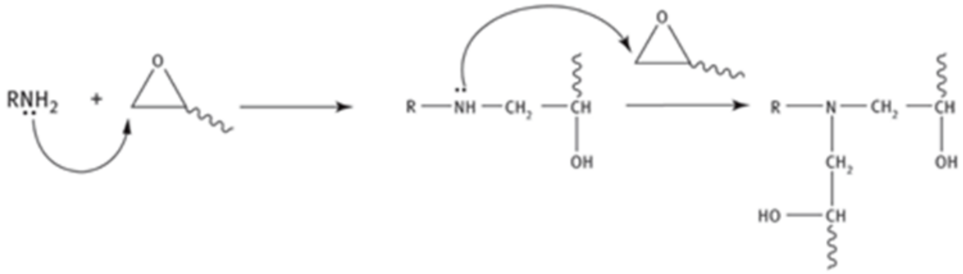


*Fig.5) Reaction of a primary amine with an epoxide group [13]*

### 2.2.2 Anhydride Curing Agents

Anhydride curing agents are mostly used in electrical encapsulation and composites since they provide good electrical and mechanical resistance [23]. Important commercial anhydrides are, for example, phthalic anhydrides (PA) or tetrahydrophthalic anhydride (THPA). The mechanism of cure is complex due to the possibility of competing reactions [5, 8]. They show low reactivity, needing therefore high temperatures or a presence of a catalytic agent [22].

### 2.2.3 Catalytic Curing Agent

Catalytic curing agents only exhibit activity with heat or photo-irradiation [8]. They promote epoxy reactions without being consumed [5]. Lewis bases, like tertiary amines, contain an atom with an unshared electron in the outer orbital and catalyze epoxy polymerization. They are used in coatings, adhesives or as accelerators for curing with other hardeners. Lewis acids, like metal halides or adducted boron trifluoride compounds, react well with epoxies and are also catalytic curing agents [5].

### 2.2.4 Conferring flexibility with curing agents

Considering that some curing agents integrate the final structure of the thermoset, it is possible to confer desirable mechanical properties by choosing the right curing agent. In order to achieve flexibility, epoxy resins can be reacted with different amines or anhydrides with a flexible backbone. Instead of changing the epoxy backbone, it is possible to maintain any kind of epoxy structure and choose amines or anhydrides with long-chain backbones, changing that way the final structure and properties of the coating [5].

## 2.3 Epoxy Formulation Development

The commercial success of the epoxy resins came along with the possibility to create combinations in order to achieve certain goals [20]. Besides resins and curing agents, diluents, fillers or other additives can also be used to manipulate final properties [21]. The challenge lies in the ability to choose and combine the ingredients and then studying the process of cure that better suits the final formulation [5].

### 2.3.1 Selection of epoxy resins and curing agents

In order to manipulate the characteristics of the final product, it is possible to choose one or more epoxy resins or curing agents [23, 24]. Knowing the features of the epoxy/curing agent molecules gives the advantage to accomplish the required properties. Ether linkages give chemically resistance and methyl groups are usually responsible for toughness. Also, the hydroxyl groups are a good option for improving adhesion and aromatic groups add rigidity to the structure, improving the high-temperature performance [21]. Nevertheless, it is important to test the mixtures and have in mind that commercial resins and hardeners do not only have reactive terminal groups. Other end groups or different molecular weights may result from the manufacturing process. Also, some products may also contain modifiers and diluents [20, 21].

### 2.3.2 Stoichiometric calculations

The stoichiometric ratio plays an important role in epoxy-based systems. When the curing agent is coreactive, like primary or secondary amines, it is proved that the resin/curing agent ratio largely affects the mechanical properties of the final product due to incomplete crosslinking status [5, 20, 25]. Theoretically, a fully crosslinked structure is obtained when equimolar quantities of resin and curing agent are combined. Suppliers set an epoxy equivalent weight (EEW) for epoxy resins and amine hydrogen equivalent weight (AHEW) for curing agents [5]. EEW is the weight of the resin (in grams) which contains one gram equivalent of epoxy and AHEW is the weight of curing agent (in grams) which contains one gram equivalent of active hydrogens [21].

Precise stoichiometric balance does not always produce a cured resin system with optimized properties. Experiments are important to establish the mix ratio that better suits the desired characteristics [4].

### 2.3.3 Curing process

Understanding the curing and the kinetics is important to design a proper curing schedule since the epoxy curing process affects the cured epoxy performance. Phenomena such as physical ageing may occur due to an incomplete cure. Physical ageing is a gradual change in physical properties over time, which results in alterations in the performance of the material. This kind of phenomena can be reduced or avoided by studying the curing process of the system [5].

The epoxy curing process can be monitored by a number of different techniques. The thermal properties of the system can reflect the degree of cure and be analysed by differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). It is also an option to monitor the reaction by analysing the functional groups through Fourier transform infrared spectroscopy (FTIR) [5].

## 2.4 Tribology

Tribology is the science in the field of mechanical engineering that studies the interaction of surfaces with relative motion, including the subfields of friction, wear, and lubrication [1].

### 2.4.1 Friction

Friction is the resistance to the movement of one solid body in contact with another. There are two types of friction: static and dynamic friction. The static friction is the friction force at the beginning of the movement and the dynamic friction force is the frictional force when the motion is already established [26, 27]. To determine the friction between these two bodies, the coefficient of friction (COF) is calculated. The COF is the ratio of the force of friction between the two bodies and the force pressing those together [26]. Considering the Fig. 6, the square moves in the direction of the applied force. F is the friction force, contrary to movement, and N is the normal force between the surfaces. In this example, the COF is calculated by the ratio of the force F and N. Lower the force F, lower the COF, which means the surfaces have good tribological behaviour.

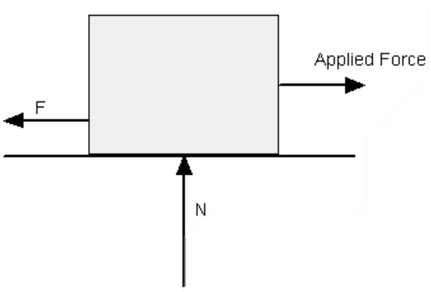


*Fig. 6) Schematic draw of the forces involved in the movement of two bodies, where the applied force promotes the movement, F is the force correspondent to the friction and N is the normal force between the surfaces.*

In certain applications, a higher value of COF may be benefic. In some cases, to stop movement, it is important to provide high friction, like in breaks of vehicles. However, in applications like bearings, higher friction might lead to wear and decrease of energy efficiency in the final application [1, 27].

### 2.4.2 Wear

Wear is the surface damage process which results from friction. There four main types of wear, described in the Fig. 7.

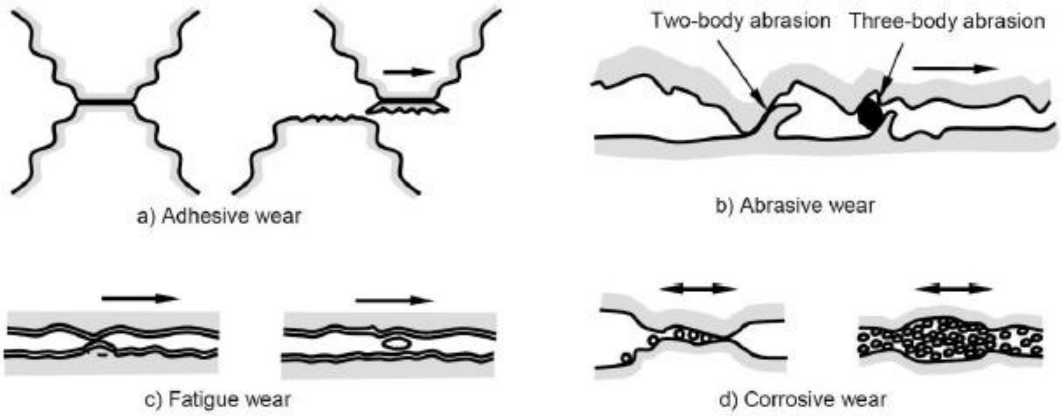


*Fig. 7) The basic mechanisms of wear are (a) adhesive, fb) abrasive, (c) fatigue and (d) chemical wear [2].*

When one surface comes into contact with another, they may adhere strongly to each other and cause adhesive wear. As illustrated in the Fig. 7 (a), relative tangential motion of the surfaces (represented by the arrow) can lead to the removal of the softer material [26].

Abrasive wear, schematized in Fig. 7 (b) may occur when one of the surfaces is considerably harder than the other (two-body abrasion) or when hard particles are introduced into the surfaces (three-body abrasion). When the harder surface moves tangentially, removal of softer material is seen as grooves or scratches [26].

Fatigue wear occurs when the materials are exposed to repeat loading and unloading cycles. Fatigue may originate large scale cracking and liberation of surface material, forming wear debris, as shown in Fig. 7 (c) [27].

Corrosion happens to some materials exposed to oxygen. The corrosion forms a film on the top of the surfaces. Due to the friction, this film is removed, and the material is again exposed to the corrosive environment. The Fig. 7 (d) shows the accumulation of corroded particles [26, 27].

### 2.4.3 Lubrication

The most common way of reducing friction and wear is to use a lubricant between the two moving materials. Lubricants can be liquids, such as oil, dispersions like grease or solids, like graphene [26]. Historically, oil and grease have been used as lubricants in a lot of applications, especially in industrial equipment. However, solid lubricants appear on the market addressing to replace them, having already proven to be an effective solution [28].

Solid lubricants are mainly important where the use of liquid lubricants is either impractical or inadequate, such as aerospace technology or automotive transport. They are generally available as powder dispersed in a resin, oil or water. Examples of effective solid lubricant are molybdenum disulphide ($MoS_2$), graphite and polytetrafluoroethylene (PTFE) [29].

**PTFE**

PTFE is a synthetic fluorinated polymer with a propensity to exhibit considerable elastic deformation under load [28]. The representation of the polymer molecule can be seen in the Fig. 8.

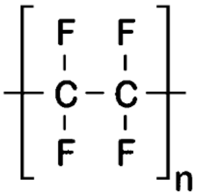


*Fig. 8) Polytetrafluoroethylene polymer representation.*

This polymer is an inert compound due to the protection of the fluorine atoms on the carbon chain. It has a coefficient of friction of 0.05 to 0.10, which is the third-lowest of any known solid material, next to aluminium magnesium boride (with a COF of 0.02) and diamond-like carbon (with COF of 0.05) [30].

### 2.4.4 Tribological Coatings

By incorporating PTFE or other solid lubricants in formulations, it is possible to create coatings with low friction and low wear. Based on that, the concept of tribological coatings emerges. A tribological coating is a film/layer applied on a substrate aiming to provide a specified friction behaviour and wear resistance [31]. Coating thickness can vary from micrometres (thin coatings) to millimetres (thick coatings). Thin coatings, despite the low thickness, already show significant alterations in substrate interfacial properties, modifying wettability, surface energy, surface reactivity, corrosion, friction, adhesion, and wear [32].

### 2.4.5 Epoxy tribological coatings

Epoxy resins by themselves have poor tribological properties. However, the addition of suitable fillers like fibres, nanoparticles or internal lubricants can contribute to a low coefficient of friction and high wear life, maintaining at the same time the great properties of epoxy resins [6, 7].

Studies have shown that the incorporation of graphene in epoxy coatings improves significantly anticorrosive and tribological performance [7, 33-37]. It has been reported that graphene exhibits extraordinary corrosion resistance and self-lubricant characteristics [33].

Also, fluoropolymer-modified epoxies were studied and it is verified that fluoropolymers such as polytetrafluoroethylene (PTFE) provide better overall tribological properties. The presence of fluorine atoms leads to chemical and thermal stability, low surface tension, low friction, hydrophobicity and oleophobicity [38-40].

Kevlar fibres [41], particles such as SiO2, TiO2, Al2O3 [6, 42], nanodiamond particles [43], or microencapsulated lubricants [44, 45] are also some examples of additives who had shown to successfully improve tribological properties of epoxy coatings.

# 3 Materials and Methods

## 3.1 Materials

For this project, three epoxy resins were chosen, described in Table 1. The epoxide equivalent weight (EEW) indicated by the suppliers is also presented.

*Table 1) Epoxy Resins used during the project*

| Epoxy resin | EEW / g·eq$^{-1}$ | Identification in samples | Description |
|---|---|---|---|
| **1BPA/F** | 195 | B | Based on a blend of **bisphenol A** resin and **bisphenol F** resin |
| **2BPA/F** | 190 | BB | Based on a blend of **bisphenol A** resin and **bisphenol F** resin |
| **Novolac** | 172 | N | Epoxidized phenolic resin – **Novolac** |

To react with the resins, two curing agents were considered, presented in Table 2. The amine hydrogen equivalent weight (AHEW) for each curing agent is also presented.

*Table 2) Curing Agents used during the project*

| Curing Agent | Molecular Structure | AHEW / g·eq$^{-1}$ |
|---|---|---|
| **PEPA** | Polyether polyamine | 250 |
| **CAPA** | Cycloaliphatic polyamine | 42.5 |

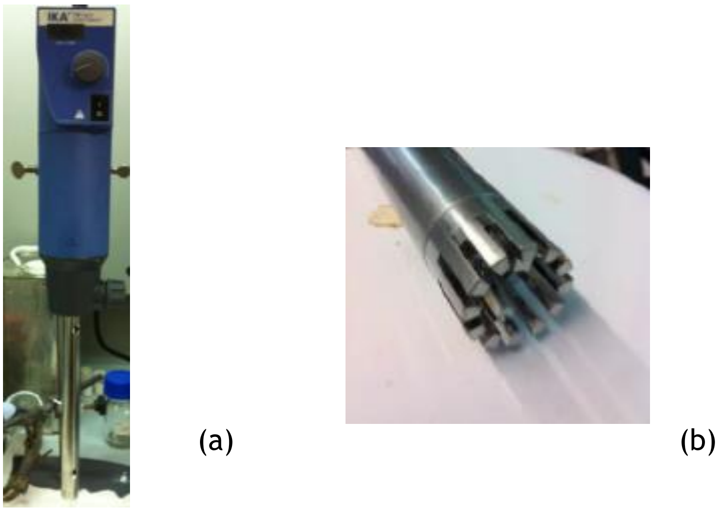
Polytetrafluoroethylene (PTFE) micropowders were incorporated in advanced stage in order to provide tribological properties.

## 3.2 Sample Preparation

For this study, 15 binders were considered. Each binder is designated by letters representing the resin (B, BB or N) and a number (1 to 5) which corresponds to the equivalent mass of different curing agents. Aiming a stoichiometric combination of the epoxy resin and the curing agents, the masses were calculated according to EEW and AHEW. The equivalent molar proportion of curing agents is represented as PEPA:CAPA. More details are presented in the

Results and Discussion chapter. In order to prepare the samples, the resin and the curing agents were weighted in a plastic cup and mixed slowly for 2 minutes.

In a second phase, PTFE was incorporated in the samples. The powder was dispersed with an IKA Ultra-Turrax T18 (Fig. 9), equipment with a rotor-stator which provides the dispersion of the micropowders.



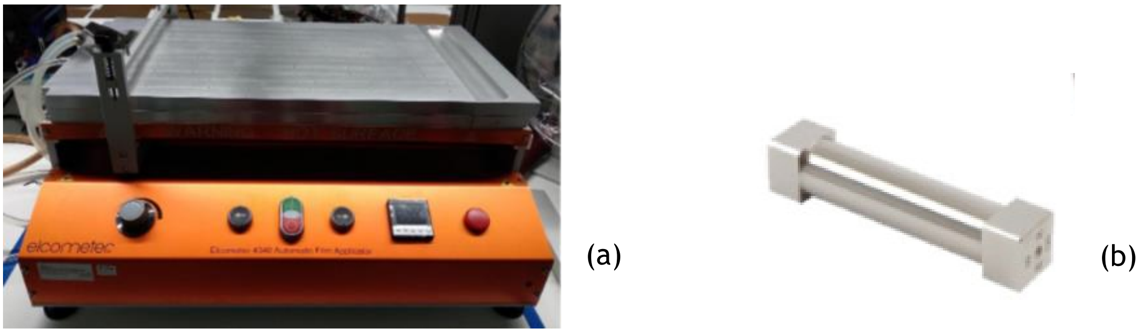
(a) (b)

*Fig. 9) (a) Ultra-Turrax and the (b) rotor-stator in detail.*

The PTFE was first incorporated in the resin with a spatula for 2 minutes. After, a Ultra-Turrax was used to disperse the powder. The dispersion was performed at 5000 rpm for 5 min.

## 3.3 Sample application

To apply the samples, it was used an automatic film applicator (Elcometer 4340) ion by doctor blade technique. The equipment is a combination of an application table with vacuum, presented in Fig 10 (a), a vacuum pump and a film applicator (type baker), presented in Fig. 10 (b).



(a) (b)

*Fig. 10) Automatic film application constituted by (a) an application table with vacuum (b) doctor-blade applicator type baker.*

The samples were applied in blasted steel DC04 sheets with a thickness of 0.4 mm. The application velocity was 40 mm·s$^{-1}$, with a wet film thickness of 60 µm.

## 3.4 Sample analysis

To analyse the curing cycle, it was used differential scanning calorimetry (DSC) technique, performed in the equipment Netzsch Polyma DSC214, under nitrogen atmosphere. The samples were analysed using an aluminium crucible with a lid. The sample's mass for liquid samples was between 12 mg and 15 mg and the solid samples between 2 mg and 4 mg. The temperature programs used are described during the Results and Discussion Chapter, since it is dependent on the sample.

A Scanning Electron Microscopy (SEM) analysis was performed in an SEM Phenom XL equipment, aiming the characterization of the coatings. Before analysis, the samples were sputtered with gold in order to provide electrical conductivity. The images can be obtained by two different detectors: SED – Secondary electron detector that provides topographic images of the samples and BSD – Backscattered detector that provide images of the elemental composition of the sample.

The thickness of the coatings was measured using an Elcometer 456 inductive coating thickness gauge with a dual sensor (Fig.11). The registered thickness is the average of ten measurements in different zones of the coating. This method allows users to measure the dry film thickness without damaging the probe or the coating. It has ±1% accuracy due to the calibrating method, which has to be performed before the measurements.

*Fig.11) Elcometer 456 inductive coating thickness gauge with a dual sensor.*

The adhesion was analysed using a TQC CC1000 Cross Hatch Adhesion Tester. The equipment allows the measurement according to the ISO 2409. First, two perpendicular cuts were performed through the coating into the substrate, forming a pattern of 25 similar squares. The pattern was brushed with a supplied brush along each of the diagonal lines, several times. Finally, an adhesive tape parallel to the pattern was applied and pulled off. The cut area was examined with a magnifying glass and the evaluation results were made following a classification table, presented in Fig. 1.1, Appendix A.

The hardness was measured with an Elcometer 3092 Sclerometer Hardness Tester (Fig. 12), which measures the hardness of a coating by moving a tip over the coating with force values changing from 1 N to 5 N. The hardness testing instrument contains a screw lock and a rounded tip which is compressed by a spring. The spring provides a certain force stipulated through the screw lock. By making short and straight movements, it was observed the force at which the tip leaves a mark or destroys the coating. That value, in Newtons, was the value registered as the hardness of the coating.

*Fig.12) Elcometer 3092 Sclerometer Hardness.*

The flexibility was measured by performing a bending test. The steel sheets were bended 90º and 180 º with a use of a mandrel.

The tribological tests were performed in a tribometer Bruker UMT-3 with a linear reciprocating module using a GCr15 steel ball with 10 mm diameter, presented in Fig. 13. The applied load was 10 N with a velocity of 5 mm·s$^{-1}$. The tests were performed during 1 h with a stroke of 10 mm.

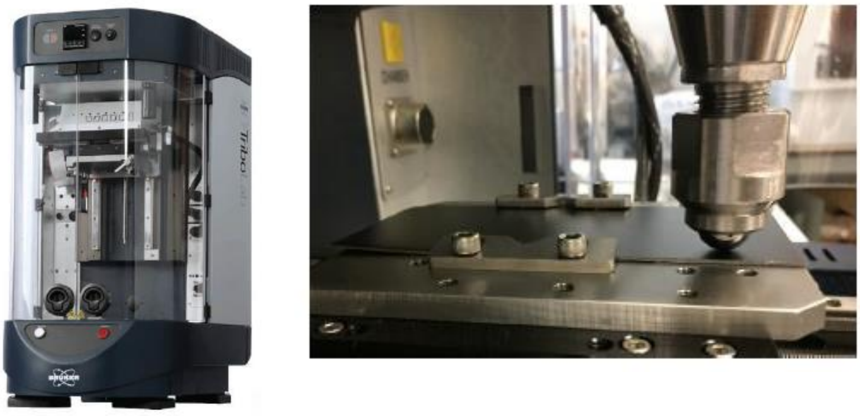


*Fig. 13) Tribometer Bruker UMT-3 and the correspondent reciprocating module.*

# 4 Results and discussion

Aiming the development of a flexible epoxy formulation for tribological applications, three main steps were acknowledged, presented in the following figure.

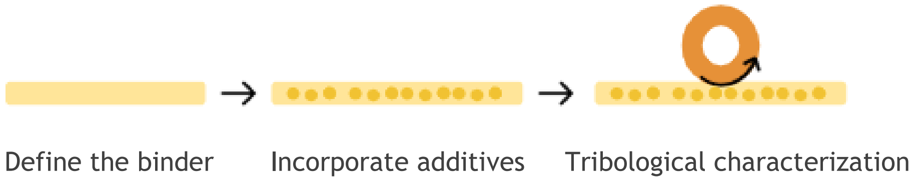


*Fig. 14) Main steps considered in the formulation development*

These main steps were performed throughout the present work, being next explored along with the results obtained.

## 4.1 Define the binder

The binder is the base of the formulation, being responsible for the main mechanical properties of the coating. This binder is constituted by an epoxy resin reacted with curing agents. The first goal is to find a flexible binder with good adhesion to the substrate.

### 4.1.1 Studied epoxy resins

Three epoxy resins were studied as candidates for the final coating: 1BPA/F, 2BPA/F and Novolac. The resin 1BPA/F is based on bisphenol-A/F and is recommended by the supplier for flexible coatings, which is the main reason why it was chosen for this project. The resin 2BPA/F is also based on bisphenol-A/F. However, besides being from a different supplier, it is already known by the company, being of interest to compare with 1BPA/F. The Novolac resin is a totally different alternative and is described as a high functionality resin that produces a higher crosslinked cured system than standard resins based on bisphenol-A/F. The choice was due to a means of comparison, in order to understand how a different type of resin may influence the final coating.

### 4.1.2 Curing agents

To provide flexibility, a polyether polyamine (PEPA) was chosen as a curing agent. The polyether polyamine molecular structure is presented in the Fig. 15. Theoretically, it is expected that a long chain backbone promotes flexibility. However, a too long chain backbone may lead to a rubbery coating. Rubbery coatings may tend to have a very high coefficient of friction and a high deformation, which is not desirable for the final application [46].

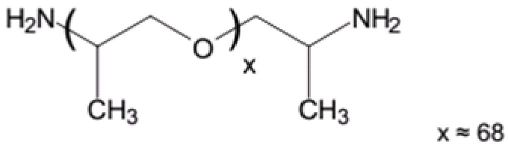


*Fig. 15) Molecular structure of the polyether polyamine curing agent used*

To overcome that, another curing agent was taken into account. A cycloaliphatic polyamine (CAPA) was used to balance the mechanical properties. Despite the specific molecular structure not being provided by the supplier, it is known that this curing agent has a higher number of reactive hydrogens per gram than the PEPA. Theoretically, it contributes to a more crosslinked system and a decrease in flexibility. The importance of this curing agent lies on the goal of finding a balance between flexibility and hardness.

In order to find the most promising binder, these two curing agents were combined in different proportions with each resin in study, culminating in a total of 15 binders, described in Table 3.

*Table 3) Molar proportion of curing agents in formulations regarding resin 1BPA/F, 2BPA/F and Novolac*

| | **Samples** | | | | |
|---|---|---|---|---|---|
| | **B1, BB1, N1** | **B2, BB2, N2** | **B3, BB3, N3** | **B4, BB4, N4** | **B5, BB5, N5** |
| **PEPA** | 100 | 75 | 50 | 25 | 0 |
| **CAPA** | 0 | 25 | 50 | 75 | 100 |

Binders of resin 1BPA/F are represented by the letter B, with the resin 2BPA/F are represented by the letters BB and samples with the Novolac are named with the letter N. All of them followed by a number from 1 to 5, which represents the equivalent molar proportion of curing agents.

### 4.1.3 Curing cycle evaluation in DSC

The first stage of the binder definition is to find the most suitable curing cycle. An epoxy system that is not properly cured may modify its mechanical properties over time. Thereby, achieving a fully cured system can guarantee a more stable product. A stable and fully cured system is also critical for a final coating because it reduces the chances of early failure in the final application [5, 47].

The strategy used to find a suitable curing cycle was based on DSC evaluation of residual crosslinking in the second heating ramp, schematized better in Fig. 16.

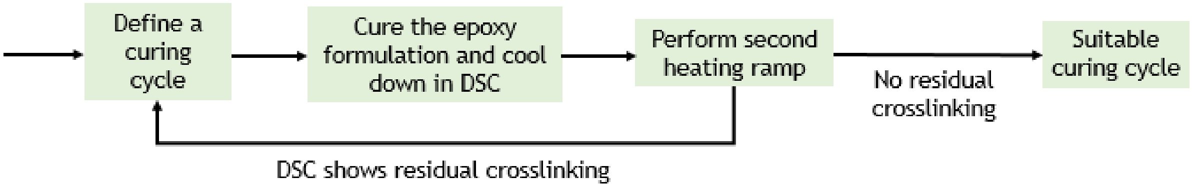


*Fig. 16) Strategy followed to find the suitable curing cycle performing the cure in the DSC*

First, a curing cycle is defined. The curing cycles are composed by a heating ramp at a heating rate of 10 °C·min$^{-1}$ followed by an isothermal. In this project, three curing cycles were considered as options, presented in Table 4. These were chosen since the company to cure epoxy systems currently uses them.

*Table 4) Curing cycles in DSC analysis with a heating ramp at 10 °C·min$^{-1}$*

| Curing Cycle | Initial Temperature / °C | Final temperature / °C | Isothermal time / min |
|---|---|---|---|
| **1** | 20 | 80 | 30 |
| **2** | 20 | 120 | 30 |
| **3** | 20 | 200 | 15 |

**Program temperature in DSC**

In order to cure the binders in DSC, the temperature program started by a heating ramp and an isothermal at the established conditions of cure. After that, the two following steps were performed:

- Cooling ramp until 20 °C at 10 °C·min$^{-1}$;
- Second heating ramp until 300 °C at 10 °C·min$^{-1}$.

By performing a second heating ramp after cure, it is possible to observe whether the cure would be complete. When the cure is incomplete, an exothermic peak is seen in the DSC thermograms, representing residual crosslinking. To better understand the strategy, Fig. 17 shows a DSC thermogram of a full temperature program performed on the sample B5 with the curing cycle 1 (presented in Table 4).

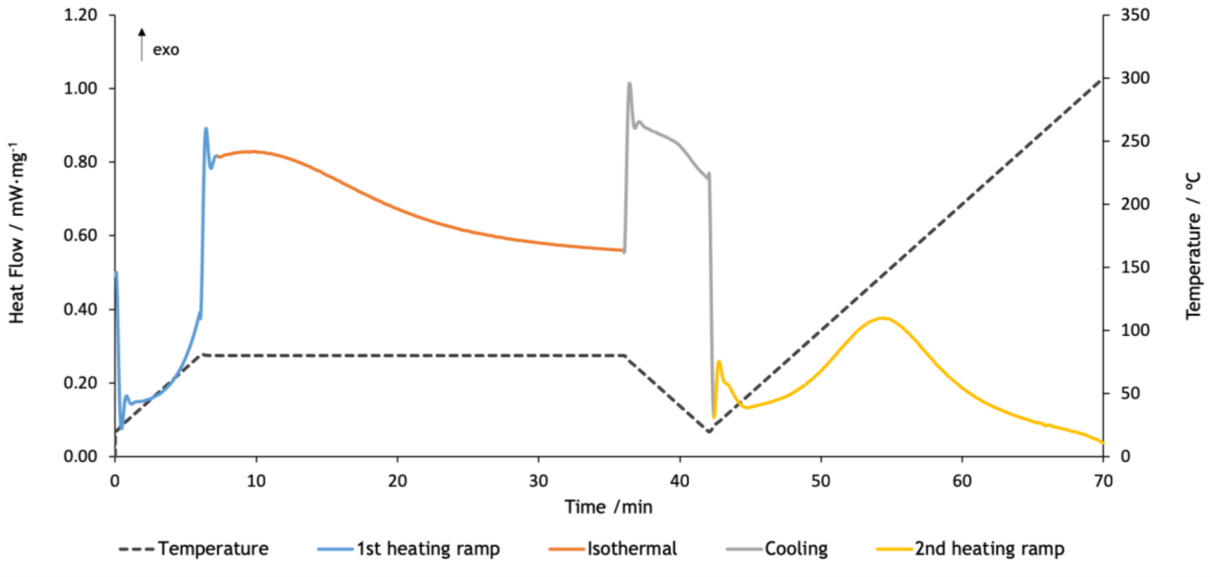


*Fig. 17) DSC thermogram of the sample B5 with the curing cycle 1.*

As expected, exothermic peaks are visible during the first heating and the isothermal run, as a consequence of the crosslinking reaction. After cooling, in the second heating ramp, a clear exothermic peak is also noticed, which area corresponds to the residual heat of the crosslinking reaction, indicating an incomplete cure in the previous process. The lower the residual heat of reaction, the higher the degree of cure and, consequently, the closer to complete crosslinking is the system [47].

With the curing cycle 3, B5 shows no exothermic peak in the second heating ramp, as seen in Fig. 18.

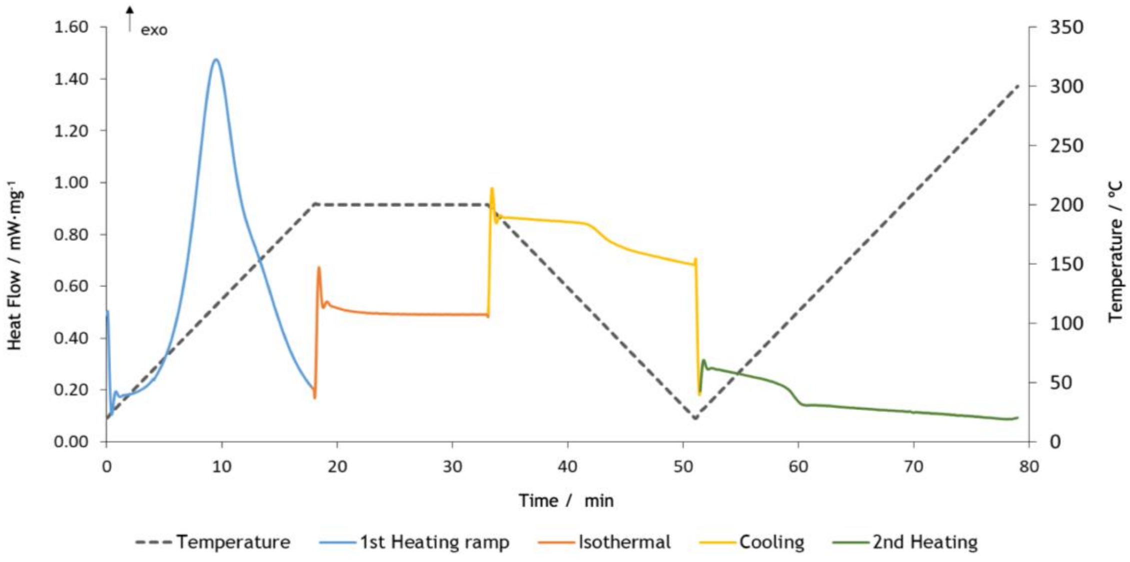


*Fig. 18) DSC thermogram of the sample B5 with the curing cycle 3.*

The glass transition is visible at around 60 min (106 °C), and it is concluded that the cure of the epoxy formulation B5 is complete using curing cycle 3.

### Suitable curing cycles

The curing cycles presented in Table 4 were simulated in DSC with the samples B1, BB1, N1, B5, BB5 and N5. These binders only have one curing agent, and it was of interest to first study the simplest epoxy binders. The selected curing cycle and the glass transition temperature (*Tg*) obtained for each sample are seen in Table 5.

*Table 5) Selected curing cycle and the glass transition temperatures obtained for the samples in study with DSC analysis.*

| | PEPA:CAPA | | | | | |
|---|---|---|---|---|---|---|
| | 100:0 | | | 0:100 | | |
| **Sample** | B1 | BB1 | N1 | B5 | BB5 | N5 |
| **Curing cycle** | 3 | 3 | 3 | 3 | 3 | 3 |
| ***Tg* (°C)** | < 20 | < 20 | < 20 | 106 | 103 | 142 |

The DSC graphics resulting from the samples B1, BB1, N1, BB5 and N5 are presented in Appendix B. Regarding the *Tg* of the samples B1, BB1 and N1, the results of the performed temperature program were inconclusive. In the Fig. 19, the second heating ramp for the curing cycle 3 corresponding the samples B1, BB1 and N1 is showed, where no *Tg* is presented. Despite no *Tg* being observed, the linear behaviour suggests a fully cured system. The PEPA is a long chain molecule which increases the distance between the crosslinking points, decreasing the crosslinking density. Consequently, in these cases, the *Tg* tends to be low. It is assumed to be lower than 20 °C, presented as < 20 in Table 3.

Between the samples B5, BB5 and N5, two main conclusions stand out. First, samples B5 and BB5 have a similar *Tg*. Despite different suppliers, the DSC thermograms did not show a difference in the behaviour of both. Secondly, the *Tg* of N5 is the highest achieved (149 °C), which is explained by a higher crosslinking density. As the Novolac resin has higher functionality than the other resins in the study, it is expected this resin would create a more crosslinked system. Combining this with the fact that the CAPA has the largest number of reactive hydrogens, makes sample N5 the more crosslinked of all.

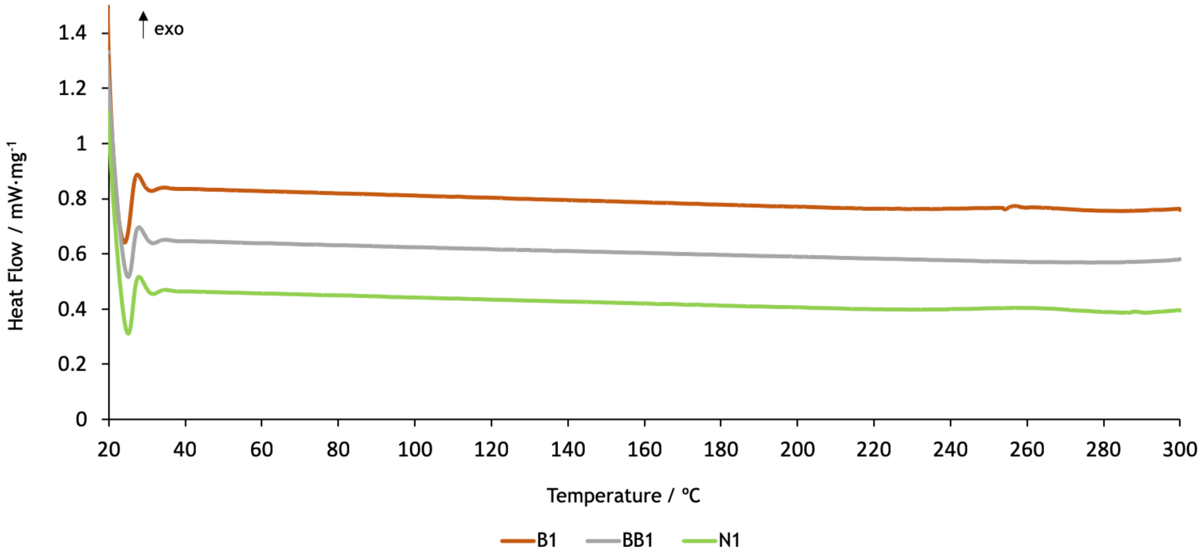


*Fig. 19) DSC thermogram of the second heating ramp at 10 °C·min$^{-1}$ performed in samples B1, BB1 and N1.*

Due to a high number of binders, it was assumed the curing cycle 3 would suit every sample and no further analysis were made using the strategy defined in Fig. 16. This assumption was tested along with the cure in the oven, explained in detail in subchapter 4.1.4.

### 4.1.4 Cure in the oven

The cure in the oven implies other factors not considered in the DSC trials, like the presence of air or a different distribution of heat. To verify if the suitable curing cycle find in the DSC also cured the samples in the oven, the strategy schematized in the Fig. 20 was performed.

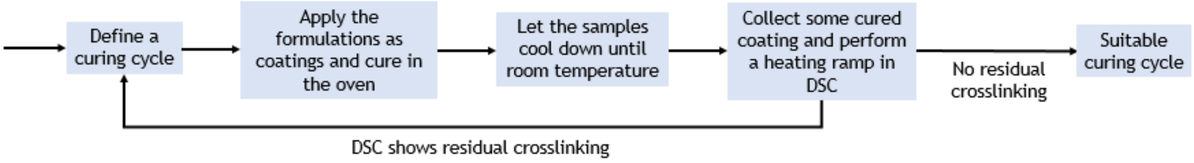


Fig. 20) *Strategy followed to find the suitable curing cycle performing the cure in the oven*

In this study, all the 15 binders were cured in the oven with the curing cycle 3 and the coatings were analysed via DSC technique, with a heating ramp from -50 °C to 250 °C at 10 °C·min$^{-1}$.

A temperature program starting with negative temperatures was used due to the fact that no *Tg* was observed in the samples B1, BB1 and N1, expecting a *Tg* lower than 20. Since the highest expected *Tg* was around 149 ºC (Sample N5), the final temperature established for the heating ramp was 250 ºC because it is thought to be enough to understand the behaviour of the samples.

The Fig. 21 presents the results of the heating ramp performed in the samples with the resin B, cured with the curing cycle 3.

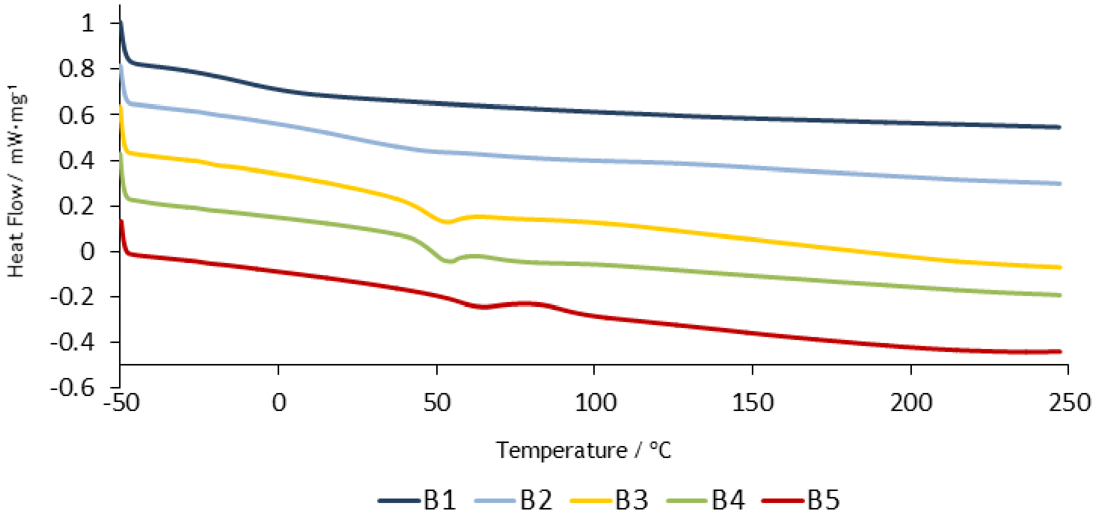


*Fig. 21) DSC thermogram of the heating ramp performed in the coatings with the resin B*

While samples B1 and B2 seemed to be fully cured, the others still showed what seems to be residual crosslinking. To overcome that, two more curing cycles were considered, described in Table 6.

*Table 6) Curing cycles in the oven*

| Curing Cycle | Initial Temperature / °C | Final temperature / °C | Isothermal time / min |
|---|---|---|---|
| **4** | 20 | 200 | 30 |
| **5** | 20 | 215 | 30 |

Table 7 summarize the suitable curing cycles for every binder, as well as the *Tg* observed. The correspondent thermograms that support the data are presented in Appendix C. The binders with the number 1 and 2 showed a linear behaviour with no *Tg*. It was assumed the *Tg* is lower than – 50. The *Tg* increased from 1 to 5, correspondent to the decrease of PEPA quantity. The *Tg* observed in samples B5, BB5 and N5 were lower than the ones obtained in the first study, presented in Table 5. It is assumed the presence of humidity and oxygen affects the curing process in the oven and consequently the *Tg*.

*Table 7) Suitable curing cycles and the Tg obtained for the samples with the resin B, BB and N cured in the oven*

| **Sample** | **B1** | **B2** | **B3** | **B4** | **B5** |
|---|---|---|---|---|---|
| **PEPA:CAPA** | 100:0 | 75:25 | 50:50 | 25:75 | 0:100 |
| **Curing cycle** | 3 | 3 | 5 | 5 | 5 |
| ***Tg* (°C)** | < - 50 | < - 50 | 50 | 72 | 97 |
| **Sample** | **BB1** | **BB2** | **BB3** | **BB4** | **BB5** |
| **PEPA:CAPA** | 100:0 | 75:25 | 50:50 | 25:75 | 0:100 |
| **Curing cycle** | 3 | 3 | 5 | 5 | 5 |
| ***Tg* (°C)** | < - 50 | < - 50 | 59 | 69 | 90 |
| **Sample** | **N1** | **N2** | **N3** | **N4** | **N5** |
| **PEPA:CAPA** | 100:0 | 75:25 | 50:50 | 25:75 | 0:100 |
| **Curing cycle** | 4 | 4 | 5 | 5 | 5 |
| ***Tg* (°C)** | < 50 | < 50 | 80 | 90 | 124 |

The DSC is a good method to understand the cure. However, in this epoxy formulations, the suitable curing cycles obtained in DSC differ from the curing cycles needed in the oven. Many factors may have influenced the complete cure on the DSC and an incomplete cure in the oven. First, a thermal inertia was considered. The heat generated in the oven is conducted not only to the samples but is also used to heat the sample sheets and the oven structure itself. Also, remembering the crosslinking reaction is exothermic, a non-linear internal heat source is generated during the curing cycle. The degree of cure may not be uniform along with the coating because of that, especially regarding areas with differences in thicknesses above 50 μm. By removing a cured sample from an area with higher thickness, the DSC results may not be representative of the remaining coating [48].

### 4.1.5 Binders mechanical properties

All the 15 binders were cured and analysed according to adhesion, flexibility and hardness. The application method was performed in order to obtain an approximately constant thickness in every coating. The application plays an important role in the characteristics of the coatings. Simple factors like the amount of uncured sample used to spread or the flatness of the steel sheets influenced significantly the final thickness and aspect of the coatings. The thicknesses defined acceptable for mechanical tests were 50 ± 10 μm, since the application thickness was 60 μm. The measured thicknesses are presented in Appendix D.

## Adhesion

Regarding adhesion, every sample presented an optimum adhesion to the substrate. In the cross-hatch performed, the edges of the cuts are completely smooth and none of the squares were detached (category 0 according to the Classification Table in Appendix A). That supports the theory that epoxy resins has a good adhesion to many substrates, including blasted steel DC04 sheets [5].

## Flexibility

To test the flexibility of the coatings, the coated steel sheets were bent in 90° and 180°. The bending was observed in the microscope in order to find indications of cracking. By bending 90°, every coating passed the test, not showing damage. When bent at 180°, three behaviours were noticed, presented in Fig 22.

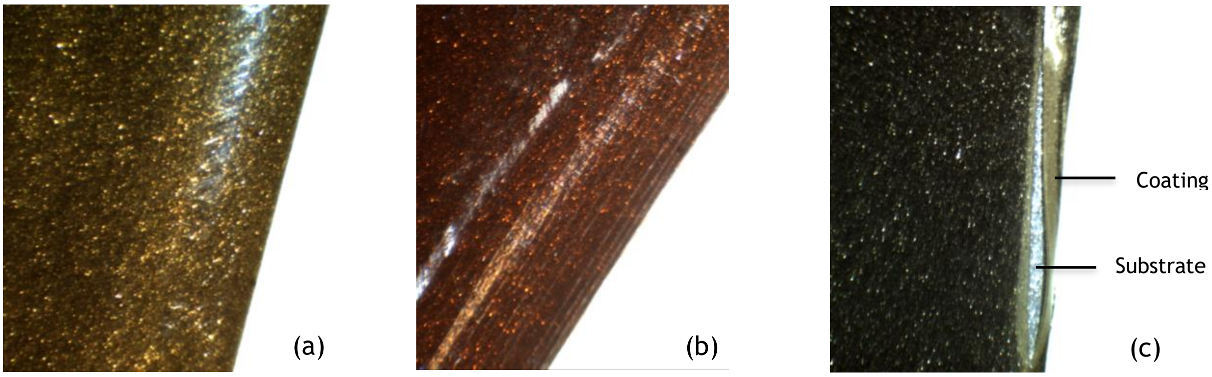


*Fig. 22) 180° bending observed in the microscope with 1.5x zoom (a) sample N2 (b) sample B4 (c) sample N5*

Coatings showing a behaviour presented in Fig. 22 (a) were considered to pass the bending test since no damage was observed. On the other hand, Fig. 22 (c) shows a complete failure, were the cracking is easily seen at the naked eye and exposes the substrate. The third behaviour is presented in binder B4 (Fig. 22 (b)), where the occurrence of crazing is apparent. Crazing is a mode of polymer fracture and is characterized by the formation of micro-gaps in a plane normal to the stress [49]. The parallel lines seen in the Fig. 22 (b) are thought to be these micro-gaps. Binders with this behaviour were assumed not to pass the bending test. However, since this theory was not supported by a detailed analysis, a SEM analysis was advised to be performed for future work.

The bending test was performed in every binder and the results are presented in table 8. The results are described as undamaged, crazing and fracture, corresponding that to the behaviours presented in Fig 22 (a), (b) and (c), respectively.

*Table 8) Results from the 180º bending test of 15 binders*

| **PEPA:CAPA** | | **100:0** | **75:25** | **50:50** | **25:75** | **0:100** |
|---|---|---|---|---|---|---|
| **Sample Number** | | 1 | 2 | 3 | 4 | 5 |
| **Resin** | B | Undamaged | Undamaged | Undamaged | Crazing | Crazing |
| | BB | Undamaged | Undamaged | Undamaged | Crazing | Crazing |
| | N | Undamaged | Undamaged | Undamaged | Crazing | Fracture |

The binders with a higher quantity of PEPA (1 to 3) passed the bending test, while the ones with none or just a few quantity failed. Only the sample N5 had the failure presented in the Fig. 12 (c). The Novolac resin tends to be more brittle than the other resins, due to higher functionality. It was noticeable the CAPA also tended to increase brittleness in the coating, as seen in samples indicated with 4 and 5. The binders which did not pass the bending test were excluded as a possibility to become part of the final coating.

**Hardness**

To understand if there is a relation between the flexibility and the hardness of the coatings, the hardness was measured (Fig.23). An adapted version of the pencil hardness test was used, allowing measurements of the force needed to scratch the coating.

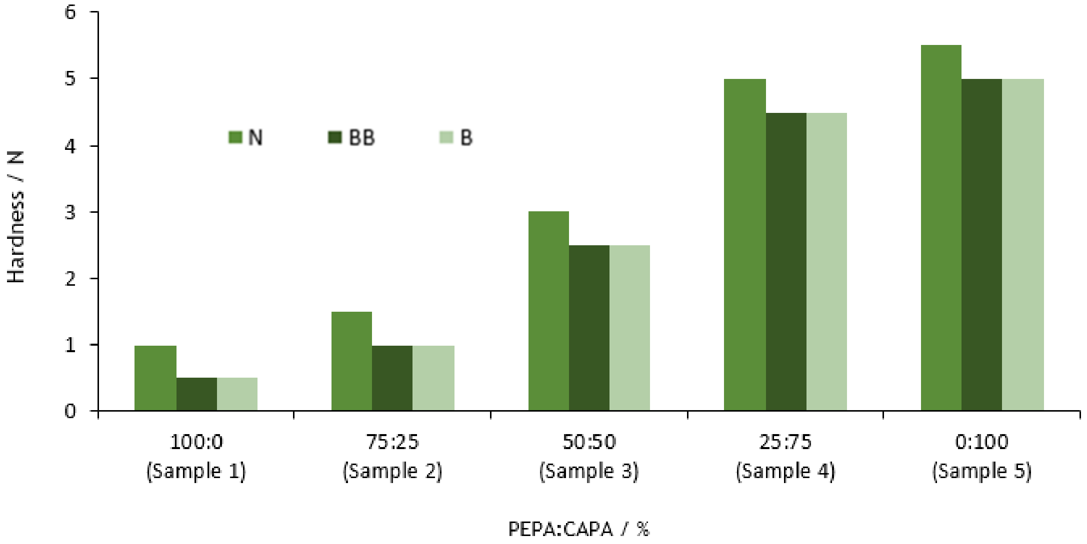


*Fig. 23) Hardness values obtained with the pencil hardness test for the 15 binders.*

As the quantity of PEPA in the binder decreased, the hardness increased. Coatings with higher flexibility were softer, as expected. The samples B1, BB1 and N1 were considered too soft and behave like rubber. Besides being easily scratched, they deform effortlessly. Samples B2 and

BB2 also showed a similar behaviour. With a higher hardness, N2 did not present these rubbery characteristics.

### 4.1.6 Final binder selection

Between all the analysed samples, 5 binders were chosen as candidates for a good flexible tribological coating. Samples B3, BB3, N2 and N3 were selected since they pass the bending test and had enough hardness not to be too rubbery. Also, to better understand the influence of hardness in the final coating, the sample BB2 was also chosen.

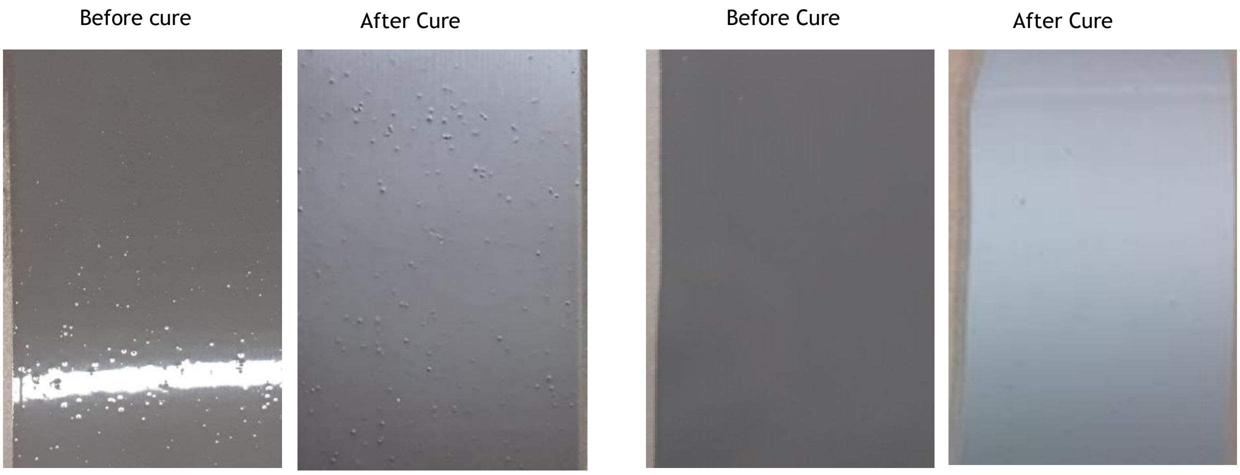
## 4.2 Incorporation of additives

To provide tribological properties, polytetrafluoroethylene (PTFE) was added as a filler to the binders (B3, BB3, N2, N3 and BB2). According to previous knowledge from the company related to epoxy formulations, it was advised to add 20 % by weight based on the epoxy resin mass. The PTFE was added along with a small quantity of surfactant, an additive for promoting PTFE wetting and dispersion. Aiming towards a constant thickness of the coating and avoid sagging effects, a rheological additive was also incorporated.

### 4.2.1 Incorporation Method

The PTFE and the remaining additives were incorporated in the epoxy resins with a high-shear mixer, the Ultra-Turrax T18. After mixing with the curing agents, the coatings were applied and cured. Since the PTFE micropowder is an inert polymer with a small size particle (average particle size around 7 μm), no effect in the curing cycle was considered. The curing cycles used were the same used to cure the binders, presented in detail in the subchapter 4.1.4. The samples with PTFE incorporated were designated by the name of the binder along with an indication of PTFE (for example, $N3_{PTFE}$ means sample N3 with PTFE).

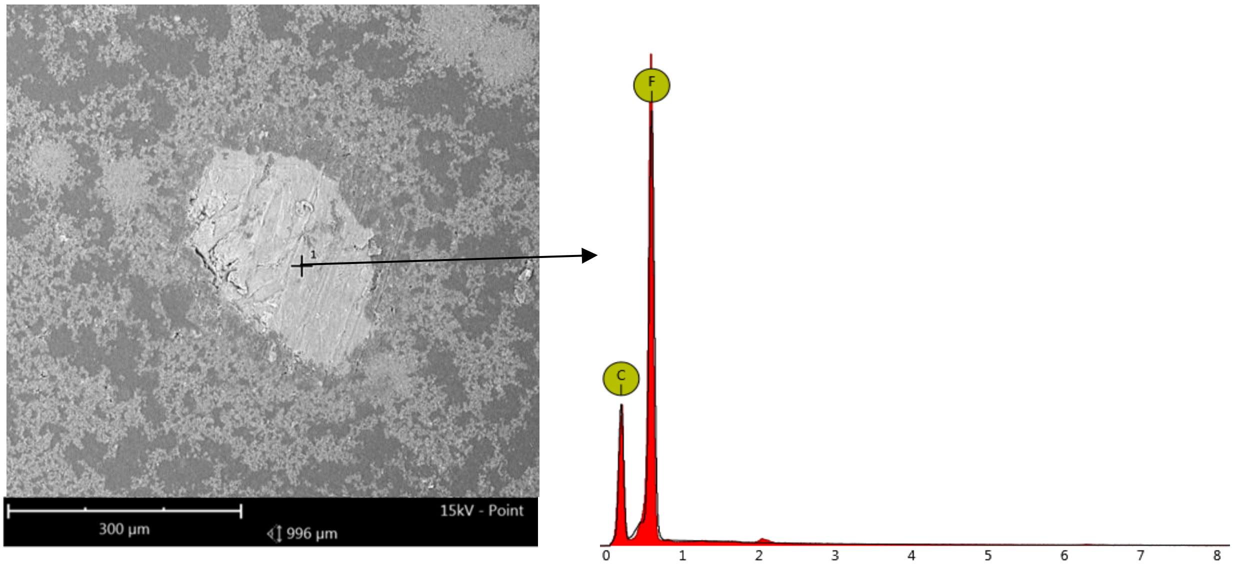
The Fig. 24 shows the samples $N3_{PTFE}$ and $B3_{PTFE}$ before and after curing. The coatings with novolac resin have the higher viscosity and it is the ones with more defects, before and after curing (Fig. 24 (a)). These defects, at naked eye, can be described as protuberances in the surface, indicating the possibility of PTFE agglomerated. With too viscous systems, not only the dispersion with the high-shear mixer might not be effective, but also the release of air incorporated during the mixing becomes more difficult. Air incorporated in viscous coating also leads to defects, which are usually holes due to the air release during cure.



(a) (b)

*Fig. 24) Images of sample (a) N3$_{PTFE}$ and (b) B3$_{PTFE}$ with PTFE incorporated before and after cure.*

Despite at naked eye the defects seemed agglomerates instead of holes, an SEM analysis was used to make sure what kind of defect it is. It was important to understand the coating defects in order to reduce them. In the Fig. 25, the results of SEM analysis along with the element analysis performed to a defect in the sample N3$_{PTFE}$ are presented.



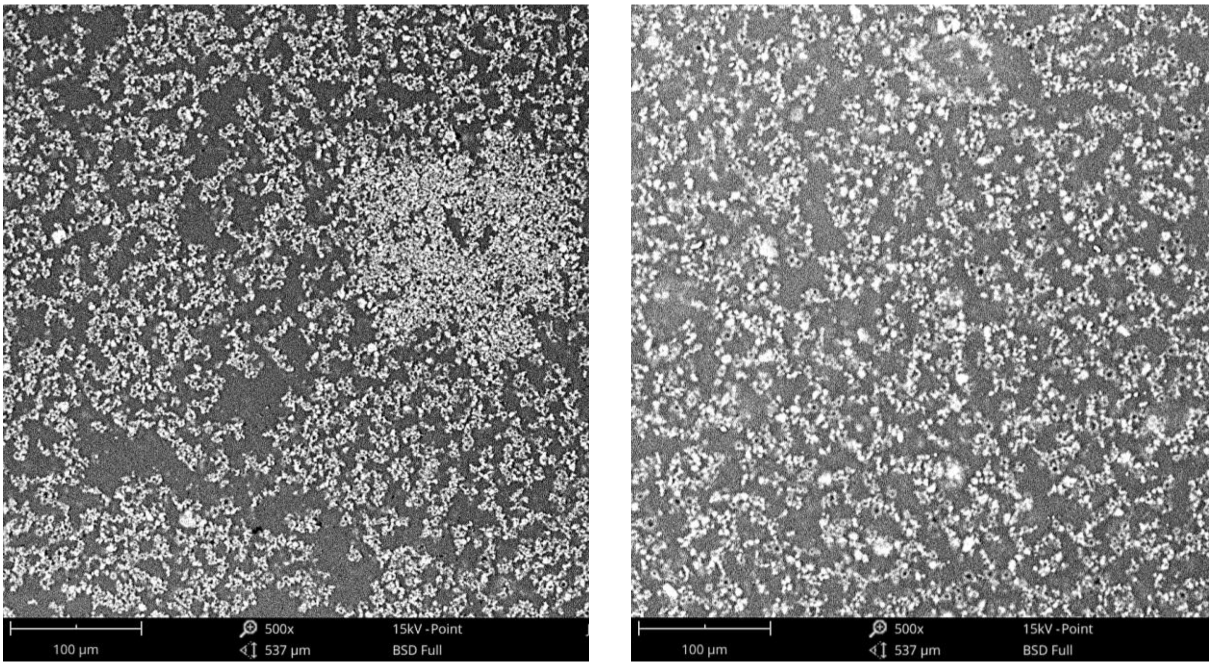
(a) (b)

*Fig. 25) Defect of the sample N3 captured by SEM (a) and the correspondent elemental analysis (b).*

The defect of the coating N3$_{PTFE}$ was composed of carbon and fluoride, which was proved to be a PTFE agglomerate. These defects were mostly seen in coatings N2$_{PTFE}$ and N3$_{PTFE}$. Coatings B3$_{PTFE}$, BB2$_{PTFE}$ and BB3$_{PTFE}$ show significantly less defects, as it is assumed a better dispersion in BPA1 and BPA2 due to a lower viscosity of these resins.

To prove that, the dispersion was observed in the SEM. The dispersion of PTFE in the samples $N3_{PTFE}$ and $B3_{PTFE}$ can be seen in the Fig. 26: the white areas are the PTFE, while the remaining is the epoxy resin with the curing agents. The sample $N3_{PTFE}$ had specific areas where the PTFE is more concentrated than others. The opposite happens with the sample $B3_{PTFE}$, where there was a good distribution of PTFE.

Despite some samples showing more defects than others, all needed optimization in order to overcome the defects. To do that, two solutions come to mind. The ideal solution would be the use of a proper dispersion equipment for viscous formulations. A roll mill equipment is the best option to incorporate PTFE, especially with the Novolac resin. Roll mills are used to mix, disperse, or homogenize viscous materials by creating a shear force with rollers [50]. Other solution lies in diluting the resin to an adequate viscosity for the higher shear mixer. However, a too low viscosity may preclude the application method used in the steel sheets.



(a) (b)

*Fig. 26) Dispersion of PTFE observed by SEM of the sample $N3_{PTFE}$ (a) and the sample $B3_{PTFE}$ (b).*

## 4.3 Mechanical analysis of the coatings

The adhesion, flexibility and hardness were measured again in order to see if the coatings maintain the same behaviour after (B3, BB3, N2, N3 and BB2) and before ($B3_{PTFE}$, $BB3_{PTFE}$, $N2_{PTFE}$, $N3_{PTFE}$ and $BB2_{PTFE}$) the incorporation of additives.

In terms of adhesion, the coatings showed optimum results (category 0 according to the Classification Table in Appendix A). The edges of the cuts are completely smooth and none of the squares were detached. The incorporation of additives did not show influence in the adhesion of the coating.

When performing the bending test, every coating also passed the test. As it is known the incorporation of PTFE has little influence on the mechanical properties of the binder polymer, it was expected to obtain good flexibility results [51].

In terms of hardness, the following graphic (Fig. 27) shows the data obtained. After the incorporation of PTFE, the hardness measured decreased in every sample comparing to the measurements in the binders. The PTFE had substantial impact on the surface properties of the binder, decreasing the coefficient of friction but making the surface softer and easier to scratch [51]. It is proved, however, that the hardness of the binder still has an influence on the coating, since the conclusions taken are similar to the ones discussed with the binder hardness. The sample $N3_{PTFE}$ is the hardest, which is justified with the fact of being prepared with a multifunctional resin with less amount of PEPA. Comparing for example the samples $BB2_{PTFE}$ and $BB3_{PTFE}$, they only differ in the amount of the PEPA curing agent. $BB3_{PTFE}$, the one with less amount, presents the higher value of hardness measured.

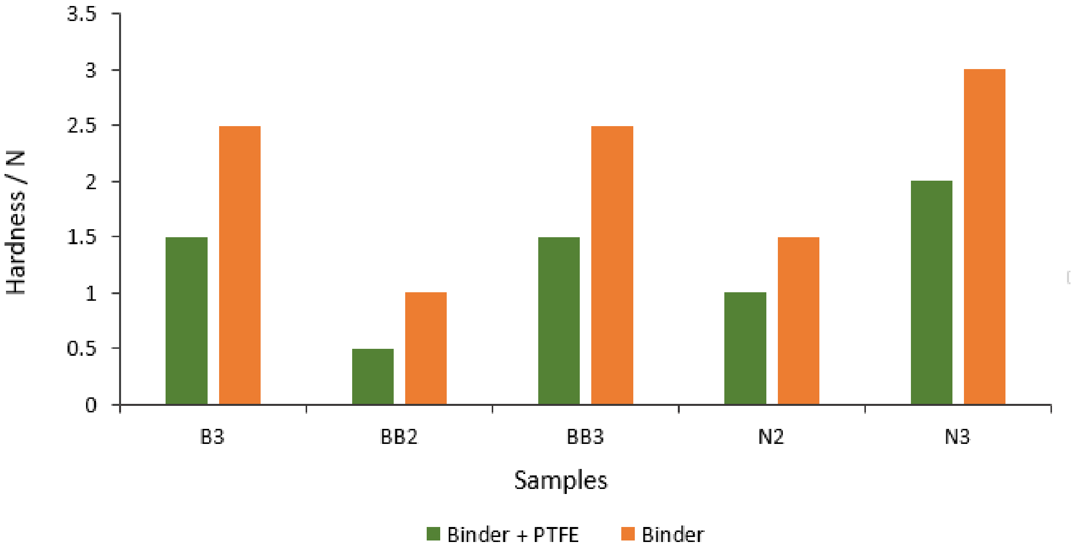


*Fig. 27) Hardness of the coated samples with and without PTFE incorporated.*

Even after the incorporation of PTFE, the adhesion and the flexibility were not affected. These results show the importance of the chemical structure of the binder in the final properties of these coatings. The hardness results demonstrate the influence of the curing agents used.

## 4.4 Tribological Analysis

Tribological tests were performed in each coating ($B3_{PTFE}$, $BB3_{PTFE}$, $N2_{PTFE}$, $N3_{PTFE}$ and $BB2_{PTFE}$), in areas with no defects. To be successful in terms of tribology regarding the final application, the coefficient of friction (COF) required should not be higher than 0.100. This requirement was defined by the company. Table 9 compiles the average COF obtained.

*Table 9) Coefficient of friction obtained in the tribological tests for the coatings*

| **Sample** | $B3_{PTFE}$ | $BB2_{PTFE}$ | $BB3_{PTFE}$ | $N2_{PTFE}$ | $N3_{PTFE}$ |
|---|---|---|---|---|---|
| **COF** | 0.136 | 0.166 | 0.117 | 0.115 | 0.112 |

Through the analysis of the COF values, it was seen the harder coatings had better tribological results than softer coatings. Between the samples $BB2_{PTFE}$ and $BB3_{PTFE}$, $BB2_{PTFE}$ was the one with more PEPA curing agent and, consequently, was softer (seen in Fig. 27). The tribological results improved significantly from the sample $BB2_{PTFE}$ (COF = 0.166) to $BB3_{PTFE}$ (COF = 0.117), where the quantity of PEPA decreases and the hardness increases. This behaviour was easily seen in the Fig. 28, showing the COF registered during time for the samples $BB2_{PTFE}$ and $BB3_{PTFE}$.

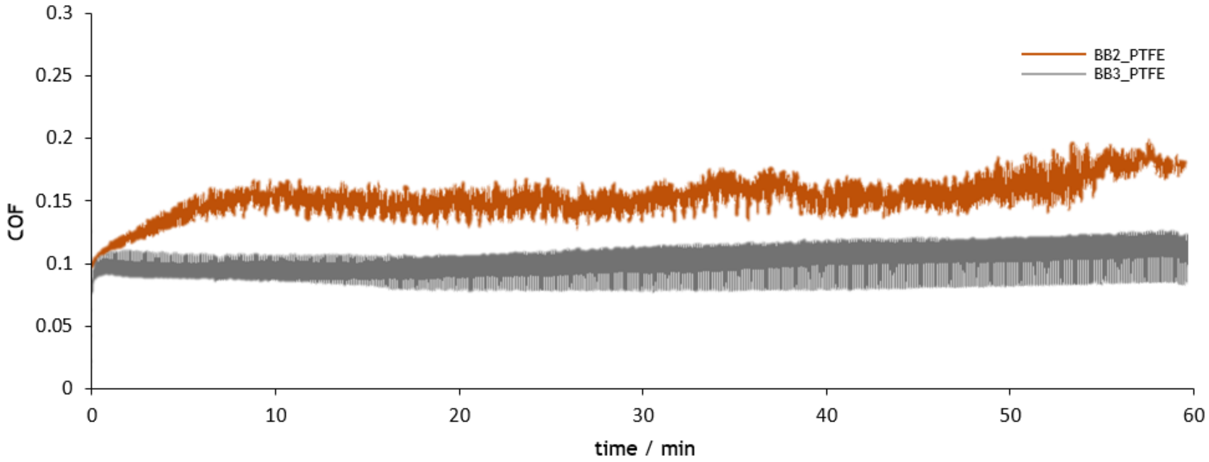


*Fig. 28) Coefficient of friction of samples $BB2_{PTFE}$ and $BB3_{PTFE}$.*

The tribological behaviour of sample $BB2_{PTFE}$ is more unstable, while the behaviour of $BB3_{PTFE}$ is constant. Softer coatings tend to deform more easily when loaded, resulting in a lot of variations in COF values.

The best tribological result comes from $N3_{PTFE}$, the hardest sample. $N3_{PTFE}$ achieved a COF of 0.112, which is the closest to the required COF of 0.100. This COF value is not so far from the one obtained by $N2_{PTFE}$ (COF = 0.115). The comparison between the tribological behaviour of $N3_{PTFE}$ and $N2_{PTFE}$ is in the Fig. 29.

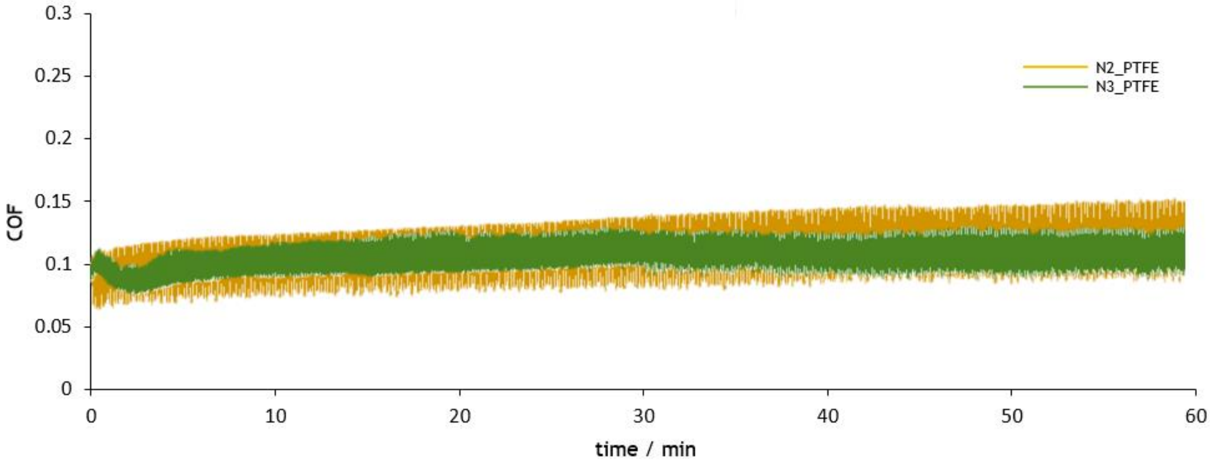


*Fig. 29) Coefficient of friction of samples N2*$_{PTFE}$ *and N3*$_{PTFE}$*.*

The samples N2$_{PTFE}$ and N3$_{PTFE}$ did not show significant differences. Both had a constant and linear behaviour, leading to conclude both samples are promising to achieve an optimum value of COF after optimization of the formulation.

Sample B3$_{PTFE}$ had a COF value (0.136) higher than expected. However, by analysing the graphic in the Fig. 30, the COF measurements had more noise than the remaining results.

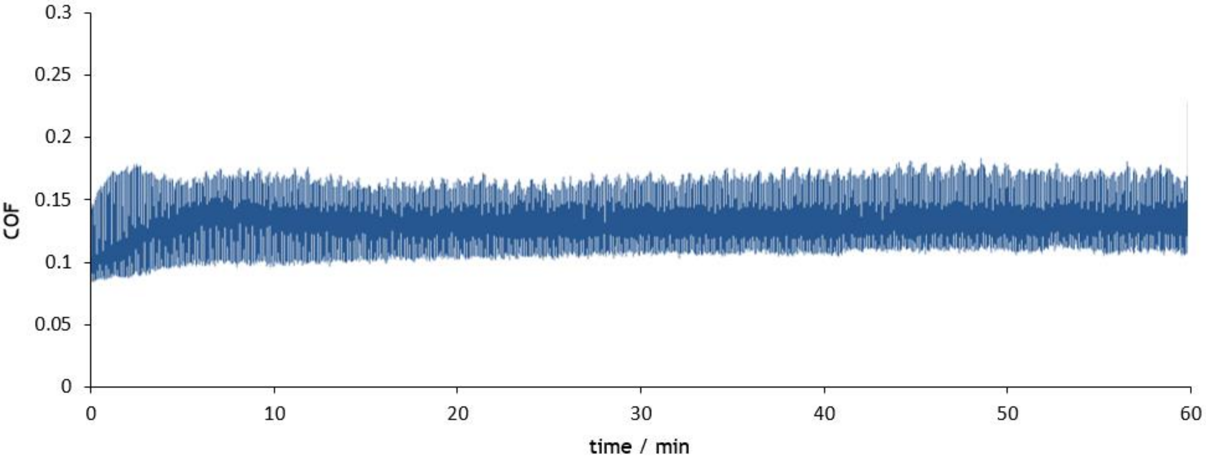
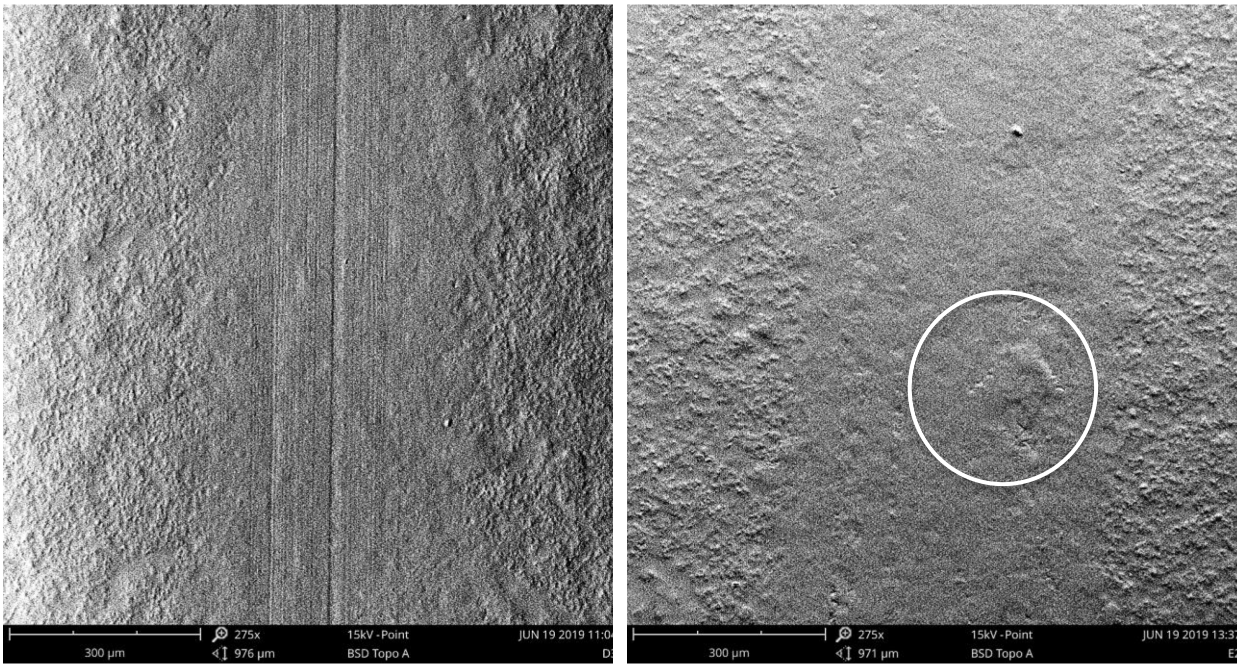


*Fig. 30) Coefficient of friction of sample B3*$_{PTFE}$*.*

The noise registered in the tribological analysis is thought to be due to bad application of the coating. This specific coating had a high roughness and too different COF values were registered during time, creating noise and resulting in a higher average COF than expected. This result obtained was not considered representative, being advised for future work to improve the application and perform the tribological tests again.

After the tribological analysis, the resultant wear was observed in SEM. The Fig. 31 sets the SEM images of samples N3$_{PTFE}$ and BB2$_{PTFE}$ after the tribological tests.

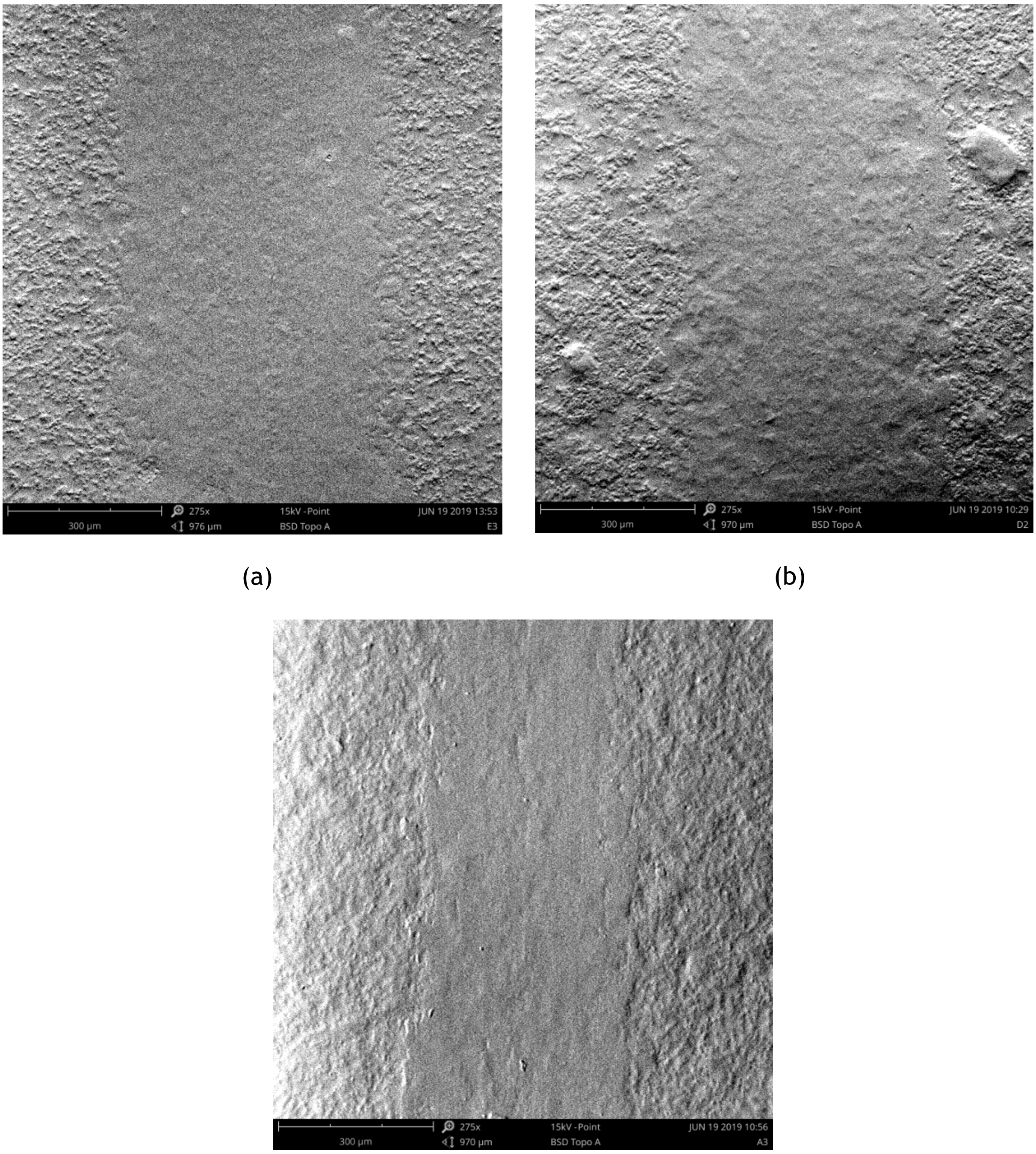


(a) (b)

*Fig. 31) SEM BSD topo A mode images of the wear of sample (a) $N3_{PTFE}$ and (b) $BB2_{PTFE}$ resultant from ball on plate tribological tests.*

The wear of sample $N3_{PTFE}$ is described by parallel lines on the coating (scratches), being interpreted as abrasive wear. The harder surface led to the removal of the softer material, resulting in grooves or scratches in the surface, as seen in the Fig. 31 (a) [2]. The sample $BB2_{PTFE}$ is mainly described by the displacement of coating that led to a lump above the original surface, marked by the white circle in the Fig. 31 (b). The material transfer is characteristic of adhesive wear. $BB2_{PTFE}$ has a lower crosslinking density than the sample $N3_{PTFE}$. That way, softer coatings tend to result in poor tribological results. When material displacement as seen in the Fig. 31 (b) happens, the coefficient of friction increases. When there is displacement of material, it acts as a foreign body in contact with the interface, increasing the friction [2]. As the hardness increases, a more abrasive wear tends to take place. Therefore, hard coatings are better for tribological properties, since the abrasive behaviour removes the particles instead of dragging them.

In the samples $BB3_{PTFE}$, $N2_{PTFE}$ and $B3_{PTFE}$ no specific type of wear was identified, seen in the Fig. 32. The applied friction in the coatings removed the PTFE from the surface, as seen by the change of roughness between the worn and non-worn areas. The results did not show significant differences between the wear of samples $BB3_{PTFE}$, $N2_{PTFE}$ and $B3_{PTFE}$. The tribological test performed, in these examples, are inconclusive. A higher load or a longer duration of the tribological test is advised for future work, in order to better understand the tribological differences between the samples.



(a)

(b)

(c)

Fig. 32) *SEM images of the wear of sample (a) BB3$_{PTFE}$, (b) N2$_{PTFE}$ and (c) B3$_{PTFE}$, resultant from ball on plate tribological tests.*

# 5 Conclusion

In order to develop a flexible epoxy formulation for tribological applications, three main steps were acknowledged:

- Obtain a flexible binder with good adhesion to the substrate using a system of epoxy resins and curing agents
- Incorporate additives to provide tribological properties
- Study the tribological properties of the final coatings

First, 15 binders were defined. Through the study of the suitable curing cycle for the binders, three curing cycles were determined:

- Curing cycle 3: Heating ramp until 200 °C at 10 $°C·min^{-1}$ and an isothermal during 15 min
- Curing cycle 4: Heating ramp until 200 °C at 10 $°C·min^{-1}$ and an isothermal during 30 min
- Curing cycle 5: Heating ramp until 215 °C at 10 $°C·min^{-1}$ and an isothermal during 30 min

The curing cycle 3 was suitable for samples B1, B2, BB1 and BB2. The curing cycle 4 fully cured the samples N1 and N2. The remaining samples cured with the curing cycle 5.

Regarding resins 1BPA/F and 2BPA/F, the results obtained are similar, showing in this case not much difference between the resins. The Novolac resin has the highest values of $Tg$ achieved in the samples N3, N4 and N5, being that explained by a higher functionality.

It was concluded the quantity of polyether polyamine has a significant influence in the curing cycle and in the $Tg$. The higher the quantity of polyether polyamine, lower the $Tg$ and less heat is necessary to completely cure the system. That is explained by the fact that the polyether polyamine is a long chain molecule which increases the distance between the crosslinking points, decreasing the crosslinking density.

The 15 binders were cured and analysed according to adhesion, flexibility and hardness. Every sample presented an excellent adhesion to the substrate. In terms of flexibility, two types of failures were identified - crazing and fracture. Samples with a higher quantity of polyether polyamine (1 to 3) had more flexibility. Sample N5 fractured and the remaining showed crazing. Then, after the study of the hardness, it was inferred that the higher the flexibility, the lower the hardness of the coating, as expected. The polyether polyamine improves the flexibility, while the cycloaliphatic polyamine improves the hardness. The Novolac resin also promotes a higher hardness of the coating.

The samples B3, BB3, N2 and N3 were chosen to proceed to incorporation of additives, since they passed the bending test and showed enough hardness to be suitable for tribological applications. The sample BB2 was also considered for that effect, in order to better understand the influence of hardness in the final coating.

The PTFE was incorporated with a high-shear mixer, which was concluded not to be effective to disperse powder in viscous resins. The coatings presented agglomerates, which were mainly noticed in coatings with the Novolac resin. A roll mill equipment is suggested as a better option to incorporate PTFE in the samples, especially with the Novolac Resin. The coatings were cured with the curing cycles defined previously, since PTFE micropowder is inert and has no effect in the curing cycle.

Regarding mechanical properties of the coatings with PTFE, the adhesion and the flexibility were not affected. The hardness decreased in every sample comparing to the measurements in the binders. However, samples with less crosslinking density tend to be softer, showing the same tendency seen with the binders. It is concluded the PTFE has substantial impact on the surface properties of the host polymer, making the surface softer and easier to scratch.

After performing the tribological tests, it was seen $N2_{PTFE}$ and $N3_{PTFE}$ showed the best results of COF (0.115 and 0.112, respectively). The worst result was obtained by $BB2_{PTFE}$ (COF = 0.166). The wear was observed in the samples. While $N3_{PTFE}$ had signs of abrasive wear, $BB2_{PTFE}$ showed displacement of material, presenting signs of adhesive wear. The results demonstrate that softer coatings tend to result in poor tribological results. As it was seen through the hardness test that more flexible coatings tend to be softer, it is mainly concluded that more flexible coatings tend to lead to a higher coefficient of friction, resulting in worst tribological performance. The most suitable coating implies, then, a balance between hardness and flexibility.

Despite the need for improvements, the best coating to pursue the optimization is $N3_{PTFE}$, since it showed the best tribological results, combining hardness and flexibility. However, longer tribological tests should be performed in order to understand better the behaviour of the coating in terms of wear. It is considered to be a good starting point for the formulation of an optimized coating that verifies the requirements for the final application.

# 6 Assessment of the work done

## 6.1 Objectives Achieved

This present work has the purpose to develop a customized epoxy based tribological coating for a mechanical system that requires, besides tribological properties, other properties such as flexibility. Inside the company's portfolio of available raw materials and polymers, epoxy resins show to be the less costly option as well as chemically versatile, being strategically interesting to explore this possibility. In this project, a flexible epoxy based tribological coating was developed. It was proved the possibility to combine epoxy resins and flexibility. Apart from that, the coefficient of friction obtained in the final samples proved that the flexible epoxy-based formulations are suitable for tribological properties. However, improvements to eliminate the defects and improve even more the tribological properties are required in order to be possible to have a product for a final application.

## 6.2 Limitations and Future Work

The first limitation was regarding the measure of the hardness. The available method measured values which allow to compare the samples between them, but the short scale and lack of accuracy didn’t allow a deep study of this property. As this property showed to be important in terms of tribology, it is advised the use of other methods.

However, the main limitation during the project the lack of availability of equipment to incorporate PTFE in viscous resins. It is advisable, for future work, to study the incorporation with other equipment like a roll mill, in order to reduce defects and improve dispersion.

For future work, is advised to change the method of incorporation of the PTFE. The coating needs optimization and it should start with the elimination of defects. After, a further study of tribological properties is important. Longer tribological tests with different loads are interesting tests which allow to better understand the tribological properties. Only by conducting such tests it is possible to know if the coating needs optimization regarding the amount of PTFE used or which other additives should be considered.

## 6.3 Final Assessment

I believe this project contributed to the development of a product with potential to be optimized for the final application. The novelty of bringing epoxy resins and flexibility together was valuable for the company. Besides, the successful incorporation of tribological properties set foundations for interest in future developments. Throughout the work done, I learned a lot about polymers and coating industry. Relevant was also the opportunity to work with a large number of new equipment and techniques. Allying that to the contact with a more professional environment, add an important value to my personal experience.

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# Appendix A Cross cut adhesion test - Classification

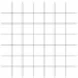
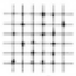
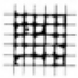
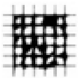
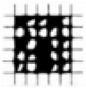
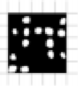
| Classification | | Description | Appearance of surface of cross-cut area from which flaking has occurred (example for 6 parallel cuts) |
|---|---|---|---|
| ISO | ASTM | | |
| 0 | 5B | The edges of the cross-cut are completely smooth: none of the squares of the lattice is detached |  |
| 1 | 4B | Detachment of small flakes of the coating at the intersections of the cuts. A cross-cut are not significantly greater than 5% is affected |  |
| 2 | 3B | The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area significantly greater than 5%, but not significantly greater than 15%, is affected |  |
| 3 | 2B | The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected |  |
| 4 | 1B | The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 65%, is affected |  |
| 5 | 0B | Any degree of flaking that cannot even be classified by classification 4 |  |

*Fig. A.1) Classification table for cross cut adhesion test.*

# Appendix B DSC evaluation

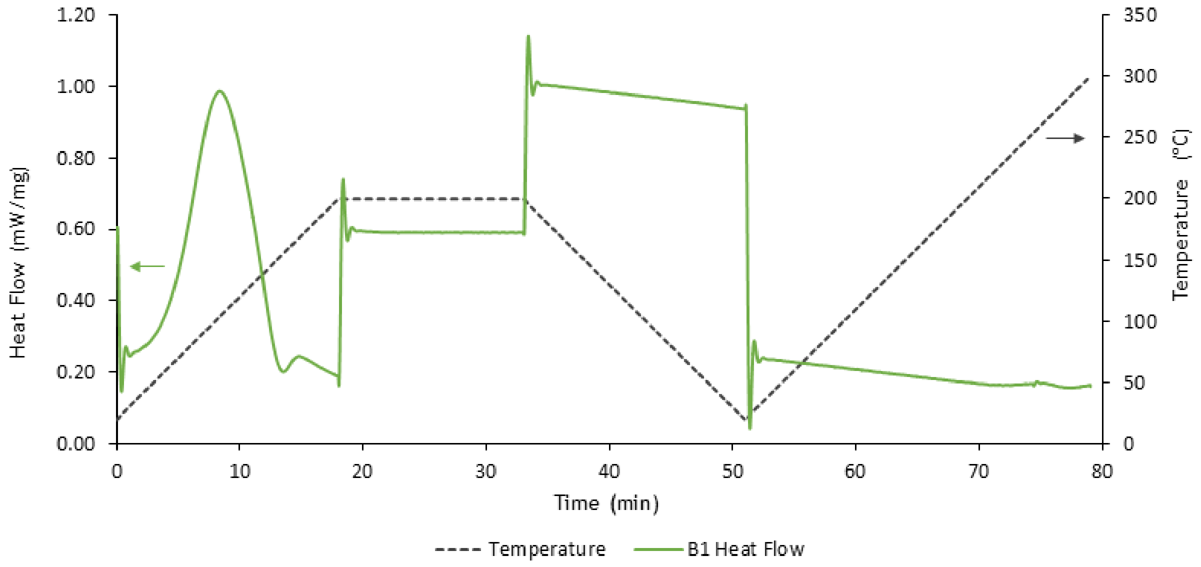


*Fig. B.1) Thermogram of sample B1, simulating the curing cycle 3.*

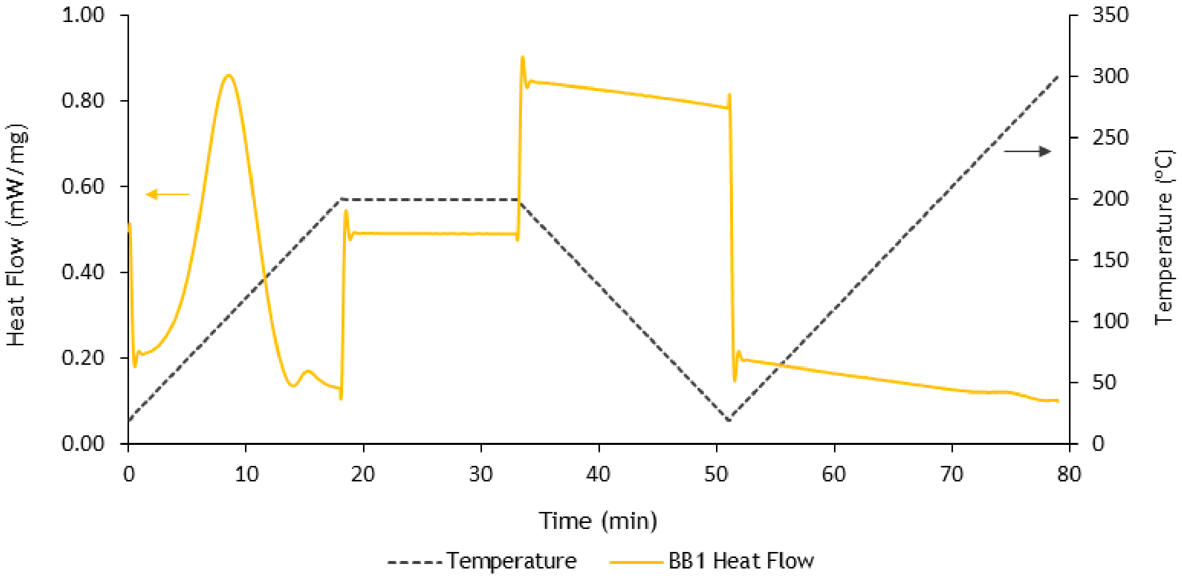


*Fig. B.2) Thermogram of sample BB1, simulating the curing cycle 3.*

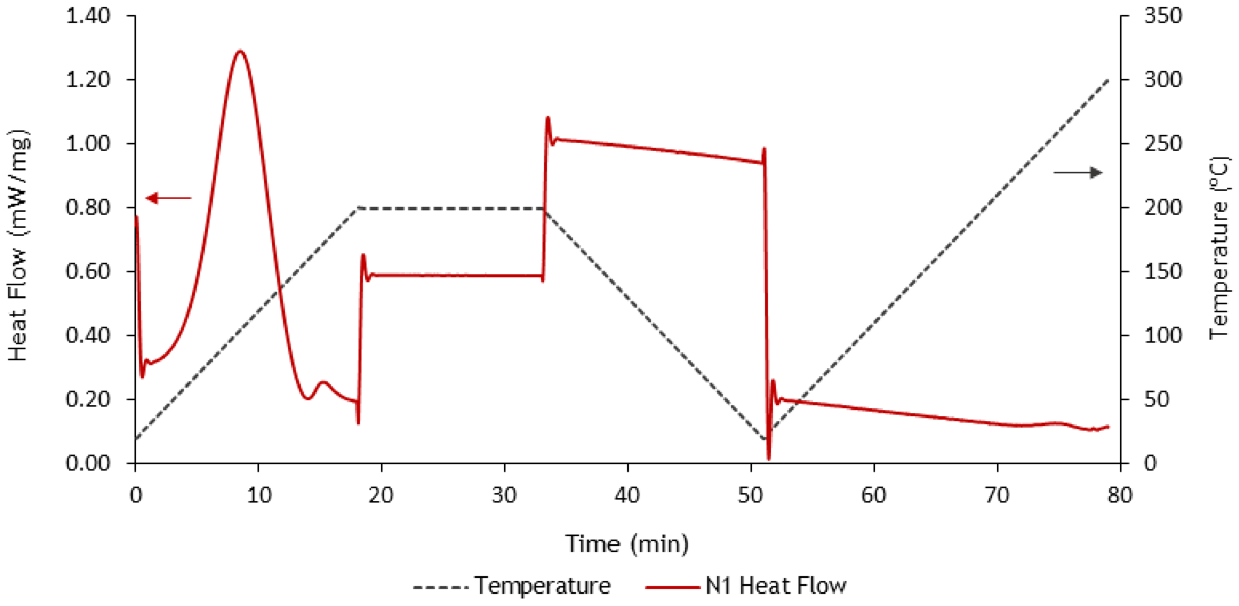


*Fig. B.3) Thermogram of sample N1, simulating the curing cycle 3.*

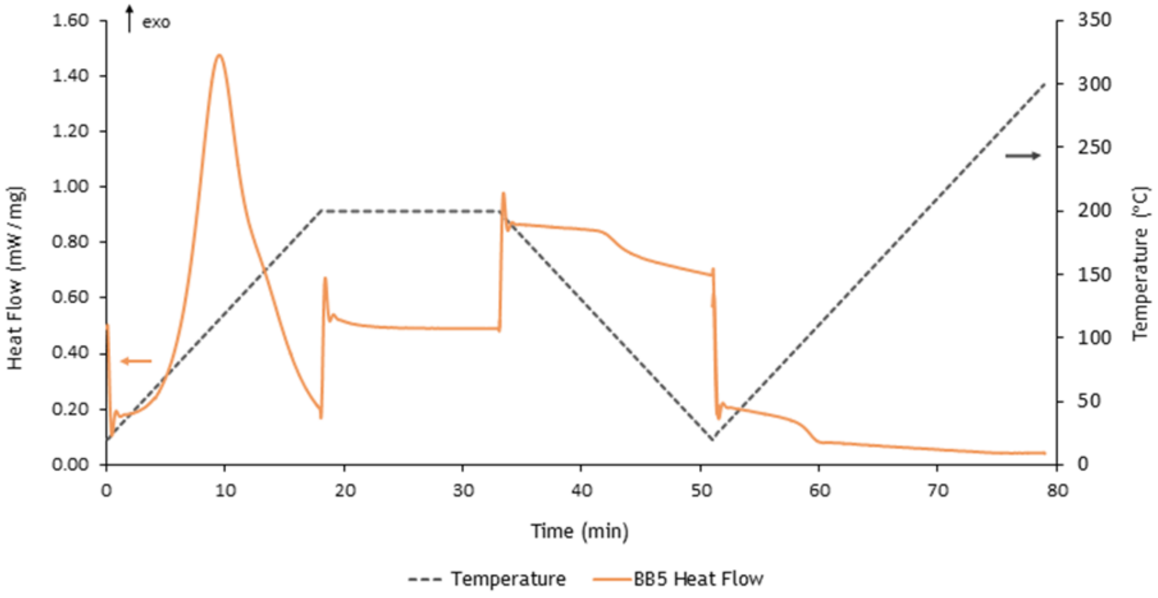


*Fig. B.4) Thermogram of sample BB5, simulating the curing cycle 3.*

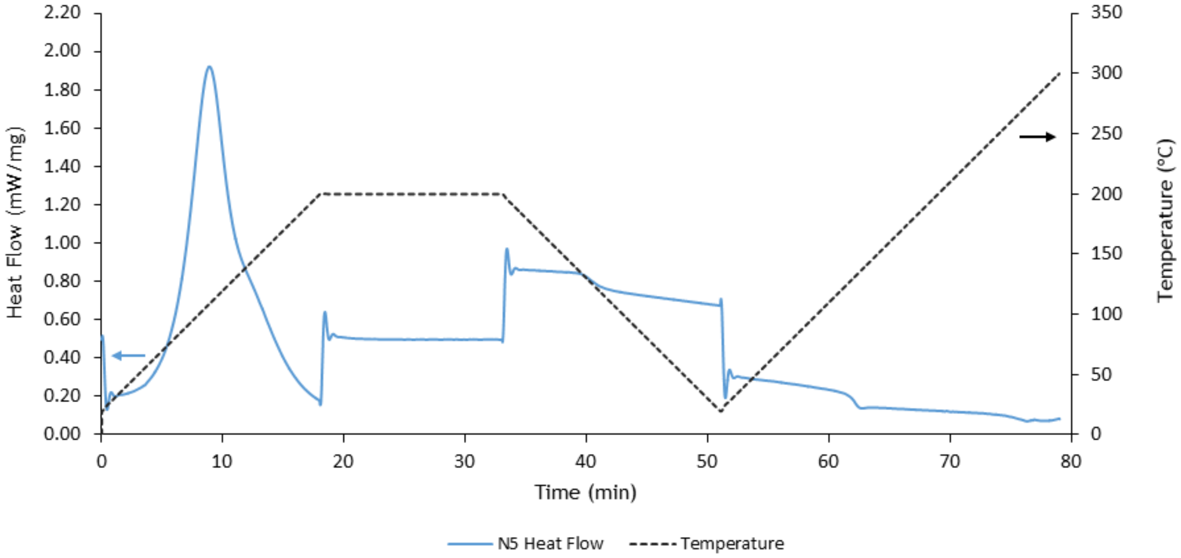


*Fig. B.5) Thermogram of sample N5, simulating the curing cycle 3.*

# Appendix C DSC heating ramp of coatings

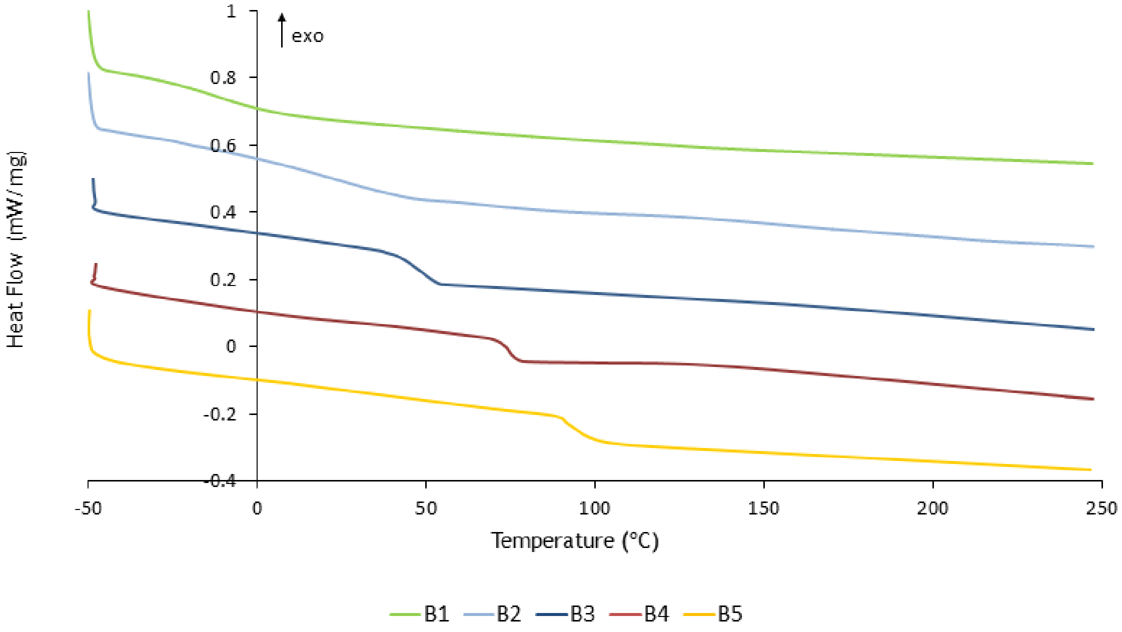


Fig. C.1) *DSC thermogram of the heating ramp performed in the coatings with the resin B with the curing cycles presented in table 7.*

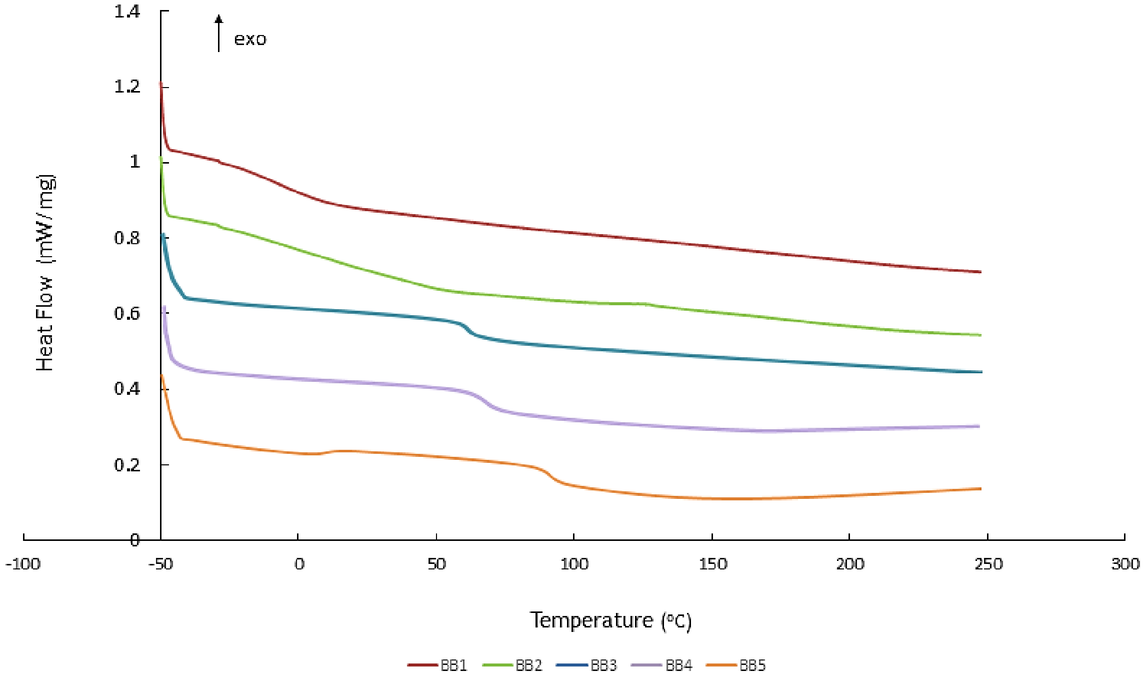


Fig. C.2) *DSC thermogram of the heating ramp performed in the coatings with the resin BB with the curing cycles presented in table 7.*

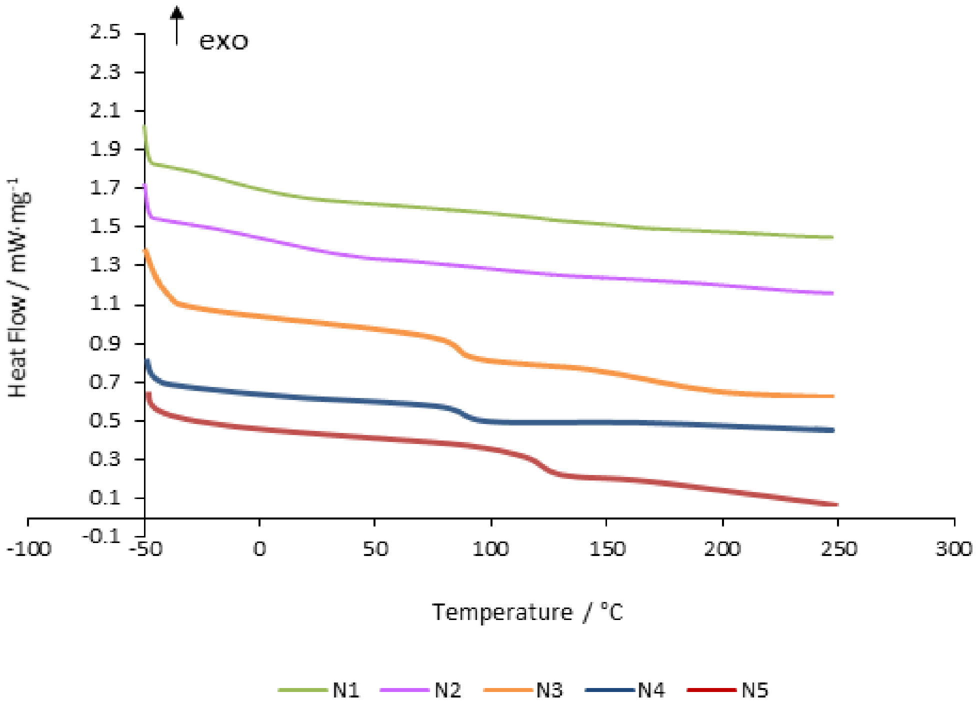


Fig. C.3) *DSC thermogram of the heating ramp performed in the coatings with the resin N with the curing cycles presented in table 7.*

# Appendix D Thickness of binders

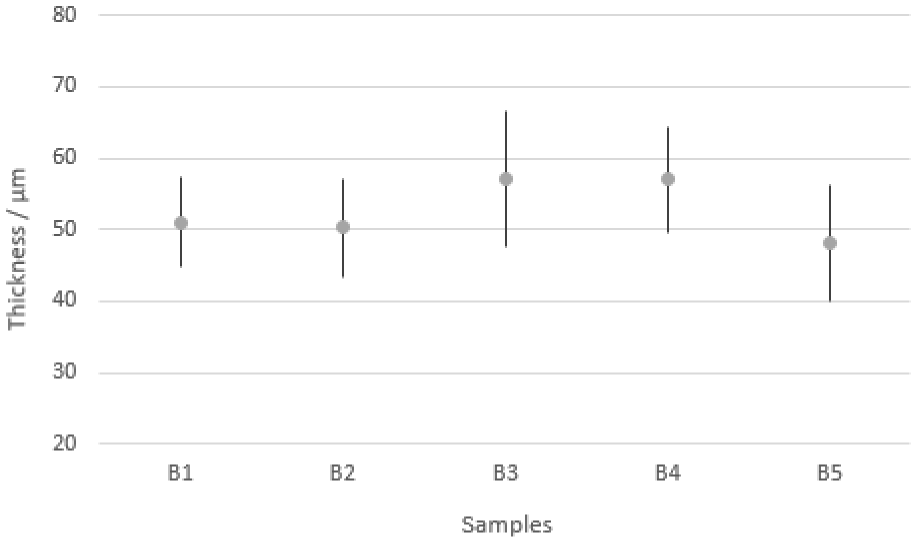


*Fig. D.1) Thickness of binders applied as coatings with resin B.*

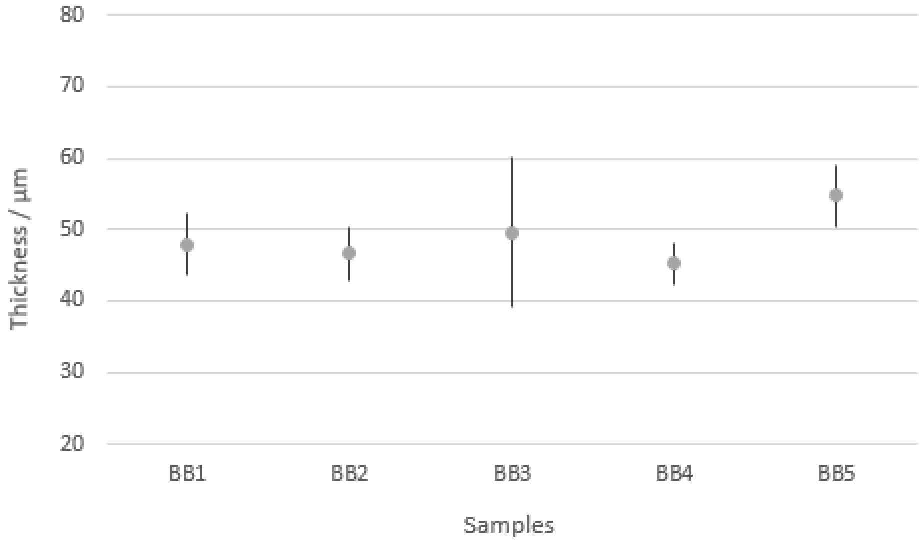


*Fig. D.2) Thickness of binders applied as coatings with resin BB.*

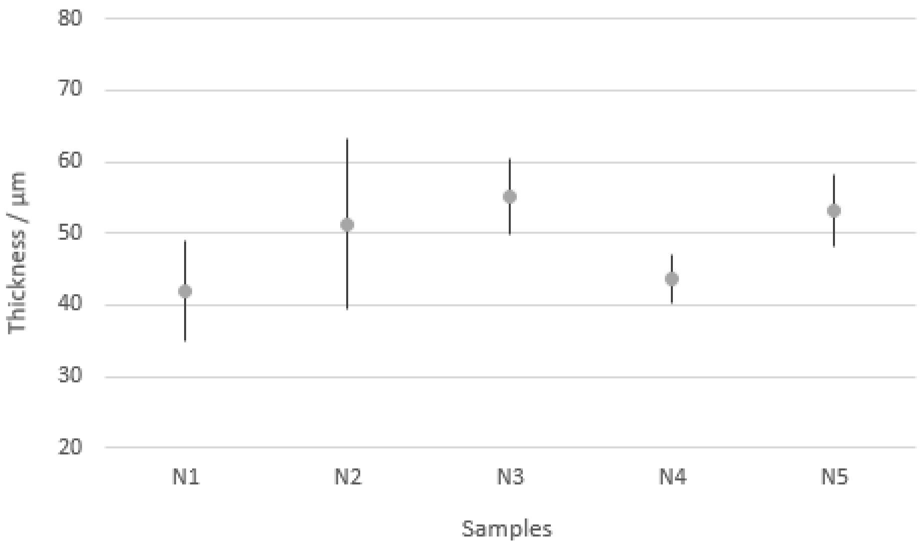


*Fig. D.3) Thickness of binders applied as coatings with resin N.*