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Optimization of Industrial Polymeric Products to Improve Quality and Reduce Environmental Impact

Cycle XXXI

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Preface

The present thesis is the result of three years' collaboration between the University of Camerino and ELANTAS Europe Srl. The strong collaboration between university and companies allows to students like others and me to do research with an industrial approach, facing with the problematics of working life.

The work was carried out among the laboratory of Organic Chemistry of Prof. Enrico Marcantoni at the University of Camerino (Camerino, Italy), the R&D laboratory of ELANTAS Europe in Ascoli Piceno (Italy) and the R&D laboratory of ELANTAS PDG INC in Saint Louis (Missouri, USA).

The thesis concern the environmental impact of some industrial polymeric materials. Polymeric materials are very important in modern society: they have considerable advantages over products of other origins with lower costs with the same performance. Nevertheless, they allow some applications that some years ago would have been unthinkable (microencapsulation, shape memory materials, and many others).

At the same time, environmental impact is a crucial topic strictly linked to polymeric materials (as all others materials), and to the period we are living. The production of such materials is constantly growing, exceeding the production of many others materials, and it is becoming increasingly important to find ways to produce them more efficiently and to recover waste products. The consequences of a production without limitation and control could be catastrophic for the whole world and humankind too.

During my PhD, I worked on three industrial products in order to reduce their environmental impact, keeping their physical properties unchanged.

After a first general introduction on polymeric materials, their uses, and their production, the second chapter concern about improving a recovery process for waste PMMA. The study allowed identifying undesirable by-products formed during the thermal depolymerization of PMMA and removing them in the consequent re-polymerization by an innovative dissolution/re-precipitation method.

The third and fourth chapters deal with two coatings for wires electrical insulation, one based on polyurethanes (PU) and the other on polyesterimides (PEI). With the PU-based one, the target was to reduce the amount of loss material during the application stage and to increase the speed of application in order to reduce the energy consumption of the process. Whereas with the PEI-based enamel the purpose was to synthesized a solvent-free product using a twin-screw extruder and using recycled PET as alternative raw material to form the polyester part. The extruder technology is less energy consuming compare to the batches ones and allows working without solvents, since it can work with high viscosity materials. Moreover, the extruded product, with an additional system, can be potentially applied onto the wire with a higher thickness compare to the respective solvent-based product, allowing a greater flow of current along the wire, thus improving the performance of the finished products (i.e. reducing the charging time of electrical motors).

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Chapter 1: Polymeric Materials

We are living in the age of polymeric materials. Discovered in the '800, to which the first uses date back, only at the beginning of the last century the German chemist Hermann Staudinger first hypothesized and then defined their macromolecular structure, winning the 1953 Nobel Prize in Chemistry for this work.

Plastic materials were widely used after the Second World War, during which the shortcomings of raw materials led to find synthetic alternatives and to an increase of polymers production, invading the civilized world. In fact, since the 1950s, the polymer materials industry has grown hugely. In those years, the first plastic products made their appearance: from bottles to packaging films, from toys to car parts, to clothes. Since then the field of application has only expanded, including paints and enamels of various types, electronic components and components for medical and pharmaceutical use, playground, food storage containers and much more. Many others examples could be cited, but to resume, the use of polymers now outstrips that of metals on volume and mass basis.

Nowadays many people objected to synthetic polymers because they are petroleum derivatives, actually the raw materials for polymers account for less than 2% of total petroleum consumption, so even an eventually substitution of synthetic polymers would not significantly contribute to the conservation of petroleum resources.

At the same time, substituting polymer materials with natural ones is unthinkable. Beside the performances of the products, for example if all the synthetized polymer fibers in use today were to be replaced by cotton and/or wool, calculations show that there would not be enough land left to feed the population.

In addition, the manufacturing processes used to produce polymers often generate considerably less environmental pollution than the processes used to produce the traditional counterparts: e.g. polyethylene film versus paper for packaging.

The fact is that there are not practical substitutes for many of the synthetic polymer used in modern society. This does not mean that there is not a serious problem with polymeric materials, but that they have not to be demonized and we must try to make a thoughtful use and especially look for ways for recycling those products that are at the end of their work life.

1.1 Introduction

A polymer is a large molecule, or macromolecule, composed of many repeated subunits. The term "polymer" derives from the ancient Greek word πολὺς (*polus*, meaning "many, much") and μέρος (*meros*, meaning "parts") and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. The basic structure of a polymer consists of a backbone and side groups. Atoms that are covalently linked and stretch from one end to the other make up the polymer backbone (which is often carbon, but can also contain other atoms such as N, O or Si). Other atoms are part of the side groups, they could be: hydrogen (-H), methyl (-CH_3), alcohol (-OH) or chloride (-Cl) groups are among the simplest of many possibilities, making for a wide variety of structures that make up polymers. Polymers are named based on the repeat unit, since that can describe a rather lengthy molecule in a quick way (Figure 1.1).

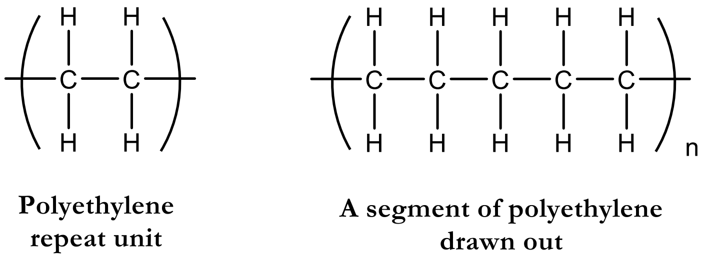
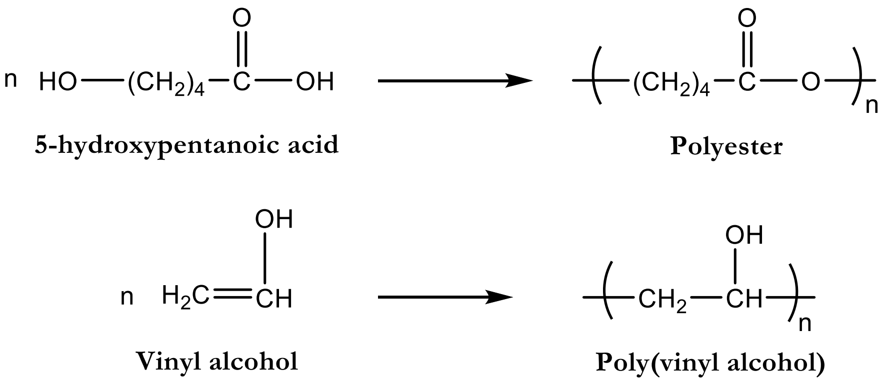


Figure 1.1. Structures of polyethylene

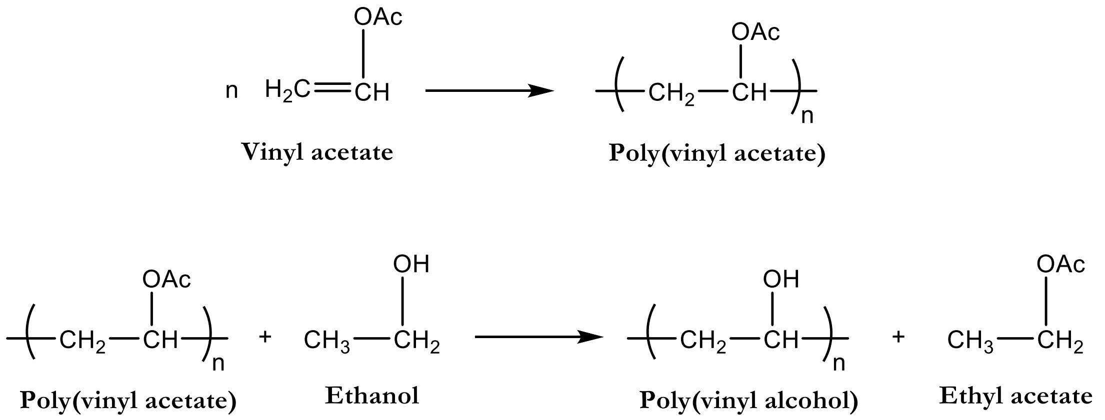
Organic chemicals can be categorized based on common functional groups that are found within a structure. These functionalities are helpful in determining if a molecule might be reactive, whether it is likely to be hydrophilic (or hydrophobic), and how (or if) a molecule can participate in a polymerization reaction.

Alcohols (-OH) are perhaps one of the more familiar functional groups, and they can be reacted with carboxylic acids (-COOH) to form an ester bond. As long as each molecule has at least two reactive functional groups, for example: a molecule with an alcohol functionality and a carboxylic acid functionality can react with itself to form a continuous polymer molecule with multiple ester linkages along the polymer backbone, yielding a polyester. Alcohols can also be found in the side groups of polymers, as in polyvinyl alcohol (PVA), where the -OH group stays intact after the reaction (Scheme 1.1).



Scheme 1.1. Some common polymers

Unlike most vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer. The monomer vinyl alcohol is unstable with respect to acetaldehyde. PVA is prepared by first polymerizing vinyl acetate, and then the resulting polyvinylacetate is converted to the PVA. The conversion of the polyesters is usually conducted by base-catalyzed transesterification with ethanol (Scheme 1.2).



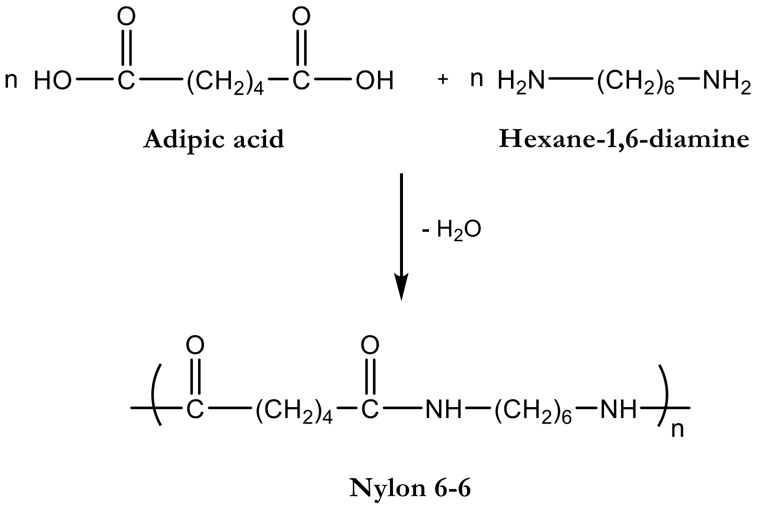
Scheme 1.2. Formation of poly(vinyl alcohol)

Some of the organic functional groups that are reactive to form polymers include alcohols, amines, carboxylic acids, and alkenes. Although alkanes (C-C bonds) are common in polymers, both in the backbone and in the side groups, they are not reactive. Other bonds commonly found in polymers include amides, esters, carbonates, imides, and urethanes.

1.1.1 Formation of polymer chain

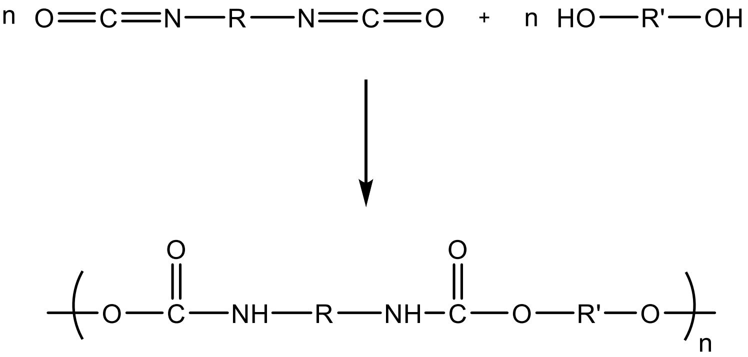
There are two reaction to form polymer: addition or condensation.

The condensation mechanism involves the formation of other side products, just like in the condensation reaction where the side product is water. This mechanism is typical of bifunctional monomers, like dicarboxylic acids, diesters, anhydrides in combination with glycols or diamines. Scheme 1.3 shows the formation reaction of Nylon 6,6 between adipic acid and hexamethylendiamine (both molecules contain six atoms of carbon, that is why “6,6”).



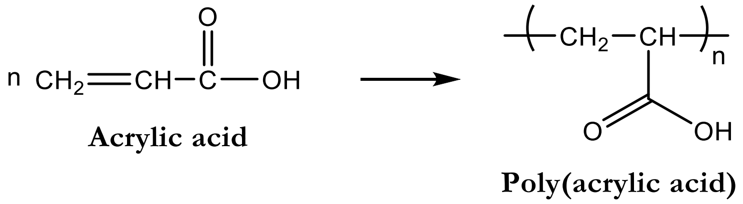
Scheme 1.3. Formation of Nylon 6,6

In the addition reaction, simple linking of monomers forms polymer without the co-generation of other products: the C-C double bond reacts forming a long-chain alkane. This kind of reaction is typical of olefins, but also of the diisocyanates. They react with polyalcohols (diols or triols) to give polyurethanes (thought industrially they are generated in a different way, Scheme 1.4).



Scheme *1.4.* Formation of a generic polyurethane

In Scheme 1.5 is showed the polymerization mechanism of polyacrylic acid and polyacrylates too. This kind of monomer, acrylic acid, although has a carboxylic functionality this would not be useful in a condensation polymerization, so the polymerization occurs on the C-C double bond, like other olefins.



Scheme 1.5. Formation of poly(acrylic acid)

1.1.2 Three-dimensional structure

Polymers could assume three different molecular structures: linear, branched, crosslinked (Figure 1.2).

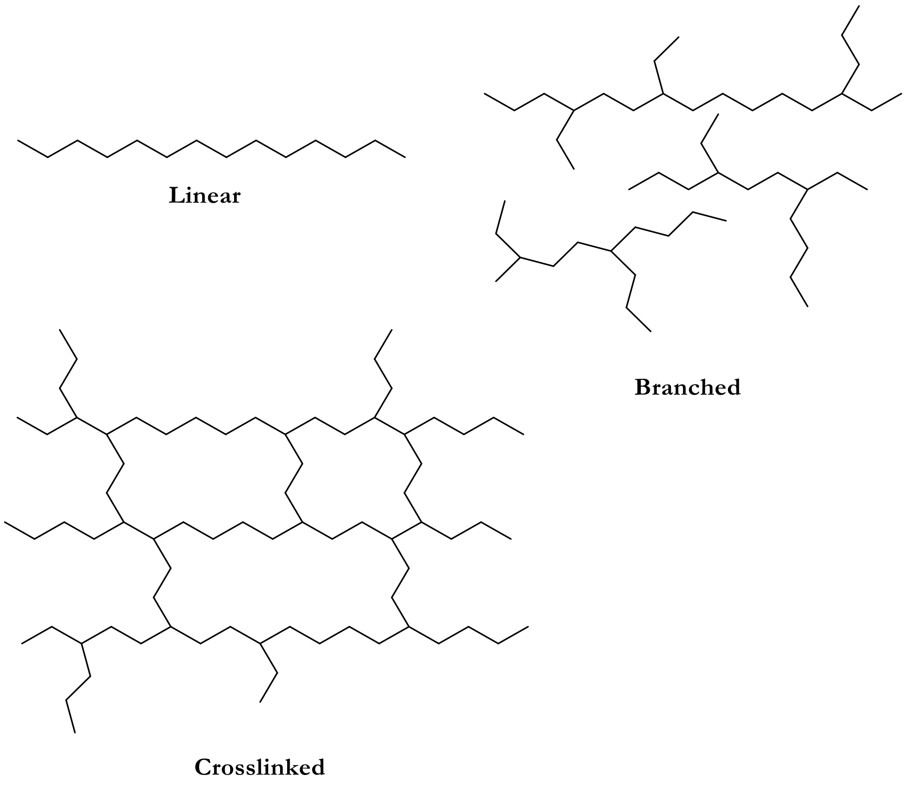


Figure 1.2. Possible molecular structure of polymer

If a polymer is built from strictly bifunctional monomers, the result is a linear polymer chain. The term linear can be misleading, because the molecules do not necessarily assume a geometrically linear conformation. Some of the better analogies for what these macromolecules look like is a bowl of spaghetti or tangled strands of yarn.

Polymers consisting of chains that contain a single repeating unit are known as homopolymers (this includes many polymers made by addition and condensation polymerization). If, however, the chains contain a random arrangement of two separate and distinct repeating units, the polymer is known as a random or statistical copolymer, or simply copolymer. A random copolymer might be formed by the addition polymerization of a mixture of two different vinyl monomers A and B (the degree of "randomness" depends on the relative amounts and reactivities of A and B, as we shall see later) and can be represented as:

AABAAABBABAAB

This is called poly(A-co-B), where the first repeating unit listed is the one present in the greater amount. For example, a random synthetic rubber copolymer of 75% butadiene and 25% styrene would be termed poly(butadiene-co-styrene). Also ter-(3-) and higher multipolymers are possible.

Under certain conditions, linear chains can be formed, that contain long contiguous blocks of two (or more) repeating units combined in the chains, termed a block copolymer:

AAAAAAAAAAAAAAAABBBBBBBBBBBBBBBBBBB

AAAAAAAAAAAABBBBBBBBBBBBBBBAAAAAAAAAAAAAA

These structures are called: the first a diblock copolymer, poly(A-b-B); the second a triblock copolymer, poly(A-b-B-b-A). Here, the b (meaning "block") replaces "co" to indicate the organized structure. These structures are important for nanotechnology as several block copolymers can self-assemble into nanospherical micelles, with the A and B blocks arranged to form the core and shell (this works especially well if the A and B groups have opposite polarities, so they prefer to segregate rather than intermingle).

If a few molecules of tri (or higher) functionality are introduced to the reaction, the resulting polymer will have a branched structure. One such example is the grafting of branches made from repeating unit B to a linear backbone of A repeating units. Here, B is said to be grafted onto A:

```
   B
   B
   B          B
   B          B
   B          B
   B          B
   B          B
AAAAAAAAAAAAAAAAAAAAAA
        B
        B
        B
        B
        B
        B
```

This copolymer would be called graft copolymer, poly(A-g-B), as the backbone repeat unit is listed first. Note that “few molecules” is key here, since if even as little as 0.1% of the reaction mixture contains monomers with functionalities of 3 or higher, a network or cross-linked structure is likely to form (particularly at higher reaction conversions).

As the length and frequency of the branches on polymer chains increase, the probability that the branches will reach from one backbone chain to another increases. When the backbone chains are connected in this way, the molecular structure becomes a network, with all the chains linked through covalent bonds. This creates a three-dimensional crosslinked polymer and the entire mass of the polymer becomes one single large molecule.

Cross-linked or network polymers may be formed in two ways: by starting with reaction masses containing sufficient amounts of tri- or higher functional monomer; or by chemically creating cross-links between previously formed linear or branched molecules (curing). The latter is exactly what vulcanization does to natural rubber.[1]

1.1.3 Types of polymer

We have already seen the classification of polymer based on their polymerization reaction mechanism or their structural organization, but there are many others ways to classified polymers. One of this is based on their thermal behavior.

We can distinguish among two different polymer: thermoplastic polymers and thermosetting polymers (or thermosets).

Thermoplastic polymer tend to soften by heating and then applying a stress could flow. When cooled again, they would reversibly regain their solid or rubbery nature. Some of the most commercially important thermoplastics include polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), and polystyrene (PS). PE is used in products ranging from plastic bags to detergent bottles and has the simplest possible repeat structure of any polymer, since all the pendant groups are hydrogens. PP is also found in a wide range of products, such as plastic storage containers, and competes with other polymers in making plastic bags and pipes. PVC is commonly found in materials as diverse as rigid drainpipes, shower curtains, and raincoats, while PS has been used in foam coffee cups and disposable cutlery. Because these materials are thermoplastics, they are typically made into pellets after polymerization, since then can be melted and extruded or shaped into final products.

Thermosetting polymers (also thermoset), although they might be heated to the point where they would soften and could be made to flow under stress once, would not do so reversibly. That is, heating caused them to undergo a “curing” reaction. Sometimes these materials emerge from the synthesis reaction in a cured state. Further heating of these thermosetting polymers ultimately leads only to degradation (the smell of a short-circuited electrical appliance attests this) and not softening and flow. Continued heating of thermoplastics will also ultimately lead to degradation, but they will generally soften at temperatures below their degradation point.

Commercially important thermosets include epoxies, polyesters, polyurethanes and phenolic resins. Each of these materials starts out as (often viscous) liquids that set by curing into a final shape. Because these materials set the first time they are made, they cannot be reheated after the polymer formation without degrading the structure.

Natural rubber is a classic example of the difference between a thermoplastic and a thermosetting polymer. Introduced to Europe by Columbus, natural rubber did not achieve commercial significance for centuries, because it was a thermoplastic, articles made of it would become soft and sticky on hot days. In 1839, Charles Goodyear discovered the curing reaction with sulfur (which he called vulcanization in honor of the Roman god of fire) that converted the polymer to a thermoset. This allowed the rubber to maintain its useful properties to much higher temperatures and led to its great commercial importance.

Polyester thermosets are used to produce fiberglass system, filament winding, repair compounds, coating. Polyurethane ones are used to make mattress, coatings, adhesives, foams, insulated systems, fibers. Polyimides could be found in parts of aircrafts or aerospace composite structures, coating materials, glass reinforced pipes. Epoxy resins are used as the matrix component in many fiber-reinforced plastics and as casting, adhesives, electronics encapsulation, coatings and constructions too.

1.1.4 Polymer morphology

For salts and metals is common and clear the concept of crystals, because these materials exist primarily as crystals when solid. The arrangement of atoms can affect the type of crystallinity, but the main effect of crystals is to bring atoms together in a regular arrangement. Thinking back to the bowl of cooked spaghetti representation of polymers, regular arrangement may seem nearly impossible (and it is for some polymers, particularly those with bulky side groups). For polymers with small side groups (such as polyethylene), large segments of polymers can arrange into crystals, but there are not polymers that are 100% crystalline.

First, a regular chain structure is necessary to allow the chains to pack into an ordered, regular, three-dimensional crystal lattice. Thus, stereoregular polymers are more likely to have sizable crystalline portions than those that have irregular chain structures. Similarly, large pendent groups, particularly if they are spaced irregularly, hinder crystallinity. Second, no matter how regular the chains, the secondary forces holding the chains together in the crystal lattice must be strong enough to overcome the disordering effect of thermal energy. So hydrogen bonding or strong dipole interactions promote crystallinity and, other things being equal, raise the crystalline melting temperature.

Polymers that do not meet the above criteria show no traces of crystallinity and they are completely amorphous. In contrast to the ordered arrangement in a crystal lattice, the chains in an amorphous polymer mass assume a more-or-less random, twisted, entangled configuration, as in the bowl of cooked spaghetti.

Despite intensive efforts, no one has succeeded in producing a completely crystalline polymer. The crystalline content may in certain cases reach 98%, but at least a few percent of non-crystalline material always remains.

Polymers have covalent bonds linking the crystalline and amorphous regions, making the interfaces between these regions more continuous. The ability to tailor and adjust crystal size and degree of crystallinity allows for a wide range of mechanical properties in polymers, from rubbery and flexible (largely amorphous with small crystals) to rigid and strong (largely crystalline).

Because weak bonds stabilize the crystal part, anything that can alter or disrupt these bonds will cause a drop in the degree of crystallinity. The first thought is the effect of temperature.

Solvents can also disrupt weak polymer bonds, thus they have an effect on crystals similar to melting. Solvents are small molecules that can diffuse into a polymer and form new weak bonds, replacing polymer–polymer interactions with polymer–solvent interactions. In a good solvent, especially in dilute solutions, polymer crystallinity disappears. Upon drying (or cooling a molten polymer), the chains can reform crystals with the crystal size and the degree of crystallinity dependent on the rate of solvent evaporation (or rate of cooling).

1.1.5 Tacticity

Tacticity is the relative stereochemistry of adjacent chiral centers within a macromolecule. The practical significance of Tacticity rests on the effects on the physical properties of the polymer. The regularity of the macromolecular structure influences the degree to which it has rigid, crystalline long-range order, or flexible, amorphous long-range disorder. Tacticity affects then at what temperature a polymer melts, how soluble it is in a solvent and its mechanical properties.

Tacticity is significant in which called vinyl polymers, in which each repeating unit with a substituent -R on the side of polymer backbone is followed by the next repeating unit with the substituent on the same side as the previous one or on the other side as the previous one. The same happens if there are two substituents -R and -R' on the side of polymer backbone.

The three possible ways for adjacent monomer units of a vinyl polymer to join are shown in Figure 1.3.

$-\!\left(\mathrm{CRR'}-\mathrm{CH_2}\right)\!\left(\mathrm{CRR'}-\mathrm{CH_2}\right)\!-$ **Head-to-tail**

$-\!\left(\mathrm{CRR'}-\mathrm{CH_2}\right)\!\left(\mathrm{CH_2}-\mathrm{CRR'}\right)\!-$ **Tail-to-tail**

$-\!\left(\mathrm{CH_2}-\mathrm{CRR'}\right)\!\left(\mathrm{CRR'}-\mathrm{CH_2}\right)\!-$ **Head-to-head**

Figure 1.3. Possible way to join for adjacent vinyl monomer units

The head-to-tail arrangement predominates for most vinyl polymers prepared by the normal methods. So assuming that only head-to-tail joining occurs, if all the same substituent (-R or -R') unit are on the same side of the plane the polymer is isotactic, alternately on opposite sides the polymer is syndiotactic, otherwise if they are randomly on either side of the plane the polymer is atactic (Figure 1.4).

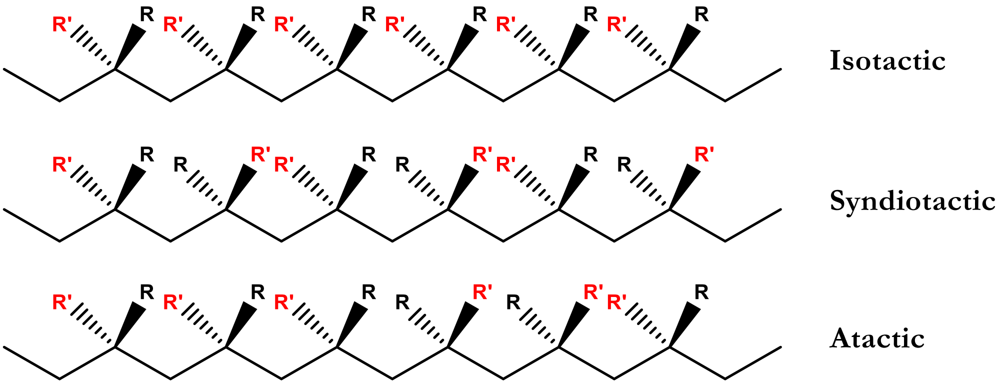


Figure 1.4. Possible stereochemistry of adjacent chiral center

A particular state of tacticity is a particular configuration of the molecule and cannot be changed without breaking and reforming bonds and there is not enough thermal energy for this to happen. Rotations around bonds produce only different conformations. A vinyl polymer is therefore unlikely to be appreciably crystalline unless it is substantially either isotactic or syndiotactic; the atactic chain cannot get into a state in which it has translational symmetry.

1.1.6 Thermal transitions in polymers

Polymers are a bit more complex in comparison to pure substances. The boiling point, for example, is largely unimportant for polymers, since they degrade well before macromolecules vaporize.

For crystalline polymers, there is a similarity with the melting point: the temperature of melting transition (T_m). With this kind of polymer as the temperature rises, bonds holding crystals together begin to come apart, resulting in a melting.

Another important temperature in polymer applications, this time for amorphous ones, is the glass transition temperature (T_g), the temperature which divides glassy from rubbery behavior. Amorphous polymers can exhibit two distinctly different types of mechanical behavior. Some, such as poly(methyl methacrylate) (PMMA) and polystyrene (PS), are hard, rigid, glassy plastics at room temperature. Other polymers, for example, polybutadiene, poly(ethyl acrylate) and polyisoprene are soft, flexible rubbery materials. If PS and PMMA are heated (to around 125 °C), they exhibit typical rubbery properties; when a rubber ball is cooled, it becomes rigid and glassy and shatters when an attempt is made to bounce it. Therefore, T_g is the temperature, or a narrow range of temperatures, below which an amorphous polymer is in a glassy state and above which it is rubbery.

Crystalline polymers, that have crystalline and amorphous portions, have both T_m and T_g temperatures, obviously each for its concerning part.[2]

1.1.7 Gel permeation chromatography

A brief discussion must be made on gel permeation chromatography (GPC), since this technique is widely used in the qualitative and quantitative analysis of polymeric materials.

As with many others analyses the first thing to do is to dilute the sample with a solvent or a mix of solvents, which could be the same eluent or a different one. Anyway, the used solvent/eluent must be compatible with the polymer to be analyzed in order that a true solution is formed. A true solution means that each polymer chain forming a random coil and the solution sufficiently dilute to avoid any interaction between individual polymer molecules. Different solvents / eluents will solvate and swell the polymer molecule to different degrees. A moderate to high degree of solvation is preferred. A polymer molecule of a certain polymer type and certain chain length in a particular solvent will occupy a particular volume.

Then the dilute polymer solution is injected on to a chromatography column containing a packing. The packings used for GPC are porous and the size of the pores will determine the molecular weight range with whom they can work.

Different packings are available dependent on the polymer type, application, and expected molecular weight range.

The analysis for the rest is identical to a typical liquid chromatography, in which the mobile phase drags the sample through the stationary phase that separates the different species and makes them reach the detector with different times. Polymer molecules of large solvated size (volume) will be unable to permeate into a portion of the packing pores and have a short residence time and will therefore get out of the column first. Polymer molecules of small solvated size (volume) will have a longer residence time in each packing pore encountered and will therefore get out of the column later (Figure 1.5).

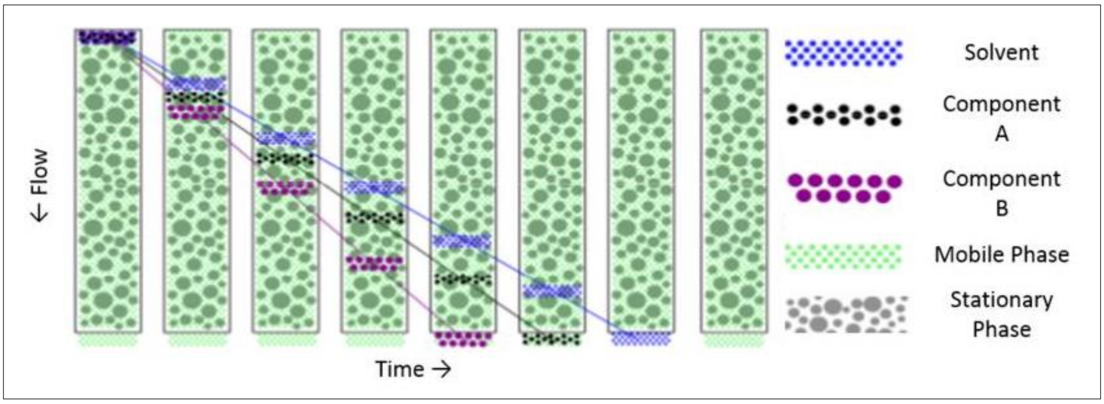


Figure 1.5. Size exclusion in the GPC column. Component B is the biggest species in the solution, component A is smaller than component B but bigger than solvent

The detector usually is a differential refractive index (DRI), but may be infrared (IR), ultraviolet (UV) or evaporative light scattering (ELS). It is used to record the amount of polymer, fractionated by molecular size, eluting from the column over time, resulting in a chromatogram (Figure 1.6).

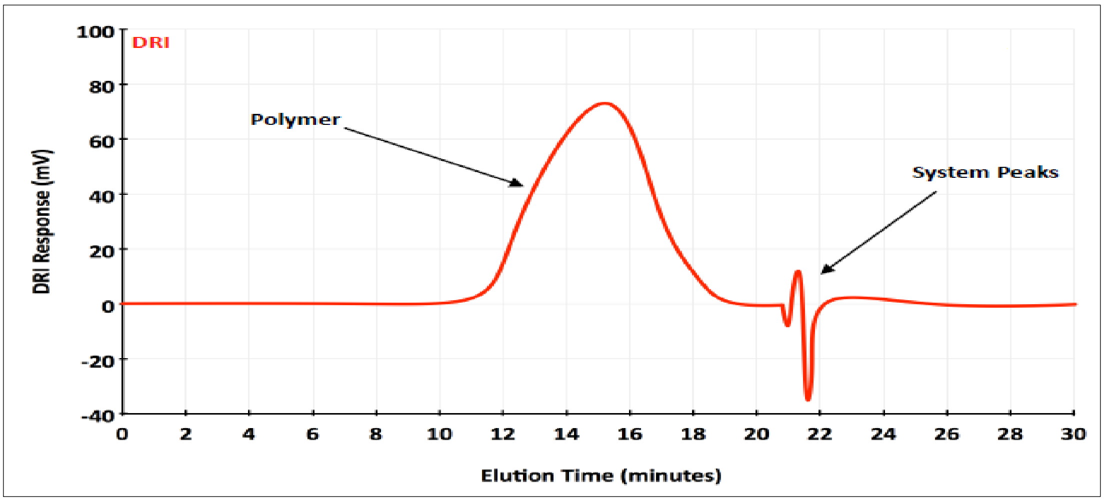


Figure 1.6. Example of GPC chromatogram

By appropriate calibration of the columns and detectors, the molecular size distribution of the polymer could be then translated to a molecular weight distribution. Computation is applied to the data to provide molecular weight values.

Among the main used average values there are number average (M_n), weight average (M_w) and polydispersity (M_w/M_n).

The number average molecular mass (M_n) is the ordinary arithmetic average of the molecular masses of the individual macromolecules. It is determined by measuring the molecular mass of n polymer molecules, summing the masses, and dividing by n:

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

The mass average molar mass (M_w) takes in account that a larger molecule will have a larger contribution than a smaller molecule. The mass average molar mass is calculated by:

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

The polydispersity index, or simply polydispersity, is a measure of the distribution of molecular mass in a given polymer sample. It is indicated with PD or M_w/M_n and is calculated by the ratio between the number average molecular mass and the mass average molar mass.

In polymers, the individual polymer chains rarely have exactly the same degree of polymerization and molar mass, and there is always a distribution around an average value. For this reason, the GPC technique becomes very useful both in the synthesis and in the analysis of polymeric materials.

Along this thesis work are shown some structures of the synthesized resins. Such figures show the abstract structure of the resins, the actual structure is an agglomeration of such molecules in different oligomers with a certain distribution. By means of GPC, we are able to detect their distribution and compare them each other.

1.2 Coatings

One of the above-mentioned applications for thermosets is coating. A coating is a covering that is applied to the surface of a substrate. The purpose of applying the coating may be decorative or functional; industrially the first purpose is to have some kind functionality, but even the eyes take their part. Functional coatings are applied to change the properties of the substrate: such as adhesion, wettability, resistance to chemical or mechanical stress, make it a conductor or to insulate one. There are several types of coating. They can be discern by their physical state (liquid, gas or solid) and/or by their application method: chemical or physical vapor deposition, chemical and electrochemical techniques, spraying, roll-to-roll process and many others. Varnishes and enamels are part of the coatings and they could be liquid, as organic solvents solution (sometimes aqueous solution), or solid, as solvent-free resins. The general enamels composition consists of:

- Resins, these are generally solid, sticky materials hold the system together. They are also called binders and, when in a solvent, they are the vehicles for the system. They may come as a “single-package” or “two package” system. Single-package is just the liquid resin or the resin in solvent. Two package means that an “A” part was blended with a “B” part to cause a chemical reaction. In both systems, we need to know the amount of solid resin present. With the two-package systems, we need to know the ratio of the solid contents to form the desired film. This ratio determine the film properties.
- Solvents, that permit to apply the coating in a liquid state. Solvents may be organic; they may even be water. They are in the formulation to aid in mixing, viscosity and application of the coating. After application, they evaporate and leave a dry film.
- Catalysts, organic or inorganic molecules that accelerate the polymerization reaction.

- Additives, these are ingredients added in small (<5%) amounts to improve some properties of the coating. They could be, for example, plasticizers or leveling agent.
- Pigments, they are the dry materials added to the coating to give it color or resistance properties, camouflaging properties and the like. Pigments can be divided into many different categories for different purposes. Some materials are primary pigments versus filler pigments. Some materials are organic in nature, and others are inorganic. Properties such as lightfastness, particle size and specific color are reasons for choice.[3]

1.2.1 Electrical insulating coatings

In modern life, electrical engines power many devices: from electrical appliance to electrical car, from the households transformers, that convert alternating current into low direct current, to industrial transformers, that convert the high currency from power plants into standard alternating current voltage and the kinetic energy obtained by traditional power plants as well as wind turbines into electricity. The Maxwell equations form the theoretical basis of understanding of electromagnetic fields, the underlying principle behind the transformation of electricity to kinetic energy and vice versa. In order to generate electromagnetic fields, electrical devices require tightly wound wire coils in which the individual wires are insulated against each other to prevent electrical short-circuits. This is the role of primary electrical insulation, applied onto wires avoids the passage of current through nearby turn in the coil. Then a secondary insulation protect electrical devices from friction, abrasion, humidity, chemicals and rotational forces.

The first materials use to insulate the conducting wires were fibrous materials such as cotton, cellulose or silk. Since 1900, these wrapped wires were also impregnated with natural product varnishes to reduce the hygroscopicity of the insulating materials. Around 1915, enamels based on synthetic materials such as phenolic resins gradually substituted natural resin-based varnishes: they made it possible to cover the wires directly without having to insulate the wires with fibrous materials first.

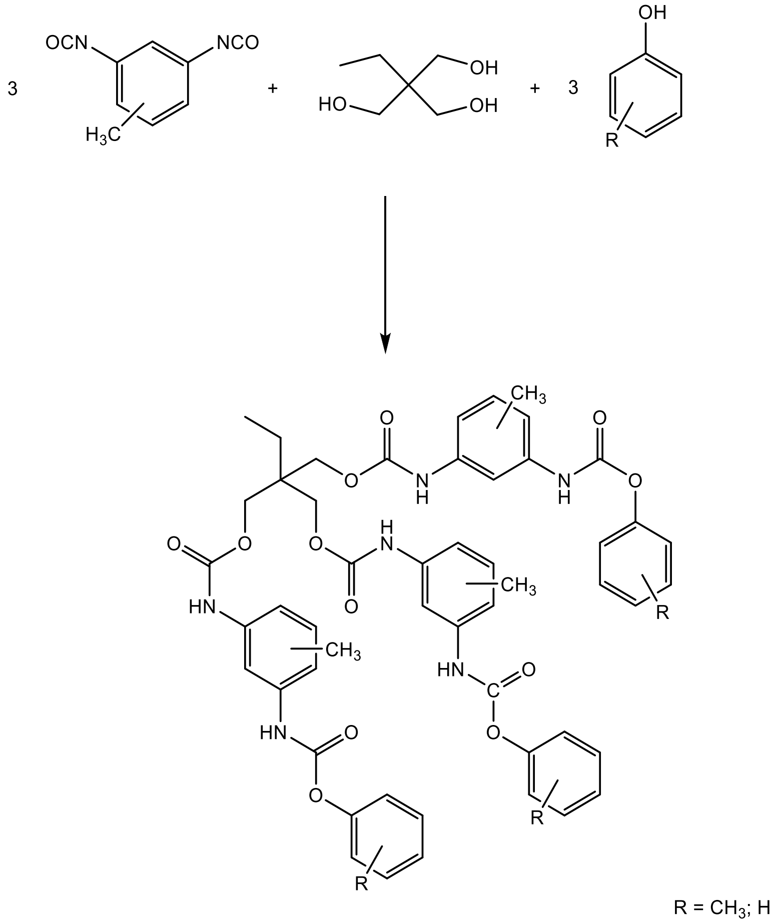
As synthetic resins replaced fibrous coating materials, motor development and motor manufacturing accelerated dramatically. With faster winding speeds required for mass production, the physical properties demanded of the wire coating also increased. Improvements in dielectric strength, abrasion, flexibility, thermal properties and chemical resistance all became more critical to the electrical industry. A new generation of wire coatings evolved with dramatic improvements in the physical properties demanded by the motor manufacturers. However, the enamel also had to be applied on the copper wire more efficiently and thus spurred the development of wire enameling machines with increased capacities.

Resins used are mainly: polyesterimides (PEI), polyurethanes (PU), polyamideimides (PAI), polyvinyl formals (PVF). Often this kind of enamels are used in combination, one as base-coat and one as topcoat. Base-coats generally show good adhesion to the copper and high flexibility and topcoats lead to high abrasion and higher temperature resistance.[4]

Polyurethane enamels

Polyurethane wire enamels (PU-WE) consists of polyurethane resin, a polyisocyanate that reacted with phenol or cresols (blocking agent) to form urethane groups, and a polyester resin, polyester polyol.

Isocyanates are blocked to reduce harmfulness and reactivity of the compound (Scheme 1.6). Isocyanates in fact have a high vapor pressure even at room temperature and they are very hazardous to human healthy due to their volatility. The toluene diisocyanate vapor pressure is 3.33 Pa at 25 °C, this means that the concentration of saturated vapors in equilibrium with the air is equal to ~30 ppm and therefore much higher than the TLV values.[5,6] By blocking the isocyanate groups and increasing the molecular weight they reduce their harmfulness. In the curing stage deblocking occurs and blocking agents diffuse to the enamel and evaporate with the solvents. The low deblocking temperature and the high reactivity of the isocyanate groups is the reason why lower oven temperatures, compared to other wire enamels, were possible.



Scheme 1.6. Structure of the blocked polyisocyanate

After deblocking the isocyanate groups, free again, re-form urethane bonds with the free -OH groups of the polyol, forming the insulated layer.

Aromatic isocyanates are used for polyurethane wire enamels because their reactivity is higher compared to the aliphatic isocyanates and the resulting enamels have a higher thermal stability. Typical isocyanates used are the toluene diisocyanate (TDI) and the methylene diphenyl diisocyanate (MDI).

The decomposition of urethane groups at high temperature is the reason for the solderability of polyurethane wire enamels. Highly cross-linked and polymeric structures increase the wire enamel cut-through temperature, while more urethane linkages improve solderability.

Polyester polyols are based on diols/triols such as ethylene glycol, diethylene glycol, glycerol and trimethylolpropane (TMP). Diacids such as terephthalic acid and isophthalic acid are employed. Aliphatic alcohols are used because of their reactivity towards isocyanates. The use of higher functional alcohol leads to branched polyester polyols. The aromatic acid are important for the thermal stability, while long chain aliphatic acids give improved flexibility.

More performant polyurethanes are obtained used an adduct of MDI, TMP and blocking agents in combination with a polyesterimide resin, formed by trimellitic anhydride, diaminodiphenylmethane and glycols.

As catalyst for the crosslinking reaction are used metal (Pb, Sn, Zn, Ti) carboxylates and alcoholates. Tertiary amine such as triethylamine and diazabicyclooctane (DABCO) have the same effect. Mixtures of tertiary amines and organo-metals compound can also be used.

Polyurethane wire enamels offer an unique combination of high flexibility, adhesion, solderability and fast coating speed. The application speed is important for improved manufacturing productivity. Thermal properties can be adjusted increasing or decreasing in imide content of the polyol (when it is participant in the formulation) and/or increasing the cross-link density of the final cured film.

This kind of enamels are mostly used on ultra-fine wires to intermediate-sized wires. Solderable polyurethane enameled wires are used in applications where highly efficient production is required. They are used for self-supporting coils, voice coils, encapsulated coils, relays and yoke coils, hair dryers, timer and clock coils, motor coils, solenoids, ignition coils, transformers, automotive relays.[7]

Polyesterimide enamels

Polyesterimides wire enamels (PEI-WE) were made with the intent of merging the good mechanical properties of polyesters with the excellent thermal resistance of polyimides. Generally, aromatic diamines and some anhydrides, often trimellitic anhydride (TMA), form the polyimide part and polyethylene terephthalates branched with glycerin or other aliphatic glycols form the ester part. Among the most used diamines is methylenedianiline (MDA), while aliphatic ones are used in special applications.

In recent time, a particular branching agent was introduced in the formulation, the *tris*-(2-hydroxyethyl)isocyanurate (THEIC). This could further improve the mechanical and thermal properties of the resulting polymer.[8]

Useful catalyst could be metal salts (as acetates or octoates of Zn, Mn, Sn and others). Titanates are also used, such as tetrabutyl titanate monomer (TBM), tetarisopropyl titanate (TiPT) or tetrabutyl titanate polymer (TBP).

PEI-WE is one of the most important insulating enamels in electrical engineering, and is used in a wide electrical equipment for the insulation of conductors and influencing the whole insulating system of a winding. They are available in all size based categories, because their application is spread over the entire possible applications palette where magnet wires are used, going from tiny motors to big transformers. They are used in transportation, automotive, household appliances, hermetics, brown goods, audio/video equipment, motors for small electric tools, and much more.

Besides standard PEI there are specialties which are optimized versions of classical PEI, which claim improved characteristic as adhesion, corrosion resistance or friction coefficient reduction. Such improved properties are obtained thanks to the addition of special additives, like cyanoguanidines, melamines, phosphates, imidazoles or fluorinated polymers. Other special applications are possible by introducing pigments or conductive materials like graphite or metal powders in the formulation.[9]

1.3 Thermoplastics

Thermoplastics are polymers that becomes pliable or moldable above their T_g temperature and solidifies upon cooling.

Most thermoplastics have a high molecular weight. The polymer chains associate through intermolecular forces, which weaken rapidly with increased temperature, yielding a viscous liquid. Thus, thermoplastics may be reshaped by heating and are typically used to produce parts by various polymer processing techniques such as injection molding, compression molding, calendaring, and extrusion.[10]

Above its T_g and below its T_m, the physical properties of a thermoplastic change drastically without associate phase change. Some thermoplastics do not fully crystallize below the glass transition temperature, retaining some or all of their amorphous characteristics. Amorphous and semi-amorphous plastics are used when high optical clarity is necessary, as light is scattered strongly by crystallites larger than its wavelength. Amorphous and semi-amorphous plastics are less resistant to chemical attack and environmental stress cracking because they lack a crystalline structure.

Brittleness can be decreased with the addition of plasticizers, which increases the mobility of amorphous chain segments to effectively lower the T_g. Modification of the polymer through copolymerization or through the addition of non-reactive side chains to monomers before polymerization can also lower it. Before these techniques were employed, thermoplastic composite would often crack when exposed to cold temperatures. These are linear or slightly branched long chain molecules capable of repeatedly softening on heating and hardening on cooling.

Many commercially products are thermoplastics, among these: polyamides (PA), polycarbonate (PC), poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(vinyl chloride) (PVC), polytetrafluoroethylene (PTFE), a terpolymer as acrylonitrile butadiene styrene (ABS), and many others.

Uses shall be as fibers, electronics component, construction materials, data storage devices (CDs and DVDs), automotive and aircraft parts, containers, ropes, carpet, disposable cutlery. In case of transparent polymers, also they serve as substitute for glass for items such as aquariums, motorcycle helmet visors, viewing ports or windows, lenses, signs or even eye lenses.[11]

1.3.1 Poly(methyl methacrylate)

PMMA is a transparent thermoplastic often used in sheet form as a lightweight or shatter-resistant alternative to glass. The same material can be used as a casting resin, in inks and coatings, and has many other uses.

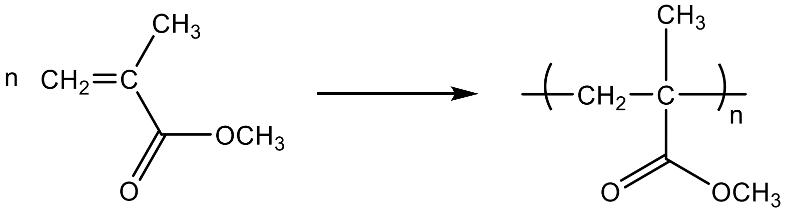
Chemically, it is the synthetic polymer of methyl methacrylate. The material was developed in 1928 in several different laboratories by many chemists, such as

William Chalmers, Otto Röhm, and Walter Bauer, and was first brought to market in 1933 by the Rohm and Haas Company under the trademark Plexiglas®.

PMMA is an economical alternative to polycarbonate (PC) when tensile strength, flexural strength, transparency, polishability, and UV tolerance are more important than impact strength, chemical resistance and heat resistance.[12] It is often preferred because of its moderate properties, easy handling and processing, and low cost.

Polymethyl methacrylate was discovered in the early 1930s by British chemists Rowland Hill and John Crawford at Imperial Chemical Industries (ICI) in England. ICI registered the product under the trademark Perspex®. About the same time, chemist and industrialist Otto Röhm of Rohm and Haas AG in Germany attempted to produce safety glass by polymerizing methyl methacrylate between two layers of glass. The polymer separated from the glass as a clear plastic sheet, which Röhm gave the trademarked name Plexiglas® in 1933. Both Perspex® and Plexiglas® were commercialized in the late 1930s. In the United States, E.I. du Pont Company subsequently introduced its own product under the trademark Lucite®. In 1936, Imperial Chemical Industries began the first commercially viable production of acrylic safety glass. During World War II both Allied and Axis forces used acrylic glass for submarine periscopes and aircraft windshields, canopies, and gun turrets. Airplane pilots whose eyes were damaged by flying shards of PMMA fared much better than those injured by standard glass did, demonstrating better compatibility between human tissue and PMMA than glass.[13] As for many other polymer materials, civilian applications followed after the war.

PMMA is routinely produced by emulsion polymerization, solution polymerization, and bulk polymerization. Generally, radical initiation is used, but anionic polymerization of PMMA can also be performed. PMMA produced by radical polymerization is atactic and completely amorphous (Scheme 1.7).



Methyl methacrylate **Poly(methyl methacrylate)**

Scheme 1.7. Formation of poly(methyl methacrylate)

The glass transition temperature (T_g) of atactic PMMA is 105 °C. The T_g values of commercial grades of PMMA range from 85 to 165 °C. The range is so wide because of the vast number of commercial compositions which are copolymers with co-monomers other than methyl methacrylate.[14] PMMA is thus an organic glass at room temperature, since it is below its T_g. The forming temperature starts at the glass transition temperature and goes up from there. All common molding processes may be used, including injection molding, compression molding, and extrusion. The highest quality PMMA sheets are produced by cell casting, but in this case, the polymerization and molding steps occur concurrently. The strength of the material is higher than molding grades owing to its extremely high molecular weight. Rubber strengthening has been used to increase the toughness of PMMA to overcome its brittle behavior in response to applied loads.

PMMA can be also joined using cyanoacrylate cement (commonly known as superglue), with heat (welding), or by using solvents such as di- or trichloromethane to dissolve the plastic at the joint, which then fuses and sets, forming an almost invisible weld. Scratches may easily be removed by polishing or by heating the surface of the material.

Laser cutting may be used to form intricate designs from PMMA sheets. PMMA vaporizes to gaseous compounds (including its monomers) upon laser cutting, so a very clean cut is made, and cutting is performed very easily. However, the pulsed laser cutting introduces high internal stresses along the cut edge, which on exposure to solvents produce undesirable "stress-crazing" at the cut edge and several millimeters deep. Even ammonium-based glass-cleaner and almost everything short of soap-and-water produces similar undesirable crazing, sometimes over the entire surface of the cut parts, at great distances from the stressed edge. Annealing the PMMA sheet/parts is therefore an obligatory post-processing step when intending to chemically bond laser cut parts together.

In the majority of applications, it will not shatter. Rather, it breaks into large dull pieces. Since PMMA is softer and more easily scratched than glass, scratch-resistant coatings are often added to PMMA sheets to protect it.

1.4 The "Impact" of Polymeric Materials

Polymeric materials offer many advantages for specific applications. They are easy to shape, do not corrode or decompose, but slowly, and the characteristics can be adapted to the specific needs by using composites or adding specific layers or additives. These characteristics are also the source of some of the problems associated with plastics.

Thanks to their versatility and their high resource efficiency, polymeric materials have become key materials in strategic sectors such as packaging, building and construction, transportation, renewable energy, medical devices, sports, and even more. Moreover, polymeric materials have enabled innovation in many other sectors allowing the development of products and solutions that could not exist today without these materials. Polymeric materials and polymeric products are extremely resource efficient along their service life, helping us to avoid food waste, to save energy and to decrease CO_2 emissions.

For example, polymeric insulation saves 250 times the energy used for it production; thanks to plastic parts, cars have four times lower environmental impact and plastic packaging extend significantly the shelve life of food reducing spoilage and waste. Moreover, food packaging reduce in many Countries the risk of spreading diseases, making sterile food and water.[15, 16, 17]

The worldwide production of polymer materials is approximately 335 million tones (in 2016), steadily increasing (Figure 1.7).

China is the largest producer of polymers (29%), followed by Europe (19%) and NAFTA (18%), then Asia (without China, 21%), Middle East Africa (7%), Latin America (4%), and CIS (2%).

In Europe, the main converter of polymeric materials is Germany and the second is Italy (Figure 1.8).

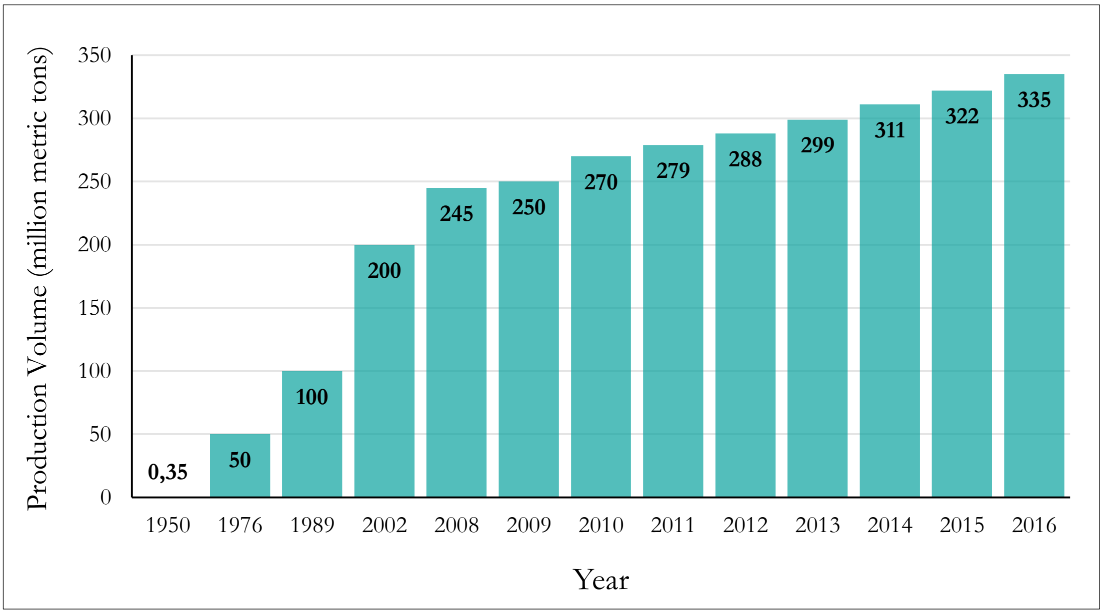


Figure 1.7. Global polymeric materials production from 1950 to 2016

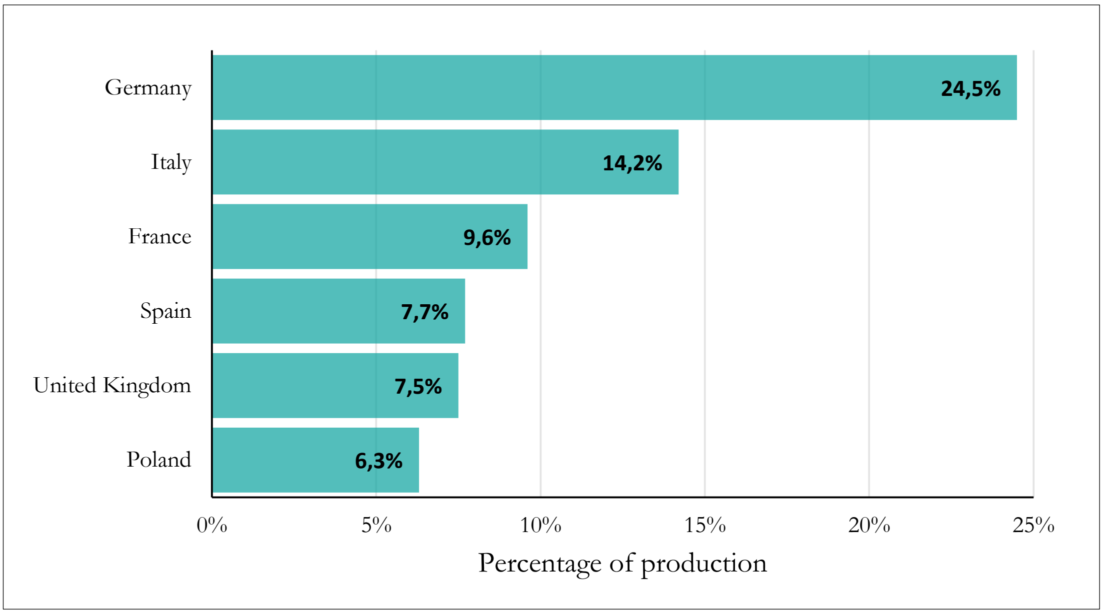


Figure 1.8. Percentage of polymeric materials production in Europe for main countries.

The six larger European countries and Benelux cover almost 80% of the European demand in 2016 (49,9 million tons). Figure 1.9 shows the main market sectors of polymeric converter.

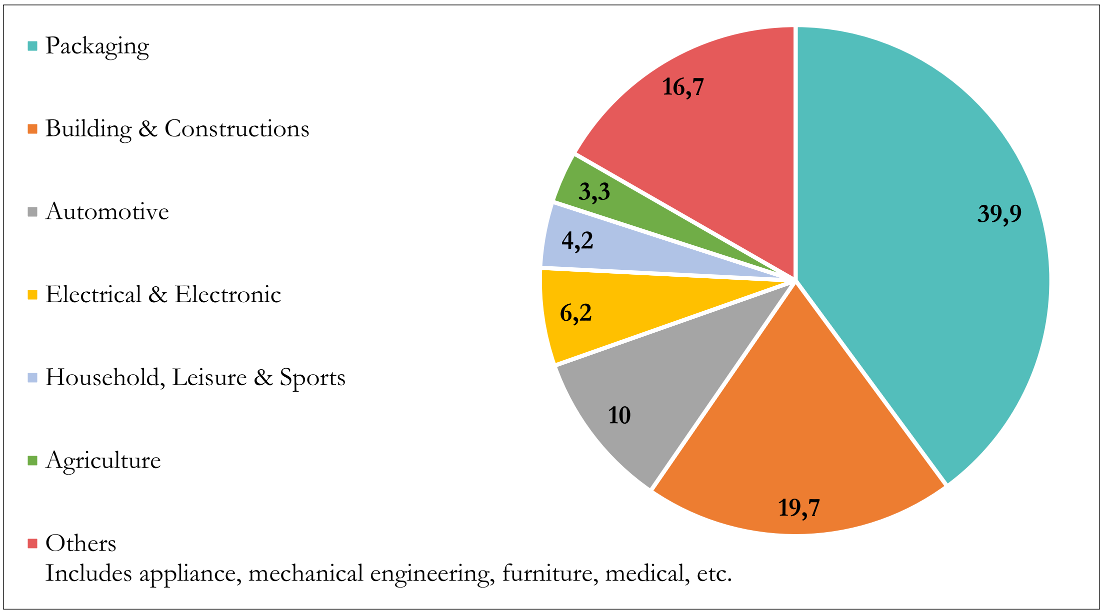


Figure 1.9. Main market sectors of polymeric converter

Whereas, the European partition regarding polymer types is shown in Figure 1.10.

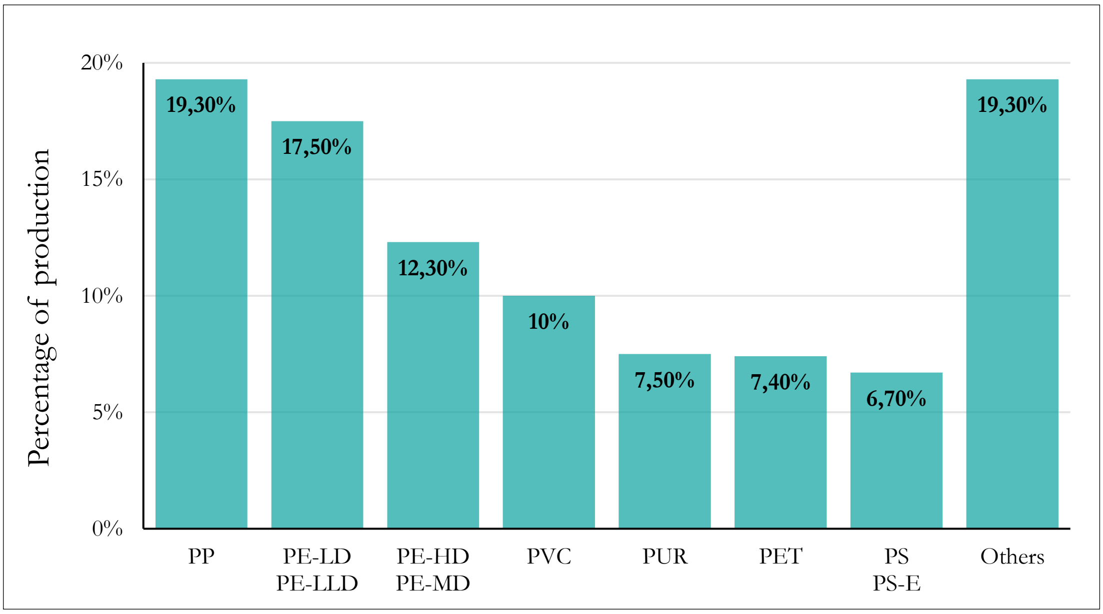


Figure 1.10. European plastics converter demand by polymer types in 2016

These data shows the big importance and the big worth of polymeric materials. Obviously, a production of this size needs a large amount of energy and resources and, nevertheless, cause a large amount of waste.

Nowadays saving and waste are two of the most important topic that need to be considered when dealing with producing any necessities or object.[18]

1.4.1 Environmental impact

Environmental impact refers to any alteration of the environment as a system of relationships between the anthropic, naturalistic, chemical-physical, climatic, landscape, architectural, cultural, agricultural and economic factors. It can be positive or negative, but often with the words "environmental impact" we refer exclusively to its negative meaning.[19] Terms such as sustainability, pollution, recycling are now more relevant than ever in both the industrial and civil sectors. For a number of years, we have also begun to talk about Anthropocene, referring to a geological epoch in which the presence of human beings and their activities are the main causes of territorial, structural, and climatic changes.[20] Nowadays it is therefore clear that the indistinct human activity needs to be regulated and curbed to avoid putting at risk the stability of the planet and the life of all its inhabitants.

The issue is so pressing that environmental impact assessments are necessary to submit a work or project and to have the authorization to complete them.

A concept strictly related to the environmental impact is that of sustainability. Sustainability is the characteristic of a process that can be maintained indefinitely at some level. In many fields, it is the process of changing in which the exploitation of resources, the investment plan, the orientation of technological development and institutional changes are all in line and enhance the current and future potential in order to meet the needs and aspirations of humankind.

The guiding principle is sustainable development, which relates, in an interconnected way, the environmental, the economic and the social. For sustainable development, development is intended to meet the needs of the present generation without compromising the ability of future generations to meet their needs. In the light of phenomena such as environmental degradation, climate change, overconsumption, population growth and unlimited economic growth in a closed system, the concrete possibility that human societies can achieve in the next future the objectives of environmental sustainability has been uncertain. Despite the commitment of individuals and companies to be oriented towards increasing sustainability.

Many modifications of the ecosystem made by man, including uncontrolled technological evolution, unbridled consumerism and the irresponsible use of raw materials, lead to the exhaustion of natural resources and a dangerous increase in environmental pollution. Humanity is living in an unsustainable manner, consuming the Earth's limited natural resources more rapidly than it is able to regenerate. Consequently, a collective social effort to adapt human consumption of these resources to a level of sustainable development is a question of paramount importance for the present and future of humanity. The devastating effects generated by continuous production and processing of products obtained without a planning can no longer be pursued. For this reason, many conferences are held periodically, organized among States all around the world, to set agendas to be pursued.

With these conferences, we try to spread the conviction that we need to intervene and raise awareness in order to finalize a complete cycle that generates a defined process that, through continuity and control guidelines, can fully manage, starting from the idea that defines a product is: its use, its durability and its recycling. Managing in such a way as to guarantee a closed cycle that reduces to zero the waste and guarantees the quality of the environment. Waste is the conclusive act of any cycle, preferably to be avoided and in any case to be controlled.

After a greater awareness of the need for sustainable development, contemporary society aims to change its behavior by focusing on the smart management of its work in respect of humankind and natural resources. It is also aimed at safeguarding future generations, in order to guarantee humankind continuity through a responsible control of the actions carried out on the ecosystem. The resources must be exploited in such a way as to encourage their regeneration in order to prevent their depletion, through process with zero impact to protect the environment.

To this end, some interventions can be carried out on the life cycle of the products of human activity: the birth of the product, the maintenance in life of the product, and the cycle of the product. The amount of waste generated during each phase represents a fundamental index to be minimized for obtaining a sustainable process. The more the gap is close to zero, the more the process from which it is generated can be defined as sustainable.

In general, the procedures that can be used to increase the sustainability of a process include: improving quality with minimum consumption of raw materials; the use of natural raw materials with minimal energy investment; during its design phase, provide for the possibility of recycling the product.

1.4.2 From waste to resources

The incorrect collection of many waste materials has caused that a large part of them were poured out into the sea, through rivers or groundwater. Every year, up to 13 million tons of plastic materials reach the ocean. It is estimated that in 2050 the total weight of plastic materials will be greater than that of fish. The plastics, once dispersed in the sea, become dangerous material for the aquatic fauna and flora. Both as they are, animals can eat them or can be trapped in some way in the plastics and this situation could compromise the possibility to carry out the necessary activities for live, and in the form of microplastics and nanoplastics. Microplastics and nanoplastics are particles of the order of micrometers or nanometers that are formed by the breakage due to atmospheric agents of the plastic materials dispersed in the sea. The micro- and nanoplastics also remain dispersed in the marine environment and enter into circulation in living organisms being ingested by fish or birds or absorbed by algae and other aquatic plants. There are studies that show an increase of the likelihood of disease in coral reef shoots up from 4% to 89%.[21] Besides, some substances used as additives in plastics are considered endocrine disruptors that alter the regular function of hormones. Otherwise, flame retardants (present inside many plastic products) are known obstruct the brain development in fetus and kids and other substances that can remain attached to the plastics, may cause cancer or birth defects (like Hg, DDT, hexachlorobenzene, and polychlorinated biphenyl).

It is known that microplastics accumulate inside fish stomach and not inside muscle tissue, so they should not move inside the human body by eating. Anyway, the effects of nanoplastics on fish and the assimilation mechanism are unknown but they could interfere at cellular level. Anyway, increasing of the amount of such plastics in the ocean could become dangerous for human health too as well as is already for fishes and other marine species.[22]

It is therefore important to take care of the wastes we produce. Solutions can be two: do not have dangerous waste (ideal concept) or re-evaluate the waste and do not consider it only as waste but as resource.

In the first sense, the so-called biodegrable or compostable products are oriented. Biodegradable polymers are polymeric materials, which are designed to exhibit a significant degradation resulting in environmentally compatible products, namely, CO_2, water, and other substances (biomass) within an acceptable period.

Degradation of these materials is achieved by various mechanisms and their combination (photo, thermal, mechanical, hydrolytic, oxidative, and biological) with the ultimate degradation exclusively carried out by biological processes, known as “mineralization”.

In addition, compostable products are not only biodegradable but also disintegrable and their decomposition process takes place in less than three months. Compostable means convertible into compost, a natural fertilizer.

These materials can be synthesized from either petrochemical or natural resources of vegetal, aquatic, and animal origins. Three main routes derive the feedstock: biosynthesis, chemosynthesis, and a direct application of natural materials with or without chemical modification.

Some biodegradable polymers are poly(lactic acid) (PLA), poly(glycolic acid) (PGA), and polyhydroxyalkanoates (PHA). These are all examples of biodegradable polymers derived from renewable raw materials. They are used for packaging or other food containers, and sometimes as biocompatible materials for the human body (threads for sutures or drug encapsulation).

However, biodegradable polymers due to their nature do not have high physical properties or are suitable for some types of applications (they have weak bonds that make them easy to degrade). This makes them not very versatile and impossible to use in some sectors. Moreover, if biodegradable products end up into the sea like the non-biodegradable ones, there are not the right conditions for degradation into the marine environment and the biodegradable products would require longer periods to degrade. For this reason, the United Nations Development Programme has rejected biodegradable polymers as possible solution for the plastic pollution.

The solution to reduce the amount of waste is to reuse the waste as more as possible by recycling or burning it to obtain energy (energy recovery).

In 2016 in Europe, around 11% of the total polymeric products were collected after their working "life". Of these, 41.6% were used for energy recovery, 31.1% recycled (63% inside Europe and 31% outside Europe), 27.3% shipped to landfill. For the first time in Europe, recycling overcomes landfill.

Worldwide, 18% of the plastic produced is recycled. Recycling is done based on the type of polymer, because each polymer has a different way of being recycled or sometimes they are very hard to recycle (Figure 1.11).[23]

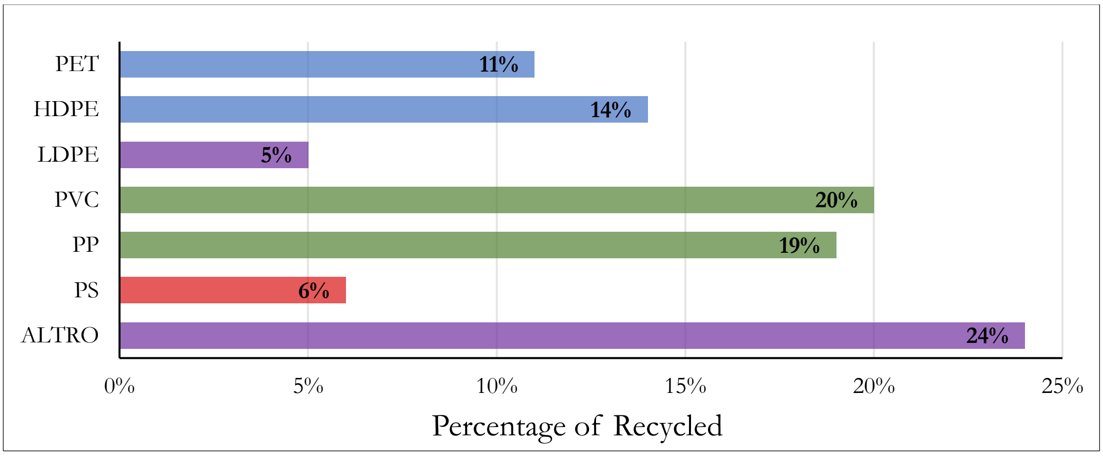


Figure 1.11. Global recycling based on types of polymers. Blue line for polymers easy to recycle, green line for manageable ones, red line for hard ones, and purple line for very hard ones.

1.4.3 Recycling and energy recovery

Today, mechanical recycling is the main technology used to recycle plastics. Mechanical recycling typically includes four steps. The collected material is first sorted, and then the sorted material is shredded, and at the end washed and dried. The material can then be melted and reprocessed to make pellets (that can be used by a manufacturer or convertor) or products directly. Below we discuss the key steps in more detail.

The first step in a recycling process is the collection of the waste and transporting it to a sorting plant to sort the plastic mix. The collected mix of plastics usually consists of various types of plastics, especially for postconsumer waste. Pre-consumer (production) waste can be relatively pure. In the case of post-consumer waste, there are usually still non-plastic impurities in the material, such as labels and little pieces of metal. These are first removed. Separation into various types of plastics is required to improve material quality. The separation of mixed plastics is challenging, and various techniques are applied in varying combinations. The process and the order in which they are used are defined by the composition of the mixed waste stream.

Eddy current separator, sink-float separation, drum separators/screens, induction sorting, X-ray technology and near infrared (NIR) sensors are the most commonly used separation techniques. Most companies use a combination of different techniques to obtain sufficiently pure streams.

The design of a sorting installation may be tailored to the incoming stream of plastic waste, to optimize sorting efficiency. The achievable purity level is a trade-off between costs and market requirements. The maximum achievable purity by separating mixed plastics waste is 94-95%. High-quality recycled material should have at least a purity of 98% to be used as input into manufacturing processes.

The next step is to reduce the size of the scrap, to enable processing larger pieces of plastic waste and to improve the density of the material for more efficient storage and transport. A shredder consists of rotating blades driven by an electric motor, some sort of grid for size grading and a collection bin. Materials are added to the shredder by a hopper. The product of shredding is a pile of plastic flakes.

After the plastics are shredded into small flakes, they are washed. Although most post-consumer waste is washed, this is not true for all input material used for recycling. Some regrind or even agglomerate is processed instantly. Cold or hot water, up to 60 °C, may be applied. Cold water use may result in increased use of chemicals (e.g. sodium hydroxide) and mechanical energy. The washed plastic flakes are dried until they contain less than 0,1 wt% moisture and are ready for reprocessing.

There are different techniques for reprocessing, with the most common ones being agglomeration and extrusion. Agglomeration is used mainly for recycling plastic films and consist of cutting the film in small pieces, heating and then cooling down by injection water. Extrusion is the most commonly applied technique. The material injected in the extruder come into contact with one or two rotating screws that force the plastic forward into a heated barrel at the molt temperature. The pressure allows the plastic to mix and melt gradually as they are pushed through the barrel. At the end, the molten plastic is pushed through a sieve to remove impurities, cooled and pelletized.

After the agglomeration or the extrusion phase, agglomerates or pellets are ready for the final processing step, the choice of which is determined by the final product: injection molding, blow molding, film blowing, and fiber extrusion.

Today high-quality recycled material can be made from HDPE, PP and PET (especially bottles). Specialized streams can also be recycled to provide high-quality recycled material. For example, in several countries, PVC window frames are collected separately and recycled into material for new window frames. However, other plastic products, especially films and foils, represent a large challenge for the recycling process. The large use of plasticizers and other additives makes it hard or impossible to guarantee a high purity of the recycled material. Hence, this material may currently be used to replace other materials than plastics (e.g. in construction) or may be incinerated for energy recovery.

Energy recovering is a valuable alternative for plastic-rich waste fractions that cannot be recycled. Plastics mainly consist of carbon and hydrogen that combusting they can develop high quantity of heat, as petroleum. Modern combined heat and power recovery plants can use plastic waste together with other high calorific materials. In Europe, the energy produced in this way account for up to 10% of some countries energy needs.

Chemical recycling consist of conversion of plastic materials into low-molecular weight products that can be reused as raw materials. Usually, is convenient only if the same plant is equipped to guarantee the further utilization of all products and residuals obtained.

The most important processes for the chemical recycling are: gasification processes, hydrogenation, pyrolysis, and blast furnace processes.

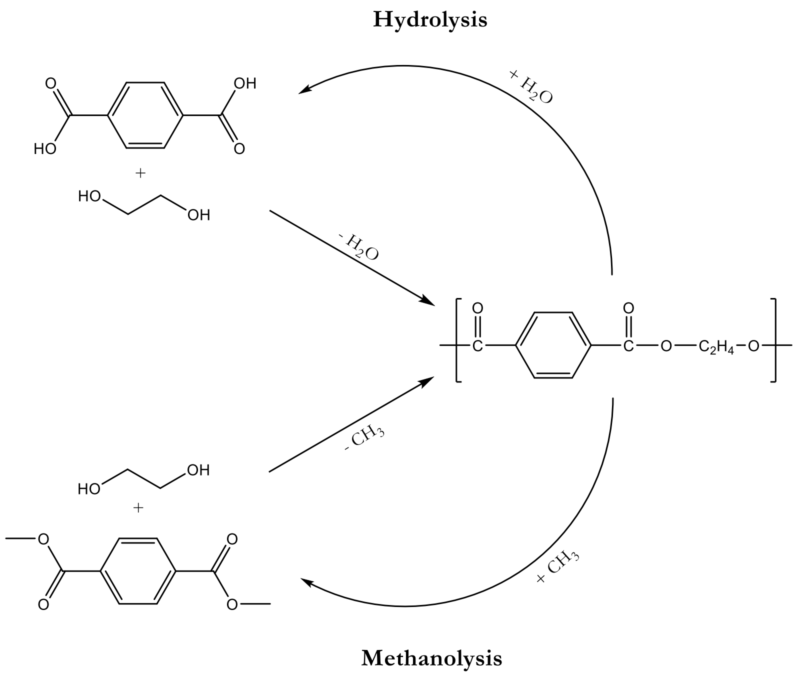
The main purpose of gasification processes is the generation of gas (CO, H_2). Possible byproducts in these processes are CO_2, H_2O, CH_4, and soot. The gasification can be described as a partial oxidation of hydrocarbons with an oxygen quantity which is under stoichiometric with respect to total combustion. The reaction temperatures range up to 1600 °C at a pressure of up to 150 bar. After the total conversion of the hydrocarbons CO_2 and H_2O can be formed. The processes uses oxygen, air, flue gas, steam, and carbon oxide as gasification agents, sometimes in combination too.

The polymer hydrogenation is derived from coal refining processes and the processing of heavy crude oil residues. After visbreaking in a depolymerization reactor at temperatures of about 420 °C, the real hydrocracking follows in a bubble-column-type reactor. Molecular hydrogen is used for this hydrogenation at approximately 200 bar and 480 °C. Less aggressive conditions can be applied when polymers are used exclusively as feedstocks. Hydro-bitumen and a synthetic crude oil as products can be further converted to chemical raw materials.

By pyrolysis a high-quality product can be obtained from a vast number of different polymers. The pyrolytic breakdown into chemical feedstocks allows a reuse in the original markets. Depending on the polymer used, a product similar to crude oil or even the monomer can be generated. The working temperatures of pyrolysis processes aimed at obtaining a high-quality product are within the range of 350±600 °C and therefore have to be classified as low temperature pyrolysis. Besides the choice of temperature, is very important choosing a suitable reactor type to have a product selectivity.

A waste polymer agglomerate could substitute for heavy oil normally necessary for the operation of the blast furnace. Iron ore as feedstock must be reduced for steel production. Carbon, carbon monoxide, or hydrogen are possible reducing agent. The gases necessary for reduction are formed as soon as the polymer material is blown into the 2000 °C hot melt at the bottom of the blast furnace. At these temperatures, the polymer is gasified instantly. As the chemical nature of waste polymer and heavy oil is very similar, waste polymer can be substituted for one oil. During the passage of the hot gases through the long blast-furnace moving bed more than 80% of the reduction potential of the gases generated from the waste polymer are utilized. At the top of the blast furnace a mixture of carbon dioxide, carbon monoxide and steam is obtained. After separation of water, the mixture has a low caloric value and is used internally in the iron works.

Pyrolysis is used also for recycling of acrylic polymers. This process consist of the thermal decomposition of the polymer chains to the monomers. For example, the depolymerization of PMMA generates stable MMA monomers under pyrolytic conditions. The processes first known used discontinuous retorts with sand as a heat transfer medium. As soon as it was realized that heat transfer was the decisive factor for pyrolytic depolymerization, other heat transfer media like superheated steam or phenol were used. Further investigations either to improve heat transfer during depolymerization or to reduce the residence time of the material in the reactor, led to processes like dry distillation and flash distillation or degradative extrusion. All these processes either showed an undesired formation of byproducts or led to deposits on the reactor walls.[24]



Scheme 1.8. Recycling mechanisms for PET

Another recycling technique is the solvolysis of polymer. Solvolysis is a general expression comprising processes like glycolysis, methanolysis, hydrolysis, acidolysis and alcoholysis. Preferentially, these processes are utilized when the polymers are classified and precleared manufacturing wastes. In this case, the processes are designed to reproduce the original monomers or starting materials from the plastics products too. An example is the complete depolymerization of PET to terephthalic acid and ethylene glycol or dimethyl terephthalates and ethylene glycol by respectively hydrolysis and methanolysis (Scheme 1.8).

Chapter 2: Optimization of a Recycling Process of PMMA

In the previous chapter, we have seen that it is possible to recycle polymethacrylates by pyrolysis. The pyrolysis process consist of the thermal decomposition at elevated temperatures usually in inert atmosphere and it involves the change of chemical composition. Commonly, the degradation of molecules during pyrolysis is caused by the break of chemical bond and the production of free radicals. When free radicals into the polymer is formed the degradation begins. Pyrolysis of poly(methyl methacrylate) (PMMA) allows high yield depolymerization.[25, 26] The monomer obtained could be used directly to produce new polymeric products. PMMA recycling by pyrolysis is widely used method because of its flexibility concerning the quality and relatively low cost.[27] But the methyl methacrylate (MMA) obtained contains traces of some byproducts as methyl isobutyrate, methyl pyruvate, 2,3-butanedione, and other organic species. The presence of these byproducts, once the repolymerization is occurred, leads to having a PMMA that differs from the pure PMMA by some undesirable characteristics: unpleasant smell, lower glass transition, different average molecular weight, and others. These characteristics make the recovered PMMA a non-first-rate product and limit its applications. The elimination of byproducts could results in obtaining a very better recovered PMMA, making possible a larger applicability. However, removing them by distillation is quite hard, because of their very similar boiling points to that of MMA.[28]
To reduce byproducts during the depolymerization, we tried to develop a process based on dissolution of PMMA into an appropriate solvent and re-precipitation into a non-solvent.

The work was carried out thanks to the collaboration between the University of Camerino, Sapienza University of Rome, and the company Delta Srl. The work involves many steps: analyses of the industrial products, pure and recovered

PMMA; depolymerization of the PMMA; analyses of the depolymerization's products; purification of the depolymerization mixture; re-polymerization of the obtained MMA; analyses of the recovered PMMA; and characterization of all PMMA structures. All of these steps need different analytical techniques. It was possible to use many different techniques only thanks to the collaboration among the involved structures. Within this study, my work mainly concerned the possibility of optimizing the recovery of obtained MMA after depolymerization of PMMA as raw material for the production of high-quality PMMA. Optimizing the process is the only way for an economical operation, making the cost of recovered PMMA competitive with the already commercially available PMMA.

2.1 Depolymerization Analyses

Analyzing molecules during pyrolysis could tell us much about the nature of the polymers. Many analytical techniques can be used to study both degradation of polymers and the obtained products. The most used for the degradation phase are thermogravimetry (TG) and differential scanning calorimetry (DSC). Whereas, degraded products could be analyzed on-line by mass spectroscopy (MS) and Fourier transform infrared spectrometry (FT-IR).

2.1.1 Gas chromatography coupled to mass spectroscopy (GC-MS)

Pyrolysis paired with GC-MS (Py-GC-MS) has been widely used for the separation and identification of the volatile pyrolysis products. Evolved gas analysis performed by GC-MS with total ion chromatogram (TIC) detector offers a number of advantages for the decomposition study. With this technique, the identification of each decomposition product it is possible by comparing the spectrum with those in a GC-MS library and the relative concentration of each compound corresponds to the relative intensity of the peak.

During the pyrolysis, the carrier gas transports volatiles into the GC column, which separate them according to their different boiling points and polarities. The separated components are then analyzed by the mass spectrometer.[29]

There are different kind of pyrolyzer. The main used are the resistive heating using platinum filaments, the Curie Point filament and the isothermal furnace. In this technique the mass spectrometer is used as the GC detector, for which its sensitivity is at least as good as that of flame ionization detectors, and even more importantly provides the opportunity to characterize the components associated with the chromatographic peaks of the pyrolysis fragments. Moreover mass spectrometers detect and measure permanent gases and other small molecules, to which flame ionization detectors are insensitive.

The coupled thermoanalytical techniques, pyrolysis-infrared (Py-IR) and pyrolysis thermogravimetry (Py-TG), are useful for rapid identification of polymeric materials and determination of weight loss characteristics, respectively.[30, 31,]

2.1.2 Thermogravimetric coupled to mass spectroscopy (TG-MS)

Thermogravimetric (TG) technique is used for the structural characterization of polymers and composites. It also finds application in the detection of residual monomers.

In combination with MS, it provides information about the qualitative aspects of the evolved gases during polymer degradation that is otherwise unavailable for TG experiments on their own.

With TG-MS, it is possible to measure directly the weight loss as a function of temperature with the use of a sensitive spectroscopic detector. The combination is via quartz glass capillary tube, one end of which is positioned close to the sample in the thermobalance and the other end is positioned inside the MS detector. TG-MS features are high sensitivity and high resolution, which allow extremely low concentrations of evolved gases to be identified, together with simultaneous weight losses that can be interpreted qualitatively.[32]

2.2 Experimental Section

2.2.1 Materials and methods

Pure and recovered PMMA were purchased from Madreperla spa, Spain. The recovered PMMA was prepared by free radical polymerization of the pyrolyzed

MMA. Solvents as toluene, xylene, dichloromethane, acetone, and *n*-hexane were purchased from Sigma Aldrich.

MS standards: Methyl methacrylate, methyl isobutyrate, methyl pyruvate, 2,3-butanedione were > 99% pure and purchased from Sigma Aldrich.

TG-MS

The Pyrolysis of PMMA was carried out by TG-MS technique using a PerkinElmer TGA7 equipment. Mass spectra of the gases evolved during the thermoanalytical experiments were recorded by a STD 2960 simultaneous DTA-TG apparatus (TA Instruments Inc., USA) using sealed crucibles with a pinhole on the top. The gaseous species were analyzed by a ThermoStar GDS 200 (Balzers Instrument) quadrupole mass spectrometer equipped with Chaneltron detector (EI, 70 eV); through a heated 100% methyl deactivated fused silica capillary tubing. Solid samples (approximately 7-8 mg) were placed within a small platinum crucible with a circular base (6 mm diameter and 3 mm height) of the TG-MS. The thermo-balance was provided with an electric oven that can operate up to 1500 °C. A thermocouple was located close to the platinum crucible for temperature monitoring and for oven control. The weight loss, together with other process variables such as temperature, and gaseous species detected by the MS were continuously monitored. The pyrolysis program for the thermogravimetric analysis of the waste materials was identical for the TG-MS. The heating rate was 10 °C/min up to temperature 400 °C, under N_2 atmosphere by a flow rate of 100 mL min^{-1} and a scanning rate of 5 °C/min. The MS was operated under a vacuum and detected the characteristic fragment ion intensity of the volatiles according to their respective mass to charge ratios (m/z).

Purification of PMMA by dissolution/re-precipitation

For the dissolution/re-precipitation technique dichloromethane was used as a solvent and n-hexane as a non-solvent.

The experimental process was carried out in a 250 mL three necked flask, attached with vertical condenser, magnetic stirrer, thermometer and temperature controller.

PMMA (2.0 g) and CH_2Cl_2 (10 mL) were added to the flask and heated to 35 °C for 30 min with continuous stirring. Then the flask was allowed to cool down to RT and the polymer solution was slowly poured into 30 mL of n-hexane in another beaker with stirring. After the precipitation in an acceptable form, stirring was continued for a while. The phase separated solvents were replaced by pure non-solvent and analyzed by GC-MS for the analysis of soluble components of pure and recovered PMMA, such as residual monomer. The purified polymer was obtained by filtering under vacuum and dried overnight in an oven at 70 °C. Then the purified polymer was grinded and the solvents used in the mixtures were separated by distillation for further reuse.

Residual monomer determination

We determined the amount of residual monomer in virgin, recycled and purified PMMA by means GC-MS. Different volumes of MMA (50-500 ppm) along with an internal standard (Hexadecane, 200 ppm) were injected in GC-MS and the obtained GC areas of MMA/internal standard were used to construct the calibration curve and calculate its equation. Reporting the GC area of polymer sample into the obtained equation, we calculated the total amount of residual monomer in all PMMA products.

2.2.2 Instrumental

HS-SPME-GC with MS and Flame Ionization Detection

The extraction of the volatile compounds was performed by SPME using fibers purchased from Supelco (Bellefonte, PA, USA). The analyses were accomplished by using the divinylbenzene/carboxen/polydimethylsiloxane fiber (DVB/CAR/PDMS, 50/30 μm, grey fiber). The analysis was performed on 50 mg of PMMA samples in a 4 mL screw cap vial (Agilent Technologies, USA), equilibrating the sample for 30 min and extracting for another 30 min, at a temperature of 70 °C. After the extraction, the fiber was conditioned in the GC injector at 260 °C for 1 h before the analysis. The qualitative analysis was accomplished by using an Agilent Technologies 6850 GC-MS equipped with a single 5973 quadrupole mass spectrometer detector (both from Agilent Technologies, USA). The capillary chromatographic column was HP-5MS from Agilent Technologies [30 m (length) × 0.25 mm (inside diameter) × 0.25 μm (film thickness)]. Desorption was performed in split less mode (4 min) at a temperature of 250 °C. The insert used in the split/split less injector was a 0.75 mm (inside diameter) liner for SPME (Supelco, Bellefonte, PA, USA). Oven temperature was held at 40 °C for 3 min, then raised to 300 °C at 15 °C/min and held at 300 °C for 8 min. The initial carrier gas (helium) flow rate was 2 ml/min. Mass analysis was performed in scan mode in the range of 29-400 Da. No solvent delay was set. Transfer line was maintained at 300 °C, ion source at 230 °C and quadrupole at 150 °C. Pure reference standards of methyl methacrylate, methyl isobutyrate, methyl pyruvate and 2,3-butanedione were purchased from Sigma-Aldrich (Milan, Italy). The volatile compounds detected in the PMMA samples have been identified by comparison with authentic standards and with reference spectra available from the data base produced in 2008 by the US National Institute of Standards and Technology (NIST) and by comparison of the linear retention indices with those available from the NIST Chemistry Web Book (NIST2011).

Differential scanning calorimetry (DSC)

The instrument was a NETZSCH DSC 200 F3 Maia. The temperature axis and the measured enthalpy were calibrated by using pure indium. 10-15 mg samples were kept in aluminum crucible and placed into the appropriate position of the instrument. The heat released was recorded at a temperature interval 25-250 °C by the scan rate of 10 °C/min to ensure complete polymerization of trace amounts of residual monomer. Then the samples were cooled to 25 °C, and their T_g was measured by heating again to 250 °C at a rate of 10 °C/min. The data obtained from the second scanning were accepted for the measurement of T_g. T_g was considered at the point where a change in the slope of the curve was observed.

Gel permeation chromatography (GPC)

The instrument used was model GPC Thermo Knauer, a differential refractive index detector, and three columns (5 μm, 500 Å, 300 x 7,5 cm; 5 μm, 1000 Å, 300 x 7,5 cm; 5 μm, 1000 Å, 300 x 7,5 cm) in series. All the samples were dissolved in 7:3 THF: DMF at a constant concentration of 2 wt %. After filtration of samples with 0,45 μm wheel syringe filter, 25 μL of each sample was injected into the chromatograph. The elution solvent was THF with a rate of 1 mL/min. Calibration of GPC was carried out with standard polystyrene samples by using the universal calibration technique.

FT-IR spectroscopy

The instrument used was an FT-IR spectrophotometer of Perkin-Elmer, UATR Two. The recorded wavenumber range was 450 to 4000 and 3 spectra were averaged to reduce the noise. A commercial software Spectrum quant v10.5.0.560 (Perkin-Elmer FT-IR C102493) was used to process and calculate the wavenumber from the spectra.

^{1}H-and ^{13}C-NMR spectroscopy

^{1}H-and ^{13}C-NMR spectra of the polymer samples were taken in CD_2Cl_2 at ambient probe temperature (ca. 25 °C) on a ^{1}H-NMR operating at 400 MHz and ^{13}C-NMR were recorded at 100 MHz on a Varian Mercury plus 400. The following abbreviations were used; s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintet, dd = double doublet, dt = double triplet, tt = triple triplet, m = multiplet.

Gas chromatography-mass spectroscopy (GC-MS)

The used instrument was a Hewlett-Packard (HP) 5890A GC-MS equipped with an HP 5971A mass spectrometer detector. The capillary column was HP-5MS from Agilent Technologies (Stationary phase: methyl siloxane, length 30 m, film thickness 0.1 mm, inside diameter 0.25 mm). Oven temperature was held at 80 °C for 3 min, then raised to 300 °C at 15 °C/min, and held for 10 min. The initial carrier gas (helium) flow rate was 5 mL/min Solvent delay was set for 4 min. Mass analysis was performed in scan mode in the range of 50-550 Da during the analysis.

Transfer line was maintained at 280 °C, ion source at 230 °C and quadrupole at 150 °C. Standard hexadecane was used as an internal standard. The peaks detected in the PMMA samples have been identified by comparison of their mass spectra with the authentic MMA and with aforementioned reference spectra from NIST and by comparison of the linear retention indices with NIST Chemistry Web Book. Quantification was carried out from the observed peak area ratio of both the MMA and internal standard.

2.3 Results and Discussion

Pyrolysis tests for PMMA have been carried out from 25 to 450 °C by heating rate 10 and 20 °C/min under inert atmosphere (Table 2.1).

Table 2.1. TG-MS ramp

Initial Temperature	Final Temperature	Heating Rate
25 °C	450 °C	20 °C/min

Figures 2.1 and 2.2 show TG-MS thermograms and their derivative of both the virgin and the recovered PMMA.

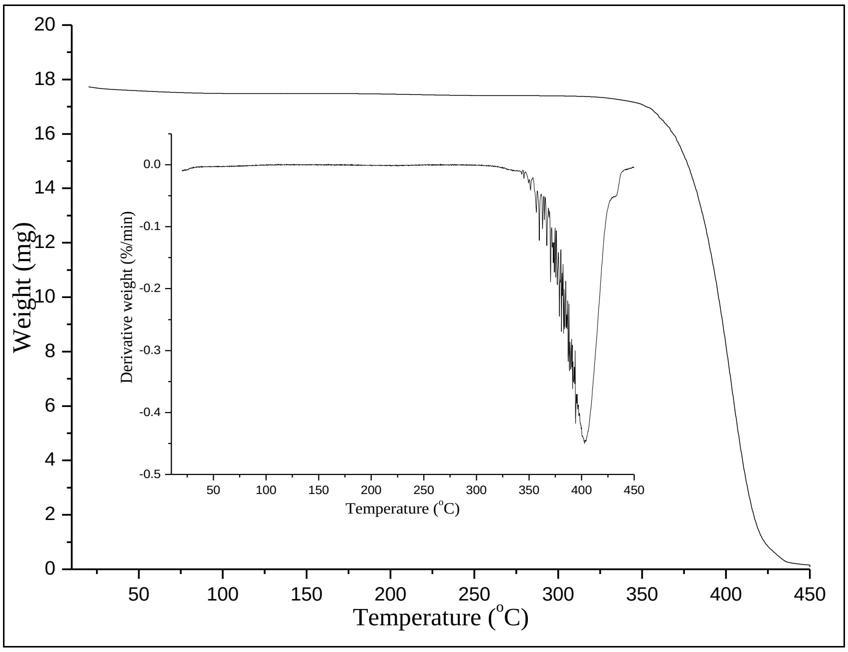


Figure 2.1. TG-MS thermogram of virgin PMMA

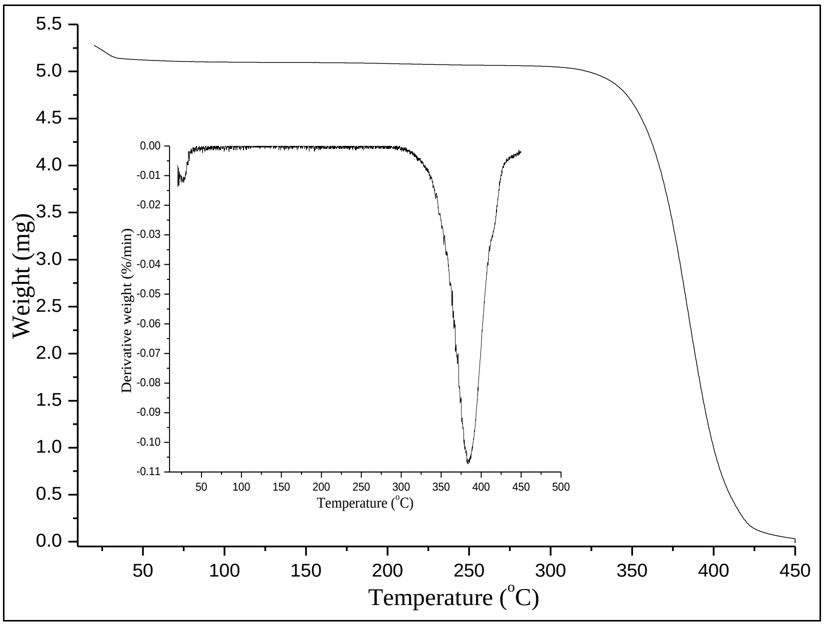


Figure 2.2. TG-MS thermogram of recovered PMMA

Both the PMMAs present a small thermal event between 0 and 100 °C, this event is indicative of the inherent moisture that is present inside the materials. Whereas in figure 2.1, one can see that major thermal events occurring between 340-430 °C and the derivative is around 404 °C. Instead, in Figure 2.2 the degradation starts at slightly lower temperature, between 310 °C, and the derivative is around 384 °C. The MS inlet was closed until 200 °C to keep the CO_2, CO, CH_4, and other gas compositions out of the MS.

Figure 2.3 shows the mass spectra of the products collected when a PMMA sample was heated to 400 °C.

The mass spectra shows a large amount of residue MMA (m/z 100 Da), together with traces of other organic species. At first, we focused our attention to the species of m/z lower than 100 Da. The peak of m/z 86 Da was assigned to 2,3-butanedione (diacetyl) and its structural assignment was confirmed in comparison with standard sample too. It is reported that 2,3-butanedione is unpleasant smelling for humans.[33]

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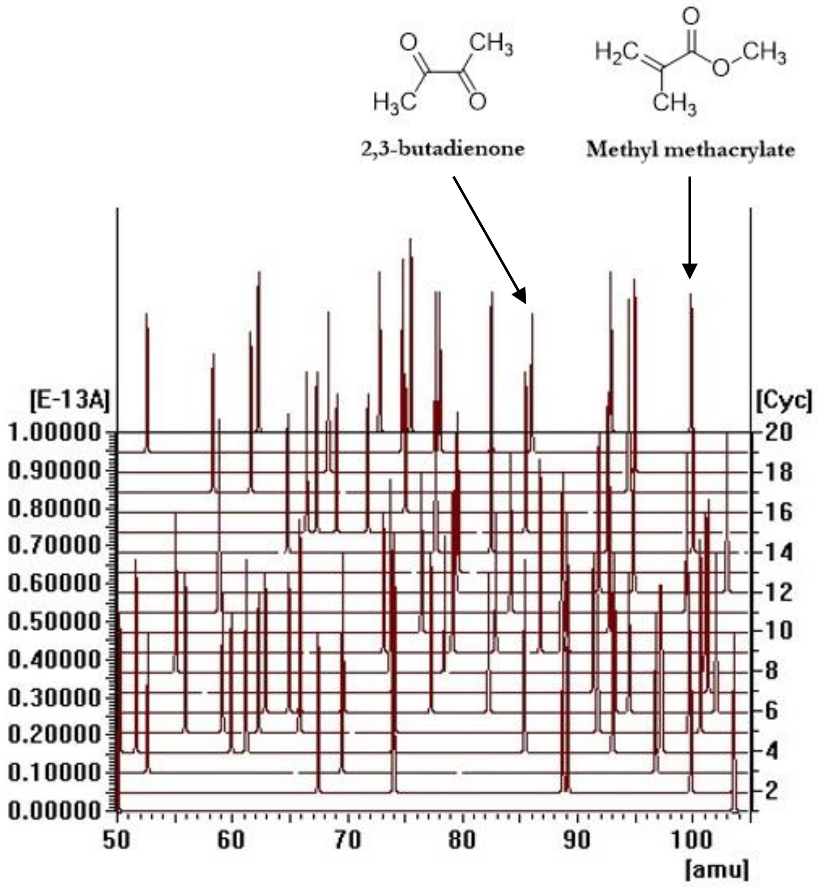


Figure 2.3. Mass spectra of PMMA

The presence of 2,3-butanedione is an interesting result, but it is necessary to understand its formation during the pyrolysis of PMMA. The intermediates during the degradation are formed in trace amounts and may have short lifetimes, for this reason the analytical technique for the detection and identification of such intermediates needs to be rapid and sensitive in order to avoid loss of valuable information on the transformation routes. Significant improvement in both speed and sensitivity can be obtained by solid-phase microextraction (SPME) technique. This technique allows identification of volatile organic compounds with unambiguous detections of degradation products of plastics including a variety of low molecular weight compounds.

Further analyses were carried out using HS-SPME/GC-MS. The principal detected compounds through the extraction technique are, except MMA: dimethyl 2-methyl-5-oxohexanedioate, 2-hydroxyethyl methacrylate, methyl pyruvate, 2,3-

butanedione, ethane-1,2-diyl bis(2-methylacrylate). In recycled PMMA the presence of 2,3-butanedione was observed, which confirms that the substance at m/z 86 Da during thermal degradation of PMMA by TG-MS was 2,3-butanedione. The gas chromatogram of recycled PMMA also showed a presence of another molecular ion with mass m/z 102 Da (Figure 2.4).

The electron ionization mass spectra fragmentation study of this compound (m/z 102) confirms unambiguously that the present compound is methyl pyruvate. It is important to note that the presence of methyl pyruvate was observed only in recycled PMMA, in pure and purified PMMA the presence of methyl pyruvate was not observed. It demonstrates that during the depolymerization of PMMA, 2,3-butanedione and methyl pyruvate also forms together with MMA. It is possible to attribute the unpleasant smell typical of pyrolyzed MMA to 2,3-butanedione, formed as byproducts during the depolymerization.

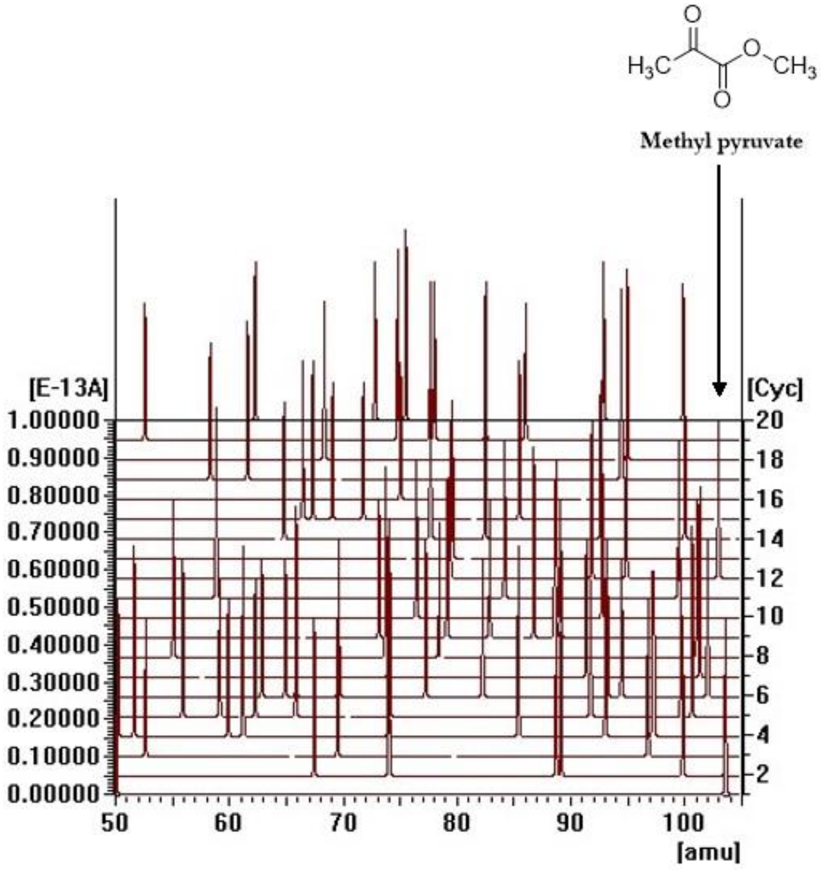
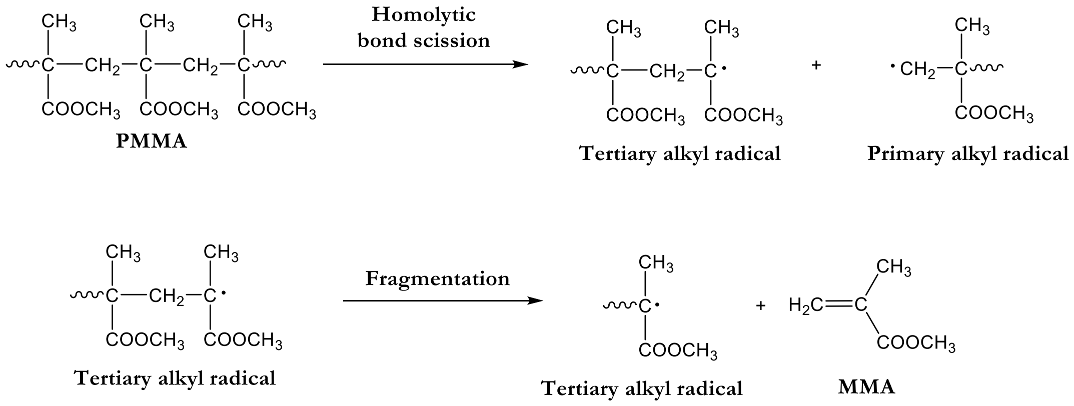


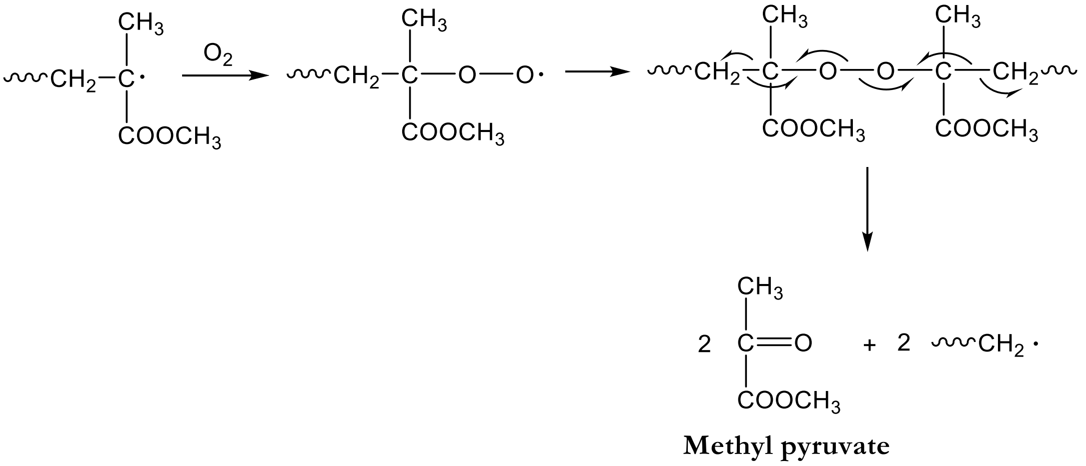
Figure 2.4. Mass spectra of PMMA

It is generally accepted that the degradation of PMMA initiates by homolytic scission of a methoxycarbonyl side group by random scission degradation.[34] The main chain scissions are kinetically inhibited relative to side group or chain end scissions due to efficient recombination of caged radicals. Whatever the initial step of the mechanism is, the exclusively degradation product obtained is MMA monomer. Above 300 °C PMMA becomes thermally instable, leading to fragmentation of tertiary alkyl radicals to yield monomer and equivalent amount of tertiary radicals (Scheme 2.1).



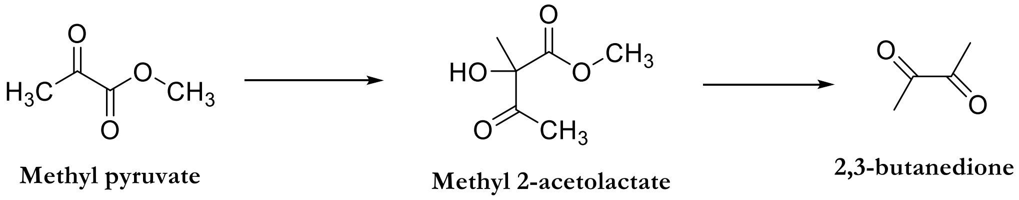
Scheme 2.1. Depolymerization of PMMA

Depolymerization by chain and chain end scissions forms MMA until the chain terminus reached as well as produces byproducts by disproportionation. During the degradation process in the system a number of small radicals can be form by disproportionation, evaporation from the sample, or integration with other radicals. The mechanism of PMMA depolymerization and generation of byproducts depends on degradation temperature, initial molecular weight of PMMA, and presence of oxygen. [35, 36] Scheme 2.2 shows the mechanism formation of methyl pyruvate.[37]



Scheme 2.2. Formation of methyl pyruvate

Poly(methyl methacrylate peroxide) units undergo O-O bond forming scission to form methyl pyruvate which is the major oxidation product. Then methyl pyruvate turn into the corresponding 2,3-butanedione (Scheme 2.3).[38]



Scheme 2.3. Formation of 2,3-butanedione

The first step of this pathway is the condensation of two methyl pyruvate molecules and concomitant decarboxylation to form methyl 2-acetolactate. The subsequent oxidative decarboxylation leads to the formation of 2,3-butanedione.

2.3.1 Purification of recycled PMMA

As mentioned, the purification process of recycled PMMA, involves dissolution/re-precipitation in an appropriate solvent/non-solvent system. The process includes the purification without modification in structure and then the reuse of the obtained purified product. Solvents studied for the dissolution of PMMA include toluene, xylene, dichloromethane, and acetone. Among non-solvents, methanol, n-hexane and cyclohexane were tested. The main criteria for the selection of solvents and non-solvents were their solubility parameter, availability, cost, toxicity, color and viscosity. Based on these criteria dichloromethane/n-hexane proved the most satisfactory system.

The preliminary experiments aim to achieve the precipitation of the PMMA in an acceptable form (i.e. to exclude formation of jelly polymer lumps, which prohibit the recovery of the solvents).

The PMMA obtained after dissolution/re-precipitation in solvent/non-solvent system was in an agglomeration form and was analyzed by SPME-GC/MS for the confirmation of volatile organic byproducts. Moreover, the filtrate was tested by GC-MS for the analysis of soluble components of PMMA, as well as the residual monomer. All the results confirmed here suggests that the purified PMMA had the similar properties of pure PMMA and could be used for further use.

2.3.2 Analyses of PMMAs

FT-IT was useful to compare the chemical structure of recovered and purified PMMA with pure PMMA. Results of FT-IR spectra are presented in Figure 2.5.

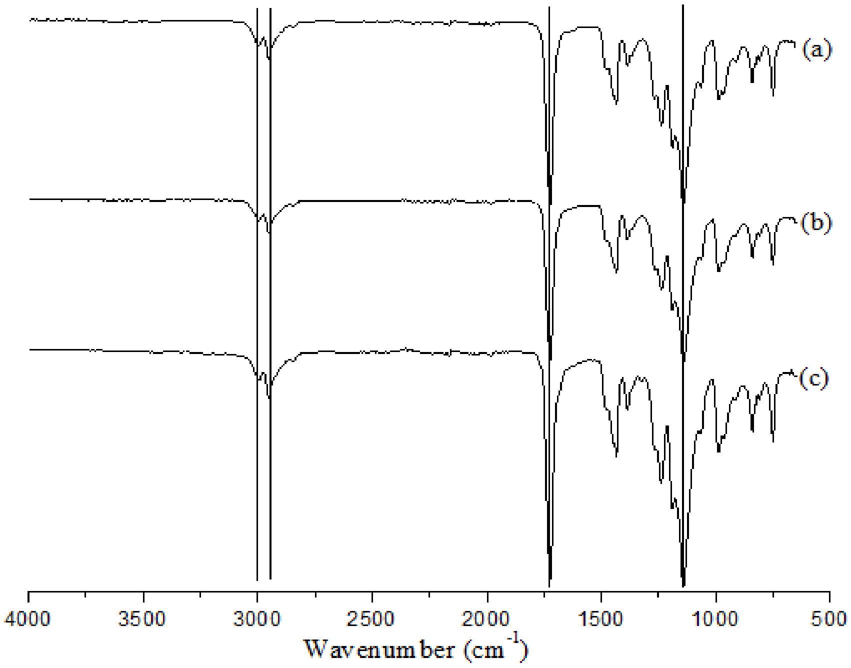


Figure 2.5. FT-IR spectra of **a)** pure, **b)** recovered and **c)** purified PMMA

One can see that the three spectra are quite the same. Especially the strong absorption band at 3000 cm^{-1} is characteristics of methyl ester stretching vibrations. Whereas the asymmetric and symmetric CH_2 stretching vibrations absorbs at 2957 cm^{-1} and the carbonyl stretching absorbs at 1722 cm^{-1}. Other characteristic band are the C-O stretching at 1142.5 cm^{-1} and two absorption peaks around the range 1260-1040 cm^{-1} for C-O-C single bond stretching vibrations.

In addition, we use the NMR spectroscopy to deduce the compositions of the polymers. ^{1}H-NMR and ^{13}C-NMR spectra were recorded to compare the integral areas of appropriately assigned signals. Figure 2.6 shows the ^{1}H-NMR resonances of three different samples of PMMA in dichloromethane-d solvent.

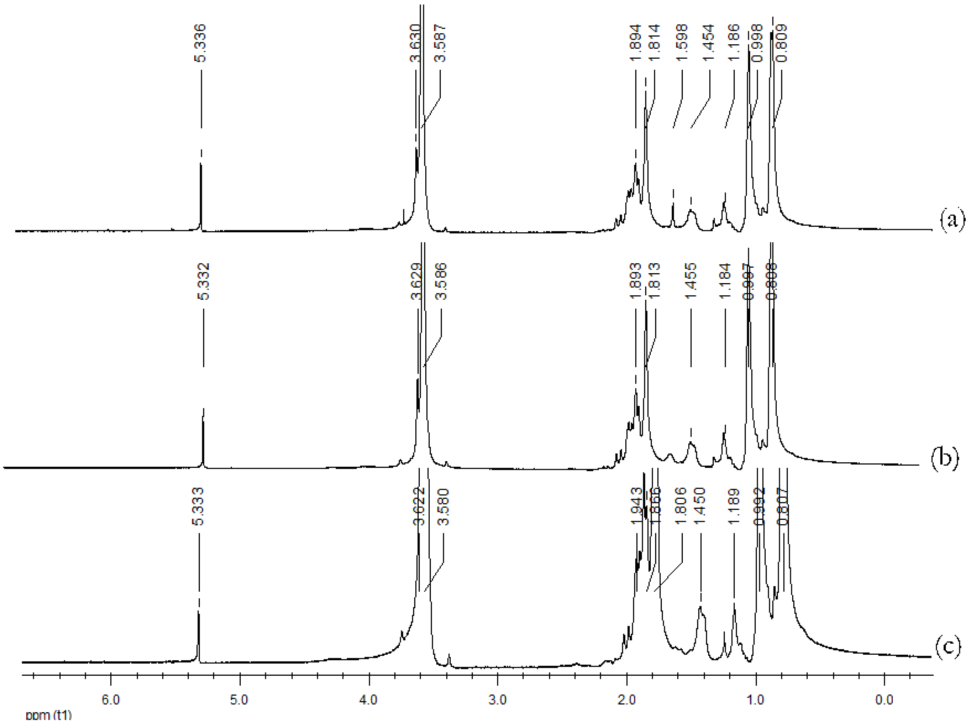


Figure 2.6. ^{1}H-NMR spectra of **a)** pure, **b)** recovered and **c)** purified PMMA

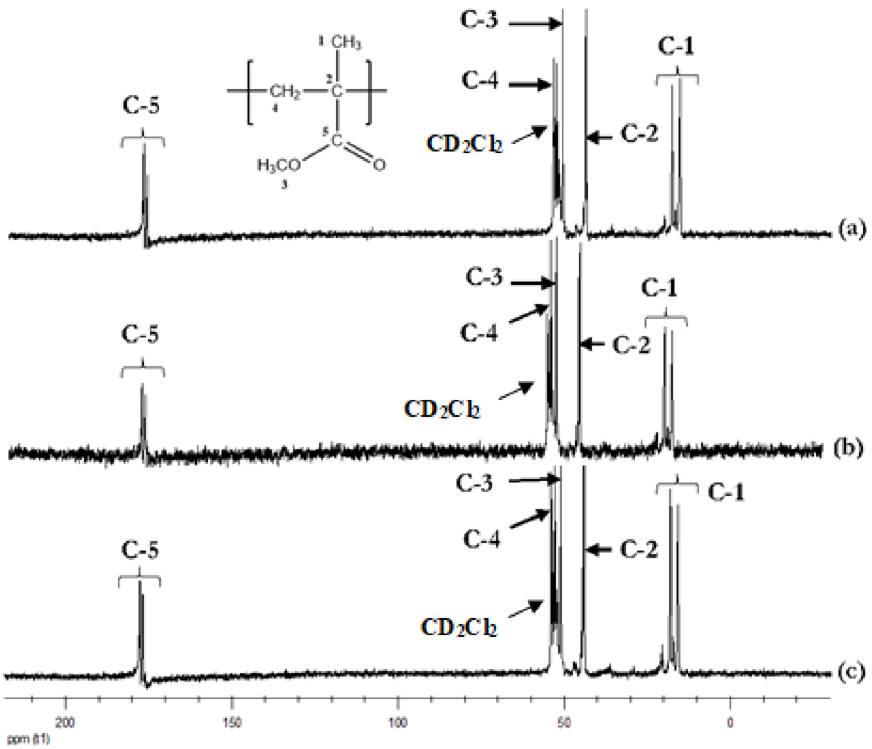


Figure 2.7. ^{13}C-NMR of **a)** pure, **b)** recovered and **c)** purified PMMA

Whereas, Figure 2.7 shows the probable assignments for ^{13}C-NMR of the three PMMAs. In the ^{1}H-NMR, the resonance band at 3,58-3,63 ppm is attributed to the methyl proton connected to the ester group. The proton resonance absorptions of methylene and the substituted methyl groups are at 1,45-1,89 ppm and 0,8-1,18 ppm, respectively. Five carbons of PMMA appeared at 16,6-19,0, 44,6-45,0, 51,83-53,9, 54,3-54,5 and 177,1-178,2 were assigned to C-1, C-2, C-3, C-4 and C-5, respectively. ^{1}H-and ^{13}C-NMR results suggests that the structure of recovered and purified PMMA are very similar to pure PMMA, the chemical shifts of recovered and purified PMMA were identical to that of pure PMMA.

Also DSC analyses were performed to determine the T_g for virgin and recovered PMMA (Figure 2.8).

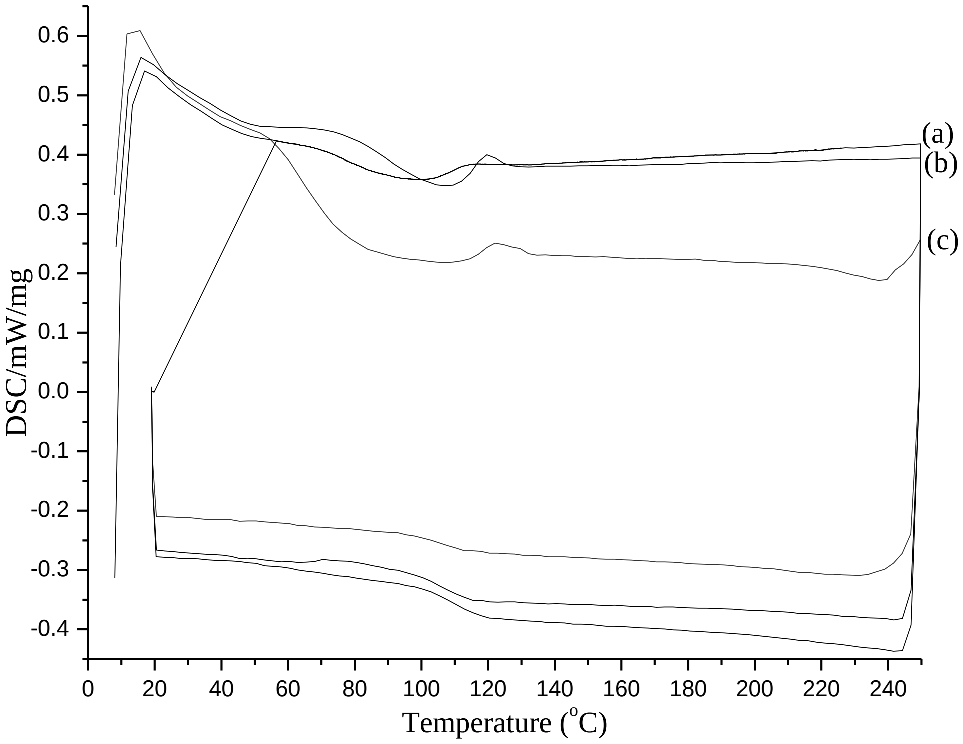


Figure 2.8. DSC thermogram of **a)** pure, **b)** recovered and **c)** purified PMMA

The glass transition temperature of virgin PMMA was measured to be between 104 and 107 °C, which is very close to the reported value of 106,5 °C for pure PMMA.[39] While the PMMA prepared by pyrolyzed MMA had the T_g approximately 10 °C lower than the pure PMMA, between 95-98 °C. The T_g of the purified PMMA was also similar to recovered PMMA. It can be explain that during the re-polymerization of recovered MMA byproducts inhibits the polymerization reaction and leads to production of macromolecules with lower average molecular weight and consequently lower T_g.

Gel permeation chromatography was used to compare pure and recovered PMMA too. Molecular weight distribution and average molecular weight are shown in Table 2.2.

Table 2.2. Molecular weights of PMMAs

Sample	M_n x 10^4 (g/mol)	M_w x 10^4 (g/mol)	M_w/M_n
Virgin PMMA	6,69	13,0	1,946
Recovered PMMA	6,10	12,4	2,043
Purified PMMA	ND	ND	ND

The number average molecular weight of virgin and recovered PMMA was 66926 and 61039, respectively. Therefore, the decrease in T_g for recovered PMMA could be attributed to the reproduction of PMMA by pyrolyzed MMA with lower average molecular weight compared to virgin PMMA.

We determined the amount of unreacted monomer in pure, recovered and purified PMMA by as aforementioned dissolution/re-precipitation technique. The amount of residual monomer in pure and recovered PMMA were 102.9 and 569.2 ppm respectively, while no residual monomer was observed in purified PMMA.

2.4 Conclusion

In this investigation considering the limitation of raw materials and environmental pollution, the recovery of MMA from waste PMMA scraps was investigated by depolymerization. The depolymerization of PMMA was studied by TGA-MS technique, also the volatile organic compounds (byproducts produced during thermal degradation) were reconfirmed by SPME-GC/MS. The pyrolysis seems to be the most promising technique resulting a high percentage of methyl methacrylate monomer with great purity. Results obtained from TGA-MS and SPME-GC/MS suggests that the main product of the pyrolysis was methyl methacrylate along with an impurity of methyl pyruvate and 2,3-butanedione which previously was believed methyl isobutyrate and responsible for unpleasant smell in recycled MMA/PMMA. We approached a method for elimination of such byproducts from the recycled PMMA, and explored the recycled PMMA free from impurities. The physical and chemical properties of obtained recycled and purified PMMA were similar to that of pure PMMA as characterize by FT-IR, 1H-NMR, 13C-NMR, DSC and GPC. Finally, to conclude that, the investigation presented here could lead the PMMA recycling technology towards utilizing the recycled PMMA.

Chapter 3: Improvement of an Industrial Coating

At ELANTAS, I worked mainly with polyurethane enamels (PU), in particular with those ones of thermal class 155. This kind of enamels are used in the manufacturing of fine magnet wires with excellent electro insulating performance. Main related applications are relays, high frequency coils and transformers, solenoids and small motors.

Two binders, various solvents, an ammine catalyst and some additives form this enamel. One binder is a polyester polyol formed by the reaction among dimethyl terephthalate (DMT), isophthalic acid (IPA), ethylene glycol, glycerin. Mn-based catalyst is used to accelerate the reaction and solvents help to keep soluble the resin reducing its viscosity and making it manageable.

The other binder is a PU intermediate that consists of an oligomer of toluene diisocyanate (TDI); the material is a mix 80/20 of the two isomers 2,4- and 2,6-TDI, trimethylolpropane (TMP), phenol and cresols as blocking agents and DABCO as catalyst. The term “blocking agent” means a substance that is used to react with the isocyanate functionality and that could be easily removed in the curing phase allowing to create the polyurethane link with the -OH group of the polyol binder. Here two solvents are used to make the resin manageable.

Mixing these two intermediates with other solvents and the catalyst (the product of polycondensation reaction of butyraldehyde and aniline) we obtain the final enamel 155 class. This kind of enamel does not have the best chemical, electrical and thermal properties, but is characterized by a high application speed (up to 1200 m/min).

Table 3.1 report some properties, the most common, and their specific values to be part of class 155, termed “minimum values”. The others, the “target values”, are the targets required. Obviously, with the progress of the technology machines for enamels application, becoming faster and more efficient, a need for more efficient enamels arise.

Table 3.1. Main properties for class 155 enamels

Properties	Minimum Value	Target Value
Tangent delta	135 °C	148 °C
Cut-through	225 °C	235 °C
Solder time	3,2 s	2,3 s
Mandrel test	OK	OK

The target with this enamel was to increase the curing speed in order to save energy (more enameled wire in a fixed time, so using the same amount of energy) and to reduce environmental impact due to the split off of low molecular weight molecules, which do not react and leave the coating during the enameling phase.

To quantify the dispersion of low molecular weight molecules during the curing phase, there is a parameter called Stack Loss and is expressed by the following formula:

$$\text{Stack Loss} = \frac{\text{Solid Content - Residual Enamel on Wire}}{\text{Solid Content}}$$

The definition of stack loss is "*that portion of the magnet-wire enamel solids, which are lost during the conductor-coating process*" (ASTM std N° D3288/D3288M-08). Therefore, it is the part of solid content that does not evaporate during the solid content measurement (in the lab oven), but does during the curing process. This means that a certain part of solid content is lost.

3.1 Enamels Application and Enameled Wire Tests

A lot of time for this thesis work was spent in the enameling department. The enameling stage is a necessary step of the work because until now it is the only and actual way to evaluate products. Only by testing the properties of the enameled wire, one can evaluate the goodness of the enamel.

In order to be able to enamel and test the applied material, I had to be trained. This required a first period of learning by people of the enameling department on how to run the enameling machine and to perform the main tests.

Applying an enamel means allowing to the molecules of the enamel in question to react with each other, forming a three-dimensional network. The layer thus formed will give the desired electrical, mechanical, chemical and thermal resistance to the wire.

All the mentioned types of enamel are manufactured in more or less the same way, biggest difference lay in used temperatures and enameling speed.

3.1.1 Enameling machine

The manufacture of good enamelled wire entails proper application of the enamel to the wire.

In order to get such result, an enamelling machine, or oven, is used, able to apply liquid enamels to the wires and cure them to create a solid film around the wires (Figure 3.1).

Figure 3.1. Enameling machine Aumann DHL 250

There are enamelling ovens for different size of wires, from less than 0,050 mm to more than 2 mm of diameter and different type of enamels. Enamels are specifically designed in terms of viscosity and solid content characteristics, to be properly applied on different diameters. For examples for fine and ultra-fine wires, it is used felts application, and enamels with low solid content and low viscosity are required, while for bigger wires it is used die application and enamels with higher solid contents and viscosities are required.

It is necessary to apply a number of passes of enamel one after the other to get the required insulating thickness, which may be in the order of 20 μm for a copper wire of 0.1 mm in diameter. The usual procedure is to pass the wire a number of times through the enameling machine.

The enameling machine is composed of different part:

- Annealing line. Annealing is the metallurgical method for heating a metal and subsequently cooling it to change its properties (such as its hardness or durability). Annealing the copper wire makes it softer and less brittle, which allows one to bend it without breaking it.
- Application system. It consist of a pump that brings the enamel into the application tank, where are dies or felts. In the case of dies, there are nuzzles that lay down the liquid enamel on the wire and then a die regulate the thickness (die are placed in order of increasing thickness, Figure 3.2).

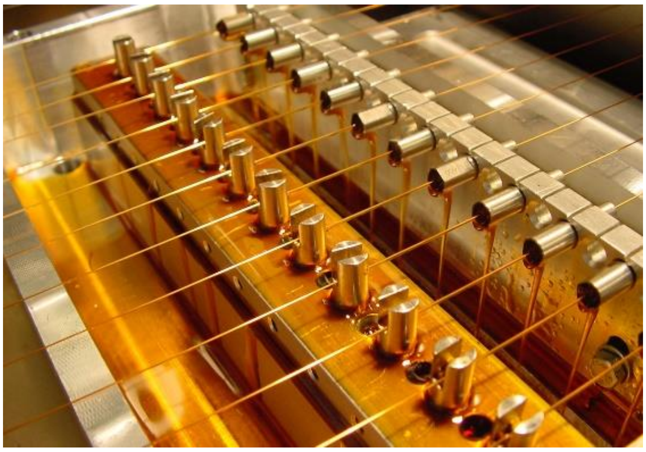


Figure 3.2. Applicator with dies

In the case of felts, three felts are needed: two small ones, placed in the tank (Figure 3.3) and a bigger one placed as bridge between them.

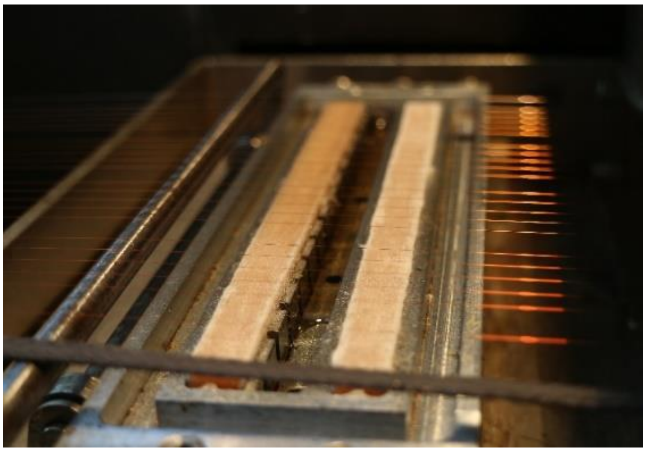


Figure 3.3. Applicator with felts

In this case, liquid enamel is pumped on the first felt and, by the bigger one placed above, it reaches the third. The wire passing through the felts takes a little amount of liquid enamel. The thickness is adjusted by the rate of the pump.

It is also possible to apply two or more different coats one over the others, using specific applicator with separate bowl.

- Curing room. The curing room is the one where the curing occurs. In this room, there are high temperatures (about 400-600 °C) that allow evaporating the solvents and making the chemical species react to form the polymer layer on the wire.

  Setting the right temperatures and the airflows is very important (incoming and out coming flows, Figure 3.4).

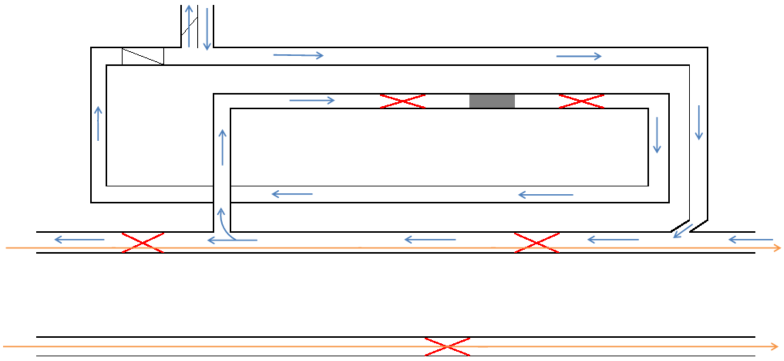


Figure 3.4. Enameling oven internal scheme. Orange arrows represent the wire, blue arrows the airflows, and red cross the resistance

- Cooling room. In this room, the enameled wire is cooled. Once cold, it can go back for another pass through the felts and the curing oven to increase the thickness, or, if the desired thickness is reached, it can go to the spooler.
- Spooler. The spooler is a machine on which there are two spools. The enameled wire winds up to a spool (Figure 3.5).

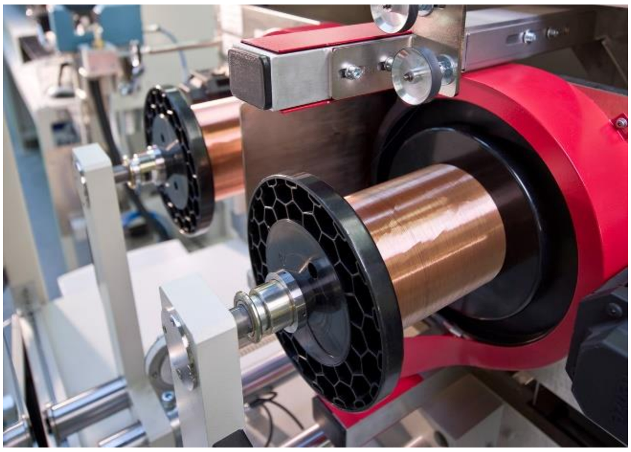


Figure 3.5. The spooler

The second spool allows switching and winding up the wire on both spools alternatively, so that one can take a sample without stopping the machine.

- PC and software. There is a software to manage the machine, i.e. the pump rate, the spools rate, the temperatures and the airflows.
- Copper wire spool. Copper wire spool is not a part of the enameling machine, but it is the source of the bare copper wire. Usually is a very big spool (250 Kg of wire or more) that allows the enamelling machine working for many hours.

The machines used may mainly be divided into two types: those in which the wire is led vertically through the furnace, and those in which it is led horizontally. The force of gravity makes a horizontal wire lie in a slight curve, which has undesirable consequences for the manufacture. The furnace of the horizontal machine must therefore be relatively short. Vertical machines, where this difficulty does not arise, can use furnaces 10 m or more in length. The short horizontal machines have the advantage that the wire can be threaded through by one man, while the attractive point of the vertical machines is that, for a given drawing rate, the wire remains longer in the curing room. This is especially important with thick wire, where the enamel is applied in relatively thick coats, and which therefore need rather a long drying time. However the advantage of this will be lost if the wire breaks often, because the whole machine has to be stopped each time a break occurs. Thick wire does not break very often, but with thin wire this possibility is higher.[40]

3.1.2 Testing of enameled wire.

Testing the final product is very important because it allows valuing the goodness of the enamels. The enameled wire is tested as regards a considerable number of properties. The uniformity of the enamel layer is of prime importance for wire to be used for winding purposes: the enamel must not show any inhomogeneities or pits, and must be applied equally thickly all-round the wire. The mechanical, electrical, thermal and chemical properties of the enamel layer are also of great importance. We shall mention a few of the methods described in standard specifications for the testing of enamelled wires in these respects.

The aspect of the insulation is detected by checking the wire with a microscope. This is a qualitative inspection, which delivers a pass/non pass result, though arbitrary ranking can be assigned by enamellers. In Elantas wires are classified from zero to six based on the presence of blisters, waves and dots, the higher the worse. A uniform thickness of the enamel layer is also checked. The thickness is measured in different points of the sample using a micrometer. Obviously, the thickness must be as uniform as possible to guarantee properties reproducibility.

Electrical properties describe the behavior of the enamel under the influence of electrical fields and voltage. Typical tests for enamelled wires include dielectric loss tangent (Tangent Delta). Dielectric strength is the maximum electric field strength that the enamel can withstand intrinsically without breaking down and experiencing failure of its insulating properties. This property depends on the material used and on the thickness of insulation.

The dissipation factor is the ratio of the resistive component of the current to the capacitive component of current and is equal to the tangent of the loss angle. It is a measure of the rate of loss of electric power of a mechanical mode, such as an oscillation, in a dissipative system in the form of heat. The tangent delta tester calculates the tangent of the curve of the dielectric loss against temperature. The tangent delta value is the temperature at which a tangent that runs in parallel with the curve after the dielectric angle has increased dramatically (when the dielectric properties have been lost) intersects a tangent of the curve that follows the initial values (Figure 3.6).

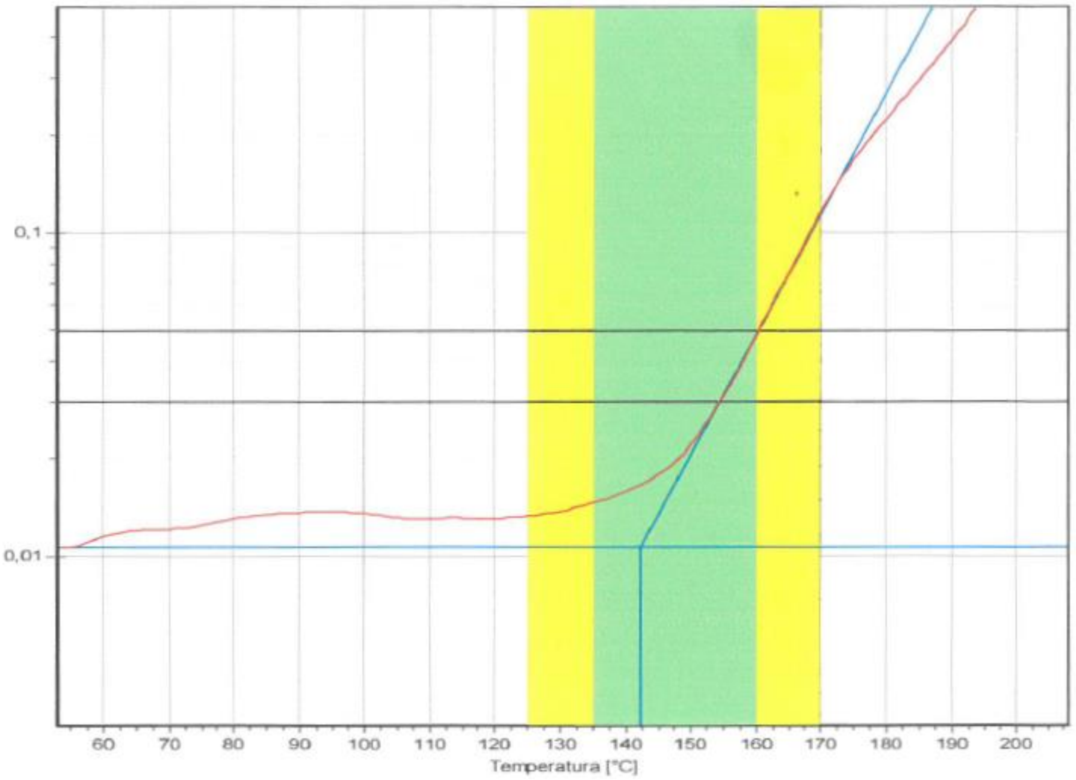


Figure 3.6. Example of Tangent Delta graph

It is an indication of the loss of dielectric properties and in several cases can also be related to the glass transition point. It is used as a measure of cure for magnet wire production.

Mechanical properties describe the behavior of the enameled wire under the influence of different mechanical stresses. Typical tests covered in the industry include elongation, jerk, flexibility, abrasion and coefficient of static and dynamic friction.

Adhesion and flexibility: after a certain elongation (from 5 to 30%), the wire is wounded around a mandrel with a typical diameter of 2 times the wire diameter.

The appearance of cracks and loss of adhesion is checked visually (using a microscope if necessary). The jerk test consists in quickly jerking the wire and checking again the appearance of cracks and loss of adhesion (Figure 3.7).

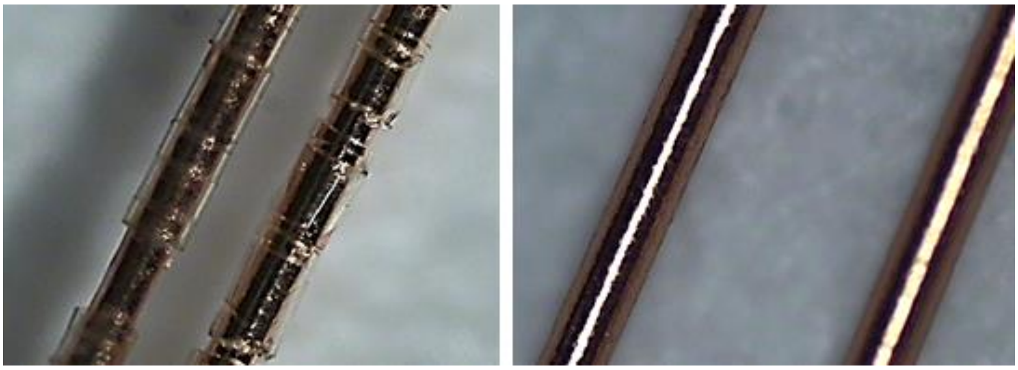


Figure 3.7. Jerk Test results: “not passed” (left) and “passed” (right)

One of the possible tests to measure the abrasion resistance is the repeated scrape test, which is widely recognized and employed as a measure of the abrasion resistance for wire coatings. The repeated scrape consists of a test wire suspended adjacent to a pendulum having a needle attached at the end thereof. The needle swings back and forth and scrapes the coating on the periphery of the wire. A defined loading is applied to the pendulum providing a controlled force to the needle against the wire. The number of strokes it takes the needle to wear through the coating is recorded. A greater number of strokes before failure indicates a higher abrasion resistance.

Thermal properties describe the capacity of the enamel to maintain its structure and properties at high temperature. Typical wire tests are heat shock, cut-through and thermal index determination.

In the heat shock test, the same tested sample used to determine the flexibility is heated into an oven at a specific temperature according to its thermal class and then cooled to ambient temperature. No cracks must be visible. This property is related to the capability of the winding to resist against thermal shocks.

In the cut-through, a standardized pressure is applied on two wires crossing each other or, for small diameter wires (to 0,100 mm), two wires crossing one and heated for 2 minutes at a given temperature. Before applying the pressure, wires are preheated at the same temperature for 1 minute. When an electrical contact between the two wires occurs due to the softening of the wire enamel film, this temperature is recorded as cut-through. This test demonstrates the flow capability of the enamel under pressure.

Chemical properties describe the capacity of the enamel to withstand chemical attacks. They can be summarized as resistance to solvents, resistance to refrigerants, resistance to transformer oil and solder time.

Solder time is the minimum time in which a sample of 4 cm of enameled wire is completely soldered for half-length by a tin-lead (80:20) alloy. The less is the time the better is the enamel's solderability.

3.1.3 The enameling stage

For the product I have worked with, we have used an Aumann DHL 250, a horizontal machine with felts applicator, as enamelling machine. The wire passes 22 times into the machine uptaking a layer of enamel each time, before being collected. We used wires of 0,100 mm and 0,071 mm of diameter. In both cases, the thickness of the insulated layer was grade 2, which means from 16 μm to 25 μm for the 0,100 mm and from 12 μm to 20 μm for the 0,071 mm wire.

To set up the enamelling conditions, we worked with a reference enamel characterized by good performance, in two steps, respectively called "Air Span" and "Speed Span" in our arbitrary procedure. The so called "Air Span" is the first step in the process of finding the best enamelling conditions for the investigated enamel. It consists in changing the airflows inside the curing room of the machine to change the curing of the product and evaluate related properties of enamelled wire. The parameters that affect airflow are:

- Recirculation fan's rate, which regulates the speed of air circulating inside the curing room. It is measured in rpm.
- Exhaust bell's opening, that controls the amount of air that comes out from the curing room. It affects the room's temperature too: by opening the bell more hot air goes out, vice versa closing the bell the hot air remains inside

heating the curing room. It is measured in degrees: at 0° it is completely open; at 90° it is completely closed.

- Fresh air fan's rate, which regulates the amount of fresh air introduced into the curing room. The higher the fan rate, the higher the amount of fresh air that lowers the temperature in the curing room. It is measured in rpm.

Other parameters that are set in the enamelling phase are the temperatures of the resistors inside the curing room. Setting such temperatures and the above described airflows defines the temperatures reached inside the curing room.

The tests are planned in order to increase the temperatures in the curing room, keeping the speed of the machine at 930 m/min.

Some tests have been made adjusting the three parameters and the temperatures, until we have found the optimal conditions for enameling. Optimal conditions occur when, in the course of the tests, the sample passes from a non-cured state to a good cured state, until it reaches a state of over-cured (Table 3.2 and Figure 3.8).

Table 3.2. Set for the "Air Span" test

Recirculation Fan	1050	1200	1400	1500	1500	1500
Bell for Exhaust	20°	20°	20°	20°	30°	40°
Fresh Air Fan (rpm)	280	300	300	300	300	300
Speed (m/min)	930	930	930	930	930	930
Polymerization Temperature (°C)	446	471	503	517	522	524
Jerk Test	OK	OK	OK	OK	OK	OK
Tangent Delta (°C)	143,7	155,4	161,0	161,3	159,5	159,9

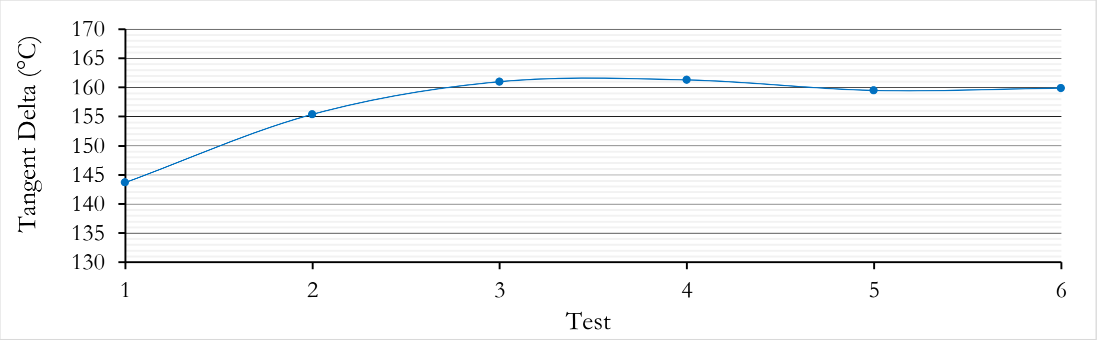


Figure 3.8. Tangent Delta values for the "Air Span" test

For each test, tangent delta and jerk test were performed; these are the tests that give a direct indication on the curing of the enamel.

From Figure 3.8, we see that the trend of the tangent delta is the one we were looking for, except for the last test in which the tangent delta should have been a little lower.

The test at which the highest value of tangent delta is recorded (in our case, test 4), is taken as the starting point to proceed with the so called "Speed Span", made as second and last step of the evaluation of the optimal enamelling conditions.

In this series of tests, the parameters concerning the airflows are fixed and the enameling speed is changed. The variation is made of ± 15% and ± 30% compared to the standard speed (930 m/min). In this case, the lower the speed the greater the degree of curing, since the wire remains for longer in the oven, and vice versa. Therefore, also in this case the resulting tangent deltas should have a Gaussian pattern, reaching the apex with the central speed (Table 3.3 and Figure 3.9).

Table 3.3. Set for the "Speed Span" test

Recirculation Fan	1500	1500	1500	1500	1500
Bell for Exhaust	20°	20°	20°	20°	20°
Fresh Air Fan (rpm)	300	300	300	300	300
Speed (m/min)	650	790	930	1070	1210
Polymerization Temperature (°C)	524	529	529	521	507
Jerk Test	OK	OK	OK	OK	OK
Tangent Delta (°C)	147,9	155,0	159,6	161,1	155,9

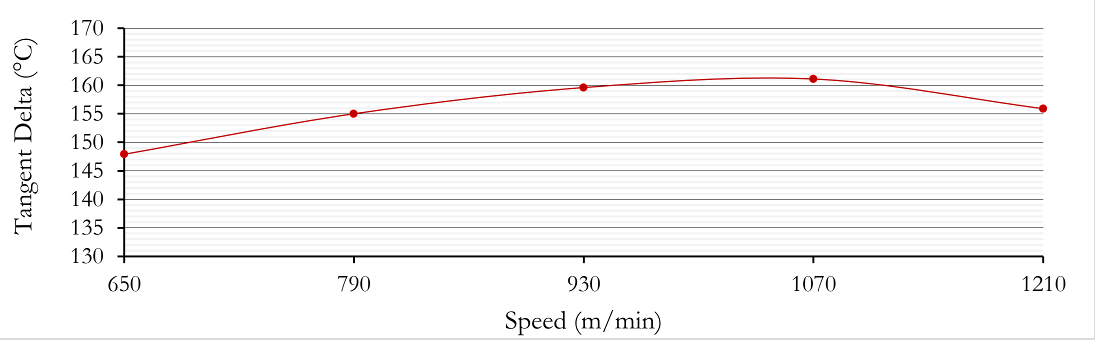


Figure 3.9. Tangent Delta values for the "Speed Span" test

To evaluate enamel properties, usually a Speed Span step is performed. Thanks to such step it is possible to see the Tangent Delta trend and then to validate the enamelling process, before checking the properties of the obtained enameled wires. Every time there is a doubt about the enamel curing or about the conditions of the machine, the reference batch of which the Speed Span profile is known is enamelled and the results are compared to the reference and used for validation.

3.2 Statistical Approach

Very often the way to conduct the research is done in the manner defined OVAT (One Variable At a Time). This is the immediate method of carrying out the research and certainly the one most used. This method by its intrinsic nature consists in doing the most plausible tests on the basis of an elementary logic: modifying a variable in a certain range and evaluate the best result, then narrow the range around the value that gives the best result to see if the result can improve. Obtained the best result fixing the variable to the value that made it and proceed by modifying a second variable in the same way, and so on until all the variables are fixed. Obviously, the tests to be carried out vary according to the number of variables, but apart from that, many tests have to be made. Furthermore, in this way we do not consider the synergy between the elements within the system. This synergy is the effect for which the variables of the system interacting with each other can have a different effect from that which they individually exert. To understand, not always the best result obtained by modifying individually the variables is the best result obtainable from the system. We have to consider the system as a single entity and not the simple sum of its individual components.

To overcome this problem and be able to evaluate the system in its entirety, we can use some statistical tools such as design of experiments. The design of experiments is a design that helps to plan the experiments to be carried out in such a way as to obtain a complete view of the analyzed system by performing the fewest possible tests. Once all the necessary tests have been performed, we can optimize the system, setting the variables in the way as to obtain the desired result.

Being a tool based on statistical and mathematical calculations, it is not easy to make the needed calculation. For this, various software can provide support both during planning and data processing and optimization.

The use of such mathematical tools has often proved successful in various sectors both in the field of scientific research and in industrial applications.

3.2.1 Preliminary activities

The first thing to do is to define the purpose and the results one wants to achieve, define in details the kind of results (responses, or Ys) and their related values, then if it is necessary to increase or decrease their value. Possible interactions among the responses are evaluated too.

The next step is the identification of the variables of the system. A list of variables is drawn up with an assessment of their impact on each response: whether strong or weak, or if they have no impact. At the end of the evaluation the variables to be inserted in the design (factors) are decided. In this phase, if necessary, preliminary tests are carried out to evaluate some factors or to reduce their number. Obviously, the greater the number of factors the greater the number of tests to be carried out. Additionally, talking to people familiar with the system/process (experts) or establishing a dedicated team could be very useful to identify and evaluate factors.

3.2.2 Planning the design

Based on the results of the discussions, or screening experiments, factors for the modeling design should be identified. All of the factors should be controllable and should have adequate measurement systems, so it is possible reliably to set them at particular values in the experiment. Possibly the chosen factors should be the ones most affecting the system.

Then define the factor levels. Factors can be numeric or categorical. For each numeric factor, it has to be decided how much to increase and decrease the factor from its current setting to see a difference in the response. For a modeling design, usually are used settings that are closer together than for a screening design. Because the modeling experiment uses only the critical few factors already determined which have a strong influence on the response, there is less need to stretch the limits.

With a modeling design, the model estimates the main effect for each factor as well as the interactions between each pair of factors. An interaction is the difference in the effect of one factor at different levels of another factor.

If we want to detect smaller shifts in the mean of the response, we need more data as possible. Therefore, to obtain more data it is possible to repeat all or some of the runs in the experiment, which is called replicating the design.

Usually when a modeling design is created, the used software randomizes the order of the experimental runs. Randomization balances the effect of uncontrollable conditions, such as changes to materials or personnel, and reduces the chance that these conditions will bias the results. Once we start carrying out the planned trials, it is important to make sure to perform the runs in random order as specified in the schedule.

The number of trials to run depends on the number of factors and the number of their levels. Usually designs have n factors and two levels, for a total of 2^n trials.

Sometimes the number can be reduced running a fractional design. A fractional design is a design in which experimenters conduct only selected subset (or fraction) of the runs in the full design. Fractional designs are a good choice when resources or time are limited or the number of factors is large because they use fewer runs than the full design.

A fractional design uses a subset of a full design, so some of the main effects and 2-way interactions are confounded and cannot be separated from the effects of other higher-order interactions. Usually experimenters are willing to assume the higher-order effects are negligible in order to achieve information about main effects and low-order interactions with fewer runs.

The design resolution should be known when choosing a fractional design. The resolution indicates the ability of the design not to confound interactions: the higher the resolution, the lower the confounded interactions. Running a fractional design, one or more of the effects are confounded, so we need to get a design with the highest possible resolution for fractionation required.

Resolution III, IV, and V designs are the most common:

- Resolution III, no main effects are aliased with any other main effect, but main effects are aliased with 2-factor interactions.
- Resolution IV, no main effects are aliased with any other main effect or 2-factor interactions, but some 2-factor interactions are aliased with other 2-factor interactions and main effects are aliased with 3-factor interactions.
- Resolution V, no main effect or 2-factor interactions are aliased with any other main effects or 2-factor interactions, but 2-factor interactions ae aliased with 3-factor interactions and main effects are aliased with 4-factor interactions.

To choose a right resolution for a fractional design we can use a table as the one shown below (Table 3.4).

Table 3.4. Resolution of designs

		Factors							
		2	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Runs	**4**	Full	III						
	8		Full	IV	III	III	III		
	16			Full	V	IV	IV	IV	III
	32				Full	IV	IV	IV	IV
	64					Full	VII	V	IV
	128						Full	VIII	VI

This kind of tables shows for each number of factors the number of runs needed to have a certain resolution. Good resolutions are from V on or a full design of course.

3.2.3 Validating measurement systems

To trust experimental results, it is necessary to verify that all the measurement systems are accurate, verifying the measurement systems that are used both to measure the response and to set the factor levels.

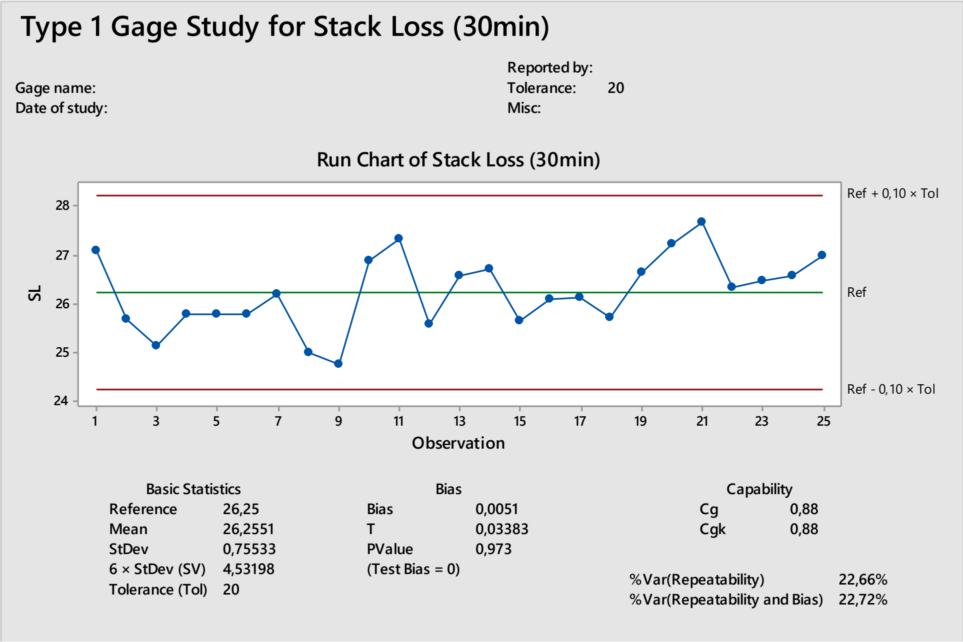
If the experiments are part of a as a six sigma project, the measurement system for the responses should have been validated previously. Make sure to verify the measurement system for the factors as well.

The process for validating measurement systems is called Measurement System Analysis (MSA). There are two types of MSA: Type 1 Gage Study or Gage Repeatability and Reproducibility (R&R). As suggested by the name in a Gage R&R repeatability and reproducibility are checked. Repeatability expresses how much variability the measurement device causes; reproducibility expresses how much variability in a measurement system is caused by differences between operators. In this analysis, different operators carry out the same measurement on the same sample with the same measurement system. With this kind of study, it is possible to assess whether a measurement system variability is small compared with the process variability and whether a measurement system is capable to distinguish between different parts.

Whereas Type 1 Gage Study assess only the variation that comes from the gage. Specifically, this study assesses the effects of bias and repeatability on measurements from one operator and one reference sample. This kind of analysis at the start of a measurement system analysis is used to focus on the gage, not on any other sources of variation. In fact, usually the Type 1 Gage Study is the first step in a complete measurement system analysis.

Below it will be briefly shown the Type 1 Gage Study, since this kind of MSA has been used during the thesis work.

To conduct a Type 1 Gage Study it is possible to make at least 25 tests of one sample (possibly a standard sample) using the same measurement system, carried out by one operator. After conducting the tests, the obtained values can be integrated into the software together with the reference and tolerance values. The software shows the results as in Figure 3.10.



Type 1 Gage Study for Stack Loss (30min)

Gage name:
Date of study:

Reported by:
Tolerance: 20
Misc:

Basic Statistics	
Reference	26,25
Mean	26,2551
StDev	0,75533
6 × StDev (SV)	4,53198
Tolerance (Tol)	20

Bias	
Bias	0,0051
T	0,03383
PValue	0,973
(Test Bias = 0)	

Capability	
Cg	0,88
Cgk	0,88

%Var(Repeatability)	22,66%
%Var(Repeatability and Bias)	22,72%

Figure 3.10. Example of MSA results given by the software

In the figure, the graph reports the values obtained from the tests, the reference value (green line) and its tolerance set as ± 10 % (red lines). The figure also shows some parameters, including: mean, standard deviation, bias, C_g and C_{gk}, %Var (Repeatability) and %Var (Repeatability and Bias).

Bias indicates how close the measurements are to the reference values. A positive bias indicates that the gage overestimates; vice versa, a negative bias indicates that the gage underestimates. The %Bias value indicates the magnitude of the bias as a percent of the process variation (usually 6 sigma).

As mentioned repeatability is the gage's ability to make consistent measurements of the same sample. Some measurement variation will be present even in a capable gage, but if the variation is too large in relation to the sample's tolerance, the gage will be too variable for its purpose. The variation of a gage's measurements should be small compared to the tolerance.

To assess a gage's repeatability, software calculate the C_g metric to compare the study variation (the spread of the gage's measurements) with a percentage of the tolerance. Values of C_g greater than 1.33 indicate the spread of the gage's measurements is adequately narrow in relation to your tolerance range.

$$C_g = \frac{\frac{K}{100} \times \text{Tolerance}}{L \times s}$$

In the equation, K is the percentage of the tolerance (20 is the default); L is the number of standard deviations that represent the entire process spread (6 is the default); s the standard deviation of measurement.

In addition to repeatability, the software also assesses the gage's bias, which is the difference between the gage's average measurement and the official reference value, the actual value that the gage targets. The %Bias value indicates the magnitude of the bias as a percent of the process variation. If a statistically significant bias exists, one concludes that the gage is consistently measuring higher or lower values than the correct ones.

The software also calculates the capability metric C_{gk} to assess repeatability and bias together. C_{gk} compares the Study Variation to the tolerance, but it also considers whether the measurements are on target. C_{gk} decreases as the difference between the gage's mean measurement and the reference value increases. A C_{gk} value of 1.33 is a common benchmark value to denote a capable gage: one that is both precise (good repeatability) and accurate (low bias).

$$C_{gk} = \frac{\frac{K}{100} \times \text{Tolerance} - \left|\overline{X}_g - X_m\right|}{L \times s}$$

In the equation, $\overline{X}_g$ is the mean of all measurement and X_m is the reference value. %Var (Repeatability) and %Var (Repeatability and Bias) indicate the variation due to the measurement system. Commonly used benchmark are smaller than 15%.[41]

3.2.4 Evaluating the design

Once running all the trials, the results can be integrated into the software for the evaluation. In this work, we used mainly Main Effect Plot, Interactions Plot and Pareto Charts.

Main Effect plots show how the different factors affect the response under consideration. It means how the responses change based on the factors levels: if they increase, decrease or remain the same (Figure 3.11).

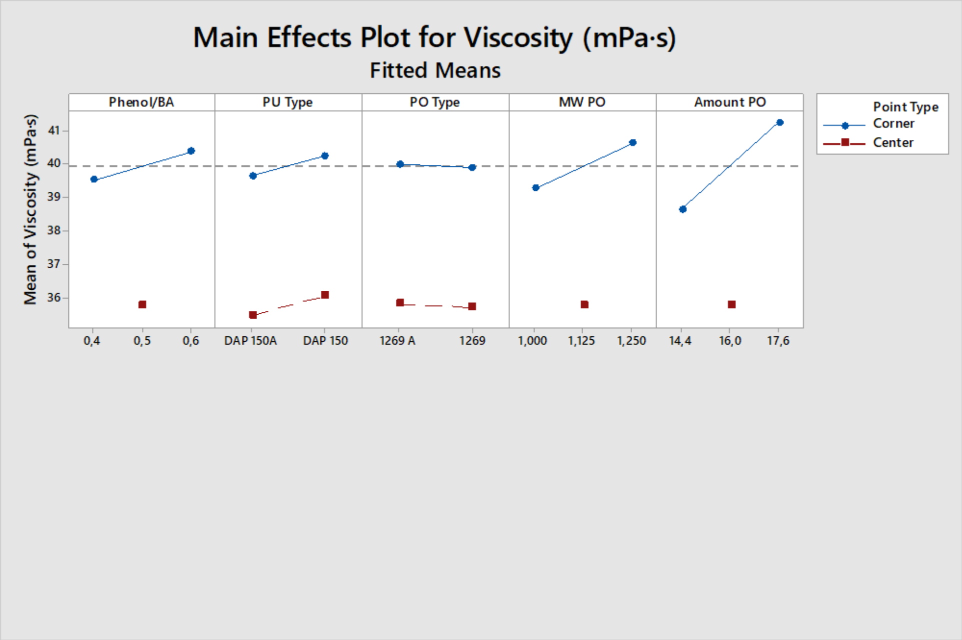


Figure 3.11. Example of Main Effects Plot

Interactions plots display how the relationship between one categorical factors and a continuous response depends on the value of a second categorical factor. We can evaluate the line to understand how the interactions affect the relationship between factors and responses: parallel lines, no interaction occurs; nonparallel lines, an interaction occurs (Figure 3.12).

The Pareto chart shows the absolute values of the standardized effects from the largest effect to the smallest effect. The chart also plots a reference line to indicate which effects are statistically significant (Figure 3.13).

The reference line for statistical significance depends on the significance level (denoted by α).

The Pareto chart is meant to determine the magnitude and the importance of the effects. On the Pareto chart, bars that cross the reference line are statistically significant. Because the Pareto chart displays the absolute value of the effects, one can determine which effects are large but cannot determine which effects increase or decrease the response. If one want to know the direction of the effects, It possible to use the normal probability plot of the standardized effects to examine the magnitude and direction of the effects on one plot.[42]

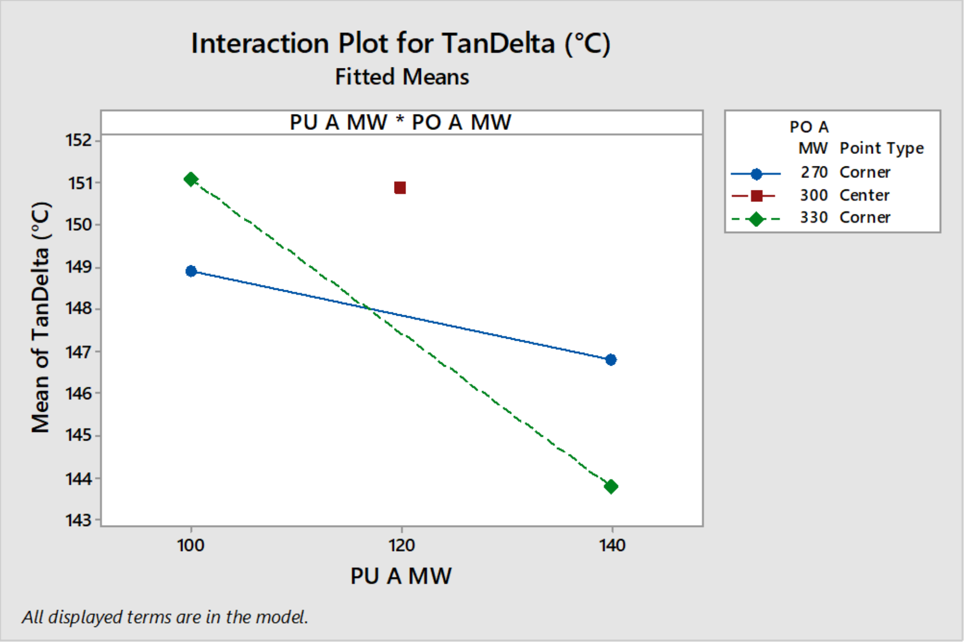


Figure 3.12. Example of Interaction Plot

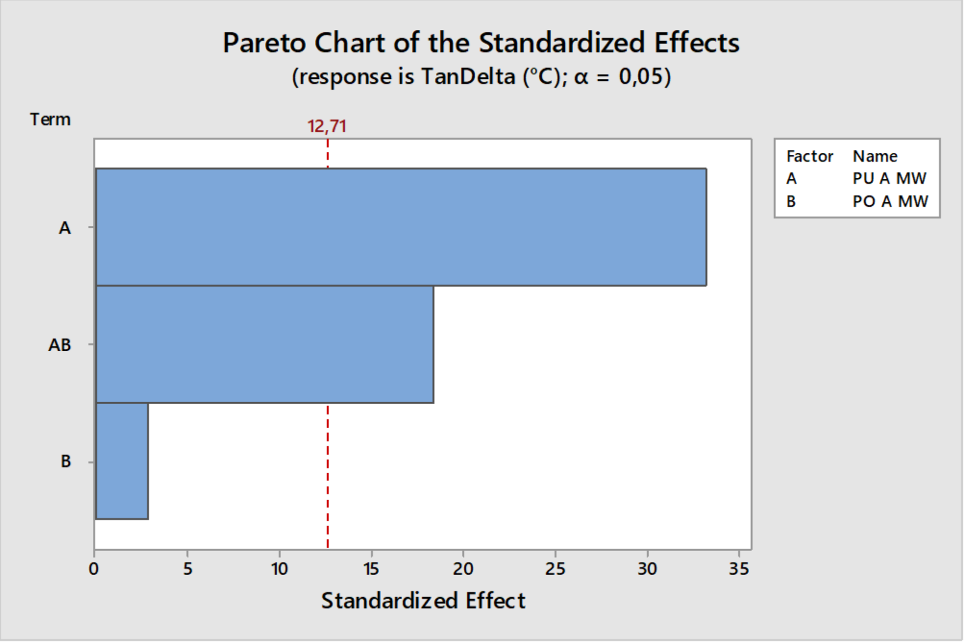


Figure 3.13. Example of Pareto Chart

3.3 Experimental Section

3.3.1 Materials and methods

All the used raw materials and solvents were purchased from various supplier all over the world. The quality of different compounds is guaranteed from the internal CQ laboratory.

All the syntheses were carried out in 5 liters round-bottom flasks with mechanical mixing and a mantles were used to heat.

3.3.2 Instrumental

Gel permeation chromatography (GPC)

The instrument used was a Knauer Azura, a differential refractive index detector, and one column (5 μm, 300 x 7,5 mm) or two identical in series for the polyester polyol analyses. All the samples were dissolved in THF at a constant concentration of 10 mg/mL. After filtration of samples with 0,45 μm wheel syringe filter, 20 μL of each sample was injected into the chromatograph. The elution solvent was also THF at a constant flow rate of 1 mL/min.

Thermogravimetric analysis (TGA)

The instrument was a Netzsch TG 209 F1 Iris® ASC. The analysis were performed weighting 15 mg of product in Al_2O_3 crucibles. A commercial software Netzsch Proteus® was used to process and calculate thermograms.

FT-IR spectroscopy

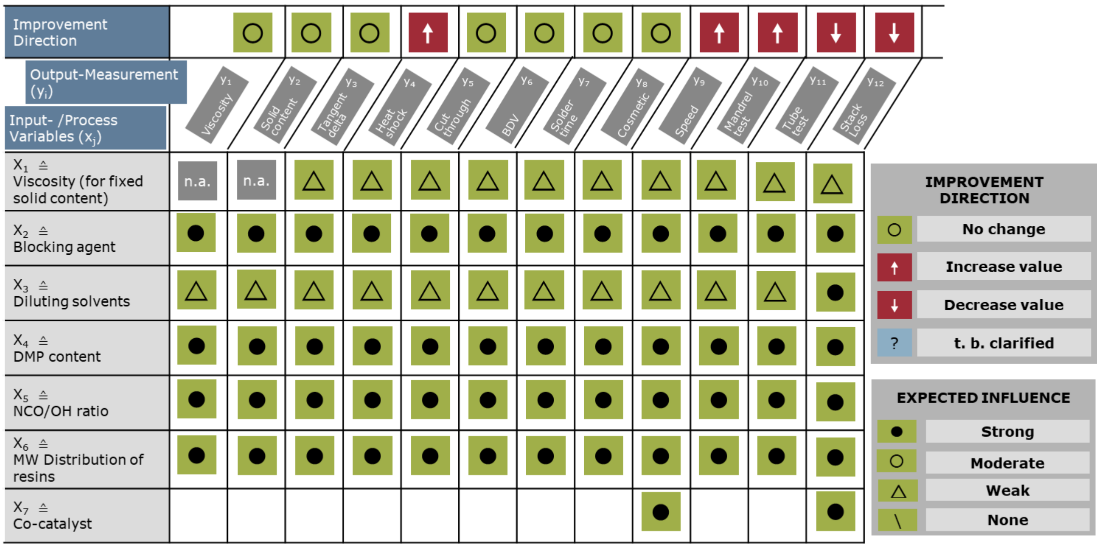
The instrument was a Thermo Scientific Nicolet iZ10 with the MART Omni-transmission accessory. The recorded wavenumber range was 450 to 4000 and 3 spectra were averaged to reduce the noise. A commercial software Thermo Scientific™ OMNIC™ Series FT-IR was used to process and calculate the wavenumber from the spectra.

3.4 Results and Discussion

As first step, the PU-team, consisting of the team leader and expert members together with the author of this Thesis, adopted a DFSS approach and identified the most impacting variables in the polyurethane system and their effects on the system.

Table 3.5 shows the expected effects of each factor on each response and the strength of these effects. On the top of the table are shown the improvement directions that the team wanted to have.

Table 3.5. Possible factors and their effects on the system



Improvement Direction	○	○	○	↑	○	○	○	○	↑	↑	↓	↓
Output-Measurement (y_i) Input- /Process Variables (x_j)	y_1 Viscosity	y_2 Solid content	y_3 Tangent delta	y_4 Heat shock	y_5 Cut through	y_6 BDV	y_7 Solder time	y_8 Cosmetic	y_9 Speed	y_{10} Mandrel test	y_{11} Tube test	y_{12} Stack Loss
X_1 ≙ Viscosity (for fixed solid content)	n.a.	n.a.	△	△	△	△	△	△	△	△	△	△
X_2 ≙ Blocking agent	●	●	●	●	●	●	●	●	●	●	●	●
X_3 ≙ Diluting solvents	△	△	△	△	△	△	△	△	△	△	△	●
X_4 ≙ DMP content	●	●	●	●	●	●	●	●	●	●	●	●
X_5 ≙ NCO/OH ratio	●	●	●	●	●	●	●	●	●	●	●	●
X_6 ≙ MW Distribution of resins	●	●	●	●	●	●	●	●	●	●	●	●
X_7 ≙ Co-catalyst									●			●

IMPROVEMENT DIRECTION	
○	No change
↑	Increase value
↓	Decrease value
?	t. b. clarified

EXPECTED INFLUENCE	
●	Strong
○	Moderate
△	Weak
\	None

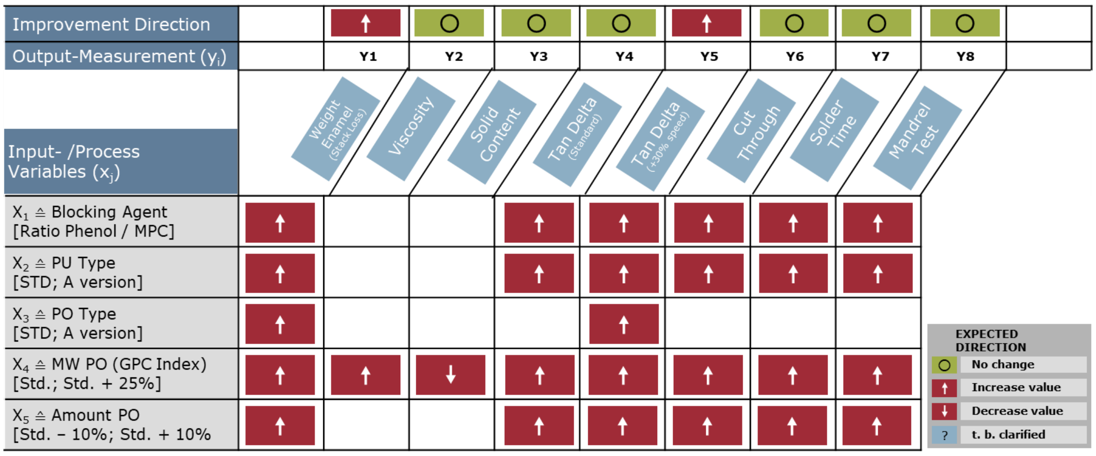
We identified as possible factors:

- Viscosity, for a fixed solid content.
- Blocking agent in the synthesis of the PU intermediate.
- The diluting solvents also used in dissolving the PU intermediates.
- Dimethyl phthalate content. DMP is a plasticizer used to improve application of the enamel.
- The NCO/OH ratio. It means the ratio between the amount of -NCO blocked groups of PU intermediate and the amount of -OH groups of PO intermediate. This ratio is very important because it is in correlation with the number of urethanes bonds that are going to be formed in the application phase.

- The molecular weight (MW) of the two intermediates. The MW affects the properties of the resins, in addition to modify the NCO/OH ratio.
- The use of a second catalyst in addition to the already included one.

After some discussions, we decide the factors to be used in our design (Table 3.6). The table shows the desired improvement direction on the top and the expected improvement directions of each factor on each response. The chosen factors and their levels are in Table 3.7.

Table 3.6. Chosen factors and their effects



Improvement Direction	↑	○	○	○	↑	○	○	○
Output-Measurement (y_i)	Y1	Y2	Y3	Y4	Y5	Y6	Y7	Y8
Input- /Process Variables (x_j)	Weight Enamel (Stack Loss)	Viscosity	Solid Content	Tan Delta (Standard)	Tan Delta (+30% speed)	Cut Through	Solder Time	Mandrel Test
X_1 ≙ Blocking Agent [Ratio Phenol / MPC]	↑			↑	↑	↑	↑	↑
X_2 ≙ PU Type [STD; A version]	↑			↑	↑	↑	↑	↑
X_3 ≙ PO Type [STD; A version]	↑				↑			
X_4 ≙ MW PO (GPC Index) [Std.; Std. + 25%]	↑	↑	↓	↑	↑	↑	↑	↑
X_5 ≙ Amount PO [Std. – 10%; Std. + 10%	↑			↑	↑	↑	↑	↑

EXPECTED DIRECTION
○ No change
↑ Increase value
↓ Decrease value
? t. b. clarified

Table 3.7. Chosen factors and their levels

	Factors	Lower value	Upper value
X_1	% Phenol/Blocking Agent	40%	60%
X_2	PU Type	STD	A
X_3	PO Type	STD	A
X_4	Molecular Weight PO (GPC Index)	Standard	Standard + 25%
X_5	Amount PO	Standard – 10%	Standard + 10%
X_6	Catalyst	Old	Old+New

PU type and PO type concern the formulations of the intermediates. Together with the standard formulations (STD) we decided to evaluate two old alternative formulations (A) known to be performant in an old version of polyurethane dismissed due to a policy of products number reduction. STDs and A versions diverge in solvents and catalysts used.

GPC Index is a way to measure the MW of a polymer, making a ratio among areas of the peaks in the chromatogram (obviously comparing the same product and getting always the same peak in different chromatograms), independently from any calibration curve.

Amount PO is the quantity of PO into the formulation; increasing or decreasing it is equivalent to decrease or increase respectively the NCO/OH ratio.

With this set of factors, the runs to have a full resolution should be 64 or 32 trials to have a VI resolution, in addition to central point and repeated runs. In order to decrease the number of trials, we decided to remove the catalyst from design. So the final factors and levels are shown in Table 3.8.

Table 3.8. The final chosen factors with their levels

	Factors	Lower value	Upper value
X_1	% Phenol/Blocking Agent	40%	60%
X_2	PU Type	STD	A
X_3	PO Type	STD	A
X_4	Molecular Weight PO (GPC Index)	Standard	Standard + 25%
X_5	Amount PO	Standard – 10%	Standard + 10%

With five factors, 16 runs are enough to have good resolution (V resolution) and a concrete saving of time. We decided to proceed with this design, adding 4 center points and their repetitions, and the software calculates all the trials to be done (Table 3.9). Center points are trials in which factors with numeric levels assume middle values, in order to check the linearity of the system. Repetitions are also important because they allow checking that the same trials give the same results and that there is nothing disturbing the system.

Table 3.9. Scheduled trials for DOE

RunOrder	CenterPoint	Blocks	% Phenol	PU type	PO type	MW PO	Amount PO
1	0	1	50%	A	A	Std +12,5%	Standard
2	1	1	66%	Standard	Standard	Standard	Std -10%
3	0	1	50%	A	A	Std +12,5%	Standard
4	0	1	50%	A	Standard	Std +12,5%	Standard
5	1	1	33%	Standard	Standard	Std +25%	Std +10%
6	1	1	33%	A	A	Standard	Std -10%
7	0	1	50%	Standard	A	Std +12,5%	Standard
8	1	1	66%	A	Standard	Std +25%	Std -10%
9	0	1	50%	Standard	Standard	Std +12,5%	Standard
10	1	1	33%	Standard	A	Std +25%	Std -10%
11	1	1	66%	Standard	A	Standard	Std +10%
12	1	1	66%	A	A	Std +25%	Std +10%
13	1	1	33%	A	Standard	Standard	Std +10%
14	1	2	33%	A	A	Std +25%	Std +10%
15	0	2	50%	A	Standard	Std +12,5%	Standard
16	1	2	66%	A	A	Standard	Std -10%
17	1	2	66%	Standard	Standard	Std +25%	Std +10%
18	0	2	50%	Standard	A	Std +12,5%	Standard
19	1	2	33%	Standard	A	STD	Std +10%
20	0	2	50%	Standard	Standard	Std +12,5%	Standard
21	1	2	66%	A	Standard	Standard	Std +10%
22	1	2	33%	A	Standard	Std +25%	Std -10%
23	1	2	33%	Standard	Standard	Standard	Std -10%
24	1	2	66%	Standard	A	Std +25%	Std -10%

3.4.1 Measurement system analysis

Before starting with the DOE, we had to check our measurement systems. This check is called Measurement System Analysis (MSA). An MSA evaluates the test method, measuring instruments, and the entire process of obtaining measurements to ensure (or evaluate) the integrity of data used for analysis and to understand the implications of measurement error for decisions made about a product or process. Being a statistical tool that correlates synthesis variables with properties of the final product, in order to make this correlation the better as possible we have to measure all properties as good as possible, being sure that the results of our measurements are as near as possible to the real values.

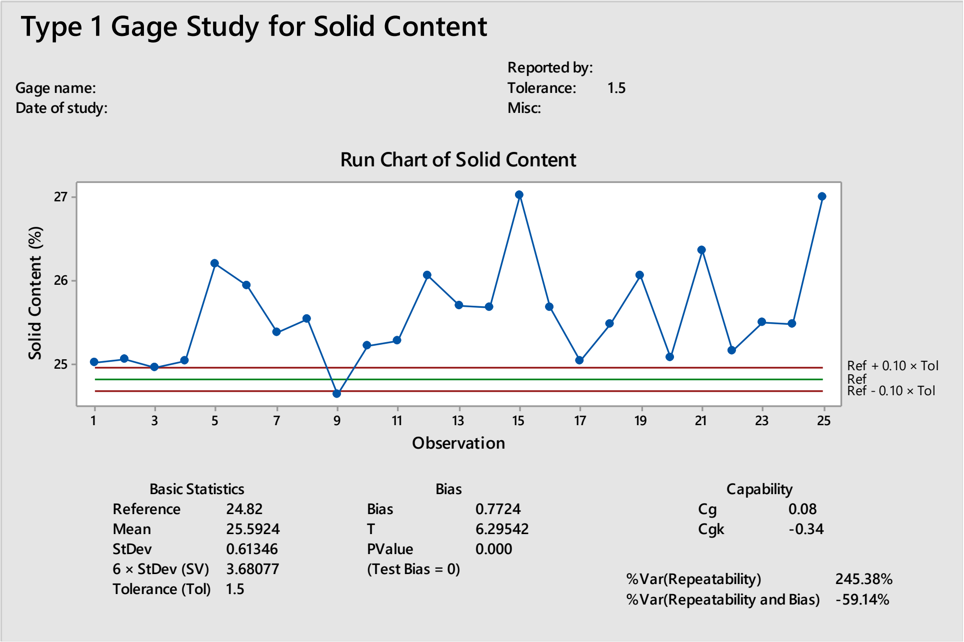
We therefore chose to do an MSA Type-I before running the DOE. MSA Type-I study assesses only the variation that comes from the gage, the measurement, and consists at least of 25 repeated tests of the same sample, carried out with the same method and by the same operator. Measurement systems that need the analysis and theirs MSA are debated below.

Solid content.

Solid content is that portion of non-volatile material contained into the enamels. The method is based on placing 1 g of enamel, weighted on an aluminum disk, in a forced circulation oven at 180 °C for 1 hour. The weight of the empty disk is taken out of the scale (tare), the weights of the disk with the enamel before (yb) and after (ya) the treatment into the oven are then taken and reported in the following equation:

$$\text{Solid Content} = \frac{y_a - \text{tare}}{y_b - \text{tare}} \times 100\ [\%]$$

For the tests we have used a product with 24,82 % of solid content. We have carried out a first MSA, from which it resulted that there is a bias, almost 1 %, a high deviation, so a very low Cg and a very high repeatability (Figure 3.14).



Type 1 Gage Study for Solid Content

Gage name:
Date of study:

Reported by:
Tolerance: 1.5
Misc:

Run Chart of Solid Content

Basic Statistics

Reference	24.82
Mean	25.5924
StDev	0.61346
6 × StDev (SV)	3.68077
Tolerance (Tol)	1.5

Bias

Bias	0.7724
T	6.29542
PValue	0.000
(Test Bias = 0)	

Capability

Cg	0.08
Cgk	-0.34

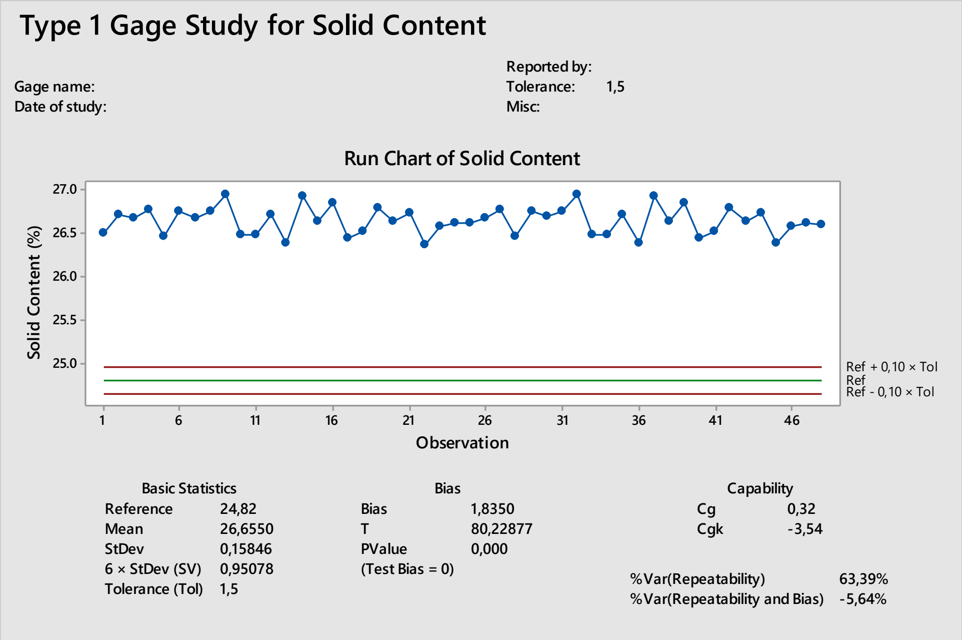
%Var(Repeatability)	245.38%
%Var(Repeatability and Bias)	-59.14%

Figure 3.14. MSA results for solid content

To improve the measurement system we thought to carry out each test as average of four contemporaneous tests. To do this we have used an especially made holder, able to contain four disks at a time (Figure 3.15).

Figure 3.15. Sample holder for solid content

Whit this expedient we have been able to increase the Cg to 0,32, four times more than the previous one, and to reduce the repeatability to 63,39 % (Figure 3.16).



Type 1 Gage Study for Solid Content

Gage name:
Date of study:
Reported by:
Tolerance: 1,5
Misc:

Basic Statistics

Reference	24,82
Mean	26,6550
StDev	0,15846
6 × StDev (SV)	0,95078
Tolerance (Tol)	1,5

Bias

Bias	1,8350
T	80,22877
PValue	0,000
(Test Bias = 0)	

Capability

Cg	0,32
Cgk	-3,54
%Var(Repeatability)	63,39%
%Var(Repeatability and Bias)	-5,64%

Figure 3.16. MSA results for solid content

After few weeks, we have changed our disk with new flatter ones (Figure 3.17), and then we have run again the MSA (Figure 3.18). First disks in fact had a little convexity at the center and the enamel, that has a very low viscosity, was distributed not uniformly on the disk. With new disks, the enamel resulted to be distributed homogeneously, allowing a better evaporation of the solvents.

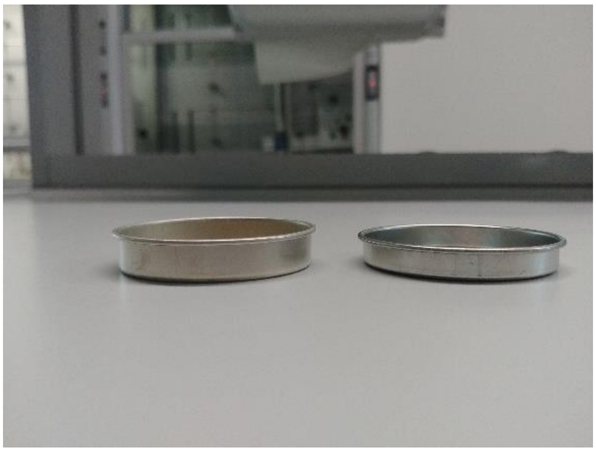
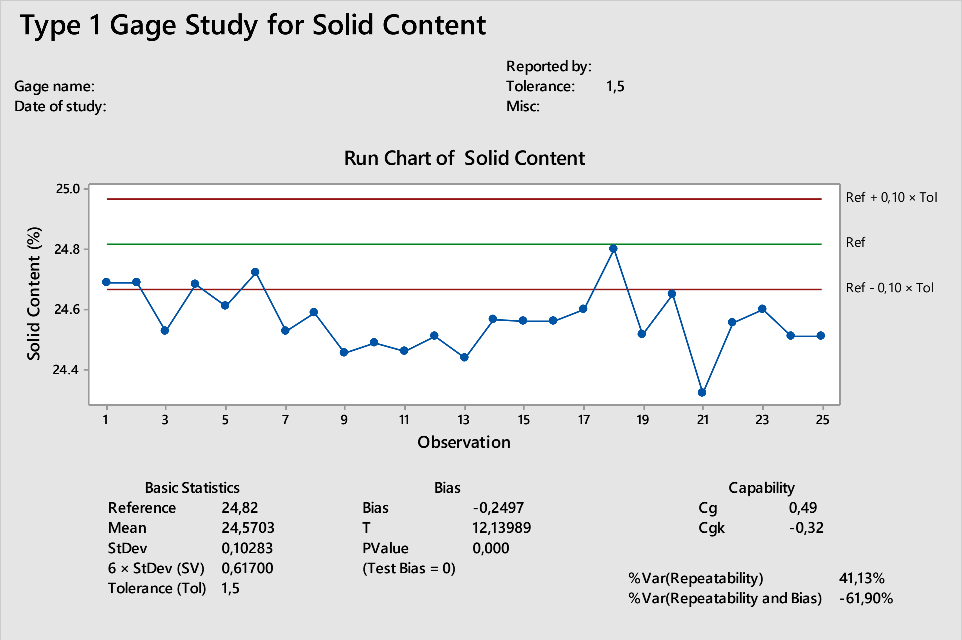


Figure 3.17. Old (on the left) and new (on the right) disks for the solid content determination

We can see that Cg is increased now to 0,49, which means six time higher than the first system, and the Repeatability is decreased to 41,13 %.

We do not reach the desired values for Cg and Repeatability, but we have improved a lot the measurement system performance and the values moved away from the average max for 0,2-0,3 % of solid content, which is not bad.



Type 1 Gage Study for Solid Content

Gage name:
Date of study:

Reported by:
Tolerance: 1,5
Misc:

Basic Statistics

Reference	24,82
Mean	24,5703
StDev	0,10283
6 × StDev (SV)	0,61700
Tolerance (Tol)	1,5

Bias

Bias	-0,2497
T	12,13989
PValue	0,000
(Test Bias = 0)	

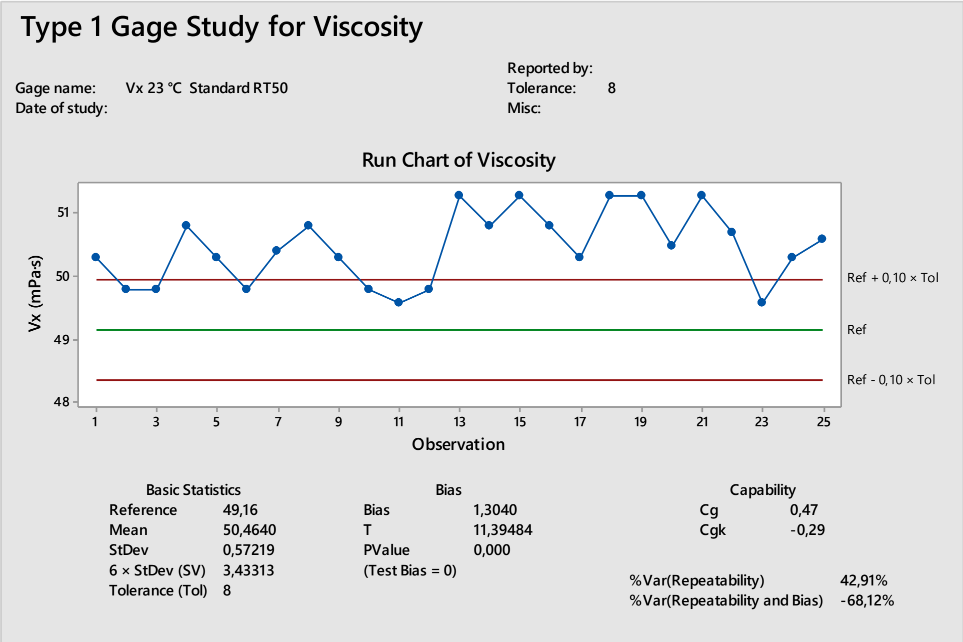
Capability

Cg	0,49
Cgk	-0,32
%Var(Repeatability)	41,13%
%Var(Repeatability and Bias)	-61,90%

Figure 3.18. MSA results for solid content

Viscosity.

Viscosity is checked by a rotatory viscometer with coaxial cylinder HAAKE VT 550, kept at the desired temperature by a thermostat. To carry out the analysis we have used a standard oil that has a viscosity of 49,16 mPa·s at 23 °C (Figure 3.19). There is a bias and a certain deviation. Cg and Repeatability are respectively 0,47 and 42,91 %. The analysis is not too good by a statistical point of view, but deviations of 1-2 mPa·s for this kind of application are considered almost insignificant.



Gage name: Vx 23 °C Standard RT50
Date of study:

Reported by:
Tolerance: 8
Misc:

Basic Statistics

Reference	49,16
Mean	50,4640
StDev	0,57219
6 × StDev (SV)	3,43313
Tolerance (Tol)	8

Bias

Bias	1,3040
T	11,39484
PValue	0,000
(Test Bias = 0)	

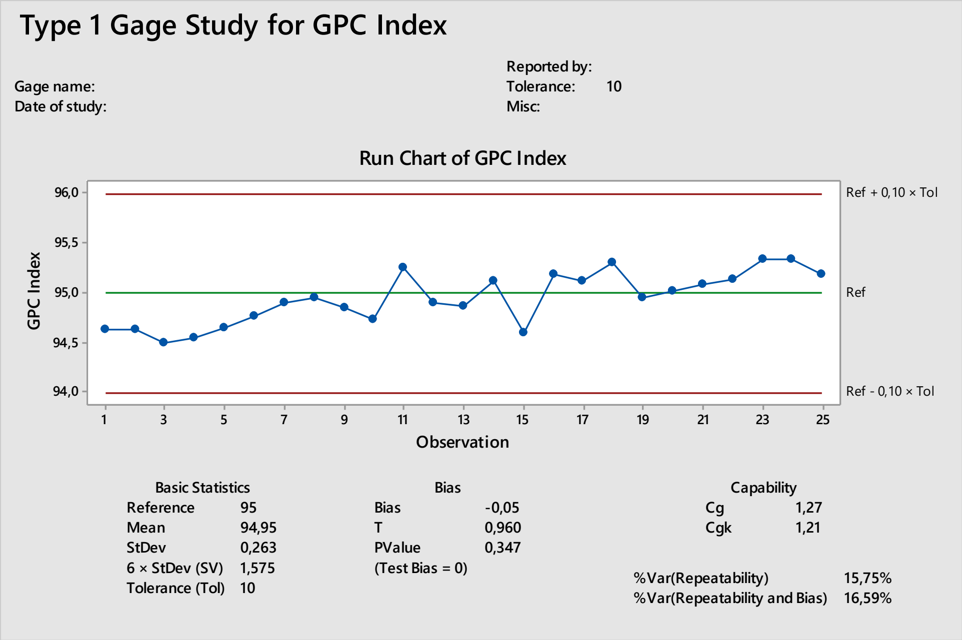
Capability

Cg	0,47
Cgk	-0,29
%Var(Repeatability)	42,91%
%Var(Repeatability and Bias)	-68,12%

Figure 3.19. MSA results for viscosity

GPC index.

The GPC index is an empirical value extrapolated from GPC chromatogram used to evaluate the molecular weight of polymers. The index is the ratio among areas of different peaks and is useful only to compare the growth of the same kind of products, but not to compare different products. MSA result shows a good deviation, a Cg of 1,27 and a repeatability of 15,75 % (Figure 3.20).

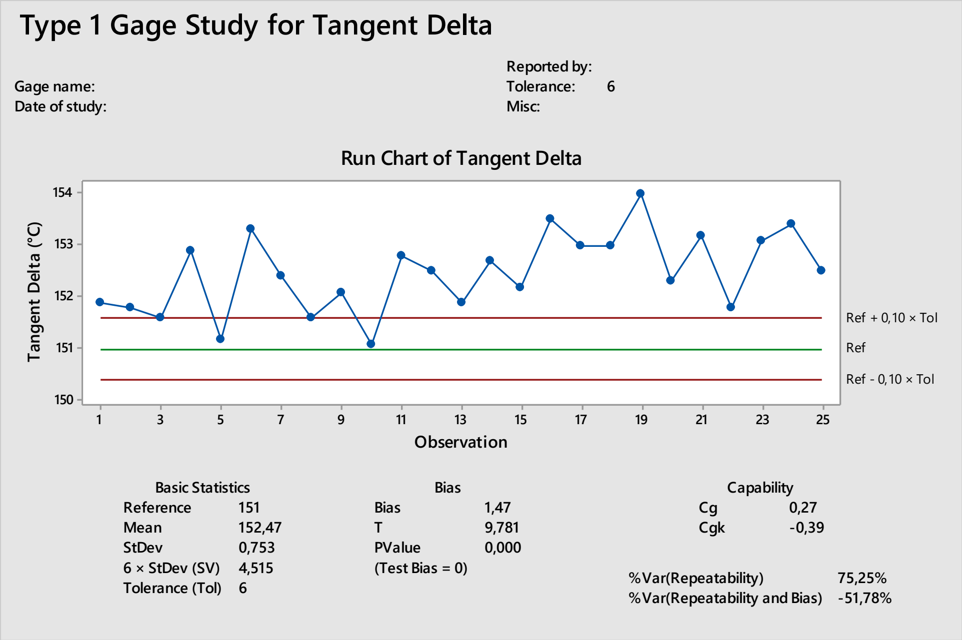


```
Type 1 Gage Study for GPC Index

                                               Reported by:
Gage name:                                     Tolerance:    10
Date of study:                                 Misc:

        Basic Statistics                 Bias                           Capability
     Reference        95          Bias          -0,05              Cg         1,27
     Mean             94,95       T             0,960              Cgk        1,21
     StDev            0,263       PValue        0,347
     6 × StDev (SV)   1,575       (Test Bias = 0)             %Var(Repeatability)            15,75%
     Tolerance (Tol)  10                                      %Var(Repeatability and Bias)   16,59%
```

Figure 3.20. MSA results for GPC index



```
Type 1 Gage Study for Tangent Delta

                                               Reported by:
Gage name:                                     Tolerance:    6
Date of study:                                 Misc:

        Basic Statistics                 Bias                           Capability
     Reference        151         Bias          1,47               Cg         0,27
     Mean             152,47      T             9,781              Cgk        -0,39
     StDev            0,753       PValue        0,000
     6 × StDev (SV)   4,515       (Test Bias = 0)             %Var(Repeatability)            75,25%
     Tolerance (Tol)  6                                       %Var(Repeatability and Bias)   -51,78%
```

Figure 3.21. MSA results for tangent delta

Tangent Delta.

A tester called BQS Burkert Quality System GmbH with TanD09 software measures this property. A piece of about 10 cm of enameled wire is inserted between two clamps of the holder. The clamps come into direct contact with the copper. After which the sample holder is inserted into the furnace, which gradually heats up the wire until it has an electrical loss. The software processes the data and returns a graph and the value of Tangent Delta. Danfoss system is used. MSA results are quite similar to what we have seen for the viscosity: a little bias, low Cg and not good repeatability (Figure 3.21); but for this measurement in the same way of viscosity, a little difference of 2-3 °C is considered almost insignificant.

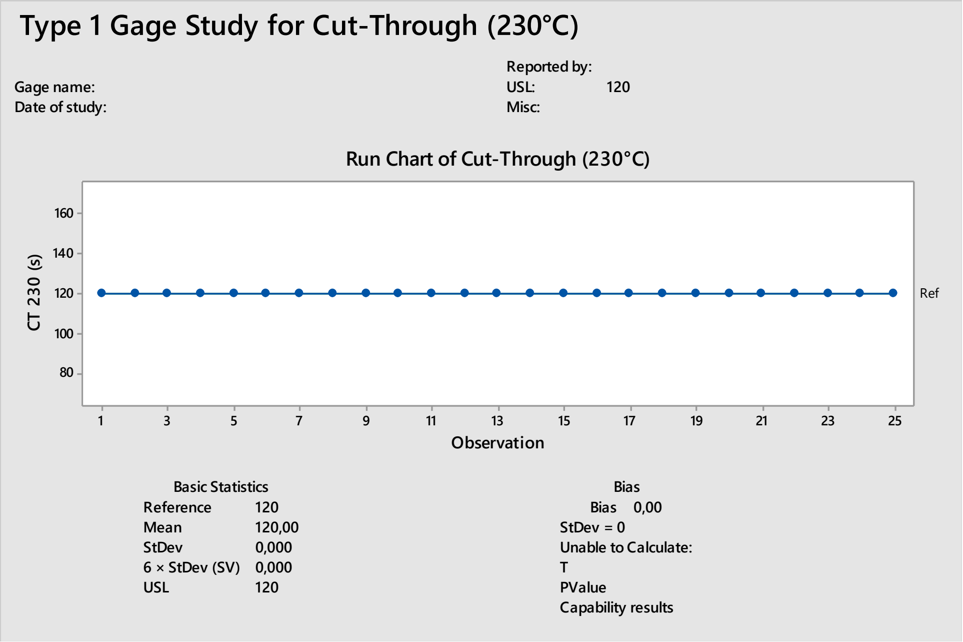
Cut-Through.

The test is run by introducing two specimens of enameled wire in the oven of the instrument in a cross section of ninety degrees. The enamel at the top of the specimens is removed and the wires are located into two clamps where an electrical current is flowing. The test starts after one minute of pre-heating at the given temperature. After this minute, a lever is moved to apply a certain weigh to the crossed wires (the weight depends on wire's diameter). If the insulation hold out for 2 minutes the test is "passed" otherwise is "not passed", at the measurement temperature. Repeating the test at 5 °C lower if "not passed" or 5 °C higher if "passed". The lowest temperature at which the test is passed for three times is referred as the CT value.

For this analysis we do not have continuous values, but only a "passed"/"not passed" result. MSA is not applicable for discontinuous results. So we decided to use it in a different way.

During the test on the enameled wires, a strength is applied for two minutes, if the enamel does not resist, the test is interrupted and the result is "not passed". We decided to take as results the time in seconds at which the test "not passed" stopped (at a given temperature). We carried out 25 tests at 230 °C, the temperature documented as CT temperature for the product, and we recorded the time when the enamel broke down and the current passed through the wires (Figure 3.22). At this temperature every tests "passed" and no one broke down before two minutes. So we carried out another set of 25 tests at the temperature immediately above (5°C higher) and we recorded again the time before failure for all the 25 tests (Figure 3.23). This time some specimens failed, about 50 % of the total.

From the analysis, we can assume that with this analysis, recording three passed results, we could make a mistake of 5 °C at most.



Type 1 Gage Study for Cut-Through (230°C)

Gage name:
Date of study:

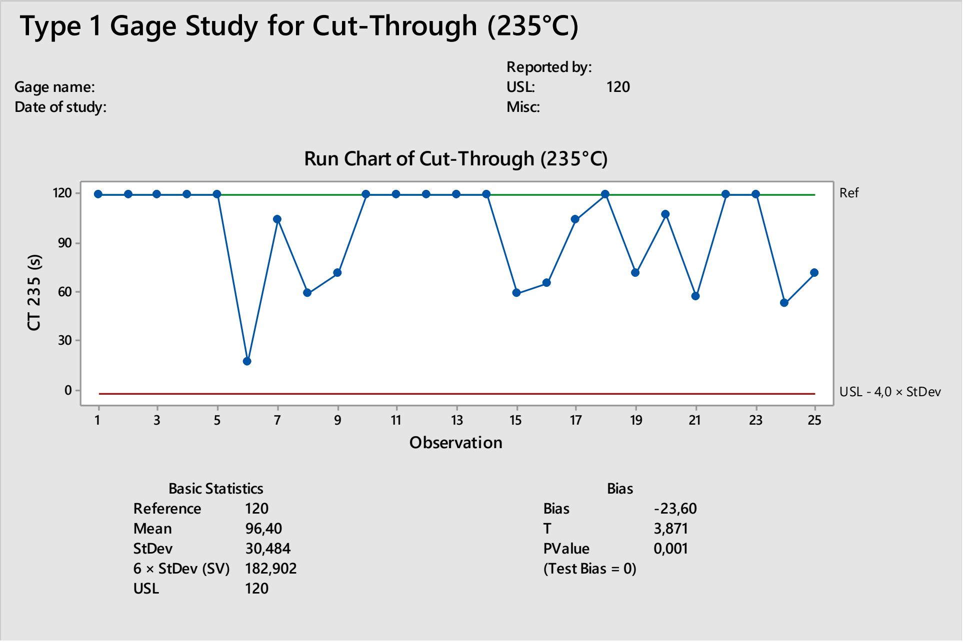
Reported by:
USL: 120
Misc:

Basic Statistics

Reference	120
Mean	120,00
StDev	0,000
6 × StDev (SV)	0,000
USL	120

Bias
Bias 0,00
StDev = 0
Unable to Calculate:
T
PValue
Capability results

Figure 3.22. MSA results for cut-through at 230 °C



Type 1 Gage Study for Cut-Through (235°C)

Gage name:
Date of study:

Reported by:
USL: 120
Misc:

Basic Statistics

Reference	120
Mean	96,40
StDev	30,484
6 × StDev (SV)	182,902
USL	120

Bias

Bias	-23,60
T	3,871
PValue	0,001
(Test Bias = 0)	

Figure 3.23. MSA results for cut-through at 235 °C

Solder Time.

Like for the Cut-Through the Solder Time has no continuous values as result: it is "passed" or "not passed" again. The analysis consists of a time controlled piston which immerses a specimen of sample into a well filled with a tin alloy (60:40 tin/lead) at a set temperature (320 °C or 370 °C for PU) in a certain time frame. If the specimen is tinplated for 2,5 ± 0,25 cm in the center of 3,8 cm submerged, the test is "passed" otherwise "not passed" (Figure 3.24).

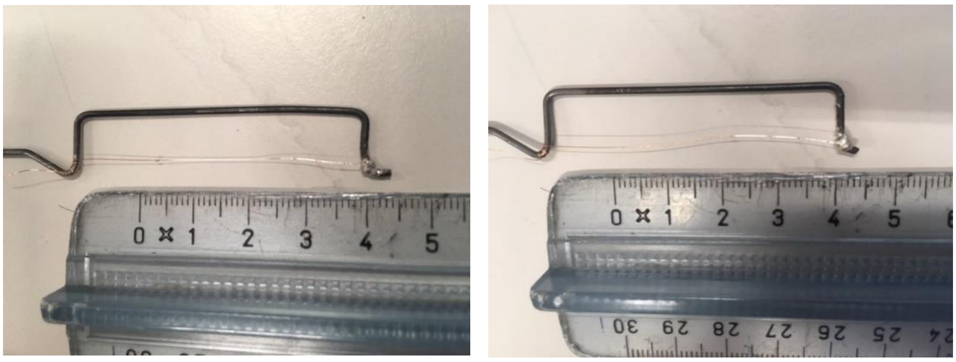
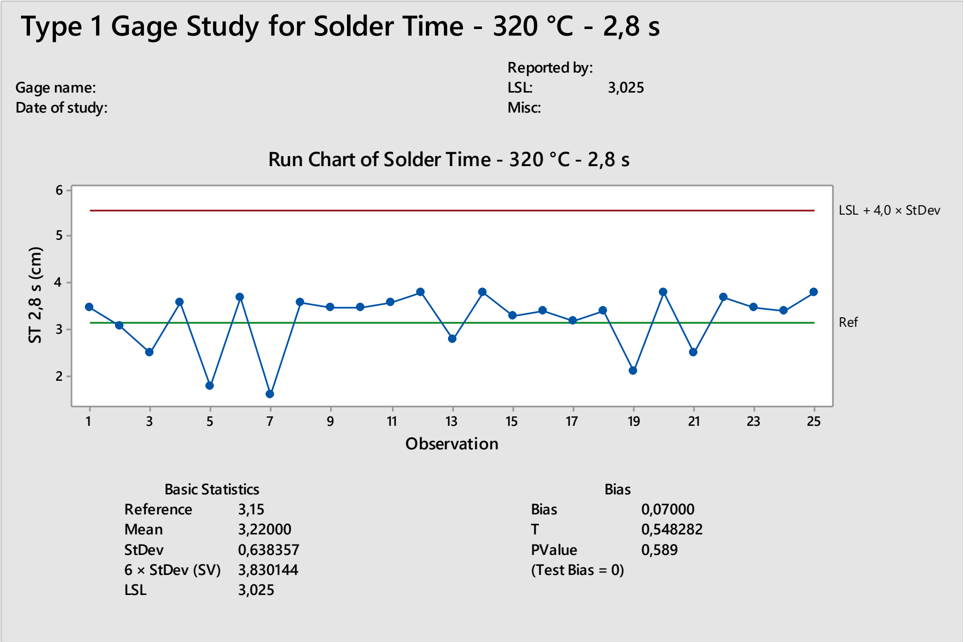


Figure 3.24. Solder time results: "passed" on the left and "not passed" on the right

The test is repeated at different periods of submersion; the lowest time at which the test is passed for three times is recorded as Solder Time.

To perform a similar MSA to that done for CT we set the temperature at 320 °C, typical solder temperature for P155 enamel, and then we carried out 25 tests at the time found as Solder Time (2,8 s) recording the length (in cm) of the tinplated part. Then we moved up to the time at which all 25 tests are passed, recording as before the lengths (Figures 3.25 and 3.26).



Type 1 Gage Study for Solder Time - 320 °C - 2,8 s

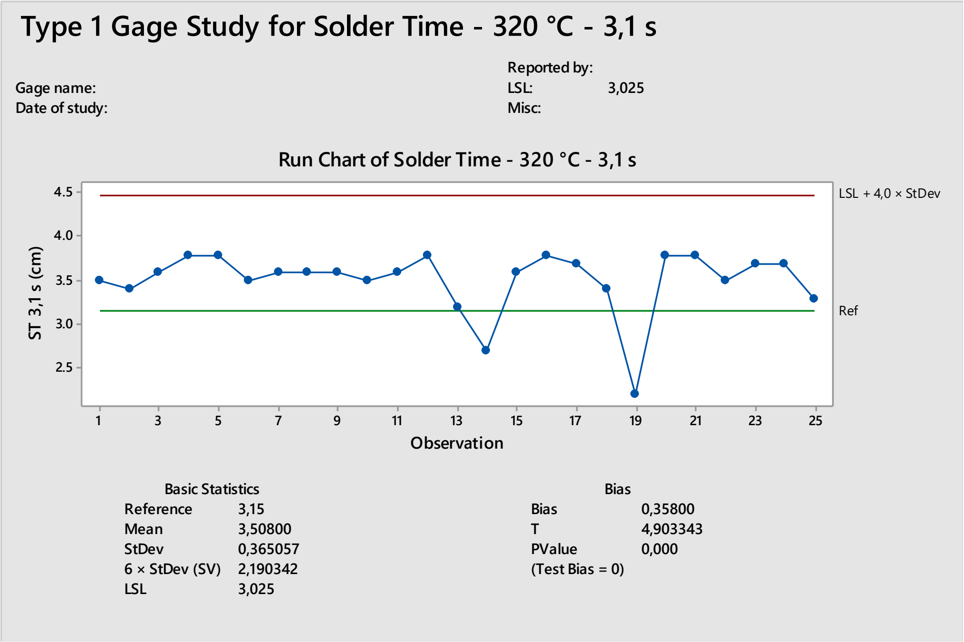
Gage name:
Date of study:

Reported by:
LSL: 3,025
Misc:

Basic Statistics	
Reference	3,15
Mean	3,22000
StDev	0,638357
6 × StDev (SV)	3,830144
LSL	3,025

Bias	
Bias	0,07000
T	0,548282
PValue	0,589
(Test Bias = 0)	

Figure 3.25. MSA results for solder time at 2,8 s



Type 1 Gage Study for Solder Time - 320 °C - 3,1 s

Gage name:
Date of study:

Reported by:
LSL: 3,025
Misc:

Basic Statistics	
Reference	3,15
Mean	3,50800
StDev	0,365057
6 × StDev (SV)	2,190342
LSL	3,025

Bias	
Bias	0,35800
T	4,903343
PValue	0,000
(Test Bias = 0)	

Figure 3.26. MSA results for solder time at 3,1 s

The first figure shows that 3 out of 25 tests failed, their length being shorter than 2,25 cm. Whereas with 0,3 s increased time all tests passed. In giving results, we can therefore suppose that our mistake is of 0,3 s.

Stack Loss.

As stated above Stack Loss is a correlation between the solid content of the enamel and the film formed after the curing process. It is therefore a difference between two left solid residues after two different evaporations of solvents: one deposited slowly at not very high temperature, the other quickly at higher temperatures. To determine the "stack loss", industrial enamellers correlate the amount of liquid enamel to the amount of enameled wire, so it is not a routine test for enamels producers and we do not have a specific method to determine Stack Loss. We had to found a way to measure this characteristic.

Unfortunately with did not have actual data for Stack Loss, since it is a property usually measured only by industrial producers of enamelled wire. Nevertheless, we had two samples for which we knew that one had lower Stack Loss than the other, respectively about 20 % and 25 % (referring to Solid Content). The one with lower Stack Loss will be termed Sample 1 below and the other one Sample 2.

ASTM std N° D3288/D3288M-08 reports a method using lab oven for Simulated Stack Loss. The method is similar to the one used to run the Solid Content analysis, consisting of weighting about 1 g (yb) of sample into a weighted empty disk (tare), putting the disk in the oven at 200 °C for 30 mins, weighting (ya) and putting it in a second oven at 250 °C for 20 mins then weighting again (yc). Simulated Stack Loss is expressed with the following formula:

$$\text{Simulated Stack Loss} = \frac{\left[\left(\frac{y_a\text{ - tare}}{y_b\text{ - tare}}\right) - \left(\frac{y_c\text{ - tare}}{y_b\text{ - tare}}\right)\right]}{\frac{y_a\text{ - tare}}{y_b\text{ - tare}}} \times 100\ [\%]$$

The results obtain from the test are shown in the graph in Figure 3.27.

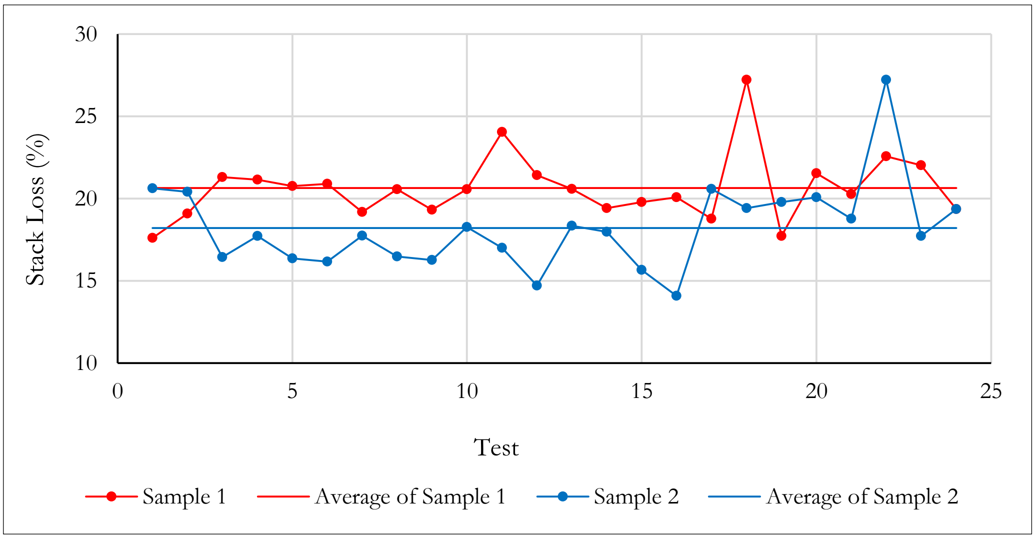


Figure 3.27. Simulated Stack Loss results

From the graph, we can see the big deviations that we have for each sample and the strange counter-trend observed: Sample 1 that should have lower Stack Loss got an average of 20,6 % in comparison with 18,2 % of Sample 2.

This analysis did not reproduce what happens in the enameling phase, so we moved ahead looking for other possible ways.

Being strictly connected to heating, we thought that the use of a thermal analysiser, like Thermogravimetric Analysis (TGA), might help in determining the Stack Loss. This kind of analysis allows to record the mass loss of a sample during the application of a temperature gradient.

The TGA instrument consists of a precision balance with a sample pan to be located inside a furnace with a programmable control temperature. The temperature is generally increased at constant rate or using ramps, including isothermal curves, to incur a thermal reaction. Thermal reaction may occur under a variety of atmospheres, e.g. ambient air, inert gas, oxidizing/reducing gases, as well as under a variety of pressures.

The thermogravimetric data collected from thermal reactions are compiled into a mass plot, or percentage of initial mass plot, on the y-axis versus either temperature or time on the x-axis.

Therefore, we tried to found a suitable method analyzing both liquid enamels and solid enamels after Solid Content analysis. We used the solid film from Solid Content analysis for two reasons: the first reason was that Stack Loss is directly linked to Solid Content; the second one was because by using a small amount of liquid enamel, like 10-15 mg, part of the solvents began to evaporate before that the analysis started, misrepresenting actual results.

To carry out these analyses we took the film resulting from the Solid Content analysis removing round disks of 4 mm diameter and shaping them in order to be able to put them into the silica pans of the instrument. Disks put into the pans reached the weight of 10 mg for each analysis.

First analysis we have carried out was until the complete burning of the product, to see different reactions at different temperatures and to individuate at which temperature the expected mass loss occurs. The heating ramp is shown in Table 3.10.

Table 3.10. TGA ramp

Initial Temperature	Final Temperature	Heating Rate
25 °C	800 °C	30 °C/min

In Figure 3.28 the TGA curve resulting from the analysis is shown. Time in minutes is reported in the X-axis and mass in percentage of initial mass id reported on the y-axis on the left. Reported values refer to two curves, in red and blue, where we see that the two samples curves cross each other during material loss. First, they are equal, then around 200 °C Sample 1 (in red) has a bigger loss than Sample 2 (in blue) up to about 300 °C when the trend changes to over 400 °C, then it changes again.

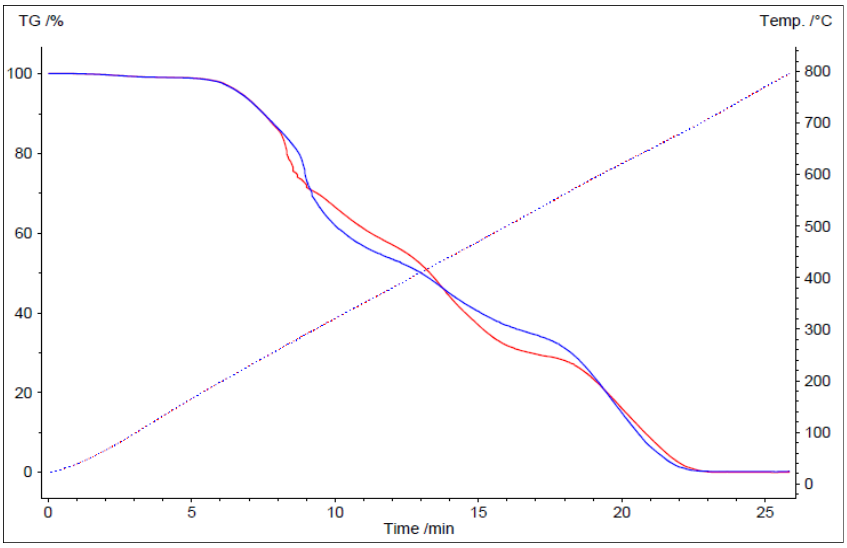


Figure 3.28. TGA curves of Sample 1 (red) and Sample 2 (blue)

In the next test, we decided to reach 350 °C and keep the temperature for some minutes in order to obtain a plateau, expecting no mass loss during constant temperature. The ramp used is reported in Table 3.11.

Table 3.11. TGA ramp

Initial Temperature	Final Temperature	Heating Rate	Isothermal Time
25 °C	350 °C	20 °C/min	10 min

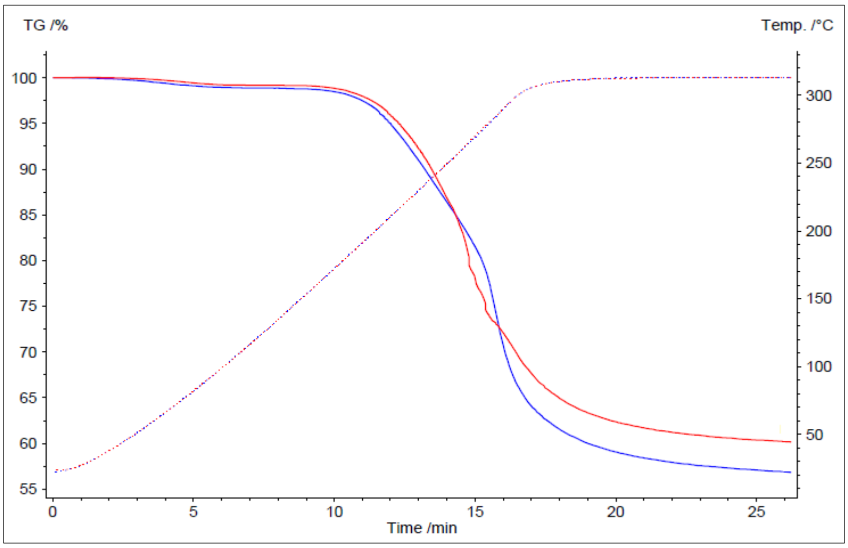


Figure 3.29. TGA curves of Sample 1 (red) and Sample 2 (blue)

The Figure 3.29 shows that this time Sample 1 has a minor loss than Sample 2, in line with what we were expecting. Nevertheless, we did not reach a plateau, the mass loss was not stable. Therefore, from this kind of analysis, we did not draw more information than the previous test and both require the same time. Furthermore, at the end of the first analysis we had empty and clean pans, whereas after this last analysis there was still material into the pans, which had to be removed by putting them into the muffle at 800 °C.

We decided to run 25 tests on Sample 2 with the first method in order to perform an MSA. The obtained curves are reported in Figure 3.30.

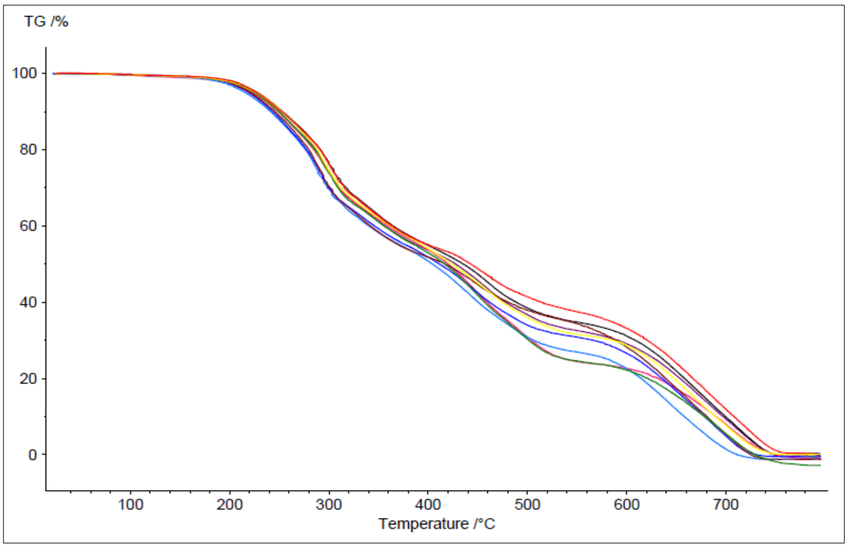


Figure 3.30. TGA curves

This time the graph had mass in percentage of initial mass on the y-axis and temperatures on x-axis. One can see that analyses did not show repeatability, not even in the area between 300 and 400 °C, in which we have the expected losses. Other few tests with Sample 1 showed the same behavior. Especially in the mentioned range, the losses of the two samples crossed themselves. Consequently, it was impossible to differentiate between the two samples.

We ran some tests using the second method (heating to 350 °C and keeping the temperature constant) obtaining the same result, e.g. no repeatability and overlapping of the samples.

After then, we moved ahead testing the liquid enamels. Our first test was carried out weighting 10 mg of each sample and using the temperature ramp reported in Table 3.12.

Table 3.12. TGA ramp

Initial Temperature	Final Temperature	Heating Rate
25 °C	270 °C	5 °C/min

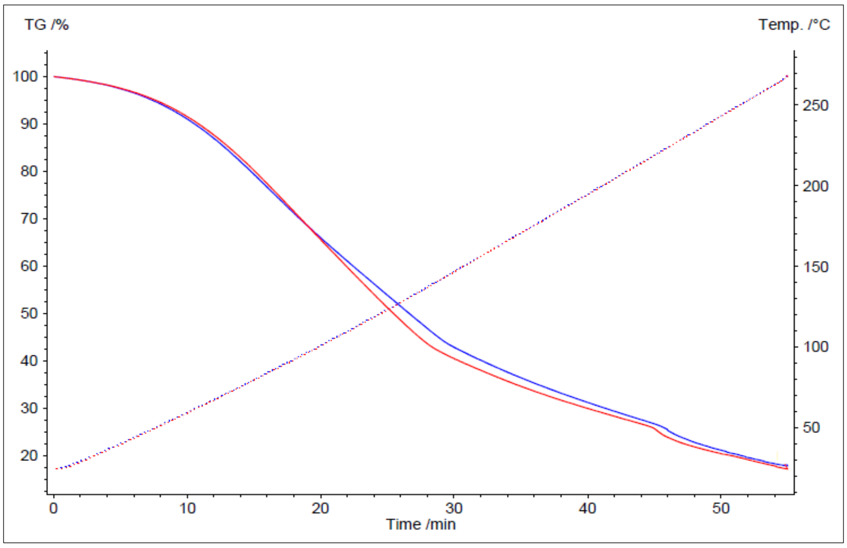


Figure 3.31. TGA curves of Sample 1 (red) and Sample 2 (blue)

The graph in Figure 3.31 as the others shows Sample 1 in red e Sample 2 in blue. The losses for both samples were quite the same, except in the center of the analysis where Sample 1 had a bigger loss, in contrast with expectations.

A second test has been run using the ramp reported in Table 3.13.

Table 3.13. TGA ramp

	1° STEP	
Initial Temperature	**Final Temperature**	**Heating Rate**
25 °C	180 °C	5 °C/min
	2° STEP	
Initial Temperature	**Final Temperature**	**Heating Rate**
180 °C	800 °C	30 °C/min

As we can see in Figure 3.32 losses for the samples were very similar and it was hard to define a difference between them.

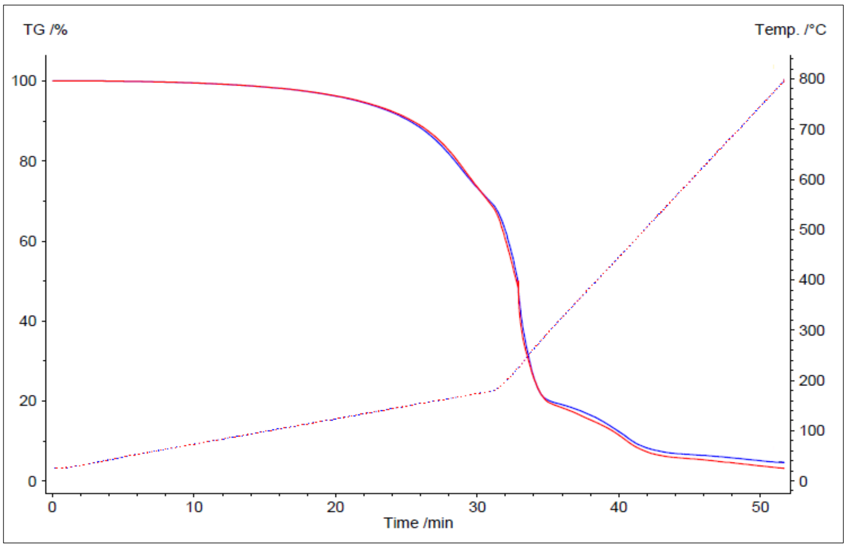


Figure 3.32. TGA curves of Sample 1 (red) and Sample 2 (blue)

Due to found difficulties, we decided to leave lab tests for a simulated Stack Loss and to use the enameling machine to measure the actual Stack Loss.

As stated, Stack Loss represents a correlation between the amount of liquid enamel and the amount of solid film on the wire after curing. The idea was to enamel for a certain period, keeping constant the film's layer on the wire (18 µm), weighting the used mass of liquid enamel and the mass of the film's layer in that period. To do this we needed a scale able to check continuously the taken amount of enamel and to know the weight of the bare copper wire to calculate the weight of enamel on wire. The scale, with a remote control, was bought and we could start with the tests.

At first, we measured the weight of the bare wire. Therefore, we ran the enameling machine at standard speed (932 m/min) without enameling, just to collect a spool of wire in a definite time (about 30 minutes). Table 3.14 shows the results.

Table 3.14. Calculation for the copper wire

Time (min)	Length of Wire (m)	Empty Spool (g)	Full Spool (g)	Mass per Meter of Wire (g)
31,69	29533,0	317,3	1351,9	350,32 x 10^{-4}
30,80	28780,6	317,7	1008,4	350,37 x 10^{-4}

Making a theoretical calculation, the mass of one-meter copper wire with 0.071 mm diameter is:

- Wire's radius:

$$r = \frac{d}{2} = \frac{7{,}1 \times 10^{-5}\ \mathrm{m}}{2} = 3{,}55 \times 10^{-5}\ \mathrm{m}$$

- Wire's cross section:

$$S = \pi \times r^2 = \pi \times (3{,}55 \times 10^{-5}\ \mathrm{m})^2 = 3{,}959 \times 10^{-9}\ \mathrm{m}^2$$

- One meter wire's volume:

$$V = S \times l = 3{,}959 \times 10^{-9}\ \mathrm{m}^2 \times 1\ \mathrm{m} = 3{,}959 \times 10^{-9}\ \mathrm{m}^3$$

- Copper density:

$$\varrho = 8960\ \frac{\mathrm{Kg}}{\mathrm{m}^3}$$

- One meter wire's mass:

$$m = V \times \varrho = 3{,}959 \times 10^{-9}\ \mathrm{m}^3 \times 8960\ \frac{\mathrm{Kg}}{\mathrm{m}^3} = 3{,}547 \times 10^{-5}\ \mathrm{Kg} = 35{,}47\ \mathrm{mg}$$

Backward, we can calculate the diameter of one-meter wire that has a mass of 35,034 mg, which is 0,070 mm. This is possible because the wire passing through the enameling machine undergoes an elongation.

The procedure to measure Stack Loss is as follows: start enameling; once the machine is to set speed and the thickness is as desired, switch the spool; as soon as the wire starts to roll up on the second spool start a chronometer and push the button on the scale's remote control. After the desired period, switch again the spool, stop the chronometer and push the scale's button when the wire starts to roll up in the new spool. From collected data, we obtained the result (Table 3.15).

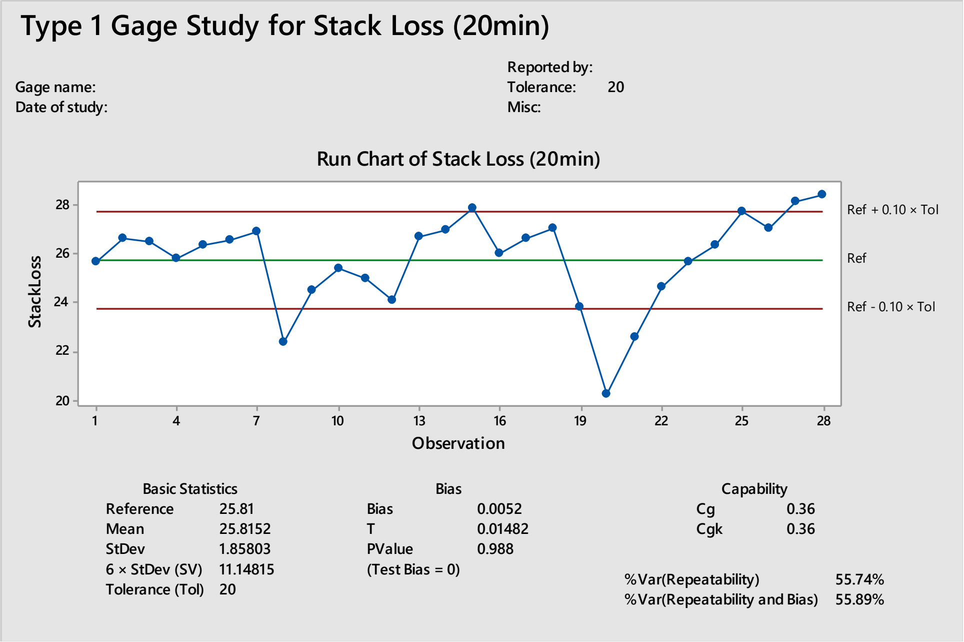
Table 3.15. Data for determination of Stack Loss

Collected Data	Calculated Data	Calculation
Speed (m/min)	Wire Length (m)	Speed x Time
Time (min)	Bare Wire (g)	Wire Length x One-Meter Wire Mass
Empty Spool (g)	Enameled Wire (g)	Full - Empty Spool
Full Spool (g)	Film Layer (g)	Enamelled - Bare Wire
One-meter Wire Mass (g)	Used Liquid Enamel (g)	Starting - Ending Liquid Enamel
Starting Liquid Enamel (g)	Residual on Wire (%)	Film Layer / Used Liquid Enamel x 100
Ending Liquid Enamel (g)		

The final Stack Loss value is obtained by the equation:

$$\text{Stack Loss} = \frac{\text{Solid Content - Residual Enamel on Wire}}{\text{Solid Content}}$$

So initially, we ran 25 tests on Sample 2 for the MSA, taking 20 minutes for each test as enamelling period. Figure 3.33 shows a low Cg and a bad Repeatability due to the high deviation. In the analyses, not having an reference value for the sample, we have used the average value as reference to calculate the Capability.



Type 1 Gage Study for Stack Loss (20min)

Gage name:
Date of study:

Reported by:
Tolerance: 20
Misc:

Basic Statistics

Reference	25.81
Mean	25.8152
StDev	1.85803
6 × StDev (SV)	11.14815
Tolerance (Tol)	20

Bias

Bias	0.0052
T	0.01482
PValue	0.988
(Test Bias = 0)	

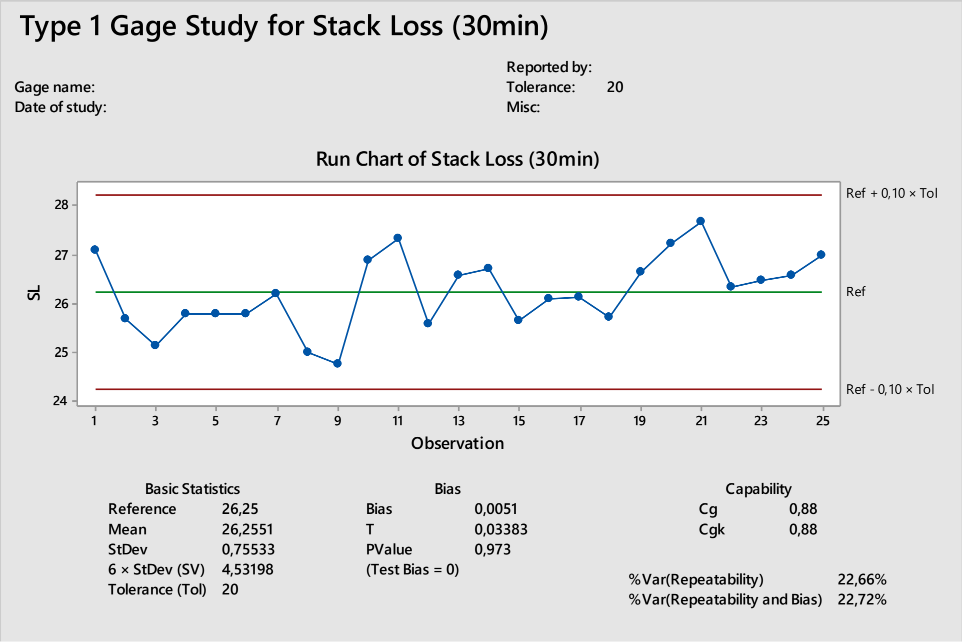
Capability

Cg	0.36
Cgk	0.36
%Var(Repeatability)	55.74%
%Var(Repeatability and Bias)	55.89%

Figure 3.33. MSA results for Stack Loss

In order to improve the analysis we decided to increase the enameling period from 20 to 30 minutes. In Figure 3.34 the results are shown. We can see a Cg of 0,88 and a Repeatability of 22,66%. Not perfect values, but acceptable.

Further increasing of time would surely improve the analysis, but it would also increase the overall time for enameling that with 30 minutes consist already in about 1 hour and half for each sample. That means days only for enameling DOE trials, which is not payed back from the entity of achieved improvement.



Type 1 Gage Study for Stack Loss (30min)

Gage name:
Date of study:

Reported by:
Tolerance: 20
Misc:

Basic Statistics	
Reference	26,25
Mean	26,2551
StDev	0,75533
6 × StDev (SV)	4,53198
Tolerance (Tol)	20

Bias	
Bias	0,0051
T	0,03383
PValue (Test Bias = 0)	0,973

Capability	
Cg	0,88
Cgk	0,88
%Var(Repeatability)	22,66%
%Var(Repeatability and Bias)	22,72%

Figure 3.34. MSA results for Stack Loss

We tested the Sample 1 to evaluate its Stack Loss. The result was 19,42 %, in accordance with what we knew. Since finding a method to evaluate Stack Loss needed a very long time, we began to run DOE trials while we were looking for a valid analysis. Therefore, the next discussion of DOE results will not include Stack Loss data, because they were not available yet.

3.4.2 DOE I

During the period spent to check the measurement system, we synthetized the needed intermediates to produce all the samples for DOE I. Once finished the syntheses and prepared the samples, we enameled them and tested the properties of the related insulated wires. Results are reported in Table 3.16.

Table 3.16. Results of DOE I

RunOrder	Viscosity (mPa·s)	Solid Content (%)	Tangent Delta (°C)	Tangent Delta +30% Speed (°C)	Cut-Through (°C)	Solder Time at 320 °C (s)
1	33	24,7	142,6	139,3	250	3,6
2	48	24,7	148,0	143,7	250	5,3
3	36	24,7	141,2	138,0	240	3,7
4	36	25,0	145,4	138,7	245	3,2
5	44	24,2	145,0	136,0	250	3,7
6	39	24,5	145,4	127,5	240	3,6
7	33	23,8	144,9	140,9	240	3,5
8	38	24,8	146,9	140,8	245	3,6
9	39	23,4	148,2	139,7	245	4,8
10	38	23,5	144,2	136,2	255	4,9
11	50	25,5	147,9	142,4	260	5
12	46	26,2	144,4	130,9	240	3,9
13	41	25,8	143,0	132,1	240	2,7
14	48	25,8	145,8	135,2	250	3,6
15	36	25,2	148,3	139,9	250	3,2
16	34	25,0	145,7	132,3	245	2,7
17	34	23,7	146,2	139,6	240	4,8
18	34	23,7	144,8	140,9	240	3,5
19	33	23,5	143,2	137,6	245	3
20	39	24,3	138,7	145,6	245	3,6
21	34	24,3	142,8	134,8	255	5,2
22	38	24,4	148,4	141,4	245	3,2
23	35	23,3	146,9	140,8	255	4,4
24	39	23,5	156,4	121,1	255	5,1

Among responses there is also Tangent Delta +30 % Speed that means the Tangent Delta value obtained for the sample run at 1210 m/min instead of 930 m/min on the enameling machine.

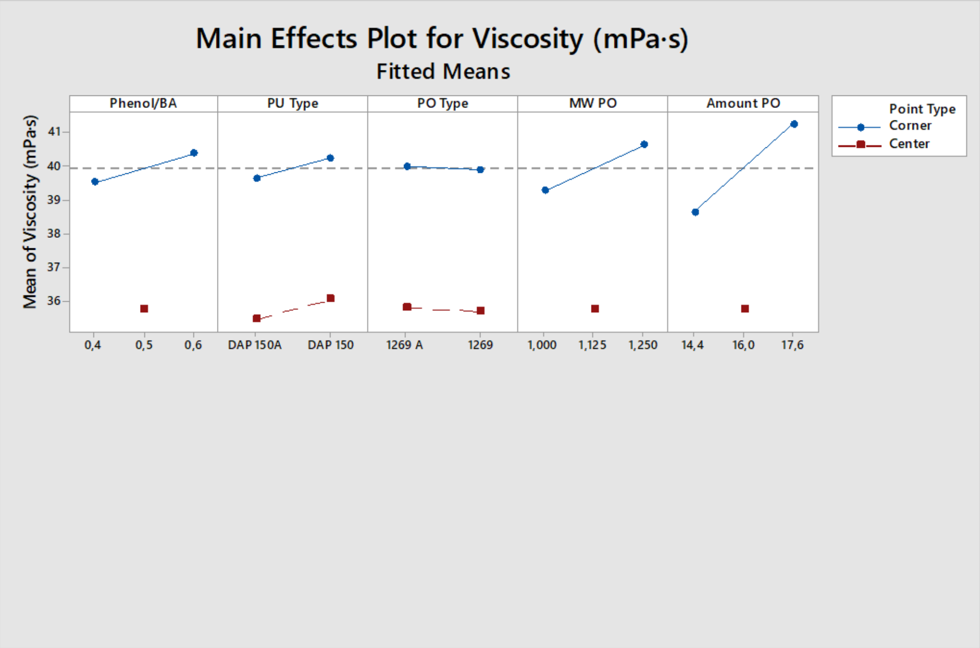
Putting all these data into the Minitab software, it can correlate results with factors chosen initially. First we can do a quickly check at the repetition trials to see if their results are equivalent.

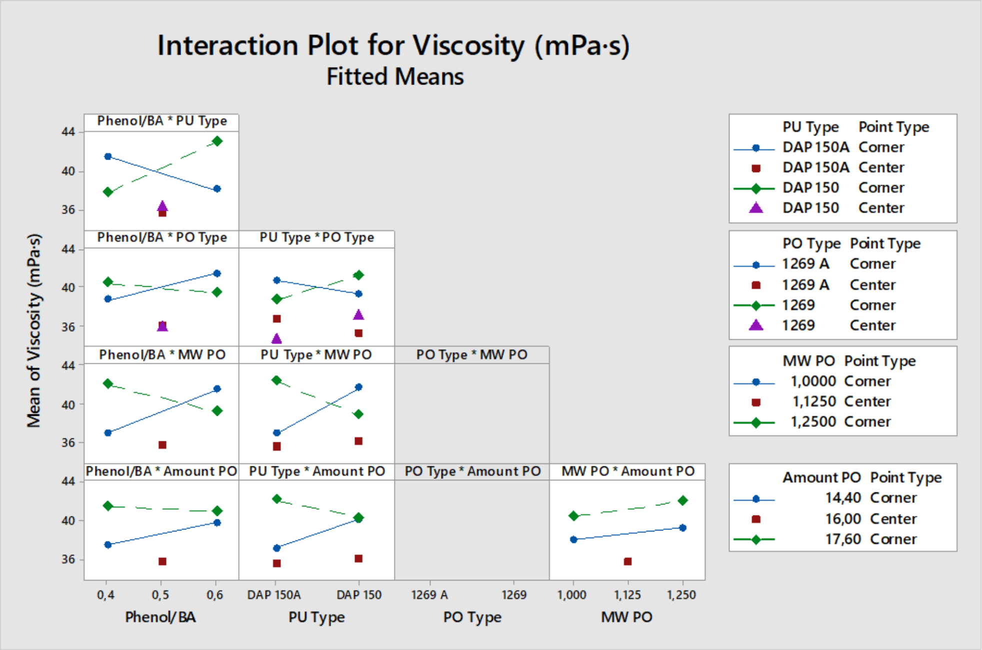
Table 3.17. Results for repited trails

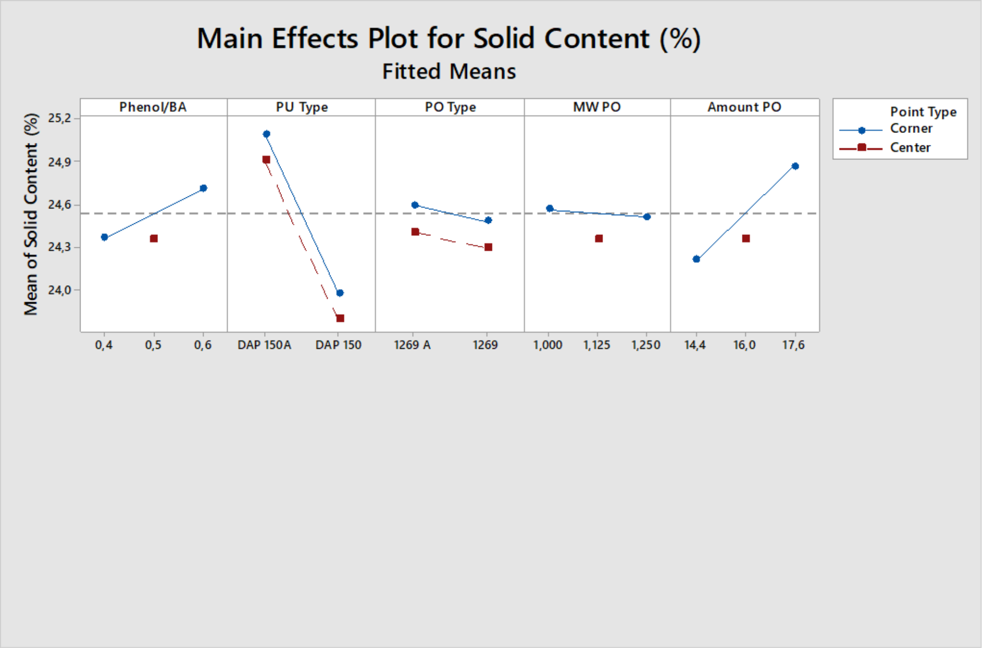
RunOrder	Viscosity (mPa·s)	Solid Content (%)	Tangent Delta (°C)	Tangent Delta +30% Speed (°C)	Cut-Through (°C)	Solder Time at 320 °C (s)
24	33	24,7	142,6	139,3	250	3,6
12	36	24,7	141,2	138,0	240	3,7
10	36	25,0	145,4	138,7	245	3,2
22	36	25,2	148,3	139,9	250	3,2
9	39	23,4	148,2	139,7	245	4,8
21	39	24,3	138,7	145,6	245	3,6
11	33	23,8	144,9	140,9	240	3,5
23	34	23,7	144,8	140,9	240	3,5

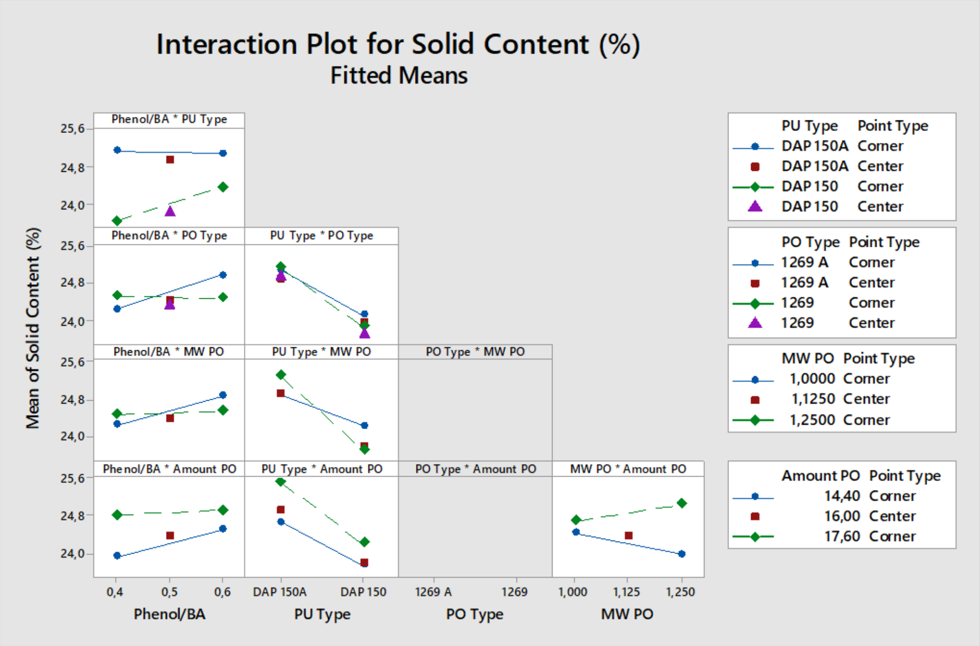
From the comparison, we can see that the results are very similar, almost identical according to the MSA. Except for the entries 9 and 21 that have completely different results: probably some mistake has been made in the preparation of one of the two samples.

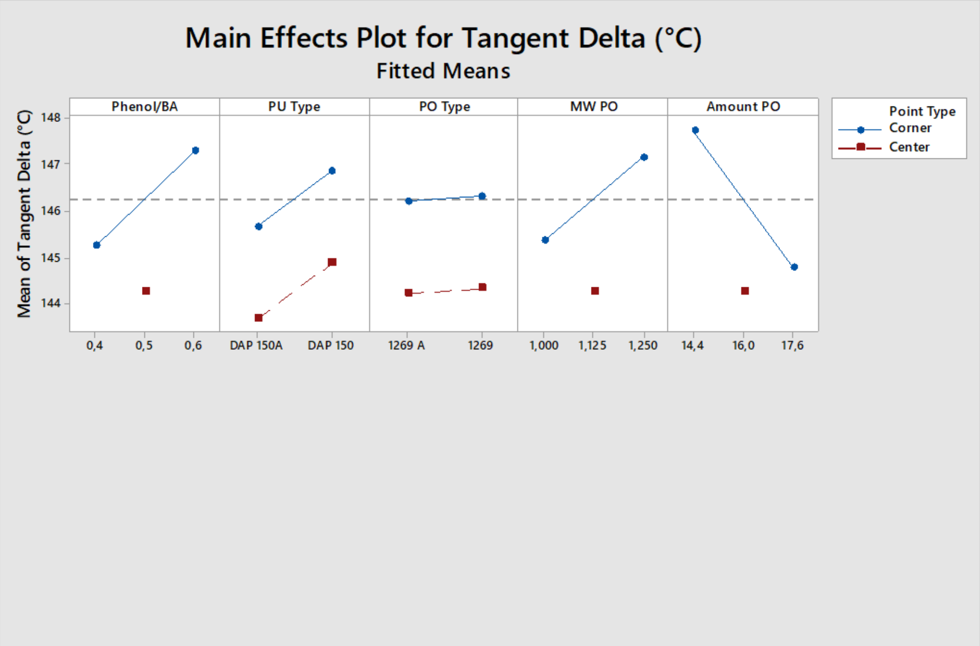
Below are reported the graphs for Main Effect and Interactions for each response (Figure 3.35).

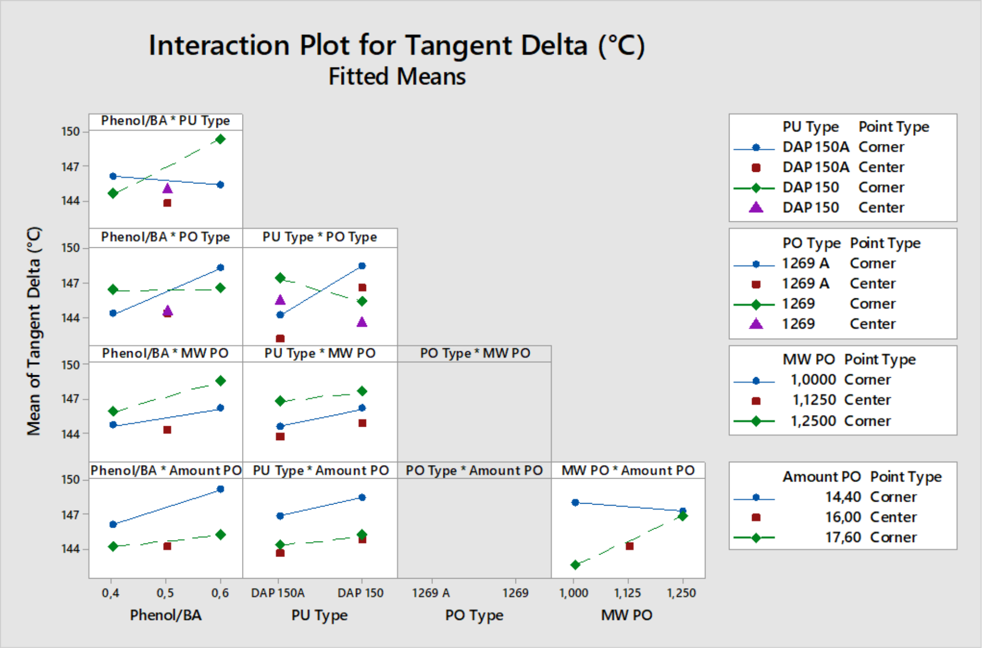


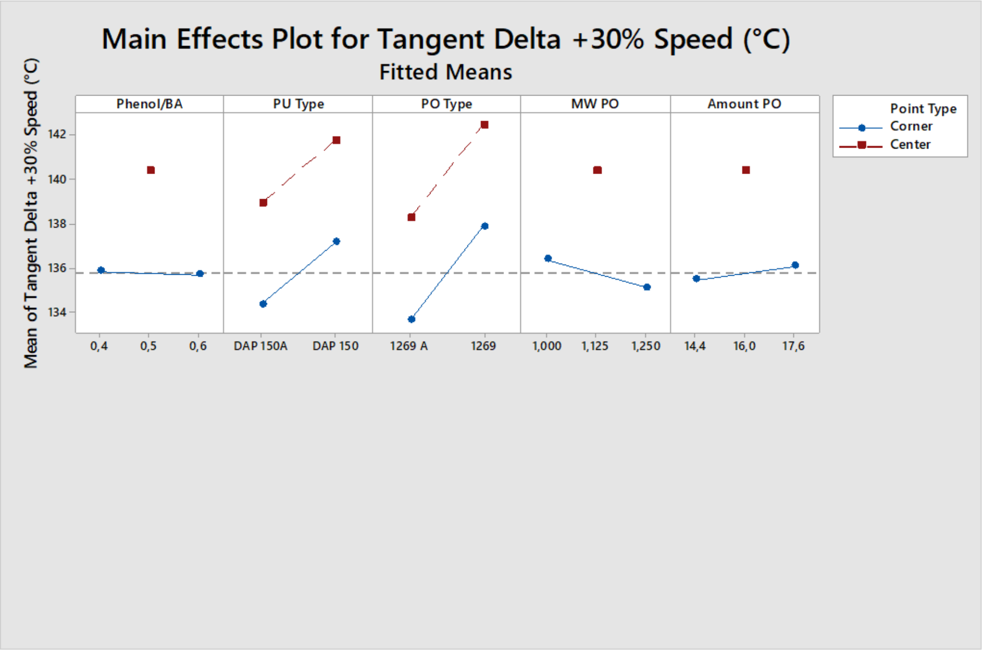

Interaction Plot for Viscosity (mPa·s)
Fitted Means
Mean of Viscosity (mPa·s)
Phenol/BA * PU Type
Phenol/BA * PO Type
PU Type * PO Type
Phenol/BA * MW PO
PU Type * MW PO
PO Type * MW PO
Phenol/BA * Amount PO
PU Type * Amount PO
PO Type * Amount PO
MW PO * Amount PO
44
40
36
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
Phenol/ BA
PU Type
PO Type
MW PO
PU Type Point Type
DAP 150A Corner
DAP 150A Center
DAP 150 Corner
DAP 150 Center
PO Type Point Type
1269 A Corner
1269 A Center
1269 Corner
1269 Center
MW PO Point Type
1,0000 Corner
1,1250 Center
1,2500 Corner
Amount PO Point Type
14,40 Corner
16,00 Center
17,60 Corner

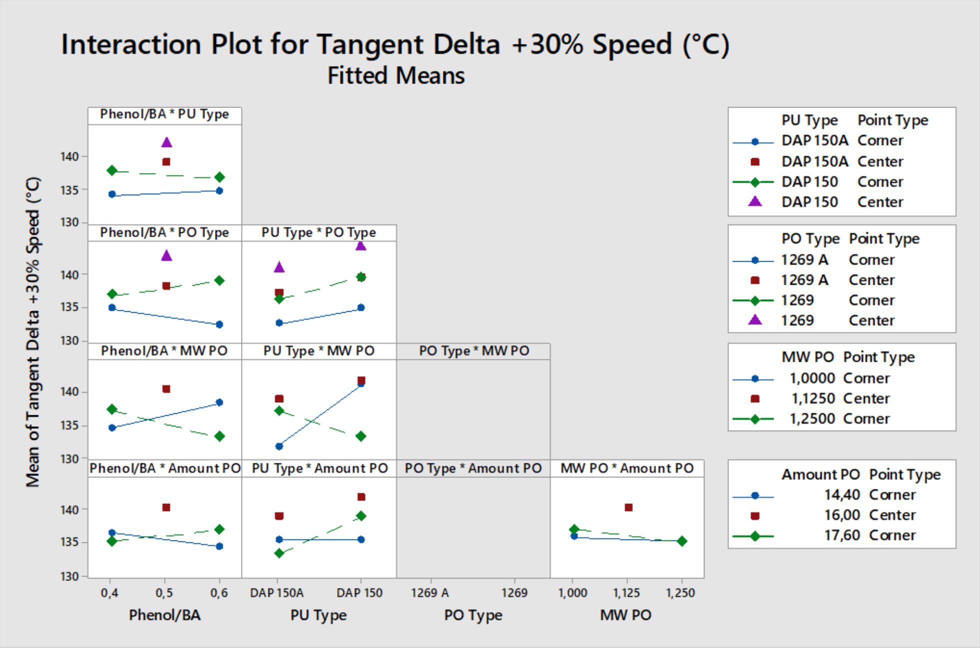

Main Effects Plot for Solid Content (%)
Fitted Means
Mean of Solid Content (%)
Phenol/BA
PU Type
PO Type
MW PO
Amount PO
25,2
24,9
24,6
24,3
24,0
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
14,4
16,0
17,6
Point Type
Corner
Center

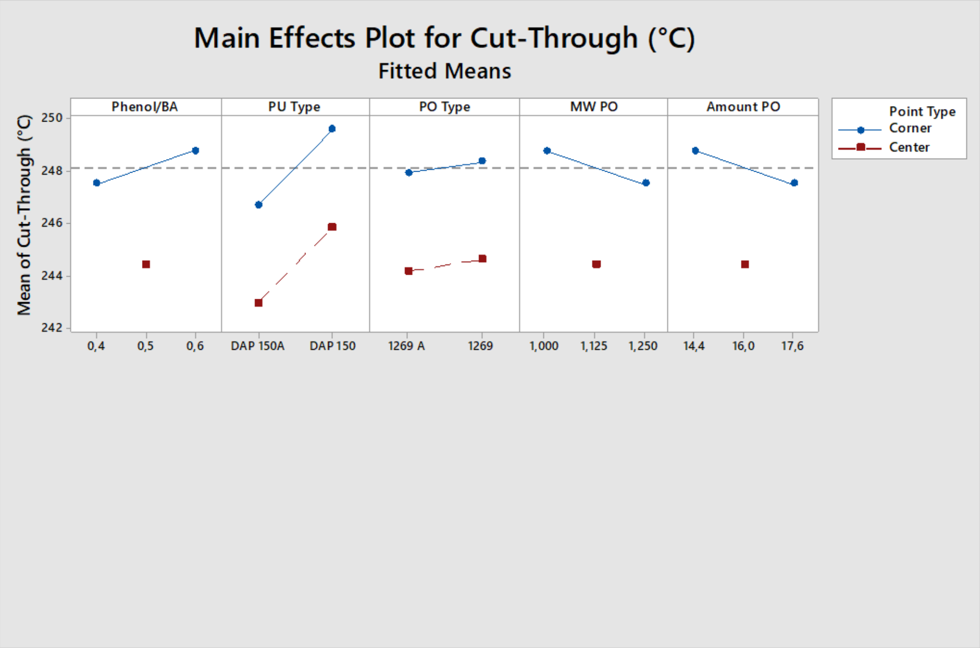

Interaction Plot for Solid Content (%)
Fitted Means
Mean of Solid Content (%)
25,6
24,8
24,0
Phenol/BA * PU Type
Phenol/BA * PO Type
PU Type * PO Type
Phenol/BA * MW PO
PU Type * MW PO
PO Type * MW PO
Phenol/BA * Amount PO
PU Type * Amount PO
PO Type * Amount PO
MW PO * Amount PO
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
Phenol/BA
PU Type
PO Type
MW PO
PU Type Point Type
DAP 150A Corner
DAP 150A Center
DAP 150 Corner
DAP 150 Center
PO Type Point Type
1269 A Corner
1269 A Center
1269 Corner
1269 Center
MW PO Point Type
1,0000 Corner
1,1250 Center
1,2500 Corner
Amount PO Point Type
14,40 Corner
16,00 Center
17,60 Corner


Main Effects Plot for Tangent Delta (°C)
Fitted Means
Mean of Tangent Delta (°C)
148
147
146
145
144
Phenol/BA
PU Type
PO Type
MW PO
Amount PO
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
14,4
16,0
17,6
Point Type
Corner
Center


Interaction Plot for Tangent Delta (°C)
Fitted Means
Mean of Tangent Delta (°C)
Phenol/BA * PU Type
Phenol/BA * PO Type
PU Type * PO Type
Phenol/BA * MW PO
PU Type * MW PO
PO Type * MW PO
Phenol/BA * Amount PO
PU Type * Amount PO
PO Type * Amount PO
MW PO * Amount PO
150
147
144
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
Phenol/BA
PU Type
PO Type
MW PO
PU Type Point Type
DAP 150A Corner
DAP 150A Center
DAP 150 Corner
DAP 150 Center
PO Type Point Type
1269 A Corner
1269 A Center
1269 Corner
1269 Center
MW PO Point Type
1,0000 Corner
1,1250 Center
1,2500 Corner
Amount PO Point Type
14,40 Corner
16,00 Center
17,60 Corner


Main Effects Plot for Tangent Delta +30% Speed (°C)
Fitted Means
Mean of Tangent Delta +30% Speed (°C)
Phenol/BA
PU Type
PO Type
MW PO
Amount PO
142
140
138
136
134
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
14,4
16,0
17,6
Point Type
Corner
Center


Interaction Plot for Tangent Delta +30% Speed (°C)
Fitted Means
Mean of Tangent Delta +30% Speed (°C)
Phenol/BA * PU Type
Phenol/BA * PO Type
PU Type * PO Type
Phenol/BA * MW PO
PU Type * MW PO
PO Type * MW PO
Phenol/BA * Amount PO
PU Type * Amount PO
PO Type * Amount PO
MW PO * Amount PO
130
135
140
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
Phenol/BA
PU Type
PO Type
MW PO
PU Type Point Type
DAP 150A Corner
DAP 150A Center
DAP 150 Corner
DAP 150 Center
PO Type Point Type
1269 A Corner
1269 A Center
1269 Corner
1269 Center
MW PO Point Type
1,0000 Corner
1,1250 Center
1,2500 Corner
Amount PO Point Type
14,40 Corner
16,00 Center
17,60 Corner


Main Effects Plot for Cut-Through (°C)
Fitted Means
Mean of Cut-Through (°C)
Phenol/BA
PU Type
PO Type
MW PO
Amount PO
242
244
246
248
250
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
14,4
16,0
17,6
Point Type
Corner
Center


Interaction Plot for Cut-Through (°C)
Fitted Means
Mean of Cut-Through (°C)
Phenol/BA * PU Type
Phenol/BA * PO Type
PU Type * PO Type
Phenol/BA * MW PO
PU Type * MW PO
PO Type * MW PO
Phenol/BA * Amount PO
PU Type * Amount PO
PO Type * Amount PO
MW PO * Amount PO
252
248
244
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
Phenol/BA
PU Type
PO Type
MW PO
PU Type Point Type
DAP 150A Corner
DAP 150A Center
DAP 150 Corner
DAP 150 Center
PO Type Point Type
1269 A Corner
1269 A Center
1269 Corner
1269 Center
MW PO Point Type
1,0000 Corner
1,1250 Center
1,2500 Corner
Amount PO Point Type
14,40 Corner
16,00 Center
17,60 Corner

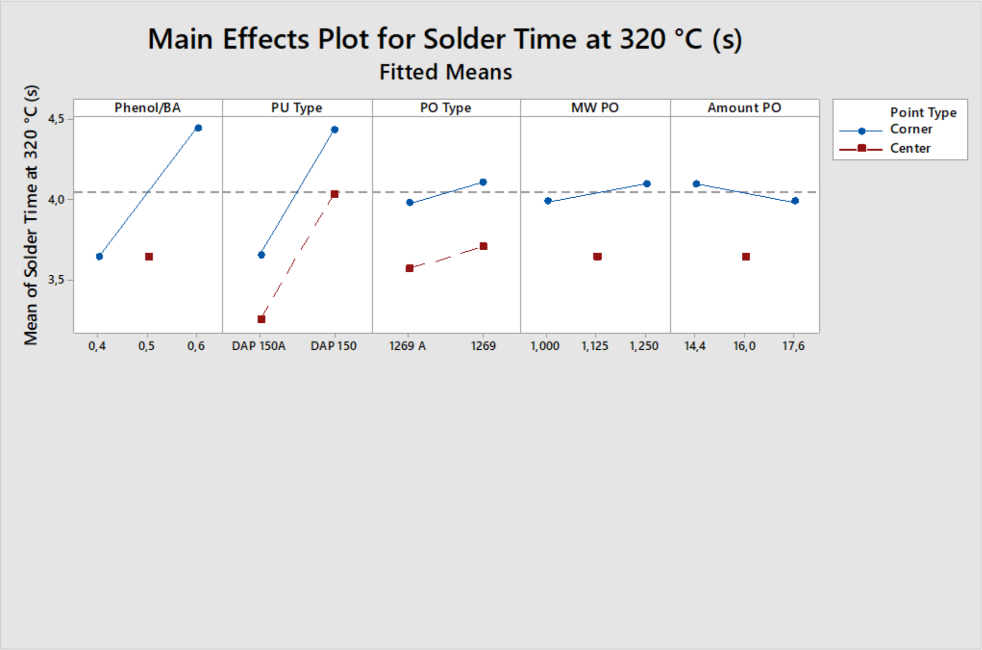

Main Effects Plot for Solder Time at 320 °C (s)
Fitted Means
Mean of Solder Time at 320 °C (s)
Phenol/BA
PU Type
PO Type
MW PO
Amount PO
4,5
4,0
3,5
0,4
0,5
0,6
DAP 150A
DAP 150
1269 A
1269
1,000
1,125
1,250
14,4
16,0
17,6
Point Type
Corner
Center

Figure 3.35. Resulting Main Effect Plots and Interactions Plot for each response of DOE I

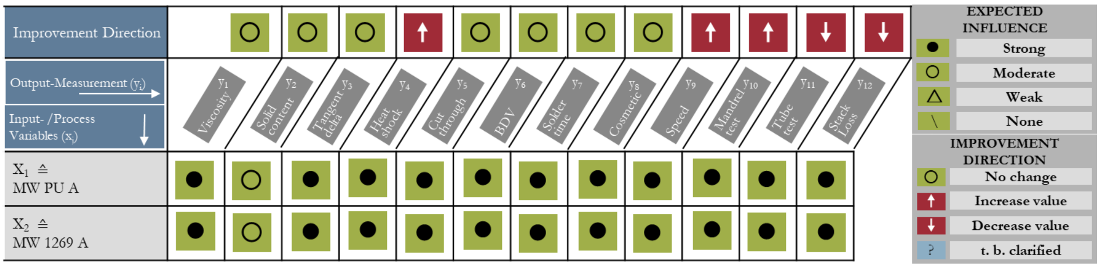
From the Interaction Plots we can see that there are lacks about the interactions between PO Type and PO Molecular Weight and between PO Type again and Amount of PO. These lacks are due to confounded interactions. It means that the system cannot distinguish the effects of the combination of those two pairs of factors. Removing these terms from the model, the software was able to use another tool to evaluate interactions among factors and responses, the *Pareto Charts*. The purpose of these charts is to highlight the most influencing factors or factors combinations for each response. Nevertheless, from the Pareto Charts analysis not every response had most influencing factors. In some cases, the model was not able to explain the variation of the response.

The problems we bumped into made us realize that probably we putted into the model too many variables, above all putting together different formulations for the intermediates. This convinced us to separate standard formulations from the alternative ones, and running two new different designs of experiment.

3.4.3 DOE II

One of the second DOEs was conducted only with the alternative formulations of the intermediates. The main goal of this design was to check if there was a combination of PU molecular weight and PO molecular weight, which could show a significant improvement comparing to the standard enamel. In Table 3.18 the expected effects are shown.

Table 3.18. Factors for DOE II and their expected effects



Improvement Direction	○	○	○	↑	○	○	○	○	↑	↑	↓	↓
Output-Measurement (y_j) → Input- /Process Variables (x_i) ↓	y_1 Viscosity	y_2 Solid content	y_3 Tangent delta	y_4 Heat shock	y_5 Cut through	y_6 BDV	y_7 Solder time	y_8 Cosmetic	y_9 Speed	y_{10} Mandrel test	y_{11} Tube test	y_{12} Stack Loss
X_1 ≙ MW PU A	●	○	●	●	●	●	●	●	●	●	●	●
X_2 ≙ MW 1269 A	●	○	●	●	●	●	●	●	●	●	●	●

EXPECTED INFLUENCE	
●	Strong
○	Moderate
△	Weak
\	None
IMPROVEMENT DIRECTION	
○	No change
↑	Increase value
↓	Decrease value
?	t. b. clarified

Since we did not have information on the ideal molecular weight for these two resins, we thought to use the same GPC Indexes of the standard resins, and based on those values we chose a range to run the new trials (Table 3.19).

Table 3.19. Factors for DOE II with their levels

	Factors	Lower Value	Upper Value
X_1	Molecular Weight PU A (GPC Index)	Standard -15%	Standard +15%
X_2	Molecular Weight PO A (GPC Index)	Standard -10%	Standard +10%

Table 3.20. Scheduled tests for DOE II

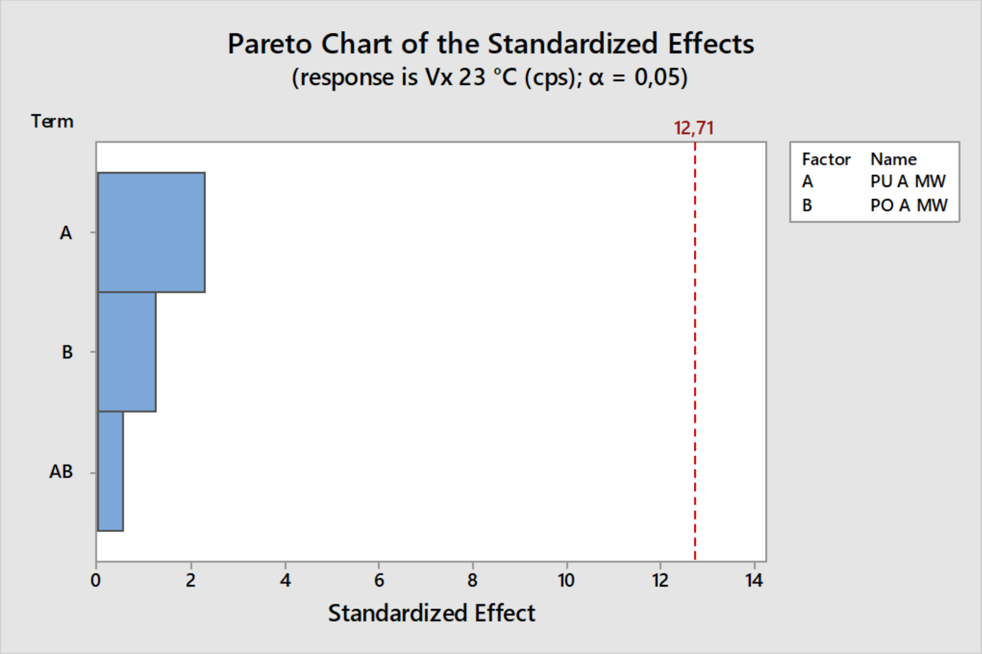
StdOrder	RunOrder	CenterPoint	MW PU A	MW PO A
6	1	0	Standard	Standard
3	2	1	Standard -15%	Standard +10%
5	3	0	Standard	Standard
4	4	1	Standard +15%	Standard +10%
2	5	1	Standard +15%	Standard -10%
1	6	1	Standard -15%	Standard -10%

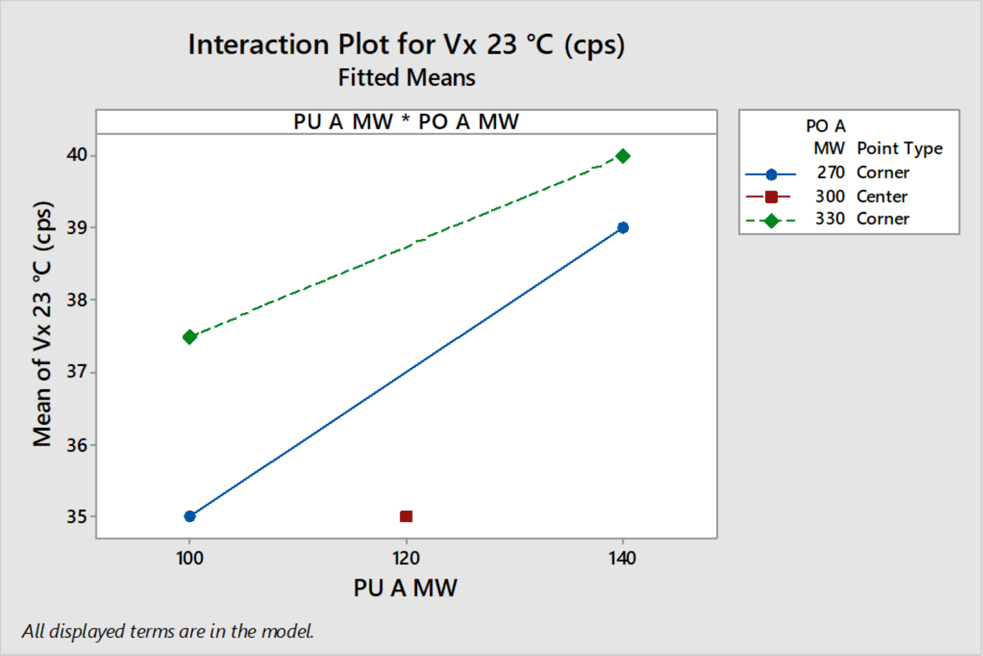
Table 3.21. Results of DOE II

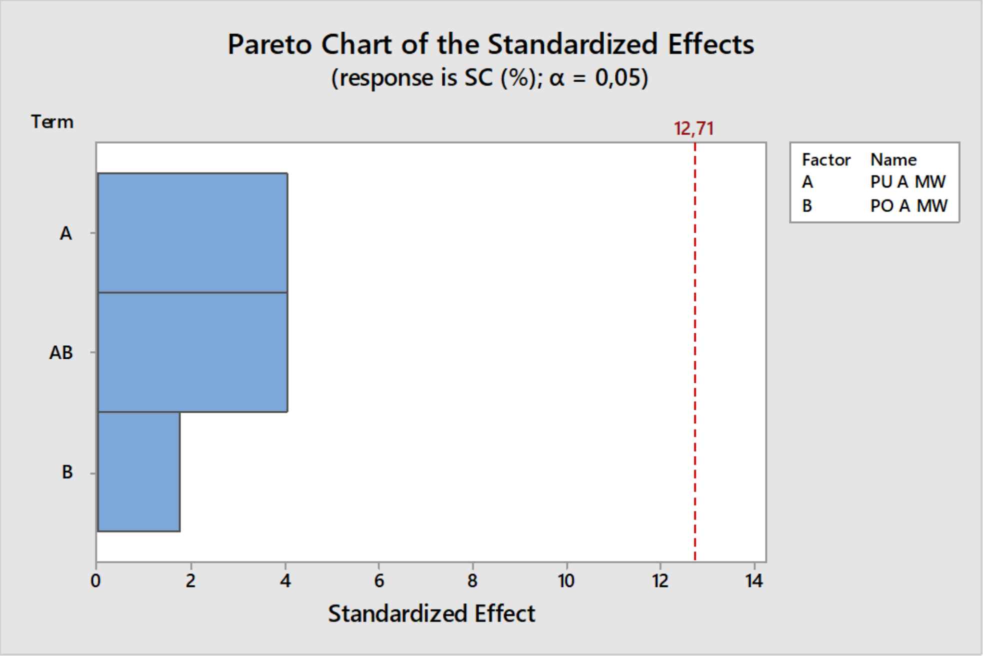
RunOrder	Viscosity (mPa·s)	Solid Content (%)	Tangent Delta (°C)	Tangent Delta +30% Speed (°C)	Cut-Through (°C)	Solder Time at 320 °C (s)
1	36,0	25,09	150,8	139,8	230	3,2
2	37,5	25,35	151,1	142,3	225	3,5
3	34,0	25,20	151,0	141,0	225	3,3
4	40,0	25,35	143,8	133,5	215	3,6
5	39,0	25,17	146,8	134,4	225	3,0
6	35,0	25,80	148,9	143,1	220	2,4

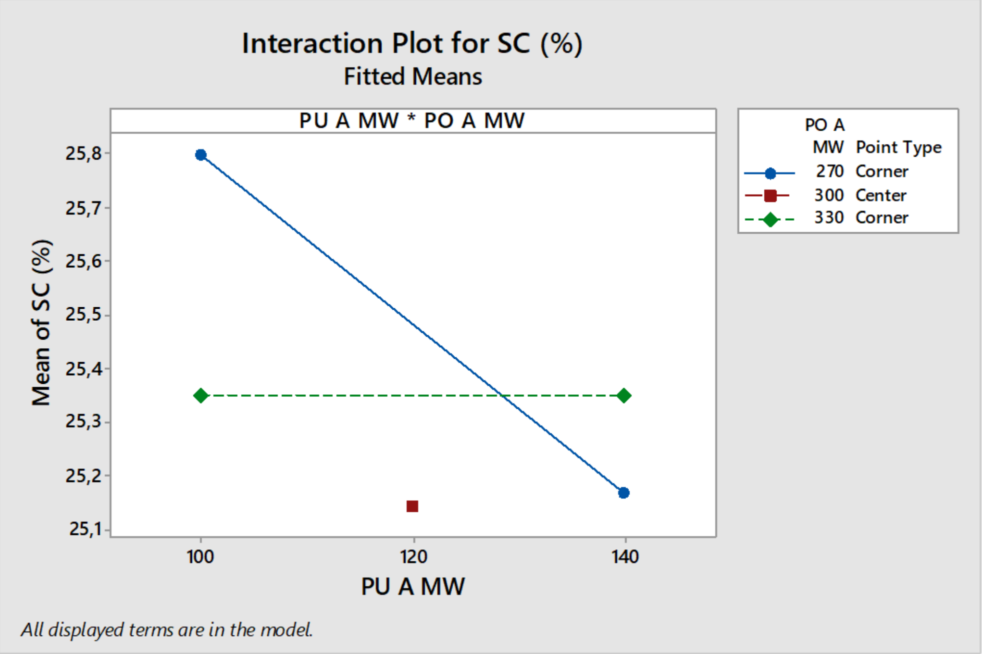
Having only two factors and two levels we had a full resolution DOE consisting of four trials, one center point and its repetition. We carried out syntheses, and ran trials in the enamelling machine. Table 3.20 reports the six proposed trials and Table 3.21 the obtained results.

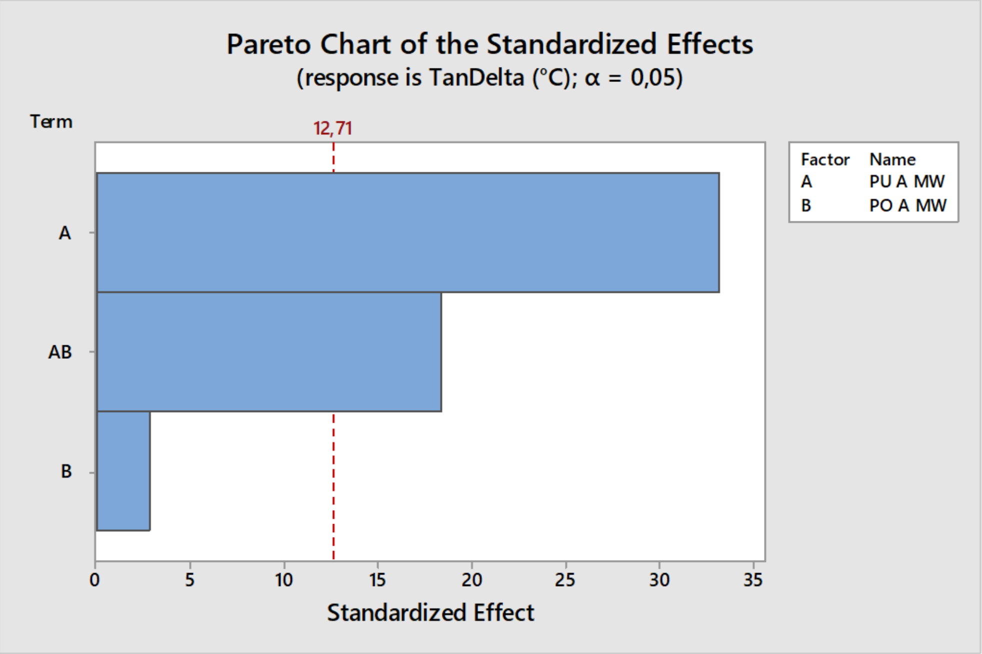
The two repetition trials (RunOrder 1 and 3) showed quite similar results. Actually, considering MSA, they can be considered identical. Below the Pareto Charts and the Interaction Plot obtained from the analysis of the model are shown (Figure 3.36).

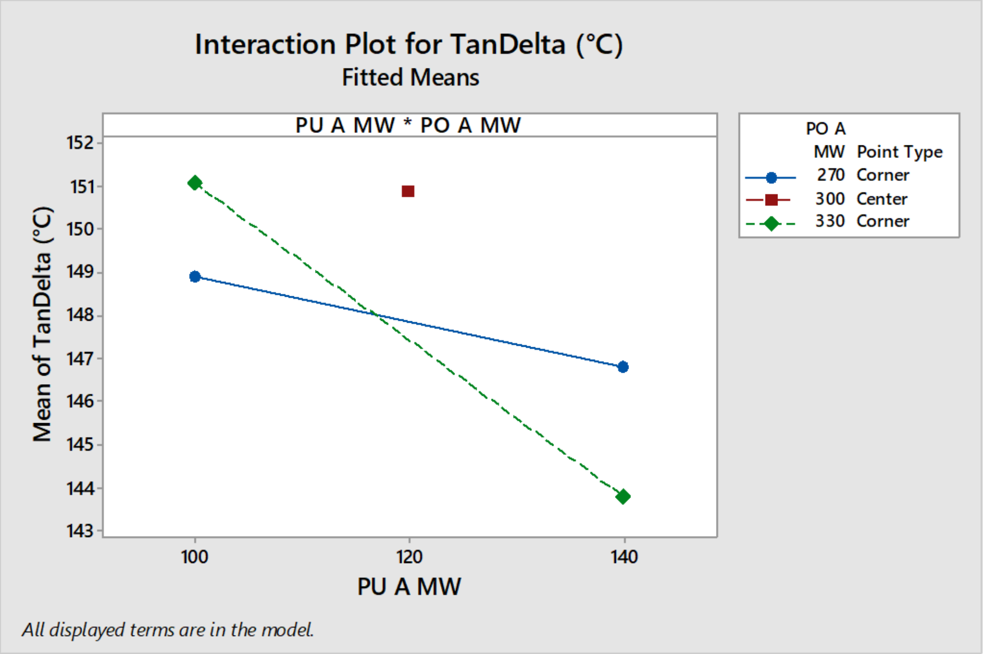


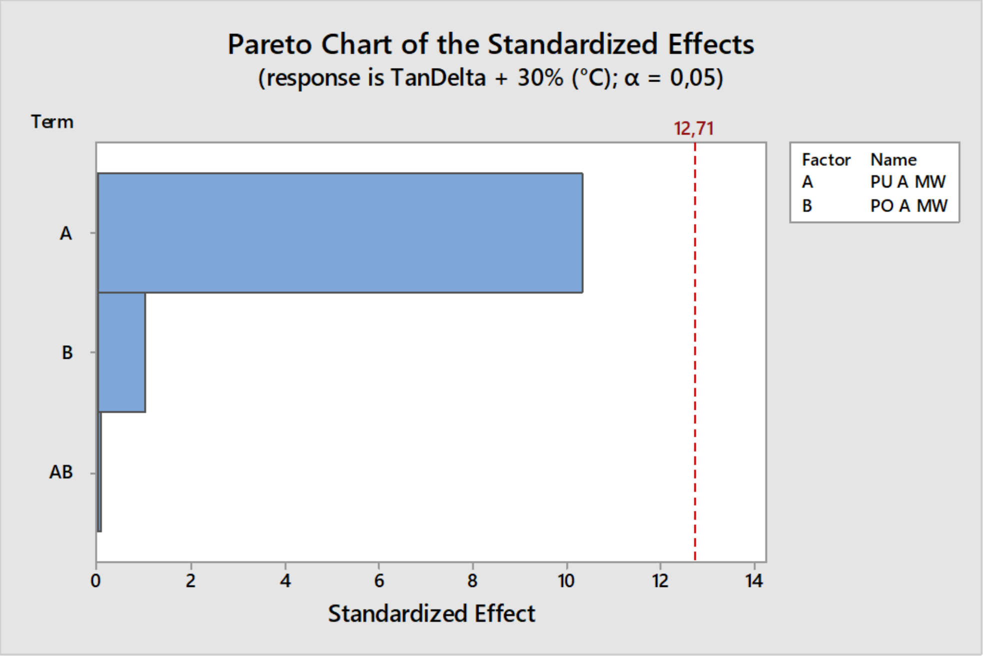

Interaction Plot for Vx 23 °C (cps)
Fitted Means
PU A MW * PO A MW
Mean of Vx 23 °C (cps)
35
36
37
38
39
40
100
120
140
PU A MW
PO A MW
Point Type
270 Corner
300 Center
330 Corner
All displayed terms are in the model.

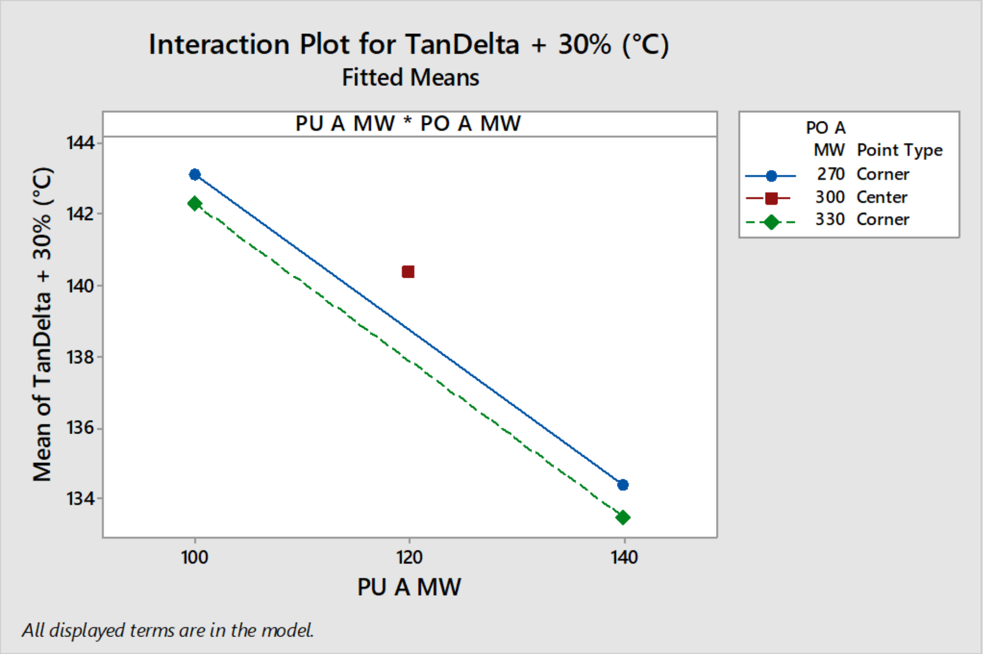

Pareto Chart of the Standardized Effects
(response is SC (%); α = 0,05)
Term
A
AB
B
12,71
0
2
4
6
8
10
12
14
Standardized Effect
Factor
Name
A
PU A MW
B
PO A MW

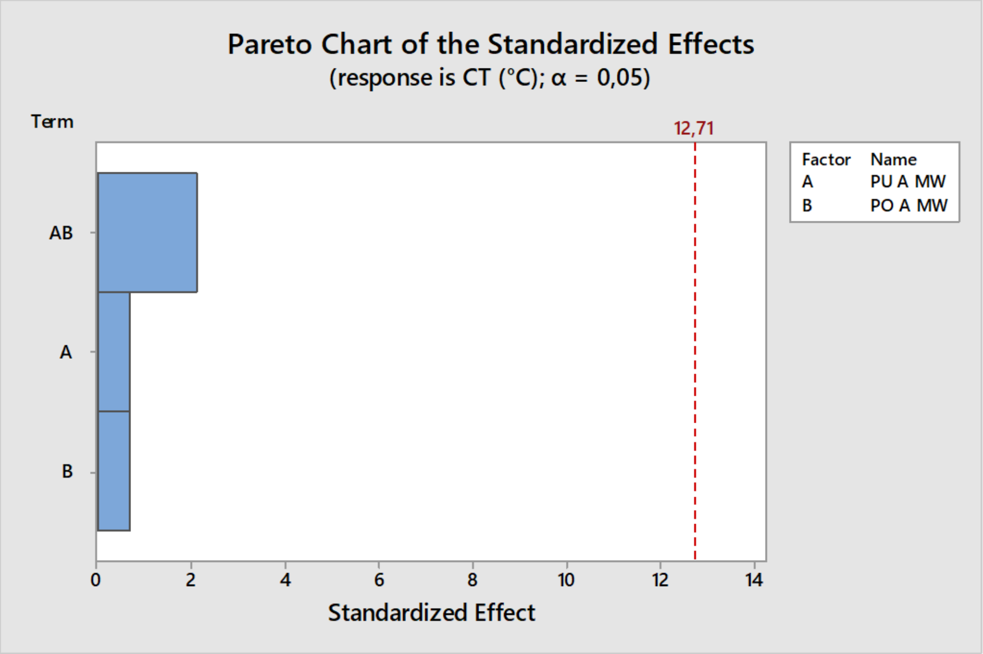

Interaction Plot for SC (%)
Fitted Means
PU A MW * PO A MW
Mean of SC (%)
25,8
25,7
25,6
25,5
25,4
25,3
25,2
25,1
100
120
140
PU A MW
PO A MW Point Type
270 Corner
300 Center
330 Corner
All displayed terms are in the model.

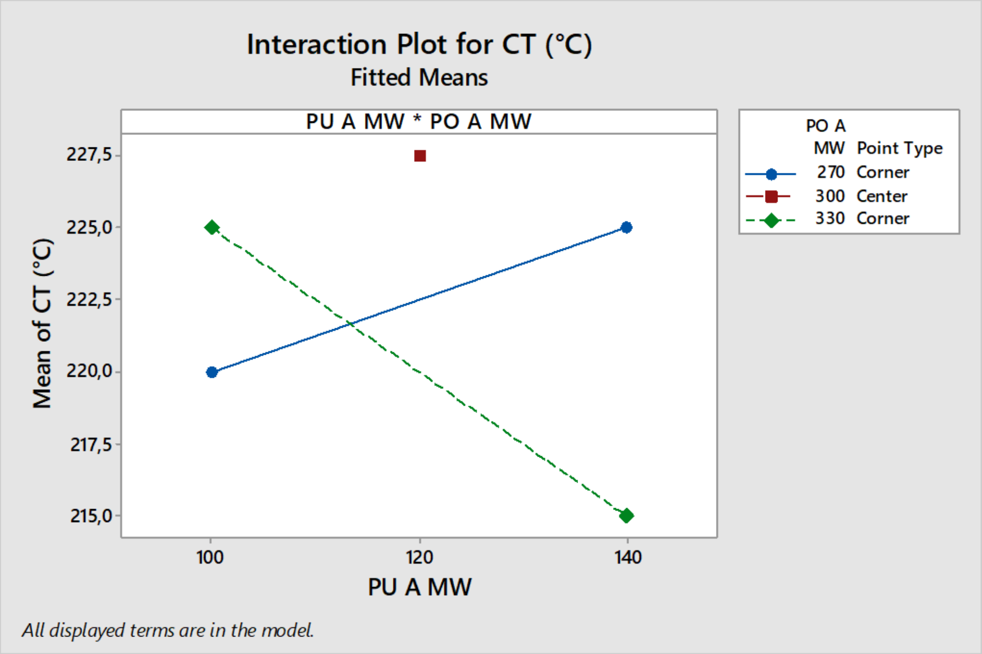

Pareto Chart of the Standardized Effects
(response is TanDelta (°C); α = 0,05)
Term
12,71
A
AB
B
0
5
10
15
20
25
30
35
Standardized Effect
Factor Name
A PU A MW
B PO A MW

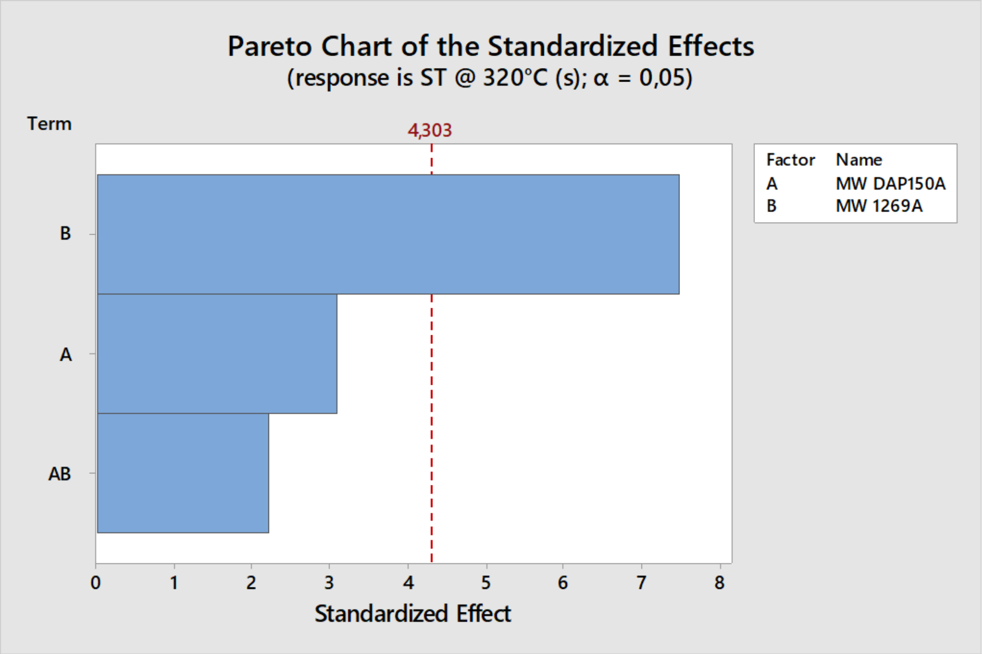

Interaction Plot for TanDelta (°C)
Fitted Means
PU A MW * PO A MW
Mean of TanDelta (°C)
152
151
150
149
148
147
146
145
144
143
100
120
140
PU A MW
PO A MW
Point Type
270 Corner
300 Center
330 Corner
All displayed terms are in the model.


Pareto Chart of the Standardized Effects
(response is TanDelta + 30% (°C); α = 0,05)
Term
12,71
A
B
AB
0
2
4
6
8
10
12
14
Standardized Effect
Factor
Name
A
PU A MW
B
PO A MW


Interaction Plot for TanDelta + 30% (°C)
Fitted Means
PU A MW * PO A MW
Mean of TanDelta + 30% (°C)
144
142
140
138
136
134
100
120
140
PU A MW
PO A MW
Point Type
270 Corner
300 Center
330 Corner
All displayed terms are in the model.


Pareto Chart of the Standardized Effects
(response is CT (°C); α = 0,05)
Term
12,71
AB
A
B
0
2
4
6
8
10
12
14
Standardized Effect
Factor Name
A PU A MW
B PO A MW


Interaction Plot for CT (°C)
Fitted Means
PU A MW * PO A MW
PO A
MW Point Type
270 Corner
300 Center
330 Corner
Mean of CT (°C)
227,5
225,0
222,5
220,0
217,5
215,0
100
120
140
PU A MW
All displayed terms are in the model.


Pareto Chart of the Standardized Effects
(response is ST @ 320°C (s); α = 0,05)
Term
4,303
B
A
AB
Factor Name
A MW DAP150A
B MW 1269A
0
1
2
3
4
5
6
7
8
Standardized Effect

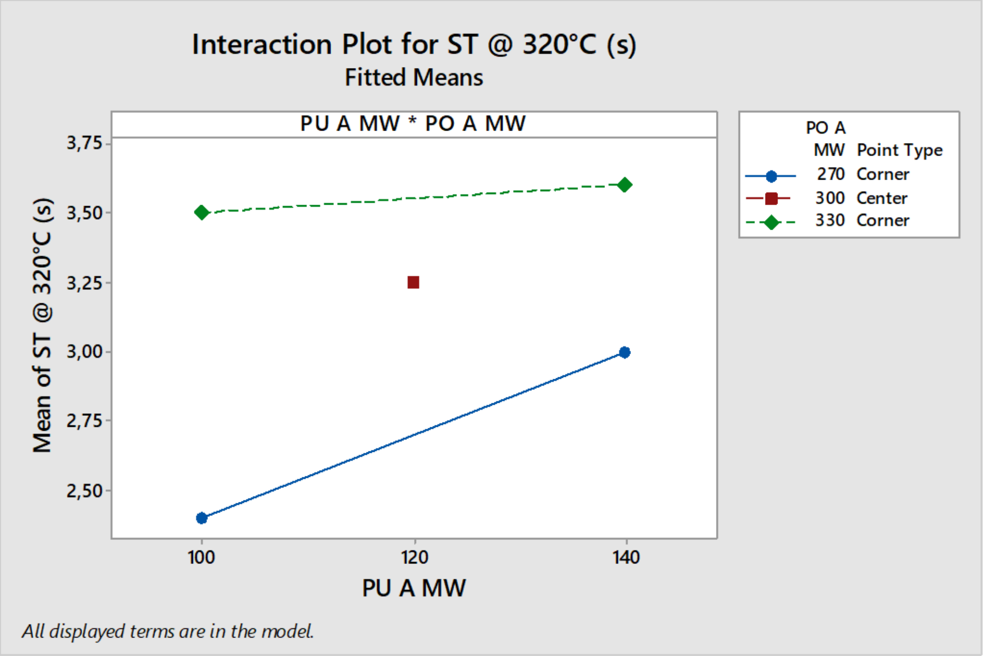


Figure 3.36. Resulting Pareto Charts and Interaction Plot for DOE II

The analysis shows that no terms can be seen as statistically significant, except for Tangent Delta and Cut-Through. For all of the others responses, performed tests are not enough to explain the system. This can occur when the effects are too small comparing to the noise in the system.

The software suggested running seven additional trial to fit the likely non-linearity of the system. The new trials provided for the combination of the center values of the factors with themselves again and the corner values (Table 3.22).

Table 3.22. Additional trials for DOE II

RunOrder	CenterPoint	MW PU A	MW PO A
7	-1	Standard -15%	Standard
8	-1	Standard +15%	Standard
9	-1	Standard	Standard -10%
10	-1	Standard	Standard +10%
11	0	Standard	Standard
12	0	Standard	Standard
13	0	Standard	Standard

However, since from the first trials we did not obtain a general good product, in fact just the last had a satisfying Solder Time, but it had also not good Cut-Through.

For this reason, we decided to leave aside, at least temporarily, this design and continue with the third DOE of which we have already made the needed syntheses.

3.4.4 DOE III

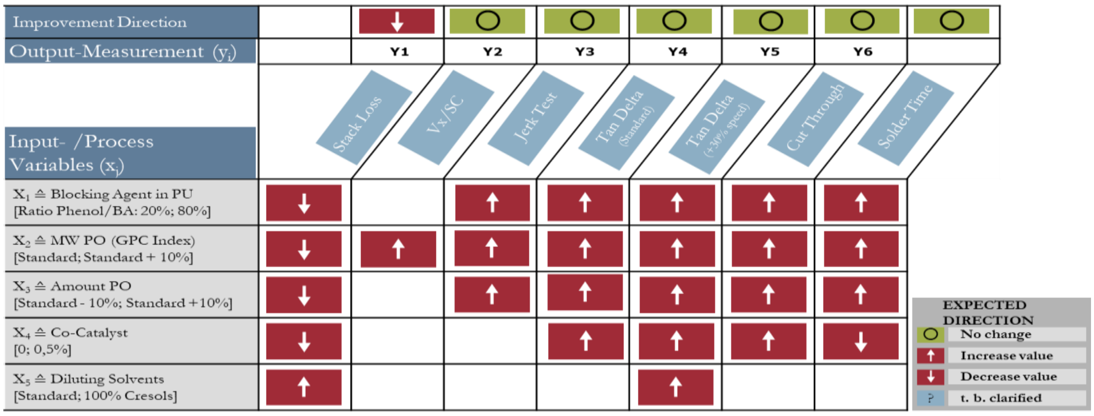
Third DOE focused on the standard resins. We decided to use three of the old factors: blocking agents' composition in polyurethane resin, molecular weight of polyol resin and amount of polyol resin in the formulation. In addition, we used two new factors: co-catalyst, e.g. a cross-linker to be added together with the standard catalyst; composition of high-boiling diluting solvents in the enamel (Table 3.23).

Table 3.23. Factors for DOE III with their levels

	Factors	Lower Value	Upper Value
X_1	Ratio Phenol/BA	20%	80%
X_2	Molecular Weight PO (GPC Index)	Standard	Standard +10%
X_3	Amount of PO in Formulation	Standard -10%	Standard +10%
X_4	Co-Catalyst	0%	0,5%
X_5	Diluting High-Boiling Solvents	Standard	100% MPC

Table 3.24 shows the expected effects of the chosen factors.

Table 3.24. Factors for DOE III and their expected effects



Improvement Direction		↓	○	○	○	○	○	○
Output-Measurement (y_i)		Y1	Y2	Y3	Y4	Y5	Y6	
Input- /Process Variables (x_j)	Stack Loss	Vx/SC	Jerk Test	Tan Delta (Standard)	Tan Delta (+30% speed)	Cut Through	Solder Time	
X_1 ≙ Blocking Agent in PU [Ratio Phenol/BA: 20%; 80%]	↓		↑	↑	↑	↑	↑	
X_2 ≙ MW PO (GPC Index) [Standard; Standard + 10%]	↓	↑	↑	↑	↑	↑	↑	
X_3 ≙ Amount PO [Standard - 10%; Standard +10%]	↓		↑	↑	↑	↑	↑	
X_4 ≙ Co-Catalyst [0; 0,5%]	↓			↑	↑	↑	↓	
X_5 ≙ Diluting Solvents [Standard; 100% Cresols]	↑				↑			

EXPECTED DIRECTION	
○	No change
↑	Increase value
↓	Decrease value
?	t. b. clarified

Having five factors with two levels each, we chose a factorial design with resolution V for 16 trials. As usual, we added a center point and one repetition of it (Table 3.25).

Table 3.25. Scheduled trials for DOE III

RunOrder	CenterPoint	Phenol/BA	MW PO	Amount PO	Co-catalyst	Diluting MPC
1	0	50%	Std +5%	Standard	0,25%	70%
2	1	20%	Std +10%	Std +10%	0%	100%
3	0	50%	Std +5%	Standard	0,25%	70%
4	1	80%	Std +10%	Std -10%	0%	100%
5	1	80%	Standard	Std -10%	0,5%	100%
6	1	20%	Standard	Std +10%	0%	40%
7	1	80%	Std +10%	Std +10%	0,5%	100%
8	1	20%	Std +10%	Std -10%	0,5%	100%
9	1	80%	Std +10%	Std -10%	0,5%	40%
10	1	80%	Standard	Std +10%	0,5%	40%
11	1	20%	Std +10%	Std -10%	0%	40%
12	1	80%	Standard	Std -10%	0%	40%
13	1	20%	Std +10%	Std +10%	0,5%	40%
14	1	80%	Standard	Std +10%	0%	100%
15	1	80%	Std +10%	Std +10%	0%	40%
16	1	20%	Standard	Std -10%	0%	100%
17	1	20%	Standard	Std -10%	0,5%	40%
18	1	20%	Standard	Std +10%	0,5%	100%

In the meantime, the latest tests on Stack Loss determination had been made, and the measurement system had been validated, so we could evaluate the Stack Loss for the new trials.

In order to obtain good Stack Loss results we decided to reduce the amount of DMP into the formulation. As mentioned DMP is a plasticizer that helps application but also affects Stack Loss, being high-boiling substance (it does not go away during the Solid Content determination at 180 °C, but it does during the enameling phase). Therefore, before preparing the needed samples we decided to review the formulation and reduce DMP amount that we considered too high from 11% to 2%.

Maybe the reduction had been too big because it was not possible enameling some samples due to very bad enamel distension and we lost part of the results (Table 3.26).

Table 3.26. Results for DOE III

Run Order	Viscosity (mPa·s)	Solid Content (%)	Tangent Delta (°C)	Tan Delta +30% Speed (°C)	Cut-Through (°C)	Solder Time at 320 °C (s)	Stack Loss (%)
1	47,0	26,89	142,6	133,4	235	2,9	18,77%
2	42,2	25,78	146,4	139,2	235	2,7	17,36%
3	50,3	26,25	143,5	137,7	230	2,8	16,19%
4	37,0	25,07	146,0	141,5	230	2,4	18,84%
5	36,1	26,34	142,8	135,6	230	2,5	20,55%
6	44,1	25,43	145,5	136,5	230	3,0	14,31%
7	42,2	26,33	143,1	135,4	230	2,4	16,94%
8	41,8	25,76	143,0	131,1	225	2,1	20,83%
9	37,5	25,95	---	---	---	---	---
10	45,6	26,65	---	---	---	---	---
11	40,6	25,15	148,2	140,6	220	2,5	20,69%
12	32,3	24,98	146,7	136,1	230	2,4	20,22%
13	45,7	26,21	138,1	---	235	2,5	17,87%
14	42,2	26,03	---	---	---	---	---
15	40,3	25,36	146,1	---	230	2,3	17,31%
16	37,5	25,12	136,0	135,7	245	2,6	20,12%
17	39,4	25,75	---	---	---	---	---
18	47,5	26,74	136,0	---	235	2,2	18,26%

In some cases it was not possible to enamel at all (runs 9, 10, 14, 17), in other cases it was not possible to enamel at the fastest speed of 1210 m/min.

With the samples not enameled at all, the enameling machine developed a lot of smoke and the coating thickness was out of control, oscillating from 14 μm to 25μm, while the wire showed big blisters (Figure 3.37). The same behavior happened at the fastest speed with that samples lacking of "Tangent Delta +30% Speed" results.

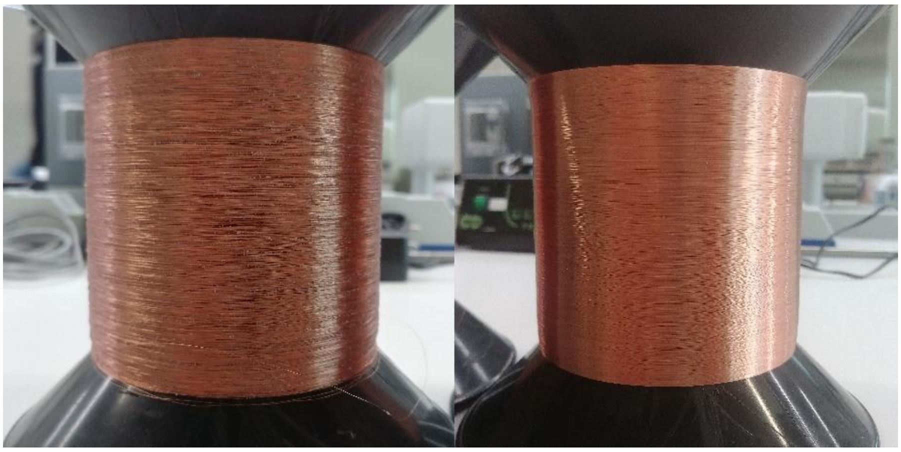


Figure 3.37. A bad wire on the left and a good one on the right

With four trials missing the effects were highly confounded, so it was impossible to calculate anything about the model.

Once again the application of the Design of Experiment approach proved to be very hard. Unfortunately, there are many variables to consider running an extremely precise tool like this, and taking care of each variable and detail is very time-consuming. Just think that from the first discussion in the team about planning DOE I to the last DOE running, almost two years have passed by. Statistical tools are a way to conduct work and a new approach that the Company is trying to introduce to evaluate its feasibility in this field of application. Since tests run so far did not lead to good results, we decided to move beyond and work on other aspects.

3.4.5 New synthesis process for polyurethane resin

As mentioned Stack Loss is a contribution of DMP and part of solid content. The solid content contribution is due to the species with low molecular weight, as confirmed by the GPC and FT-IR analyses of a yellow granular solid found on the sides of the enamelling machine after product application (Figure 3.38 and Figure 3.39).

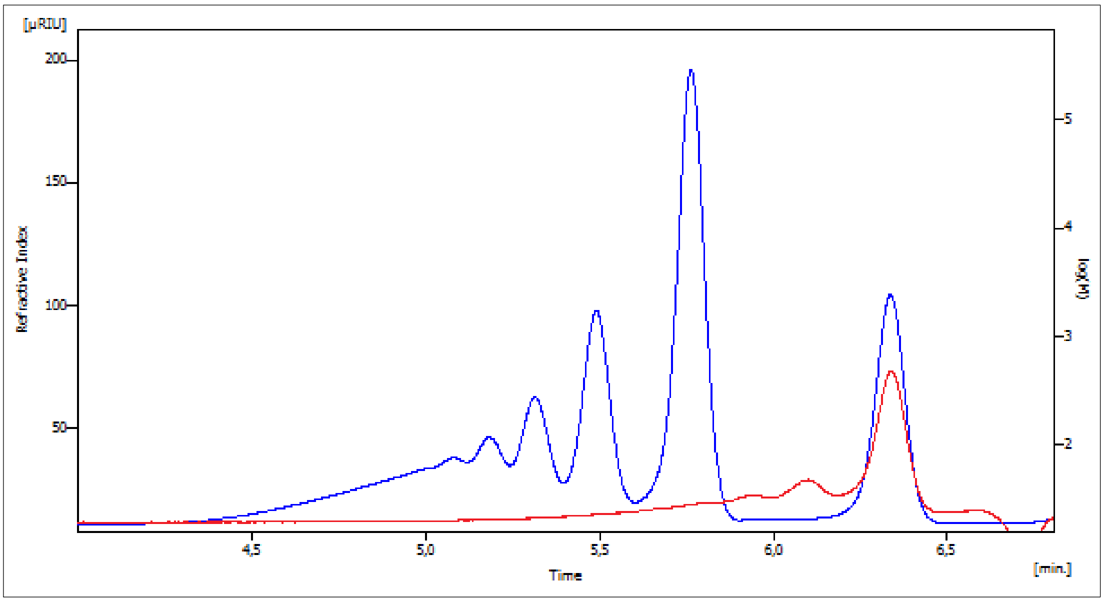


Figure 3.38. GPC chromatogram comparison between the powder taken from the sides of the enameling oven (in red) and the polyurethane prepolymer (in blue).

From the GPC chromatogram we can see that the yellow granular solid is composed of the lowest molecular weight species.

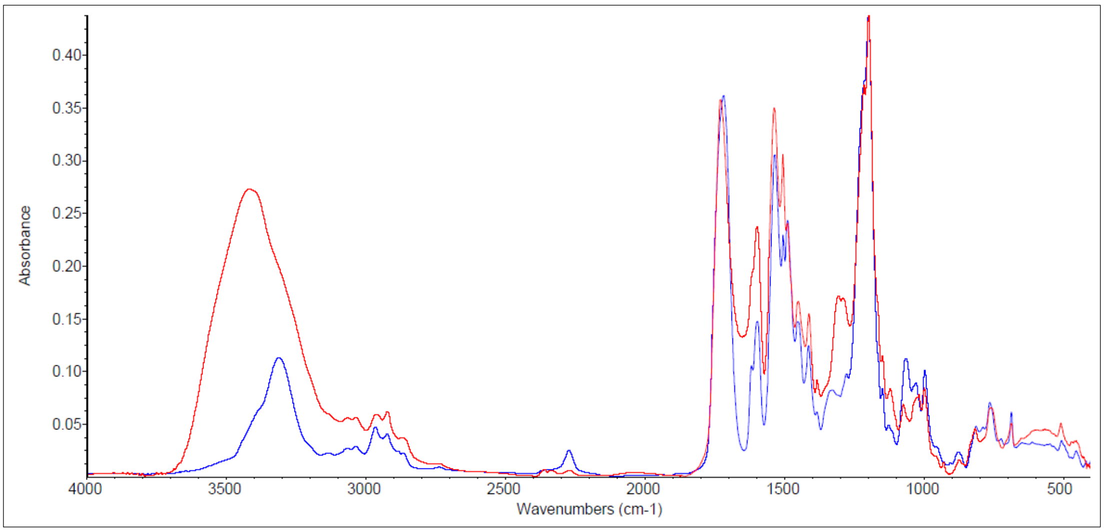
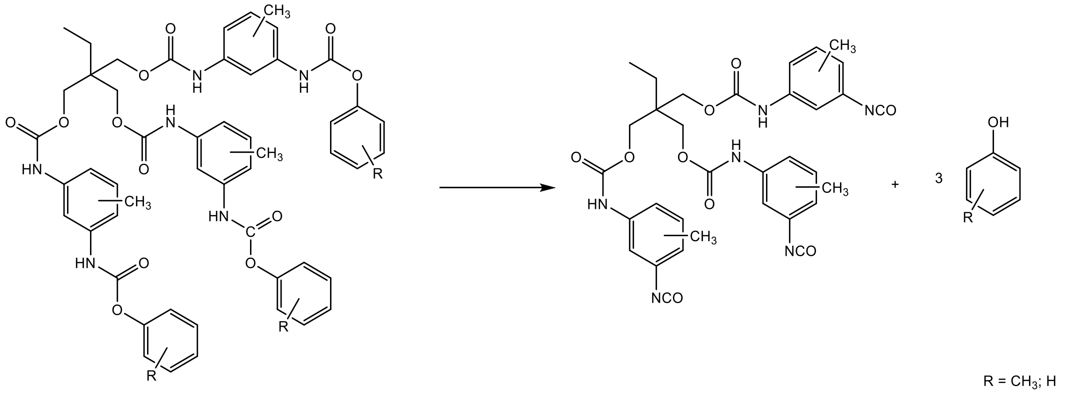


Figure 3.39. FT-IR spectra comparison between a yellow granular solid found on the sides of the enameling oven (in red) and the polyurethane prepolymer (in blue).

In both spectra the -OH group stretching vibration is clearly seen at 3550-3200 cm^{-1}, and may be attributed to residual triol and to residual cresylic acids. CH stretching vibrations originate bands in the range of 3100-2840 cm^{-1}. The peak at 1715 cm^{-1} is typical of CO stretching vibration, present in urethane groups. The most characteristic peak is that of isocyanate group NCO at 2270 cm^{-1}, which is visible only in the polyurethane prepolymer because of a partial unblocking of urethane groups during the drying in the laboratory oven, which allows cresylic acids to evaporate, moving the equilibrium towards unblocked NCO groups (Scheme 3.1). Apart from these issues, a striking similarity in the fingerprint region (1500-500 cm^{-1}) tells us that the yellow granular solid is a blocked aggregate of polyurethane prepolymer.



Scheme 3.1. Unblocking reaction in the PU intermediate.

We have seen that removing DMP is a problem because it affects the application of the enamel. Therefore, we thought we could work on the resins to avoid or reduce the formation of lower molecular weight species.

For this reason, we begun to work on the polyurethane synthesis, choosing to work with the alternative intermediate, being characterized by a different production method that could bring to reduced low molecular weights structures.

The synthesis of the standard PU intermediate consist in the complete blocking of TDI, as first step before oligomers formation. In this way, a certain amount of TDI based low molecular weight molecules remain into the resin and then into the final enamel. This unreacted part, being the lowest molecular weight species (except solvents), contributes to the Stack Loss, as we have seen.

For the new synthesis, TDI and TMP were reacted first, creating desired oligomers, and then blocked with phenol and cresols. The name of the new intermediate was polyurethane AM (PU AM).

Figure 3.40 shows that with the new synthesis the amount of low molecular weight substances is considerably decreased compared to the standard intermediate.

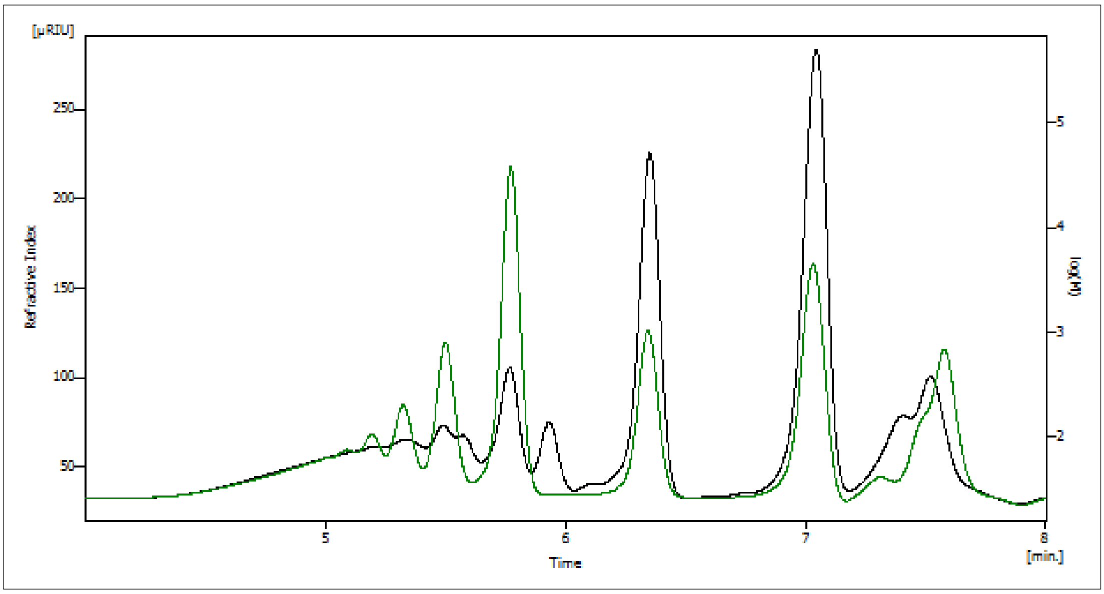


Figure 3.40. GPC chromatogram comparison between old PU intermediate (in black) and new PU intermediate (in green)

The resin has been tested together with the PO A to evaluate the properties of the final enamel. Results are reported in Table 3.27.

Table 3.27. Enameling results

Tan Delta -30% Speed (°C)	Tangent Delta (°C)	Tan Delta +30% Speed (°C)	Cut-Through (°C)	Solder Time At 320 °C (s)	Stack Loss (%)
140,0	143,0	133,7	230	2,1	20,0

As one can see, the results are enough good in generally and very well concerning Stack Loss.

Professional enamellers confirmed good performance of newly developed version and acclaimed for its general properties, asking for industrial batches for extended tests, therefore we had to scale up the product for the industrial plant.

The two industrial resins were made and so the resulting final enamel. Figures 3.41-3.43 show the comparison between the molecular profiles of the three lab products and the same three production products and in Table 3.28 and Table 3.29 are reported their molecular weight values.

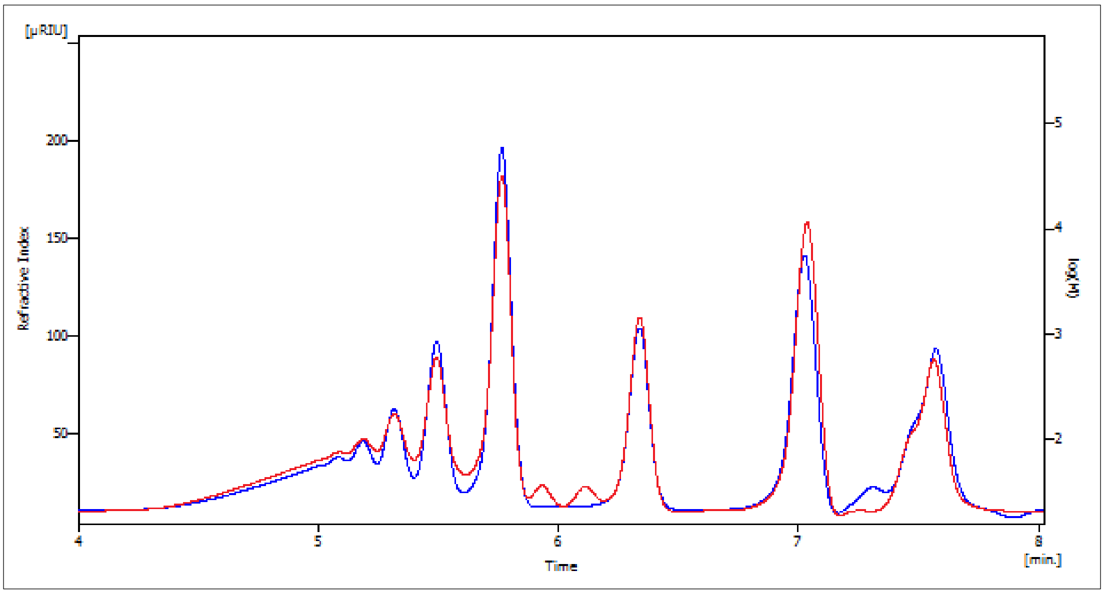


Figure 3.41. GPC chromatogram comparison between PU intermediate: lab synthesis (in red) and production synthesis (in blue)

Table 3.28. Molecular weight values of PU intermediates

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
Lab	1328	2523	1,90
Production	1295	2353	1,82

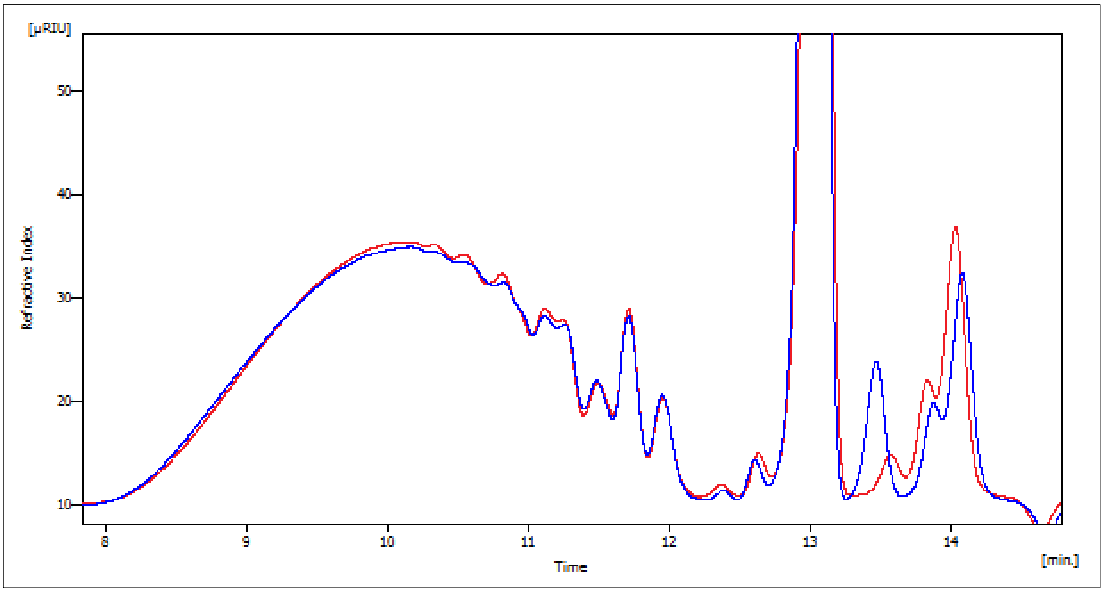


Figure 3.42. GPC chromatogram comparison between PO intermediate: lab synthesis (in red) and production synthesis (in blue)

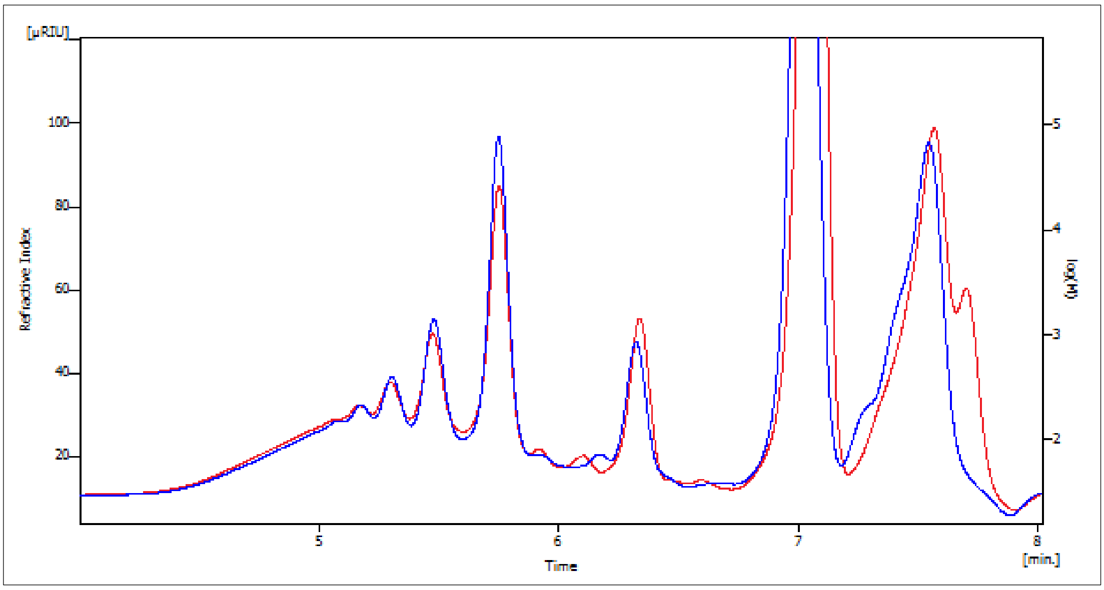


Figure 3.43. GPC chromatogram comparison between final enamel: lab synthesis (in red) and production synthesis (in blue)

Table 3.29. Molecular weight values of final enamels

Sample	**M_n (g/mol)**	**M_w (g/mol)**	**M_w/M_n**
Lab	1368	2597	1,90
Production	1338	2441	1,82

From the figures and the reported molecular weight values, we can see the successful scale-up of the resins and the final enamels. There were just few small differences, probably insignificant. Indeed the industrial batch was tested and positively assessed by professional enamellers. Especially in terms of enamelling speed and Stack Loss, so in term of energy saving, making the whole product development a successful process.

3.5 Conclusions

The aim of this project was to improve an industrial PU-based wire enamel in order to reduce its energy consumption (increasing the enameling speed) and its material loss during the application phase (decreasing the Stack Loss).

The project was also useful to try to introduce in the chemical field of insulating enamels statistical tools like Design of Experiment and Measurement System

Analysis. Unfortunately, the use these statistical tools needs a very long time and the period available for the author of this thesis to carry out the work has proved to be not sufficient to reach satisfying results. The starting product proved to be very sturdy and therefore not easily influenced by small changes made during the study. Moreover, it is probably not performing enough to reach the high target required.

For this reason, it was necessary to change the product synthesis process, as well as to move to a revisited formulation to obtain good results.

In fact, with the newly developed product we managed to get very promising results, confirmed by the industrial enamellers themselves who praised the new product in terms of performance and properties of the resulting enameled wire. In particular we managed to lower the Stack Loss by about 30% and guarantee excellent results even at high enameling speed (about + 30% vs standard speed). Nevertheless, the work carried out with the MSA was useful and effective to improve some of the measurement systems used and to know the error done and the confidence interval of the same ones. So the DOE, even not bringing immediate results, can be considered as a valid tool for product optimization.

Chapter 4: Innovative Synthesis for Insulating Coatings.

During my PhD, I spent a period at the laboratories of ELANTAS PDG in St. Louis, Missouri (USA). The project I worked on involved the implementation of a new synthesis process of a polyesterimide resin on a reactive extruder. Thus, an alternative process to the batch ones, typically used for the synthesis of such products. The use of a reactive extruder includes some advantages, among which: greater safety since you work with smaller quantities of materials per time; the possibility of working with high viscosity products, therefore the possibility of working without using solvents; and the possibility of working continuously. Developing a solvent-free enamel, equivalent to the solvent-based, would reduce the amount of needed raw materials and energy consumption. Moreover, by using an appropriate system, it would be possible to apply the enamel in the molten state on the wire. In this way, it is possible to reach greater thicknesses of insulation compare with the current solvent-based enamels. Applying a greater thickness of insulation would mean allowing the passage of a higher electric current through the wire, making the applications more efficient (i.e. more performing electric motors with reduced charging times).

A further advantage with the reactive extruder is the possibility to use recycled PET to form the ester part of the resin, replacing the used DMT and part of the glycol. This is a good way to reuse a material scraped from other productions, avoiding waste and replacing some virgin raw materials.

4.1 Extrusion applications

The possibilities to use an extruder as a polymerization reactor were already recognized in 1950. A patent of those years described a polymerization unit in which a single-screw extruder was used as the main polymerization device.[43] For the first part of the polymerization process, when low viscosities prevailed, a continuous stirred-tank reactor with a residence time of 90h was used as a prepolymerizer, after which the material was transferred to the single-screw extruder for the high-viscosity part of the reaction. In this extruder, a residence time of 18h was necessary for the thermal polymerization of styrene.

The first polymerizations described in open literature were the polymerization of nylon and several polycondensation reactions.

In the middle of 70s, the first theoretical considerations concerning reactive extrusions appeared. Extruder was identify as the best plug flow reactor for viscous materials, with some implication with the distribution in molecular weight of the polymer formed that cannot be prevented. For this reason, a prepolymerization is advised to avoid low viscous material to be fed to the extruder.

Then twin-screw technology was proposed for reactive extrusion because of difficulties in scaling up single screw extruders that could be avoided in twin-screw extruders. Residence times of half an hour were possible in self-wiping twin-screw extruders. A combination of a stirred-tank reactor, a single-screw extruder, and a twin-screw extruder was identified the most suitable system for the production of polyesters.[44]

In more recent years, the radical polymerization of several methacrylates was studied in a counter rotating twin-screw extruder.[45, 46, 47, 48]

Apart from these polymerizations mentioned, the counter rotating extruder was also used for the polycondensation of urethanes and the anionic polymerization of ε-caprolactam.[49, 50] Several other studies also debated the possibilities for reactive extrusion of urethanes.[51, 52, 53]

Other reactions have been described in various types of extruders, like the use of co-rotating twin-screw extruders for the anionic polymerization of ε-caprolactam.[54, 55, 56] Some patents also describes the synthesis of high-impact polystyrene (HIPS).[57]

Reactive extrusion is also attractive for grafting or modification reactions, where micromixing is an important factor for obtaining a homogeneous product. Typical examples are the free radical grafting of maleic acid, glycidyl methacrylate, or acrylic acid onto polyolefines

The resulting functionalized polymers can be used for blending with other polymers; also the adhesive properties of these polymers to metals or glass fibers improve.[58] Apart from the desired grafting reactions, unwanted side reactions such as cross-linking of polyethylene and chain scission in polypropylene may occur.[59] Little is known about the stability of the reactive extrusion process. Especially if a transition of very low to very high viscosities occurs, as is the case during polymerizations starting from low-molecular-weight monomers, a sharp transition between high conversion and low conversion of the reaction can occur as a result of very small changes in operating conditions.

Reactions involving polymers that have been performed in extruders can generally be divided into five categories:

- Polymerization. During polymerization reactions the viscosity of the polymer–monomer mixture increases sharply as the reaction progresses. Due to this increase in viscosity both mixing and heat transfer become restricted. During addition reactions a polymer chain is formed in a very short time, until it terminates and stops growing. During condensation reactions, all polymeric chains keep growing during the whole reaction time and often a low-molecular-weight by-product is formed. The removal of this by-product by evaporation is often the limiting factor for the reaction speed.
- Graft and functionalizing reactions. The production of both graft polymers and functionalized polymers involves the reaction of a polymeric chain with molecules of a monomer or a mixture of monomers. In functionalizing reactions, single units of the monomer are chemically linked to the backbone polymer. In grafting reactions, short chains of the monomer units are linked to the main chain polymer. Due to the longer side chains, the viscosity of the reacting mixture increases more drastically during grafting reactions than during functionalizing reactions.

- Interchain Copolymerization. This is a reaction between two or more polymers to form a copolymer. This type of reaction often involves the combination of reactive groups of the different polymers to form a graft copolymer. However, contrary to normal graft reactions, no monomers are used in this process, so the viscosity increases very fast.
- Coupling or branching reactions. These reactions involve the increase of the molecular weight of homopolymers by coupling the polymeric chains through a polyfunctional coupling agent.
- Degradation reactions. This technique is used to decrease the molecular weight of polymers in order to meet a specific product performance. The degradation is often achieved by simple shear heating or by the addition of chemical reactive like peroxides. Because large chains have a bigger chance being cut, degradation often occurs together with a narrowing of the molecular weight distribution.

Besides polymerization reactions and modification reactions of polymers, other types of reactions can also be performed in extruders: cyclization of chemical components, isomerization of chemicals, depolymerization of polymers, hydrolysis of esters and polyurethanes, and others.

From a processing point of view, all reactions can be divided into two main groups: single-component and multicomponent reactions.

Single-component reactions can occur throughout the bulk of the material. At the start of the reaction only one component, monomer or prepolymer, is present, or the components used are well miscible and premixed. For this group of reactions the temperature of the mixture plays an important role, as well as macromixing over the length of the extruder, which is related to the residence time distribution. Both parameters determine the progress of the reaction.

Whereas multicomponent reactions occur predominantly between immiscible components. Because the reaction proceeds mainly at the interface between the components, micromixing plays an important role. Normally, this type of reactions becomes diffusion limited as the reaction progresses due to the buildup of reaction products at the interface between the components. To overcome this diffusion limitation, extensive micromixing is necessary. In addition to micromixing, temperature and macromixing play an important role.[60]

4.2 Experimental Section.

4.2.1 Materials and methods

All the used raw materials and solvents were purchased from various supplier all over the world. The quality of different compounds is guaranteed from the internal CQ laboratory.

All the syntheses were carried out in 5 liters or bigger round bottom flasks with mechanical mixing and heated by a mantle.

4.2.2 Instrumental

Gel permeation chromatography (GPC)

The used instrument was a Agilent Technologies 1260 Infinity, a differential refractive index detector, and two columns in series (PL-gel 5 μm Mixed -D, 300 x 7,5 mm). All the samples were dissolved in THF at a constant concentration of 2 wt%. After filtration with 0,45 μm wheel syringe filter, 20 μL of each sample was injected into the chromatograph. The elution solvent was also THF at a constant flow rate of 1 mL/min.

Thermomechanical analysis (TMA)

The instrument was a TA Instrument Q400 TMA. The penetration probe was used with an applied force of 0,1 N and a 5 °C/min heating rate from 25 °C to 250 °C.

Extrusion

The used extruder was a Brabender Twin Screw Extruder TSE 20/40 EC with co-rotating twin screws (Figure 4.1). For the tests, we used a screw design already employed for a previous processing of a polyester resin. The design alternated screw pieces, which allow the passage of molten raw materials along the barrel, to kneaders and toothed blocks pieces, which mix the raw materials together.

Figure 4.1. Brabender extruder

4.3 Results and Discussion.

The enamel consists of a single binder formed of trimellitic anhydride (TMA), 4,4'-methylenedianiline (MDA), ethylene glycol (MEG), 1,3,5,-tris(2-hydroxyethyl)isocyanurate (THEIC, Figure 4.2), dimethyl terephthalate (DMT), catalyst, additives and solvents.

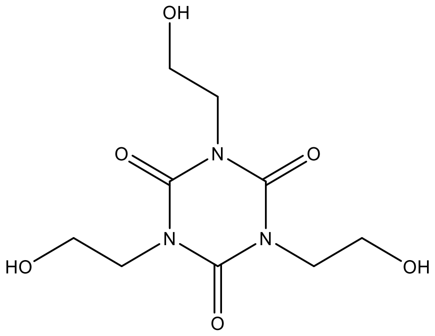


Figure 4.2. Structure of THEIC

In classical synthesis, the formation of the resin takes place in the presence of solvents. After the resins formation, additives and dilution solvents are added TMA and MDA form the imide part of the enamel, which confers high thermal and chemical resistance. DMT esterified with the glycols forms the ester part, which gives flexibility to the enamel (Figure 4.3).

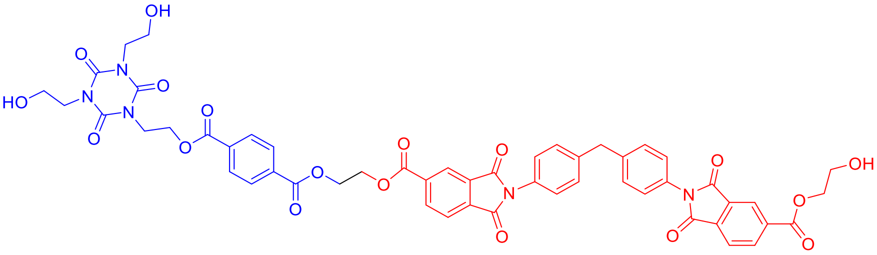
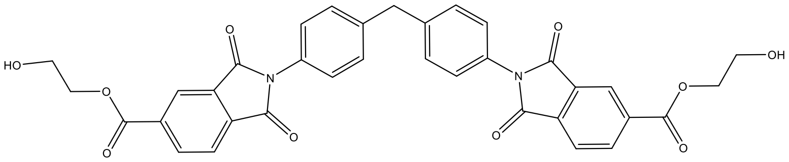
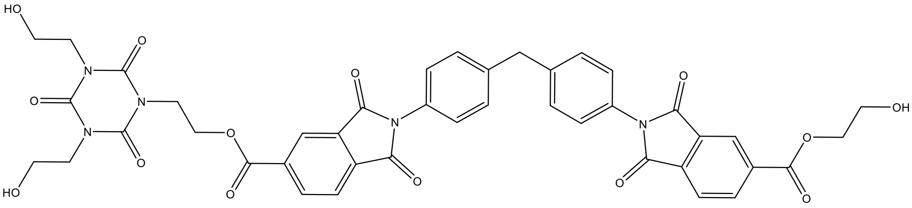


Figure 4.3. Structure of the esterimide resin. In blue the ester part and in red the imide part

The reaction involves the use of ethylene glycol, which is a liquid reagent. To use a liquid is not an efficient procedure with our extruder, because being a liquid it tends to settle on the bottom of the barrel and it is harder to mix together with others materials. For this reason, we decided to synthesize a preliminary polyesterimide intermediate to be loaded into the extruder. The intermediate was prepared with TMA, MDA and MEG and with or without THEIC. Indeed, there was two possible routes: one by synthesizing an intermediate, called diimidediester (DIDE), with TMA, MDA and MEG and then load it into the extruder with PET and THEIC; the other by synthesizing a similar intermediate with the addition of THEIC (DIDET) to be loaded into the extruder with only PET. The two intermediates are shown in Figure 4.4.



DIDE

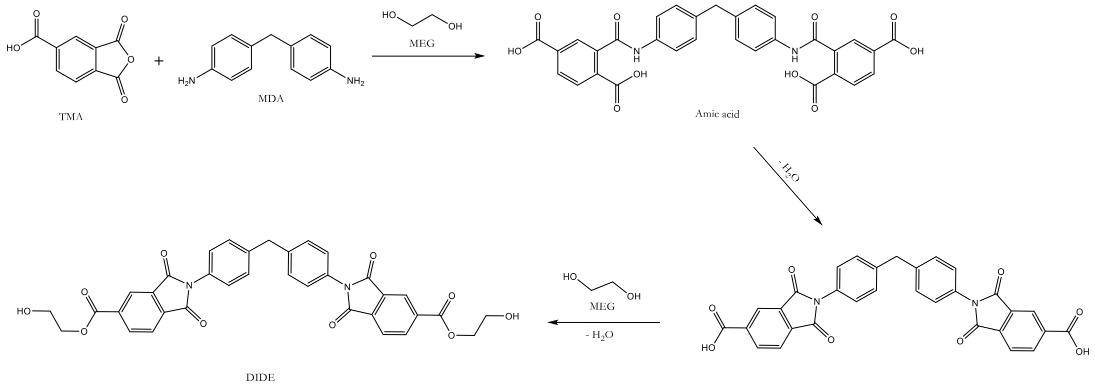


DIDET

Figure 4.4. Structure of the two possible intermediates

4.3.1 Formation of DIDE

Both syntheses are not so far from the original one. The main problem consists in the absence of solvents. The synthesis passes for the formation of the amic acid, insoluble in ethylene glycol, but its esterified form, DIDE, is soluble (Scheme 4.1).



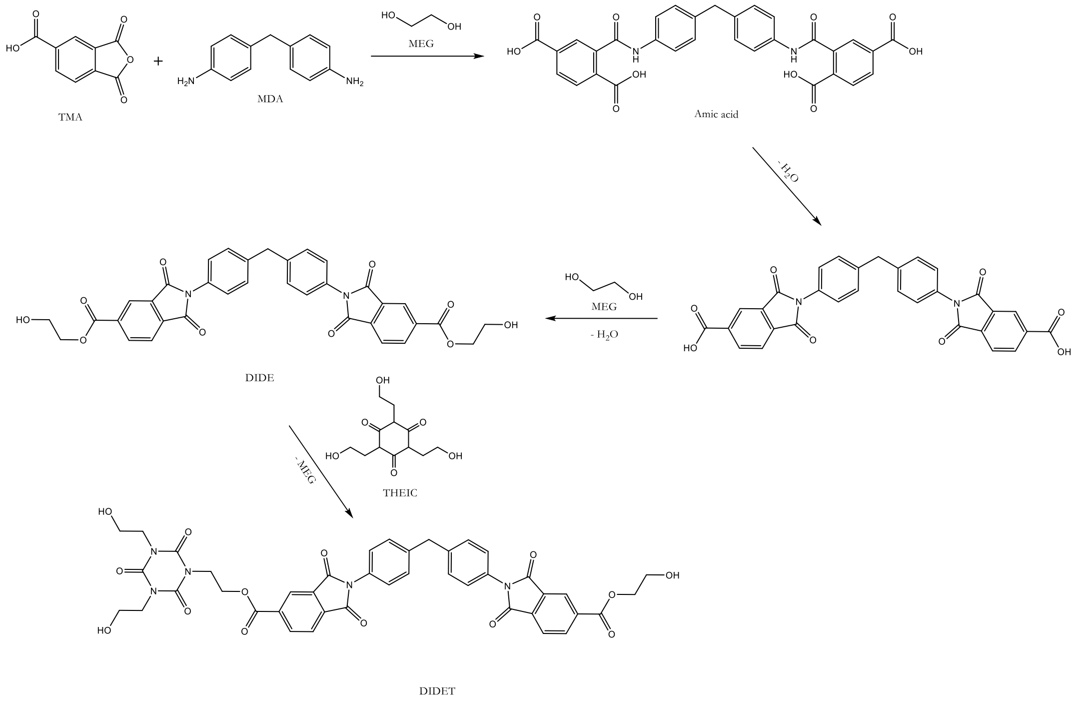
Scheme 4.1. Formation of the DIDE intermediate

By using a large excess of ethylene glycol, then recovered as distillate, it is possible to keep the solid in suspension, having good mixing and good esterification times. Once esterified the compound is completely soluble in ethylene glycol and the reaction proceeds with the formation of the oligomer and the elimination of excess glycol by condensation and distillation.

The product obtained is a solid glassy resin and it is possible to reduce it to powder in order to use it on the extruder.

4.3.2 Formation of DIDET

The procedure for the formation of the alternative preliminary intermediate is identical, except for the addition of THEIC after esterification of the amic acid (Scheme 4.2).



Scheme 4.2. Formation of the DIDET intermediate

In Figure 4.5, we can see the difference between the chromatograms of the two resins.

The second intermediate obtained is a solid too, but this time it is not possible to reduce it to powder because, unlike the other, it is a little bit elastic (DIDET-1).

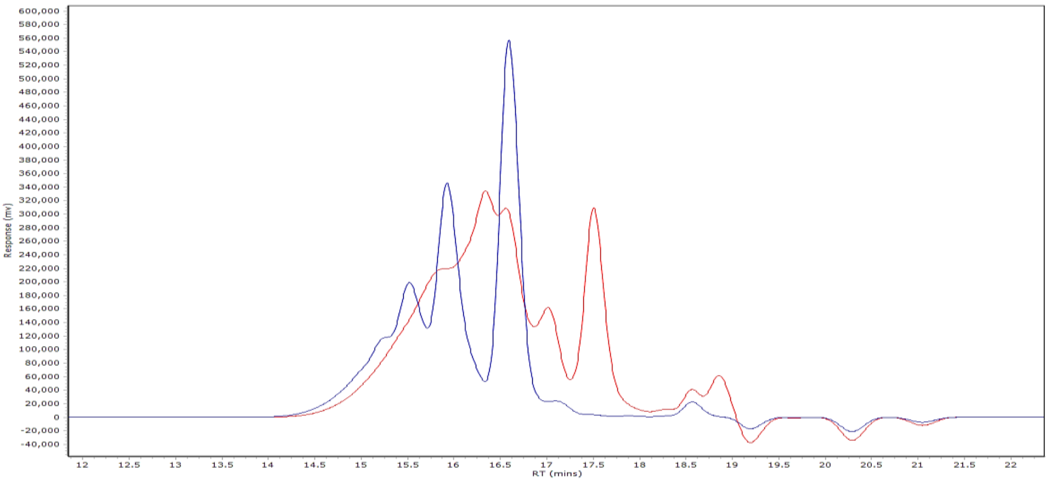


Figure 4.5. Chromatograms of DIDE (in blue) and DIDET-1 (in red)

It was therefore decided to carry out a second synthesis, increasing the degree of condensation and so the molecular weight of the intermediate to obtain a compound that was no longer elastic (DIDET-2). We can see from Figure 4.6 that the molecular weight of DIDET-2 was actually greater then DIDET-1.

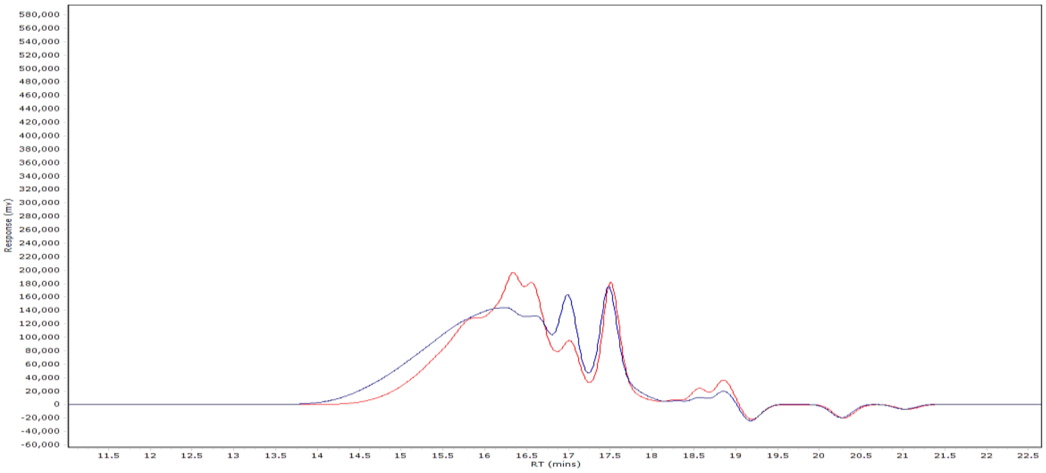


Figure 4.6. Chromatograms of DIDET-1 (in red) and DIDET-2 (in blue)

Table 4.1 shows the molecular weight values of DIDET-1 and DIDET-2.

Table 4.1. Molecular weight values.

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
DIDET-1	890	1409	1,583
DIDET-2	923	1704	1,846

Despite the greater molecular weight, the solid obtained was still sticky. In fact, it was much more difficult to break it compare to DIDE and once on the extruder feeder it was stuck to the walls.

The possibility of further increasing the molecular weight has been excluded, since as can be seen from Figure 4.7 the molecular weight is already high compare to the industrial product as reference, further increasing of the molecular weight would lead to a product with very high molecular weight and very different properties.

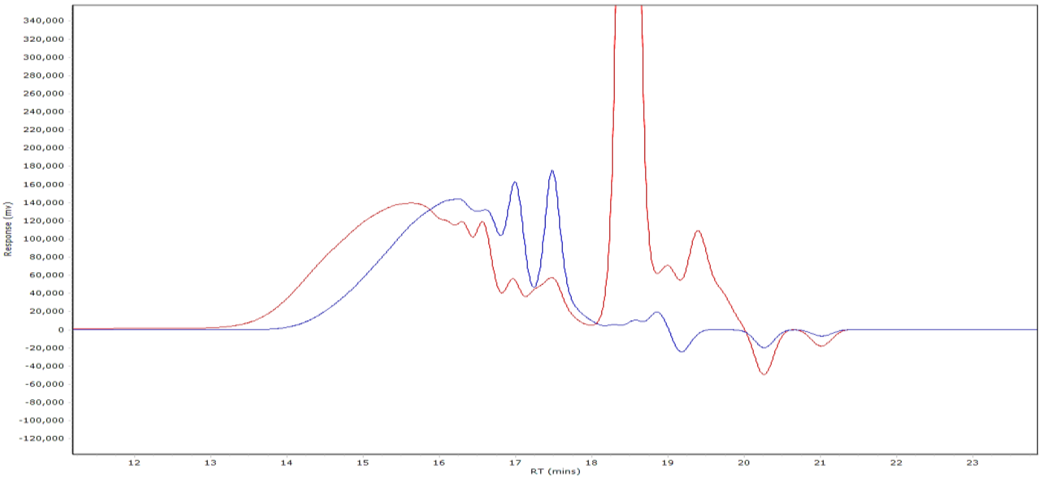


Figure 4.7. Chromatograms of DIDET-2 (in blue) and the reference (in red)

4.3.3 Tests on the extruder

It was decided to proceed with the tests on the extruder using the DIDE intermediate.

The intermediate was then reduced to powder and mixed with THEIC (powder too) and loaded into a feeder. A second feeder was dedicated to PET.

In the first tests performed, we changed the operating temperature to see the effect on the product. Temperatures of 250 °C, 280 °C and 310 °C were tested. The obtained results are shown in Figure 4.8 and Table 4.2.

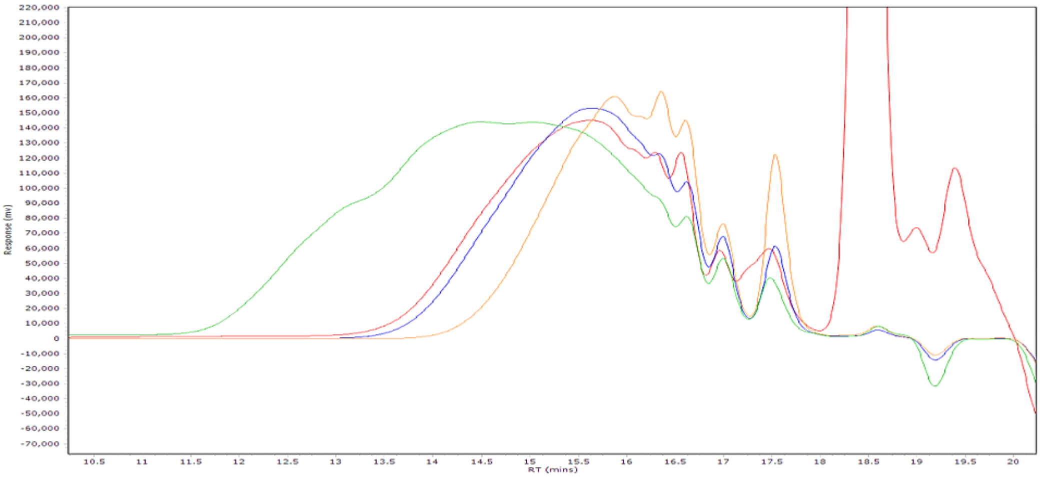


Figure 4.8. Chromatograms of the reference (in red), the product at 310 °C (in green), the product at 280 °C (in blue) and the product at 250 °C (in orange)

Table 4.2. Molecular weight values

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
250 °C	1132	1963	1,734
280 °C	1504	3005	1,998
310 °C	2657	15530	5,845
Reference	1510	3320	2,199

As we expected increasing the temperature, the molecular weight increases. From the comparison with the reference, we can see that 280 °C can be a good operating temperature, considering at higher temperatures we have a very high molecular weight and at the temperature of 250 °C, we have obtained a product not clear and not very soluble in THF, solvent used for GPC analysis. This is probably because PET at 250 °C is not completely melted and it cannot react with the other components remaining separate into the product.

Once the operating temperature has been set, the subsequent tests have been carried out by varying the feeding amount.

The condensation reaction among the species at stake is continued removing ethylene glycol, since it is a by-product of the condensation. Indeed, to remove ethylene glycol from the mixture means moving the chemical equilibrium to the products and so allowing the reaction going ahead by promoting the transesterification and producing oligomers. Decreasing the feeding amount the space inside the barrel of the extruder is bigger and ethylene glycol has more chance to separate from the reaction mixture increasing the molecular weight of the resin. On the contrary increasing the feeding amount the available space into the barrel is less and ethylene glycol stays longer in contact with the reaction mixture changing less the chemical equilibrium and slowing the reaction, in this way the resulting molecular weight will be smaller. To check the feeding amount effect, we have run some tests changing it (Figure 4.9).

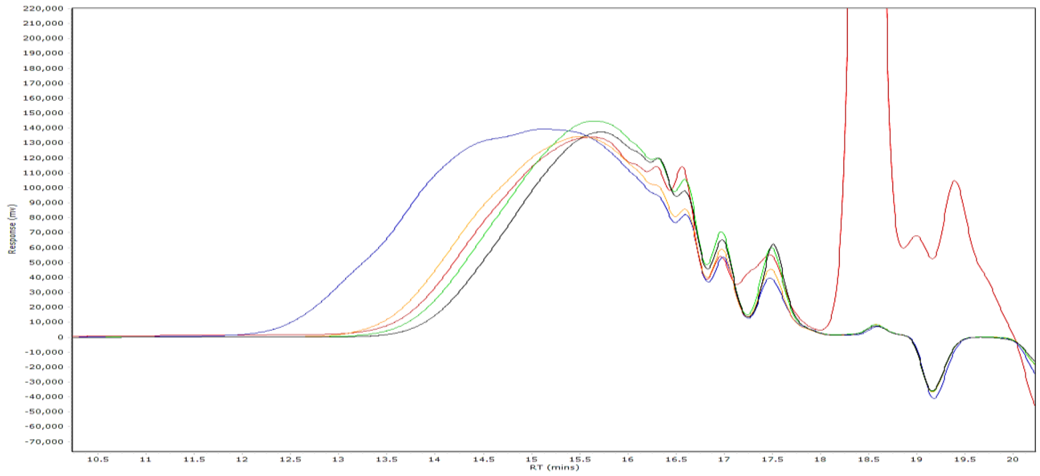


Figure 4.9. Chromatograms of the reference (in red) and the products loading: 30 g/min (in blue), 60 g/min (in orange), 90 g/min (in green), and 120 g/min (in black)

The figure shows the chromatograms of the tests done loading 30, 60, 90, and 120 g/min. Table 4.3 shows the values of the molecular weight. We can see increasing the feeding the molecular weight decreases as expected.

Table 4.3. Molecular weight values

Feeding (g/min)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
30	2203	6808	3,090
60	1704	3723	2,185
90	1501	3100	2,065
120	1414	2721	1,924
Reference	1510	3320	2,199

Still making a comparison with the reference (Figure 4.9), we can see that the best feeding amount was halfway between 60 g/min and 90 g/min, so it was decided to carry out a test loading 75 g/min.

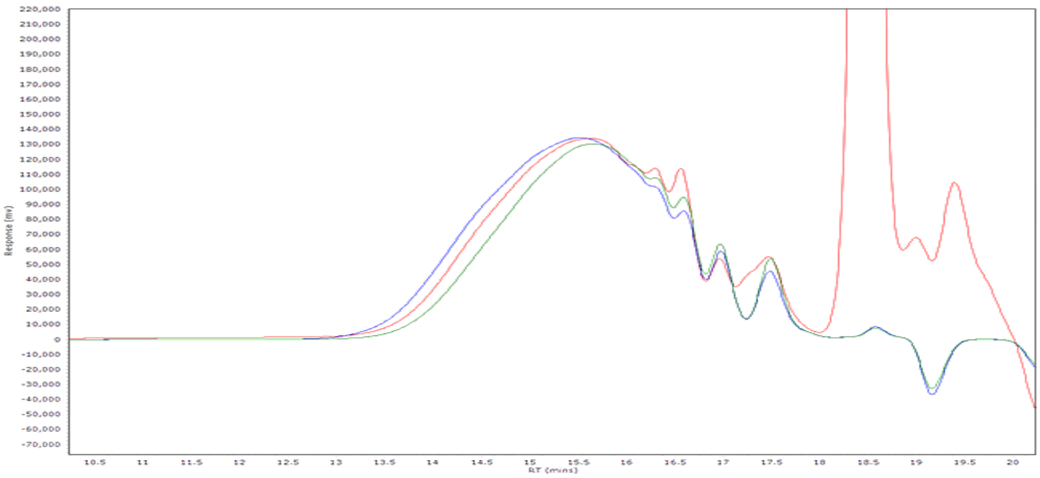


Figure 4.10. Chromatograms of the reference (in red), the product at 60 g/min (in blue) and the product at 90 g/min (in green)

The obtained resin feeding 75 g/min was then diluted with solvents and additives used for the solvent-based enamel. Figure 4.11 shows the comparison with this enamel and the reference, and Table 4.4 shows the molecular weight values. As we can see, the product was very similar to the reference.

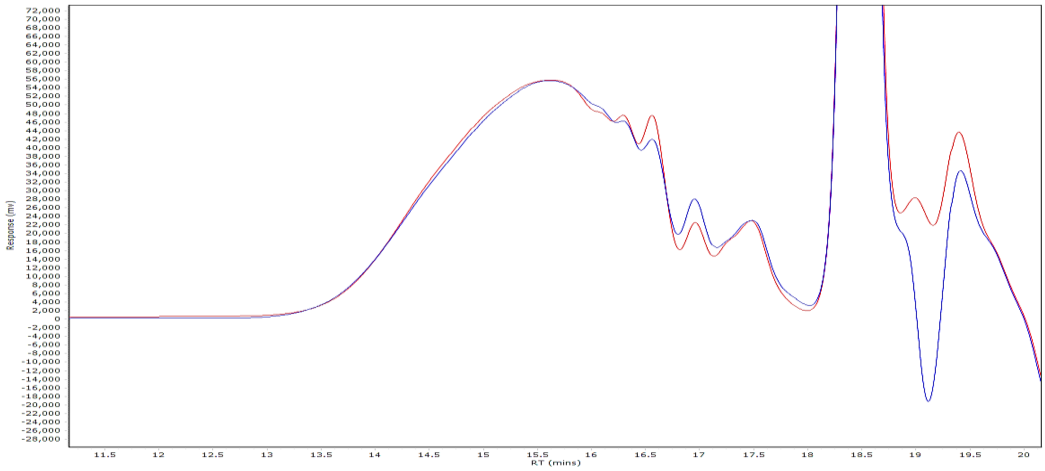


Figure 4.11. Chromatograms of the reference (in red) and the diluted product at 75 g/min (in blue)

Table 4.4. Molecular weight values

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
75 g/min	1452	3226	2,222
Reference	1510	3320	2,199

Once set the operating temperature and the right feeding amount, we decide to prepare different products, changing the ratio of the raw materials. In particular, we decided to change the amount of PET and THEIC into the formulation: ± 30% of PET and ± 30% of THEIC.

In Figure 4.12 are shown the chromatograms of the standard, + 30% THEIC and - 30% THEIC.

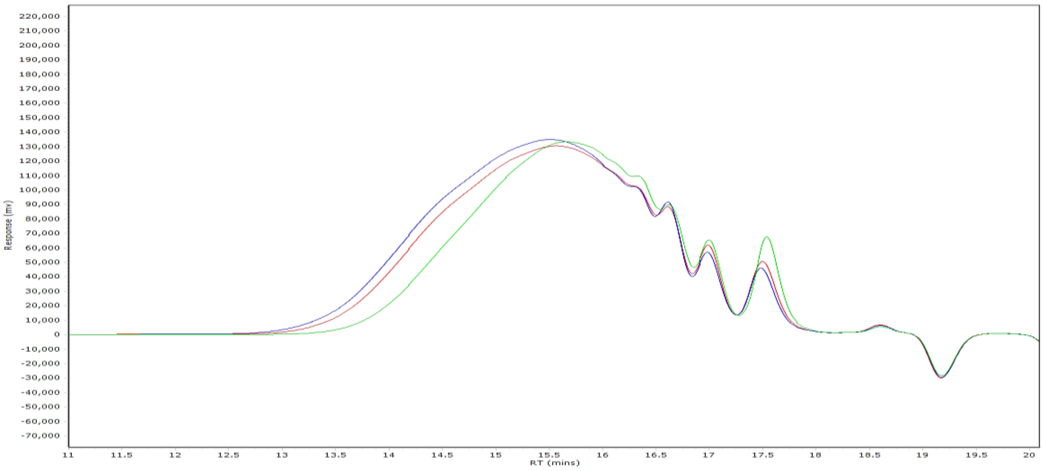


Figure 4.12. Chromatograms of product with standard ratio (in red), + 30% THEIC (in green) and - 30% THEIC (in blue)

Table 4.5 shows the molecular weight values for the three products.

Table 4.5. Molecular weight values

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
Standard	1646	3652	2,219
- 30% THEIC	1751	4016	2,294
+ 30% THEIC	1427	2927	2,051

One can see that the molecular weight decreases increasing the amount of THEIC. That is why THEIC has three -OH group, so more possibility to react, and a lower molecular weight compared to PET.

Then we changed the PET amount. Figure 4.13 shows the comparison of the standard trial and the other two with - 30% PET and + 30 % PET.

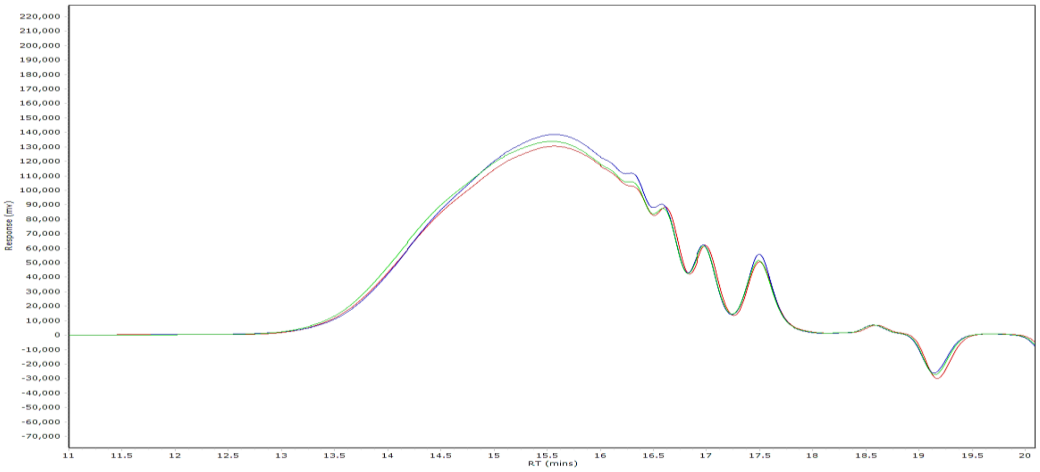


Figure 4.13. Chromatograms of product with standard ratio (in red), + 30% PET (in green) and - 30% PET (in blue)

Table 4.6 shows the molecular weight values for the three products.

Table 4.6. Molecular weight values

Sample	M_n (g/mol)	M_w (g/mol)	M_w/M_n
Standard	1646	3652	2,219
- 30% PET	1653	3651	2,209
+ 30% PET	1687	3797	2,251

This time we obtained very similar products. Despite the close molecular weight, a change in the amount of PET could lead at different properties of the final enamel.

4.3.4 Products properties

In the previous chapter, I explained that the only way to evaluate properly an enamel is testing the properties of the enameled wire. With the available technologies solvent-based products are required for the application. Therefore, we diluted the extruded resin first heating the material to 160 °C and then adding solvents, catalysts and additives.

At first, we have run some tests using the thermomechanical analyzer. The thermomechanical analysis consist of the measurement of a change of a mechanical property of the sample while it is subjected to a temperature regime. In particular with thermomechanical analysis we evaluate a change of a dimension of the sample under a little force acts on it while it is subjected to a thermal ramp. Increasing the temperature the sample starts to expand until a certain temperature at which the samples becomes soft. A probe checks the variation of the surface and the instrument records the thermogram. That temperature is taken as results of the analysis.

This kind of test does not replace the enamelling stage, which remains the best way to evaluate the enamel, but could give a preliminary indication of the thermal properties of the product.

To run this analysis we coat the diluted product on an aluminum panel at 40 μm thickness and we cure it into the oven at 260 °C for 30 minutes. A piece of the cured panel was removed and used for the thermal analysis. The analysis result should be near to T_g temperature of the cured enamel.

Figure 4.14 shows the analysis result for the reference sample.

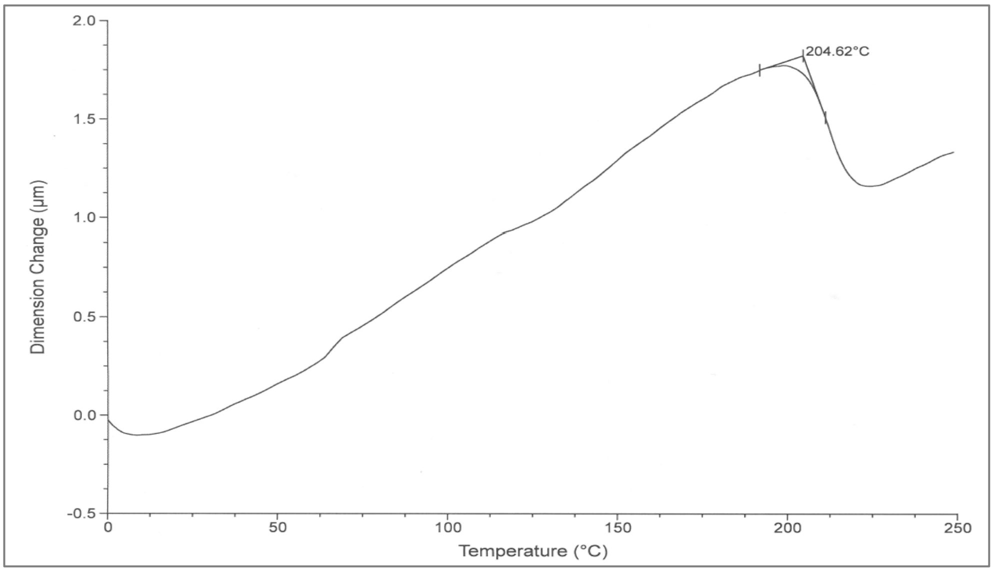


Figure 4.14. Thermogram of the reference

The reference shows a value of 204,6 °C. Below are shown the resulting thermogram for all the other samples (Figures 4.15-4.18).

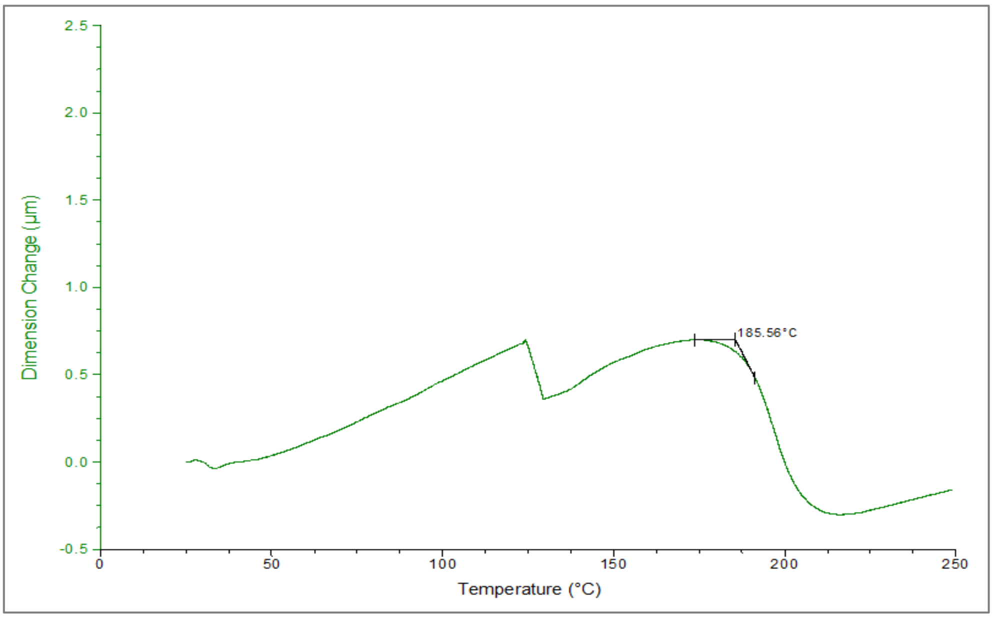


Figure 4.15. Thermogram of the product with standard ratio

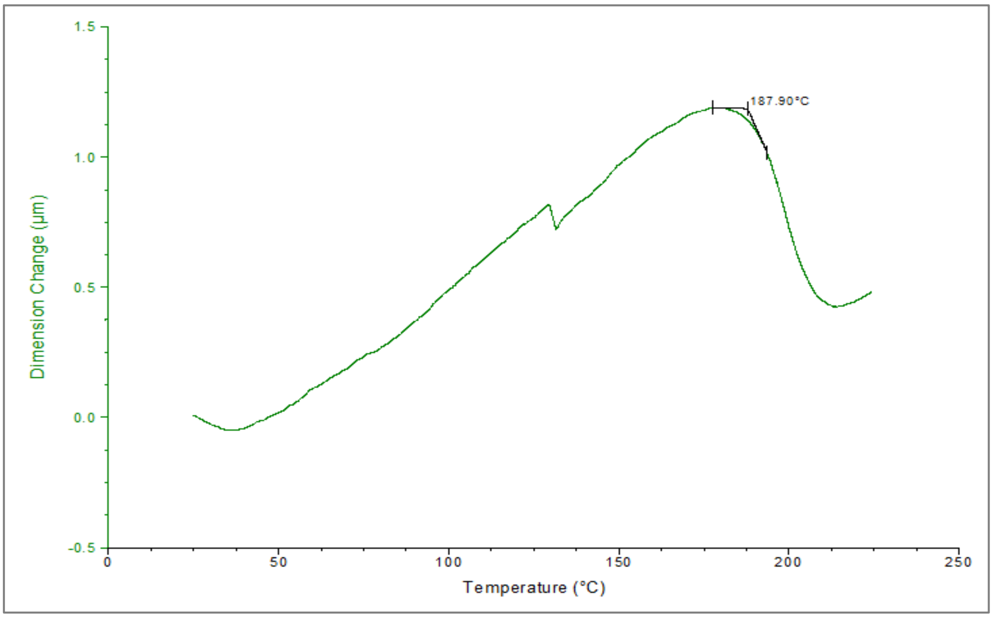


Figure 4.16. Thermogram of the product with standard - 30% THEIC

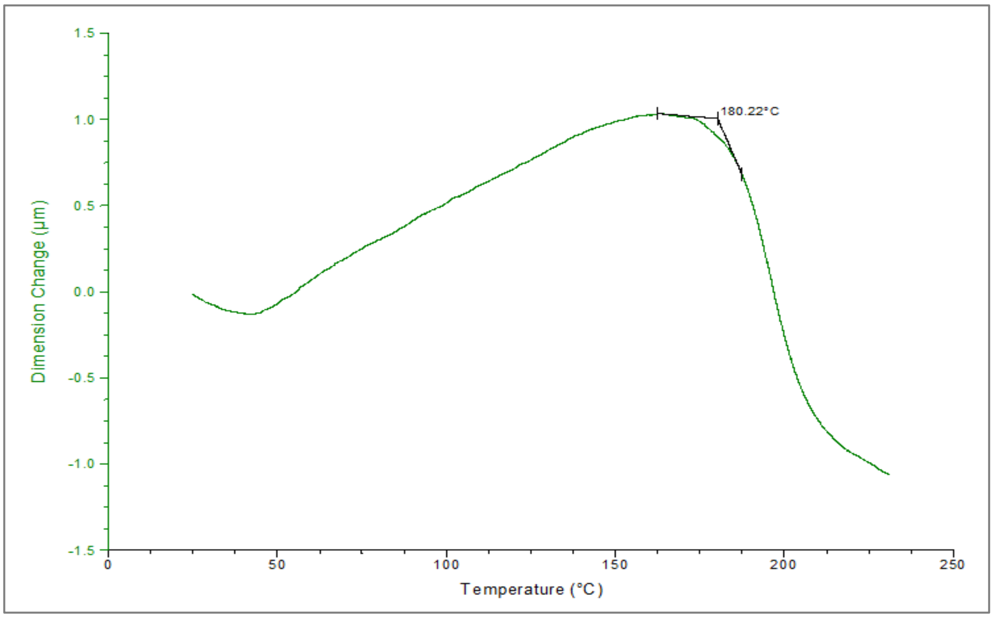


Figure 4.17. Thermogram of the product with standard + 30% THEIC

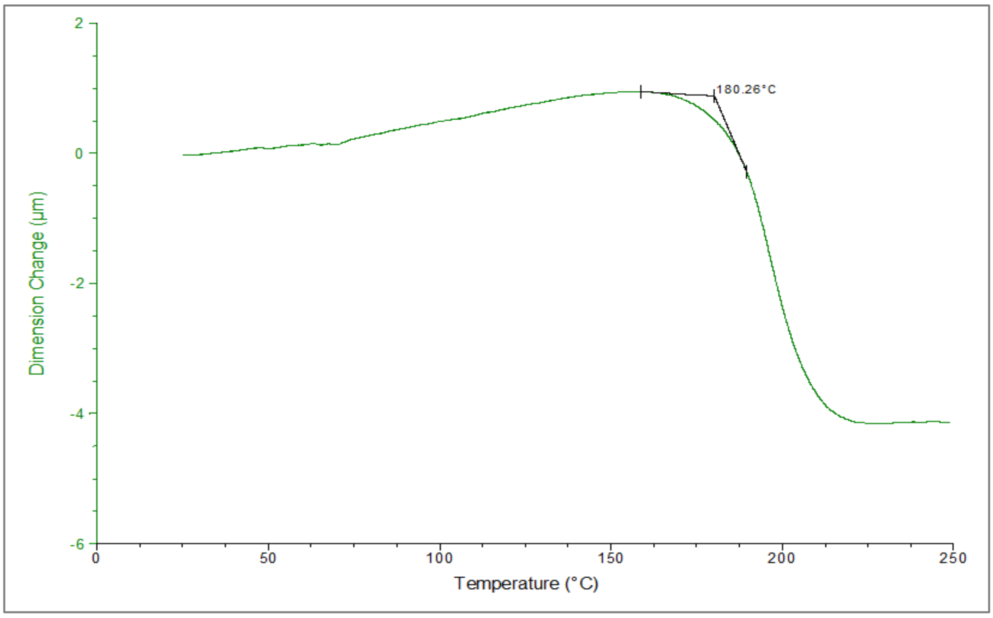


Figure 4.18. Thermogram of the product with standard - 30% PET

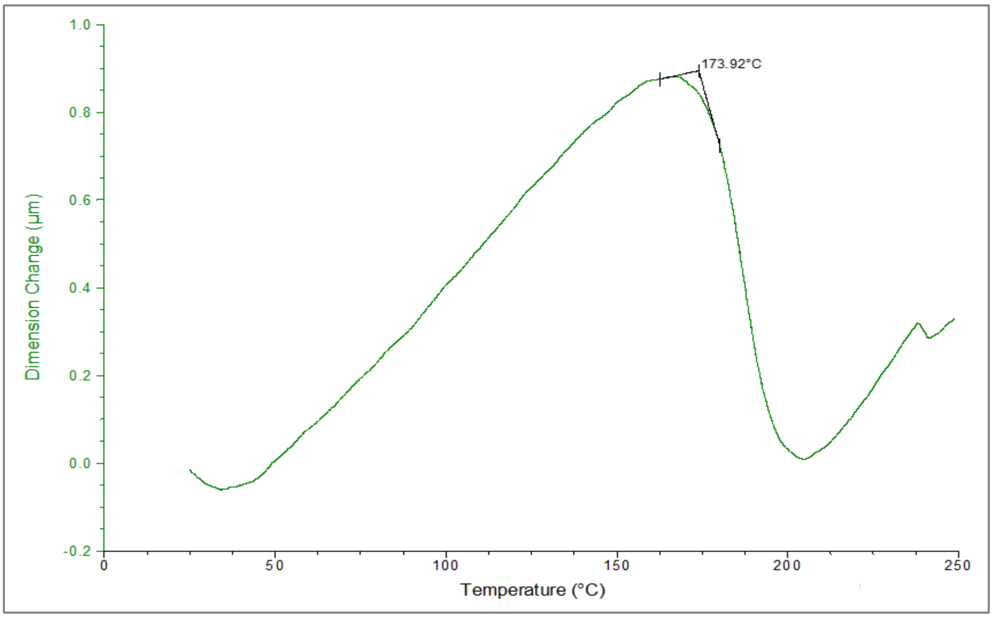


Figure 4.19. Thermogram of the product with standard + 30% PET

The results are summarized in Table 4.7.

Table 4.7. Thermomechanical results

Sample	**Softening Temperature (°C)**
Reference	204,6
Standard	185,5
- 30% THEIC	187,9
+ 30% THEIC	180,2
- 30% PET	180,2
+ 30% PET	173,9

From figures , one can see that the products had generally a lower temperature in comparison to the reference. Changing the THEIC amount the temperature increases increasing the molecular weight (Figures 4.16 and 4.17).

Whereas in both the trials with more and less PET the softening temperature were lower than the product with standard ratio (Figures 4.18 and 4.19). Being a no usual method, it is hard to draw conclusions from these results, but it could be that a higher amount of imide part in relation to PET and THEIC is necessary to achieve the reference properties.

Enamelling results

Once diluted products were prepared, they were enameled. The results compare to the reference are reported in Table 4.8.

Table 4.8. Enamelling results

Sample	**Reference**		**Standard**		**- 30% THEIC**		**+ 30% THEIC**		**- 30% PET**		**+ 30% PET**	
Speed (m/min)	42	46	42	46	42	46	42	46	42	46	42	46
Mandrel Test	OK		OK		OK		OK		NOT OK		OK	
Tan Delta (°C)	201,3	197,5	172,6	163,7	176,2	170,1	172,8	163,6	178,1	163,3	164,9	156,6
Cut-Through(°C)	380		370		350		370		380		360	
Heat Shock @ 220 °C	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK

The enamelling stage was performed at two different speed (42 and 46 m/min) to evaluate different curing degrees. From the reported results, one can see that generally the samples were of lower level compared to the reference. No one of them reached the desired properties, but they did not too bad characteristics. Unfortunately, since no more time was available, we did not have the chance to do other tests. Nevertheless, the obtained results are promising and by doing some other tests changing the ratio of the raw materials (i.e. the imide part) or the extrusion process (i.e. modifying the design or the speed of the screws) we could achieve the target.

4.4 Conclusions

This project born with the intention to use the extruder to synthetize polyesterimide insulating enamels. The extrusion technology has some advantages compared to batch syntheses, among them: the possibility to work without solvents, the possibility to work in continuous, and the possibility, with the suitable implementation, to apply the solvent-free products with more thickness on the supports, increasing the properties of the final product. The use of such technology could improve the production of insulating enamels, especially from an environmental point of view: the process would be less energy consuming, the used raw materials would be less and the final product, the insulated wire, would be more performing. Moreover, the process considers using recycled PET instead of terephthalic acid (or dimethyl terephthalate) and ethylene glycol.

The obtained results were not yet satisfying, but they were very promising. Indeed the carried out tests had some good properties considering the completely new approach used.

As mentioned, the project was interrupted for time reason, but will be the basis for the future development of the product.

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