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ADVANCED INDUSTRIAL APPROACH TO BIOBASED REPLACEMENT OF FOSSIL-BASED RAW MATERIALS: FROM THE SYNTHESIS TO THE EVALUATION OF THE PERFORMANCES

PhD Candidate
Edoardo Parrucci

Supervisor
Prof. Enrico Marcantoni

Co-supervisor
Dr. Giovanna Biondi

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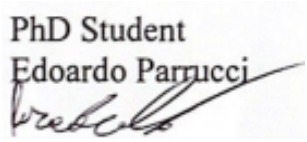
AUTHOR'S DECLARATION

I declare that the work in this dissertation was carried out in accordance with the requirements of the University's Regulations and Code of Practice for School of Advanced Studies, and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate's own work. Work done in collaboration with, or with the assistance of others, is indicated as such. Any views expressed in the dissertation are those of the author.

Signed



Date

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PREFACE

In the last 150 years the humanity has gained an enormous quantity of knowledge about the world in every field, from medicine to engineering, but to fuel this development resources have been depleted with little care, and the demand on nature are so high that the current estimates are that humanity is using the resources 1.7 times faster than our planet's biocapacity can regenerate per year. These 150 years packed with knowledge led to the develop of industries that used fossil fuel. Those fossil fuel were created and stored in the hearth of the earth for millions of years, those high energy fuels were used to pump industries to produce more and more. Human population start rising rapidly like never before and this convinced even more that produce more was the right thing to do. As humans, we should have felt that something was off when we realized that the oil we were burning had taken so long to form. This should have been a clear sign that we were heading in the wrong direction. Understandably, at that time, the main focus was not on the environment but on generating profit and improving individual living conditions. However, I still see this mindset prevailing in much of the population, even among some scientists who should be fighting against the very system that has brought us to where we are now. The paradox we are living is that in which the most versatile and least expensive material, considering costs of production, the wide ranges of application and CO_2 emitted, for individuals and the planet, is plastic—the same material polluting every natural element on Earth, raising the planet's CO_2 levels, and disrupting its climate balance, including marine and atmospheric currents.

The work herein was carried out in the Prof. Marcantoni's research group, at the University of Camerino (Italia) with the collaboration of Elantas Europe company, from November 2021 to November 2024. This study has the main focus on the partial substitution of fossil based raw materials with the bio based trying to lower the impact of final product, in this case wire enamels.An introduction on wire enamels and its chemistry is described in the first chapters. An introduction on conformal coating and its chemistry is described 8.1. The experimental section is described in chapter 5, 6 and 8. It is necessary to say that the work done in Chapter 8 was conducted in Elantas GmbH, Hamburg (Germany). Additionally, in chapter 7 there is a novel aromatic diamine determination in a polyamic acid matrix solution.

Edoardo Parrucci

LIST OF CONTENTS

SECTION 1: INTRODUCTION TO COATINGS

PART 2: EXPERIMENTAL SECTION

PART I

THEORETICAL INTRODUCTION SECTOR

This dissertation explores the background of magnet-wire insulating systems and their applications. It also includes a brief overview of the classification of wire enamels and the procedures for testing finished products. Subsequently, the discussion will shift to a chemical perspective, examining the composition, synthesis, and characterization of wire enamels.

1. Introduction to coating

To construct a functional electric machine, it is essential to direct the electric current in predetermined pathways. This is typically accomplished by employing electric wires composed of a material capable of conducting electric current with minimal resistance, which in the vast majority of cases is copper. To compel the electric current to flow in a specified direction, rather than along the path of least resistance, it is crucial to prevent the bare conductors from coming into contact with one another. The simplest means to achieve this is by maintaining a distance between the conductors that exceeds the flashover distance for the applied voltage. However, this principle proves unsuitable for machines such as electric motors or generators, hence air, as an insulating material, has been substituted by materials insulators superior to air, primarily varnishes based on synthetic resins. This substitution enables the conductors to be brought into closer proximity.[1] As a result, copper wires are now coated with a thin layer of organic polymer, serving as the insulating material.

1.1 OVERVIEW ON COATINGS

Coatings are liquid, paste, or powder products that are applied to surfaces using a variety of methods and equipment, forming layers of specific thickness. These layers create adherent films on the surface of the substrate. Film formation can occur either through physical or chemical processes. Physical film formation from liquid coatings, commonly known as drying, involves the evaporation of organic solvents or water, while for powder coatings, it involves a melting process. Chemical film formation becomes necessary when the coating components are in a liquid or paste state; the transition to a solid film occurs through a chemical reaction between the coating constituents. These reactions are initiated by energy sources, such as heat or radiation, after the application of the coating. Coatings are required to meet numerous functional demands. They protect the substrate from corrosion, environmental factors, and mechanical damage; they may also serve decorative purposes (e.g., automotive coatings, household appliances, furniture); provide information (such as on traffic signs, informational signage, or advertising); or exhibit other specific properties.[1] Since this work focuses primarily on organic coatings, a brief overview of this category is provided. There are three main types of coatings, classified according to their intended purpose:

1. *Architectural coatings:* These include paints and varnishes (clear coatings) used to decorate and protect buildings, both exterior and interior.
2. *Original Equipment Manufacturer (OEM) coatings:* Applied in factories on products such as automobiles, appliances, furniture, and magnet wires.
3. *Special coatings:* Industrial coatings applied outside the factory setting, such as automotive refinish coatings, marine coatings for ships, and maintenance paints.

Organic coatings are often composite materials, as they consist of more than one distinct phase. The matrix, referred to as the binder, holds the other components of the coating together and typically forms the continuous phase in the dry coating, which is usually an organic polymer. Examining the composition of organic coatings in greater detail, we observe that these materials are complex mixtures of chemical substances that can be grouped into four major categories:

1. Binders: These materials form the continuous film that adheres to the substrate and are also known as resins. In the realm of organic coatings, binders are generally polymers. In some instances, the binders may be lower molecular weight substances, such as oligomers, which are mixed with other components of the coating and undergo

polymerization after application. The binder largely dictates the properties of the final coating film.

2. Volatile components: These are the solvents essential for both the synthesis and application of the coatings. Their primary function is to make the coating sufficiently fluid for application on the substrate; during the application process, these solvents evaporate.

3. Pigments: Finely divided, insoluble solid particles dispersed within the binder, which remain dispersed after the coating is applied. The primary function of pigments is to provide colour and opacity, though they can also influence application properties and mechanical behaviour.

4. Additives: Substances incorporated into the coating to modify specific properties. Examples include catalysts, stabilizers for light and heat, and wetting agents [2].

2. Wire Enamels

This chapter introduces and explains wire enamels, followed by a discussion of coating technology and the main performance indicators. The chemistry of these resins will be explored in greater detail in Chapter 3.

2.1 Introduction

Numerous electrical devices influence our daily lives, surrounding us at home, in our cars, and at work. In private residences, electrical machines power household appliances, while transformers charge phone batteries, operate TVs, computers, and other devices. Electric motors control car windows, adjust seats, mirrors, and headlights, and serve as the primary propulsion system in electric and hybrid vehicles. In industry, large transformer units convert the high currents from power plants into standard AC voltage, and they also transform kinetic energy from both traditional power plants and wind turbines into electricity.

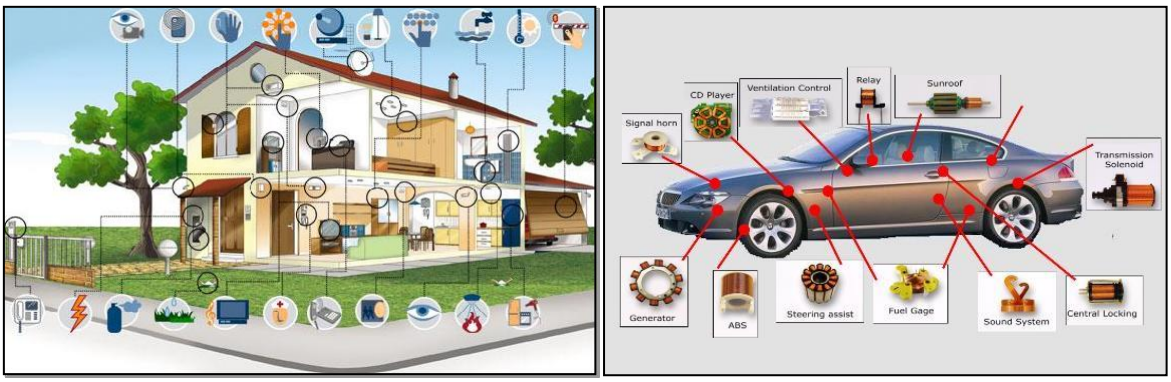


Figure 1. Electrical devices in a vehicle and in a smart house. Note: from Elantas internal database.

To construct functional electrical devices and machines, electromagnetic fields must be generated by directing electric current along specific paths. This is accomplished using wire coils made from a conductive material, typically copper. Copper wires must be insulated to ensure that the electric current travels along the desired path rather than opting for the path of least resistance. The simplest method to achieve this is by keeping the conductors spaced farther apart than the flash-over distance of the voltage. While this approach is still used in printed circuits, it is not practical for use in electrical motors or generators.

Such machines would be excessively large and challenging to operate efficiently, which is why the insulating medium (air) has been replaced by polymeric materials, resulting in the creation of enameled magnet wires. This allows copper windings to be placed very close together without causing short-circuits. Although referred to as “enameled,” this wire is not actually coated with enamel paint or vitreous enamel made from fused glass powder. Instead, it is coated with a thin layer of polymer film insulation. Wire enamel is typically composed of a blend of oligomeric compounds dissolved in a solvent system, which also contains latent catalysts, cross-linkers, and specialized additives. This mixture is applied to the wires, providing electrical insulation necessary for generating the magnetic field needed for the device’s operation. During the enameling process, the solvents evaporate, and the oligomers undergo reactions to form insoluble, infusible macromolecules, resulting in a cured film on the wire’s surface (Figure 2). The properties of this film depend on the chemical composition of the enamel and the enameling process conditions. Often, a dual-coat system is used: a base coat that offers good adhesion to copper and flexibility, and a topcoat that provides high abrasion resistance and high temperature tolerance.

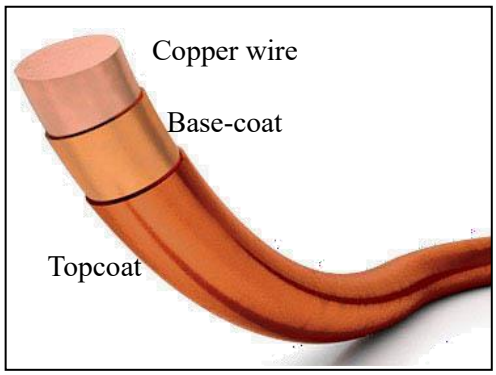


Figure 2. Enameled copper wire section. Note: from Elantas internal database.

Enameled wires are used in various applications, and in electric motors or environments with high wear conditions, they are subjected to friction, abrasion, humidity, and rotational forces. To protect these components and extend their lifespan, impregnating agents made from alkyd, phenolic, epoxy, or unsaturated polyester resins are applied to electrical devices. These agents provide mechanical support, prevent excessive movement, enhance heat transfer, and improve thermal endurance, a process known as secondary insulation (Figure 3 and Figure 4).

Figure 3. Component of an electric motor: the enameled magnet wires are wound within the rotor

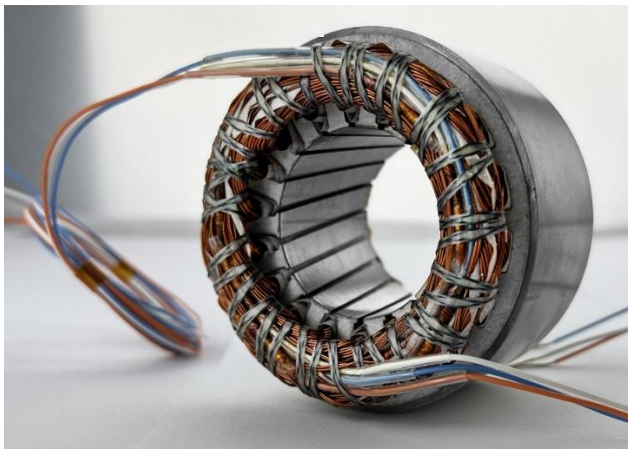


Figure 4. Component of an electric motor: the enameled magnet wires are wound within the stator

2.2 History & Development of magnet wire insulations

The history of electro-insulating coatings dates to the 19th century when natural fibers such as cellulose, silk, flax, cotton, wool, and later asbestos, were used to wrap and insulate the wires in the stators and rotors of the first dynamo machines, invented by Siemens. However, these fibrous materials had a major drawback—they were hygroscopic, meaning that over time they will absorb moisture, this will lead to a significantly diminishing of the insulating properties. To address this issue, alternative materials were introduced in the early 20th century, such as oil bitumen, which led to the development of "black enamel," and copal, which produced the so-called "blond enamel".[3] These products, being derived from natural materials, often lacked batch consistency. Around 1915, synthetic material-based enamels, such as those made from phenolic resins, began to replace natural resin-based varnishes. These new enamels allowed wires to be coated directly, eliminating the need for initial insulation with fibrous materials. A particularly successful innovation was the introduction of polyvinyl acetal (PVA)-based varnishes, such as Formvar®, developed in 1938 by Hoechst and General Electric. [3-4] By 1940, polyamide (nylon)-based varnishes had been introduced, and three years later, terephthalic polyester-based varnishes were simultaneously developed by General Electric in the USA and Dr. Beck in Germany. [5-6] The 1950s was the year the introduction of polyurethane, polypropylene, and polycarbonate coatings. [7] Although these early materials lacked the advanced properties of modern versions, they sparked a wave of new applications in electrical insulation. During this period, the concept of dual coatings emerged. The first dual-coating system was introduced in 1953 when a polyamide film was applied over Formvar, polyester, polyurethane, and acrylic films, reducing surface friction and improving resistance to mechanical damage during high-speed winding. In the early 1960s, Dr. Beck & Co. GmbH developed polyester-imides, combining the mechanical strength of terephthalic acid polyesters, used since the mid-1950s as copper wire coatings, with the excellent thermal resistance of polyimides, which DuPont had introduced as wire coatings around the same time.[8-9] Polyamide-imides were commercialized in the late 1960s by Amoco.[10] Around the same time, Schenectady introduced a new branching agent, tris-(2-hydroxyethyl) isocyanurate (THEIC), which further enhanced the mechanical and thermal properties of the resulting polymer. This innovation led to the development of a new generation of THEIC-modified polyester-imides, which remain the top-performing version of polyester-imides to this day. [11] The history of wire enamels is summarized in Table 1.

Year	Chemical basis	Inventor	Properties	Importance today
1900	Oil-bitumen		Poor thermal properties, Excellent humidity resistance	None
1915	Tung oil, copal, phenolic resins		Improved hardness, solvent resistance flexibility and	None
1938	Polyvinyl acetal	General Electric	Excellent mechanical properties and adhesion, low solids	Reduced
1940	Polyamide		Improved mechanical properties, flexibility, low coefficient of friction, self-bonding	Overcoat, self-bonding
1950	Polyurethane	Bayer	Solderable, fast enameling	Many
1954	Polyester (glycerin)	General Electric, Beck	Excellent solvents and humidity resistance, good thermal endurance	Reduced
1959	Polyimide	DuPont	Outstanding thermal resistance, high raw material costs	Special application
1961	Polyester-imide (glycerin)	Beck	Improved cut through and thermal endurance, increased enameling speed	Reduced
1965	Polyester-imide (THEIC)	Schenectady	High cut through, hydrolytic stability, Freon resistance	Great
1966	Polyamide-imide	Amoco	Excellent thermal, mechanicalproperties	Great
1967	Polyester (THEIC)	Schenectady	Improved thermal endurance, adhesion, base coat in dual coat systems (PAI as overcoat)	Great
1968	Polyhydantoin[12]	Bayer AG	Excellent thermal properties andadhesion, high raw material cost	None
1973 – 1980	Alternative enameling technologies	Beck, Herberts	Hot melts, water and mild solvent enamels, dispersion, powders, extrusion resins, Electrophoretic enamels	None
1988	Corona resistant wire enamels[13]	General Electric	Resistant to partial discharges ininverter driven motors	Special applications

Table 1. Wire enamels history.

The global wire enamel market is expected to grow significantly in the coming years, mainly driven by improvements in how energy is transmitted and distributed. Key factors behind this growth include the booming solar energy industry, more investments in smart grids, and the push for energy-efficient motors. As technology advances, there's also a shift toward making things smaller, more efficient, and sustainable, which is opening new opportunities for businesses in the market.

At the same time, stricter government regulations on VOC (volatile organic compound) content are pushing manufacturers to adopt greener and more eco-friendly practices. Top companies are pouring resources into research and development to create innovative and cost-effective products that meet these regulatory requirements. Despite this progress, the industry still faces challenges, such as high formulation costs, fluctuating prices for raw materials, and navigating tough government regulations on VOCs. Currently, global wire enamel production stands at approximately 300,000 tons annually, with the primary resins used being polyester-imides (PEI), polyurethanes (PU), polyester (PES), THEIC-modified polyesters, polyamide-imides (PAI), and polyvinyl-formals (PVF) (Figure 5). [14]

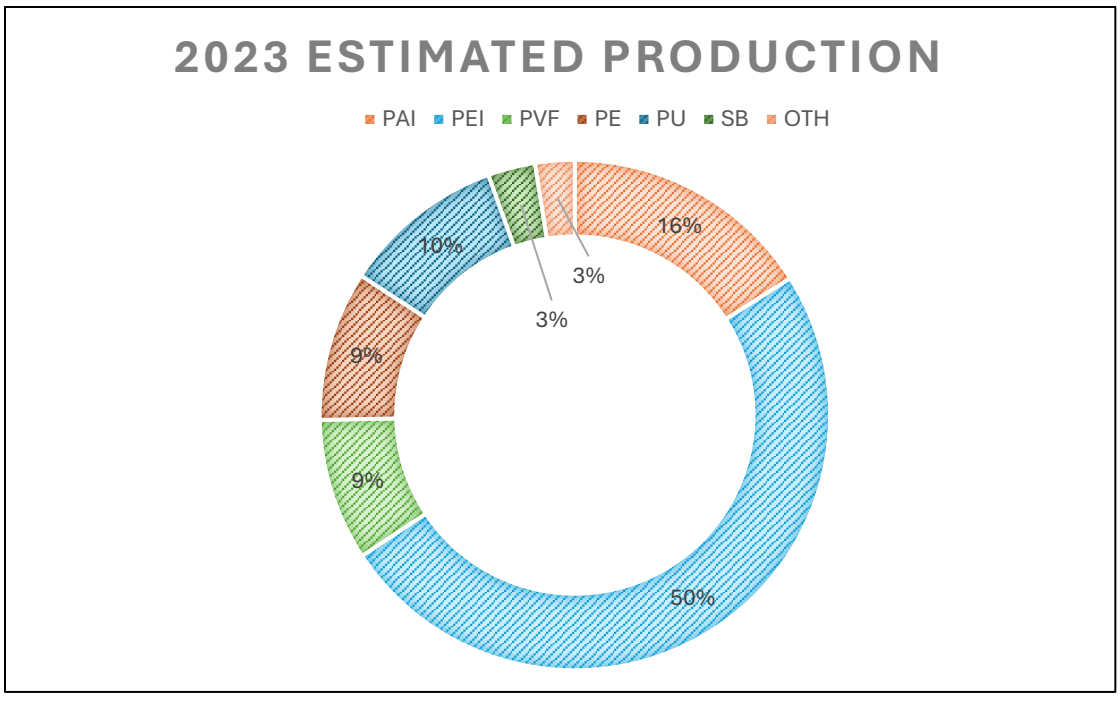


Fig.5 European estimated production of 2023

The electric motor market is largely dominated by coatings based on THEIC-modified PEI or THEIC-modified polyester, typically paired with a PAI topcoat. THEIC-modified PEI and polyester coatings deliver exceptional adhesion to copper and high flexibility, while the PAI topcoat enhances abrasion resistance and ensures durability at high temperatures. This technology is widely used in power tools, ceiling fans, household appliances, air-moving motors, hermetic motors for cooling and refrigeration, and electric motors in automobiles. In the automotive sector, the magnet wire market varies significantly, with different electrical components such as solenoids, motors, starters, and generators requiring specialized magnet wire coatings. However, polyurethane coatings are the most used in this context.[15]

2.3 Magnet Wire Coating Technology

The enameling process is a crucial step in research, as it remains the only reliable method to assess the quality of products. Evaluating the properties of enameled wire is the sole way to determine the effectiveness of the enamel. Applying enamel involves allowing its molecules to interact and form a three-dimensional network, which imparts the wire with the desired electrical, mechanical, chemical, and thermal resistance. To produce high-quality enameled wire, the enamel must be properly applied using an enameling machine or oven. These ovens apply liquid enamel to the wires and cure it to create a solid coating. The enamel must be processable, meaning its viscosity and solid content should fall within specific ranges, and the solution should be homogeneous without precipitates or gels. The selection between vertical and horizontal ovens for curing is influenced by factors such as wire diameter, resin viscosity, and solid content. Vertical ovens (Figure 6) are ideal for larger-diameter wires (both round and flat) and for varnishes with medium to high viscosities (2,000–10,000 cPs at 23°C). In contrast, horizontal ovens are better suited for medium to fine wires, where low to medium viscosity varnishes (100–2,000 cPs at 23°C) are preferred. Different applicators, such as dyes or felts, are selected based on wire diameter and resin viscosity. Dyes are typically used for medium to large diameter wires (> 0.2 mm) with enamel viscosities greater than 200 cPs. Felts are used for fine wires (0.05 to 0.2 mm in diameter), where less viscous varnishes (viscosity < 200 cPs) are required.

Figure 6. Vertical enameling oven.

In both oven configurations, the application procedure is identical. The process begins with annealing and cleaning the bare wire at high temperatures in a reducing atmosphere of steam. This step softens the copper wire, making it more malleable while also removing dirt and oils. Next, enamel is applied to the wire surface using dies or felts (Figure 7), just before the wire passes through the oven chamber multiple times. This phase, known as the "curing step," involves several key processes:

- Increase in the molecular weight of polymer chains
- Cross-linking reactions (occurring in polymers with reactive functionalities along the chains or when crosslinking agents are present)
- Evaporation of solvents
- Intra-chain reactions, such as Diels–Alder reaction.

The oven temperature typically ranges from 500 to 700°C. Six to eight layers of enamel are applied, with each layer measuring about 0.002 to 0.005 mm in thickness. Multiple coatings help cover any tiny blowholes or bare spots caused by rapid solvent vaporization or poor wetting, reducing the number of defects in the enamel film to nearly zero. Additionally, the quick curing of thin films allows for a significant increase in enameling speed. [16-17]

Figure 7. Applicators with dies

Enameling machines are equipped with air-recirculation systems and catalytic ovens designed to oxidize solvent vapors into CO_2 and steam (Figure 8). In these ovens, solvent vapors from the varnish pass over a heated catalyst mesh (up to approximately 600°C). The exhaust is then recirculated back to the oven inlet, providing additional heat. This design makes these ovens highly energy-efficient and reduces the emission of harmful fumes into the atmosphere. Once the desired enamel thickness is achieved, the enameled wire is wound onto a spool using a first spooler. A second spooler is used to switch and wind the wire onto both spools alternately, allowing samples to be taken without stopping the machine.

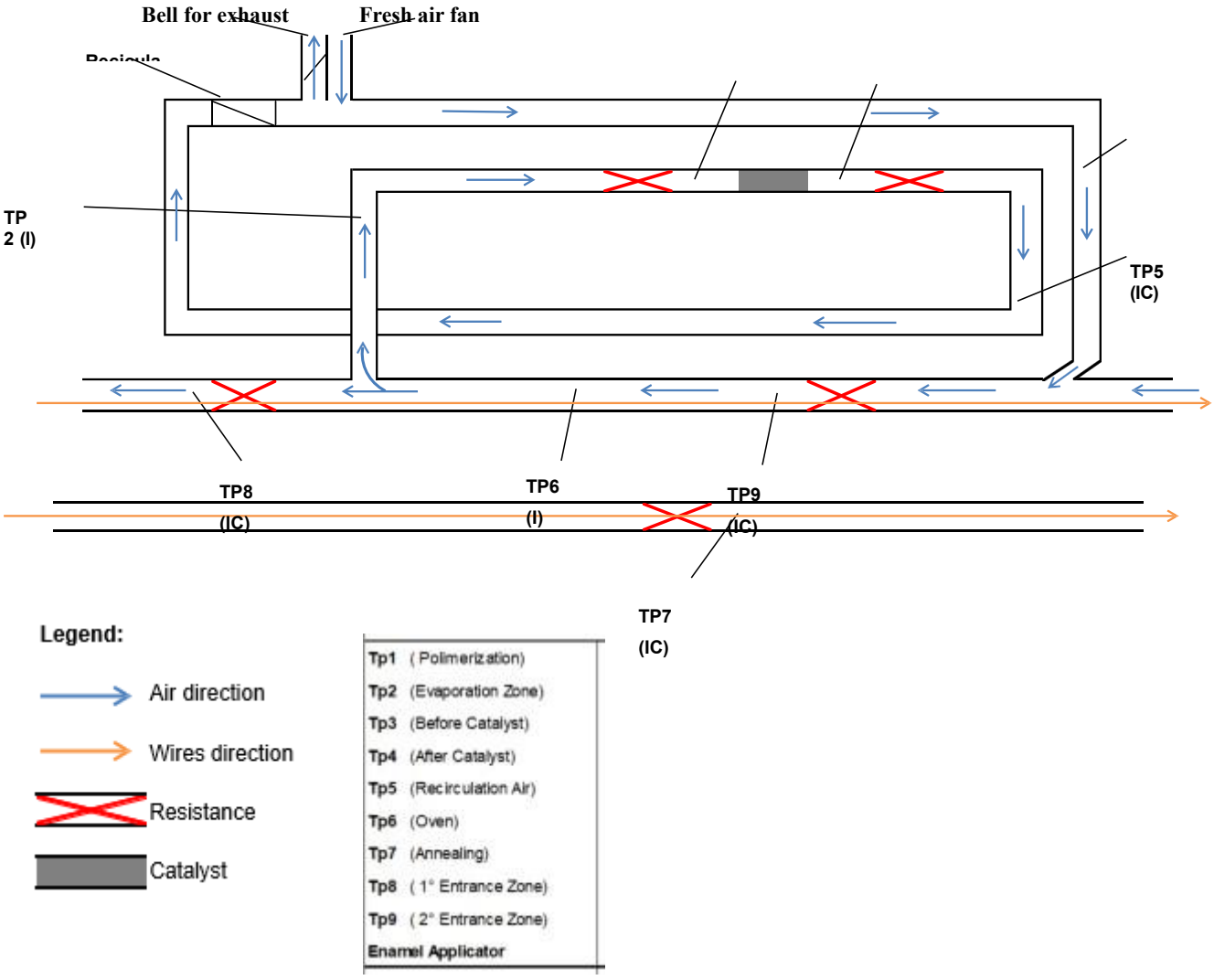


Figure 8. Schematic view of an enameling oven.

This second spooler then enables the wire to be wound alternately onto two spools, allowing for sample collection without interrupting the machine's operation (Figure 9).

Figure 9. Spooler.

2.4 Test and Properties of enameled wires

Once the enamel has been properly applied and cured on the wire, the resulting conductor-coating system exhibits specific properties that are then evaluated for quality. The insulation's appearance is inspected using a microscope, a qualitative check that provides a pass/fail result, although enamellers may assign arbitrary rankings. At Elantas, wires are rated from zero to three based on the presence of blisters, waves, and dots, with higher numbers indicating poorer quality. The uniformity of the enamel layer's thickness is also assessed using a micrometer at various points on the sample. Uniform thickness is crucial to ensuring excellent performance and reproducibility of properties, particularly when these depend on coating thickness. To allow users to compare materials from different manufacturers, the properties of enameled wires have been standardized by international organizations such as the IEC (International Electrotechnical Commission), UL (Underwriters Laboratories), ISO (International Organization for Standardization), IEEE (Institute of Electrical and Electronics Engineers), and various national standards bodies like NEMA, DIN, EN, BS, CEI, NF, AS, JIS, and IS. Among these, IEC standards are the most widely recognized. [18] According to these standard commissions, the properties of enameled wires can be categorized into four main types:

- Mechanical
- Thermal
- Electrical
- Chemical

2.4.1 Thermal Properties

Electric and electronic devices are exposed to thermal stress, which can arise from external environmental factors or, more commonly, from Joule heating caused by the residual resistance of electrical conductors and the friction of moving parts. This is particularly relevant for high-performance electric motors or high-voltage AC/DC transformers, often operating in confined and thermally insulated spaces. To prevent short-circuits resulting from the softening or thermal degradation of polymeric films, magnet wires must effectively manage these conditions. Testing the thermal properties of these wires is crucial to ensuring the longevity and reliability of the final product. These properties reflect the enamel's ability to maintain its structural integrity and performance at elevated temperatures. Key tests include:

- **Thermal Class:**

Thermal class, or heat classification, is represented by the “temperature index,” which indicates the temperature at which the insulating film can endure a specified voltage for 20,000 hours. To reduce the duration of testing, an accelerated procedure is employed. Wire samples are aged at temperatures higher than the expected class temperature, with failure times periodically checked at room temperature under a defined voltage (e.g., 1,000 V for a 1 mm diameter wire). These results are extrapolated to 20,000 hours using the Arrhenius equation to determine the wire enamel’s thermal index.

- **Heat Shock:**

The same test sample used to assess flexibility is heated to a specific temperature corresponding to its thermal class and then cooled to room temperature. The sample must show no visible cracks, demonstrating its ability to withstand thermal shocks, which is essential for the winding’s durability.

- **Cut-through Test:**

In this test, two magnet wire specimens are placed on a hot plate in a perpendicular cross-section so that they touch at a single point where a standard weight is applied. (Figure 10) The test determines the maximum temperature at which the two metal parts of the wires do not make contact (resulting in a short circuit) within a 2-minute timeframe. This test is closely related to

the enamel's ability to resist flow under pressure. Modern enamels with a thermal class of 200°C typically have cut-through temperatures exceeding 320°C. This value provides an estimate of the safety margin for a winding in the event of a hot spot. This test will be conducted on the magnet enameled wires developed in this work.

Figure 10. Cut-through tester.

2.4.2 Electrical Properties

The electrical properties of enameled wire relate to its ability to withstand electrical fields (such as electrical resistance and dielectric loss), and voltage (like breakdown voltage and coating continuity) generated by the current passing through the conductor. According to the International Electrotechnical Commission (IEC 60317), these properties can be summarized as follows:

- **Continuity of Covering:** This measures the uniformity of the enamel coating by applying a specified potential difference to ensure consistent insulation.

- **Dielectric Loss Tangent (Tangent Delta or Tgδ):** The magnet wire specimen is coated with graphite to form a condenser, where the enamel serves as the dielectric. This test evaluates the material's dielectric performance. (Figure 11)

Figure 11. Tangent delta tester.

The dissipation factor (CoD) is plotted against increasing temperature (Figure 12). When the dissipation factor rises sharply, the point where the tangents of the curve intersect indicates the corresponding temperature, referred to as "Tgδ." This is the temperature at which the material loses its ability to maintain a low CoD, meaning its dielectric properties have been lost. The tangent serves as an indicator of the degradation of dielectric properties and is related to the material's glass transition temperature. This measurement is used to assess the curing process in magnet wire production.

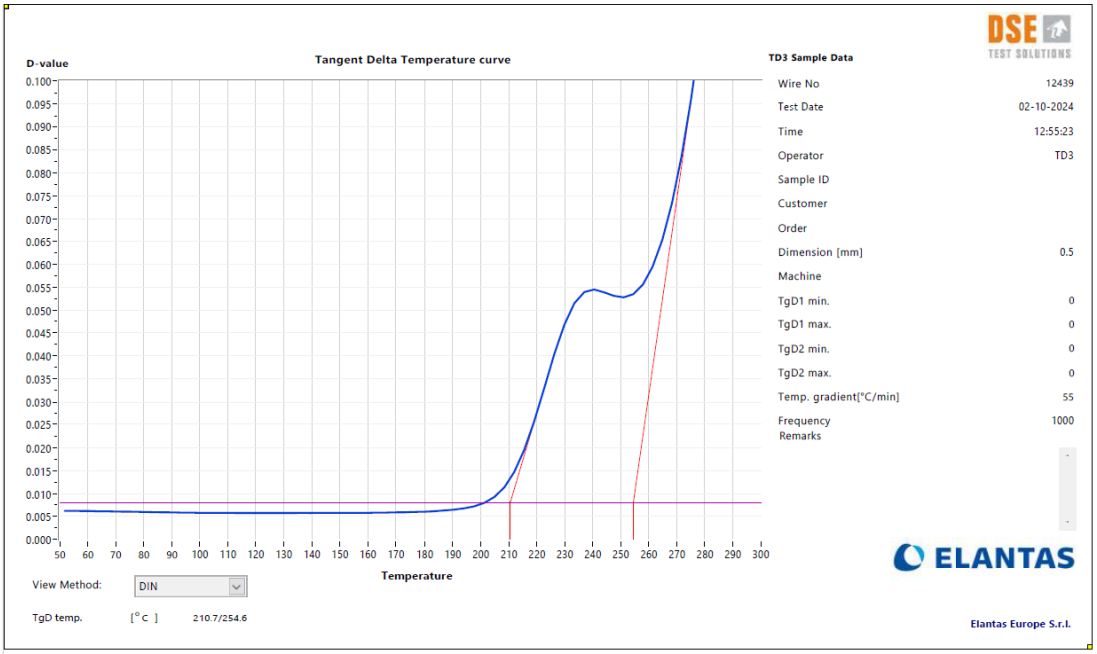


Figure 12. Example of tangent delta test result on a PEI (Polyester imide) 210°C.

- **Breakdown Voltage (BDV):** A twisted wire pair is prepared as a specimen and placed in a tester. The voltage, typically at a frequency of 50 or 60 Hz, is gradually increased until the enamel fails. The breakdown voltage represents the maximum A.C. voltage the enamel can withstand without its insulating properties breaking down. This property depends on both the thickness and the material of the enamel. (Figure 13)

Figure 13. Breakdown voltage tester.

These tests will be conducted on the final batches produced in this work.

2.4.3. Chemical Properties

Chemical properties refer to the ability of enamel to resist chemical attacks. This resistance is crucial in preventing electrical breakdown caused by the absorption of solvents or oils present in certain electrical devices, which can lead to corrosion or friction in moving parts. As defined by the International Electrotechnical Commission (IEC 60317), these properties can be summarized as follows:

- **Resistance to Solvents:**

This test measures the wire's ability to retain its hardness after being exposed to a specific solvent mixture. The wire is submersed in solvents (e.g. butanol, white spirit, styrene, xylene) at a fixed temperature for a set time. Afterward, the hardness is tested by scratching the enamel with pencils of decreasing hardness. The enamel's resistance is indicated by the hardness code

of the pencil at which it withstands the scratching. For some solvents like ethanol, a microscope is used to check for micro ring formations, though this test is not part of IEC standards.

- **Resistance to Refrigerants:**

This property is expressed as the percentage of mass retained after the wire is treated with refrigerants, such as Freon R22 or R134.

- **Resistance to Transformer Oil:**

This measures the breakdown voltage and adhesion loss of the enamel after being heated in wet transformer oil within a sealed system. Three wire specimens are placed in a calorimetric bomb containing transformer oil and heated to a specific temperature (e.g., 150°C) for a set duration, ranging from days to weeks. Afterward, the wires are examined for appearance and retained breakdown voltage (BDV).

- **Solderability:**

The wire is submerged in a solder bath containing a metal alloy, heated to specific temperatures (e.g., 320°C or 370°C), until the enamel breaks down. The time required for solder formation provides the solderability value of the enamel. The tests that will be performed are mechanical (flexibility), thermal (cut-through, thermal class), and electrical (Tgδ, BDV) tests will be conducted. The following table presents a comparison of various wire enamel types.

3 Chemistry of Wire Enamels

A coating is a protective or decorative layer applied to the surface of a substrate. In industrial applications, the primary goal of coating is functionality, though aesthetics also plays a role. Functional coatings are designed to modify the properties of the substrate, such as adhesion, wettability, resistance to chemical or mechanical stress, conductivity, or insulation. Coating comes in various forms, categorized by their physical state (liquid, gas, or solid) or by their application method, such as chemical or physical vapor deposition, electrochemical techniques, spraying, and roll-to-roll processes.

Wire enamels, a type of functional coating, can be in liquid form, such as organic solvent solutions or aqueous solutions, or in solid form, such as solvent-free resins. A typical organic enamel consists of several key components:

- **Binders**

Binders, also called resins, are sticky materials that hold the coating system together. They form the majority of the solid content in the coating and are crucial for determining the properties of the final film. In solution, they act as the vehicle for the system, influencing adhesion, flexibility, and durability.

- **Volatile Components**

Solvents are included to allow the coating to be applied in liquid form. These may be organic solvents or water, depending on the formulation. Solvents aid in mixing, adjusting viscosity, and improving workability and application. Once applied, they evaporate, leaving behind the solid enamel film.

- **Catalysts**

Catalysts, either organic or inorganic, speed up the polymerization reaction of the enamel, allowing it to cure more efficiently. They ensure the formation of a stable and durable coating film in a shorter period.

- **Additives**

Additives are introduced in small amounts, typically less than 5%, to enhance specific properties of the coating. For example, plasticizers may improve flexibility, while leveling agents ensure a smooth surface finish.

- **Pigments**

Pigments are solid particles added to the enamel to provide color or improve specific performance characteristics, such as UV resistance. Pigments can be organic or inorganic and are selected based on factors like lightfastness, particle size, and specific color requirements.

- **Crosslinkers**

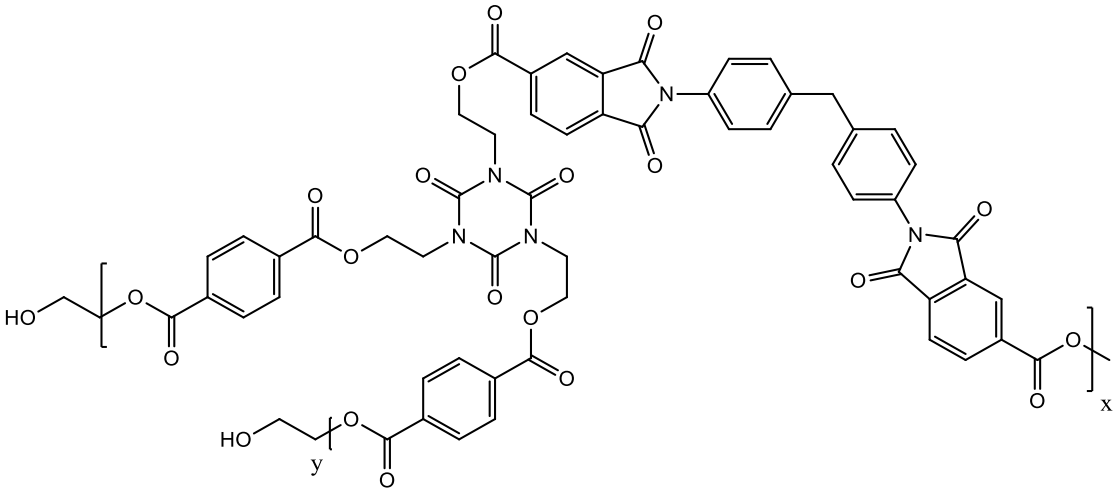
Crosslinking is essential for forming the polymer network within the coating film. Crosslinkers hold polymer chains together through ionic or covalent bonds, creating a network that enhances the electrical, mechanical, thermal, and chemical properties of the enamel. Crosslinkers can be categorized into two major types. One type consists of functional segments that are incorporated directly into the polymer chains, while the other involves chemical agents that are distinct from the polymer itself. These agents are introduced during a secondary processing step, after the polymer has been formed. The degree of crosslinking, known as crosslink density, affects the rigidity of the polymer. A higher crosslink density results in a more rigid coating, while excessive crosslinking can lead to embrittlement. Crosslinking also reduces segmental motion within the polymer, often raising the glass transition temperature and improving the overall durability of the coating.

3.1. Binders

In this chapter, a deep focus on properties and synthetic route of the binder used in my works will be addressed, polyester-imide (PEI). Since there is a huge difference in the type of product and scope the poly(ester)urethane-acrylate will be treated in a different chapter.

3.1.1. Polyester-imide: Properties and applications

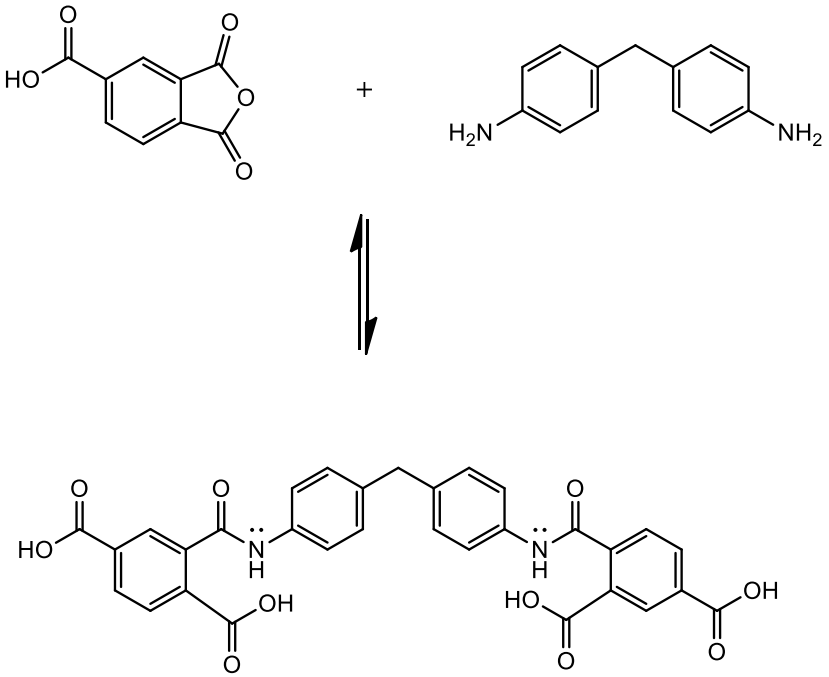
Polyester-imides (PEI) were created to combine the excellent mechanical properties of terephthalic acid polyesters, which have been used as copper wire coatings since the 1950s, with the superior thermal resistance of polyimides, while avoiding the processing challenges and low storage stability associated with the latter.[19] The first development of polyester-imides took place in the early 1960s by Dr. Beck and Co. GmbH.[6] Around the same time, Schenectady introduced a specific branching agent, tris-(2-hydroxyethyl) isocyanurate (THEIC), that could further enhance the mechanical and thermal properties (notably cut-through resistance, temperature index, and tan δ steep rise) of the polymer. This led to the creation of THEIC-modified polyester-imides, which remain the highest performing version of commercially available polyester-imides to date (Scheme 1).[11] Due to these properties, PEIs are among the most important wire enamels, widely used in virtually all electrical equipment for conductor insulation, influencing the overall insulating system of windings.[20]

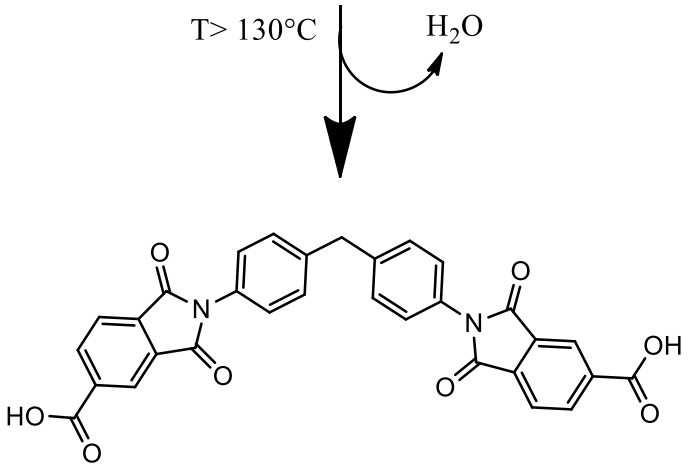


Scheme 1. THEIC-modified Polyesterimide general structure.

3.1.2. Synthesis of Polyester-imides

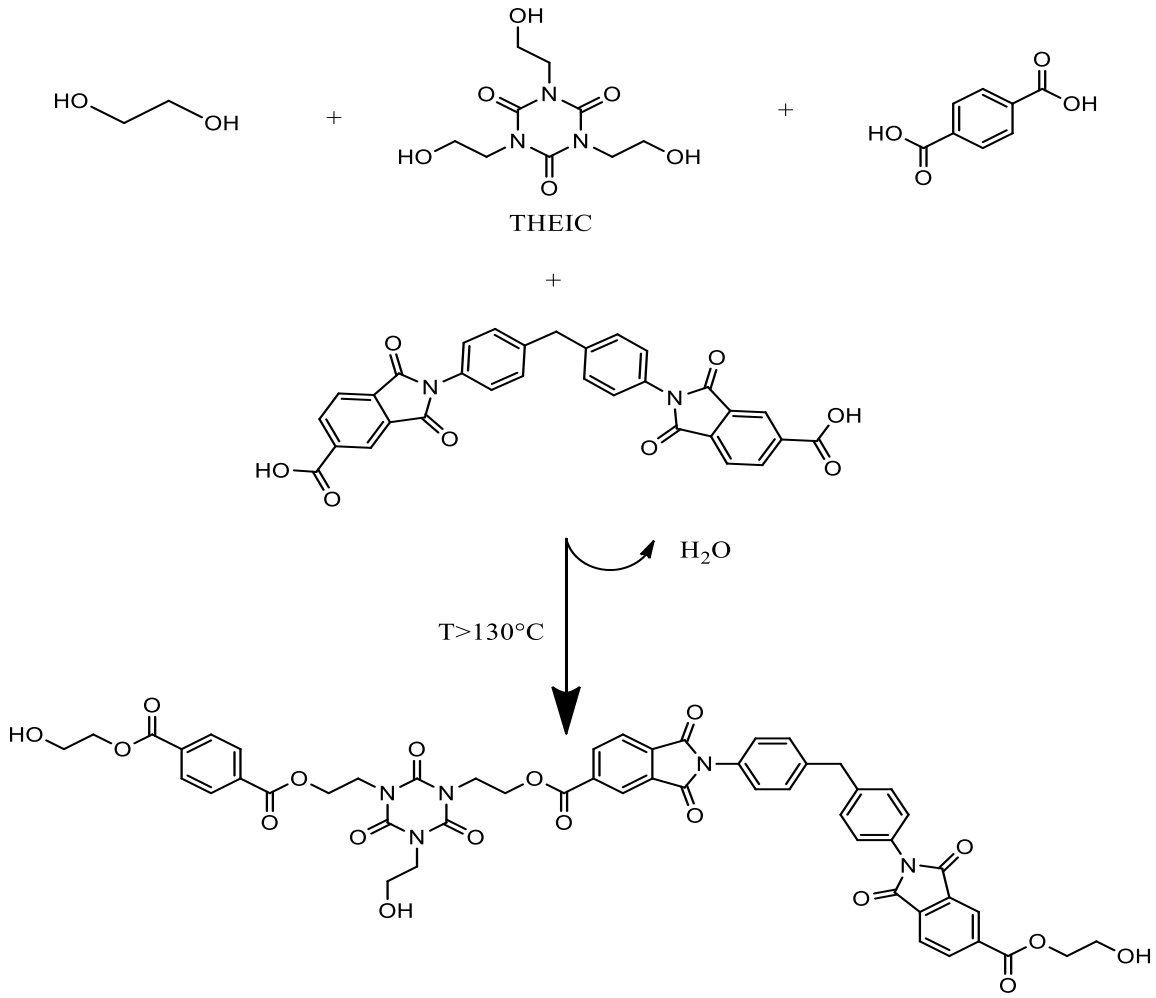
The synthesis of polyester-imide involves forming ester and imide groups, which serve as the fundamental building blocks of the polymer structure. The process begins by creating an aromatic dicarboxylic acid with imide moieties. This is accomplished by reacting two equivalents of an aromatic anhydride, like trimellitic anhydride, with one equivalent of an aromatic diamine (Scheme 2). The most commonly used diamine is 4,4'-methylenedianiline (MDA), as aromatic diamines are now favored over previously used aliphatic ones like ethanolamine. Aromatic diamine offers better resistance to oxidative degradation and enhance the polymer's hardness. [21-22] Due to the different reactivity of the carboxylic and anhydride functional groups towards amines, the formation of amic acid is preferred over the formation of amide. This leads to the production of a diimide carboxylic diacid, known as DIDA (Scheme 2), following the ring closure of the amic acid with the release of water. DIDA is initially an insoluble substance but becomes soluble in the polyester mixture once esterified. However, there is a risk of forming a dense precipitate (referred to as "yellow cake") that could potentially block the stirrer. Therefore, careful control of stirring, process temperatures, addition times, and other parameters is essential to ensure a smooth process.





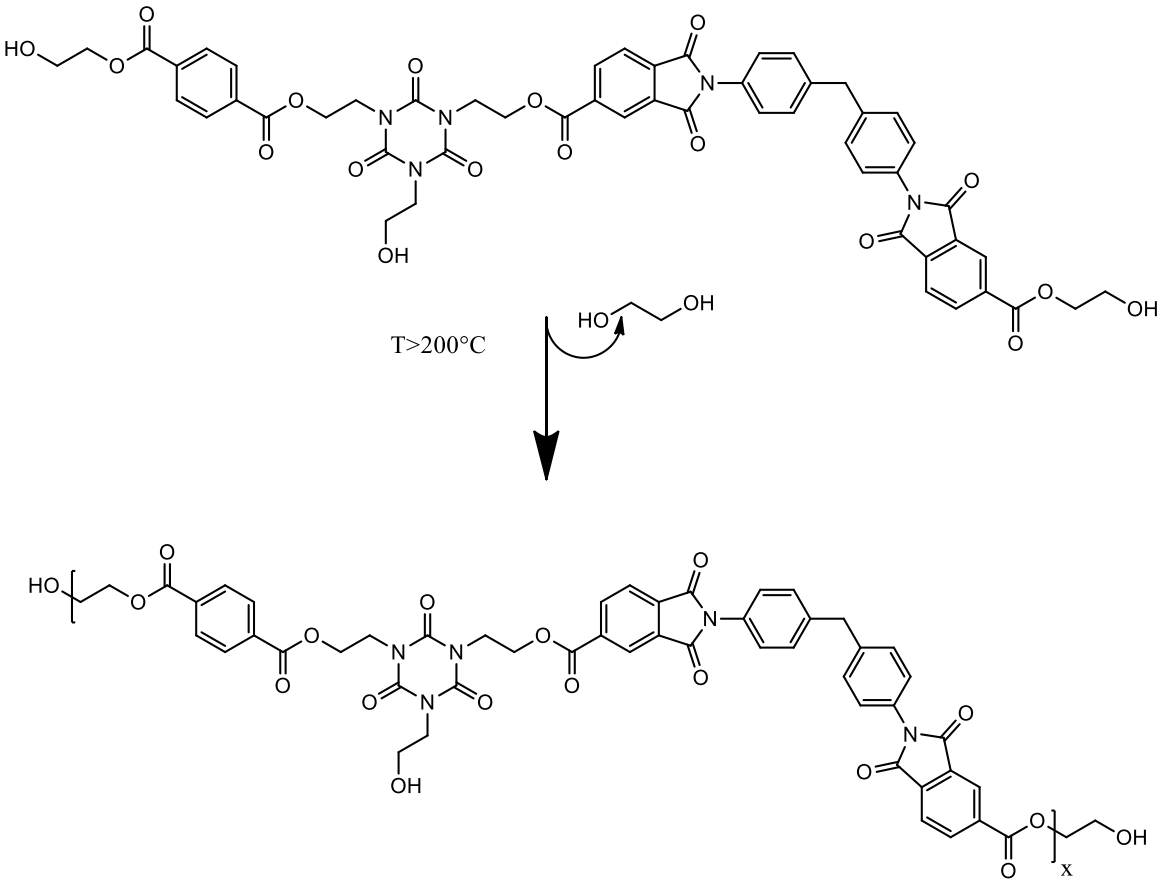
Scheme 2. DIDA's reaction scheme.

Simultaneously, random esterification takes place between one equivalent of DIDA and other carboxylic diacids such as terephthalic acid, along with an excess of diols and triols like ethylene glycol or THEIC. This reaction forms low-molecular-weight polyester oligomers (Scheme 3) through a polycondensation reaction with water elimination. The resulting oligomers retain unreacted hydroxyl (OH) groups due to the excess of diols and triols. It is crucial that all the DIDA reacts, as any remaining acid crystals in the varnish could lead to surface defects on the copper wire during the enameling process.



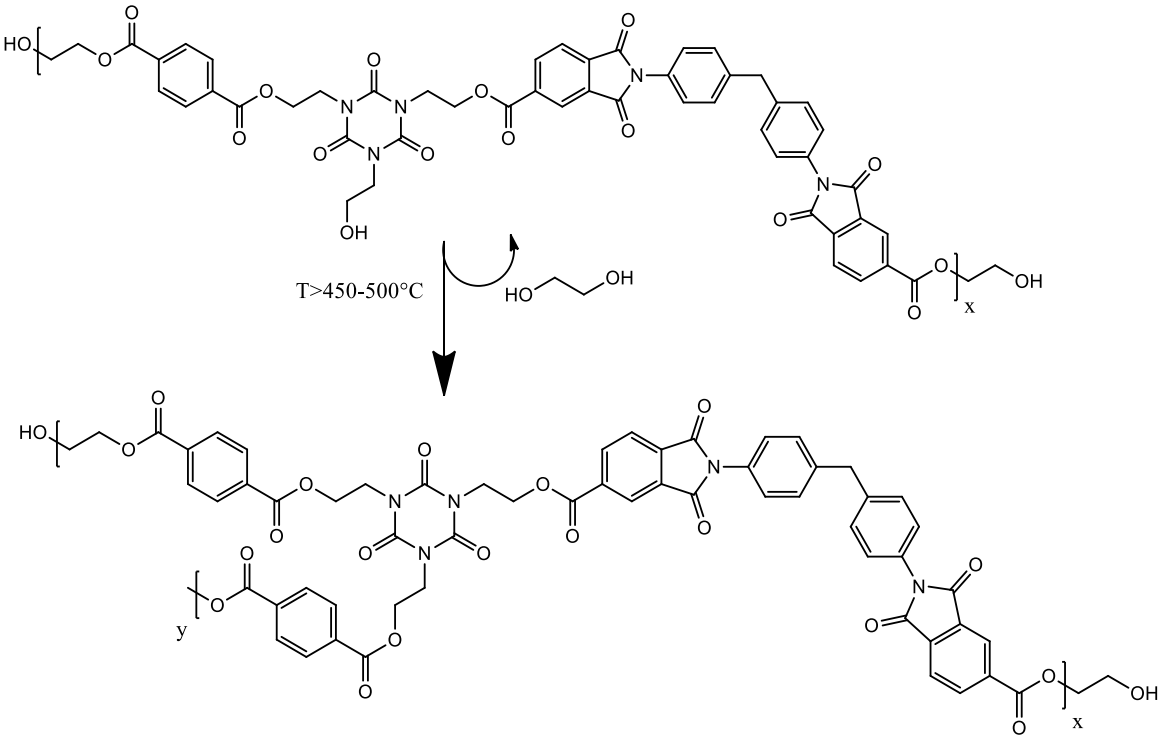
Scheme 3. Reaction product between DIDA, diol triol and diacid

Finally, transesterification takes place between the terminal hydroxyl groups through a polycondensation reaction, with glycol being removed and distilled off (Scheme 4). This step is essential for increasing the molecular weight of the polyester-imide. However, excessive removal of ethylene glycol can lead to polymer gelling due to cross-linking reactions. More specifically, a polymer that has become gel can be defined as a single 3D macroscopic molecule that is not movable, so useless for our scopes.



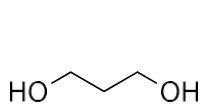
Scheme 4. Transesterification reaction.

When the desired molecular weight is achieved, the polymerization is stopped, and the resulting resin is applied to copper wires for curing. During this process, cross-linking occurs between the unreacted hydroxyl (OH) groups (Scheme 5).

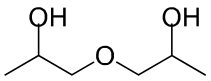


Scheme 5. Cross-linking reaction

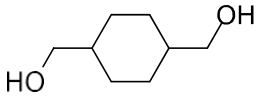
Esterification reactions can be catalyzed in various ways, such as using metal salts (e.g., Mn, Sn, Zn acetates or octoates) or titanates like titanium butoxide monomer and polymer (TBM and TBP) or titanium isopropoxide (TiPT). TBP is preferred in industrial applications because it produces high-quality polymers (minimizing side product formation) and allows for better waste management, as no catalyst residue needs to be washed out and the excess glycol can be recovered in a relatively pure form. [23-25]



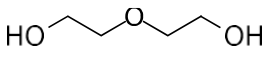
Propylen Glycol



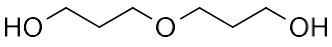
Dipropylene glycol and its isomeric mixture

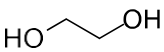


1,4-cyclohexanedimethanol



Diethylene Glycol

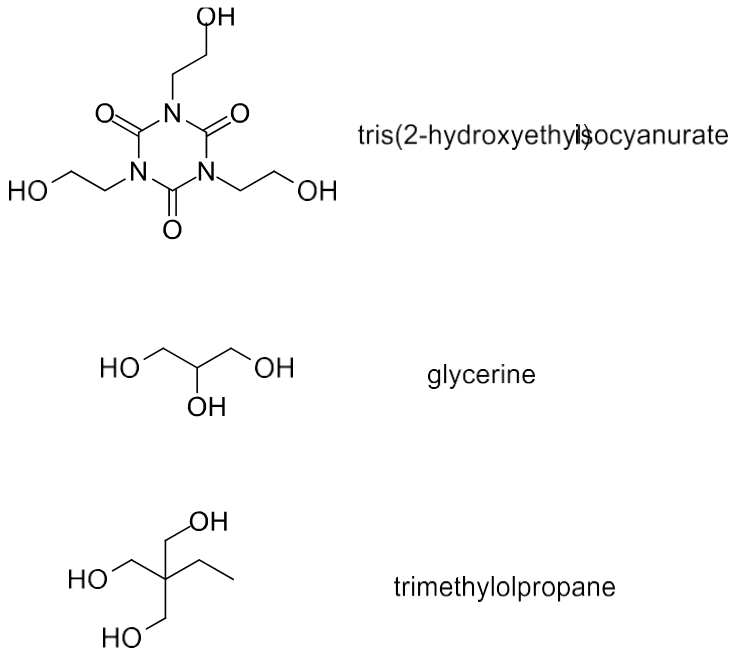




Ethylene Glycol

Scheme 6. Widespread diols in PEIs

Due to its lower boiling point compared to other diols, MEG is preferred for its ability to be easily driven off during the transesterification step in oven applications, as well as its easy removal from the coating film through diffusion and evaporation. Longer-chain diols are primarily used to improve polymer flexibility and enhance resistance to degradation. [28-29] Triols are introduced as branching agents to increase the thermal stability of cured enamels. The most commonly used triols include glycerin (Gly), trimethylolpropane (TMP), and tris(2-hydroxyethyl) isocyanurate (THEIC) (Scheme 7).

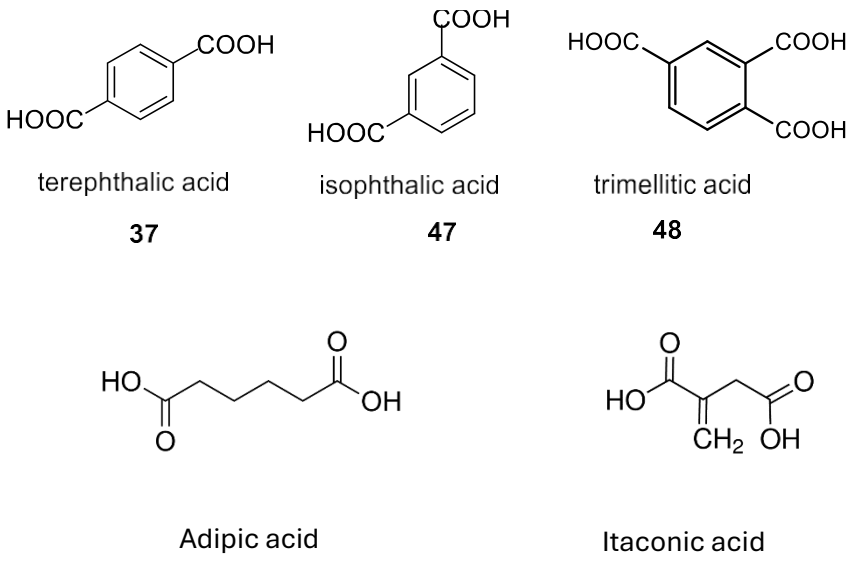


Scheme 7. Most used triols in PEIs.

When tris(2-hydroxyethyl) isocyanurate is incorporated into polyester-imides, the resulting materials are referred to as THEIC-modified PEIs. These modified PEIs exhibit enhanced thermal properties, such as approximately 30% higher cut-through resistance compared to glycerin-based PEIs, a 30% increase in thermal index, and a 25% increase in tan δ. Alternatively, THEIC can be produced in situ from isocyanuric acid, although this method can lead to unwanted by-products that compromise the overall quality of the film.

Various diacids, reported in the literature and patents, have been explored for their ability to impart different properties to polyester-imides. [30-33]. The most commonly used carboxylic diacid monomers include terephthalic acid (PTA), isophthalic acid (IPA), and trimellitic acid.

Recently also new bio-based diacids are getting interesting by an industrial point of view like itaconic acid and adipic acid (Scheme 8).



Scheme 8. Most widespread di- and tri-acids in PEI

Reagents can be introduced on various ratios and at different stages of the reaction. The process conditions largely dictate the resulting polymeric (or more accurately, oligomeric) composition, meaning that different conditions lead to different oligomer distributions. Although there is considerable flexibility in loading monomers, industrial applications typically employ one of four main process types: [34-39]

- **One-step process**: All components are added sequentially, beginning with polyols at room temperature. As the temperature increases, the other components are introduced.

- **Two-step process**: Components are partially loaded as in the one-step process. Initially, esterification or transesterification occurs at high temperatures, forming imides. The mixture is then cooled, and the remaining reagents are added for further reaction.

- **Multi-step process**: In the first step, polyols and the acid component are combined with the catalyst, leading to esterification (or transesterification). The diamine is then slowly introduced at elevated temperatures, promoting the formation of the imide group within the polyester mixture. Alternatively, trimellitic anhydride (TMA) can be withheld in the first step and added later, with subsequent additions split into two or more steps.

- **Aza-micheal variant process:** When dealing with an aza-Michael adduct, the process begins by loading glycol, followed by the diacid (e.g. itaconic acid,), TMA, and then the diamine. The mixture is allowed to react until the exothermic reaction stops (formation of the aza-micheal adduct). When reached 150°C TBM is added. As the temperature increases (by the heating mantle), water is distilled off because of the esterification and imidation reactions.

Industrial syntheses are typically conducted in batches ranging from a few to several tens of tons, depending on reactor capacity. The reaction can occur in solvents like cresylic acids (a mixture of phenol derivatives: m,p-cresol, xylenols, ethylphenol…) or with an excess of glycol, which is removed during the condensation phase. To assess the polymerization, also called the "condensation grade," a simple method is to measure the viscosity of the mixture, which increases proportionally to molecular weight until the desired specification is reached. Alternatively, molecular weight growth can be tracked directly using gel permeation chromatography (GPC), which allows monitoring of the polymerization process and the formation and consumption of oligomers during condensation.

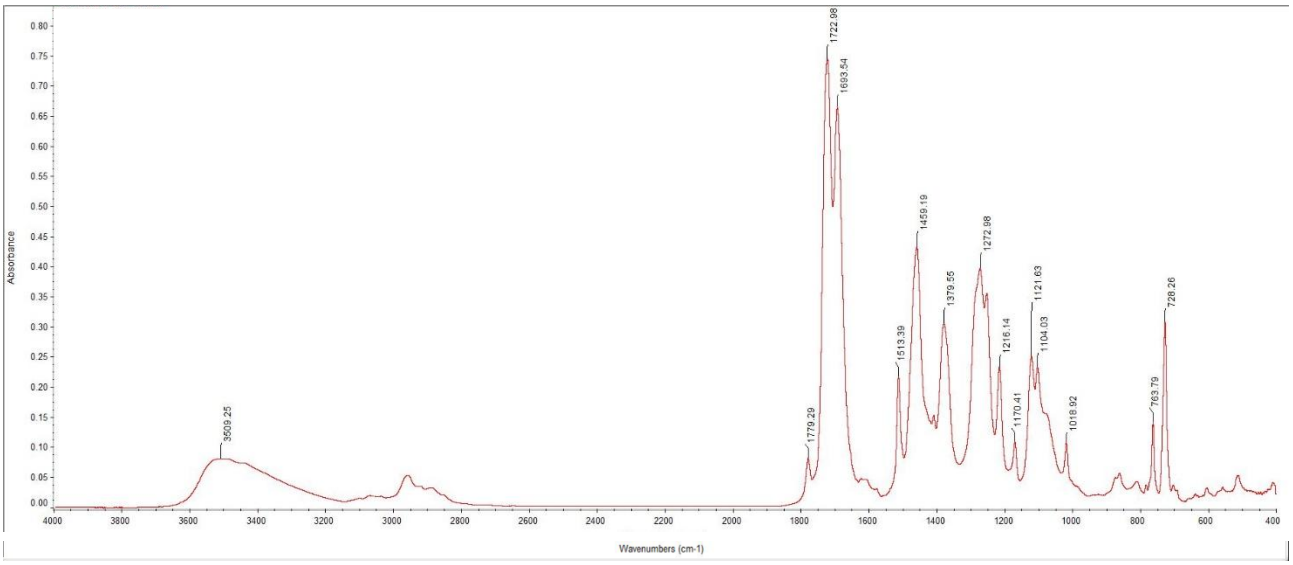


Figure 14. FT-IR spectra of a THEIC-modified PEI.

In the FT-IR cured PEI (Figure 14), the main absorption bands of the carbonyl groups, which are part of the imide ring, carboxylate groups, and isocyanurate ring, appear in the 1800–1600 cm^{-1} range. Specifically, the symmetric and asymmetric stretching peaks of the imide ring carbonyl (C=O) are observed in 1716 and 1775 cm^{-1}, while the ester bond's C=O stretching

vibration occurs at 1690 cm^{-1}. [40] Absorption intensities vary depending on the different raw material ratios.

PEIs are supplied as mixtures of cresylic solvents and hydrocarbons. During wire oven curing, solvents and volatile monomers such as ethylene glycol are removed, allowing the prepolymer to increase molecular weight through transesterification, forming a fully cured polymer. This reaction is catalyzed by titanium esters like butyl titanate. [41-42]

3.1.3 Polyurethanes properties and applications

Polyurethanes (PUs) represent a unique class of polymeric materials, distinguished by several characteristics that set them apart from most other plastics. They can be integrated into a diverse array of products, including paints, liquid coatings, elastomers, insulators, elastic fibers, foams, and integral skins. Many of the PU forms used today are merely improvements upon the original invention by the German scientist, Professor Dr. Otto Bayer, and his colleagues.[43] Figure 15 illustrates the primary types of PUs and some common examples of their uses. Bayer's development of the diisocyanate polyaddition technique in 1937 marked the birth of the PU industry, with PU initially synthesized from the reaction between diisocyanate and polyester diol. [44,45]

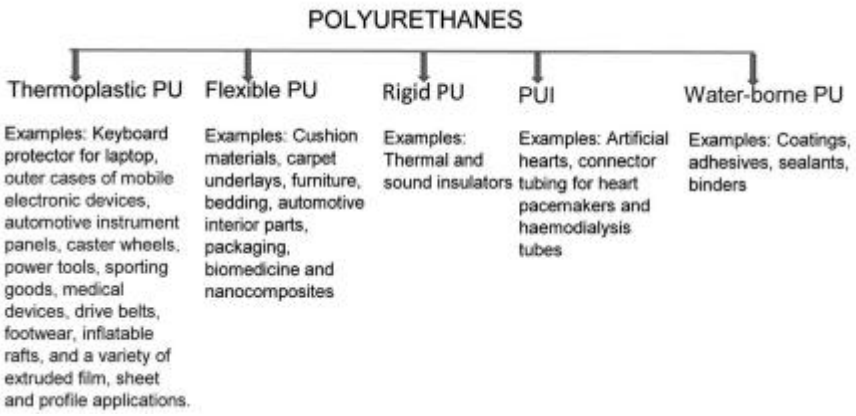


Figure 15. Types of PU and examples of their common applications.

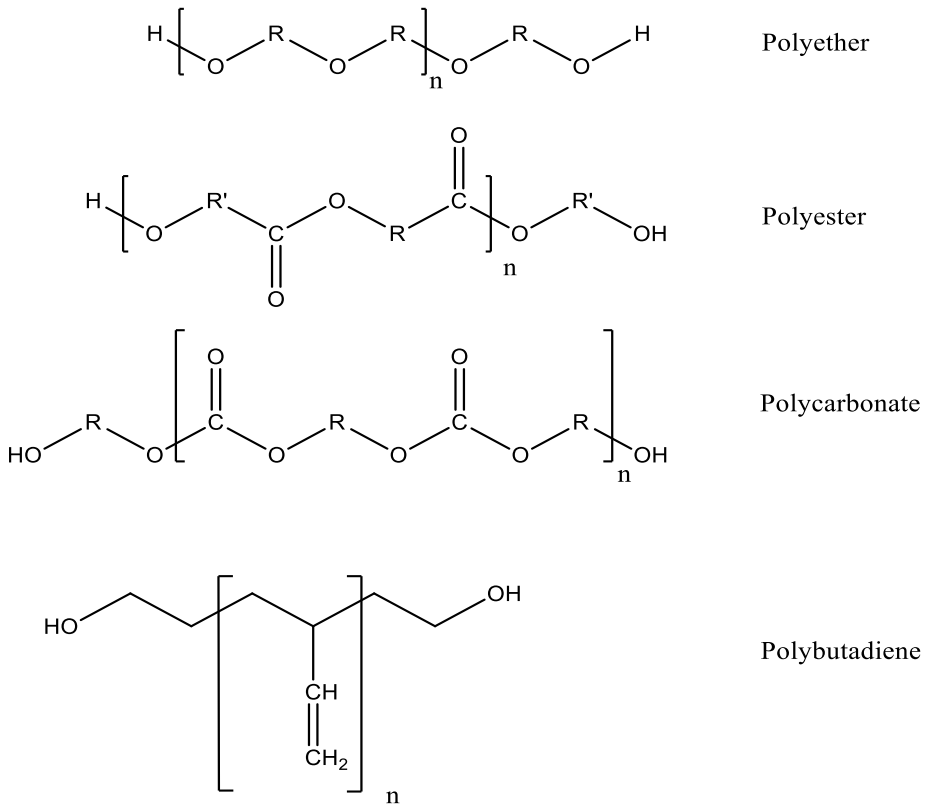
Polyurethanes were first introduced as a substitute for rubber during World War II. The material's versatility and ability to replace other scarce resources quickly led to its adoption in numerous applications. For example, PU coatings were used for impregnating paper and creating garments that were resistant to both mustard gas and corrosion. They also served as

chemically resistant coatings for wood, masonry, and metal, as well as high gloss finishes for airplanes.[46] Early industrial production of PU coatings featured specialized formulations for different purposes. By the mid-1950s, PUs had become common in elastomers, coatings, rigid foams, and adhesives. [47] Later in the decade, flexible foams emerged, offering comfort and practicality in cushions, which were commercially available by then.[46] The development of flexible foams from low-cost polyether polyols led to a range of applications in automotive and upholstery industries that remain relevant today. Continuous advancements in processing techniques, additive types, and formulations have allowed PUs to be utilized in a wide variety of applications. [48,49] Nowadays, PUs are one of the most commonly used, versatile, and well-studied materials globally. [50] They combine the durability and strength of metals with the elasticity of rubber, making them suitable for replacing metals, plastics, and rubber in various engineered products.[49,51] PUs are extensively applied in industries such as biomedical, construction, automotive, textiles, and many others, owing to their superior hardness, elongation, strength, and modulus properties.[48,50,52–56] The primary repeating unit in PUs is the urethane group, formed by the reaction between an alcohol (–OH) and isocyanate (NCO); however, PUs also contains other functional groups, such as ethers, esters, ureas, and aromatic compounds.[50,57] Given the vast array of sources from which PUs can be synthesized and the wide range of their applications, PUs are classified into various categories based on their specific properties: rigid, flexible, thermoplastic, waterborne, binders, coatings, adhesives, sealants, and elastomers.[58] Nowadays, polyurethane-coated wires are primarily used in the communication and electronics industries. These coatings offer the advantage of allowing for high enamelling speeds and enable the coated wires to be directly soldered.[59]

3.1.4. Chemistry of Polyurethanes

The chemistry of PUs leads them to be categorized with other compounds often collectively known as reaction polymers. These include phenolics, unsaturated polyesters, and epoxies.[60,61] Generally, PUs are typically synthesized from a reaction between isocyanates and polyol molecules, which happens either with the help of a catalyst or by activation through ultraviolet light.[62] These molecules—both isocyanates and polyols—should contain two or more isocyanate groups ($R-(N=C=O)n \geq 2$) and hydroxyl groups ($R'-(OH)n \geq 2$), respectively.[60]

The physical properties shown by PUs depend on the specific types of polyols and isocyanates that have been used.[63] Typically, soft elastic polymers come from long, flexible polyol segments, while rigid, tough polymers are produced with higher degrees of cross-linking. Stretchy polymers, on the other hand, result from long chains with low cross-linking, whereas harder polymers are derived from shorter chains with higher cross-linking. Additionally, combining long chains with an intermediate level of cross-linking results in polymers that are ideal for foam production.[52] Due to this cross-linking within PUs, they frequently have an effectively infinite molecular weight and a three-dimensional network structure. This is why a portion of PUs may be described as giant molecules, and it explains why typical PUs do not soften or melt when heated. By incorporating different additives with isocyanates and polyols, along with adjusting processing conditions, a wide variety of features can be achieved, making PUs adaptable for numerous applications.[64] Polyols used in PU synthesis often feature two or more –OH groups. Various kinds of polyols (Scheme 9) can be prepared in laboratories through different methods. For instance, polyether polyols come from the copolymerization of propylene oxide and ethylene oxide with a suitable polyol precursor,[65]. while polyester polyols are synthesized similarly to the production of polyester polymers. A specific type of polyether polyol, poly(tetramethylene ether) glycol, is obtained by polymerizing tetrahydrofuran and is used for high-performance elastomeric applications.[66] An example of isocyanate-terminated prepolymers produced using polytetrahydrofuran, along with related characterization studies, has been reported by Rajendran and colleagues.[67] Polyols are often used as mixtures of molecules that are similar but have different molecular weights.



Scheme 9. Example of possible functionalities inside a polyol.

These molecules can vary in the number of –OH groups they contain, so it is necessary to specify the average functionality of the polyols.[65] Despite the complexity of these polyol mixtures, industrial-grade polyols are formulated carefully to ensure consistent properties, which are essential for producing PUs with specific attributes. For example, rigid PUs are made from polyols with low molecular weight (a few hundred), while flexible PUs come from polyols with higher molecular weights (ten thousand and beyond).[65] Different structures of polyols are illustrated in Scheme 9.

A comparative analysis of the advantages and disadvantages of various polyols is presented in Table 2

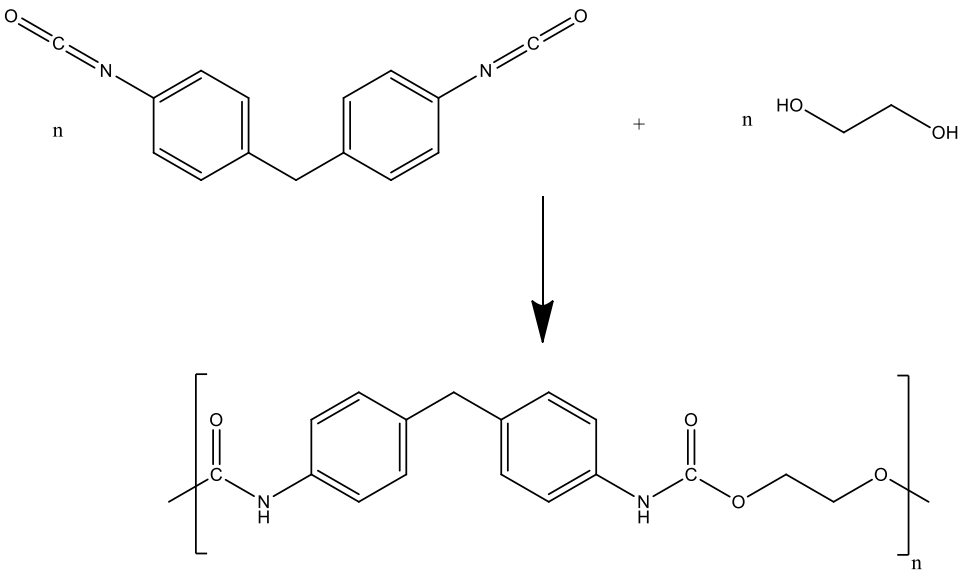
Polyol type	Advantages
Polyether polyols based on propylene oxide and ethylene oxide	Hydrolytic stability, cost, viscosity, flexibility
Aliphatic polyester polyol	Oxidative stability, modulus/strength
Aromatic polyester polyol	Flame retardance, modulus/stiffness
Polyether polyols based on tetrahydrofuran	Hydrolytic stability, modulus/strength
Polycarbonate polyols	Hydrolytic stability, oxidative stability, modulus/strength
Acrylic polyols	Hydrolytic/oxidative stability, hardness
Polybutadiene polyol	Low temperature flexibility, solvent resistance

Table 2. Advantages of different polyols

In contrast, isocyanates are incorporated into PU synthesis via a hydroxyl-group-containing compound because of their high reactivity, although the reaction rate can be slow at room temperature.[68] This slowdown may occur due to phase incompatibility between the polar, less dense polyol phase and the relatively non-polar, denser isocyanate phase. As a result, surfactants and suitable catalysts are needed to speed up the reaction. The catalyst functions by polarizing either the isocyanate or hydroxyl compound through polar interactions. According to the model, enhancing the electrophilic nature of isocyanates can be achieved by reducing electron density from the nitrogen or oxygen atoms within the NCO group. Aromatic isocyanates, such as toluene diisocyanate (TDI) and diphenylmethane diisocyanate (MDI), tend to be more reactive than their aliphatic counterparts, like isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HDI). Most isocyanates are difunctional, meaning each molecule contains two isocyanate groups, though there are exceptions, such as diphenylmethane diisocyanate, which consists of a mixture of molecules that contain two or more isocyanate groups. In this case, the average functionality of the compound tends to exceed two, typically averaging around 2.7, due to the higher number of isocyanate groups. Modifications to raw materials and changes in the synthesis process determine the final properties of PU products.

3.1.5. Synthesis of Polyurethanes

Polyurethanes (PUs) can be synthesized through a variety of methods.[61] The most common and practical approach involves the reaction between a polyol (a molecule containing two or more hydroxyl groups) and a diisocyanate. [43,52,69] Scheme 10 illustrates the synthesis process of a typical PU, figure 16 shows a typical ATR-IR spectra of a polyurethae.



Scheme 10. Common synthetic approach for Polyurethane.

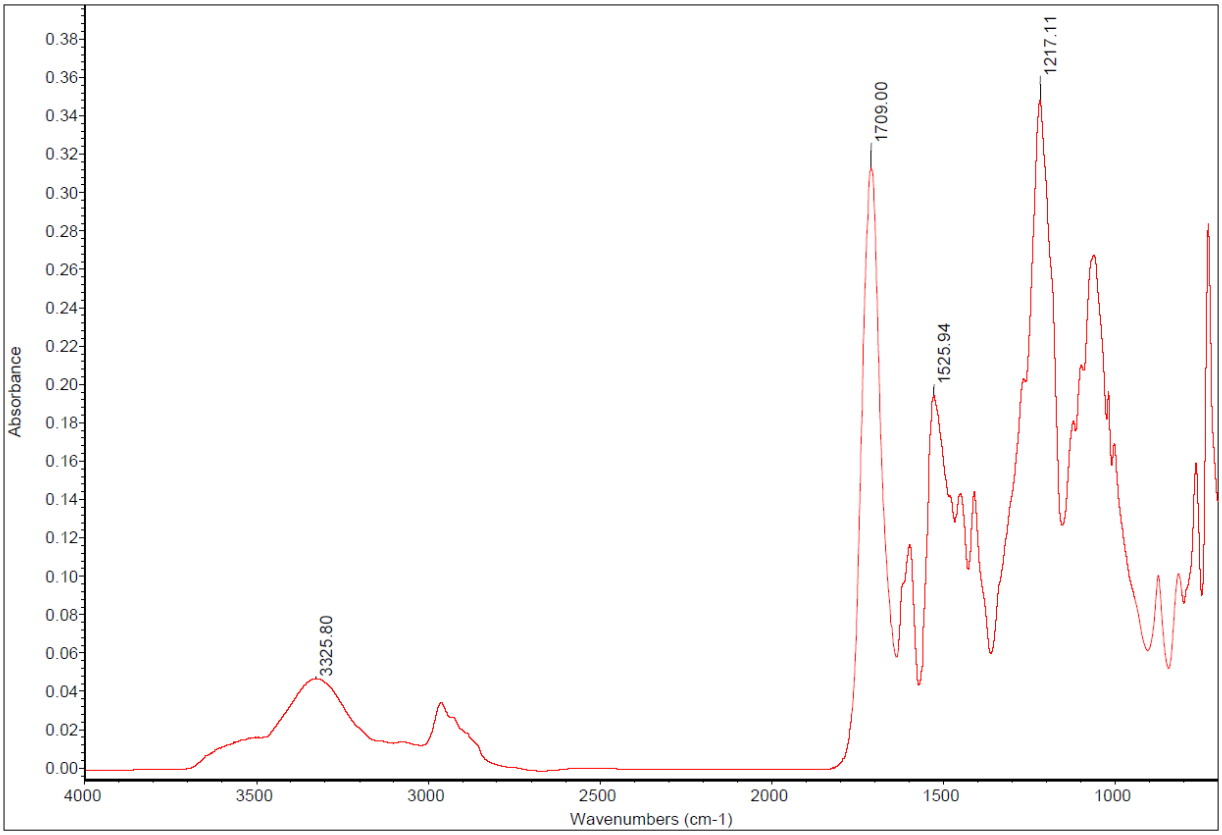


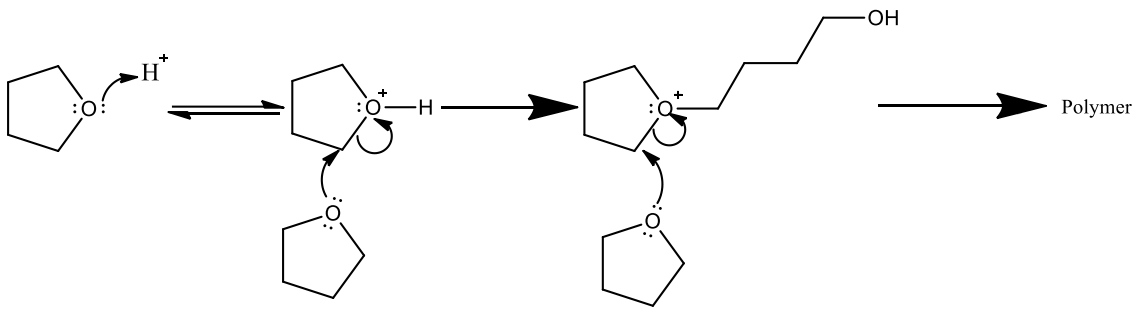
Figure 16. FT-IR spectra of a PU.

In the cured PU spectra (Figure 16), it is possible to spot in the picture where the single N-H stretch occurs at 3326. The 1709 cm^{-1} peak is linked to the hydrogen-bonded or "associated"

carbonyl groups.[104] Typically, these secondary urethane C=O stretching peaks are found between 1725 cm^{-1} and 1705 cm^{-1}. Keep in mind that, for polyamides, there's a notably strong N-H in-plane bending vibration. [105,106] Urethanes display this peak as well, found at 1525 cm^{-1} . This peak typically shows up in the 1540–1520 cm^{-1} range, overlapping with secondary amides. The C-O stretch of polyurethane is seen at 1217 cm^{-1}. Normally, this peak falls between 1265cm^{-1} and 1200 cm^{-1} in urethanes. Various additives and catalysts can also be introduced during PU synthesis. Common additives include flame retardants, pigments, cross-linkers, fillers, blowing agents, and surfactants. By adjusting the quantity and type of polyol, isocyanate, or additives, PUs can be fabricated with a wide range of properties, such as different levels of hardness and density. Table 3 outlines the typical components found in PUs and their specific purposes.

Additives	Reasons for use
Isocyanate	Responsible for the PU reactivity and curing properties
Polyols	Contributes flexible long segments, which produces soft elastic polymers
Catalysts	To speed up the reaction between the isocyanate and polyols and to allow reaction at a lower reaction temperature
Plasticisers	To reduce material hardness
Pigments	To produce coloured PU materials, especially for aesthetic purposes
Cross-linkers/chain extenders	For structural modification of the PU molecule and to offer mechanical support that will enhance the material properties
Blowing agents/surfactants	To aid the production of PU foams, to help control the formation of bubbles during synthesis and to control the foam cell structure
Fillers	To minimize cost and to improve the material properties, such as stiffness and tensile strength
Flame retardants	To reduce material flammability
Smoke retardants	To reduce the rate of possible smoke generation when the material is burnt

Table 3. Compounds Found in Polyurethanes (PUs) and their purpose [70]



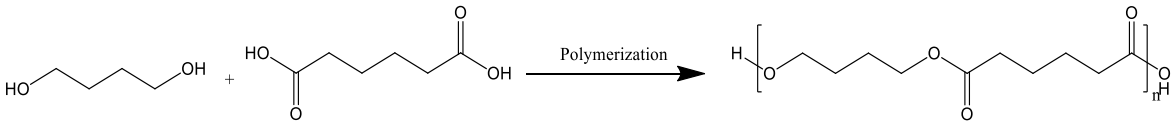
Scheme 11. Ring-opening mechanism of THF.

3.1.5.1 Polyols

Polyols are generally categorized into either polyether polyols or polyester polyols. Polyether polyols are formed by the reaction of an epoxide with an active hydrogen-containing compound. They can also be created via the ring-opening polymerization of epoxy monomers [70-71]. In contrast, polyester polyols are synthesized through the polycondensation of hydroxyl compounds and multifunctional carboxylic acids. Polyols can also be classified based on their intended use. High molecular weight polyols (ranging from 2,000 to 10,000 molecular weight) are primarily used in flexible PU production, while low molecular weight polyols are used to create rigid PUs. [52,72,73] Polyols for flexible PUs often involve initiators with low functionality, such as glycerine (f = 3), dipropylene glycol (f = 2), or a mixture of water and sorbitol (f = 2.75). Conversely, polyols for rigid PUs require initiators with higher functionality, such as sorbitol (f = 6), Mannich bases (f = 4), sucrose (f = 8), and toluenediamine (f = 4). Typically, ethylene oxide and/or propylene oxide is added to the initiators until the desired molecular weight is achieved. It's important to note that both the amount and the sequence in which the oxides are added can significantly influence the properties of the polyols.[74] This includes their solubility in water, reactivity, and compatibility. Polyols derived solely from propylene oxide generally terminate with secondary hydroxyl groups [54] and tend to be less reactive than polyols with ethylene oxide, which contain primary hydroxyl groups. Graft polyols, also known as polymer or filled polyols, consist of finely dispersed acrylonitrile, styrene-acrylonitrile, or polyurea polymer particles chemically grafted onto a high-molecular-weight polyether backbone. These graft polyols are often used in high-resilience, low-density foams to enhance load-bearing capacity, and they may also be added to improve the toughness of cast elastomers and microcellular foams. Additionally, low-molecular-weight polyols for rigid foams can be produced using initiators like triethanolamine or ethylenediamine, which impart inherent catalytic properties due to nitrogen atoms in the backbone. Another notable polyether polyol is poly(tetramethylene ether) glycol (PTMG), obtained from the polymerization of tetrahydrofuran, and it is mainly used in high-performance elastomers, coatings, and wetting applications. (Scheme 12)

Scheme 12. Ring-opening mechanism of THF.

Polyester polyols are produced from virgin raw materials through the direct polyesterification of highly pure diacids and glycols, such as 1,4-butanediol and adipic acid. (Scheme 13)



Scheme 13. Polyester reaction between 1,4-butanediol and adipic acid.

Polyester polyols are usually more viscous and expensive compared to polyether polyols, but they remain significant due to their ability to produce PUs with superior abrasion, solvent, and cut resistance. Another class of polyester polyols is derived from recycled materials through transesterification, also known as the glycolysis of recycled polyethylene terephthalate (PET) or the distillation byproducts of dimethyl terephthalate (DMT) with glycols, like diethylene glycol. These aromatic polyols, typically with low molecular weight, are commonly used in the production of rigid foams, offering cost savings and improved flame-retardant properties in polyisocyanurate (PIR) boardstock foams and PU insulation foams.

3.1.4.2 Speciality Polyols

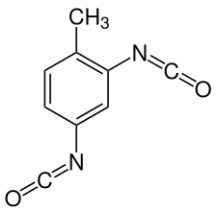
A group of specialty polyols is necessary for the production of sealants, elastomers, and adhesives that need to withstand challenging chemical and environmental conditions. Examples of these specialty polyols include polysulfide polyols, polycaprolactone polyols, polycarbonate polyols, and polybutadiene polyols. Polyols can also be sourced from renewable materials, such as vegetable oils. These renewable sources may include fatty acids or dimer fatty acids. [72,75] The vegetable oils used to produce polyols include castor, soybean, Pongamia glabra, neem, and cottonseed oils.[76] Polyols from vegetable oils are primarily used to create flexible molded foams, flexible bun stocks, and elastomers. The presence of triacylglycerides in vegetable oils makes them particularly suitable for manufacturing a variety of polymeric materials. [77-79]

When reacted with isocyanates, polyols from renewable sources can form PUs with unique properties, suitable for a broad range of applications.[80] One study explored modifications to soybean oil and castor oil to make them viable for rigid PU foam production. The resulting foams exhibited reduced mechanical properties compared to commercial polyol-based foams. However, they showed potential for rigid PU foam production due to their renewable origins.[81] In another area of research, the copolymerization of tetrafluoroethylene or chlorotrifluoroethylene with hydroxyl-alkyl vinyl ethers has led to the production of fluoroethylene vinyl ether (FEVE) polyols. Fluorinated PUs, synthesized from the reaction of polyisocyanate with FEVE polyols. Owing to the high concentration of fluorine-carbon bonds (one of the strongest chemical bonds), fluorinated PUs exhibit excellent resistance to UV radiation, alkalis, chemicals, acids, solvents, corrosion, weathering, fungi, and other microbial attacks. These properties make them ideal for use in high-quality paints and coatings.

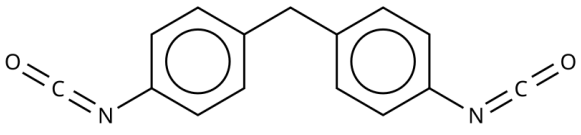
2.2.2.3 Isocyanates

Isocyanates are crucial components in the production of polyurethanes (PUs). They can be classified as either difunctional or heterofunctional, and further divided into aromatic or aliphatic categories. Among the various available options, the most commonly used isocyanates are methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), and aliphatic diisocyanates. Some common isocyanate structures are shown in Scheme 14. Typically, MDI and TDI are more cost-effective and reactive compared to other isocyanates. Industrial-grade MDI and TDI, which are usually isomeric mixtures, often consist of polymeric materials. These are predominantly used to produce flexible foams, such as molded foams for car seats or slabstock foams for mattress production. [42] They are also used in making rigid foams, such as insulating materials for refrigerators, and in elastomers (like shoe soles), among other applications. Modifications to isocyanates can be achieved by partially reacting them with polyols or by adding specific substances to reduce their volatility and toxicity. This process can also lower their freezing point, making them easier to handle, while simultaneously enhancing the properties of the resulting polymers. Less commonly used isocyanates include aliphatic and cycloaliphatic isocyanates, which are used in applications such as coatings where transparency and color stability are important. This is because aromatic isocyanate-based PUs tends to darken when exposed to light. [82] Some common examples of aliphatic and cycloaliphatic isocyanates are 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate,

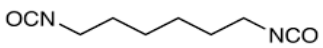
IPDI), 4,4'-diisocyanato dicyclohexylmethane (hydrogenated MDI or H12MDI), and 1,6-hexamethylene diisocyanate (HDI).



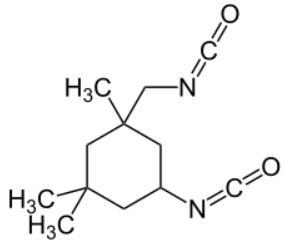
Toluene



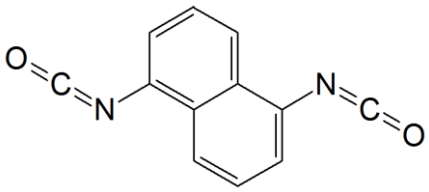
Methylene diphenyl diisocyanate



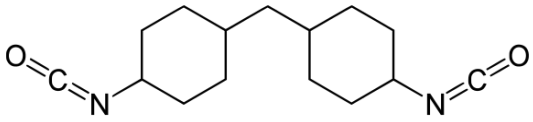
Hexamethylene diisocyanate



Isophorone diisocyanate



Naphthalene diisocyanate

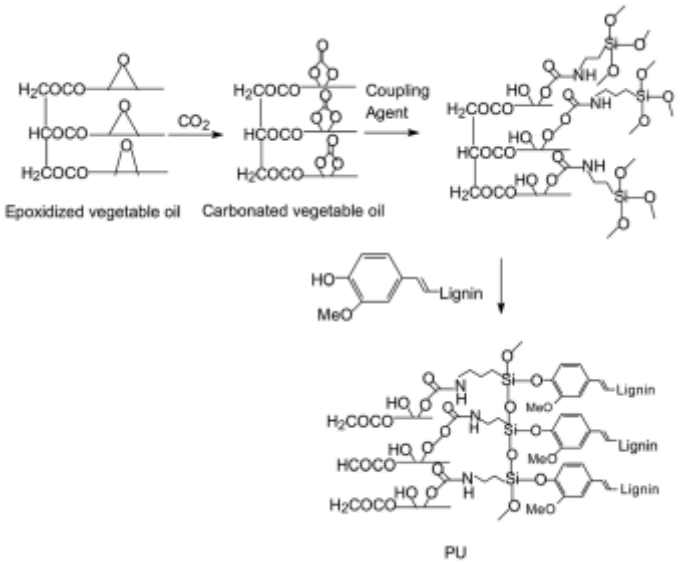


Hydrogenated methylene diphenyl diisocyanate

Scheme 14. Most used diisocyanates

Despite the widespread use of diisocyanates, environmental and health concerns have led researchers to explore alternative routes to minimize or avoid their use, with a focus on reducing the environmental impact and toxicity associated with diisocyanates. For instance, one study investigated producing sustainable PUs from carbonated soybean oil, 3-aminopropyltriethoxysilane, and lignin.[83] This non-isocyanate route involved the reaction of cyclic carbonates with amines,[84] while the polyol was derived from lignin using an oxypropylation method,[85] In another example, oligomeric polybutadiene diisocyanate was used for lignin-based PU production. [86]. Similarly, lignin-aminated polyol was reacted with diphenyl diisocyanates to synthesize PUs. Most studies found that the properties of non-

isocyanate-based PUs largely depend on the lignin content, which affects the material's cross-linking and modulus. A typical synthetic route is depicted in Scheme 15.



Scheme 15. Polyurethane preparation starting from vegetable oil (castor oil) and lignin, isocyanate free

3.2 Solvent System

Solvents are essential in wire enamel formulations and, more generally, in organic coatings, as they provide the necessary viscosity for the curing process, which leads to film formation. Choosing the right solvents in appropriate proportions is critical for producing a high-performance wire enamel that is free of surface defects. Volatile components in the formulation influence popping, sagging, leveling, as well as adhesion, corrosion resistance, and durability. To use solvents effectively, it is important to understand what constitutes a solvent, the different types available, and their potential hazards to human health and the environment.

Solvents can be categorized into three main types: weak hydrogen-bonding, hydrogen-bond acceptor, and hydrogen-bond donor/acceptor.

- **Weak Hydrogen-bonding solvents:**

These are petroleum-distillate mixtures of aliphatic and aromatic hydrocarbons, known as naphthas. They vary in volatility and aromatic content. Commercial aliphatic naphthas are blends of straight-chain, branched-chain, and alicyclic hydrocarbons, with relatively low aromatic hydrocarbon content. One advantage of aliphatic naphthas is their low cost,

particularly by volume, as they have low density and price per unit of weight. Aromatic hydrocarbon solvents, while more expensive than aliphatic, can dissolve a wider range of polymers.

- **Hydrogen-bond acceptor solvents:**

Oxygenated solvents, such as esters, ester ethers, and ketones, fall into this category. Ketones are generally less expensive than esters with comparable evaporation rates. However, in some cases, esters and ester ethers may be preferred over ketones due to their lower odor levels.

- **Hydrogen-bond acceptor/donor solvents:**

Among oxygenated solvents are those with active hydrogens that act as strong hydrogen-bond donors/acceptors, such as hydroxy compounds, both aliphatic and aromatic. Common volatile alcohols include methyl, ethyl, isopropyl, n-butyl, sec-butyl, and isobutyl alcohols. Less volatile compounds, such as phenol and alkylated phenols (e.g., cresols, xylenols, ethyl phenols, and trimethylphenols), are also used. Additionally, nitroparaffins are highly polar hydrogen-bond acceptor solvents. Due to their increased electrical conductivity from high polarity, nitroparaffins are useful in electrostatic spraying applications.[87]

3.2.1. Solvent Selection

Selecting an appropriate solvent is essential, as it must meet several key criteria:

- It should not react with the reactants.
- It must effectively dissolve the final polymer.
- It has to remain stable throughout its shelf life.
- It must not cause issues during application and curing.
- It should be cost-effective.
- It must be non-toxic.
- It needs to have at least 2 industrial providers in an industrial scale.

Another important consideration is the molecular weight of the polymer, which significantly impacts its solubility. In a specific solvent at a given temperature, higher molecular weights tend to reduce polymer solubility. A similar trend is observed with crosslinked polymers—higher degrees of crosslinking reduce solubility, as the crosslinks hinder interactions between polymer chains and solvent molecules, preventing the polymer chains from dissolving.

3.2.1.1 Hansen Solubility Parameters

A useful approach for selecting solvents is through Hansen solubility parameters (HSP), as proposed by Charles M. Hansen. He identified three types of intermolecular forces that determine solubility:

- Dispersion forces (δd)
- Polar forces (δp)
- Hydrogen bonding (δh)

These forces are represented in a three-dimensional "Hansen space," where solvents and solutes are positioned based on their δd, δp, and δh values. The closer two substances are in Hansen space, the more likely they are to dissolve in each other. This follows the principle of "like dissolves like," meaning substances with similar bonding tendencies tend to mix well. [88-90]

The total solubility parameter (δ) is calculated using the equation:

$$\delta = (\delta_a^2 + \delta_p^2 + \delta_n^2)^{1/2} \quad \text{(Eq. 1)}$$

For solvent mixtures, a weighted average of the partial solubility parameters can be calculated:

$$\delta_{d(mix)} = (\varphi\delta_d)_1 + (\varphi\delta_d)_2 + \cdots + (\varphi\delta_d)_n$$

$$\delta_{p(mix)} = (\varphi\delta_p)_1 + (\varphi\delta_p)_2 + \cdots + (\varphi\delta_p)_n \quad \text{(Eq. 2)}$$

$$\delta_{h(mix)} = (\varphi\delta_h)_1 + (\varphi\delta_h)_2 + \cdots + (\varphi\delta_h)_n$$

Several methods can be used to determine or calculate three-dimensional solubility parameters, including the HSPiP software, which contains a database of solvents, chemicals, and polymers. The software can also predict solubility parameters based on a substance's Simplified Molecular Input Line Entry System (SMILES).[91]

No.	Solvent	δD	δP	δH	Score	RED	MVol
52	Benzene	18.4	0	2	0	1.723	89.5
325	Ethanol	15.8	8.8	19.4	0	1.504	58.6
181	Cyclohexane	16.8	0	0.2	0	1.928	108.9
585	Propylene Glycol	16.8	10.4	21.3	0	1.550	73.7
456	Methanol	14.7	12.3	22.3	0	1.891	40.6
368	Ethylene Glycol	17	11	26	0	2.062	55.9
406	Glycerol	17.4	11.3	27.2	0	2.178	73.4
9999	Dihydrolevoglucosenone	18.9	12.4	7.1	1	0.308	100
9999	Astrobio Ap-3	17.53	11.51	8.63	-	0.436	100
9999	Cardanol	17.5	2.3	6.2	-	1.310	100
9999	Methoxy Phenol	19.19	7.6	12.3	-	0.630	100
9999	Timol	17.8	4.0	7.2	-	1.068	100
9999	Eugenol	18.5	5.6	9.5	-	0.797	100
9999	Estragol	18	4.5	4.8	-	1.114	100

Figure 17. Examples Hansens solubility parameters. Note, from screenshot of HSPiP software.

To determine whether a solvent and polymer are compatible, an interaction radius (R_0) is assigned to the solute, defining a sphere in Hansen space with the solute's Hansen parameters at its center. The distance (Ra) between the solvent and solute in Hansen space is calculated as:

$$(R_a)^2 = 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 \qquad \text{(Eq. 3)}$$

This can be combined with the interaction radius to calculate the Relative Energy Difference (RED) of the system:

$$RED = R_a/R_0 \qquad \text{(Eq. 4)}$$

- If RED < 1, the molecules are compatible and will dissolve.

• If RED = 1, partial solubility occurs.

• If RED > 1, the system will not dissolve.

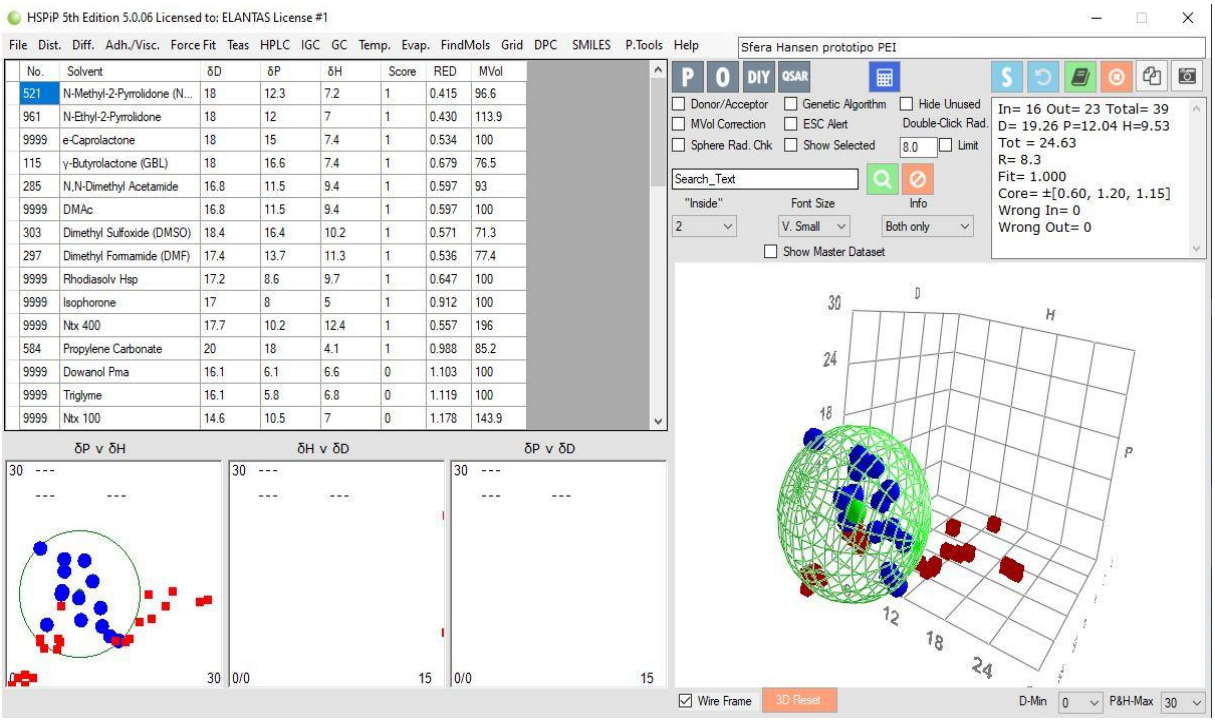


Figure 18. Hansens solubility sphere. Note, from screenshot of HSPiP software

3.2.2. Solvent system in wire enamels

In wire enameling, the solvent system typically comprises two key components: one serves as a reaction medium to dissolve monomers and initiate the reaction (referred to as solvents), while the other, known as thinners, dilutes the resin, modifying the system's boiling characteristics and viscosity.

The reaction medium consists of high-boiling, highly polar aprotic solvents that are both hydrogen bond donors and acceptors. Common examples include NMP (N-methyl-2-pyrrolidone), DMF (dimethylformamide) and DMAc (dimethylacetamide).

Thinners, on the other hand, are made up of medium-boiling-point solvents, such as aliphatic and aromatic hydrocarbons like naphtha and xylene, as well as some high-boiling-point solvents. "Naphtha" refers to a group of chemicals derived from petroleum distillates and

natural gas condensates, typically with distillation ranges around 160–180°C. These are clean, flammable solvents, customizable for various applications. Common high-boiling solvents include phenol, cresols (a mixture of meta- and para-cresols), xylenols (isomers of dimethyl phenols), cresylic acids (a mix of phenol, cresols, xylenols, and other alkylated phenols), and synthetic alkylated phenols. These solvents have distillation ranges between 190°C and 250°C.

Thinners are added primarily to reduce the viscosity of resins, improving their workability and application to wire. They are more cost-effective than highly aprotic solvents, lowering the overall cost of the enamel. Additionally, thinners evaporate faster than NMP during wire enameling, which helps cool the varnish mixture, preventing surface crusting and blistering in the film. The choice of varnish solvents must ensure proper evaporation rates, aligning with the curing oven's temperature profile and the desired enameling speed to produce smooth, regular films.

For uniform evaporation during baking, efforts are made to achieve a consistent evaporation pattern as the composition of the changing azeotrope evolves. Abrupt changes can lead to surface defects in the cured enamel film, such as blister formation (illustrated in Figure 19).

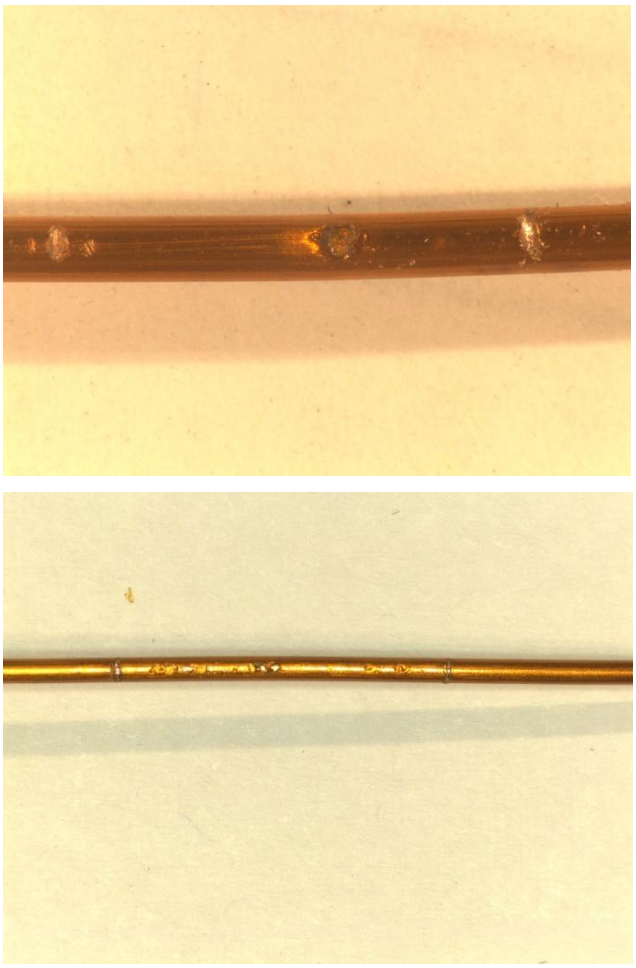


Figure 19. Blister formation on enameled wires (Source: Elantas internal database).

As previously mentioned, solvents are crucial during film formation in the enameling ovens, where they evaporate while the polymer cures on the copper wire. Therefore, the evaporation rates of solvents are treated with special care to ensure a flawless finish.

3.2.2.1. Key aspects and variables on evaporation

The rate at which a solvent evaporates is influenced by four key variables: vapor pressure, temperature, surface-to-volume ratio, and airflow rate over the surface. The temperature to consider is that of the area at and near the surface, while the vapor pressure refers to that of the solvent at the temperature where evaporation occurs. The surface area-to-volume ratio plays a crucial role because evaporation happens at the interface between the solvent and air. For example, if 10 g of solvent are spread over an area of 100 cm^2, it evaporates much more rapidly

compared to when the surface area is just 1 cm². As a result, when solvent evaporates from thicker films with the same surface area, the resin solution's concentration and viscosity increase at a slower and steadier pace. Additionally, the airflow rate plays a key role because the evaporation rate depends on the partial pressure of the solvent vapor at the air-solvent interface. If the vaporized solvent isn't removed quickly from the surface, the partial pressure builds up, slowing down the evaporation process.. Airflow rates can vary considerably, depending on the application method, and therefore, the solvents used in a coating must be chosen carefully for the specific application conditions [92,93].

In terms of selecting solvents, the most critical factor is vapor pressure. A common mistake is to assume that boiling points (the temperatures at which solvents have a vapor pressure of 1 atm) are directly proportional to vapor pressures at other temperatures. Thus, many use boiling points to estimate evaporation rates. However, boiling points are poor indicators of vapor pressure, and the two values can vary significantly for the same solvent, making it difficult to predict how much faster one solvent will evaporate compared to another based on vapor pressure data alone. Because of this, it became necessary to establish the relative evaporation rates (see Eq. 5).

$$E = \frac{t_{90}(\text{n-butyl acetate})}{t_{90}(Test\ Solvent)} \qquad \text{(Eq. 5)}$$

This equation is used to determine the relative evaporation rate of a solvent (E) compared to that of n-butyl acetate. In the equation, t_{90} represents the time required for 90 wt% of a sample to evaporate in a specific type of apparatus under controlled conditions. Therefore, the higher the E value, the faster the evaporation rate. The relative evaporation rate is influenced by numerous parameters such as vapor pressure, temperature, and surface area, since evaporation is primarily a surface-driven phenomenon. To determine relative evaporation rates, measurements must be taken under standardized conditions. Focusing on the coating film formation process, it can be stated that the resin components initially have little or no effect on the rate of solvent evaporation. However, as the solvent continues to evaporate from the coating, a point is reached where the evaporation rate decreases sharply. At this stage, the viscosity of the coating rises, reducing the available free volume, and the solvent loss rate becomes dependent on the rate of diffusion of the solvent through the film rather than the evaporation rate itself. Two distinct phases of solvent evaporation can be identified. During the initial phase,

the evaporation rate is determined by the same factors that govern the evaporation of solvent mixtures. After a transitional phase, evaporation slows down, and the rate of solvent loss becomes reliant on the diffusion rate of the solvent molecules through the film. In this second phase, the diffusion rate is predominantly controlled by the availability of free volume. Essentially, the solvent molecules move through the film by jumping from one free volume void to another. The most significant factor controlling free volume availability is the difference between the temperature (T) and the glass transition temperature (Tg). If solvent evaporation takes place at a temperature well above the Tg of the solvent-free resin, diffusion rate will not limit the evaporation rate at any point during drying. However, as the Tg of the resin nears the temperature at which drying occurs, solvent evaporation becomes increasingly governed by diffusion rate as (T-Tg) diminishes [94].

3.3. The Polymerization reactions

Here, we discuss the two primary classes of polymerization processes that contribute to the formation of organic coatings: chain-growth and step-growth polymerization. Chain-growth is often referred to as addition polymerization, though this term can be somewhat misleading. While all chain-growth polymerizations involve addition reactions, not all addition reactions correspond to chain-growth mechanisms. Chain-growth polymerization operates through four main mechanisms: free radical, anionic, cationic, and coordination polymerization. Additionally, three essential types of reactions are always part of this process: initiation, propagation, and termination. Sometimes, a side reaction called chain transfer plays a role, causing the termination of one growing chain and the formation of another radical capable of starting a new chain. Initiation begins when an initiator reacts to produce an active free radical, which quickly adds to a monomer molecule, forming another free radical. This leads to the propagation stage, where the free radical adds rapidly to successive monomer molecules, extending the polymer chain. The process of propagation is incredibly fast, and during this stage, the concentration of monomers and polymers is much higher than that of the growing polymer chains. Finally, the growing chain ends through termination, which typically occurs via either combination or disproportionation reactions. In most cases of free radical polymerization, the propagation rate is quicker than the initiation rate, as the formation of the first free radical tends to be the slowest step [95].

3.3.1. Step-Growth Polymerization

When it comes to step-growth polymerization, this process is particularly important to us because it's the method used for many of the polymers found in wire insulation enamels, including polyesters, polyamides, and polyurethanes, among others.

In the early phases of step-growth polymerization, the increase in the degree of polymerization happens quite slowly as functional groups are converted. This is primarily because a significant number of end groups need to be consumed to create each high-molecular-weight polymer chain. However, as the polymerization progresses, even small changes in conversion can lead to substantial increases in molecular weight, thanks to the combination of larger molecules.

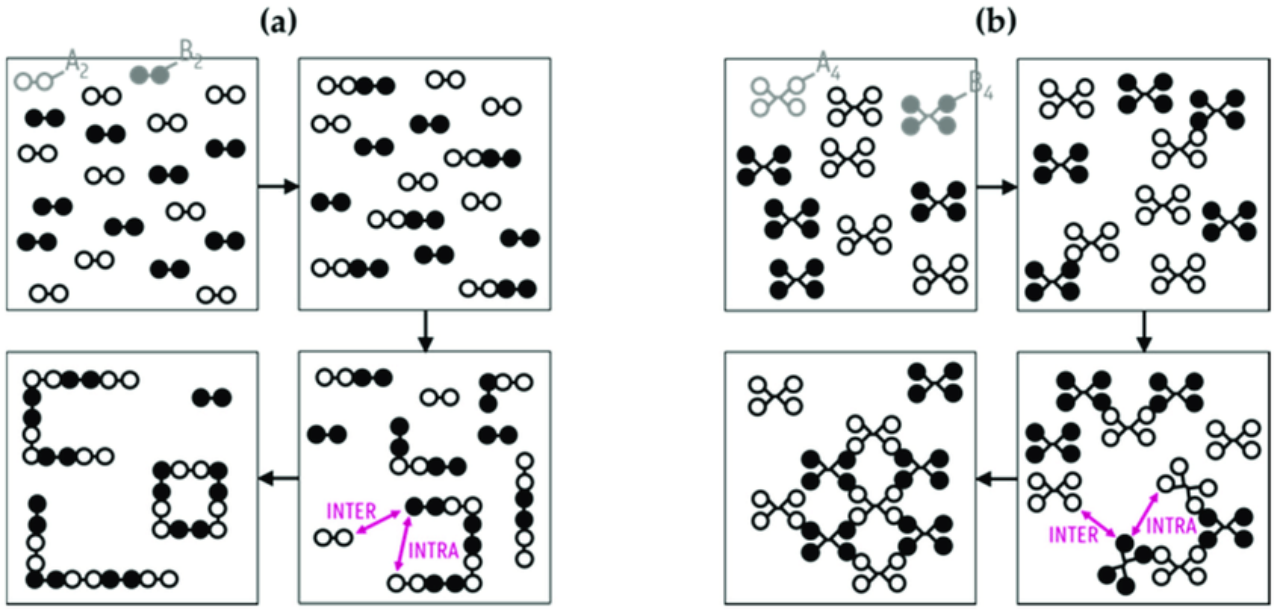


Figure 20. Step grow polymerization kinetics for (a) two bifunctional reagents and (b) two multifunctional reagents.

Typically, the final conversion and, consequently, the average molecular weight in step-growth processes are constrained by the reaction's equilibrium. The concentrations of functional groups at equilibrium are influenced by the presence of eliminated compounds. By removing these byproducts from the reaction medium, their concentration decreases, reducing the rate of the reverse reaction. This encourages the continued consumption of functional groups and promotes

the formation of higher-molecular-weight polymers. To achieve high molecular weight in polymers, the reaction needs to be pushed towards very high conversions. However, this can make the reaction medium quite viscous, which poses a challenge. High viscosity hinders the diffusion of condensation byproducts through the medium, making it difficult for them to be removed. Since the removal of these byproducts is crucial for the growth of polymer chains, mass transfer often becomes the bottleneck in step-growth polymerizations.

To facilitate the removal of condensation byproducts, many polycondensation reactor designs maximize surface area to improve mass transfer from the polymer phase. In certain processes, applying a high vacuum can further enhance the removal of these byproducts. (Figure 21)

Figure 21. High vacuum pump for industrial plants

Polycondensation can be conducted through various polymerization techniques, including melt polymerization and solution polymerization. A brief summary of these processes will follow in the next paragraphs [96].

3.3.2. Melt polycondensation

In melt polycondensation, the step-growth reactions happen when the polymer is in a molten state, with the temperature raised above its melting point. To help get rid of any byproducts created during the process, a vacuum can be used to pull out these volatile substances, or an inert gas can be pumped in to reduce their concentration near the polymer. This approach produces polymers that are usually very pure, apart from any catalysts or additives used to tweak their appearance or stability, like pigments or stabilizers.

As the polymerization progresses, the polymer mass becomes much more viscous, which makes it harder for small byproduct molecules to escape. This step of removing the byproducts actually slows down the whole process. On top of that, the high temperatures needed to keep the polymer in a molten state can sometimes lead to unwanted side reactions, creating other byproducts that aren't useful [97].

3.3.3. Solution polycondensation

In industry, solution polycondensation is a go-to method for producing materials like polyurethanes, polycarbonates, and certain polyamides and polyesters. This process is especially useful when keeping the reactants in the same phase in bulk polymerization is difficult, or when the final polymer has an exceptionally high melting point. Since it operates at lower temperatures than melt polymerization, solution polycondensation allows for better heat control because the viscosity is lower. However, it comes with extra steps: once the reaction is done, the polymer must be separated from the solution, the solvent has to be recovered, and the polymer itself needs to be thoroughly washed and dried. [98,99]

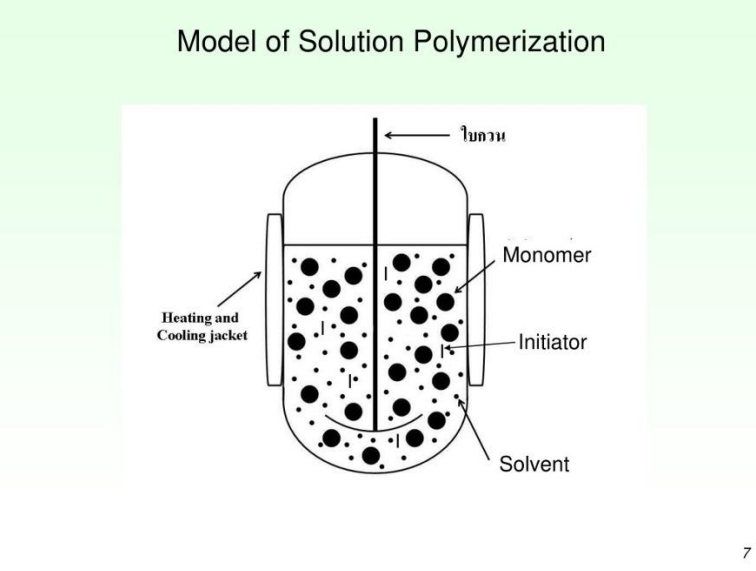
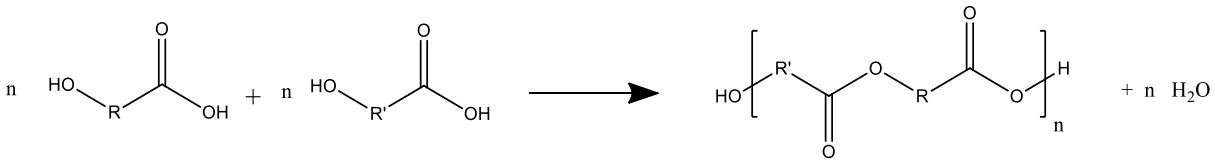


Figure 22. Model of solution polymerization

3.3.1.1. Step growth polymerization reaction kinetics and molecular weight distribution

To quantify the kinetics of step-growth polymerization, it's essential to take into account the reactivities of the functional groups on both the monomers and the growing polymer chains. A key assumption in most step-growth systems is the equal reactivity of functional groups[100]. This means that the frequency with which functional groups collide and react, which largely dictates the polymerization rate, is fairly uniform, whether the group is on a small molecule or at the end of a polymer chain. Additionally, in many cases, the presence of other nearby groups doesn't significantly alter the reactivity of a functional group. As a result, the polymerization rate can often be expressed simply based on the overall concentration of functional end-groups. One of the critical characteristics of condensation polymers is their molecular weight. To illustrate, consider a linear step-growth polymerization involving AB-type monomers, where A might be a hydroxyl group and B a carboxylic acid group, leading to the formation of a polyester.



Scheme 16. Linear step-growth polymerization.

The goal is to model how the polymer chain length distribution (CLD) evolves at different stages of conversion. In step-growth polymerization, the symbol p (rather than x) is typically used to indicate the conversion of the limiting functional group. This conversion can be interpreted as the probability that any given functional group in the starting reaction mixture (e.g., −OH) has reacted with another group (e.g., −COOH). Based on this reasoning, Flory [100] demonstrated that the probability of a molecule having a chain length n can be described as follows: (Eq. 6)

$$P(n) = p^{n-1}(1-p) \qquad \text{(Eq. 6)}$$

The formation of a polymer chain that consumes exactly n monomers requires $n - 1$ independent chain-linking reactions, each occurring with probability p. Additionally, one hydroxyl group at the end of the polymer remains unreacted, which has a probability of $1 - p$.

This results in what's known as the most probable distribution (MPD), or Schulz–Flory distribution. Interestingly, the MPD can also appear in chain-growth polymerization systems. The probability *P(n)* represents the mole fraction of an *n*-mer, denoted as *x(n)*. For instance, at 90% conversion ($p = 0.9$), the mole fractions are as follows: monomer ($n = 1$) has a mole fraction of 0.09, dimer ($n = 2$) is 0.081, and trimer ($n = 3$) is 0.0729. As the chain length increases, the mole fractions become progressively smaller. As the conversion approaches $p \rightarrow 1$, the mole fractions of small molecules diminish, and larger molecules become more prevalent. Next, by using Equation 6, it's possible to derive an expression for the weight-based CLD for this AB-type polymer system. Let *N* be the total number of molecules left at conversion *p*, and N_0 the initial number of monomer molecules. Thus, $N = N_0(1 - p)$, and the mole fraction of *n*-mer becomes Equation 7

$$x(n) = \frac{N_n}{N_0(1-p)}$$

Since $x(n) = P(n) = p^{n-1}(1 - p)$, the number of moles of n-mer is (Equation 8)

$$N_n = N_p p^{n-1}(1-p)$$

and the weight fraction of n-mer is: (Equation 9)

$$w(n) = \frac{N_n(nw_n)}{N_0 w_m} = \frac{N_0(1-p)^2 p^{n-1} n}{N_0} = (1-p)^2 p^{n-1} n$$

In this case, w_m represents the molecular weight of a repeat unit, under the assumption that the total mass of repeat units in the polymer chains far exceeds the mass of the end groups. Figure 23 illustrates the weight chain length distribution (CLD) curves for three distinct conversion values ($p = 0.96, 0.97, 0.98$). As the conversion rate increases, you'll notice that the peak of the CLD curve shifts rightward, and the distribution itself becomes broader. This broadening indicates that higher molecular weight species are becoming more prevalent as the reaction progresses.

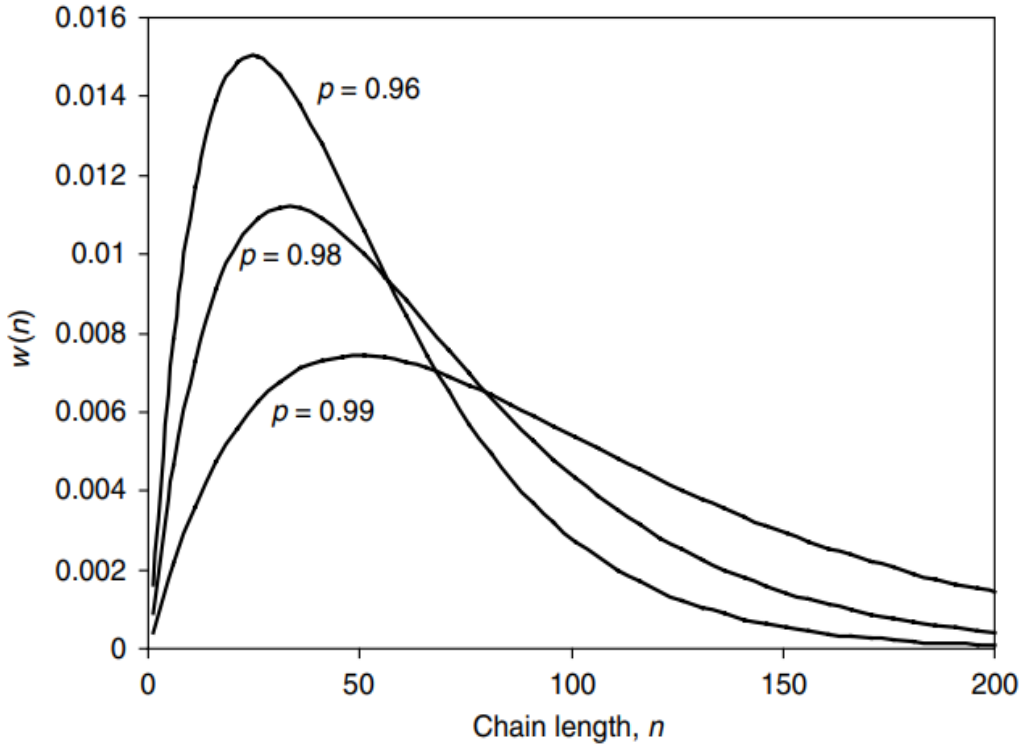


Figure 23. Weight chain length distribution at different end group conversions.

The number-average degree of polymerization (DPn) and the weight-average degree of polymerization (DPw) can be determined using the number and weight chain length distribution (CLD): (Equation 10,11)

$$DP_n = \sum_{n=1}^{\infty} nx(n) = \sum_{n=1}^{\infty} (1-p)np^{n-1} = (1-p(1+2p+3p^2+\cdots)$$

$$= \frac{1-p}{(1-p)^2} = \frac{1}{1-p}$$

$$DP_w = \sum_{n=1}^{\infty} nw(n) = \sum_{n=1}^{\infty} (1-p)^2 n^2 p^{n-1} = (1-p)^2(1+2^2p+3^2p^2+\cdots) = \frac{1+p}{1-p}$$

The polydispersity index (PDI), defined as DPw/DPn, is equal to 1 + p. Since p is usually very close to 1.0 for linear high-molecular-weight step-growth polymers, the polydispersity is approximately 2.0. The molecular weight averages can be calculated from the conversion, and for high-molecular-weight polymers, the conversion (p) must approach 1.0. For instance, when p = 0.99, the number-average degree of polymerization is 100.

3.3.1.2. Non-stoichiometric composition effect

In chapter 3.3.1.1., the focus was on the polymerization of AB-type monomers. In these systems, the structure of the monomer ensures an equal number of functional end-groups of both types, unless there are impurities or additives in the mixture. However, in AA and BB systems, there can be a stoichiometric imbalance, which can significantly affect polymerization. The initial molar ratio of the two monomers in a batch reactor, along with any loss of monomers or oligomers during the reaction, dictates the molar ratio of A and B functional groups available for polymerization. This loss of volatile monomers, which alters the ratio of functional groups, is a notable issue in industrial polymerizations involving volatile monomers, such as HMD in nylon 6,6 production or diphenyl carbonate in polycarbonate production.

Now, consider a scenario where there's a slight excess of BB monomers at the start of an AA and BB polymerization, with no loss of molecules from the mixture. To understand how the average molecular weight of a polymer can be calculated, it's important to first define a few key concepts. (Equation 11)

$$N_{A0} = number\ of\ A\ groups\ present\ at\ t = 0$$

$$N_{B0} = number\ of\ B\ groups\ present\ at\ t = 0$$

$$r = \frac{N_{A0}}{N_{B0}} (< 1; B\ groups\ in\ excess)$$

$$p = conversion\ (based\ on\ A\ gropus, limit\ reactant)$$

Then, the initial number of molecules is: (*Equation 12*)

$$n_0 = \frac{N_{A0} + N_{B0}}{2} = \frac{N_{A0}}{2}(1 + \frac{1}{r})$$

The total number of chain ends after reaction progresses to conversion p is (*Equation 13*)

$$N_{total} = N_{A0}\{2(1-p) + \frac{1-r}{r}\}$$

Since the total number of molecules at conversion p is $N_{total}/2$, the number-average chain length can be expressed as: (*Equation 14*)

$$DP_n = \frac{initial\ number\ of\ molecules}{final\ number\ of\ molecules} = \frac{(N_{A0}/2)(1+(1/r))}{(N_{A0}/2)\{2(1-p)+(1-r)/r\}}$$

$$= \frac{r+1}{2r(1-p)+1-r}$$

To understand how to calculate the polymer's average molecular weight, let's define "chain length" as the total number of monomer molecules used to form a polymer chain. In an AB polymerization, it's the number of repeat units plus one, while in an AA + BB polymerization, it's roughly the number of repeat units times two. *Equation 15* shows that when the initial amount of AA and BB monomers is equal (r = 1), $\bar{X}_n = 1/(1-p)$, which is the same result as in *Equation 10* for AB polymerization. *(Equation 15)*

$$DP_n = \frac{r+1}{2r(N_A/N_{A0})+1-r} = \frac{N_{A0}+N_{AB}}{2N_A+N_{B0}-N_{A0}}$$

If Z is the number of moles of polymer linkages formed, then

$$N_{A0} = N_A + Z$$

$$N_B = N_{B0} - N_{A0}p$$

And

$$N_{B0} = N_B + N_{A0}p$$

$$= N_B + N_{A0}p$$

$$= N_B + N_{A0} - N_A$$

$$= N_B + Z$$

Finally, the following equation describing the number-average chain length in AA and BB polymerization is obtained: (*Equation 16*)

$$DP_n = \frac{N_A + N_B + 2Z}{N_A + N_B} = 1 + \frac{2Z}{N_A + N_B}$$

The derivation of *Equations 6-16* assumes that linear polymer molecules are formed, with a functional group at each end. However, in step-growth polymerization systems where a significant number of cyclic oligomers or polymer molecules are created—those that lack

functional end groups. *Equations 10, 11, 14, 15 and 16* tend to overestimate the actual average chain lengths. The likelihood of forming cyclic oligomers, whether in AB or AA + BB systems, depends on factors like the size and shape of the monomer molecules, as well as the thermodynamic stability of the different cyclic molecules that can form [96].

3.3.1.3 Non-linear step-growth polymerization

When monomers with more than two reactive end groups (like trifunctional or tetrafunctional monomers) are involved, step-growth polymerizations lead to the formation of non-linear polymer structures, such as hyperbranched polymers, dendrimers, and crosslinked polymers, as shown in Figure 24. Dendrimers, characterized by highly organized branching patterns with a precise geometric structure, are usually synthesized through multiple synthetic steps. Each step requires purification, leading to low overall yields. The process of dendrimer growth starts from a core, expanding radially outward through stepwise addition of monomers. For instance, the dendrimer depicted in Figure 24 originates from a tetrafunctional molecule, B4, with subsequent additions of AB2 forming trifunctional branching points. One downside is that the secondary forces within dendrimers are weaker than in linear polymers because the molecules can't pack tightly together. As a result, no chain entanglement occurs, and this limits their strength for use in fibers and plastics. However, dendrimers show high solubility and good miscibility with other substances, making them useful as viscosity modifiers [101].

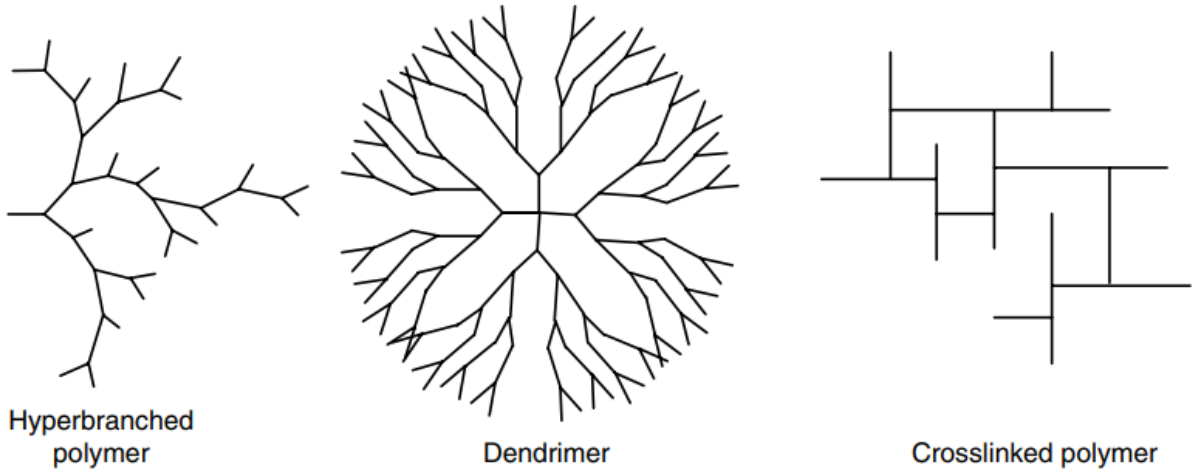


Figure 24. Different Branched polymer structures that could be produced using step-growth polymerizations.

In contrast, hyperbranched polymers, which have less organized structures than dendrimers, can be synthesized in just one step using multifunctional monomers of the type ABn (where n ≥ 2), or by mixing linear and multifunctional monomers (like AA and B_3). The irregular branching of hyperbranched polymers prevents crystallization, which makes them valuable as functional modifiers in crosslinked polymers, as well as components in adhesives and coatings. Examples include polyphenylenes, polyesters, polycarbonates, polyureas, polyurethanes, and polyethers. There are excellent reviews available in the literature on both hyperbranched polymers and dendrimers. [102,103] When hyperbranched polymers are created using AB_n monomers, most of the functional end-groups are type B, making it difficult for large molecules to combine and form larger crosslinked gel-like structures. However, adding AA monomer into an AB_n mixture (or co-polymerizing AA with Bn) can lead to crosslinking and gelation. The crosslinked structure seen in Figure 24 could be produced in various ways, such as by using linear molecules (e.g., AB or a combination of AA and BB) along with trifunctional crosslinkers (e.g., AB_2, A_3, or B_3). Tetrafunctional branching (which forms an X structure at the branch point instead of a T) can be achieved by using tetrafunctional molecules like B_4. Increasing the mole fraction of multifunctional monomers will boost crosslink density.

3.3.1.4 Impact of functionality on molecular weight growth

In sections 3.3.1.1., relationships were built between conversion and molecular weight, assuming each monomer has two functional groups. This section expands on those results to include branched polymer chains formed with monomers that have more than two functional groups. In such cases, the average functionality $\boldsymbol{f_{av}^*}$ is defined for a stoichiometrically balanced system, where the average number of functional groups per monomer molecule varies. Multifunctional monomers can feature either a single group type (e.g., A_3) or multiple types (e.g., AB_2). *(Equation 17)*

$$f_{av}^* = \frac{\sum n_i f_i^*}{\sum n_i}$$

Where f_i^* represents the functionality of monomer species *i* within the reacting mixture. If n_0 is the initial number of molecules and *n* is the total number of molecules at time *t*, then the initial number of functional groups is given by $n_0 f_{av}^*$. The fractional conversion of these functional groups is: *(Equation 18)*

$$p = \frac{2(n_0 - n)}{n_0 f_{av}^*} = \frac{2}{f_{av}^*}\left(1 - \frac{n}{n_0}\right)$$

Therefore, *(Equation 19)*

$$DP_n = \frac{n_0}{n} = \frac{2}{2 - p f_{av}^*}$$

If the average functionality is 2.0 (for example, using only AB monomer), *Equation 19* simplifies to *Equation 10,* $DP_n = 1/(1-p)$. In non-stoichiometric mixtures where $N_A < N_B$, reactions cease once all A groups are consumed, making it easier to consider the conversion of the limiting functional group rather than the total conversion. Here, the effective average functionality f_{av}^* equals the total number of functional groups available for reaction (twice the number of deficient A groups) divided by the initial number of molecules containing A or B groups. Using this definition, the fractional conversion of A is described by *Equation 18*, and the number-average chain length is given by *Equation 19,* also known as the Carothers equation (named after W.H. Carothers [107]). Keep in mind that DP_n refers to the number-average chain length for the entire mixture, including any unreacted monomers. Additionally, the derivation of *Equation 19* assumes that each step-growth reaction involves combining two molecules into one larger molecule, with cyclization reactions being neglected. Analyzing the denominator in *Equation 19* reveals that DP_n approaches infinity as *p* approaches $2/f_{av}^*$ Therefore, when $2 \geq f_{av}^*$ and the conversion of the limiting groups is sufficiently high, the number-average chain length can become infinite, leading to polymer gelation. Gelation refers to the formation of large molecules that are insoluble in the polymer solution or melt. Predicting the onset of gelation is crucial, as large gel molecules can create imperfections in polymer products and cause significant fouling in polymerization equipment. It's important to note that the presence of only a few extremely large molecules does not make the number-average chain length infinite. Gel formation and the associated issues begin at conversions below $2/f_{av}^*$ [96].

3.3.4. Molecular weight determination: Gel permeation chromatography

Size-Exclusion Chromatography (SEC), commonly known as Gel Permeation Chromatography (GPC), is a separation technique that operates based on the hydrodynamic volume or size of molecules. This method is entropically controlled, meaning that the separation process is influenced by the entropy associated with molecular configurations in solution. In SEC, molecules pass through a column filled with porous materials; larger molecules are excluded from entering the pores, while smaller molecules can permeate the pore structure. As a result, larger molecules elute first, followed by smaller ones, allowing for effective separation based on size (Figure 25) [108].

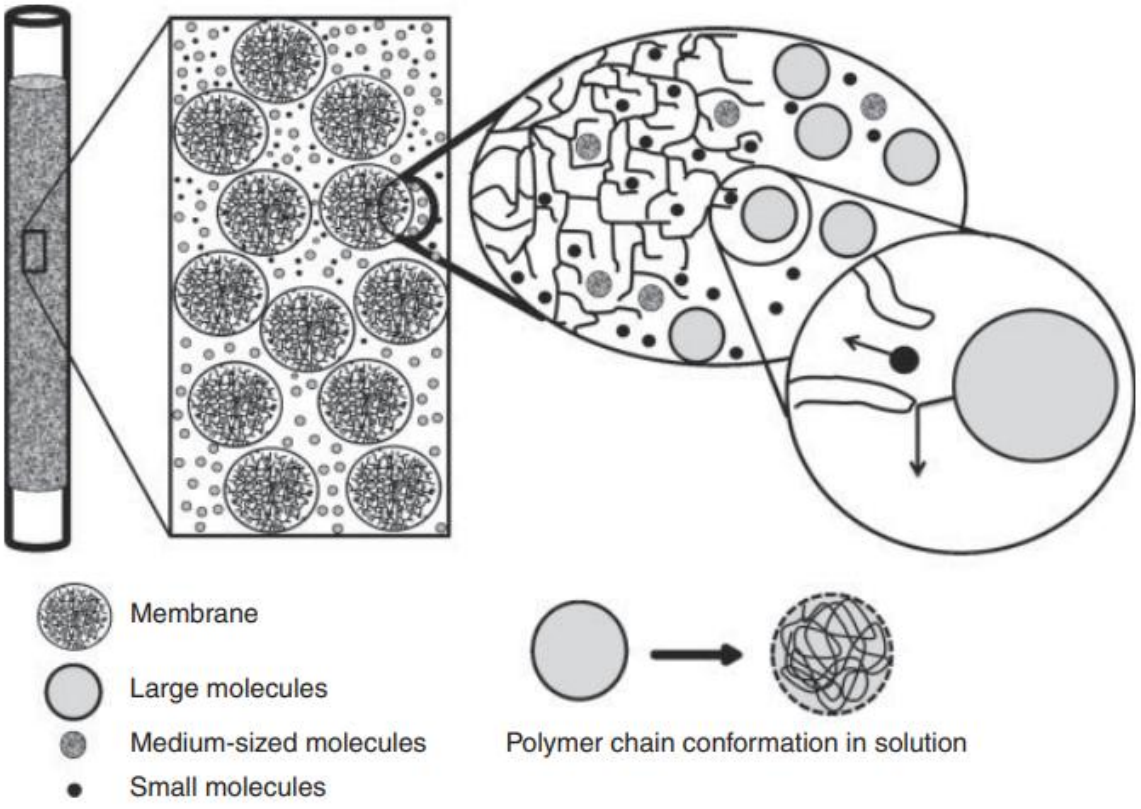


Figure 25. Chromatographic separation by size

One key characteristic that differentiates synthetic polymers from simple molecules is that it's impossible to assign an exact molar mass to a polymer. This is because, during polymerization, the chain length varies based on random factors. In condensation polymerization, the chain

growth depends on the availability of compatible reactive groups, while in addition reactions, it depends on the lifespan of the chain carrier. As a result, polymerization leads to a mix of chains with varying lengths, creating a chain length distribution that often follows statistical patterns. Rather than a single molar mass, polymers are better described by a distribution of molar masses and their averages. These distributions, which can be represented by various averages (as shown in Figure 26), reflect the nature of the sample. Since different measurement techniques apply unique averaging methods, using multiple techniques can provide a fuller characterization of the sample. Colligative methods, like osmotic pressure measurements, are examples of such approaches that yield complementary molar mass data.

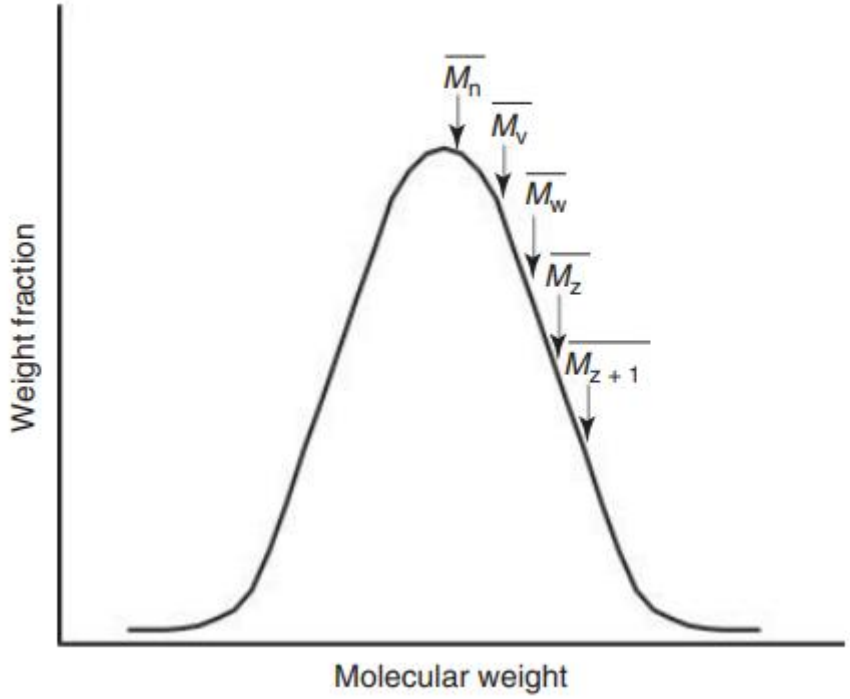


Figure 26. Different average of molecular weight distributions.

The M_n is defined as: *(Equation 20)*

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} = \frac{\sum w_i}{\sum (w_i/M_i)}$$

Here, N_i represents the number of molecules of species i with a molar mass M_i. An alternative form for expressing this uses the mass $w_i = N_i M_i/N_A$, where N_A is Avogadro's constant. A weight-average molar mass M_W is instead defined as: *(Equation 21)*

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum w_i M_i}{\sum w_i}$$

Statistically, $\bar{M}_n$ represents the first moment of the number distribution, while $\bar{M}_w$ is defined as the ratio of the second to the first moment. A higher level of averaging, called the z-average, is then calculated by: *(Equation 22)*

$$\bar{M}_z = \frac{\sum N_i M_i^3}{\sum N_i M_i} = \frac{\sum w_i M_i^2}{\sum w_i}$$

This calculation results in an even higher average known as the *(z+1)* average molar mass, which is often essential for accurately describing certain mechanical properties of polymers. Another important aspect to take into account is the polydispersity index, commonly referred to as PDI. The PDI serves as an indicator of the distribution of molecular weights of polymer chains within a specific polymer sample. For a monodisperse polymer, or a uniform polymer, the PDI value is close to 1. *(Equation 23)*

$$PDI = \frac{\bar{M}_w}{\bar{M}_n}$$

In addition polymerization, the polydispersity index (PDI) typically ranges from about 1.5 to 2.0, reflecting a moderate distribution of molecular weights. This range can vary based on specific polymerization conditions and the type of monomers used. In the case of step-growth polymerizations, the PDI usually averages around 2 [96].

3.4 Synthetic Polymers: innovation or pollution?

Polymeric materials, known widely as plastics, bring significant advantages across diverse applications due to their versatility, corrosion resistance, and adaptability. By incorporating

composites or additives, these materials can be tailored to meet specific needs. Contrary to common perceptions, plastics are resource-efficient throughout their lifecycle. For instance, polymer insulation conserves 250 times the energy required for its production, while plastic components in vehicles reduce environmental impact, and plastic packaging prolongs food shelf life, lowering spoilage rates and reducing waste. [109-112] However, the environmental costs of global plastic production are substantial, requiring considerable energy and creating extensive waste, greenhouse gases, and microplastics that pollute air, soil, and water. Around 25 million tons of plastic accumulate annually, with degradation rates so slow that it may take 100–500 years to break down. To address these impacts, the development of biodegradable biopolymers aims to offer similar utility with a reduced environmental footprint. Yet, renewable sourcing alone doesn't guarantee sustainability. To fully assess the environmental impact, Life Cycle Assessment (LCA) is essential, especially as we explore bio-based monomers and solvents to reduce reliance on petrochemical resources in specific fields, such as wire enamels. [113] In the experimental section, there will be a study where the LCA was calculated by some of ELANTAS Europe's internal R&D team, aiming for the highest possible accuracy. They considered every stage of the product's production, beginning with raw material sourcing, then through the transport system, and up to the company gate, where the product exits as varnishes. This approach, known as "cradle to gate," provides a clear endpoint for the assessment. It's also essential to note that LCA is one of the few reliable tools we have to gauge whether a product has a higher or lower environmental impact, and the findings can sometimes be quite surprising.

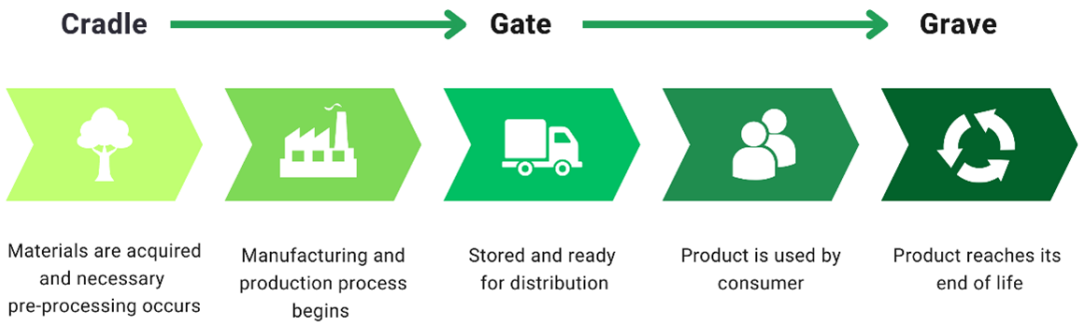


Figure.27 Product life cycle.

3.5 Bio-based raw materials

Biorefineries, in many ways, operate much like traditional oil refineries. The main difference is that they're designed to transform renewable bio-based feedstocks into valuable chemicals, moving away from fossil resources. [114-117] Biomass, our renewable resource here, regenerates relatively quickly and generally falls into two main categories: first-generation and second-generation feedstocks. First-generation feedstocks are made up of easily fermentable sugars from edible sources like corn, sugarcane, and vegetable oils. Although some studies suggest that it is possible to sustainably co-produce biomass for food, fuel, and other bio-based materials[118-119], first-generation biomass remains ethically controversial due to potential competition with food resources, particularly in local and vulnerable communities.[120] Currently, around 0.02% of global agricultural land use is allocated to the production of bioplastic precursors. [121] However, a complete transition from fossil resources to biomass for plastic production is unlikely, underscoring the need for reduced consumption and more efficient recycling processes. A full replacement of the annual 170 million tonnes of global packaging plastics with bioplastics alone could require up to 54% of current corn production and would demand 60% more freshwater than Europe's annual consumption.[122] Second-generation biomass consists of various non-edible biowastes, which offer a more ethically acceptable and readily available, even though more complex, alternative. [123]

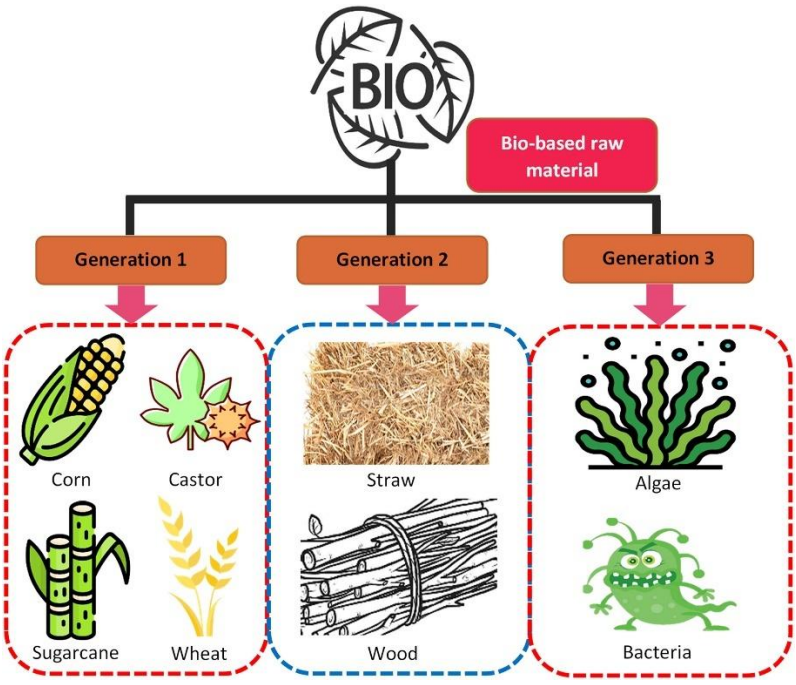


Figure 28. Different sources of bio based raw materials

Each year, more than a billion tonnes of agricultural and food waste pile up globally, with around 20% of household waste consisting of food scraps. [124-126] In light of this, biorefinery research is now exploring ways to convert lignocellulosic biomass—waste from crops like wheat straw and sugarcane bagasse—into fermentable sugars. This approach not only offers a use for otherwise discarded materials but also taps into a sustainable source for bio-based production. These agricultural byproducts are usually cost-effective but require extra pretreatment to release cellulose and hemicellulose sugars from the crosslinked, phenolic lignin polymer network. [127-130] Seaweed, particularly brown and red algae, presents another promising source of polysaccharides. Alginates, found in brown algae and comprising up to 40% of their dry weight, can gel with divalent or trivalent cations and blend well with starches, producing biodegradable films with desirable gas permeability and mechanical properties. [131,132] Vegetable and plant oils offer pathways to various monomers essential for bio-based plastics. However, using edible oils raises concerns about competition with food supplies and deforestation. [133,134] In contrast, non-edible or waste oils are more sustainable options [131]. Vegetable oils contain triglycerides with unsaturated fatty acids that can be epoxidized to produce epoxy resins. [135,136] Additionally, polyols found in certain fruits and vegetables are used in creating bio-based polyurethanes (bioPUs). Another bio-based option includes terpenes, isoprene-containing compounds sourced from plant oils; polyisoprene, for instance, is produced on a multimillion-tonne scale and widely used as natural rubber. Limonene, a terpene from lemon peel, can be processed to create bisphenol A-free bio-based polycarbonates (bioPCs) by reacting limonene epoxide with CO_2 [137,138]. CO_2 itself, abundant yet low in energy potential, is also emerging as a direct feedstock for polymer synthesis, thanks to advanced catalytic methods. [139,140] This approach effectively sequesters CO_2 from the atmosphere within polymers, keeping it stored until its release through incineration or composting. High-CO_2 emissions sources like NH_3 factories and coal-fired power plants, with concentrations around 97% and 15% respectively, provide a viable CO_2 supply for the production of polyurethanes, polycarbonates, and other valuable chemicals. [141-144] While crude oil remains the principal source for most traditional, durable polymers, it also continues to support certain biodegradable polymers. Due to the environmental impacts associated with extracting and incinerating fossil resources, crude oil is generally considered a non-sustainable feedstock. Each bioplastic feedstock type poses distinct challenges, and improving the conversion efficiency of renewable resources into functional chemicals in biorefineries is essential. Advances include enhanced pretreatment techniques and more resilient microorganisms for fermentation, which could drive more efficient bioprocessing. [119,145,146]

PARTI II

EXPERIMENTAL SECTION

4.1 Project Overview for Wire Enamels

This section will discuss three studies. The first study focuses on developing a modified polyester-based enamel for magnet wire, in which conventional materials are partially replaced with bio-based materials (including both reagents and solvents). The aim is to achieve approximately 25-30% substitution while maintaining standard thermo-electrical and mechanical properties. This study will be exploited in chapter 5.

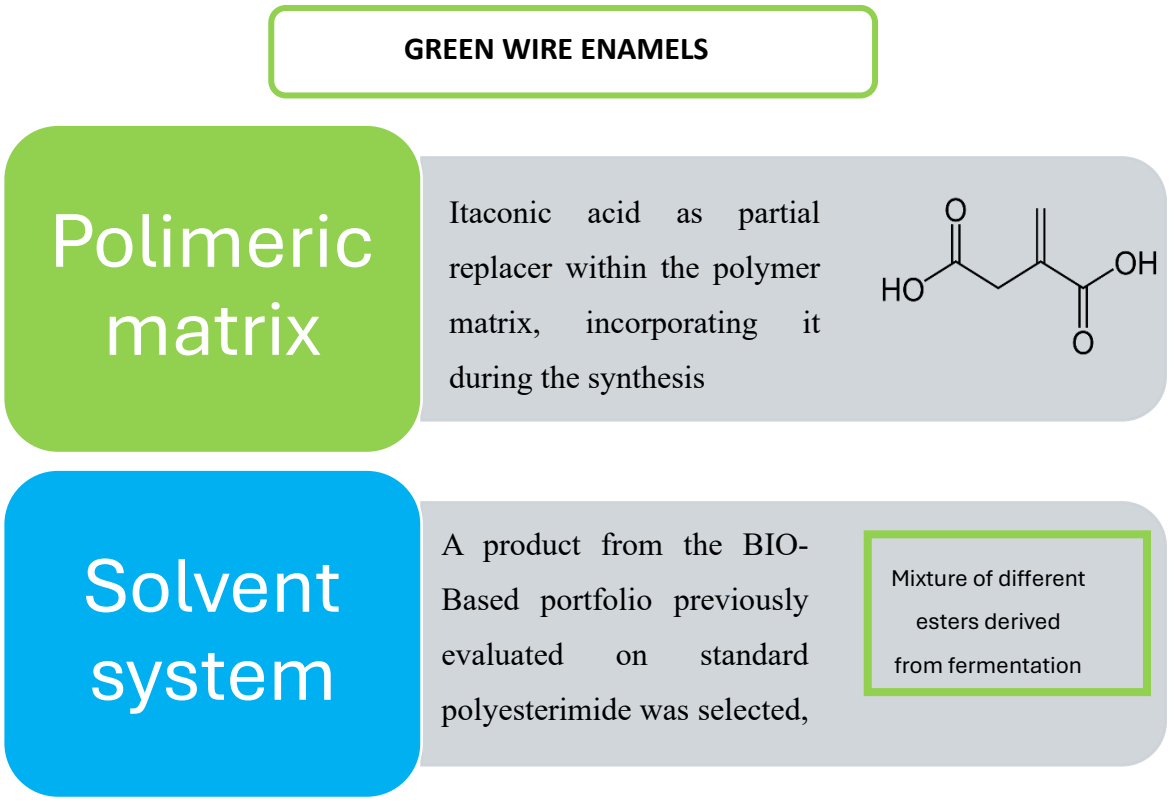


Figure 29. Green Wire enamels work overview

During the synthesis GPC and ATR-IR analysis were performed, then, all batches were applied and cured on copper wires by the Company's operators, following an internal standardized enameling procedure. After that, thermo-electrical and mechanical tests (Chapter 2) were done to assure that the new product was comparable to the standard PEI already present in the market.

The second study is about the replacing of Cresylic Acids, more specifically a mixture of isomers of cresols, xylenols, ethyl phenols and alkylated phenols like guaiacol, anisol, trimethylphenols and similar molecules, and even more specifically a technical mixture of cresols isomers. The aim of the project is to replace the cresylic acids present in the formulation maintaining the thermo-electrical and mechanical performance of the obtained material, as well as its dry content and its viscosity in the same range of the standard reference material, in this case the enamel "TEREBEC MT533-39 TP" (Polyester-imide). In this study several solvents were selected as candidates and many factors were taken in consideration. This work will be addressed to chapter 6.

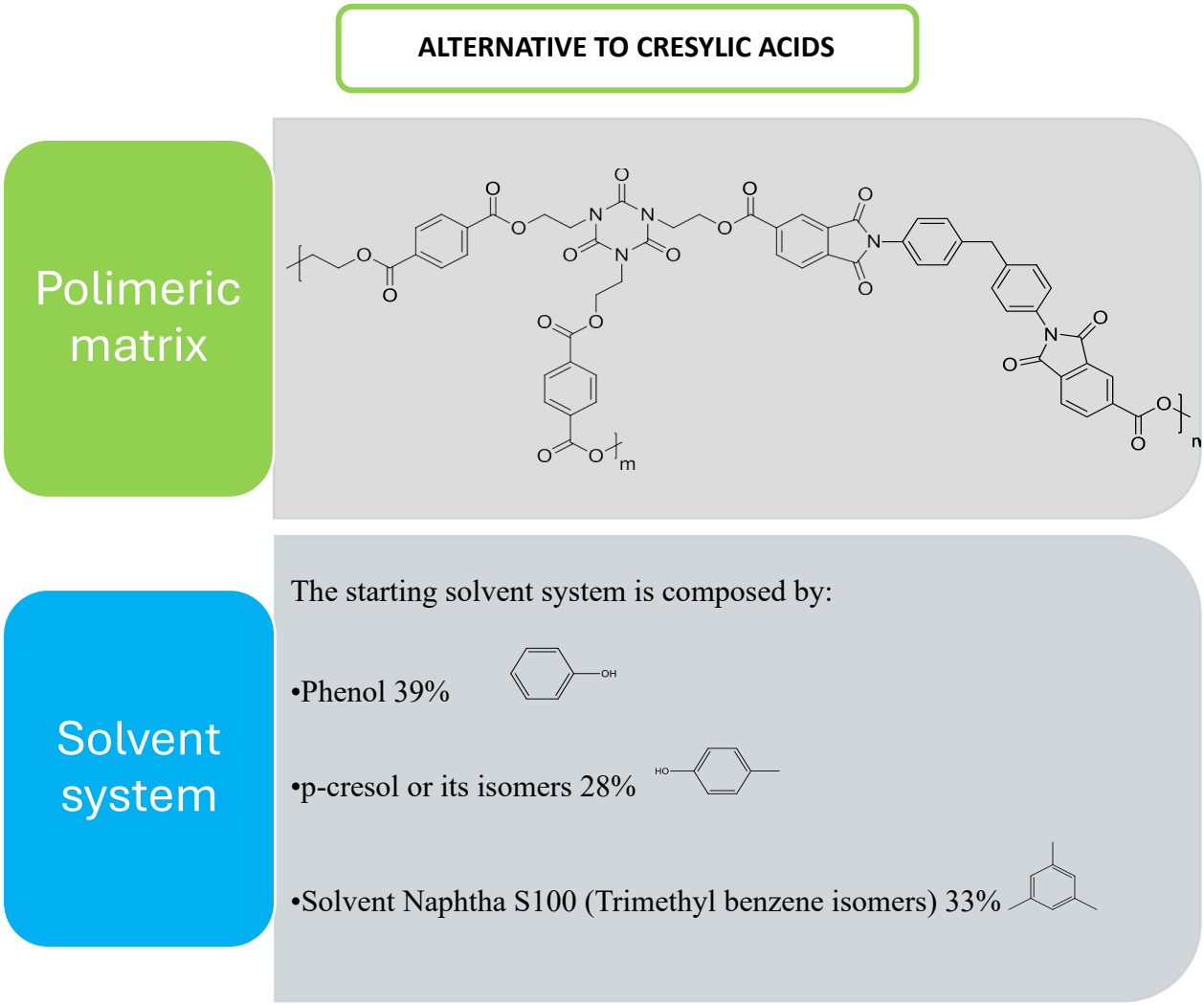


Figure 30. Alternative to cresol work overview.

GPC analyses were performed, then, all batches were applied and cured on copper wires by the company's operators, following an internal standardized enameling procedure. After that,

thermo-electrical and mechanical tests (Chapter 5.1) were done to assure that the new product was comparable to the standard PEI already present in the market.

In order to harmonize what is going to be done, it is necessary to show the main processes of a wire enamel production from the synthesis to the application, unfortunately is not possible to go deep in the detail of the processes for non-disclosures reasons.

However, we can summarize the main step in this graph:

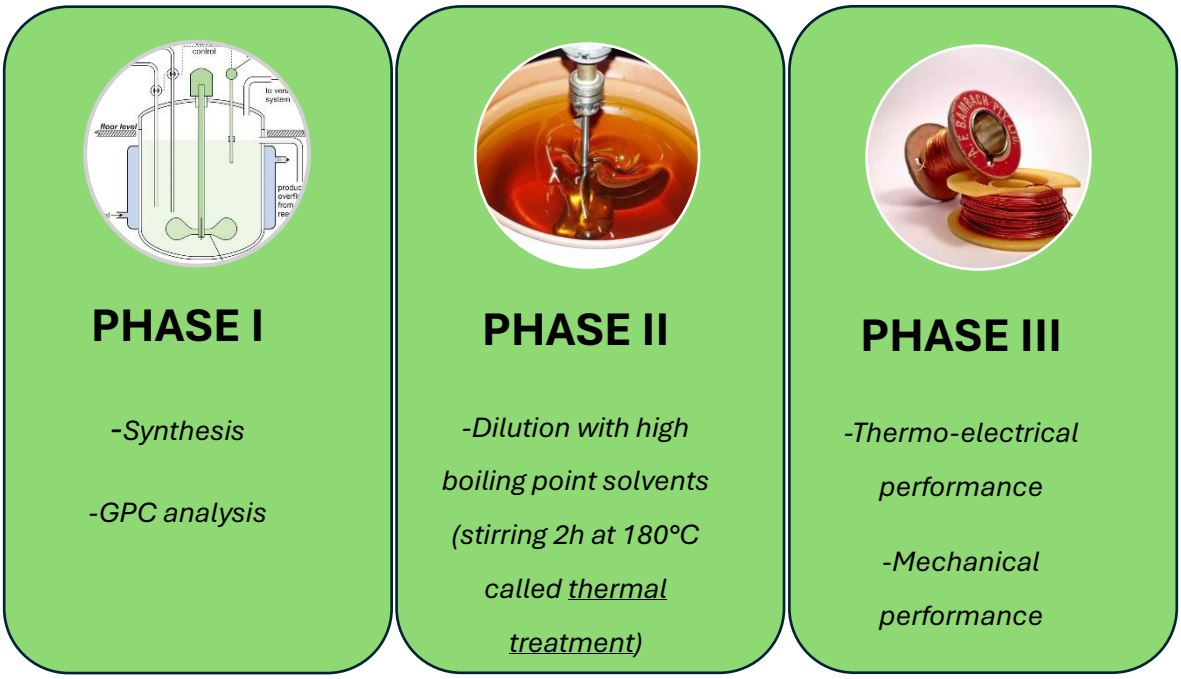


Figure 31. Main phases for wire enamel production

These three phases are representative for the two first works. The third work will be about the analytical chemistry of wire enamels, more specifically, a quantitative determination of a aromatic diamine residue that, depending on its quantity the safety data sheet will change and so the limit of import/export of that product. Finally in chapter 7 will be exploited the third work, since it is a different technology with a specific application, there will be a brief introduction on conformal coating and then the development of a Polyurethane acrylate (PUA).

4.2. Materials

All reagents and solvents were purchased from commercial suppliers and used as received, without additional purification unless specified otherwise. The quality of the compounds used was verified by the internal Quality Control (QC) laboratory. Depending on the enameling oven used, there will be a bigger or a smaller batch of synthesis. For the horizontal enamelling machine (called "oven" from now on), where the magnet wire has a diameter of 0,5mm, all syntheses were performed in a 2-liter round-bottom glass vessel fitted with a five-necked glass head and a mechanical stirrer, with heating provided by a mantle. A laboratory vacuum pump and distillation apparatus were utilized as specified in the procedures.

When the enameling step have been conducted in the vertical oven, where the magnet wire has a diameter of 1 mm and more liquid enamel vs smaller diameter is required during the enamelling process, all syntheses were performed in a 6-liter round-bottom glass vessel fitted with a five-necked glass head and a mechanical stirrer, with heating provided by a mantle. A laboratory vacuum pump and distillation apparatus were utilized as specified in the procedures.

4.3 Instruments and Methods

4.3.1. Gel Permeation Chromatography

GPC analyses were conducted on a *Thermo Knauer* instrument, assembled with a Smartline 1000 pump and a Smartline 2300 differential refractometric detector. The column setup included three columns in series: Agilent™ PLgel 10^4Å, 7.5 x 300 mm, 10^3Å, 7.5 x 300 mm and 500Å, 7.5 x 300 mm all with particle sizes of 5 μm. The eluent was a 70:30 solution of THF and DMF. Both the eluent and column compartment were maintained at 33°C. Prior to analysis, resin samples were dissolved in the appropriate eluent solution at a solid concentration between 30 and 50 mg/mL depending on the dry content of the sample. Samples were filtered through a 0.45 μm PTFE syringe filter from Agilent™ before injecting 100 μL of each filtered sample into the instrument loop.

4.3.2 Infrared Spectroscopy

Infrared spectroscopy was performed using *a Thermo Scientific Nicolet iZ10*, equipped with a Smart Omni-transmission accessory with KBr support and a diamond crystal ATR module.

Spectra were recorded over a wavenumber range from 450 to 4000 cm^{-1}, with an accumulation of 16 repeated scans for both background and sample analyses. Spectral data were processed and absorption band wavenumbers were calculated using *Thermo Scientific™ OMNIC™ Series FT-IR* software.

4.3.3. Viscosity Determination

Viscosity measurements were performed using a Haake VT550 viscometer at a constant shear rate at 23°C. All samples were measured without dilution, and viscosity values were reported in mPas (millipascal per second).

4.3.4. Solid Content Determination

Solid content determination was carried out by placing 1 gram of sample on a metal disk of 5.1 cm and heating it at 180°C for 1 hour. The solid content (R.S.%) was calculated using the formula:

$$R.S.\% = \frac{W_2}{W_1} * 100$$

Where W_1 is the initial sample weight and W_2 is the weight after heating.

4.3.5 HSPiP Software

Hansen solubility parameters were calculated using the HSPiP software.

4.3.6 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

The GC-MS analysis was performed using a Perkin Elmer Clarus 680 Gas Chromatograph (GC) equipped with an Elite-5MS capillary column (30 m x 0.25 mm i.d., film thickness 0.25 µm). Helium (He) was used as the carrier gas at a constant flow rate. The GC was coupled to a Perkin Elmer Clarus SQ8S mass spectrometer (MS), operated in electron ionization (EI) mode.

The following parameters were used for the GC analysis:

- Injection volume: 0.2 µL

- Temperature program:
    - Initial temperature of 45°C, held for 2.5 minutes
    - Ramp 1: 10°C/min to 225°C, hold for 11.5 minutes
- Total run time: 40 minutes

For the MS analysis, the parameters were set as follows:

- Ion source: Electron ionization (EI+), source temperature 200°C
- GC line temperature: 200°C
- Electron energy: 70 eV
- Ion energy: 1.5 V

4.3.7. Determination of the biobased carbon percentage

The samples were dated using the radiocarbon method (ASTM 6866-18) via Accelerator Mass Spectrometry (AMS) at the Center for Dating and Diagnostics (CEDAD) of the University of Salento. The extracted material was converted into carbon dioxide through combustion at 900°C in an oxidizing environment and subsequently reduced to graphite. Hydrogen (H_2) was employed as the reducing agent, with iron powder serving as the catalyst. Radiocarbon concentration was measured by comparing the currents of ^{12}C and ^{13}C, as well as ^{14}C counts, to reference values obtained from sucrose C_6 standards supplied by the IAEA. Conventional radiocarbon dating results were corrected for isotopic fractionation effects by directly measuring the $\delta^{13}C$ term using the accelerator and accounting for measurement background levels. Quality control of the results was ensured using reference samples with known concentrations of oxalic acid provided by the National Institute of Standards and Technology (NIST). Finally, the radiocarbon content was converted into the biogenic fraction using a contemporary radiocarbon reference value of 101 pMC (percent Modern Carbon).

5.1. Green Wire Enamels

Elantas is more and more committed to sustainability aspects to pursue improvements in the environmental footprints, with a particular focus on CO_2 reduction and increased carbon-14 content. A partial replacement of fossil origin materials with bio-based materials is an important step to accomplish such targets.

- Objective: to set up a modified polyester or polyester-imides based resins enamel (for magnet wire) where reference materials are partially replaced by biomaterials (both monomers and solvents) to have about 25 - 30% replacement.

In order to have a reference a PEI already commercially available from ELANTAS Europe that will be depicted as **EP0**. In particular, itaconic acid was selected as a candidate in the replacement of components for the polymer matrix part. A full replacement of the fossil-based reagents is not possible due to the high performance requested to this product. Since the itaconic acid is a low price bio-based di-carboxylic acid with high chemical value it's been selected as candidate.

For the solvent system it's been replaced half of cresylic acid content with a commercial product that is a mixture of esters from organic acid generated from the fermentation of biomass, it is going to be named as **BIOSOLV1**. This product has been selected because of its solvency power (Table 4) and its boiling point (242-246°C). The solvency power (RED) has been calculated as written in chapter 3.2.1.1. selecting as solute the **EP0.**

Solvent	δ_d	δ_p	δ_h	RED
m-Cresol	*18,5*	*6,5*	*13,7*	-
BIOSOLV1	*19,4*	*16,5*	*5,1*	**0,725**

Table 4. Hansens solubility parameters for m-Cresol and BIOSOLV1

5.1.1. Synthesis and characterization: Green Wire Enamel

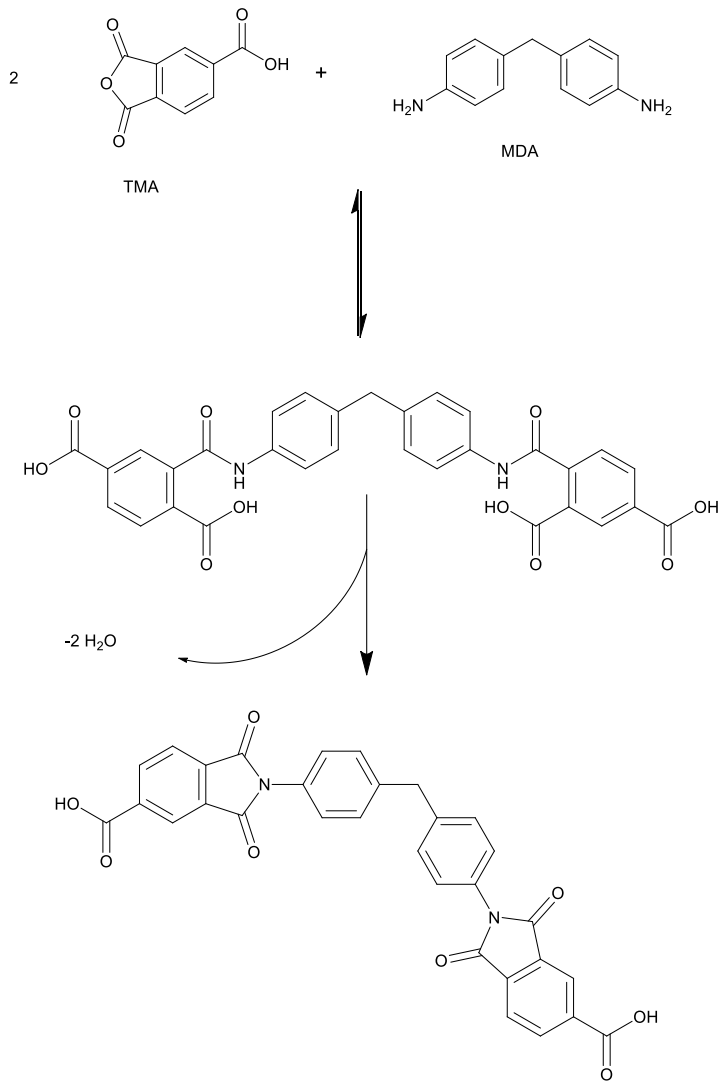
Polyester-imides were synthesized according to the multi-step process and the aza-Micheal variant process described in chapter 3.1.2. Itaconic acid was used to synthesize different batches of polyester-imide by replacing the total amount of terephthalic acid leaving the synthesis process unchanged. Every batch done was subjected to standardized internal tests since it is needed to reach specific values for the thermo electrical and mechanical properties. The molar ratio between reagents (diacids, diols and TMA) were changed from one batch to another to tailor the performances. The data on the molar ratios were re-elaborated to avoid disclosing the exact molar or equivalent ratios, given the commercial desirability of this product. Nevertheless, the data effectively represent trends, showing that as the molar amount of one component increases or decreases, the percentage of that specific reagent also changes accordingly. The equivalent ratio between components consistently remains close to 1:1 to achieve the highest possible conversion, as discussed in Chapter 3.3.1.1. A table where those values are reported is here below:

BATCH	*Mol PTA*	*Mol TMA*	*Mol Itaconic Acid*	*Mol THEIC*	*Mol Glycerin*
Ref. EP0	0,4	0,3	1,3	0,83	-
EP01	0,4	0,3	1,3	1 **(+20%)**▲	-
EP02	0,1 **(-75%)**▼	0,6 **(+50%)**▲	1,3	1	-
EP03	0,1	0,6	1,3	1,2 **(+20%)**▲	-
EP04	0,1	0,6	1,3	1,2	0,83 ▲
EP05	0	0,8	1,2 **(-7%)** ▼	1,2	-

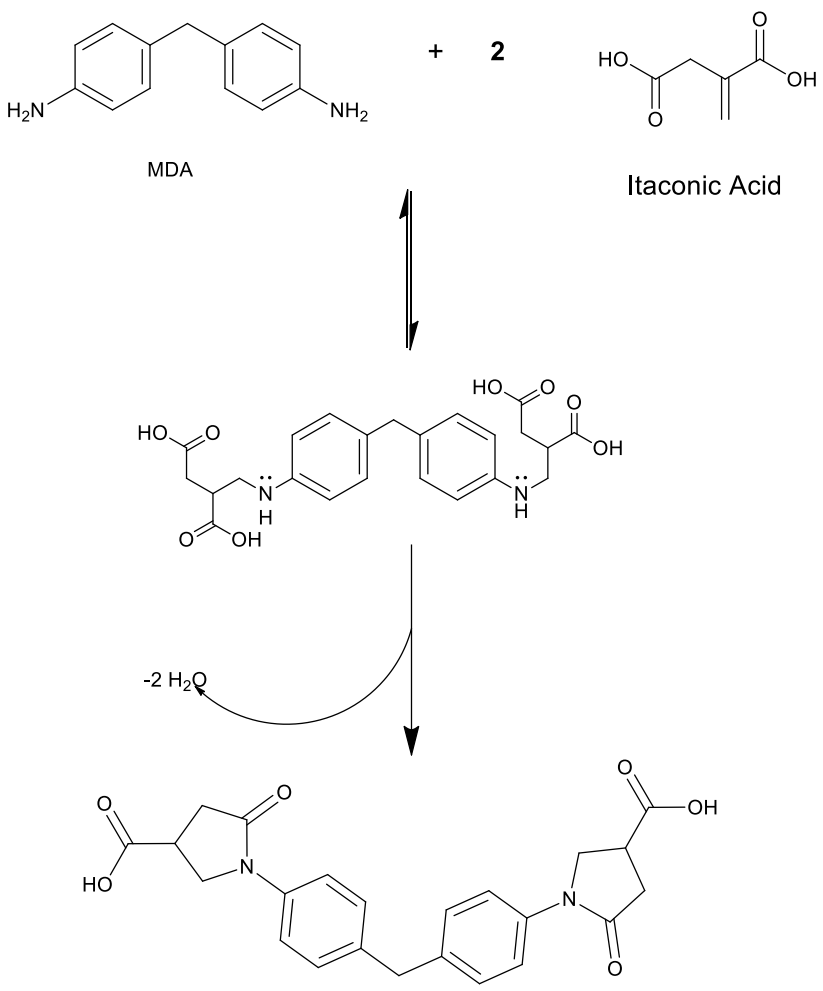
Table 5. Different molar contribution of reactants.

Polyester-imides (PEIs) were synthesized using the process described below. In a 2 L, five-necked round-bottom glass vessel equipped with a mechanical stirrer, thermocouple, Vigreux

column, and distillation apparatus, an excess of ethylene glycol was added. The reaction was conducted with excess ethylene glycol as the reaction medium, which was later removed during the transesterification step with the help of a vacuum pump. The glycol and the diamine and the temperature were setted to 90°C. Then the Itaconic acid and the TMA were added to the reation mixture, exothermy is observed up to 130°C most probably as a result of the formation of DIDA and DPDA (respectively Scheme 17 and Scheme 18). Then the Titanate butyl monomer and THEIC is added as catalyst and the reaction temperature was set to 150°C. Then the temperature is increased +10°C/h until 200-210 °C. Here follows different reaction scheme with an appropriate explanation of the main reactions that are occurring in the reaction bulk:

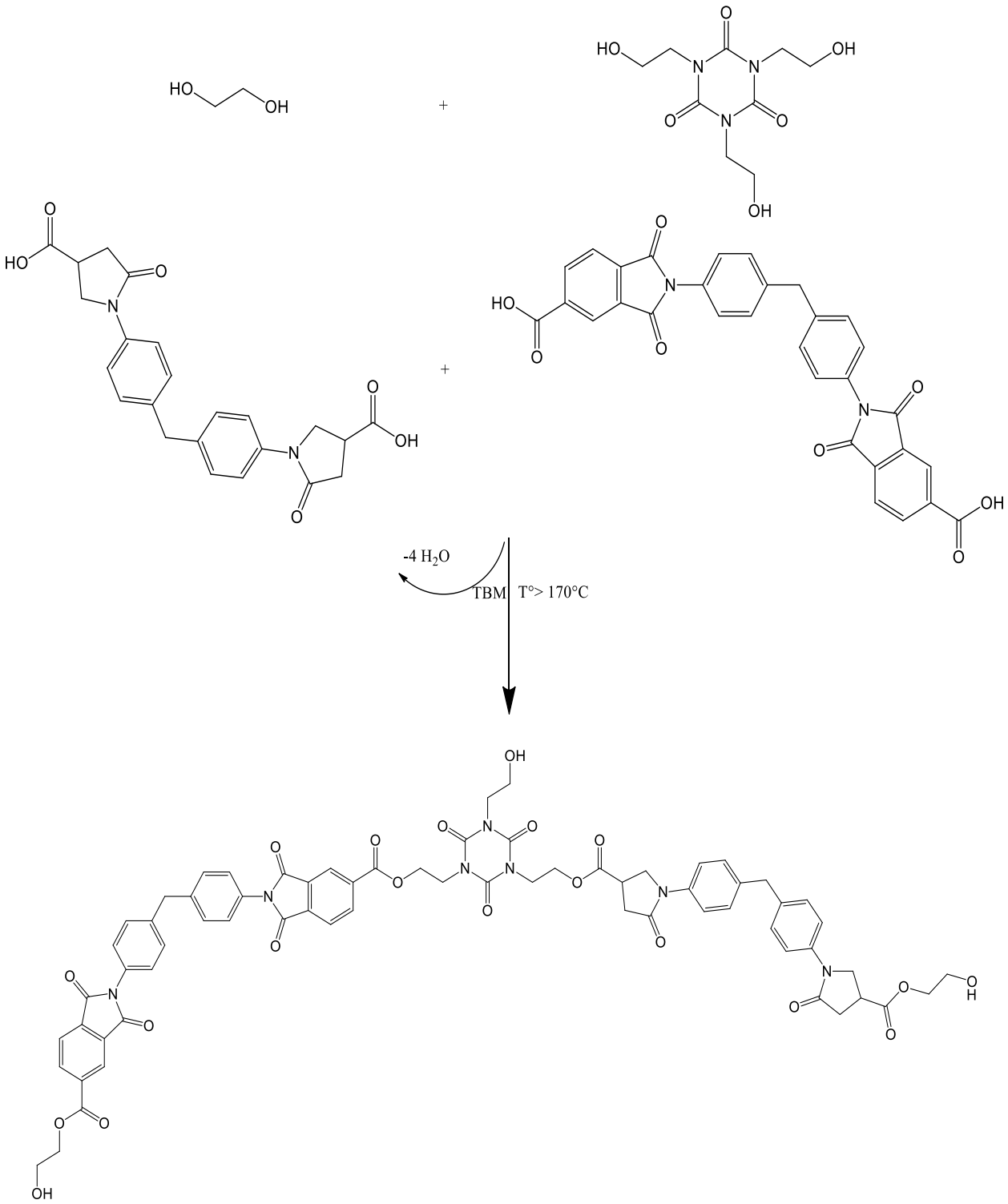


Scheme 17. DIDA reaction formation.



Scheme 18. DPDA reaction formation.

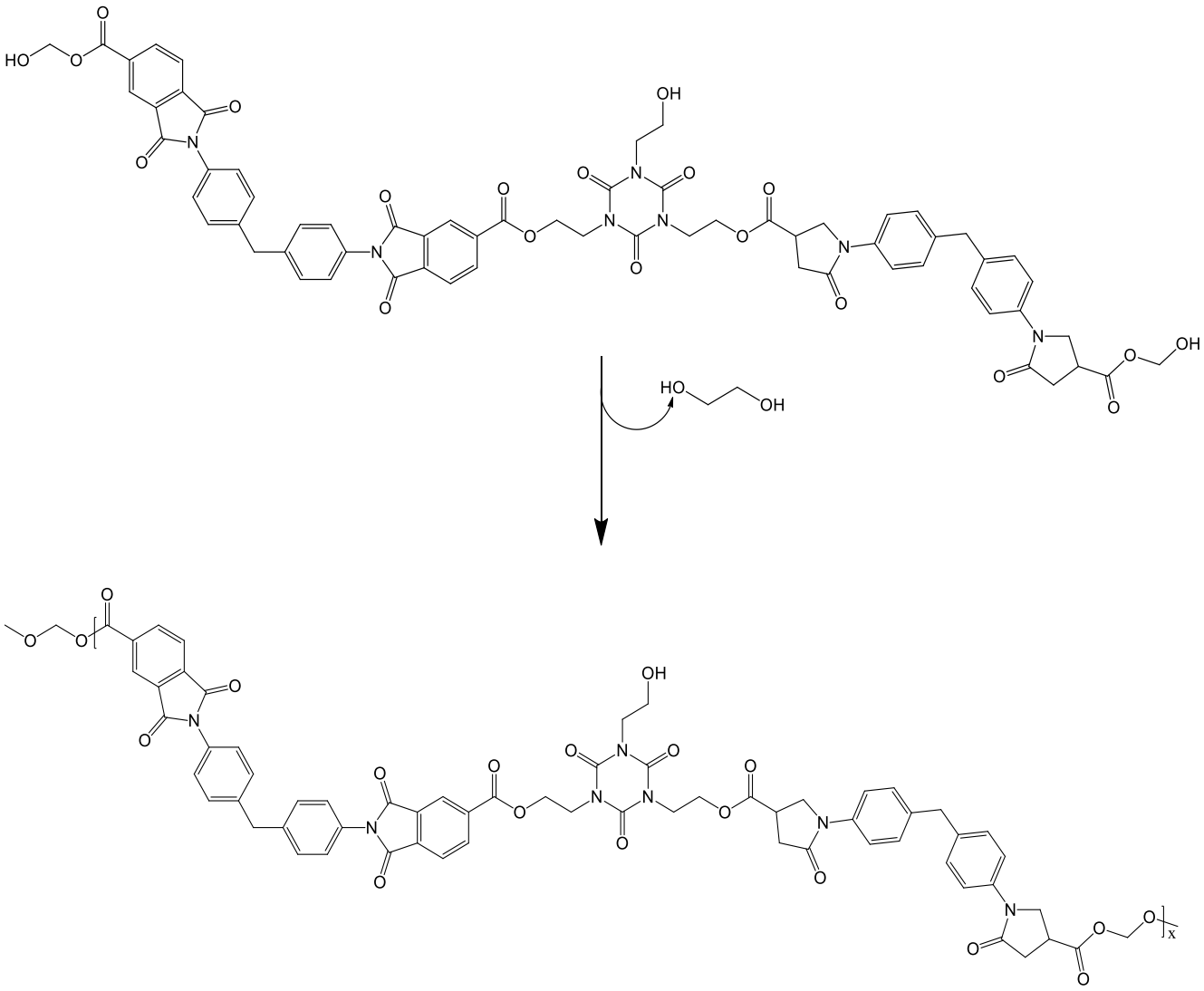
After these two reactions, ethylene glycol and THEIC react toward DIDA, DPDA, PTA and the acid group of TMA to form ester intermediates and oligomers, while water is distilled off (see Scheme 19).



Scheme 19. Esterification reactions.

Conditions were maintained until the temperature in the overhead column began to drop, indicating that all condensation water had been completely distilled off. When the overhead column temperature reached 75°C, the temperature of the reactor was set to 210°C, and the

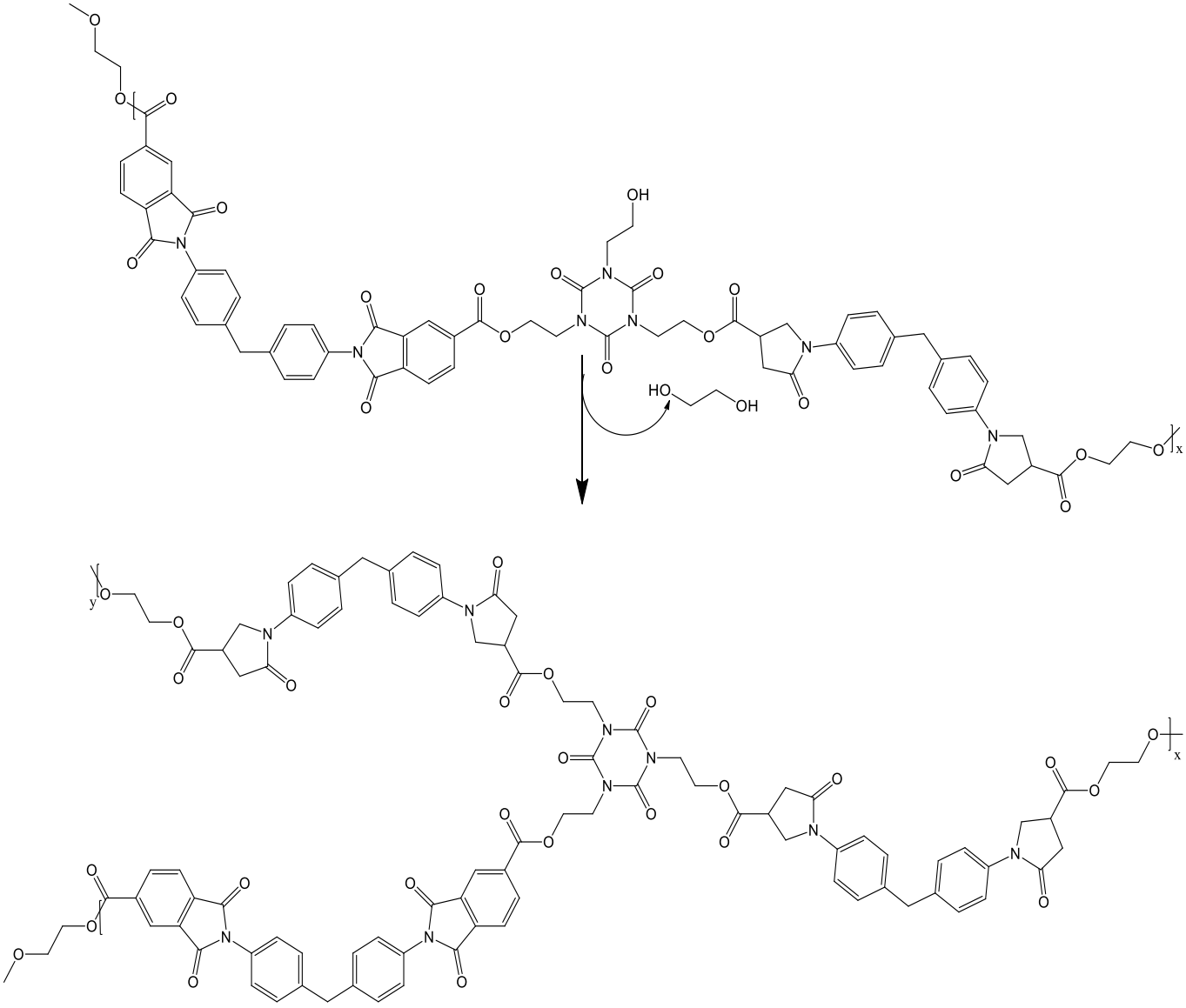
vacuum pump was connected and configured to operate at 400 mBar. These stable conditions facilitate the transesterification of ester oligomers by eliminating ethylene glycol, resulting in an increase in the molecular weight of the polyester-imide (see Scheme 20).



Scheme 20. Trans-esterification reaction.

At this stage, reactions were controlled via GPC, and the condensation step was completed when the polymer's molecular weight equaled or exceeded that of standard PEI (**EP0**). At this point, the vacuum pump and heater were turned off, and a cresylic mixture along with **BIOSOLV1** was added to adjust the viscosity and the dried residual content of the mass. The final products were characterized using GPC and IR spectroscopy. The resulting resins were then applied to copper wires, where additional inter-chain transesterifications (cross-links)

occurred in the enameling oven at around 500°C, producing cured PEI-enameled copper wires (see Scheme 21 for cross-linking during the curing step). Finally, the mechanical, thermal, and electrical properties were evaluated.



Scheme 21. Crosslink reaction.

Here below there are the GPC overlaps between batches: in each chromatogram, the red line represents the reference (EP0), while the black line corresponds to one of the EP samples from 1 to 5.

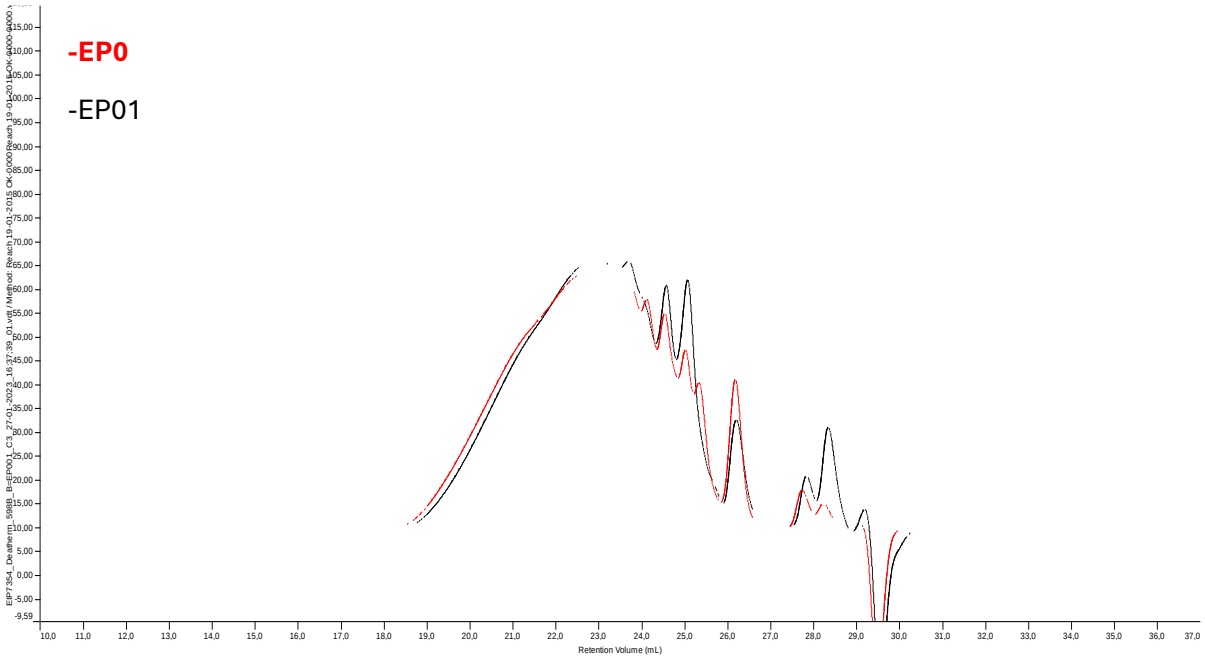


Figure 32. Overlaps of GPC chromatograms: In red EP0, reference in black EP01.

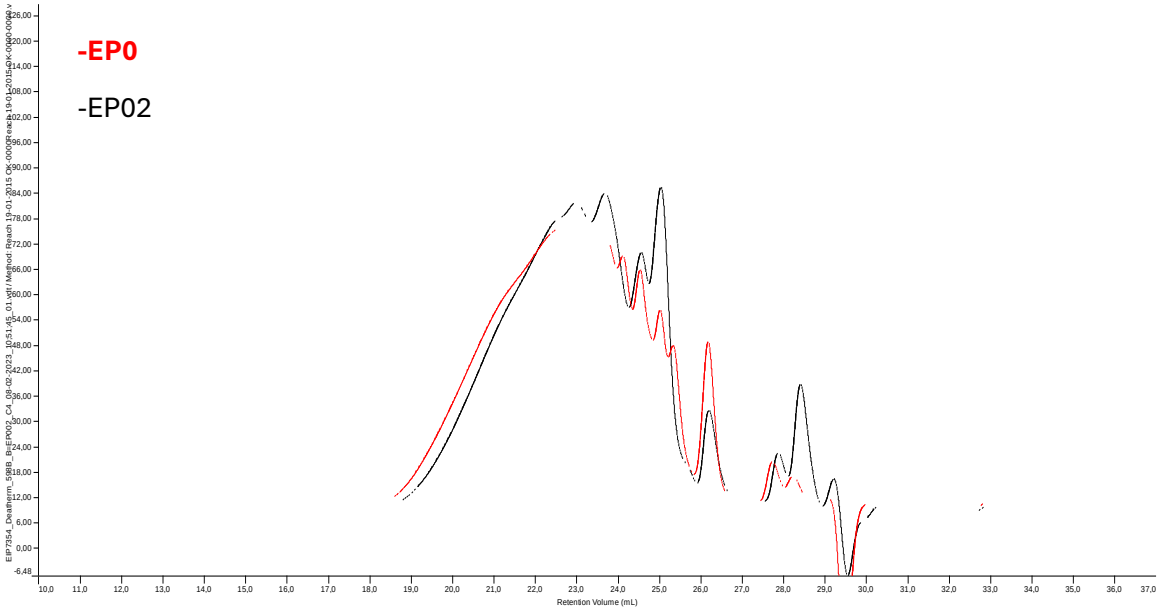


Figure 33. Overlaps of GPC chromatograms: In red EP0, reference in black EP02

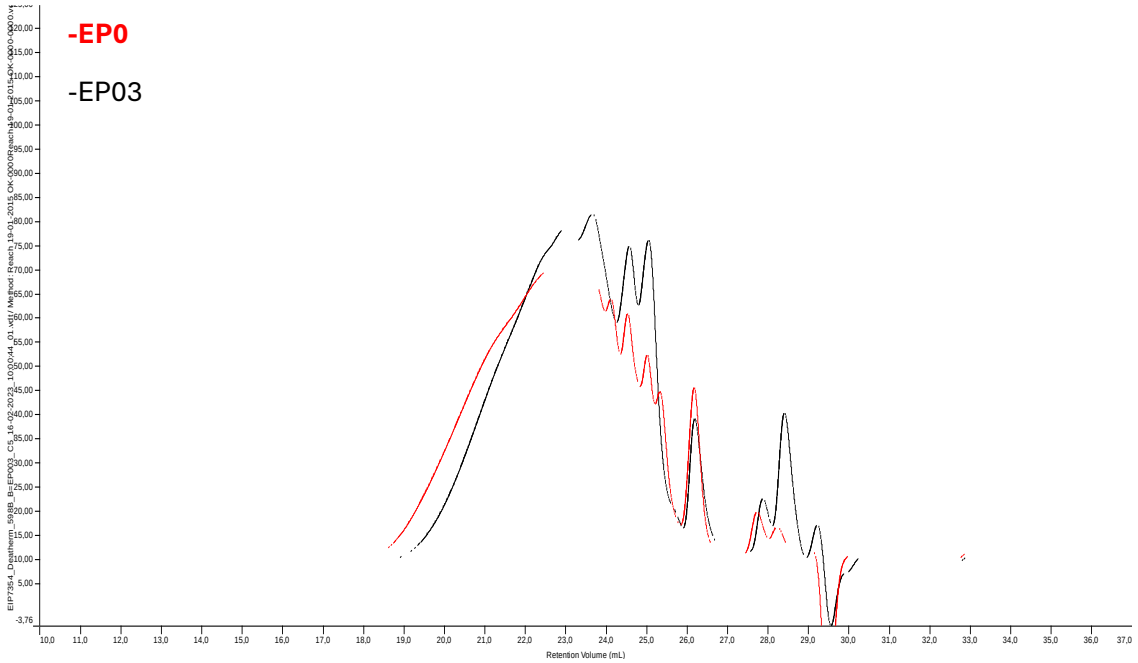


Figure 34. Overlaps of GPC chromatograms: In red EP0, reference in black EP03.

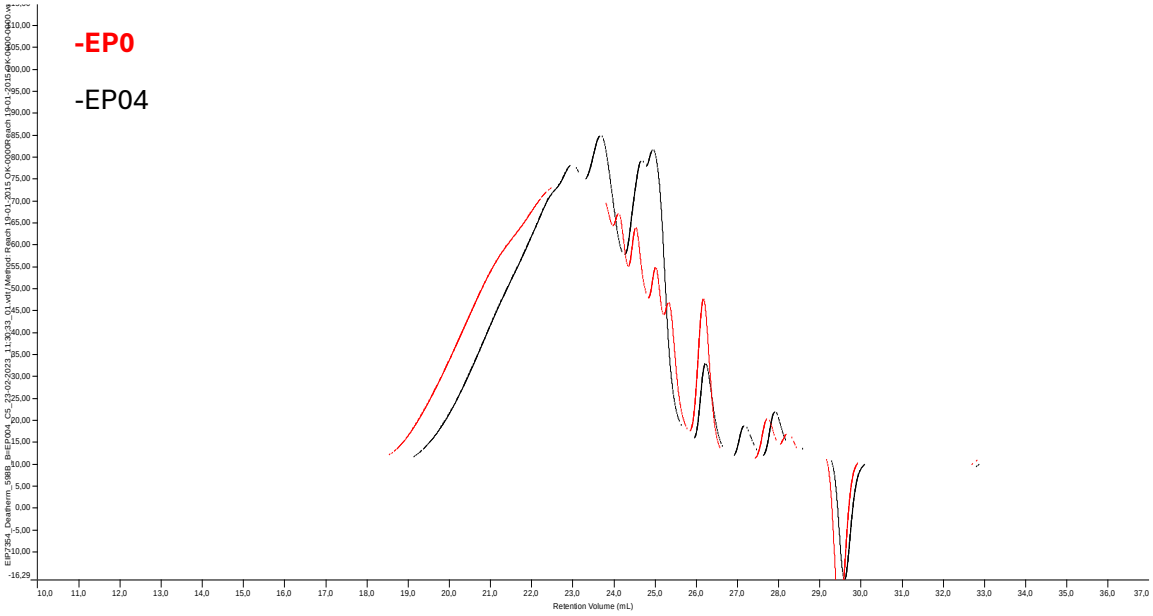


Figure 35. Overlaps of GPC chromatograms: In red EP0, reference in black EP04.

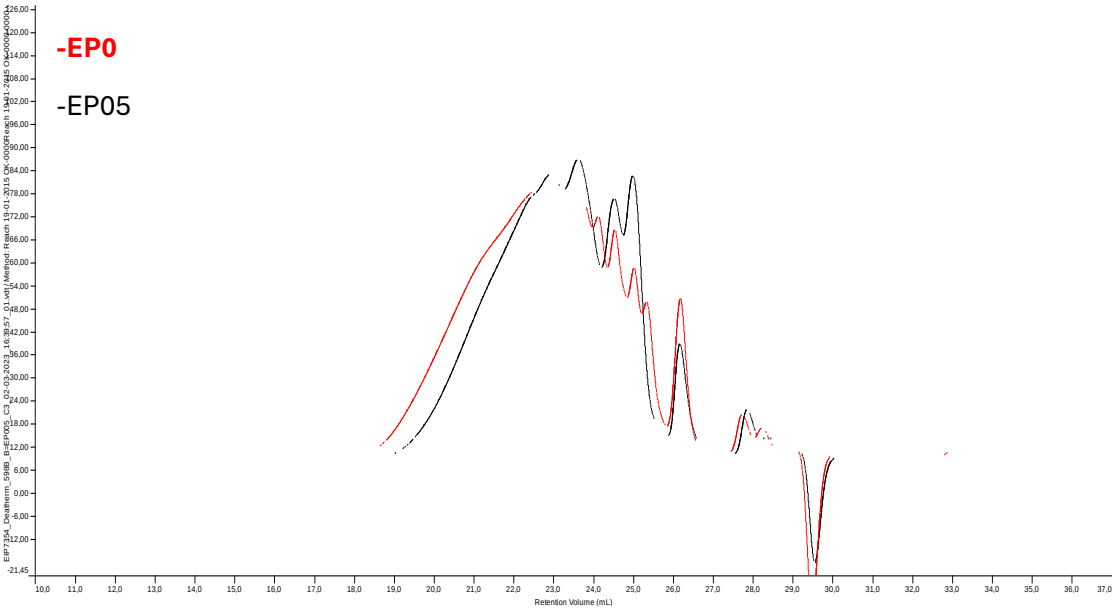


Figure 35. Overlaps of GPC chromatograms: In red EP0, reference in black EP05.

Between EP01 and EP05, the only variable is the molar ratio, so ATR-IR cannot distinguish among these five samples. However, it is still useful to obtain an ATR-IR spectrum for the most representative sample, which is EP05.

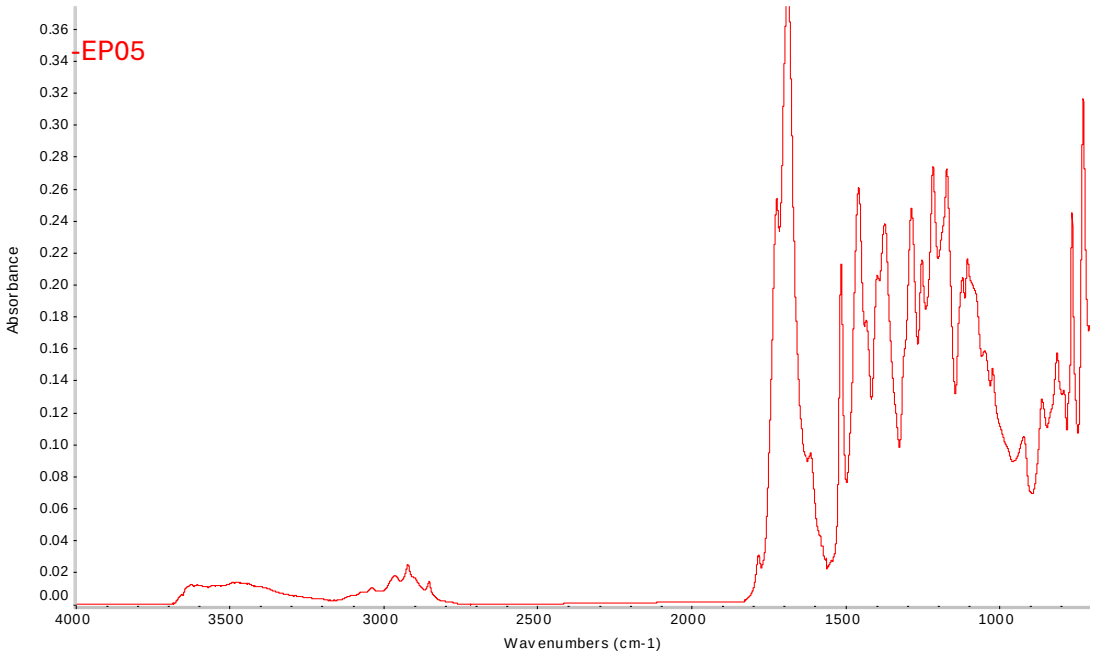


Figure 36. ATR-IR spectrum of EP05.

The thermo-mechanical and electrical properties of the cured enameled wires were evaluated and compared to those of a commercial PEI batch.

5.1.2. Results and Discussions

Product	M_w *(g/mol)*	M_n *(g/mol)*	M_w/M_n
Ref. EP0	**5417**	**2616**	**2,07**
EP01	4844	1992	2,43
EP02	4619	1926	2,39
EP03	4119	1775	2,32
EP04	4214	2244	1,87
EP05	4362	2357	1,85

Table 6. Molecular weight distributions, reference and samples.

Product	*Wire Aspect*	*Flexibility (%)*	*Cut Trough (°C)*	*Tan Delta (°C)*	*BDV (kV)*
Ref. EP0	*good*	*passed at 15%*	***≥380***	***≥195***	***≥11***
EP01	***Wavy and blistered***	*passed at 30%*	*420*	***179,3***	*13,5*
EP02	***Wavy and blistered***	*passed at 30%*	*400*	*187,4*	*11,8*
EP03	*Wavy*	*passed at 30%*	*410*	*187,8*	*11,8*
EP04	*good*	*passed at 30%*	*370*	*183,8*	*9,7*
EP05	*good*	*passed at 30%*	*410*	*197,0*	*12,4*

Table 7. Enameled wire tests: thermo-mechanical and electrical. (Enameling speed = 42m/s)

To better clarify the changes that have been made between batches a visual representation of the data in Table 5 is presented here below. (Figure 37)

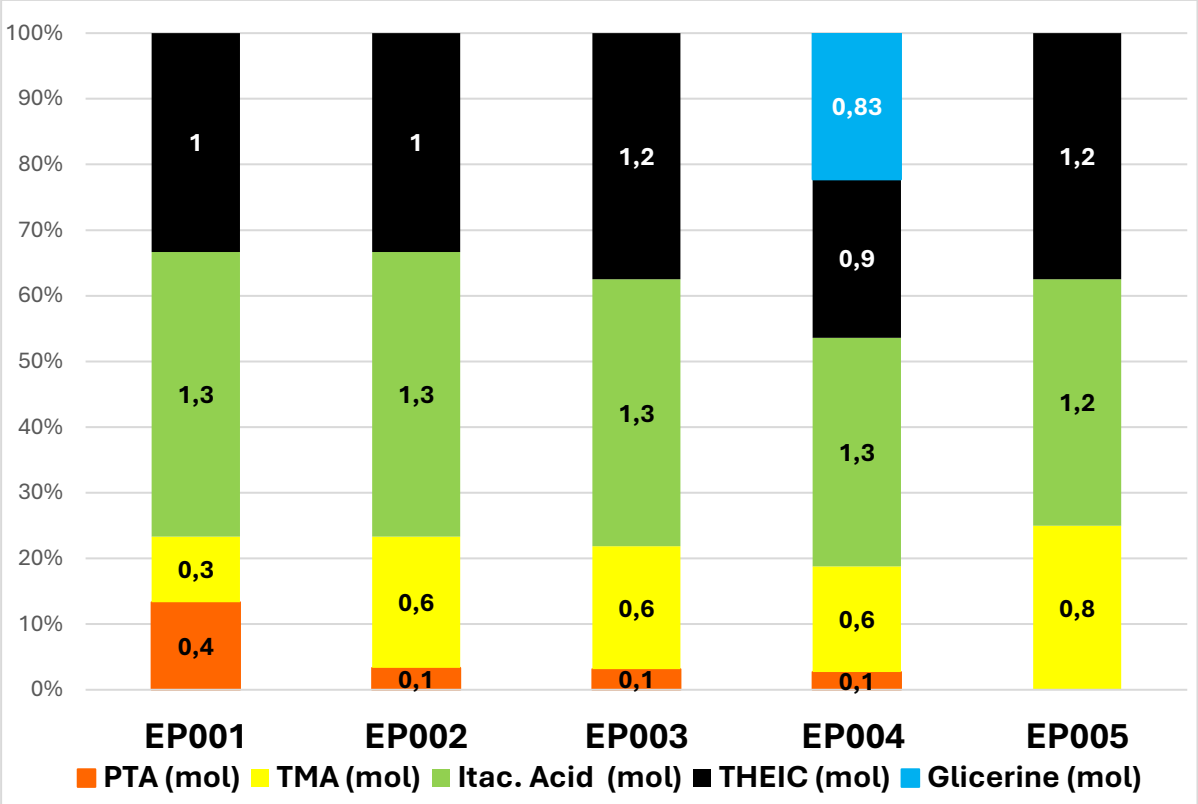


Figure 37. Graphic representation of the molar ratio used between reactants.

In the cured PEI ATR-IR spectra (Figure 36), the main absorption bands associated with the carbonyl groups in the imide ring, carboxylate groups, and isocyanurate ring appear within the 1800–1600 cm^{-1} range. Specifically, the symmetric and asymmetric stretching peaks of the imide ring carbonyl (C=O) are observed at 1716 and 1775 cm^{-1}, while the C=O stretching vibration of the ester bond occurs at 1690 cm^{-1}.[40]

Three versions of this product (EP005) were developed;

- EP005 polymer matrix + Solvent System: 50% BIOSOLV1 + 50% m,p-cresol(Final dry content of 39%) depicted as **EP005 BIO**

- EP005 polymer matrix + Solvent System: 30% m,p-cresol, 45% Phenol, 15% Xylene and 10% Naphtha SN100 (Final dry content of 27%) depicted as **EP005-27 CA**

- EP005 polymer matrix + Solvent System: 45% BIOSOLV1 + 41 % m,p-cresol + 12% Naphtha SN100(Final dry content of 27%) depicted as **EP005-27 BIO**

The first two versions were subjected at biogenic C14 determination analysis and to Thermal Index analysis in ELANTAS PDG, USA.

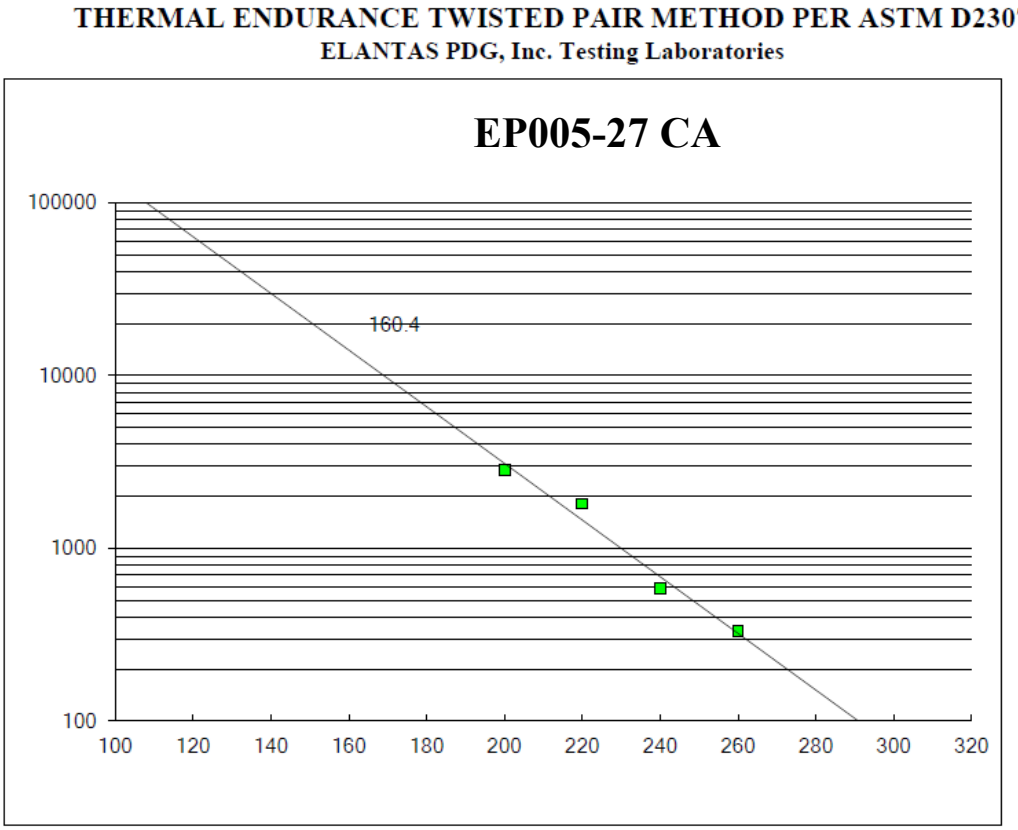


Figure 38. Thermal Index for EP005-27 CA (160,4°C).

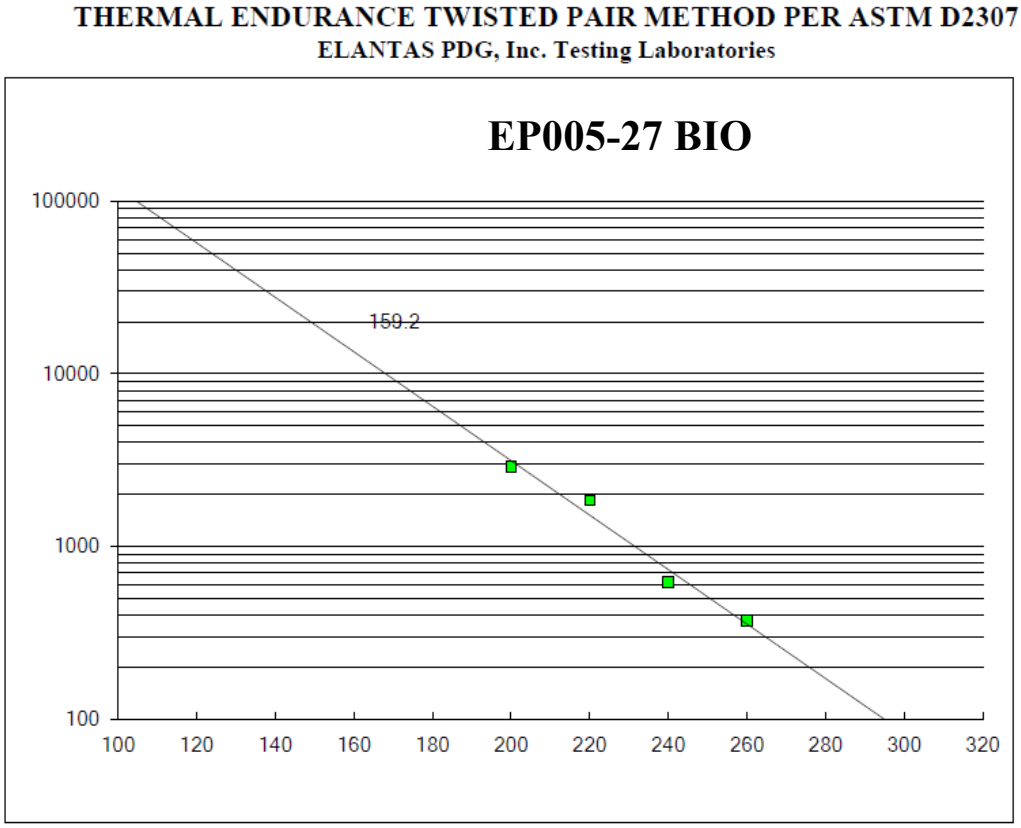


Figure 39. Thermal Index for EP005-27 BIO (159,2°C).

5.1.3. Conclusions

In all the versions created, the minimum limit of bio-material content, indicated in the target, was exceeded, there is a **40,2%** in weight of bio-based material present in the **EP005-27 BIO**. Both reagents and solvents have been partially replaced by bio-based materials. The polymer matrix was obtained by replacing approximately 50% by moles of the TMA with a biomaterial, Itaconic acid, which reacts with MDA to form a pyrrolidone adduct at the expense of the imide part of a Theic-modified standard PEI. PTA was totally eliminated. The resin obtained showed general characteristics aligned to the reference product but with a thermal class of 155°C and a thermal index of approximately 159 -161°C, LCA of **EP005** showed a carbon footprint very similar vs standard PEI (CO_2 eq/Kg: 6,41 vs 5,94). This product with 39% solid content was diluted at 27% with 2 different solvent curves, one standard (**EP005-27 CA**) and the other containing almost 50% of a non-fossil original solvent (**EP005-27 BIO**). Also, C14 content was determined for both products, obtaining resp. values of 17,7% and 6,4% for std and BIO

versions. Both products at 27% have been sent to consolidated costumers of the Company. In general, good properties were observed for both versions, aligned to standard PEI. Only wire cosmetics (surface appearance) would eventually need to be optimized. It is important to highlight that the bio-based material, that comes from fermentation of biomasses, used are non-toxic and safer with respect to the ones used in classic THEIC-modified PEI. It's very interesting also the paradox that comes out from this work, the product made with the bio-based material has a bigger CO_2 impact compared to the product with only fossil-based materials (even when taking in consideration credit of $C0_2$ for bio-based raw materials and a CO_2 debt for the fossil-based material). This should let us understand that the "green" and "bio" words are not always the solution for every problem and every action to reduce the climate impact has to be calculated and evaluated.

6.1 Alternative to Cresylic acids

Cresylic acids (CA), are a mixture of aromatic organic compounds, in particular alkylated phenols, like cresols, xylenols ethylphenols, trimethylphenols, anisols, guaicols, and other minor components, derived primarily from petroleum and coal tar. An important group of cresylic acids is formed by cresols isomers, especially para and meta (named as metaparacresol or m,p-cresols). Cresols can appear as a colorless, yellowish, brownish-yellow, or pinkish liquid. Cresol has three structural isomers: o-cresol, m-cresol, and p-cresol, which vary slightly in their physical properties. The boiling points for these isomers are 191.0°C for o-cresol, 202°C for m-cresol, and 201.9°C for p-cresol, while their melting points are 29.8°C, 11.8°C, and 35.5°C, respectively. The names of the compounds indicate the position on the benzene ring where hydrogen has been replaced. Cresols are generally obtained from coal tar or petroleum. Due to their similar boiling points, it is impractical to separate a mixture of the three isomers into pure components; instead, the mixture derived from coal tar is called metaparacresol (or cresols), an important industrial product used in disinfectants, resin production, and the manufacture of tricresyl phosphate.

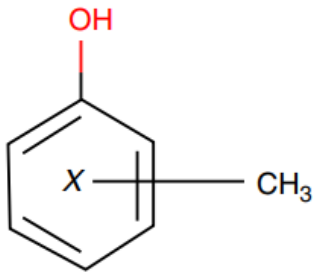


Figure 41. Cresol generic structure

Cresols are valuable as raw materials for various chemicals, disinfectants, and synthetic resins. The o-cresol isomer is particularly useful as a precursor for herbicides, including 4,6-dinitro-o-cresol and 2-methyl-4-chlorophenoxyacetic acid. The m-cresol and p-cresol isomers are utilized in the production of phenol–formaldehyde resins and are converted into tricresyl phosphate (a plasticizer and gasoline additive) and di-t-butyl cresols (antioxidants known as butylated hydroxytoluene). Professions that involve exposure to coal or wood combustion may have increased exposure to cresols compared to the general population. Environmental tobacco smoke is also a significant source of cresol exposure. The average concentration of cresol can vary depending on the brand and type of cigarette. In a 45-cubic-meter chamber with six cigarettes smoked, cresol concentrations ranged from 0.17 to 3.9 mg/m³. While cresols can also be detected at low levels in certain foods and tap water, these sources typically do not contribute significantly to overall exposure for most individuals. Detectable levels of cresols have been reported in various environmental settings.[145] Let's now define the project scope and the SS requirements.

✓ Project Scope:

- Individuate possible alternative to CA candidates (pure solvents or mixtures)
- Define solvent systems without CA able to replace solvent systems with CA in PEI enamels
- PEI (polyesterimide) resin to be soluble and stable in the resulting enamel composition.
- The resulting enamel to be able to give a wire with comparable properties vs. standard.

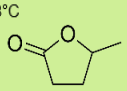
✓ SOLVENT SYSTEMS REQUIREMENTS:

- Final enamel specifications matched
- No resin depolymerization in the operating conditions
- No severe HSE classification (not higher than reference CA based solvent systen

Table 8. Project scope and SS requirements.

With the help of the HSPiP software that uses the Hansen solubility parameters, we can predict how the selected solvent will behave in solubilizing the polymer, in this case a 35% solution of Polyesterimide. The molar ratio of the building blocks of the PEI will stay the same. The solvent system is the mixture of solvents that are going to be used to solubilize the PEI. The standard solvent system used for years for the standard PEI is composed of: Phenol / m,p-cresol / Naphtha SN100 (39/28/33). Solvent naphtha (SN100 or SNI) is an intermediate hydrocarbon liquid derived from crude oil refining used as diluent in different types of chemical industries to reduce the price and the viscosity. The portion of solvent system that needs to be changed is the m,p-cresol (metaparacresol) one. The first two parameters that we must stick to before even enameling is: the residual dry content and the viscosity of the enamel. To be reproducible the main phases (Figure 31) previously showed were used for every batch for this project.

Table 9. H&SE, IP, Regulatory constraints, Boiling point, RED(%).

Product	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
Gamma-valerolactone CAS 108-29-2 Biomaterial	H319: Causes serious eye irritation H315: Causes skin irritation	FTO	Registered and manufactured in and / or imported to Europe, at ≥ 1 to < 10 t/y	BP: 207-208°C 	RED: 0,532

Those candidates were selected evaluating different characteristics; one of them is the availability of the product taken in consideration: it must be available in big quantities and continuously. The H&SE section concerns the safety of the substance, and the risk phrases associated with that substance. In the standard PEI there are already present the following risk phrases:H222 (Extremely flammable aerosol), H302+H312 (Harmful if swallowed or in contact with skin), H314 (Causes severe skin burns and eye damage.), H341 (Suspected of causing genetic defects), H373 (May cause damage to organs through prolonged or repeated exposure), H412 (Harmful to aquatic life with long lasting effects). When searching for some alternative, a worsening in the risk phrases is not acceptable, so, substances with more harmful new phrases are not accepted. In the IP/Reference country sections it is possible to see acronymous like FTO/ EU that means Freedom to Operate in Europe (if not Europe there will be depicted another country); the optimal condition is when there is FTO. The regulatory constraints sector describes where the registration of the substance has been submitted, where is manufactured and in which quantity per year this substance can be imported in Europe (linked to REACH registration). In the Boiling Point and Properties sector, the general properties of the substance or mixture and the range in which it boils are reported. This is very important because we know

that the distillation range of the solvents influence a good application of the enamel on the wire, especially regarding levelling of the enamel and curing of the coating; in general, the slower is the distillation/evaporation rate of the solvent from the enamel, the better will be the cosmesis of the enameled wire. The last sector (RED) has been explained in 3.2.1.1 chapter. Given the aim of this study to evaluate alternatives to the widely recognized cresylic acids, standard solid PEI, commonly utilized in industrial applications, was sourced directly from the Company's production sector. This approach avoids the initial polymerization phase (Phase I), which typically requires 2-3 days per batch. Moreover, using this method enhances reproducibility, as all tests are conducted on the same PEI batch. Otherwise, each trial would necessitate new PEI synthesis, where maintaining consistent molecular weight distribution across batches proves challenging, despite using identical molar ratios between reactants.

5.1 Results and Discussions

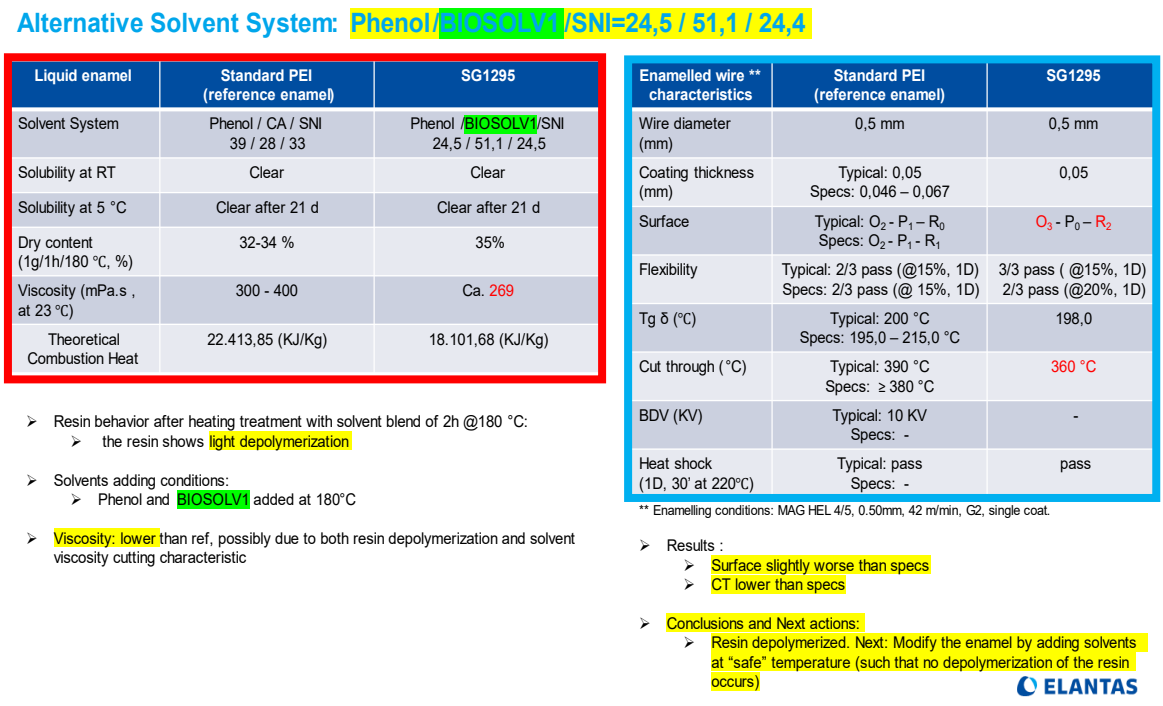


Figure 42. Example of a result presentation for a solvent substitution.

In red, on the left table are highlighted the properties that we are evaluating on the LIQUID enamel.

In blue, on the right table are highlighted the properties that we are evaluating on the ENAMELED WIRE.

Moreover, below the left table there are comments for that section and below on the right there are comments for that section. In the red table of the example above we can see that the viscosity needs to be in the range of 300-400 mPas at 23°C but instead is 269 mPas at 23°C. Is it possible to see that the theoretical combustion heat is lower than the reference. The Higher heating value (HCV) indicates the upper limit of the available thermal energy produced by a complete combustion of fuel. It is measured as a unit of energy per unit mass or volume of substance, this parameter has been used to calculate the release of heat from a SS (Solvent System) and so is depicted under every new SS tested. Enamelling machines recover energy from the solvent during wire enameling through incineration of the evaporated solvent in a catalytic plate located inside the oven and the energy recovered is used to power the enameling ovens themselves. A lower heat calorific value (HCV) in the solvent means that customers will need to use more current to operate the enameling ovens, bringing to higher production costs. Therefore, the higher the solvent's HCV, the more energy can be recovered, so HCV was selected as another parameter to take in consideration. Moreover, a GPC analysis has been done on the polymer before and after the thermal treatment (see the main phases, Figure 31). Every batch here reported follows the three main phases in Figure 31. During Phase II, (Figure 31) during the heating treatment there is only phenol or a mixture of cresols such as m,p-cresol, and this leads to a well-known light depolymerization. As we can see from the liquid enamel comment section, written below the liquid enamel table, in the heating treatment there is the presence of **BIOSOLV1**. This solvent is a mixture of materials among which esters. The presence of these components led to a significant depolymerization, which is possible to check by GPC. We can also see an impact of the depolymerization on the enameled wire performances. As we can see from the table of enameled wire(blue) there is a lowering in the surface cosmesis and in the Cut through, that could possibly be coherent with the lowering of the molecular weight distribution. Here below is shown a GPC analysis on the SG1295 (purple) and the standard Standard PEI (dark red). To better understand the influence of this depolymerization effect another batch has been produced but, in this case, we loaded the BIOSOLV1 solvent at 140°C, after the heating treatment, where the temperature should be safe enough not to let the solvent react with the polymer. These are the results:

Candidate used: BIOSOLV1

Product	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
BIOSOLV1 Organic esters blend Biomaterial	H319: Causes serious eye irritation	FTO / EU		BP: 175-242 °C. Mixture of esters	RED: 0,725

Table 10. Overview of the parameteres of BIOSOLV1.

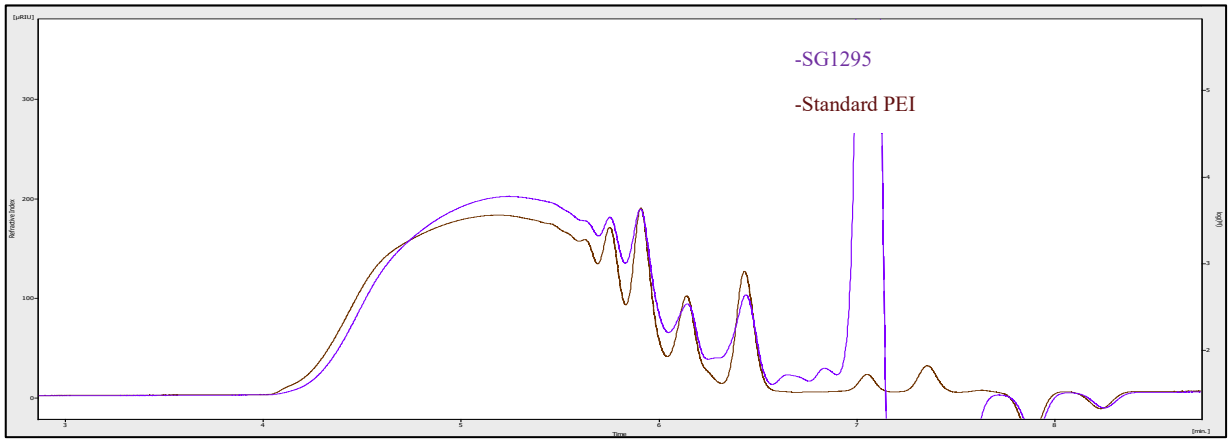


Figure 43. Superimposed GPC analysis of SG1295 and standard PEI

Alternative Solvent System: Phenol/BIOSOLV1 /SNI=24,5 / 51,1 / 24,4

Liquid enamel	Standard PEI (reference enamel)	EP0029
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol /BIOSOLV1/SNI 24,5 / 51,1 / 24,5
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear after 21 d
Dry content (1g1h180 °C, %)	32-34 %	35%
Viscosity (mPa.s , at 23 °C)	300 - 400	264
Theoretical Combustion Heat	22.413,85 (KJ/Kg)	18.101,68 (KJ/Kg)

Enamelled wire ** characteristics	Standard PEI (reference enamel)	EP0029
Wire diameter (mm)	0,5 mm	0,5 mm
Coating thickness (mm)	Typical: 0,05 Specs: 0,046 – 0,067	0,05
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_2 - P_0
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	3/3 pass (@15%, 1D) 3/3 pass (@20%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	203,4
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	380 °C
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

- Resin behavior after heating treatment with phenol of 2h @180 °C:
  - No depolymerization
- Solvents adding conditions:
  - Phenol added at 180 °C and BIOSOLV1 added at 140°C
- Viscosity: lower than ref, due to solvent cutting property

** Enamelling conditions: MAG HEL 4/5, 0.50mm, 42 m/min, G2, single coat.

- Results :
  - Wire properties in specs
- Conclusions and Next actions:
  - The studied SS shows Vix lowering below specs

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Figure 43. EP029 varnish and enameled wire characteristics.

It is possible to observe that the viscosity in this case is nearly equivalent to that of the previous batch. However, in this instance, the Cut Through has returned to within the specified

parameters. This suggests that the primary impact on viscosity is likely due to the lower solvency power of BIOSOLV1 compared to cresylic acids (CA). Here below is shown a GPC analysis on the EP029 (purple) and the standard Standard PEI (green).

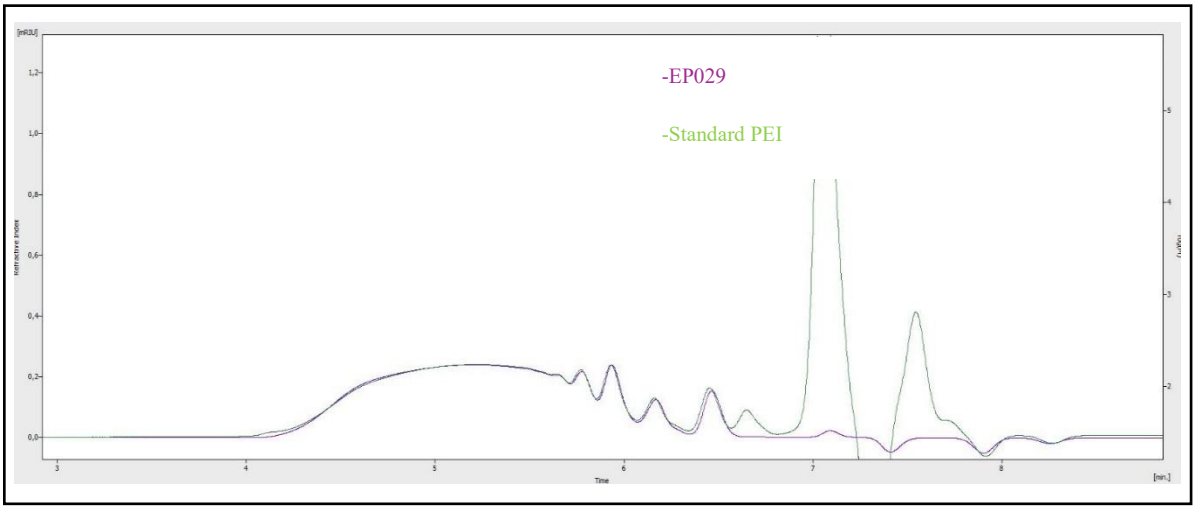


Figure 44. Superimposed GPC analysis of EP029 and the standard PEI.

The project focus is the substitution of Cresylic acids, so the presence of phenol is tolerated and almost obligated, anyway it's had been done some trials without phenol.

Next candidate used:

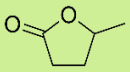
Product	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
Gamma-valerolactone CAS 108-29-2 Biomaterial	H319: Causes serious eye irritation H315: Causes skin irritation	FTO	Registered and manufactured in and / or imported to Europe, at ≥ 1 to < 10 t/y	BP: 207-208°C 	RED: 0,532

Table 11. Overview of the parameteres of Gamma-Valerolactone.

Alternative Solvent System: Gamma-Valerolactone (GVL) / BIOSOLV1 / SNI 24,4 / 51 /24,6

Liquid enamel	Standard PEI (reference enamel)	EP0032
Solvent System	Phenol / CA / SNI 39 / 28 / 33	GVL/BIOSOLV 1 /SNI 24,4/ 51/ 24,6
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear
Dry content (1g/1h/180 °C, %)	32-34 %	38,4 %
Viscosity (mPa.s , at 23 °C)	300 - 400	288
Theoretical Combustion Heat	22.413,85 (KJ/Kg)	11.717 (KJ/Kg)

Enamelled wire ** characteristics	Standard PEI (reference enamel)	EP0032
Wire diameter (mm)	0,5 mm	0,5 mm
Coating thickness (mm)	Typical: 0,05 Specs: 0,046 – 0,067	0,05
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_2 - P_0
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	2/3 pass (@15%, 1D) 1/3 pass (@20%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	207,3
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	380 °C
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

- Resin behavior after heating treatment of 2h :
  - GVL added at 180°C : No depolymerization
- Solvents adding conditions:
  - GVL added at 180°C and Astrobio added at 145°C
- Viscosity: lower than ref, due to solvent cutting property

** Enamelling conditions: MAG HEL 4/5, 0.50mm, 42 m/min, G2, single coat.

- Results :
  - Wire properties in specs
- Conclusions and Next actions:
  - The studied SS shows Vix lowering below and very low combustion heat.

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Figure 45. EP032 varnish and enamelled wire characteristics.

In the EP032 table is it possible to notice that is possible to create a solvent system (SS) able to solubilize the polymer (standard PEI) even with optimum characteristics of enameled wire. The main problem of not using phenolic compounds consists in the fact that the viscosity, the price and the theoretical combustion heat are no more in the range where they normally are. So, it is not convenient for market purposes. The remarkable aspect of this batch is the discovery that the γ-Valerolactone lactone (GVL) does not depolymerize the PEI, even at high temperatures.

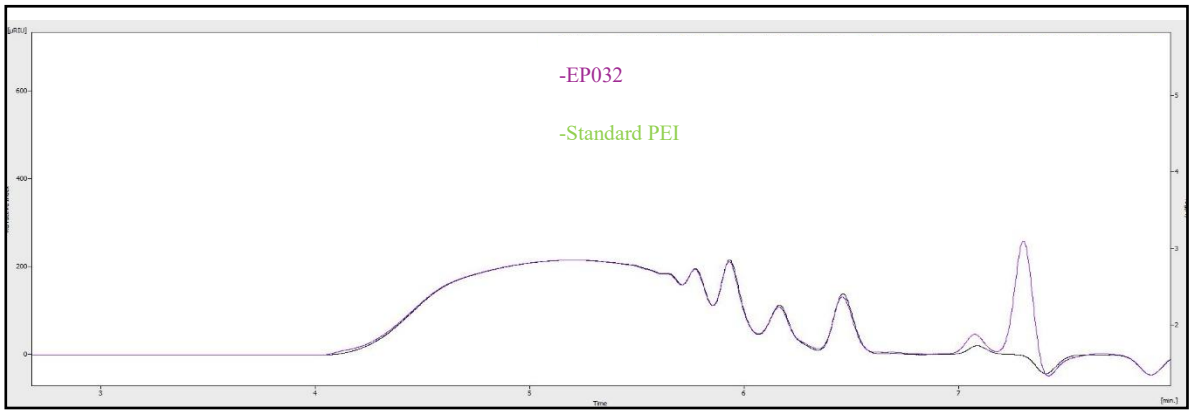

Figure 45. Superimposed GPC analysis of EP032 and the standard PEI.

Next candidate used: Benzyl Alcohol

Product CAS n°	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
Benzylic alcohol CAS 100-51-6	H319: Causes serious eye irritation	FTO	Registered and manufactured in and / or imported to the European Economic Area, at ≥ 10000 t/y. On the list of the Community rolling action plan (CoRAP) as suspected sensitizer	BP: 205°C	RED: 0,862

Table 12. Overview of the parameteres of Benzyl alcohol

Alternative Solvent System: GVL/Benzylic Alcohol/ SNI 38,3/ 41,7/ 20

Liquid enamel	Terebec MT 533 35N (reference enamel)	EP0037
Solvent System	Phenol / CA / SNI 39 / 28 / 33	GVL / BA / SNI 38,3/41,7/20
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear
Dry content (1g/1h/180 °C, %)	32-34 %	34,96%
Viscosity (mPa.s , at 23 °C)	300 - 400	100
Theoretical Combustion Heat	22.413,85 (KJ/Kg)	21.684,43 (KJ/Kg)

- Resin behavior after heating treatment of 30min at 200 °C :
  - GVL : No depolymerization
- Solvents adding conditions:
  - GVL added at 200 °C stirred and mantained 30 min, 180 °C stirred and maintained 2 h, SNI and BA added at 140 °C

Enamelled wire ** characteristics	Terebec MT 533 35N (reference enamel)	EP0037
Wire diameter (mm)	0,5 mm	0,5 mm
Coating thickness (mm)	Typical: 0,05 Specs: 0,046 – 0,067	0,05
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_2 – P_1
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	2/3 pass (@15%, 1D) 0/3 (@20%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	204,0
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	390
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

** Enamelling conditions: MAG HEL 4/5, 0.50mm, 42 m/min, G2, single coat.

- Results :
  - Enamel not in specs
- Conclusions and Next actions:
  - The studied SS shows Vix lowering much below specs No further actions on this SS.

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Figure 46. EP037 varnish and enameled wire characteristics.

BIOSOLV1 has a very low theoretical combustion heat so, if present in the 50%wt of the SS it will overall decrease this value in a significative way as we can see in the EP032. In the EP037 (Figure 46) is it possible to see the effect of benzyl alcohol where the theoretical combustion heat has been mostly recovered but the viscosity is very low. It was therefore decided to go back in the phenol-based SS.

Next candidate used: Butyl Glycol Acetate (BGA)

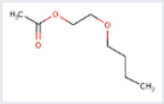
Product CAS n°	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
Butyl glycol acetate (2-butoxyethyl acetate) CAS: 112-07-2	H312: Harmful in contact with skin H332: Harmful if inhaled	FTO 	Registered and manufactured in and / or imported to Europe, at ≥ 10 000 to < 100 000 t/y	BP: 192°C My lead to transesterification reactions	RED: **0,971**

Table 13. Overview of the parameteres of Butyl Glycol Acetate.

Alternative Solvent System: Phenol/Butyl Glycol Acetate/SNI 55/ 25/ 20

Liquid enamel	Terebec MT 533 35N (reference enamel)	EP0040
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol /BGA/SNI 55 / 25 / 20
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear
Dry content (1g1h180 °C, %)	32-34 %	36,57%
Viscosity (mPa.s , at 23 °C)	300 - 400	375
Theoretical Combustion Heat	22.413,85 (KJ/Kg)	22.190,2 (KJ/Kg)

- Resin behavior after heating treatment of 30min at 190 °C:
  - BGA : Depolymerization observed
- Solvents adding conditions:
  - BGA and Phenol added at 190 °C stirred and maintained 30 min, then at 180 °C stirred and maintained 2 h, SNI added at 140 °C

Enamelled wire ** characteristics	Terebec MT 533 35N (reference enamel)	EP0040
Wire diameter (mm)	0,5 mm	0,5 mm
Coating thickness (mm)	Typical: 0,05 Specs: 0,046 – 0,067	0,05
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_2– P_1
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	3/3 pass (@15%, 1D) 2/3 pass (@20%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	168,4
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	310
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

** Enamelling conditions: MAG HEL 4/5, 0.50mm, 42 m/min, G2, single coat.

- Results :
  - Wire properties in specs
- Conclusions and Next actions:
  - Add BGA at lower T and increase phenol (60/20/20)

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Figure 47. EP040 varnish and enameled wire characteristics.

From GPC (Figure 48) analysis done after the heating treatment to the PEI with Butyl Glycol Acetate (BGA) it was possible to notice a depolymerization, this is reflected on the characteristics of the enameled wire, where we can see a decrease in the Tg δ and in the Cut

through, confirming the hypothesis that depolymerized resin shows a decrease of CT. In the next tables there will be the test done with BGA loaded after the heating treatment.

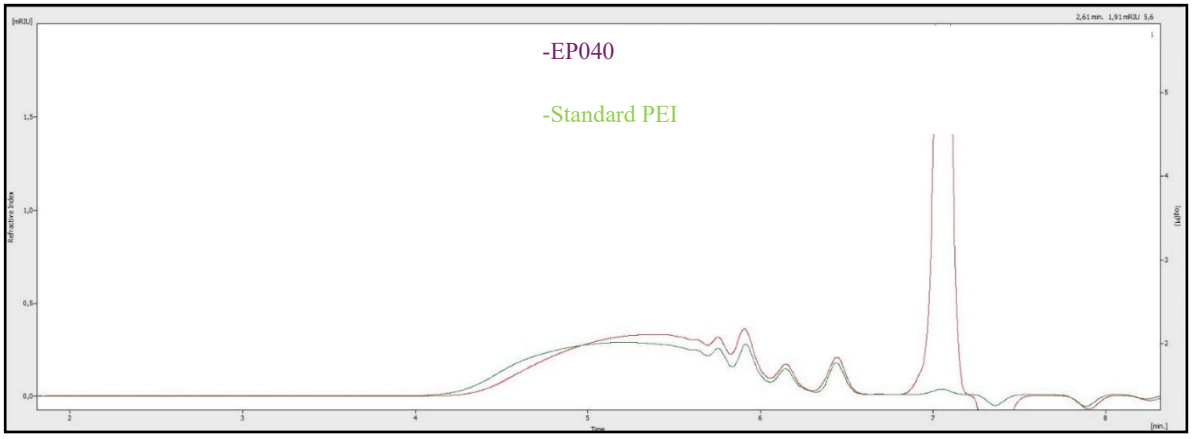

Figure 48. Superimposed GPC analysis of EP040 and the standard PEI.

In the BGA tests we decided to make an enamel at increased solid (39%) for which we took its specific reference in the family of standard PEI. Such high solid version is enamelled on a different oven used for the curing, a vertical oven on which the wire used has a diameter of 1mm, to verify if different application systems can give coherent results.

Alternative Solvent System: Phenol/Butyl Glycol Acetate/SNI= 60 / 20 / 20

Liquid enamel	Standard PEI (reference enamel)	EP0045
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol / BGA /SNI 60 / 20 / 20
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear
SC (1g1h180 °C, %)	38-40 %	38,13%
Viscosity (mPa.s , at 23 °C)	800-900	880
Theoretical Combustion Heat	22.594 (KJ/Kg)	20.830 (KJ/Kg)

- Resin behavior after heating treatment with Phenol of 2h at 180 °C:
  - the resin shows light depolymerization
- Solvents adding conditions:
  - Phenol added at 180°C and BGA and SNI added at 140°C

Enamelled wire ** characteristics	Standard PEI (reference enamel)	EP0045
Wire diameter (mm)	1 mm	1 mm
Coating thickness (mm)	Typical: 0,08	0,08
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_1 – P_1
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	2/3 pass (@25%, 1D) 2/3 pass (@30%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	204,8
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	400 °C
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

** Enamelling conditions: VET 375 Destro, 1 mm, 55 m/min, G2, single coat.

Results :
- Surface in specs
- CT in specs

- Conclusions and Next actions:
  - New SS to decrease Vx: 60 / 10 / 30: Phen / BGA / SNI

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Figure 49. EP045 varnish and enameled wire characteristics

Alternative Solvent System: Phenol/Butyl Glycol Acetate/SNI= 60 / 10 / 30

Liquid enamel	Terebec MT 533 39T P (reference enamel)	EP0047
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol / BGA /SNI 60 / 10 / 30
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear
Dry Content (1g/1h/180 °C, %)	38-40 %	39,1%
Viscosity (mPa.s , at 23 °C)	800-900	898
Theoretical Combustion Heat	22.594 (KJ/Kg)	21.778 (KJ/Kg)

- Resin behavior after heating treatment with Phenol of 2h at 180 °C:
  - the resin shows light depolymerization
- Solvents adding conditions:
  - Phenol added at 180°C and BGA and SNI added at 140°C

Enamelled wire ** characteristics	Terebec MT 533 39T P (reference enamel)	EP0045
Wire diameter (mm)	1 mm	1 mm
Coating thickness (mm)	Typical: 0,08	0,08
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_1 – P_2
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	2/3 pass (@15%, 1D) 1/3 pass (@20%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	199,7
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	390 °C
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

** Enamelling conditions: VET 375 Destro, 1 mm, 55 m/min, G2, single coat.

Results :
- Surface in specs
- CT in specs

- Conclusions and Next actions:
  - No further actions on this SS

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Figure 50. EP047 varnish and enameled wire characteristics

Next candidate solvent: Dibasic Ester (DBE)

Product CAS n°	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
DBE (dibasic esters) (dimethyl adipate, dimethyl glutarate, dimethyl succinate) CAS _ EC / List no.: 937-156-2	No hazard	FTO	Notified C&L	BP: 196-225°C My lead to transesterification reactions	RED: 0,842

Table 14. Overview of the parameteres of Dibasic esters.

Alternative Solvent System: Phenol/DiBasic Esters/SNI 60 / 20 / 20

Liquid enamel	Terebec MT 533 35N (reference enamel)	EP0042
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol /DBE/SNI 60 / 20 / 20
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear
Dry Content (1g/1h/180 °C, %)	32-34 %	37,7%
Viscosity (mPa.s , at 23 °C)	300 - 400	307
Theoretical Combustion Heat	22.413,85 (KJ/Kg)	19.850,9 (KJ/Kg)

- Resin behavior after heating treatment of 30min :
  - DBE at 190°C: Polymerization observed
- Solvents adding conditions:
  - DBE and phenol added at 190 °C stirred and mantained 30 min, then at 180 °C stirred and maintained 2 h, SNI added at 140 °C

Enamelled wire ** characteristics	Terebec MT 533 35N (reference enamel)	EP0042
Wire diameter (mm)	0,5 mm	0,5 mm
Coating thickness (mm)	Typical: 0,05 Specs: 0,046 – 0,067	0,05
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_2– P_1
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	3/3 pass (@15%, 1D) 3/3 pass (@20%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	129
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	290
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

** Enamelling conditions: MAG HEL 4/5, 0.50mm, 42 m/min, G2, single coat.

- Results :
  - Wire properties not in specs
- Conclusions and Next actions:
  - The introduction of aliphatic chains in the polymer led to a decrease in the thermo -electric characteristics
  - Next action: charging DBE at 150 °C

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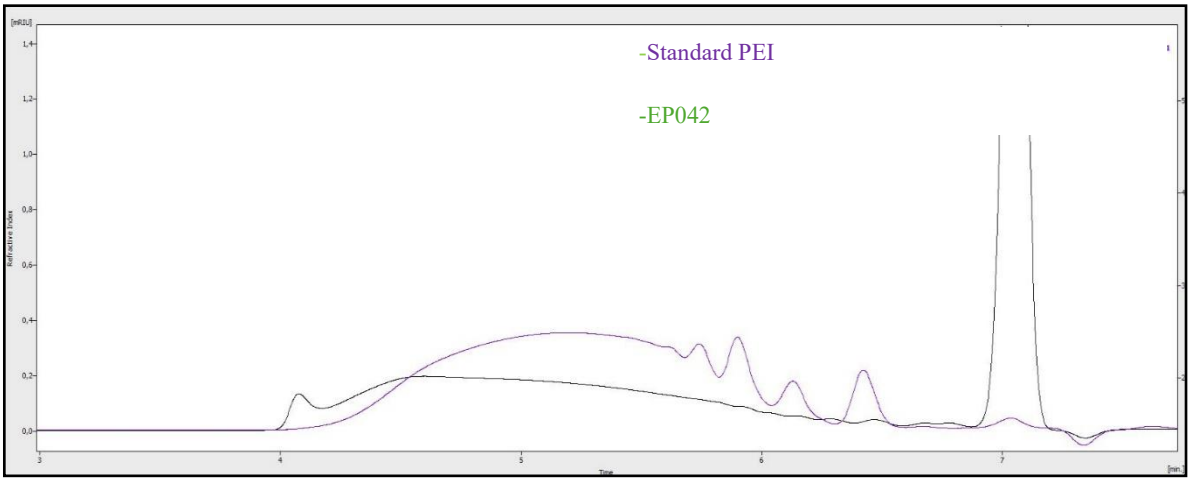
Figure 51. EP042 varnish and enameled wire characteristics



From GPC analysis done after the heating treatment to the PEI with Dibasic Esters (DBE) it was possible to notice a polymerization when added at 190°C. Since that it is known that the introduction of aliphatic chains leads to a decrease of the thermo-mechanical performances respect to an introduction of aromatic moieties, and we confirm this hypothesis by the enameling results. (DBE composition: mixture of dimethyl adipate, dimethyl glutarate, dimethyl succinate)

Figure 52. Superimposed GPC analysis of EP042 and the standard PEI.

Introducing this solvent in a "safe" temperature to avoid any polymerization phenomena could be the solution, so it has been tried and hereafter is it possible to check the results:

Alternative Solvent System: Phenol/DiBasic Esters/SNI 60 / 20 / 20

Liquid enamel	Terebec MT 533 35N (reference enamel)	EP0049
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol /DBE/SNI 60 / 20 / 20
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	In evaluation
Dry Content (1g/1h/180 °C, %)	38-40 %	40,0%
Viscosity (mPa.s , at 23 °C)	800-900	855
Theoretical Combustion Heat	22.594 (KJ/Kg)	19.850,9 (KJ/Kg)

- Resin behavior after heating treatment with Phenol of 2h at 180 °C:
  - the resin shows light depolymerization
- Solvents adding conditions:
  - Phenol added at 180 °C and DBE and SNI added at 140 °C

Enamelled wire ** characteristics	Terebec MT 533 39T P (reference enamel)	EP0049
Wire diameter (mm)	1 mm	1 mm
Coating thickness (mm)	Typical: 0,08	0,08
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_1 – P_2 – R_o
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	2/3 pass (@25%, 1D) 1/3 pass (@30%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	197
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	380 °C
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

** Enamelling conditions: VET 375, 1 mm, 55 m/min, G2, single coat.

Results :
- Surface not in specs
- CT in specs

- Conclusions and Next actions:
  - No further actions on this SS

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Figure 53. EP049 varnish and enamelled wire characteristics.

The hypothesis was correct, loading the DBE at 140°C didn't lead to noticeable chemical reaction between the polymer and the solvent. It has also been tried a solvent called Proglyde DMM (dipropylen Glycol Dimethyl ether, Figure 54), a very interesting candidate solvent since it doesn't have any reactive group towards PEI in those specific operative conditions.

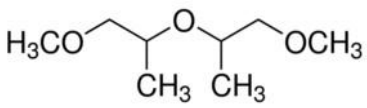


Figure 54. Dipropylen Glycol Dimethyl ether

Next candidate solvent: Proglyde DMM (dipropylen Glycol Dimethyl ether)

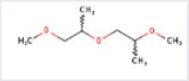
Product CAS n°	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
Proglyde DMM (Dipropylene Glycol Dimethyl Ether) CAS 111109-77-4	H319: Causes serious eye irritation H315: Causes skin irritation H335: May cause respiratory irritation	FTO 	Registered and manufactured in and / or imported to Europe, at ≥ 100 to < 1000 t/y	BP: 175°C	RED: 1,482

Table 15. Overview of the parameteres of Proglyde DMM.

Alternative Solvent System: Phenol/Proglyde DMM/SNI 60 / 20 / 20

Liquid enamel	Standard PEI (reference enamel)	EP0043
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol / PDMM /SNI 60 / 20 / 20
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear
SC (1g1h180 ℃, %)	32-34 %	31,7%
Viscosity (mPa.s , at 23 ℃)	300 - 400	331
Theoretical Combustion Heat	22.413,85 (KJ/Kg)	22.382,2 (KJ/Kg)

- Resin behavior after heating treatment of 30min :
  - PDMM at 190°C: No change in the molecular profile observed
- Solvents adding conditions:
  - PDMM and Phenol added at 190 °C stirred and maintained 30 min, then at 180°C stirred and maintained 2 h, SNI added at 140 °C

Enamelled wire ** characteristics	Standard PEI (reference enamel)	EP0043
Wire diameter (mm)	0,5 mm	0,5 mm
Coating thickness (mm)	Typical: 0,05 Specs: 0,046 – 0,067	0,05
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_2– P_1
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	3/3 pass (@15%, 1D) 3/3 pass (@20%, 1D)
Tg δ (℃)	Typical: 200 °C Specs: 195,0 – 215,0 °C	203
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	370
Heat shock (1D, 30' at 220℃)	Typical: pass Specs: -	pass

** Enamelling conditions: MAG HEL 4/5, 0.50mm, 42 m/min, G2, single coat.

- Results :
  - Wire properties in specs
- Conclusions and Next actions:
  - The PDMM seems a good choice since it has a good solvency power that can lead to an increase of the SNI
  - New SS: Phen / PDMM / SNI : 60 / 10 / 30

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Figure 55. EP043 varnish and enamelled wire characteristics.

This time, since this solvent has no reactive groups towards PEI, in these specific operative conditions, we can load it at 180°C and maintain it at that temperature for 2h as in a real production plant. The GPC analysis revealed that there is not a significant change in the molecular weight distribution.

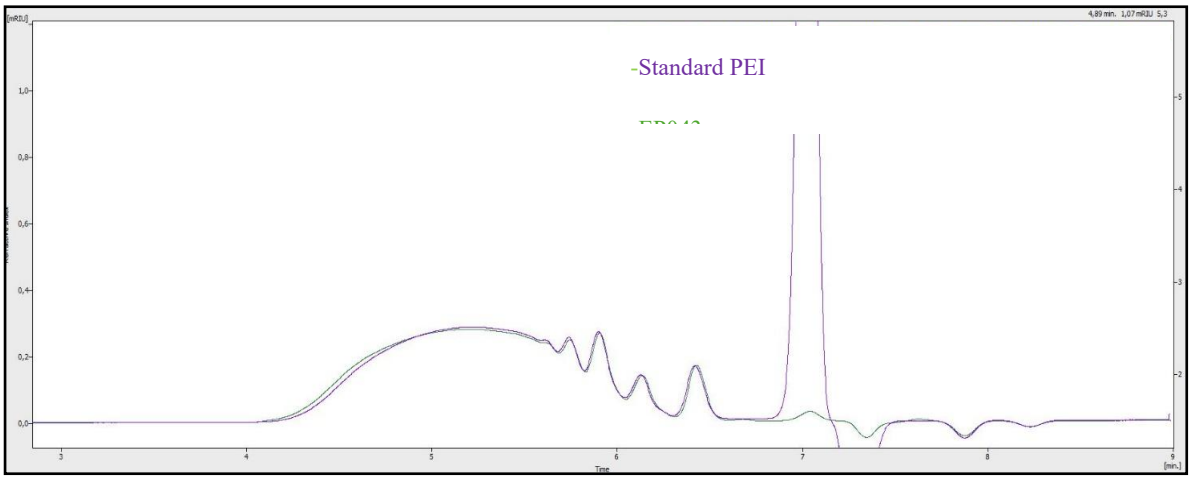

Figure 56. Superimposed GPC analysis of EP043 and the standard PEI.

It has been done another test with this solvent in the vertical oven. This time the solvent system has changed due to cost reduction and viscosity adjustments.

Alternative Solvent System: Phenol/Prolgyde DMM/SNI 60 / 10 / 30

Liquid enamel	Standard PEI (reference enamel)	EP0050
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol / PDMM /SNI 60 / 10 / 30
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	In evaluation
SC (1g1h180 °C, %)	38-40 %	38,40%
Viscosity (mPa.s , at 23 °C)	800-900	860
Theoretical Combustion Heat	22.594 (KJ/Kg)	22.706 (KJ/Kg)

- Solvents adding conditions:
  - Phenol added at 190°C stirred and mantained 30 min, then at 180°C stirred and maintained 2 h, SNI added at 140 °C

Enamelled wire ** characteristics	Standard PEI (reference enamel)	EP0050
Wire diameter (mm)	1 mm	1 mm
Coating thickness (mm)	Typical: 0,08	0,08
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_1 – P_1 – R_o
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	2/3 pass (@25%, 1D) 1/3 pass (@30%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	204
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	390 °C
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

** Enamelling conditions: VET 375, 1 mm, 55 m/min, G2, single coat.

Results :
- Surface not in specs
- CT in specs

- Conclusions and Next actions:
  - No further actions

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Figure 57. EP050 varnish and enameled wire characteristics.

The properties of the wire are in specs.

As last trial it has been tried the Mesitol, this has been used for year in this company as partial replacer of cresylic acids. In this case the total substitution of Cresylic acid with Mesitol has been tried.

Next candidate solvent: Mesitol

Product CAS n°	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
Mesitol **2,4,6-trimethyl phenol** **CAS 527 – 60 - 6**	H302 + H312 Harmful if swallowed or in contact with skin. H314 Causes severe skin burns and eye damage. H317 May cause an allergic skin reaction. H335 May cause respiratory irritation. H341 Suspected of causing genetic defects. H373 May cause damage to organs through prolonged or repeated exposure.		Registered and manufactured in and / or imported to Europe, at ≥ 100 to < 1000 t/y	BP: 221 °C	RED: **1,17**

Table 16. Overview of the parameteres of Mesitol.

Alternative Solvent System: Phenol/ Mesitol /SNI= 47 / 23 / 30

Liquid enamel	Terebec MT 533 39T P (reference enamel)	EP0044
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol / Mes /SNI 47 / 23 / 30
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	In evaluation
SC (1g1h180 ℃, %)	38-40 %	38,33%
Viscosity (mPa.s , at 23 ℃)	800-900	830
Theoretical Combustion Heat	22.594 (KJ/Kg)	22.706 (KJ/Kg)

- Resin behavior after heating treatment with Phenol of 2h at 180 °C:
  - the resin shows light depolymerization
- Solvents adding conditions:
  - Phenol added at 180°C, Mesitol and SNI added at 140°C

Enamelled wire ** characteristics	Terebec MT 533 39T P (reference enamel)	EP0044
Wire diameter (mm)	1 mm	1 mm
Coating thickness (mm)	Typical: 0,08	0,08
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_2 – P_1 – R_1
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	2/3 pass (@25%, 1D) 2/3 pass (@30%, 1D)
Tg δ (℃)	Typical: 200 °C Specs: 195,0 – 215,0 °C	203,4
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	390 °C
Heat shock (1D, 30' at 220℃)	Typical: pass Specs: -	pass

** Enamelling conditions: VET 375, 1 mm, 55 m/min, G2, single coat.

Results :
- Surface in specs
- CT in specs

- Conclusions and Next actions:
  - No further action on this SS

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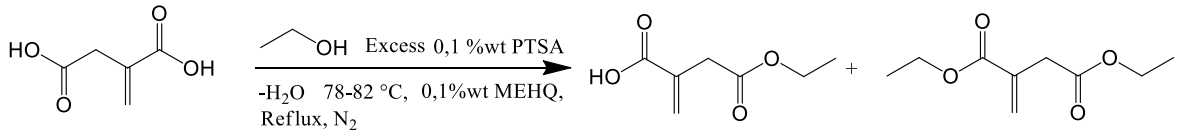
Figure 58. EP044 varnish and enameled wire characteristics.

6.1.2 Synthetic approach to Alternative to Cresol project: Synthesis of a bio-based solvent

A completely-bio based solvent has been synthesized and characterized through FT-IR and GC/MS-MS. The synthesis involved the esterification of itaconic acid by ethanol, that works as solvent and as reagent, in the presence of para-toluene sulfonic acid (PTSA) as the acidic catalyst and toluquinone as the stabilizer of itaconic acid homopolymerization. This synthesis was conducted mainly to check if this completely-biobased solvent is able to replace the m,p-cresol. In a 2 L, five-necked round-bottom glass vessel equipped with a mechanical stirrer, thermocouple, Vigreux column, and distillation apparatus, an excess of ethylene glycol was added. The reaction was conducted with excess ethanol as the reaction medium, which was later removed. The reaction conditions were: 14 h reflux at 78-82°C with a 1:10 Itaconic acid: ethanol molar ratio with a 0,1wt% of catalyst (PTSA) and 0,1%wt of stabilizer (MEHQ). The acidity of the solution was used to determine the end of the reaction expressed in mg KOH/g product as per internal standard procedure. When the acidity drops under 10 mg KOH/g product, we consider the reaction terminated. The residual acidity is given by the catalyst, the itaconic acid not reacted and by the mono-esterified itaconic acid-ester. Following the reaction, ethanol is distilled off. The mixture of product (mono and di-esterified diacid) has a melting point of about 57-59°C, the itaconic acid is not soluble in the hot mixture of products, so, two rounds of hot vacuum filtration were performed to remove unreacted itaconic acid. ATR-IR and GC-MS analyses were subsequently carried out. This batch was named **EP51.**



Scheme 22. Di and mono esterified itaconic acid.

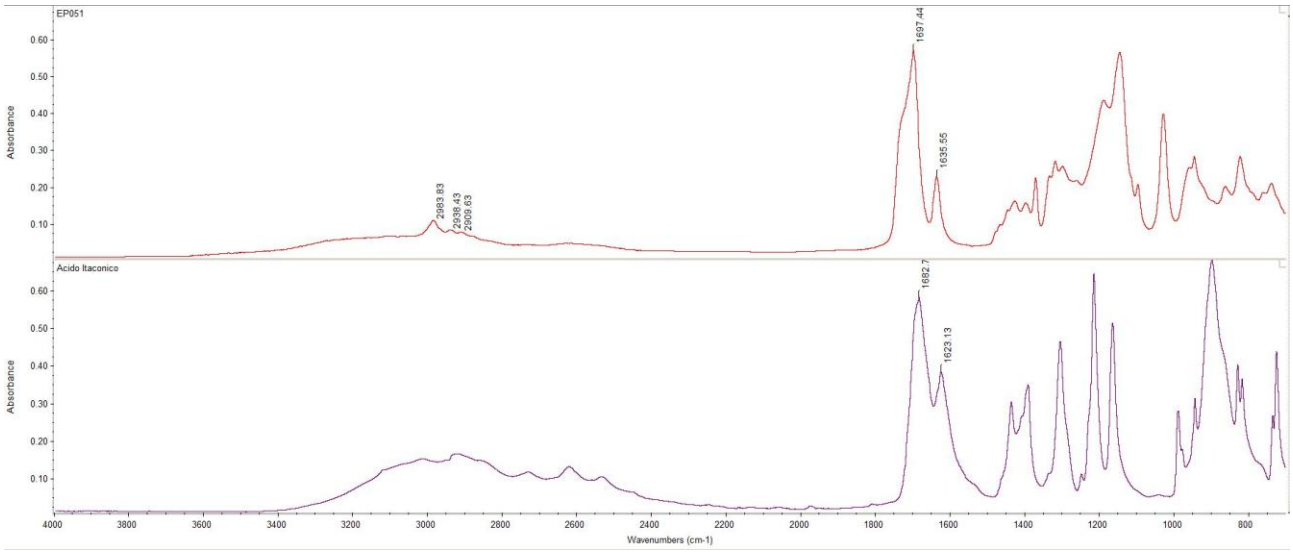


Figure 59. ATR-FTIR comparison between EP51(red) and pure Itaconic acid (purple)

This analysis alone is not enough to confirm what it's been synthesized, so a GC-MS analysis has been done, the parameters and the method are reported in chapter 4.3.6.

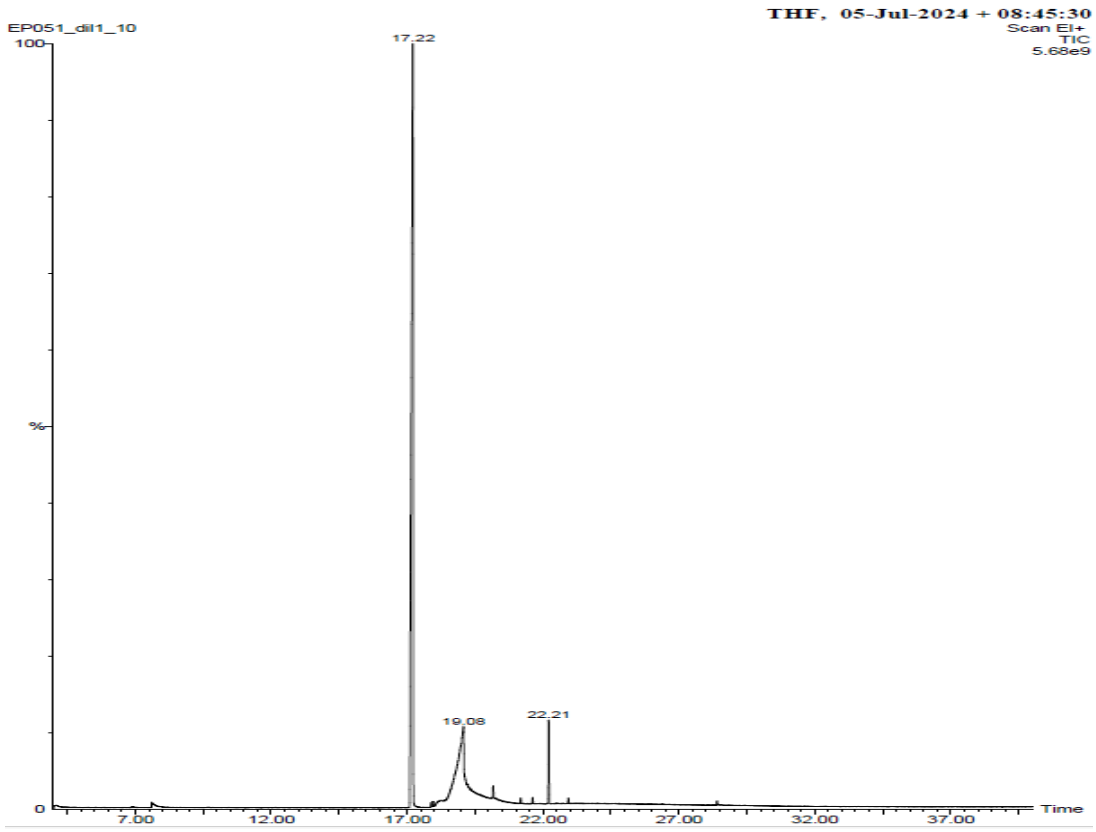


Figure. 60 GC analysis of EP51.

Hereafter it's shown the mass spectrum analysis on the peak at 17.22 min and at 19.08 min . The peak at 22.21 min has been identified as MEHQ, the stabilizer of the itaconic acid used to prevent side reaction e.g. homopolymerization.

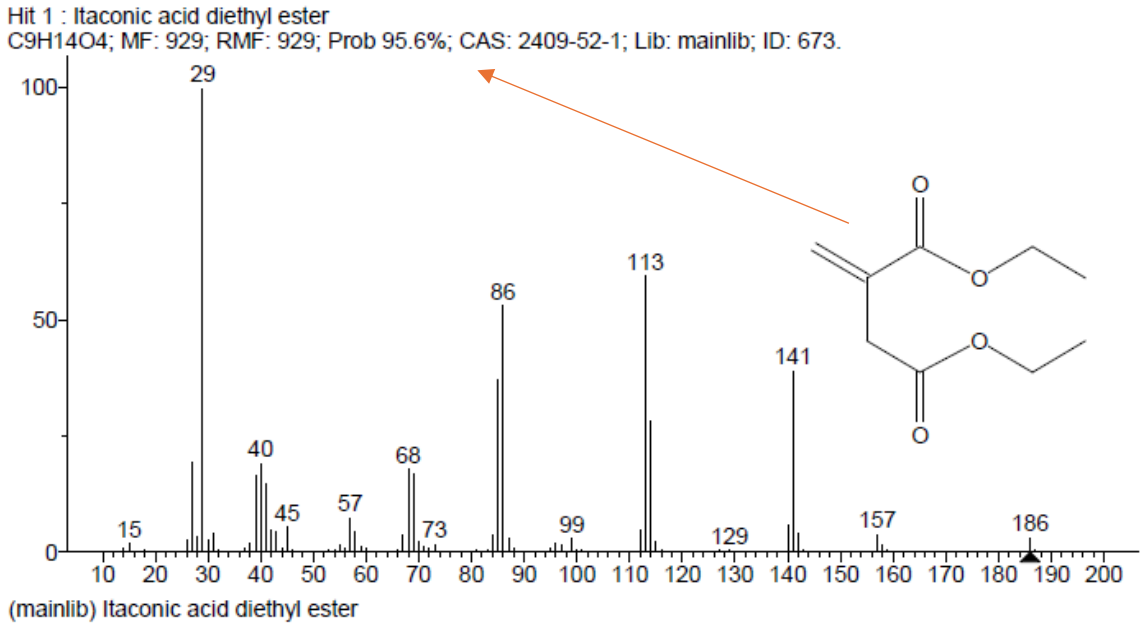


Figure. 61 Mass spectrum of the peak at 17,22.

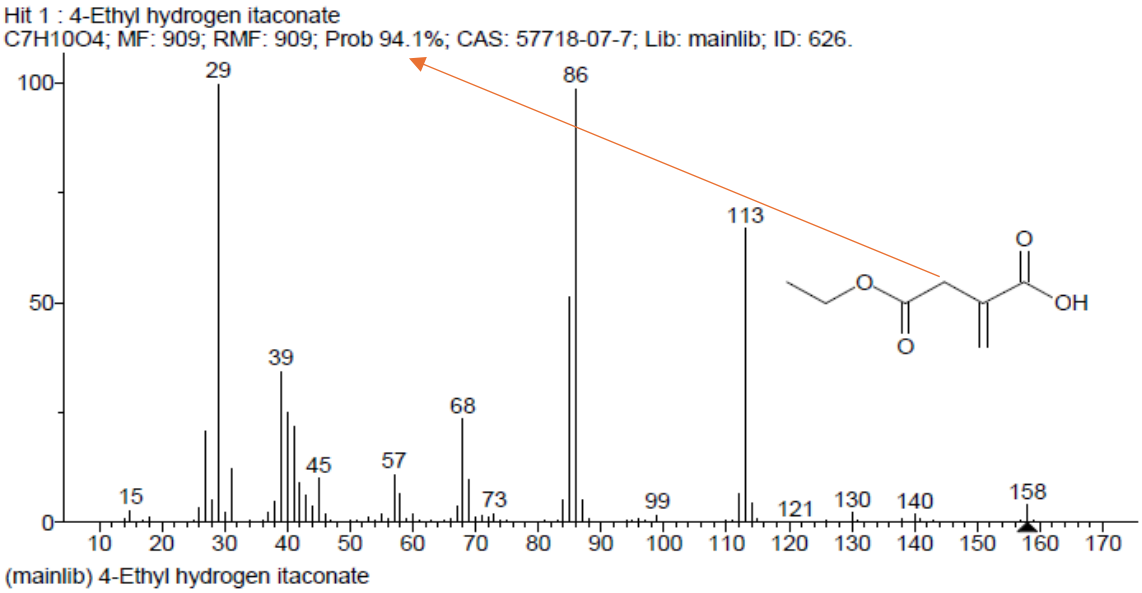


Figure. 62 Mass spectrum of the peak at 19,09.

The aim of this synthesis is to evaluate the use of this solvent for wire enamel applications, following the same procedure used in previous batches, we report here below the results.

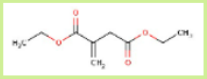
Product CAS n°	H&SE	IP / Reference country	Regulatory Costraints	Boiling Point (°C) and Properties	35% PEI 533 resin dilution
Diethyl itaconate (Diethyl 2-methylenesuccinate) CAS 2409-52-1 Biomaterial	H319: Causes serious eye irritation		Pre-registration process	BP: 228°C	RED: 0.977

Table 17. Overview of the parameteres of Di-ethyl itaconate.

Alternative Solvent System: Phenol/Diethyl Itaconate/SNI 53 / 17 / 30

Liquid enamel	Terebec MT 533 35N (reference enamel)	EP0052
Solvent System	Phenol / CA / SNI 39 / 28 / 33	Phenol / DEI /SNI 53 / 17 / 30
Solubility at RT	Clear	Clear
Solubility at 5 °C	Clear after 21 d	Clear
Dry content (1g/1h/180 °C, %)	32-34 %	33,97%
Viscosity (mPa.s , at 23 °C)	300 - 400	312
Theoretical Combustion Heat	22.413,85 (KJ/Kg)	23.084(KJ/Kg)

- Solvents adding conditions:
  - Phenol added at 190 °C stirred and maintained 30 min, then at 180 °C stirred and maintained 2 h, SNI and DEI added at 140 °C

Enamelled wire ** characteristics	Terebec MT 533 35N (reference enamel)	EP0052
Wire diameter (mm)	0,5 mm	0,5 mm
Coating thickness (mm)	Typical: 0,05 Specs: 0,046 – 0,067	0,05
Surface	Typical: O_2 - P_1 – R_0 Specs: O_2 - P_1 - R_1	O_2– P_0
Flexibility	Typical: 2/3 pass (@15%, 1D) Specs: 2/3 pass (@ 15%, 1D)	3/3 pass (@25%, 1D) 3/3 pass (@30%, 1D)
Tg δ (°C)	Typical: 200 °C Specs: 195,0 – 215,0 °C	200,2
Cut through (°C)	Typical: 390 °C Specs: ≥ 380 °C	370
Heat shock (1D, 30' at 220°C)	Typical: pass Specs: -	pass

** Enamelling conditions: VET 375, 1 mm, 55 m/min, G2, single coat.

Results :
- Surface in specs
- CT not in specs

- Conclusions and Next actions:
  - No further action on this SS

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Figure 63. EP052 varnish and enameled wire characteristics.

To summarize this big stream of datas, tables with the best alternative have been reported here below:

Summary of best performing Solvent Systems on 0,5mm wire

Batch No:	Solvent System	V(x) 23°C (cPs)	Dry content (%)	Cosmetics	Flex	Cut-t (°C)	Tan δ (°C)	HCV (KJ/Kg)
Standard PEI	**Phenol / CA /SNI 39/28/33**	300-400	33-35	*Slightly ruvid*	Passed at 15%	≥ 380	195,0 – 215,0	23.368
EP035	**Phenol / BA /SNI 38,3/ 41,7/ 20**	320	34,66	*Good*	Passed at 15% Passed at 20%	380	206	21.578
EP036	**Phenol / GVL /SNI 55/ 25 / 20**	370	34,72	*Good*	Passed at 15% Passed at 20%	380	205	20.250

Enamelling conditions: MAG HEL 4/5, 0.50mm, 42 m/min, G2, single coat.

Table 18. Summary of the best performing solvent on horizontal oven

Summary of best performing Solvent Systems on 1 mm wire

Batch No:	Solvent Syste	V(x) 23°C (cPs)	Dry content (%)	Cosmetics	Flex	Cut-t (°C)	Tan δ (°C)	HCV (KJ/Kg)
Standard PEI	**Phenol / CA /SNI 39/28/33**	800-900	38-40	*Good*	Passed at 15%	≥ 380	195,0 – 215,0	22.594
EP041	**Phenol / GVL /SNI 55/ 25 / 20**	880	39,67	*Slightly ruvid*	Passed at 15% Passed at 20%	390	204	22.250
EP046	**Phen / BA / SN100 50 / 20 / 30**	830	40,0	*Good*	Passed at 25% Passed at 30%	380	207,5	22.221
EP047	**Phen / BGA / SN100 60 / 10 / 30**	898	39,1	*Good*	Passed at 15% Passed at 20%	390	199,7	21.778
EP048	**Phenol /GVL/SNI 70 / 10 / 20**	890	38,36	*wavy*	Passed at 15% Passed at 20%	390	200	20.796
EP050	**Phenol / PDMM /SNI 60 / 10 / 30**	860	38,4	*Good*	Passed at 25% Passed at 30%	390	204	22.706

Enamelling conditions: VET 375, 1 mm, 55 m/min, G2, single coat.

Table 19. Summary of the best performing solvent on vertical oven

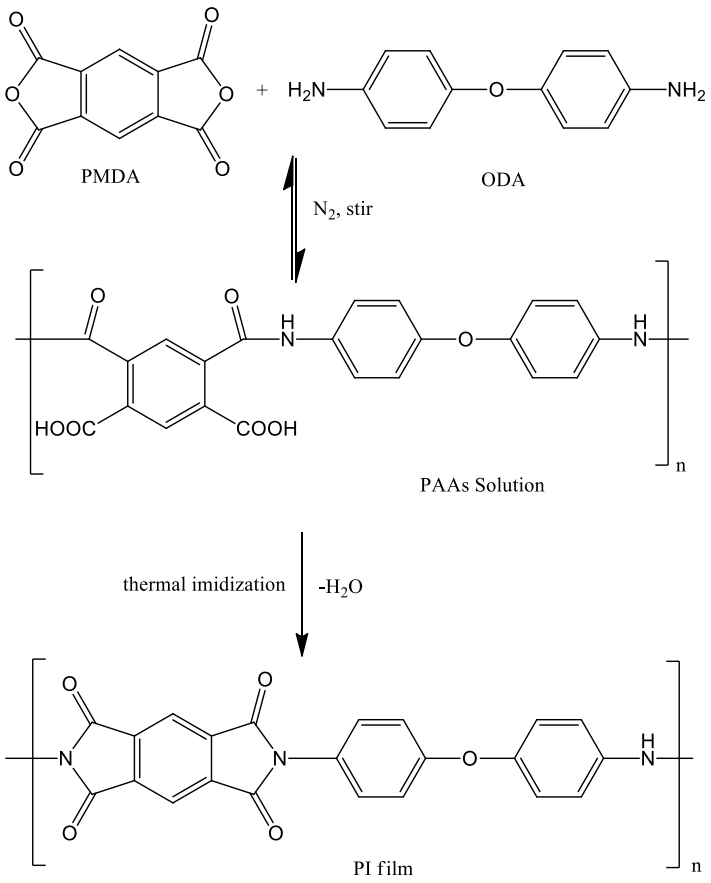
6.2 Conclusions

In a rapidly evolving world, having “second sources” for strategic raw materials and cost-effective and readily available (e.g.not bound to import issues) backup solutions is crucial to guarantee business continuity. This study explores alternatives to cresylic acids. Hansen solubility parameters were employed to identify potential solvents for testing, highlighting its value as a powerful tool that warrants further exploration. The proposed alternatives must effectively preserve both the product's characteristics and performance. Several substitutes were validated, including: γ-Valerolactone, Butyl Glycol Acetate, Proglyde DMM and Benzyl alcohol. While these alternatives demonstrate comparable effectiveness to the standard Solvent system (SS) in terms of properties, specific pricing details are not disclosed due to privacy considerations, nevertheless they have been considered among imposed boundaries to properly select candidates. It is important to note that raw material prices are subject to fluctuations driven by unpredictable geopolitical factors. As of now, the developed alternatives are similarly priced or even more economical vs reference, but future costs remain uncertain. Additionally, the choice of solvent and loading conditions can influence depolymerization phenomena, which should be carefully considered. To mitigate this issue, one solution is to perform solvent loading at a lower temperature (150°C) than reference process, or to use a solvent without reactive groups toward ester bonds under process specific conditions (eg. γ-Valerolactone or Proglyde DMM). An in-house synthesis was conducted to produce a completely bio-based solvent that is able, together with phenol, to solubilize the standard Polyester-imide. A step forward for this work could be to solubilize the PEI developed in the first work with the SS of the EP052.

7.1 Residual aromatic diamine determination in a polyamic acid solution

7.1.1. Introduction

Generally, an aromatic or aliphatic polyimide (PI) is produced by two step method: First step is polyamic acid (PAA) synthesis from dianhydride and diamine monomers through exothermic polycondensation reaction in a dipolar solvent (N, N dimethyl acetamide (DMAC), N, N dimethyl formamide (DMF), N-methylpyrollidone (NMP) etc.) and second step is imidization reaction which is applied after solvent elimination from PAA as seen in Scheme 23. High temperature resistance, mechanical and chemical stability, high glass-transition temperature (Tg), optical transmittance, low dielectric constant properties are characteristic for PI materials. All the mentioned properties of PIs can vary depending on chemical structure and macromolecular conditions such as molecular weight (MW), crystallinity or intermolecular forces. PI flms are used as thermal control coatings and a protective layer for electronic devices and space applications thanks to remarkable optical properties (transparency and low solar absorption and infrared emission), high thermal stability and wide service temperature (−300 – +300 °C), radiation resistance, enhanced electrical insulation (dielectric constant 3.4- 3.5), low density, toughness, flexibility, and high mechanical stability. In the context of scientific environmentalism, the study of the possible fate of polymeric materials at the end of their lifecycle takes on considerable importance, as it depends more on the residual monomer content than on the polymer chain itself. ODA and its salts are listed in Annex VI of Regulation (EC) No. 1272/2008 among the harmonized classified hazardous substances, being classified as carcinogenic 1B and mutagenic 1B. Its presence in a mixture at concentrations equal to or exceeding 0.1% w/w results in the classification of the entire mixture within the same hazard categories [148]. The high toxicity of ODA, together with its significant contribution to determining the physicochemical properties of the corresponding polyimides (PIs), highlights the need for accurate quantification of its residual content in polymeric materials throughout their entire lifecycle. To address this, a novel method for extracting and quantifying aromatic diamines in high thermal resistance polyamic acid (PAA) solutions has been developed. The accurate quantification of 4,4'-oxydianiline (ODA) in PAA solutions presents challenges due to the equilibrium between the monomer and the corresponding polymer. (Scheme 23)



Scheme 23. Industrial synthetic pathway for PIs production.

This system is prone to depolymerization under the influence of moisture and heat [149]. Consequently, improper sample preparation conditions can lead to an overestimation of the residual monomer content. Furthermore, the presence of the polymeric fraction and other interfering species can compromise the analysis and may even damage the analytical instruments. These factors highlight the essential role of the sample preparation step, in conjunction with the instrumental analysis, in achieving reliable results. To this end, the HPLC-MS/MS techniques was selected for the quantification of aromatic diamines. Here, we propose an accurate and fast analytical method to determine the residual monomer content in the precursor PAA solution, rather than in PI, permitting the evaluation of free ODA at the early stage of the production process increasing the overall sustainability of this class of powerful HPPs. In this study, we propose a precise and rapid analytical method to determine the residual monomer content in the precursor PAA solution, instead of the final PI. This allows for the evaluation of free ODA during the early stages of the production process, improving the overall sustainability of this class of high-performance polymers (HPPs).

7.2 Materials and methods

The 4,4'-oxydianiline (ODA) used in this study was provided by Elantas Europe S.r.l. and stored at 5 °C. HPLC-grade water was obtained using a Milli-Q system, while HPLC-grade methanol, DMSO, and formic acid were purchased from Sigma-Aldrich.

7.2.1. Sample preparation for HPLC-MS/MS analysis

Twenty-three samples of PAAs were provided by Elantas Europe S.r.l., 50 milligrams of each sample were dissolved in 2.5 mL of DMSO, yielding a clear solution without any visible signs of precipitation. The solution was then diluted 1:1000 using the mobile phase (MeOH/H_2O-Milli-Q, 50:50) and maintained in an ultrasonic bath for 30 minutes. Precipitated polymer was removed by centrifugation at 6000 rpm for 10 minutes. A portion of the supernatant was microfiltered through a 0.2 μm filter and injected into the HPLC-MS/MS system.

7.2.2. Liquid Chromatography-Tandem Mass Spectrometry (HPLC-MS/MS)

HPLC-MS/MS analyses were conducted using an Agilent 1290 Infinity Series HPLC system coupled to an Agilent 6420 triple quadrupole mass spectrometer (Agilent Technologies, Santa Clara, California, USA) equipped with an electrospray ionization (ESI) source operating in positive ionization mode. Separation was performed on a Purospher STAR RP C18 column (250 mm × 4.6 mm). The mobile phase was a 50:50 mixture of Milli-Q water and methanol, containing 0.1% formic acid, under isocratic conditions, with a flow rate of 0.8 mL/min. The injection volume was set to 2 μL, and the column temperature was maintained at 25 °C. In the ionization source, the drying gas temperature was 300 °C, the gas flow rate was 12 L/min, the nebulizer pressure was 40 psi, and the capillary voltage was 4000 V. Detection was carried out in multiple reaction monitoring (MRM) mode, using the most abundant product ion for quantification, while a minor product ion was used for qualification.

7.2.3. Optimization of the extraction method

The sample preparation process was designed to prevent the injection of the polymeric fraction into the HPLC while maximizing the recovery of residual ODA. The difference in solubility between the monomer and the polymer was a key factor in achieving a fast, simple, and effective extraction of ODA from the PAA solution. Both fractions are fully soluble in organic solvents such as NMP and dimethylsulfoxide (DMSO). Precipitation is a critical step in sample preparation, as a portion of the target analyte can become physically incorporated into the solid residue in an unpredictable manner, which may lead to reduced precision and accuracy. To mitigate this issue, polymer precipitation was performed in an ultrasonic bath for at least 30 minutes to ensure effective separation and recovery. The reproducibility of the extraction step was initially poor. To overcome this issue, a preliminary dissolution step was introduced using DMSO, a solvent capable of solubilizing both the polymeric fraction and the monomer. Precipitation of the polymer was performed only after the solution became clear and the sample was homogeneously dissolved. This was achieved using a 50:50 mixture of water and methanol, with the solution subjected to ultrasonic treatment for at least 30 minutes. The optimized procedure yielded improved precision and consistent results. HPLC-tandem mass spectrometry (HPLC-MS/MS) was selected as the most effective analytical technique, providing high sensitivity and specificity for the quantification of the target analyte.

7.3. Mobile Phase and detector optimization

Mass spectrometric detectors preclude the use of inorganic buffers, requiring the testing of various mobile phases. The best results were achieved with a 50:50 mixture of water and methanol, containing 0.1% formic acid, under isocratic conditions. The presence of formic acid in the mobile phase was essential to facilitate and maximize the formation of the ODA pseudo-molecular ion $[M+H]^+$. Collision energy was optimized to generate product ions at m/z 108, 93, 80, and 53. Based on their relative abundances, the transition from 201 to 108 m/z was chosen as the quantifier, while the transition from 201 to 80 m/z was selected as the qualifier [150].

7.4. Results and Discussions

The method was applied to several batches produced in the R&D Department of Elantas Europe S.r.l. The samples were prepared under different synthetic conditions, which cannot be disclosed due to confidentiality agreements. The monomer content exhibited significant variability, ranging from 0.01% to 2.4% (Table 20). The data obtained was essential for optimizing the PAA synthetic pathway on both pilot and industrial scales, reducing the residual monomer concentration to a minimum. Despite the specificity of tandem mass spectrometry, the analysis of real samples revealed an additional peak at a higher retention time, which responded to both qualitative and quantitative transitions (Fig. 64). This suggested the presence of dimers or oligomers that were not fully precipitated during the sample preparation. Under the optimized chromatographic conditions, these species were easily separated from the monomer. It is hypothesized that these species contributed to the generation of free ODA within the ionization source, resulting in signals indistinguishable from the actual residual monomer. In this case, chromatography remains the only method to differentiate between the two contributions, with the latter being considered an artifact of the instrument.

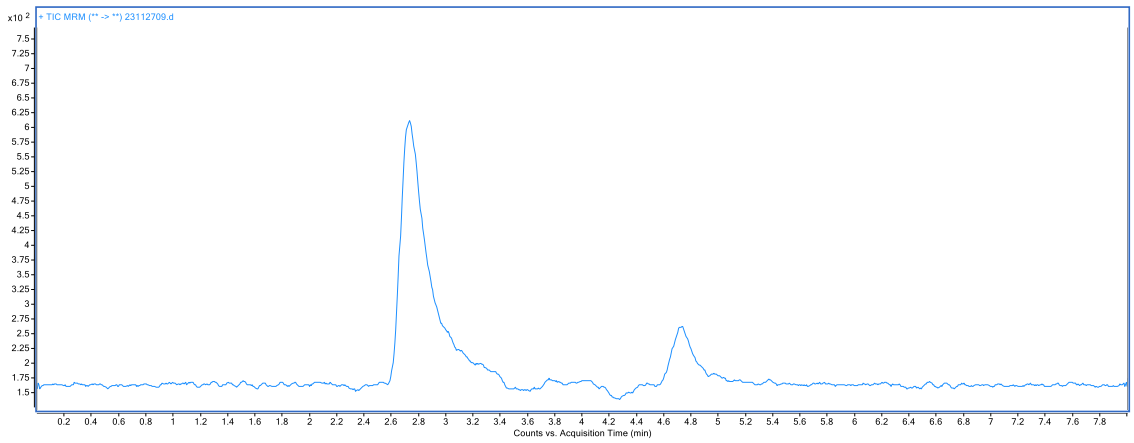


Figure 64. HPLC-MS/MS chromatographic profile of sample of PPA.

Sample	% ODA	Std. Dev. %
PAA 1	0,080	3,6
PAA 2	2,463	4,6
PAA 3	0,172	0,2
PAA 4	1,052	0,3
PAA 5	1,127	3,2
PAA 6	0,109	1,0
PAA 7	0,233	5,0
PAA 8	0,075	0,5
PAA 9	0,282	1,0
PAA 10	0,073	3,3
PAA 11	0,099	9,7
PAA 12	0,100	4,6
PAA 13	< LOD	
PAA 14	0,181	20,5
PAA 16	0,109	1,8
PAA 17	0,108	23,9
PAA 18	0,020	28,35
PAA 19	0,010	10
PAA 20	0,020	2,35
PAA 21	< LOD	
PAA 22	0,010	18,6
PAA 23	0,020	4,6

Table 20. PAA sample analyzed.

7.5 Conclusions

Polyimides (PIs) are considered high-performance polymers (HPPs) due to their superior chemical and physical properties, as well as their stability even under severe conditions of use. These characteristics, resulting from the presence of aromatic groups, make their replacement in specific applications challenging. Consequently, enhancing the sustainability of PIs can be achieved by improving recyclability and minimizing the environmental impact across their entire life cycle. In both cases, it is essential to reduce or eliminate residual monomers, particularly when they are classified as toxic substances. Achieving these goals requires the availability of effective and accurate analytical methods capable of quantifying residual monomer content from the early stages of polymer production. In this study, we developed a new, fast, and precise analytical method for determining residual aromatic diamines, such as ODA, in PAA solutions, which serve as precursors to PIs. The application of the developed method to real samples has facilitated the optimization of PI synthesis, enabling a reduction in the residual monomer content. This enhancement improves the sustainability of PIs in multiple ways: by reducing adverse impacts on human health and the environment throughout the polymer life cycle, ensuring compliance with current regulations, and enabling the safer use of these difficult-to-replace high-performance polymers.

8.1 Brief introduction to conformal coatings

The following work, including bibliographic research, tests and syntheses, was carried out in Germany, specifically at the Hamburg site of Elantas GmbH, with the support of Dr. Simon Rost. Conformal coatings are polymeric or other protective materials used to shield electronic assemblies from a wide range of life-cycle contaminants. These coatings provide high insulation levels and exhibit resistance to numerous solvents and harsh environments encountered throughout the product's lifespan. Conformal coatings also serve to immobilize various particulates on the assembly surface and act as protective barriers for the board’s components. (Figure 64)

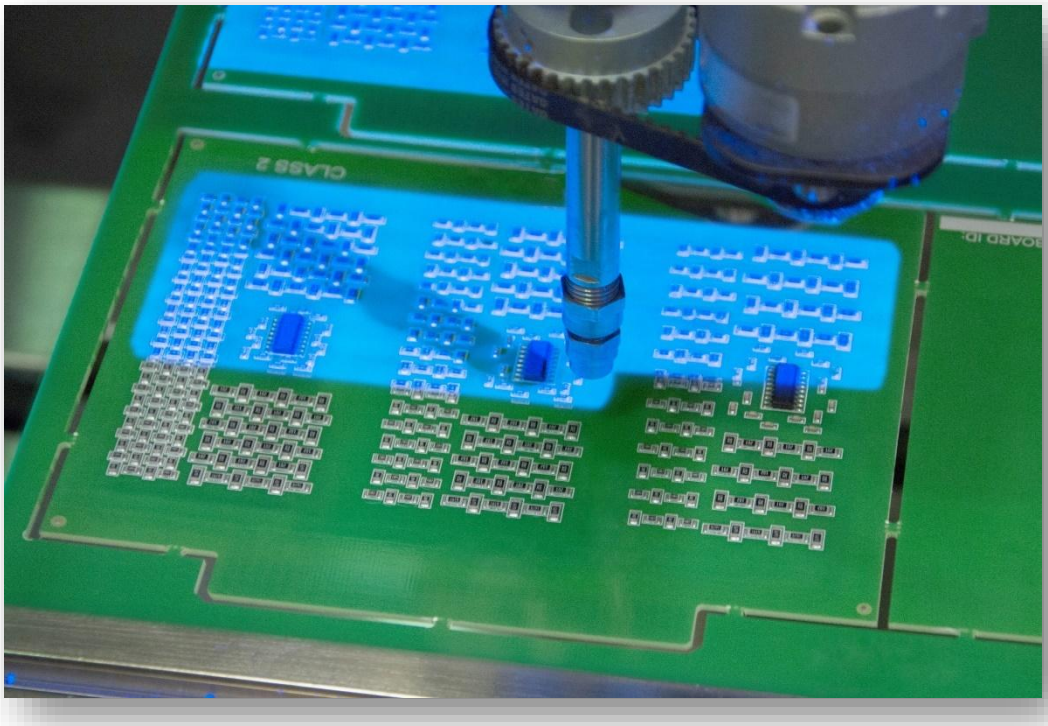


Figure.65 Automated spray technology.

Their moisture and humidity resistance helps reduce risks associated with leakage currents, "crosstalk," electrochemical migration (ECM), conductive anodic filament (CAF) formation, dendrite growth (Figure 65), and arcing. These issues are becoming increasingly critical due to shrinking component sizes, reduced pitch and circuitry spacing, thinner laminates, higher operating voltages, and the increasing frequency of signal transmission. The shift toward

compact electronics designed for outdoor or harsh environments further underscores the importance of conformal coatings. Once a printed circuit assembly (PCA) is fully assembled, tested, and inspected, environmental protections are then applied to safeguard its functionality. [151]

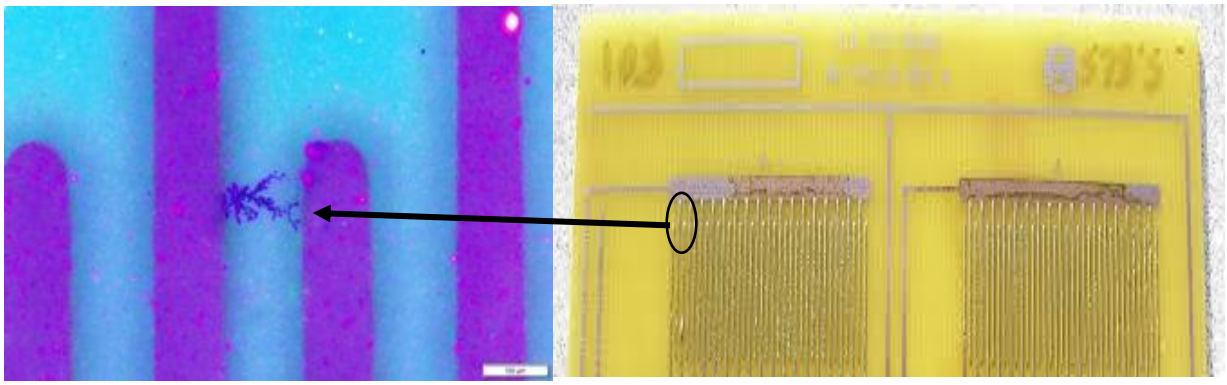


Figure 66. Zoom of a dendrite growth.

Conformal coating materials are commonly classified [152] into at least four groups based on their chemical composition: epoxy (ER), acrylic (AR), urethane (UR), and silicone (SR). Urethane and acrylic coatings are typically based on liquid, often solvent-based materials. A fifth category is associated with distinct processes for particular applications. Selecting the appropriate material provides properties tailored to the application. For instance, the abrasion resistance of a rigid material like epoxy differs greatly from that of a compliant material like silicone. Urethane is unsuitable for repairs but withstands humid environments and offers excellent chemical resistance. In contrast, acrylic lacks solvent resistance but does resist humidity and is easily repairable. Within any given chemistry, such as acrylic [153], factors like the curing agent and the type of monomer are important in achieving desired properties, such as an effective humidity barrier. Silicone coatings offer higher temperature resistance but can act as a product contaminant. A new advancement in conformal coating chemistry combines acrylic and urethane chemistries. This material is distinct in two keyways: it is solvent-free and features UV curing properties, despite also requiring thermal curing. The UV curing step provides immediate protection and allows for instant handling, streamlining the industrial process. However, the dual-cure process requires humidity and needs a couple of days to achieve full curing and adhesive strength. Controlling layer thickness is crucial for managing humidity diffusion and reducing the cycle time in the dual-cure process.[154]

8.1.1. Conformal Coating applications methods

Conformal coatings can be applied using various methods, including:

- **Manual Coating with a Brush**: This method enables precise application, without setup time or high equipment costs. It is commonly used for touch-ups on thin spots in previously coated areas, for coating replaced components, and for accessing areas where spray or automatic nozzles cannot reach. It's especially effective for smaller, unique items but can be highly variable.
- **Dip Coating**: Ideal for coatings with a long pot life, such as solvent evaporation-cured coatings and one-part materials, this method involves immersing the board in the coating solution. A long pot life reduces waste since unused coating remains in the dip tank. Dip coating is not suited for layering thicker coatings with acrylics, as solvents in the bath can dissolve prior layers, and any uncoated areas should be completely masked. Boards can be partially dipped if needed.
- **Hand Spray Coating**: This technique is suitable for all liquid coating types. The board is sprayed multiple times, rotating it 90° with each pass to ensure even coverage. Care is needed to avoid shadowing by tall components, which can block spray from reaching lower-profile parts. A witness strip can be sprayed simultaneously to measure coating thickness. Controlling viscosity is crucial to reduce bubbles, cobwebbing, and variations in thickness.
- **Automatic Conveyor Spray Coating**: High-volume applications benefit from semi-automatic spray machines, which provide consistent in-line coating by spraying the board as it moves along a paper-covered conveyor. Rotating or reciprocating spray heads ensure full-width coverage but may struggle with shadowing, as individual areas cannot be specifically targeted. Complete masking of areas to be left uncoated is essential. After one side is coated, the board can be partially or fully cured, then flipped for coating on the opposite side.
- **Selective Robotic Coating**: This method employs a robotic nozzle to apply coating precisely to certain areas of the board, offering high accuracy and repeatability. This selective approach is ideal for complex assemblies with sensitive components that may not need coating.

Each application method has distinct advantages, from the precision of manual brushing and robotic nozzles to the efficiency of automated systems for high-volume production. The choice of method depends on factors like the desired thickness, coating type, volume, and specific board requirements. In this case, study the method that is going to be used will be the **Selective Robotic Coating**.

8.1.2. Curing methods in conformal coatings

Room Temperature Vulcanization (RTV)

Some silicone-based coatings use the RTV curing process, which requires moisture from the environment to complete the cure. Humidity control is essential, as curing in a dry oven can lead to improper or incomplete curing.

Heat Cure

Oven-curable systems rely on an extended baking period, which can range from 15 minutes to several hours, to fully cure. Thermally activated systems need elevated temperatures to initiate curing, while thermally accelerated systems can eventually cure at room temperature but are typically baked to speed up the process and enhance material properties. Generally, higher temperatures result in faster curing and a harder final material. However, it's crucial to consider any thermally sensitive components that may be affected if high temperatures are used to accelerate the cure.

UV Cure

UV-curable materials are common in high-volume production. Assemblies pass through a booth with high-intensity UV lamps immediately after coating, allowing for rapid curing so they can move to the next assembly stage, such as coating the opposite side. UV-curable materials do not fully cure beneath components, where the coating isn't exposed to light. For this reason, most UV-curable coatings include a secondary curing mechanism, such as heat or moisture curing, to ensure the complete curing of the coating in a single baking or moisture step, or in ambient conditions within the final product. Since different coatings respond to specific UV wavelengths, coordinating the UV light source with the coating supplier is essential.[155]

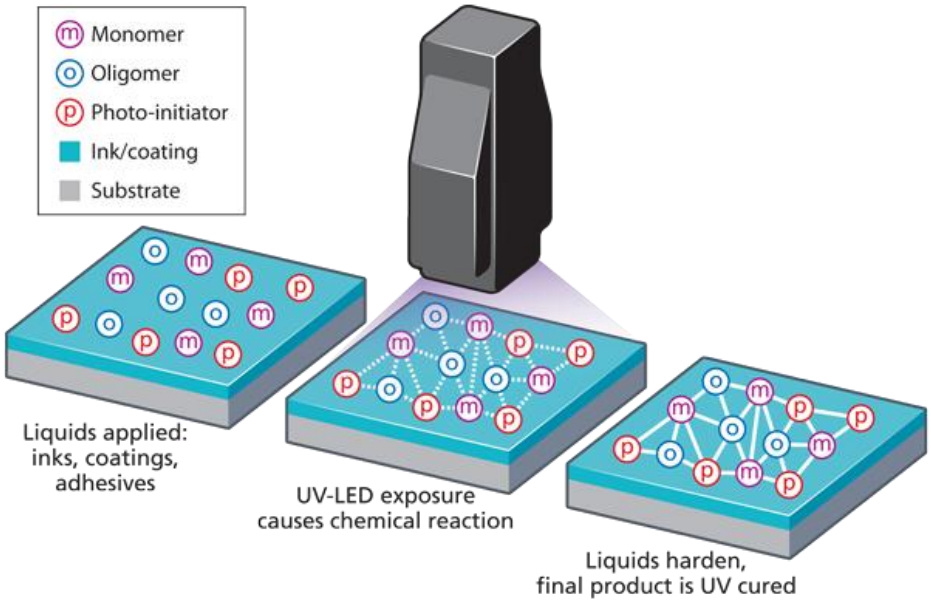


Figure 67. UV-curing step.

8.1.3. SIR test

High-reliability electronics are particularly vulnerable to failure when operating in harsh environments, such as high temperatures and high humidity. These risks are amplified by ionic contaminants from the manufacturing process that remains on the substrate surface. This combination of moisture, electrical potential (voltage bias), and ionic residues creates a high risk of electrochemical failures, such as dielectric breakdown and current leakage. These issues can lead to performance degradation or even complete hardware failure, making it crucial to ensure proper cleaning and insulation during manufacturing to mitigate these risks. [156] The Surface Insulation Resistance (SIR) test is a commonly used standard for evaluating the effects of assembly materials and manufacturing processes (e.g., residual materials) on hardware operating in hot and humid environments. (Fig. 67) [157]This test measures the change in current overtime between two electrical conductors, providing insight into inadequate electrical insulation caused by the breakdown of insulating materials such as solder masks or conformal coatings. SIR testing involves applying a voltage to conductors on a printed wiring board (PWB) and measuring the returning current. The insulation resistance (IR) between non-

common conductors is then calculated using Ohm's Law. By simulating harsh conditions—typically involving elevated heat and/or humidity—the SIR test helps ensure the reliability of electrical isolation in challenging environments.[156]

Figure. 68 Temperature Humidity Test Chamber

8.2. Materials

All reagents and solvents were purchased from commercial suppliers and used as received, without additional purification unless specified otherwise. The quality of the compounds used was verified by the internal Quality Control (QC) laboratory. Depending on the enameling oven used, there will be a bigger or smaller batch of synthesis. All syntheses were performed in a 2-liter round-bottom glass vessel fitted with a five-necked glass head and a mechanical stirrer, with heating provided by a mantle.

8.3. Instruments and Methods

8.3.1 Gel Permeation Chromatography

GPC analyses were conducted on a *Thermo Knauer* instrument, assembled with a Smartline 1000 pump and a Smartline 2300 differential refractometric detector. The column setup included three columns in series: Agilent™ PLgel 10^4Å, 7.5 x 300 mm, 10^3Å, 7.5 x 300 mm and 500Å, 7.5 x 300 mm all with particle sizes of 5 μm. The eluent was a 70:30 solution of THF and DMF. Both the eluent and column compartment were maintained at 33°C. Prior to analysis, resin samples were dissolved in the appropriate eluent solution at a solid concentration between 30 and 50 mg/mL depending on the dry content of the sample. Samples were filtered through a 0.45 μm PTFE syringe filter from Agilent™ before injecting 100 μL of each filtered sample into the instrument loop.

8.3.2 Infrared Spectroscopy

Infrared spectroscopy was performed using *a Thermo Scientific Nicolet iZ10*, equipped with a Smart Omni-transmission accessory with KBr support and a diamond crystal ATR module. Spectra were recorded over a wavenumber range from 450 to 4000 cm^{-1}, with an accumulation of 16 repeated scans for both background and sample analyses. Spectral data were processed and absorption band wavenumbers were calculated using *Thermo Scientific™ OMNIC™ Series FT-IR* software.

8.4 Results and Discussions-Conformal Coating Project #1

It is necessary to develop an in-house synthesis of urethane acrylates and isocyanate prepolymers, since they are used in UV coatings. Today the company is buying a product that we are going to call **EP100,** the problem arises when considering the increasing demand of this product compared to the the availability of this product, very limited. The company uses the **EP100** as a binder in a formulation for the conformal coating, the actual demand of this product is 16 tons/a. It is needed to synthesize a product with similar properties.

Hereafter we have a screen shot of the SDS of the material:

EP100 is an undiluted isocyanate aliphatic functional urethane acrylate designed for use in UV/EB coatings and in two component dual cure systems for coatings on wood, plastic and metal.

SPECIFICATIONS

Color, Apha	max. 150
NCO content, %	7.0 - 8.0
Viscosity, 23°C, mPa.s	12000 - 20000

TYPICAL PHYSICAL PROPERTIES

Density, g/cm³ at 20°C	1.10
Flash point, °C	> 100
Functionality, acrylate groups	1
Functionality, NCO groups	2.2

Figure 69. EP100 Material Data Sheet.

Since this product has two types of curing: moisture curing and UV, they depicted in the "typical physical properties" (Figure 68) the NCO and the acrylate groups functionalities (end capping), this is the number average groups of those chemical functions as end groups per molecule of **EP100**. An FT-IR, GPC, ^{1}H-NMR, ^{13}C-NMR analysis has been done to characterize the material.

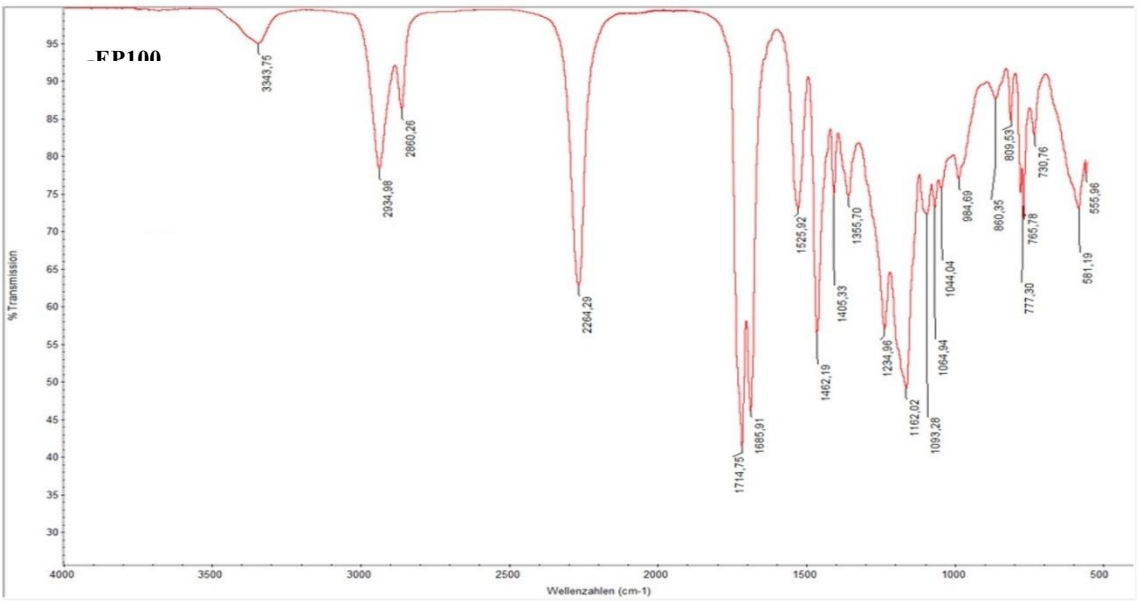
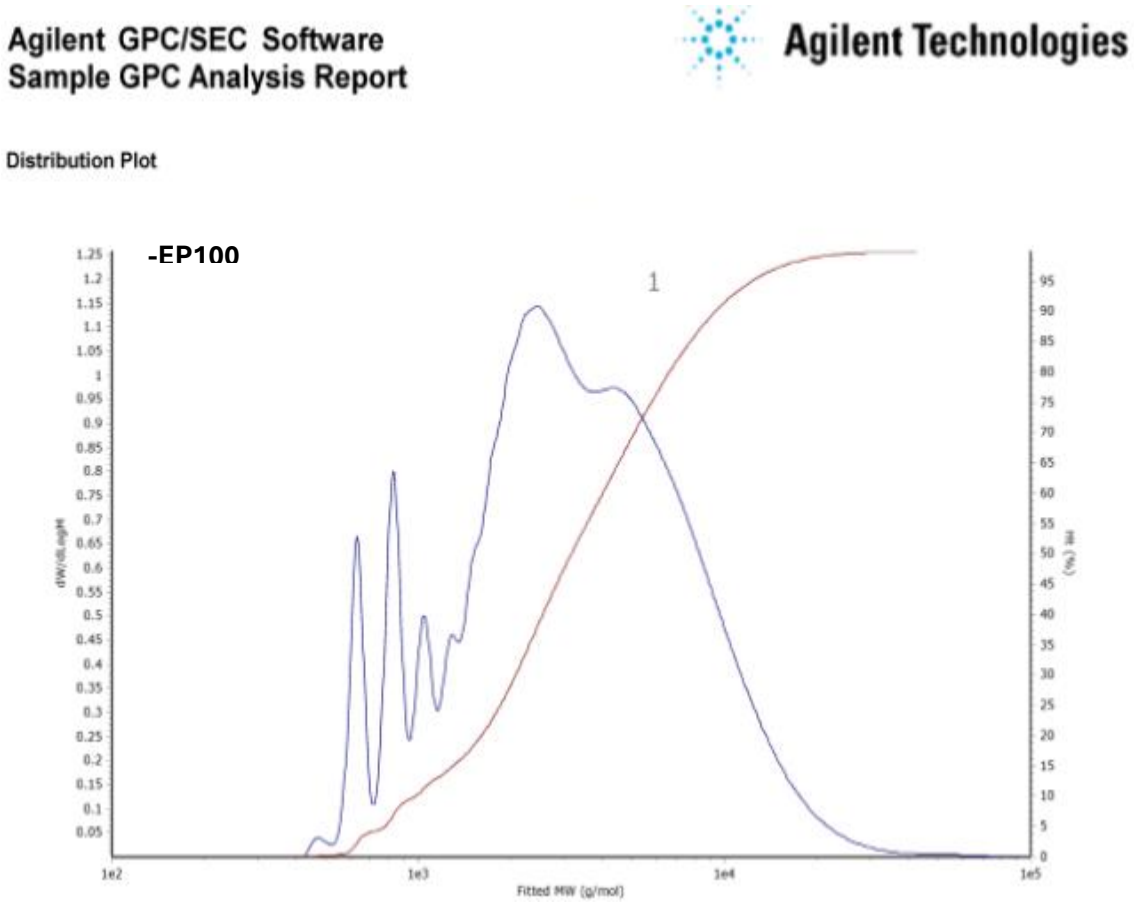


Figure 70. FT-IR analysis of EP100.

The stretching vibration of the carbonyl (C=O) group in the ester appears as a peak at 1715 cm^{-1}. Additionally, the stretching vibration of the C–O bond within the HEMA ester group produces an absorption peak at 1162 cm^{-1} [158], the characteristic absorption peak of the -NCO group was detected at 2264 cm^{-1}.[159] The N-H stretching region of the spectra of these urethanes shows a single 3343 cm^{-1} band.[160] In order to undestrand the distribution of molecular weight a GPC analysis has been done.



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	2452	2285	4495	8697	16771	7890	1.967

Figure 71. GPC analysis of EP100.

NMR Characterization: EP100

^{1}H NMR: (500 MHz, $CDCl_3$) δH = 8.60 (m), 6.43, 6.43- 6.38 (m), 6.15-6.10 (m), 5.85- 5.82 (t, triplet), 4.70 (s, broad), 4.17-4.14 (m) , 4.06-4.04 (t, triplet), 3.88-3.83 (m), 3.71- 3.70 (m),

3.30-3.27 (m), 3.145 (m), 2.31-2.28 (m), 1.67-1.59 (m), 1.59-1.48 (m), 1.41-1.32 (m), 1.27-1.25 (t, triplet).

^{13}C NMR: (125 MHz, $CDCl_3$) δC = 173.70, 173.68, 173.54, 156.85, 156.44, 154.54, 149.09, 131.32, 131.03, 122.07, 43.73, 43.02, 43.00, 42.98, 42.95, 40.94, 40.54, 34.29, 34.25, 34.18, 31.30, 31.28, 31.21, 30.05, 29.94, 29.61, 29.57, 29.18, 29.13, 28.87, 28.66, 28.48, 27.81, 27.77, 26.69, 26.50, 26.44, 26.42, 26.37, 26.36, 26.27, 26.23, 26.20, 25.73, 25.66, 25.60, 24.77, 24.71, 24.60.

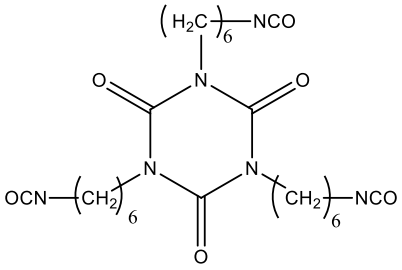
To get a PUA it is needed to react a poly-isocyanate with a hydroxy acrylate, this is done in presence of a catalyst (DBTL), a reactive solvent that is used to lower the viscosity and to have a homogeneous solution. Since SIR tests can take up to three months, the goal is to synthesize different structures and analyze them together, allowing me to complete all testing within my six-month period abroad. When the batch number is red, it indicates that the product will undergo SIR testing.

Batch No	*DEMSODUR N3300 (mol)*	*HECLA (mol)*	*Phenoxy Ethyl acrylate (%)*	*ME HQ (%)*	*CATALYST (%)*	*Viscosity mPas at 23°C*	*Application Batch*
EP22	***0,2***	***0,2***	***30***	***0,035***	***0,03 DBTL***	***1671 mPs***	***EP31, EP32***

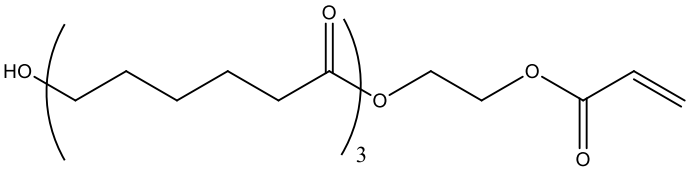
Table 21. Molar content and results of EP22.

The reagent used in this synthesis are reported here below:

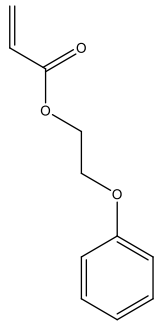
DESMODUR N3300



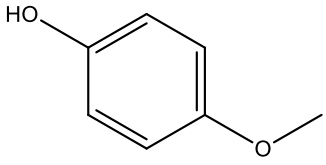
HECLA (Hydroxycaprolactone acrylate)



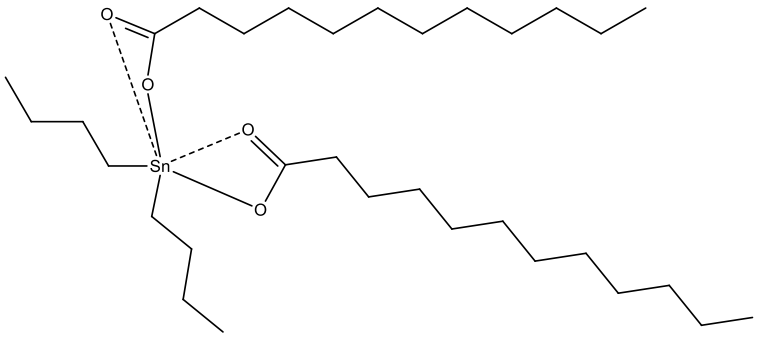
Phenoxyethyl Acrylate



MEHQ (4-Methoxyphenol)



DBTL (Dibutyltin dilaureate)

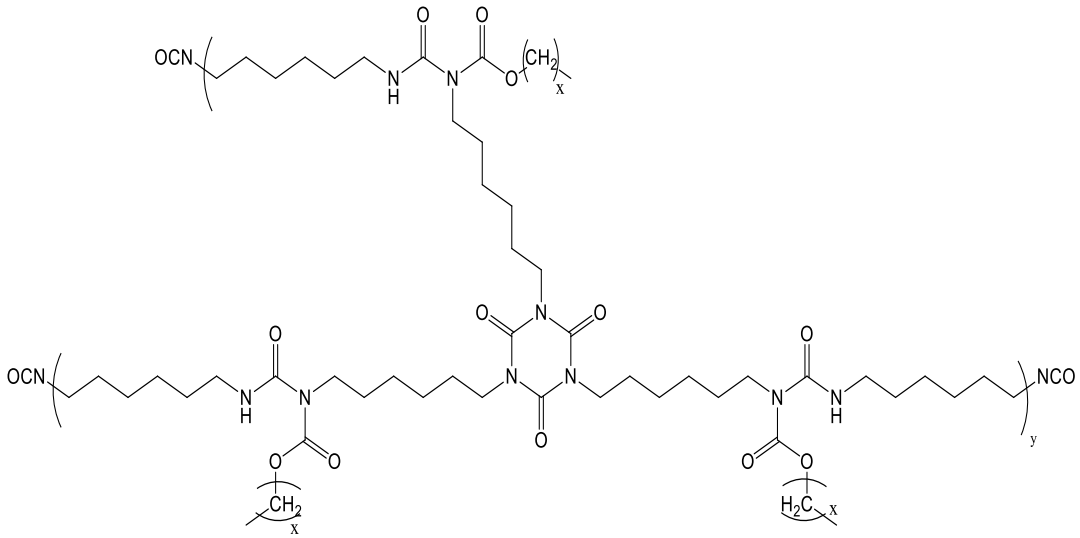


Scheme 24. Chemical structures of EP031 and EP32 reactants.

Batch No	*BASONAT HA 3000 (mol)*	*HECLA (mol)*	*Phenoxy Ethyl acrylate (%)*	*ME HQ (%)*	*CATALYST (%)*	*Viscosity mPas at 23°C*
EP20	***0,2***	***0,2***	***30***	***0,035***	***0,03 DBTL***	***625 mPs***

Table 22. Molar content and results of EP20.

- *BASONAT HA3000*



Scheme 25. Idealized BASONAT HA3000 structure.

Since the FT-IR spectrum of this PUA is very similar to the **EP100**, the BASONAT HA 3000 has been selected as starting polyisocianate prepolymer.

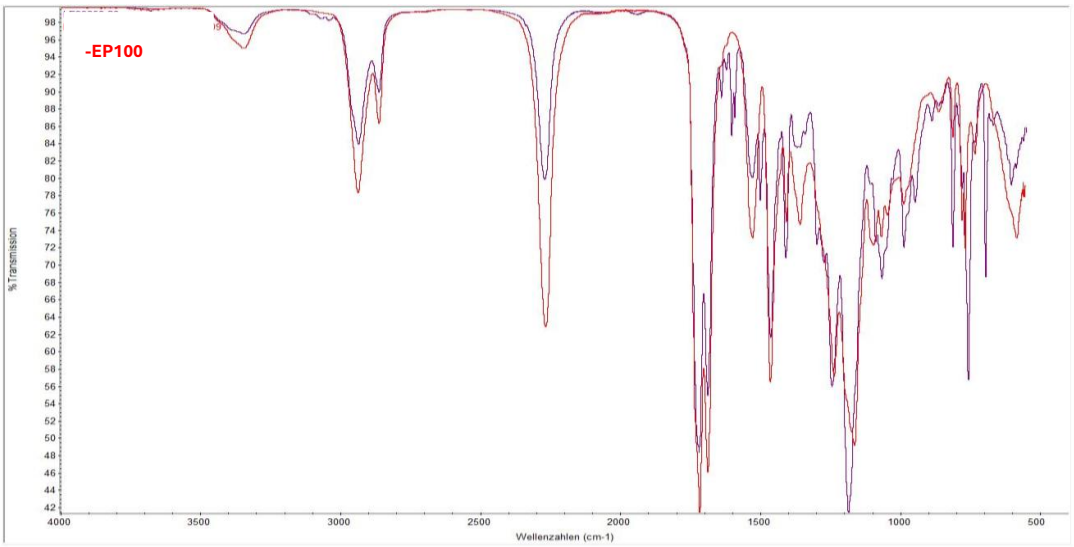


Figure 72. FT-IR Comparison in red EP100 in purple EP20.

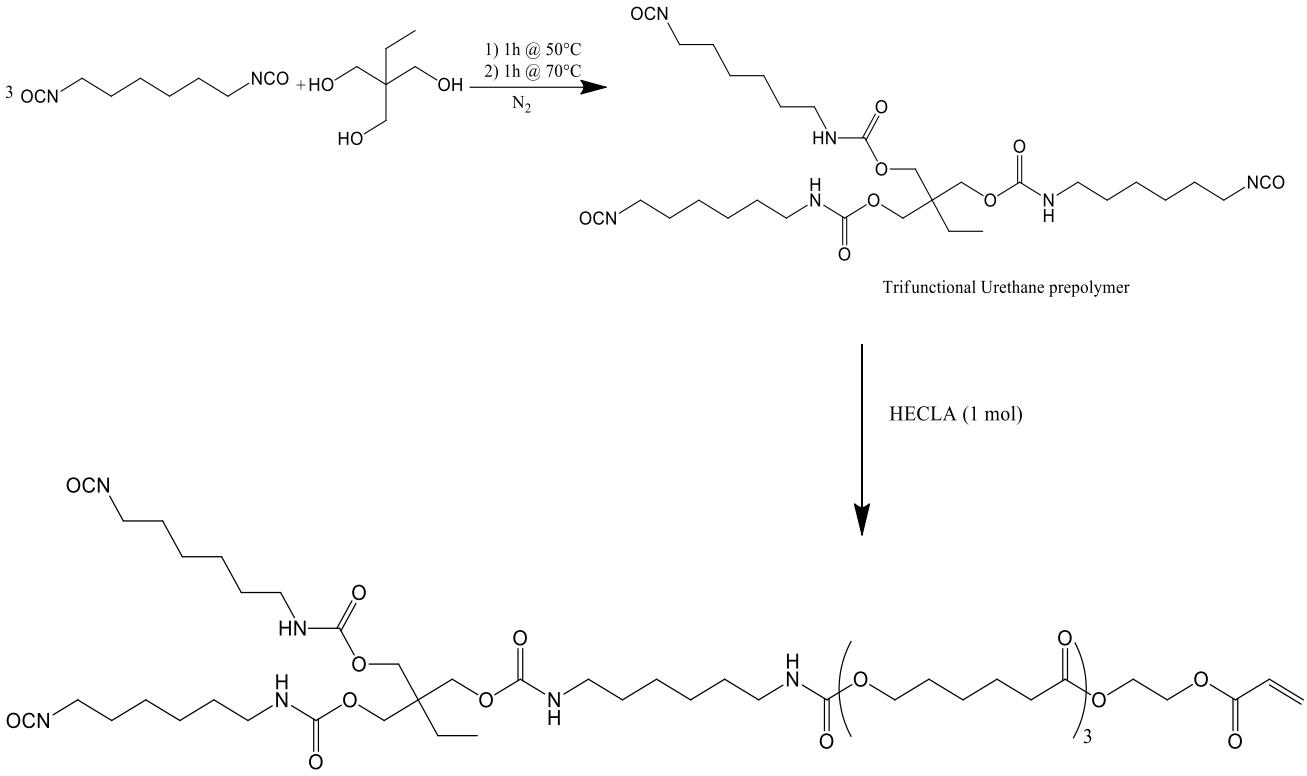
The reason for using HEMA (hydroxyethyl methacrylate) is that it is one of the most widely used hydroxy acrylates on the market. Given that the previous FT-IR spectrum of the PUA synthesized with BASONAT HA 3000 (Figure 71) closely resembled that of EP100, we decided to focus the efforts on this synthesis. However, as shown in the table, the synthesis proved to be non-reproducible and underwent gelation. Therefore, we reverted to the synthesis starting with HDI while reviewing the literature for a possible explanation of this behavior.

Batch No	Basonat HA3000 (mol)	HEMA (mol)	Phenoxyethyl acrylate (%wt)	MEHQ (%)	CATALYST %	Viscosity mPas at 23°C
EP24	**0,25**	**0,249**	**30**	**0,035**	**0,03 DBTL**	**GEL**
EP26	**0,25**	**0,249**	**30**	**0,070**	**0,03 DBTL**	**GEL**
EP27	**0,25**	**0,249**	**30**	**0,14**	**0,03 DBTL**	**GEL**
EP29	**0,25**	**0,249**	**30**	**0,14**	**0,01 DBTL**	**GEL**
EP30	**0,25**	**0,249**	**30**	**0,14**	**0**	**GEL**
EP33	**0,2**	**0,2**	**30**	**0,14**	**0,1 DABCO**	**GEL**
EP34	**0,2**	**0,2**	**30**	**0,35**	**0,05 DABCO**	**GEL**

Table 23. Basonat HA300 tests.

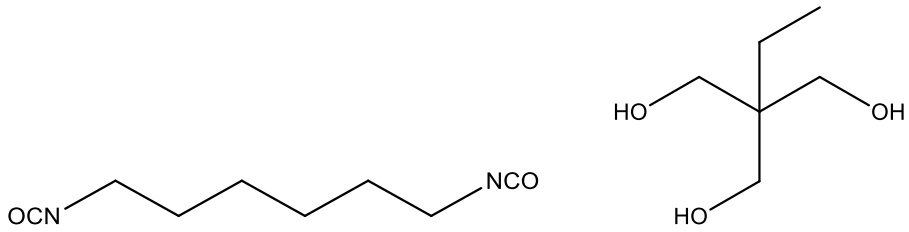
Batch No	HDI (mol)	TMP (mol)	HECLA (mol)	Phenoxyethyl acrylate (%)	MEHQ (%)	CATALYST (%)	Viscosity mPas at 23°C	Application Batch
EP35	**0,9**	**0,3**	**0,3**	**38,7**	**0,063**	**0,015 DBTL**	**7204 mPas**	**EP42**

Table 24. Molar content and results of EP35.



Scheme 26. EP35 reaction scheme.

Hexamethylene diisocyanate (HDI) TMP (trimethylolpropane)



Scheme 27. Chemical structures of EP035's reactants.

After conducting bibliographic research, several patents were identified that utilize benzoyl chloride or polyphosphoric acid as stabilizers for polyurethane (PUA) prepolymers.[161] These stabilizers help mitigate issues caused by unreacted polyols, moisture, or bases, which can interact with the isocyanate (NCO) functionality and trigger chain reactions, potentially leading to gelation of the system. To evaluate these claims experimentally, I carried out the EP36

synthesis. While the product remained in its liquid state, it was divided into two separate flasks. To one of these, two drops of pure benzoyl chloride were added for comparison.

Batch No	Basonat HA3000 (mol)	HECLA (mol)	Phenoxyethyl acrylate (%)	MEHQ (%)	CATALYST %
EP36	***0,2***	***0,2***	***30***	***0,35***	***0,05 DABCO***

Table 25. Molar content and results of EP36.

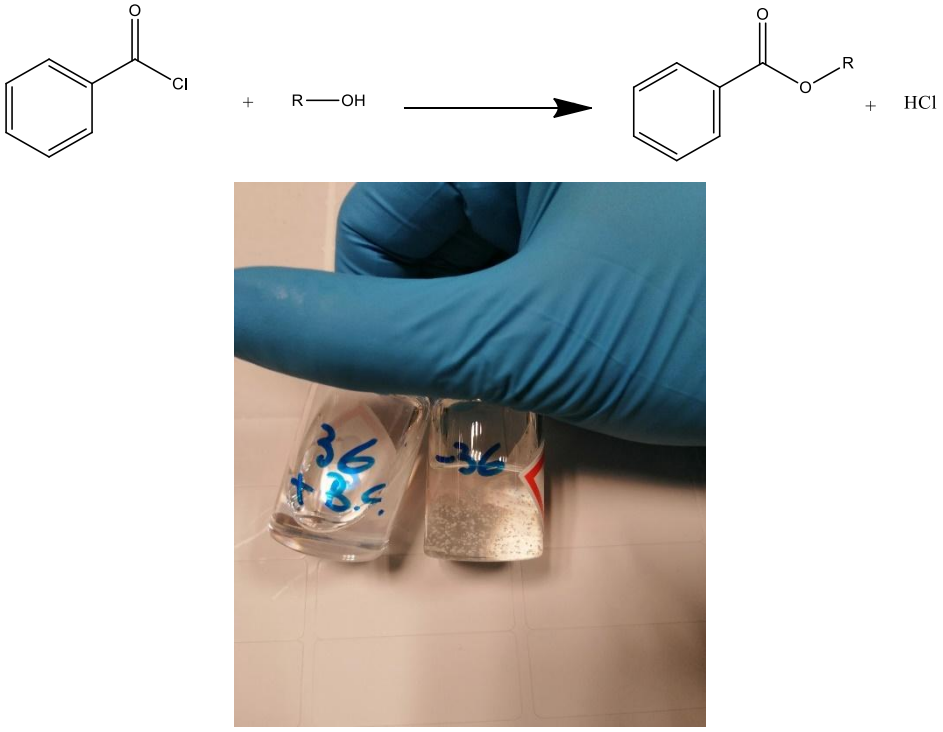
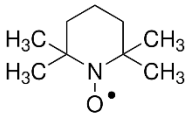


Figure 73. Gelation results on 36+Benzoyl Chloride (no gel, left) and 36 (gel, right)

Reproducing the previous synthesis using Basonat HA3000 (EP34), I modified the formulation by changing the photo inhibitor to TEMPO and introducing $Zn(Oct)_2$ as the catalyst. According to scientific literature, $Zn(Oct)_2$ is considered a weaker catalyst for PUA synthesis in terms of conversion efficiency. Despite this, the batch exhibited no signs of gelation. (Figure 73)

Batch No	*Basonat HA3000 (mol)*	*HEMA (mol)*	*Phenoxyethylacrylate (%)*	*TEMPO (%)*	*CATALYST %*	*Viscosity mPas at 23°C*	*Application Batch*
EP37	***1***	***1***	***31,8***	***0,04***	***0,1 Zn(oct)2***	***309 mPas***	***EP43***

Table 26. Molar content and results of EP37.



- TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl)

Scheme 28. Chemical structures of TEMPO.

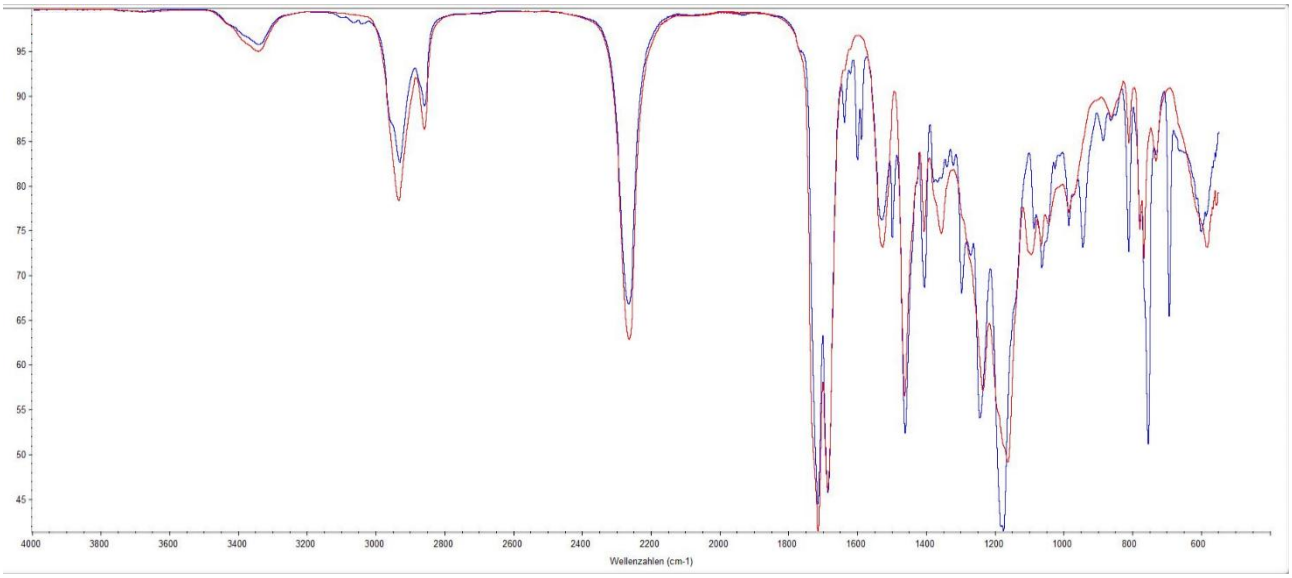


Figure 74. FT-IR overlay of EP37 and EP100.

To create a product incorporating biobased material, a promising molecule, ricinolein, was identified. Ricinolein, the primary component of castor oil, is a triglyceride of ricinoleic acid (Figure 75). This molecule is particularly notable due to its structure, which contains three hydroxyl groups and three unsaturations. These functional groups provide reactive sites suitable

for both urethane synthesis and UV curing, making ricinolein an excellent candidate for biobased applications.

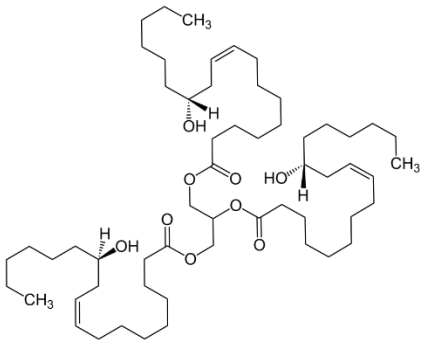


Figure 75. Chemical structure of Ricinolein.

Batch No	*HDI (mol)*	*Castor Oil (mol)*	*HECLA (mol)*	*Lauryl acrylate (%)*	*MEHQ (%)*	*CATALYST (%)*	*Results mPas*	*Application Batch*
EP40	***3***	***1***	***1***	***30,4***	***0,063***	***0,015 DBTL***	***1332***	***EP45***

Table 27. Molar content and results of EP40.

Batch No	*HDI (mol)*	*Castor Oil (mol)*	*Phenoxyethylacrylate (%)*	*MEHQ (%)*	*CATALYST (%)*	*Results mPas*	*(NCO/ACRY)*
EP52	*3*	*1*	*38,7*	*0,046*	*0,015 DBTL*	*1522*	*3/0*

Table 28. Molar content and results of EP52.

Batch No	*EP52 (mol)*	*HECLA (mol)*	*Phenoxyethylacrylate (%)*	*Results*	*(NCO/ACRY)*	*Application Batch*

EP53	*2.5*	*0,5*	*38,23*	*2071 mPs*	*2,5/0,5*	*LF99350-53*

Table 29. Molar content and results of EP53.

Batch No	*LF99350-52 (mol)*	*HECLA (mol)*	*Phenoxyethylacrylate (%)*	*Results*	*(NCO/ACRY)*	*Application Batch*
EP54	*2.0*	*1.0*	*38,23*	*2809 mPs*	*2.0/1.0*	*LF99350-54*

Table 30. Molar content and results of EP54.

The final NCO/acrylate ratio can be adjusted to tailor the product for either enhanced UV curability or improved moisture curability. This adjustment is evident in the IR spectrum, where changes in the NCO band (2260 cm^{-1}) can be observed. Specifically, the NCO band decreases in intensity (red spectrum) for a 2:1 NCO/Acrylate ratio compared to the blue spectrum for a 2.5:0.5 NCO/Acrylate ratio. This demonstrates how varying the ratio affects the available reactive groups and, consequently, the curing behavior. (Fig 76)

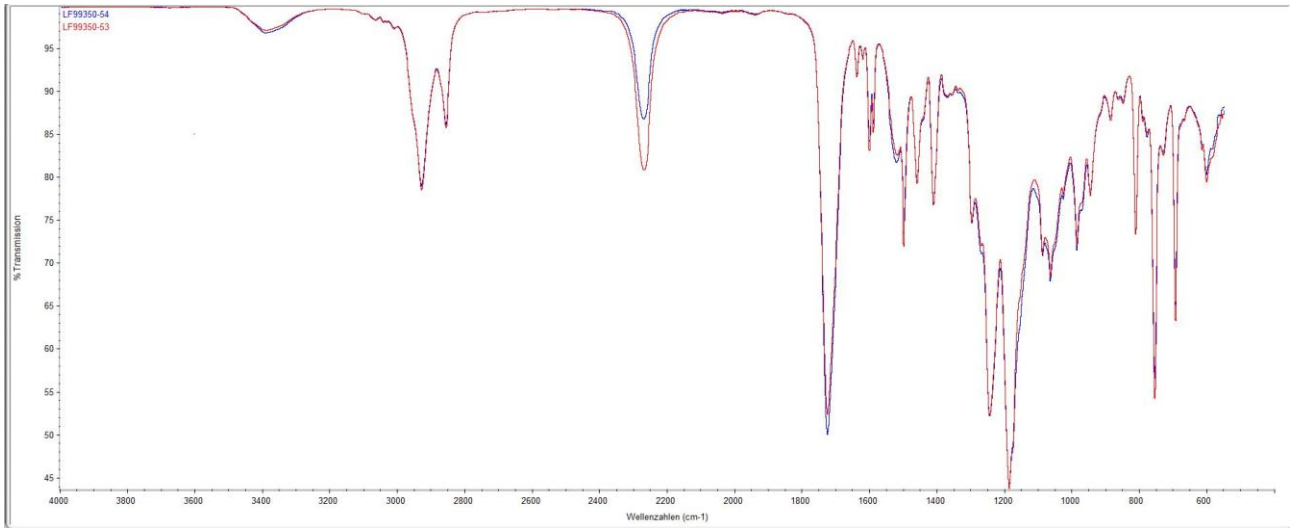


Figure 76. FT-IR overlay of EP53 and EP54.

It's important to clarify that the synthesized polymers listed in the tables all come to application batches. This means that the synthesized polymer has been mixed with a series of other compounds to produce the final product. At the Elantas Hamburg site, they develop specific formulations for each product they sell. To ensure an accurate comparison between my product and the standard one, I recreated the formulation of PT4700 (Figure 76), a commercial product made by Elantas Hamburg. In this formulation, EP100, the material I need to emulate, is used as the binder.

8.5. Conclusion- Conformal Coating project #1

The results of the SIR test are summarized below. The legend includes not only the newly developed products but also two standard products that the company typically sells. These standard products represent different formulations using the same binder, EP100. The data show

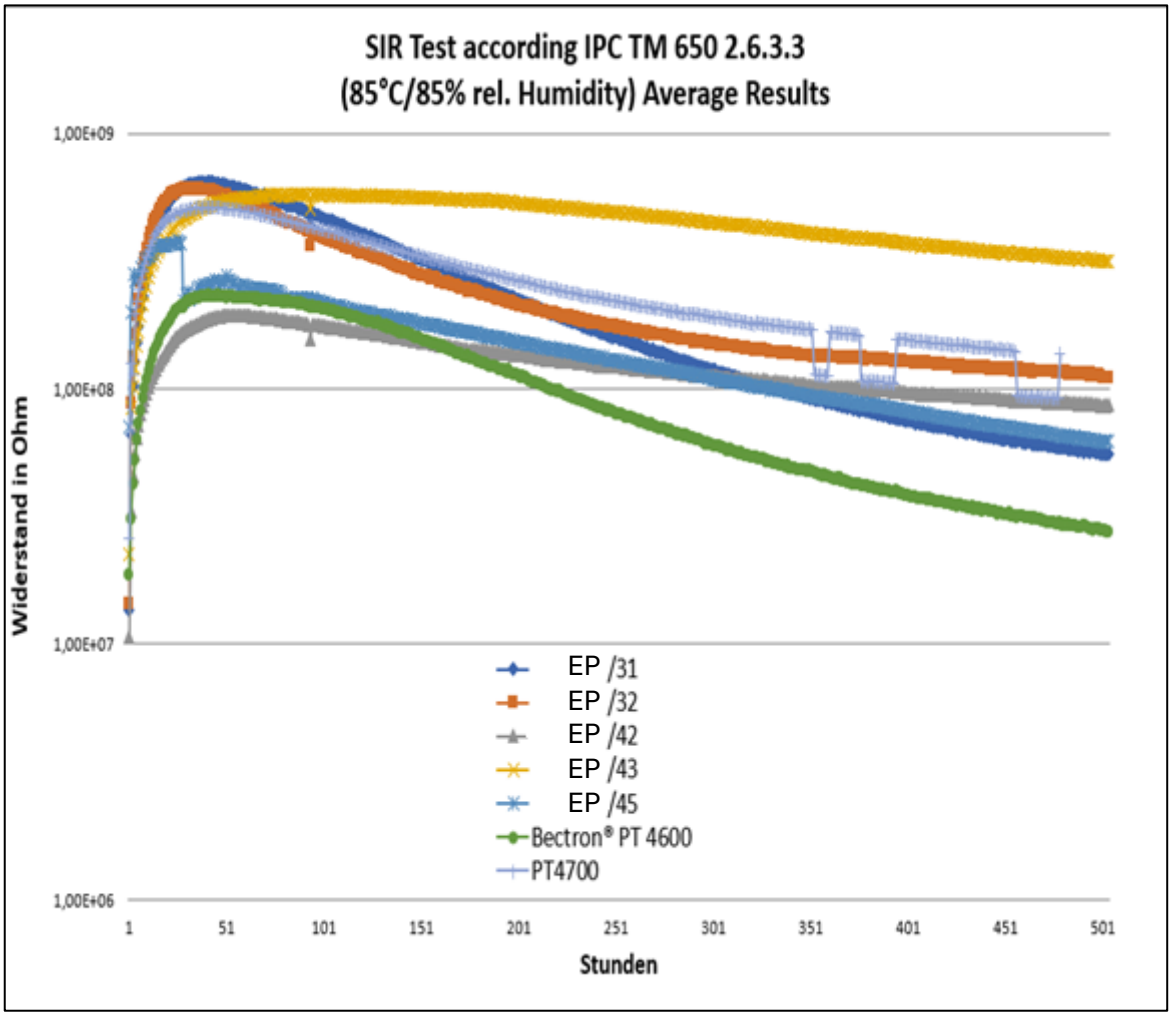
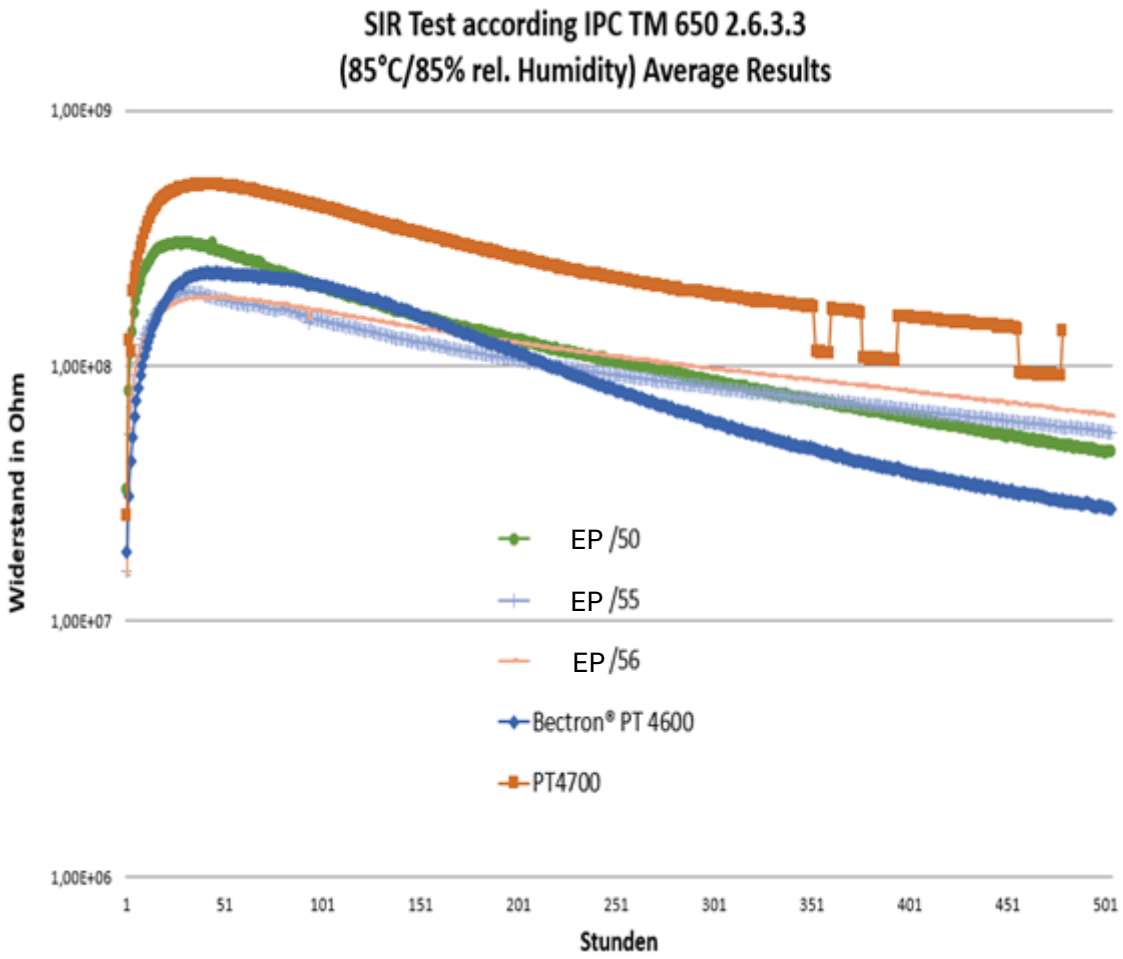


Figure 77. SIR analysis of EP31,32,42,43,45 and the two standard materials.



that most of the developed samples fall within the same range of surface insulation resistance (SIR) as the two standard products. Notably, one batch, EP43, exhibits a higher surface insulation resistance compared to the two standard products, demonstrating its superior performance in this aspect. (Fig 77,78)

Figure 78. SIR analysis of EP50,55 and 56 the two standard materials.

The conclusions for this project are included in Chapter 8.7.

8.6 Results and Discussions-Conformal Coating Project #2

In this second project, the focus is on synthesizing a polymer (binder) for conformal coating technology with properties comparable to those of a commercially available binder. Let's refer to the commercial binder as **EP200**. According to the documentation, EP200 is a polyester-based urethane diacrylate. To characterize the compound, it began with an ATR-FT-IR, ^{1}H-NMR, and GPC analyses. The characterization of EP200 starts with an ATR-FTIR shown here below: (Figure 79)

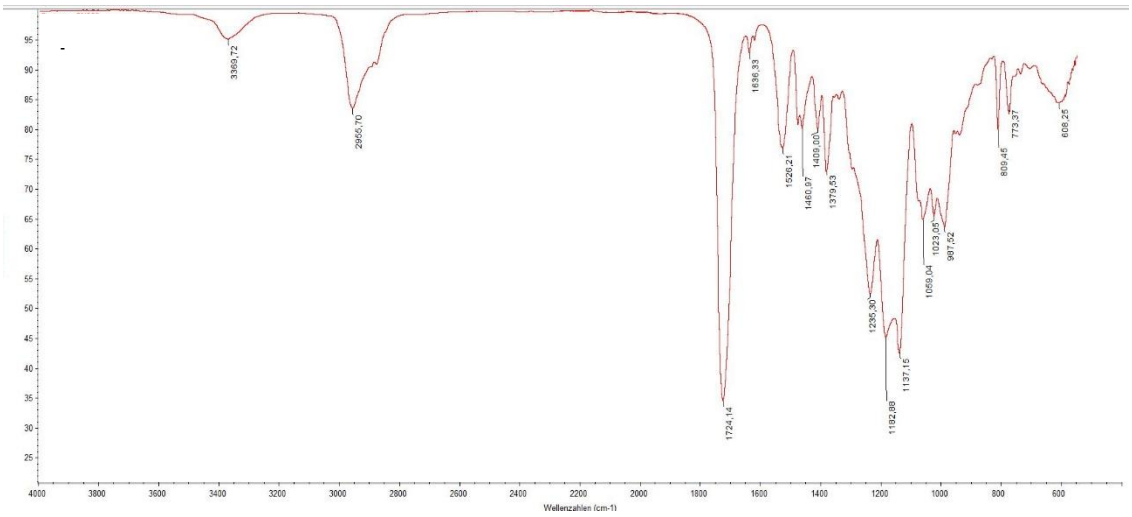
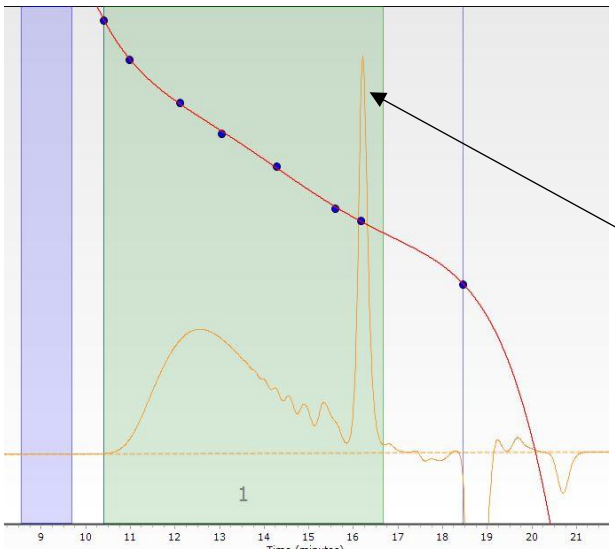


Figure 79. ATR-FTIR spectra of EP200.

In Figs. 79 show the absorption peaks of typical polyurethane acrylate (PUA) 3340–3380 cm^{-1} (NH, hydrogen-bonded), 2975-2870 cm^{-1} (CH_2 and CH_3), 1724 cm^{-1} (C=O), and 1526 cm^{-1}



Mn (g/mol)	Mw (g/mol)
1760	5170

Phenoxyethyl acrylate

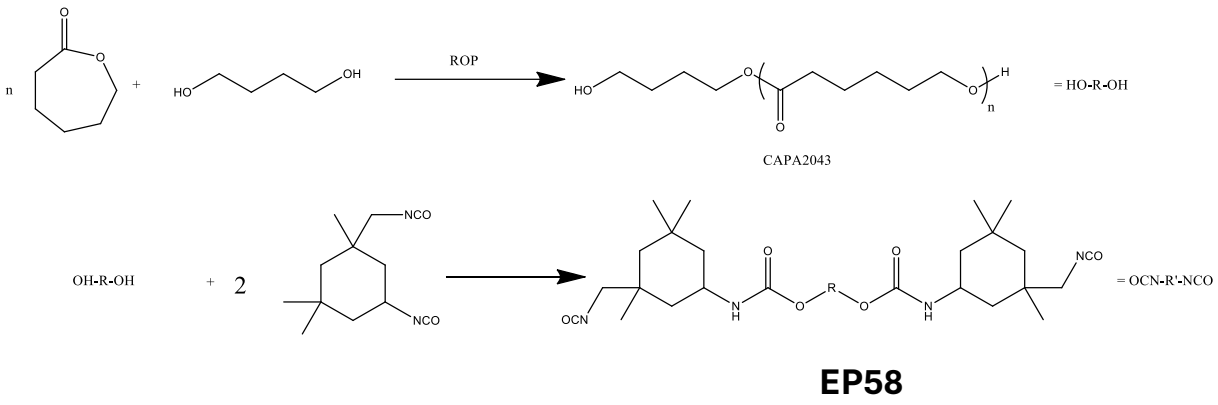
(NH), respectively additionally, the FT-IR spectra shows the absorption peaks at 1636 cm^{-1} (C=C), 1409 cm^{-1} (=CH_2), and 810 cm^{-1} (=CH), which is from the double bond of the acrylate functionality.[160] A GPC analysis was conducted to check the molecular weight, the analysis was done using 10mg of sample solubilized in 1 ml of Phenoxyethyl acrylate. (Figure 80)

Figure 80. GPC analysis of EP200.

NMR Characterization: EP200

^{1}H NMR: (500 MHz, CDCl3) δH= 6.43 (m) 6.16- 6.10 (m), 5.85 (m), 4.36-4.25 (m), 3.86 (s, single), 2.92-2.90 (s, single), 2.36-2.31 (m), 1.64-1.61 (m), 1.06-1.02 (m), 0.97-0.87 (m).

To start the synthesis, it is needed to synthesize a polyester based urethane prepolymer, as polyester it's been used the CAPA2043 that is a polyester made from a ring opening polymerization in presence of ethylene glycol.

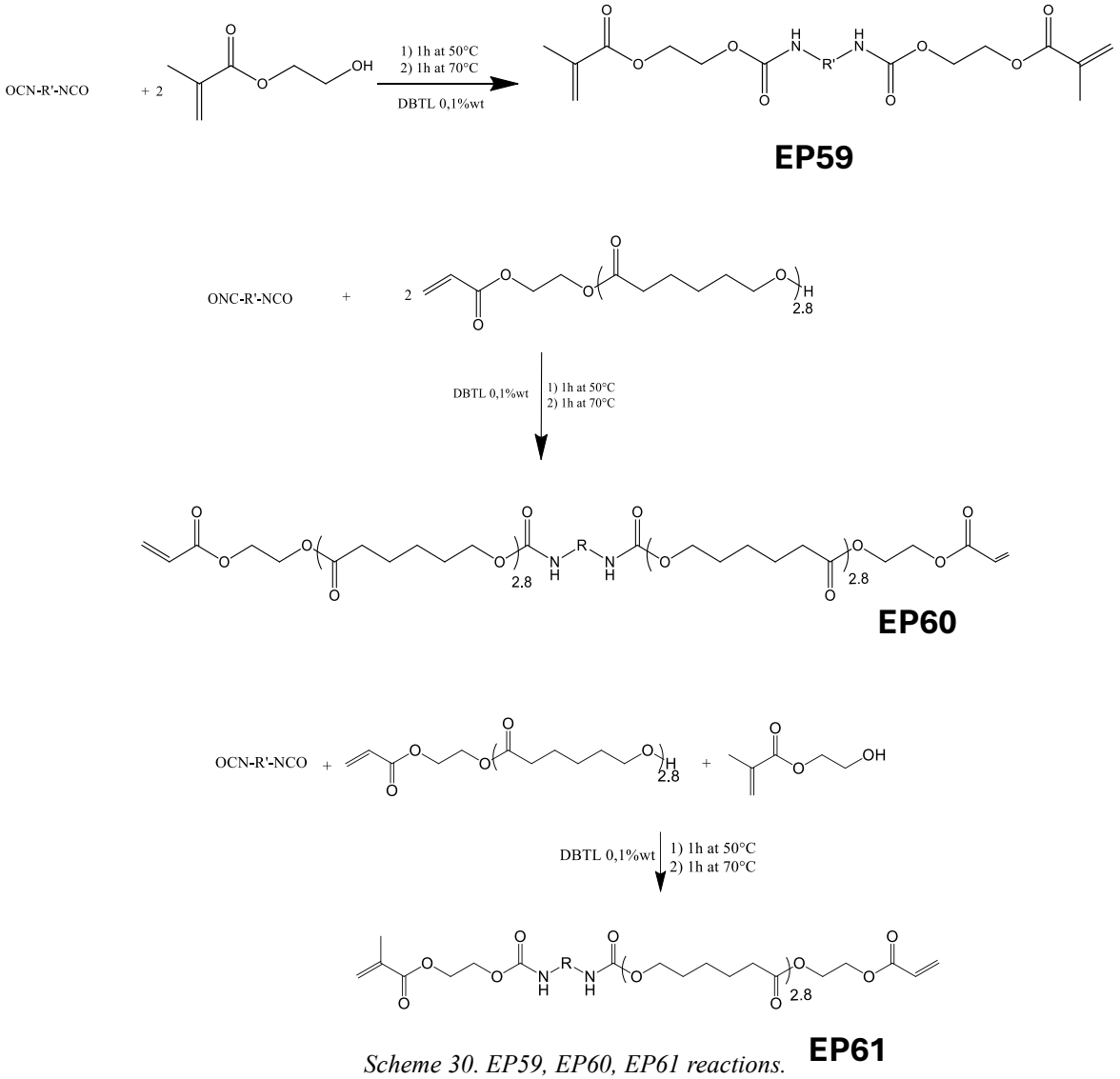


Scheme 29. Ester and ester urethane prepolymer synthesis.

The product of the second reaction (OCN-R'-NCO) **EP58**, the urethane prepolymer has been characterized by ^{13}C-NMR:

^{13}C NMR: (125 MHz, $CDCl_3$) δC= 173.70, 167.30, 156.67, 156.06, 136.10, 126.16, 66.53, 64.61, 64.24, 63.92, 63.05, 62.77, 61.44, 54.99, 47.14, 46.46, 44.65, 41.94, 36.50, 35.16, 34.27, 34.24, 34.20, 31.97, 31.91, 29.77, 28.85, 28.45, 27.73, 25.80, 25.64, 25.42, 24.74, 24.69, 24.67, 23.34, 18.45, 18.43.

From the ^{13}C-NMR spectra is it possible to verify that the urethane group is absent in CAPA2043 and present in the reaction product **EP58**. This is the polyester-based urethane prepolymer from which we are going to start for the synthesis of the PUA, I've prepared 3 different PUAs:



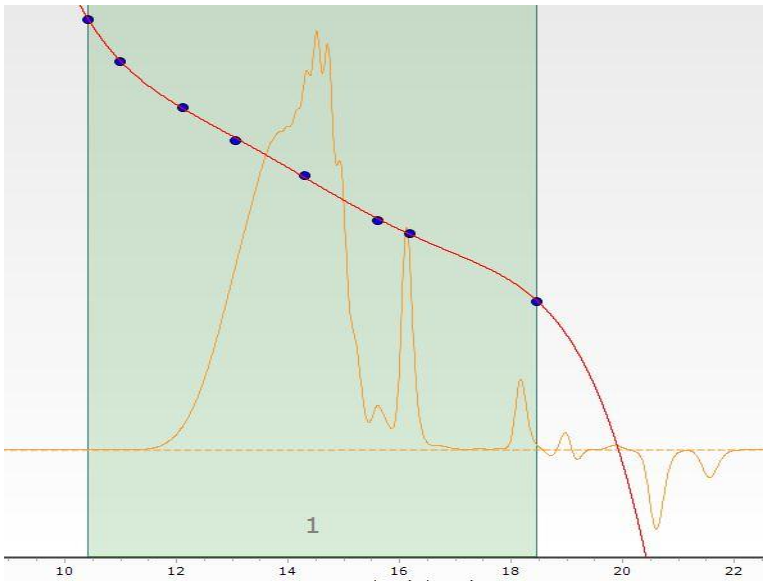
Scheme 30. EP59, EP60, EP61 reactions.

- **EP59** is end-capped with 2 mol of HEMA.
- **EP60** is end-capped with 2 mol of HECLA.
- **EP61** is end-capped with 1 mol of HEMA and 1 mol of HECLA.

HEMA: hydroxyethyl methacrylate

HECLA: hydroxyethyl caprolactone acrylate

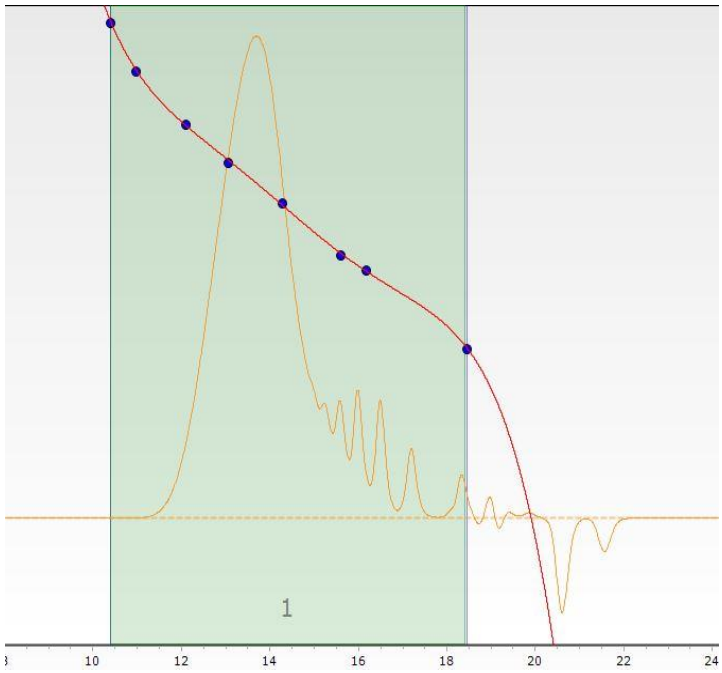
A GPC and ^{13}C-NMR characterization has been done, the structures in the *Scheme30* have been confirmed.



Mn (g/mol)	Mw (g/mol)
1665	2791

EP59

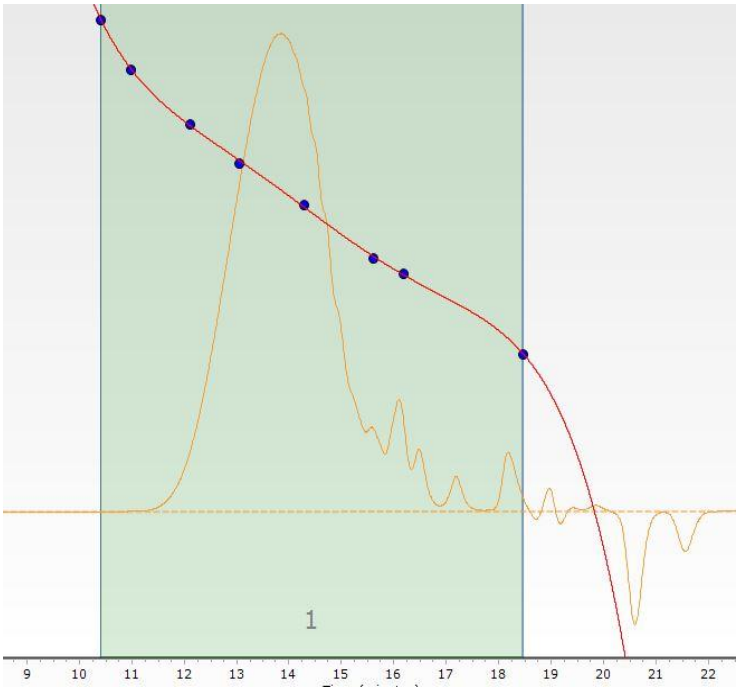
Figure 81. GPC analysis of EP59.



Mn (g/mol)	Mw (g/mol)
1889	3475

EP60

Figure 82. GPC analysis of EP60.



Mn (g/mol)	Mw (g/mol)
1844	3258

EP61

Figure 83. GPC analysis of EP61.

- **EP59: ^{13}C NMR**: (125 MHz, $CDCl_3$) δC= 173.70, 167.30, 156.67, 156.06, 136.10, 126.16, 66.53, 64.61, 64.24, 63.92, 63.05, 62.77, 61.44, 54.99, 47.14, 46.46, 44.65, 41.94, 36.50, 35.16, 34.27, 34.24, 34.20, 31.97, 31.91, 29.77, 28.85, 28.45, 27.73, 25.80, 25.64, 25.42, 24.74, 24.69, 24.67, 23.34, 18.45, 18.43.
- **EP60: ^{13}C NMR**: (125 MHz, $CDCl_3$) δC= 173.70, 173.37, 166.00, 156.07, 131.55, 131.51, 128.16, 128.08, 66.32, 64.26, 64.23, 63.92, 62.73, 62.38, 62.11, 61.32, 54.97, 44.66, 42.01, 36.50, 35.17, 34.34, 34.23, 34.20, 34.02, 32.43, 31.97, 28.85, 28.45, 28.43, 27.74, 25.64, 25.58, 25.42, 24.75, 24.68, 24.58, 23.34.
- **EP61: ^{13}C NMR**: (125 MHz, $CDCl_3$) δC= 173.74, 173.68, 173.36, 165.99, 157.22, 156.66, 156.05, 136.08, 131.54, 128.17, 128.07, 126.14, 66.51, 64.81, 64.57, 64.25, 64.22, 63.91, 63.04, 62.76, 62.70, 62.37, 62.10, 61.40, 54.98, 47.13, 46.45, 44.63, 41.99, 36.49, 35.15, 34.26, 34.22, 34.19, 34.01, 31.96, 31.90, 28.84, 28.44, 28.42, 27.73, 25.79, 25.63, 25.56, 25.44, 25.41, 24.73, 24.67, 24.65, 24.57, 23.33, 18.42.

It is needed to say that at the end of the synthesis the material made is very similar to EP200 in terms of Mn, color and viscosity. This is not much but is a clear indication that we are taking

the right way. To check if those prepolymers has the same properties of the EP200 we must create an application batch for every polymer developed. The commercial product where the EP200 is present is called Bectron BC1226. This commercial product has in it the EP200 as binder and various additives and solvent to reach that specific characteristic.

Batch	Application Batch name
EP59	**Bectron BC1226_Alternative 1T, 2**
EP60	**Bectron BC1226_Alternative 3T, 4**
EP61	**Bectron BC1226_Alternative 5T, 6**

Table 31. Application batch assignation and corresponding binders.

It is noticeable from the table that for every synthesis batch we've done there are 2 application batch for example the EP59 has 2 application batches:

- Bectron BC1226_ Alternative 1**T**
- Bectron BC1226_ Alternative 2

The difference between these two is just the presence (marked by the **T**) or the absence of the Microtalc IT extra. This was done in order to verify if the presence of this talc can give thixotropy behaviour. All batches undergo material dispersion and are vacuum-treated to eliminate any bubble formation. After curing the material for 5 min in a UV lamp, we start with the physical test to check the polymer properties. We start with the wipe test; this test is done to check if the cured material resists to solvent mechanical attack. The wipe test assesses adhesion and curing quality by rubbing the coated surface with a solvent-soaked material, ensuring proper bonding, coverage, and resistance to chemical interaction. The solvent that are going to be tested are aceton, iso-propanol, metil ethyl ketone and butyl acetate.

WIPE TEST

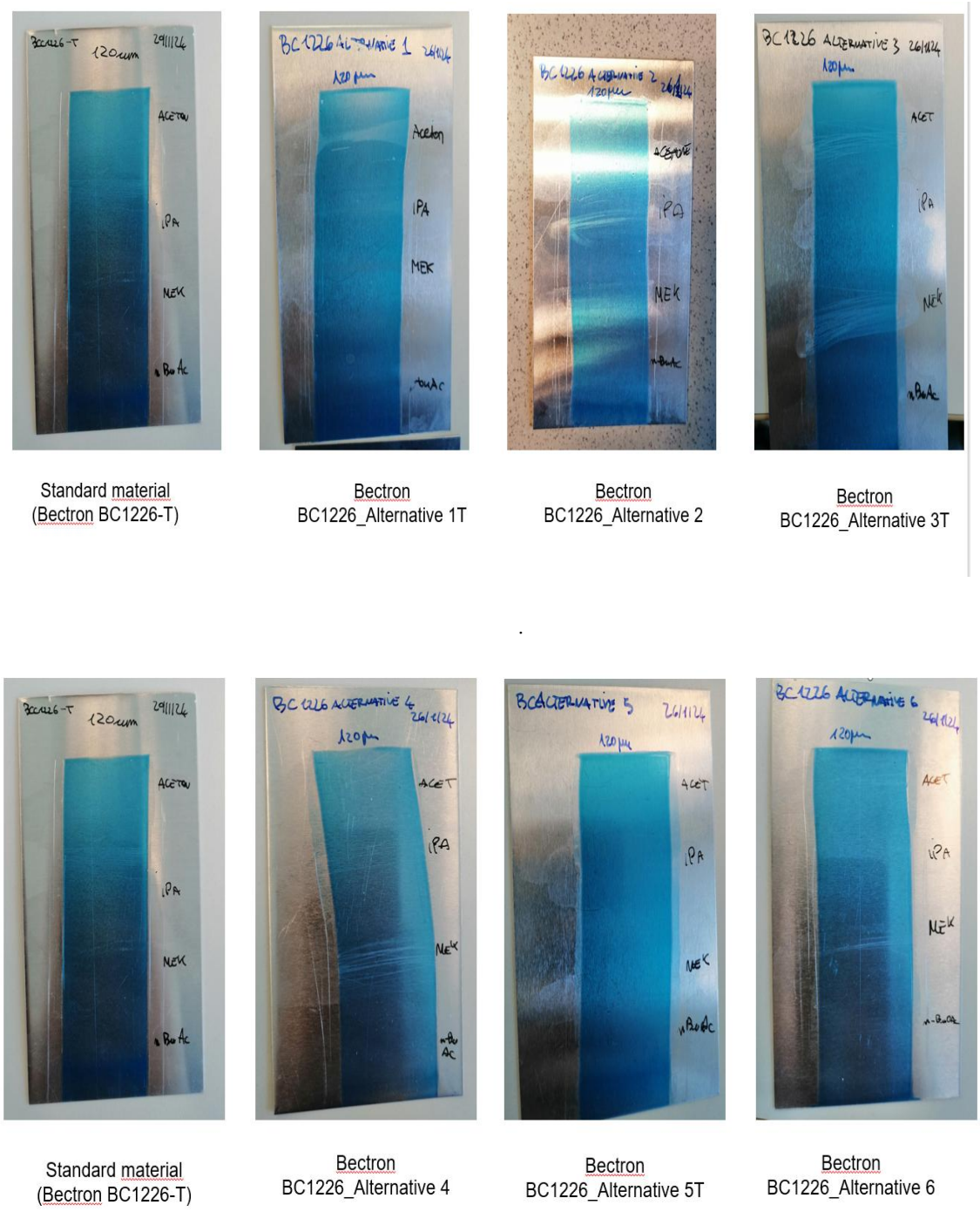


Figure. 84 Wipe test, standard material(left) vs various alternatives.

Alternative 5T and 6 are the ones that behaves the best in this test.

CROSS CUT TEST

On a surface of at least 10 × 10 cm, use a cutter or suitable metal blade to make grid incisions that reach down to the substrate. Space the incisions evenly (8–10 mm apart) both horizontally and vertically to form a lattice pattern on the test area. Apply adhesive tape over the incised area, press firmly, and then remove it with a quick, vigorous motion. Examine the surface to evaluate the results.

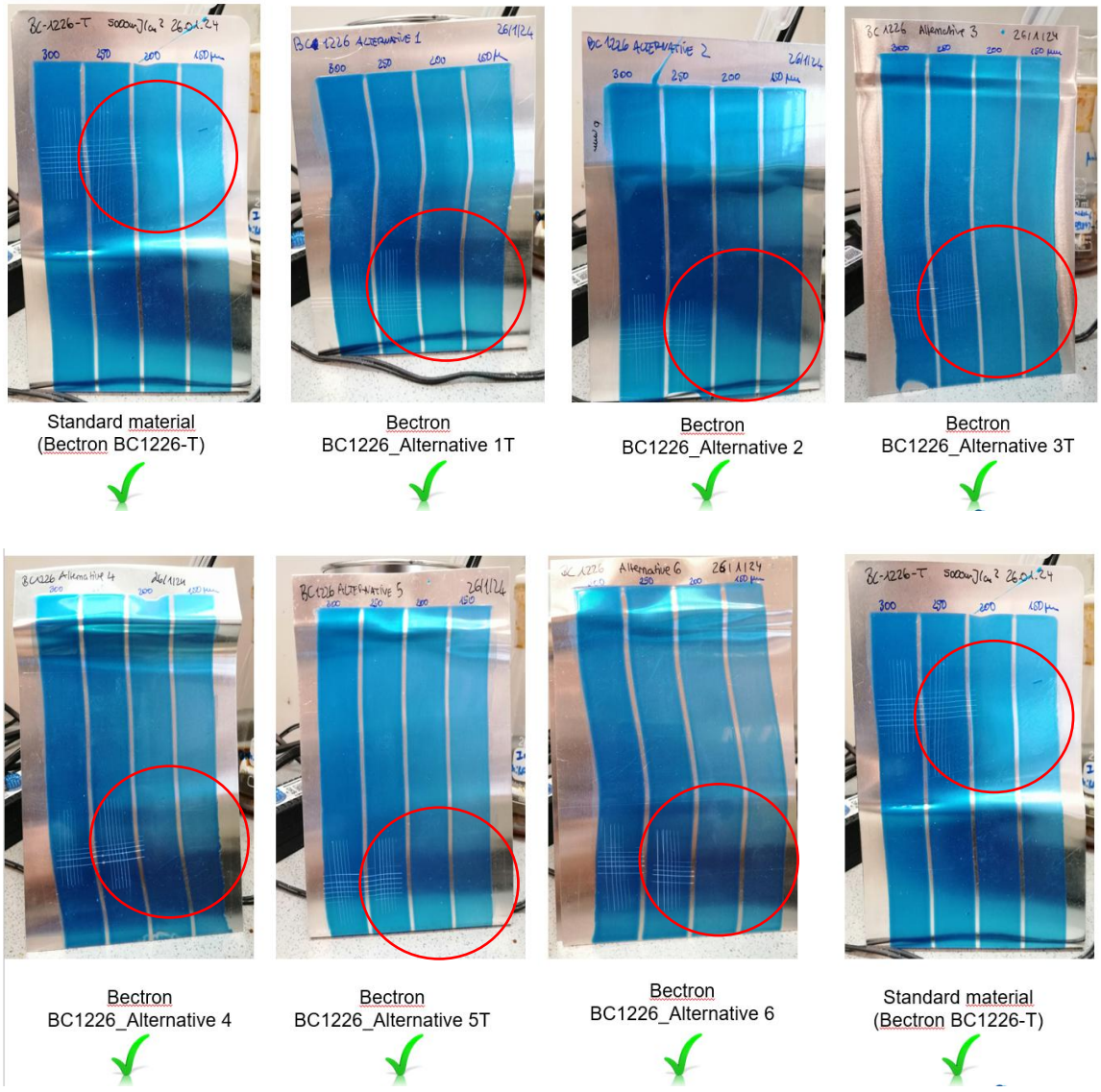
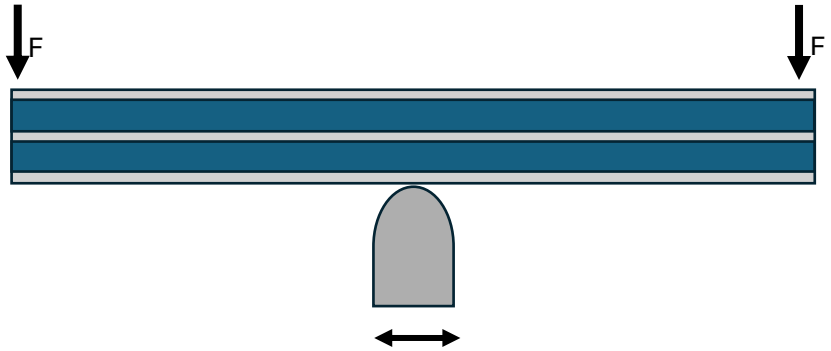


Figure 84. Cross cut test, on the left, standard material vs the various alternatives.

FLEXIBILITY TESTS

The flexibility test in conformal coatings evaluates the coating's ability to withstand bending or deformation without cracking or peeling, ensuring durability and performance under mechanical stress or dynamic environmental conditions; is conducted by bending the aluminum foil, where the polymer is applied and cured, over a 3 and 6 mm (example):



3 or 6 mm wide

As it is noticeable from the picture, the thinner the point where the bending will be done, the more the flexibility we are evaluating. We lower the thickness of the bending point until it breaks.

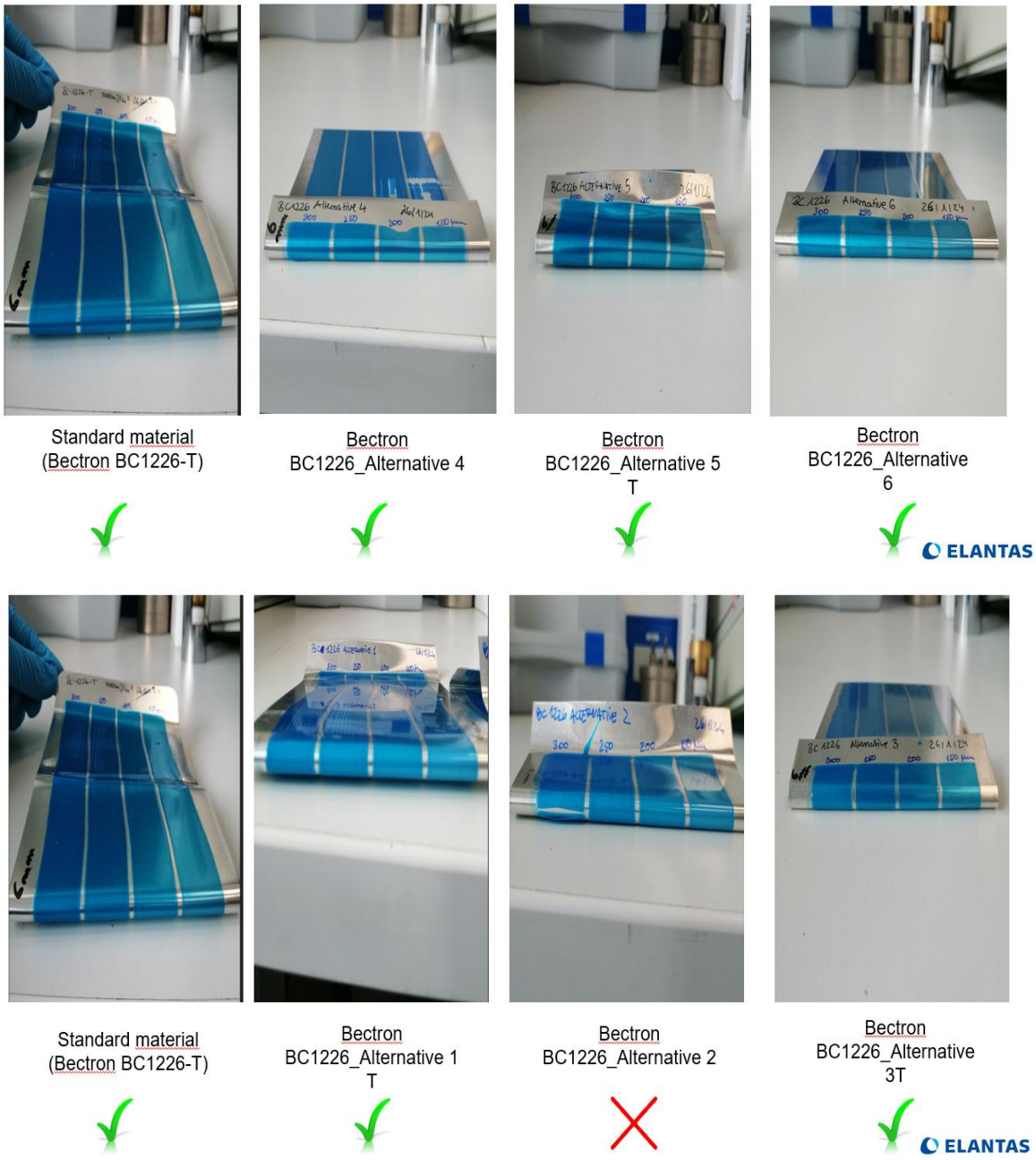


Figure 86. 6mm wide flexibility test.

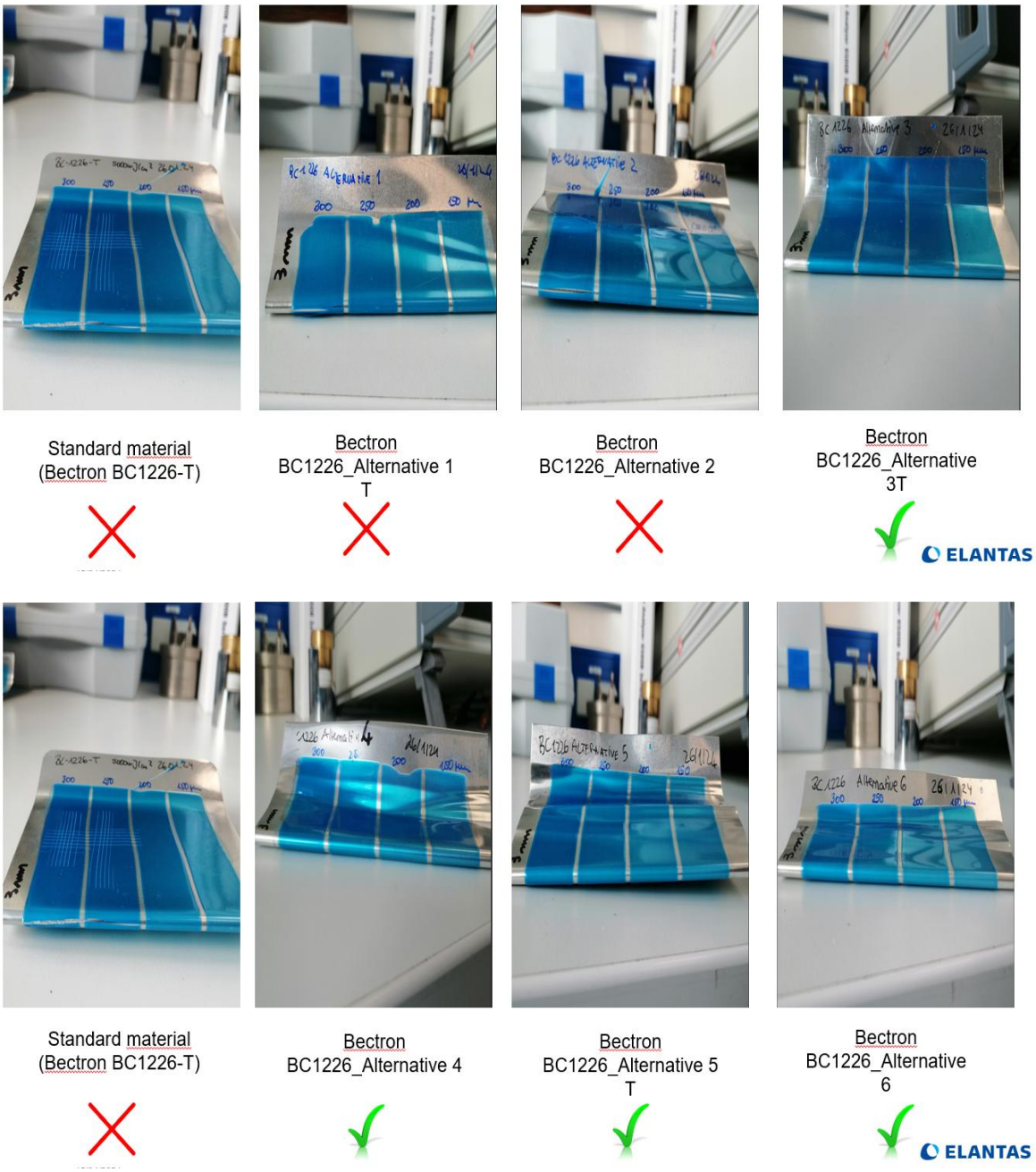


Figure. 87 3mm wide flexibility test.

It is important to notice that the standard material has a lower flexibility compared to the alternative 3T, 4, 5T and 6.

Viscosity and thixotropic behaviour of Bectron BC1226_Alternative 1T & 2

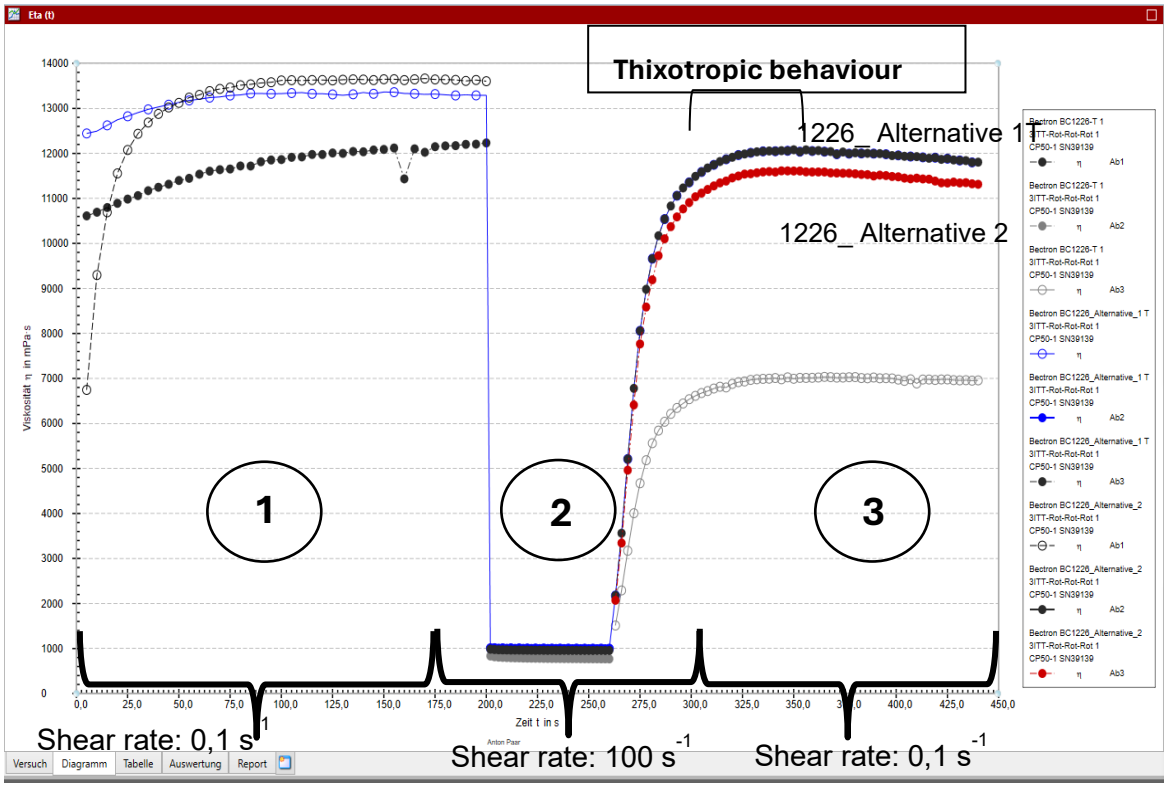


Figure 88. Viscosity and thixotropic behaviour evaluation of BC1226_Alternative 1T & 2.

This graph shows the change in viscosity when the applied rotational force changes.

-From 0 and 200 s the speed is 0,1 s^{-1} (1)

-From 200 s to circa 262 s the speed is 100 s^{-1} (2)

-From 262 s to 450 the rotational speed is 0,1 s^{-1} (3)

Thixotropy is a time-dependent, reversible rheological property observed in certain gels and fluids. These materials are thick or viscous under static conditions but flow more easily (become less viscous) when subjected to stress, such as shaking, agitation, or shear. Importantly, they gradually recover their original viscosity when the stress is removed, making them ideal for applications where structural recovery is critical.[163] The rapid change in rotational speed during testing is used to evaluate this thixotropic behavior. An ideal thixotropic material regains its viscosity almost instantly after being allowed to rest. This behavior is particularly important in conformal coating applications, where the product is sprayed onto surfaces. For example,

when coating a cube, if the material remains too liquid after application, it will flow off, leaving the edges and corners uncoated. In contrast, a material that quickly becomes highly viscous when no force is applied will stay on the edges longer, allowing for proper curing and fixation. To achieve an effective coating, the material should have the same or higher initial viscosity compared to the standard reference product (e.g., Bectron BC_1226). Each graph during evaluation also includes the standard product's behavior for comparison, ensuring the new material meets or exceeds performance expectations.

Viscosity and thixotropic behaviour of Bectron BC1226_Alternative 3T & 4

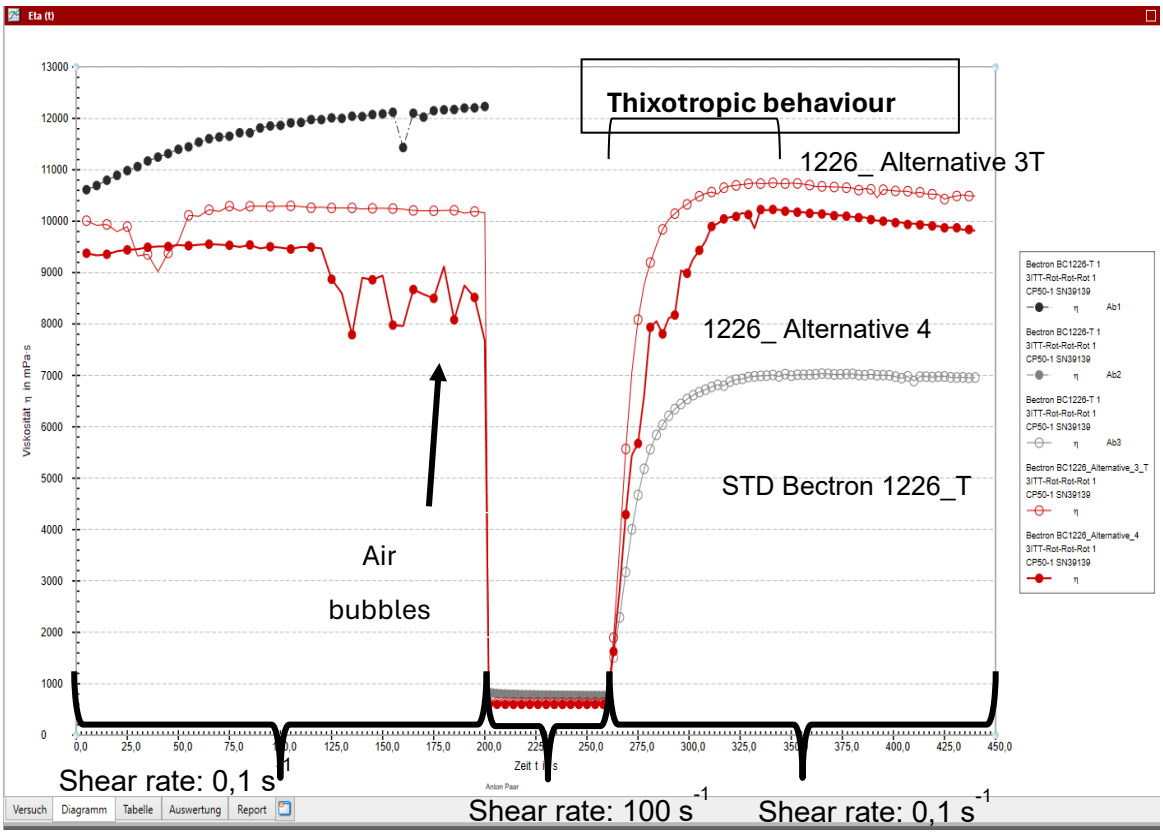


Figure 89. Viscosity and thixotropic behaviour evaluation of BC1226_Alternative 3T & 4.

Viscosity and thixotropic behaviour of Bectron BC1226_Alternative 5T & 6

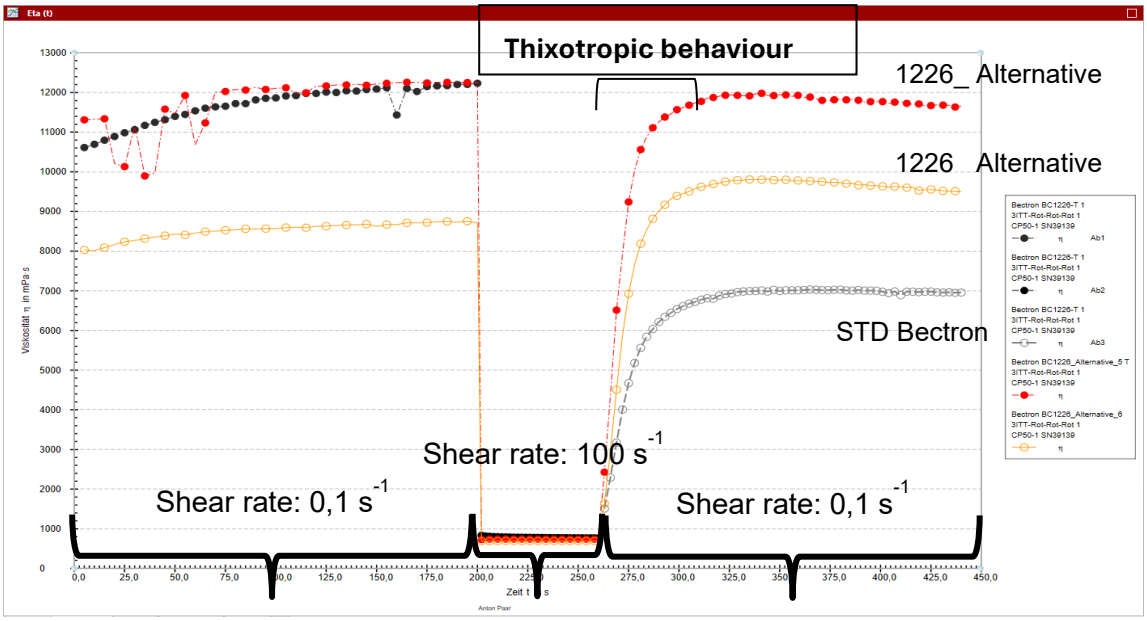


Figure 90. Viscosity and thixotropic behaviour evaluation of BC1226_Alternative 5T & 6.

A summary of mechanical tests is reported below:

Tests	Alternative 1 T	Alternative 2	Alternative 3T	Alternative 4	Alternative 5T	Alternative 6	STD Bectron 1226_T
Wipe test	🔴	🟡	🔴	🟡	🟢	🟢	🟢
Cross Cut	🟢	🟢	🟢	🟢	🟢	🟢	🟢
6 mm flex	🟢	🔴	🟢	🟢	🟢	🟢	🟢
3 mm flex	🔴	🔴	🟢	🟢	🟢	🟢	🔴
Viscosity*	🟢	🟢	🔴	🔴	🟢	🔴	🟢
Tixotropy behaviour	🟢	🟢	🟢	🟢	🟢	🟢	🟡

Table 32. Summary of mechanical tests.

Batch	Application Batch name
LF99350-59 (end capped with 2 HEMA mol)	Bectron BC1226_Alternative 1 T, 2
LF99350-60 (end capped with 2 HECLA mol)	Bectron BC1226_Alternative 3 T, 4
LF99350-61 (end capped with 1 HEMA and 1 HECLA mol)	Bectron BC1226_Alternative 5 T, 6

Table 33. Batch name and Application batch name assignation.

* When Viscosity = 🔴 means that the Viscosity measured at 0,1 s^{-1} is lower than the STD Bectron 1226_T

8.7 Conclusions

Conformal coating technology is a different field compared to wire enamel technology, these two conformal coating projects helped to understand how the work of research is full of new technologies and applications. Both the project starts with a deep characterization of the product that it is needed to get close to the chemical structure and so, the applicative performances; followed by a series of trials and errors that finally led to a product comparable with the commercial one. In these two project the introduction of bio-based material was very challenging, but some valid alternatives are now getting interesting in the industrial landscape. Bio-based isocyanates (for example 1,5-pentamethylene diisocyanates and their polyisocyanates) will be the dawn of the bio-based conformal coatings together with the use, like in this manuscript, of the ricinolein. In the first conformal coatings project the electrical characteristics were evaluated and the target was reached successfully as reported in the SIR testing images (Figure 77,78). When evaluating the use of bio-based raw materials for the production of a commercial product, it is crucial to consider the Life Cycle Assessment (LCA). As demonstrated in the Green Wire Enamel project, good intentions do not always result in reduced CO_2 emissions per kilogram of product. Overall, I've successfully emulated 2 different alternatives from 2 different commercially available products. From this last work we can also understand that is very possible to "play" with the functionalities and with the molecular structure to change properties such as flexibility. This work is a starting point for future work in synthesizing in-house products with a partial bio-based content.

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