Univerza v Mariboru

Fakulteta za strojništvo

CHEMICAL RECYCLING OF FUNCTIONALISED POLYETHYLENE TEREPHTHALATE IN FOOD PACKAGING

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1 INTRODUCTION

The origin of the word plastic goes back to the Ancient Greece. Attending to the etymology of the word, we can see that it comes from the word “plastikos” that means or is translated as “mouldable”. We can also find de the word “plasticus” in Latin language and means “belonging to moulding or shaping” [1].

These old definitions are directly related with some of the properties of nowadays plastics because they all are able to have a desired shape and properties for every specific application. The ways or techniques for manufacturing and treating plastics are mostly heat and pressure.

1.1 Origin of plastics

Historically, the first known use of plastics was in the old American cultures. They used a kind of latex (natural rubber) that was liquid and sticky in its natural state. This way, it was possible to make objects with a desired shape that persisted when the latex was dried.

It wouldn’t be until thousands of years later, in the XIX century, when the Industrial Revolution in England let the Chemical Industry make progress. This advantage on the sector allowed Charles Goodyear’s in 1839 to discover the chemical process known as “vulcanization”. This process consisted in heating the natural rubber in presence of sulphur, what made the rubber harder. This would be the first commercial thermostable plastic. In 1909, Baekeland would create the first synthetic polymer (Bakelite) [2].

In the next few years plastics became to be widely accepted because of the properties and advantages they offered, but World War II would be the inflexion point. After this historical event plastics entered in large-scale to many different industrial and daily-life applications [3].

2 APPLICATION OF PLASTICS

Since plastics were discovered in 1839, the development of the industry has allowed to reduce production costs. For this main reason, consumption of plastics has increased considerably on the last years, until becoming one of the most used material worldwide because they have let to increase the comfort and standard of living of the population. Nowadays we can´t imagine a life without plastics but, don't recycle or remove in a proper way it's becoming a problem.

Collecting some data of production of plastics in the last years [4] we can create a graph and have a look how the production (which is directly related with consumption) has increased:

Table 1-Production of plastics per year (million tons)

Year	1950	1977	1989	2002	2009	2011	2015
Production (million tons)	1,5	50	100	200	250	280	322

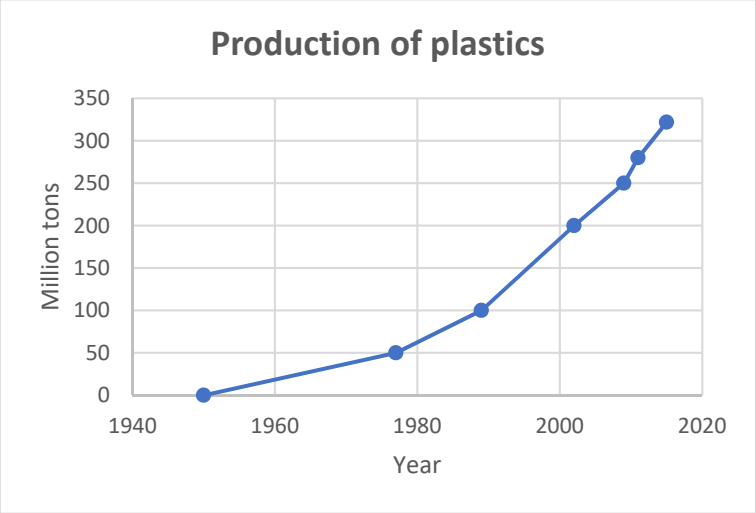

Figure 1: Production of plastics per year (million tons)

Attending to Figure 1, we can conclude that in the last 70 years, the production or consumption of plastics has been increased in more than a 20,000%.

But plastics not only have a positive aspects, we should also take into account the negative effects they have. Some advantages and some disadvantages are [5]:

Table 2: Advantages and Disadvantages of plastics

Advantages	Disadvantages
Low price	Production's pollution
Mouldable	Mixed plastics have low quality
Low weight	Expensive recycling
No corrosive	Limited use of recycled plastic
High resilience	Long life
Electric and thermic insulating	No high temperatures
They can be recycled	Large volume
Versatility	

Attending to the list of advantages and disadvantages (Table 2) we can conclude that the advantages they offer are greater than the disadvantages. Their characteristics make possible a large number of applications. Furthermore, if you work properly with plastics, some of the negative effects can be minimized or even removed.

For that reason, plastics are widely accepted and their use is extended to lots of different fields. Looking for some statistics about the consumption of plastics in the different sectors, we can make a graph in order to see how it is distributed [6]:

Table 3: Consumption of plastics in the different sectors

Packaging	Construction industry	Textile Industry	Other
35,9%	16,0%	14,5%	33,6%

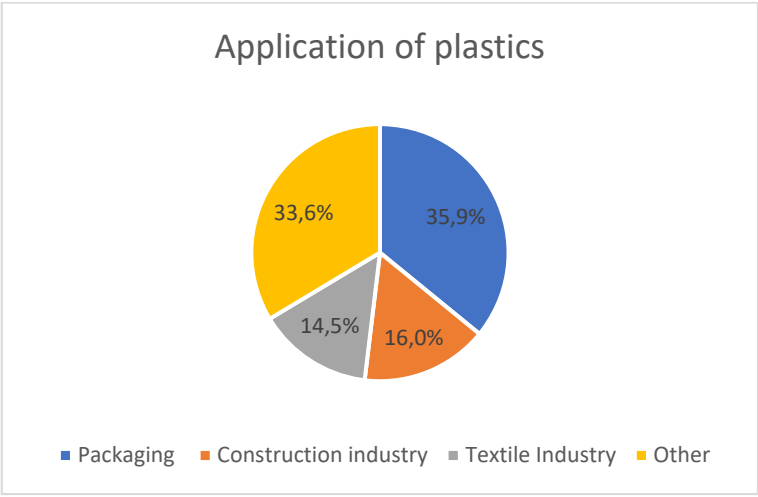

Figure 2: Application of plastics in the different sectors

On Figure 2, we can see that more than one third of the total made plastics is destinated for packaging sector, what means that it is the most important one. This also means that packaging sector is quite important for the economy.

2.1 Food packaging

In packaging sector we can distinguish different application fields, like healthcare, cosmetic and personal care or consumer packaged goods, among others. Food packaging is one of the most extended applications and, due to its advantages, in the recent years this field has been developed considerably. According to Gordon L. Robertson, food packaging has four different objectives [7]:

- The main objective of food packaging is to protect food against physical, chemical or microbial contaminants, what it is understood as an hygienic issue. Plastics offer a high resistance, so they let food to be conserved optimally. These methods of food conservation are understand like maintaining food quality level, minimizing possible damages and making duration longer (preservation). Packages also try to avoid liquid spills or bad smell, among others.
- The second one is about containing the product, what makes possible transportation, storage or distribution. Recently, has been developed something call “active packaging”, “intelligent packaging” or “smart packaging”. All these terms are referred to packages that usually contain preserving substances that extend the time that food is conserved optimally. They can also send information about freshness or quality or even modify conditions inside the package. Safety is also improved.
- The third one is about convenience, which is understood as fitting to customer’s demand, increasing accessibility and reducing time, effort or frustration. It is conceived as an enhancement of the product through the package. For example, adapted size of packages or packages for eating or drinking directly without a negative impact for human health.
- The last one makes reference to communication of food packaging labels. This prints include basic data such as the ingredients or nutritional data, and some other information like weight, production/limit dates or even instructions.

Despite in food industry are used different materials like metal (e.g., metal cans), paper and paperboard or glass, the most used packages are made of plastic because its low production cost and its nice mechanical properties. They are also easy-processable and it's easy to modify some properties like rigidity, elasticity, colour or even degradability.

Several different plastics are used, it depends on what they are designed for. Nevertheless, the most used plastic resins in food packaging sector are polystyrene (PS) and its varieties like expanded polyestyrene (EPS), polyethylene (PE) and its varieties (PET, HDPE, LDPE) and polypropylene (PP). Recently, also some other kind of polymers like lactic polyacid (PLA), which is similar to PET but biodegradable, and bioriented polystyrene (OPS), which is obtained from PS and easy-recycling, have been introduced.

Collecting some data about European consumption of food packaging plastics for year 2016 we have [8]:

Table 4: Consumption of plastics in food packaging (2016)

Kind of plastic	Use in Europe (%)	Applications
Polystyrene (PS) - Expanded polystyrene (EPS)	6.7%	Trays and food containers
Polyethylene terephthalate (PET)	7.4%	Mainly used in bottles for liquids. Also used in food containers.
High-Density polyethylene (HDPE)	12.3%	Tetrabrik (milk bottle) and bottles
Low-Density polyethylene (LDPE) -	17.5%	Trays, food containers and transparent film for food packaging
Polypropylene (PP)	19.3%	Food containers and bottle caps
Others (PVC…)	36.8%	No application in food packaging

However, some other statistics place polyethylene terephthalate (PET) as one of the most used material in food packaging. It is estimated that the production of this kind of packages is higher than 15 million tons each year [9]. This packages can be found worldwide but its presence is higher in Occidental Europe.

3 OVERVIEW OF THE PROBLEM

Fast development and the lack of sources have to face different global challenges like population growth, food safety or global warming. For that reason, efficient solutions have to be taken in order to get a sustainable development.

A sustainable development can't be thought without a transition from a linear economy, which consists mainly in "extract, manufacture, consume and throw", to a circular one. Circular economy is understand as the logical and viable alternative, which corrects the main problems of the linear one. Goods are not unlimited and they generate waste that is impossible to manage. The Circular Economy tries to ensure that products, components and resources still having their usefulness and value during their whole life. It is also understood like zero waste, what is done by sharing, repairing, reusing, re-manufacturing and recycling. Definitely, circular economy is focused on efficiency.

Thanks to plastic's versatility and its extended applications it has been possible to avoid lots of wastes, for example, food wastes. Circular economy proposes that at the end of the plastic's life, they should be repaired or reused instead of becoming a residue. Once this can't be done again, that residue can be recycled and used as a new source or raw material or even energy. This way, the circular economy's loop is closed.

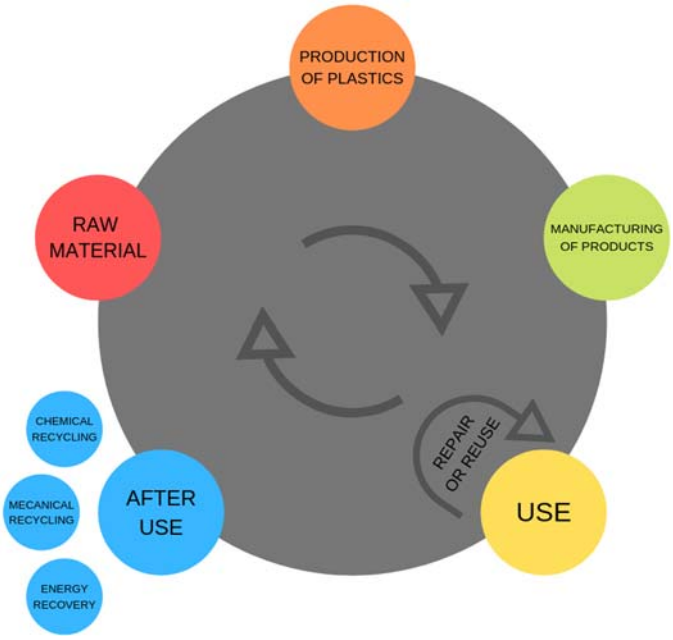

Figure 3: Circular economy's loop

The problem is that it doesn't exist the perfect circular economy, because there are still being large amounts of plastics that after their use, instead of being repaired or reused, are thrown in landfills.

Despite in the last 10 years the amount of recycled tons have increased in almost an 80% and the amount for energy recovery has increased near a 60%, the tons of plastic that are thrown still being large. It is estimated that these wastes have decreased in more than a 40%.

Finding information about what happen with plastic food-packages at the end of their life, we have [10]:

Table 5: Plastic food packages at the end of their life

Recycling	Landfill	Energy recovery
40,9%	20,3%	38,8%

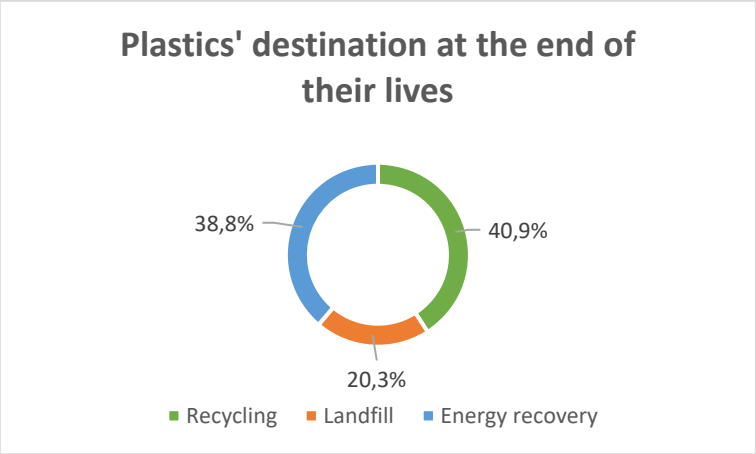

Figure 4: Plastics' destination at the end of their lives

This means that, of every 15 million tons of PET that are destined for food packaging, 6,135 million tons are recycled, 5,882 tons are destined for energy recovery and 3,045 tons are deposited in landfills.

For this reason among others, plastics are a current environmental issue that involves finding more environmentally friendly materials (for example glass) or some other different ways of recycling or removing plastics.

3.1 Bisphenol A or BPA problem

In the last years, this chemical product has been added in several plastic food packages in order to improve some of their properties. Mostly is used to improve the durability so food can be conserved optimally the most possible time [11].

However, reusing or repairing plastic containers as circular economy tries to introduce can have some side effects on human health. Despite foetuses, pregnant women and children are the most vulnerable for that problem, everybody can suffer some diseases like [12]:

- Cardiovascular and arterial diseases
- Diabetes and obesity
- Hormonal and fertility problems
- Disturbance of immune system
- Hyperactivity
- Anxiety

As BPA has become one important human health issue, plastic industry destinated for food packaging has to face the problem and try to find some new alternatives. Luckily, the consumption of this chemical is being reduced every day but, because of this problem, it's still impossibly reusing some plastics for food packaging.

For textile industry, BPA it isn't ~~a~~ so big problem because it doesn't have so~~any~~ negative consequences for human health. Every day more synthetic fibres are made of PET (mostly used PET bottles), which is becoming something widely accepted.

4 SOLUTIONS

As we have mentioned before, reusing or repairing plastics can be not safe for humans. However, don't reuse or repair it doesn't mean throwing plastic waste to landfills. According with Cintil Jose Chirayil, Raghvendra Kumar Mishra and Sabu Thomas in their report "Materials Recovery, Direct Reuse and Incineration of PET Bottles", we can classify all the different ways of treating plastic residues at the end of their life in order of preference [13]. As we will be able to see, the acting preferences of this classification are similar or based on the Circular Economy principles.

4.1 Primary recycling or ''Reusing''

The first one is understood as reusing. As we have already mentioned, it exists the BPA problem but, in case the plastic it isn't recovered with this chemical compound, there shouldn't be any kind of problem.

Despite it is thought that PET containers, like bottles, can't be reused because they can release some toxic elements it isn't this way. Chemically there are only two different substances that can harm human health which are antimony, which is used as a catalyst during PET fabrication, and formaldehyde or acetaldehydes (that sometimes cause the 'plastic flavour').

The truth is that, under some specific conditions, this harmful substances can be released, but the main problem is bacterial contamination. However, there shouldn't be any problem taking into account the number of cycles of each plastic and having some considerations like [14]:

- Don't fill the same containers lots of times and don't extend excessively their life cycle
- Don't mix the food or liquid they are containing or have contained. Never fill them with spoiled food or liquids.
- Don't leave the packages exposed to the sunlight
- Try to avoid high temperatures
- Clean the packages with soap and water, rinsing and drying them properly
- Don't share
- This preventive ways of acting should make safe reusing plastic or PET containers.

4.2 Secondary recycling or ''Mechanical Recycling''

Nowadays, mechanical recycling is the most used way of recycling plastics. However, not every plastic is valid for this kind of recycling. There are stablished some conditions in order to make it possible [15]:

- Non very degraded plastics are the only ones valid.
- It can't be possible to mix different kinds of plastics. For that reason, it has to be a previous separation of all the different kinds or a selective pick up of plastics is needed.
- There can't be external trash.
- Large amounts of plastic waste are needed in order to make the process viable (industrially and economically).

Therefore, this process is perfectly settled and developed, so we can distinguish two main mechanical recycling stages [16]:

4.2.1 Preparation of plastic waste

First of all, raw material (plastic waste), has to be cleaned in order to make possible to obtain a high valued final product. This stage is also for making longer the life of the machines that are involved during the whole process.

As we have already said in the stablished conditions, it can't be possible recycling different kind of plastics at the same time. For that reason, next step is separating and classifying into all different kinds. Nowadays, the techniques that are being used are based on differences of density (floatation techniques), techniques with solvents or spectroscopic techniques, among others.

After this previous steps, plastic waste is crushed into small grains, generally using stainless steel blades, and plastic grains are cleaned again in order to remove any impurities that may have. Then, they are dried by spin-dry. After that, another crushing process is carried on.

4.2.2 Obtaining pellets

Once it is obtained the desired granulometry, next step is melting process. The reason for making plastic almost dust is in order to make this stage easier. Melting process is part of the homogenization. Then, the melt is moulded into filaments (extrusion process). This filament has to be cut into small pieces using an helix. Finally, using water the cut melt is cooled obtaining the pellets, which later are dried by a spin-dry so they can be packed.

However, as we have already said before, the limitations of this kind of recycling still being not solved. For that reason, we have to think if this is the most viable choice. We should discuss if a transition to new ways of recycling are needed.

4.3 Tertiary recycling or ''Chemical Recycling''

Chemical recycling is a process, only possible for plastics, that consists in the decomposition of polymers into raw materials (called monomers) that can be used, among others, to make new plastics. The importance of this kind of recycling is because it helps plastic industry to achieve a properly natural resource management. It also maximizes the process of energy recovery [17].

Depolymerization is an alternative to primary recycling. Mechanical recycling needs large amounts of clean and homogeneous plastic waste in order to carry it out successfully. Otherwise, the obtained recycled product would have lower quality than the original one. Despite this way of recycling plays an important role in plastic waste management, considering this option as the only one means ignoring some economic and environmental benefits.

Therefore, chemical recycling solves all these problems, selection of plastics is not needed and heterogeneous or mixed plastics can be easily treated. It reduces collection and selection costs, and high quality final products are manufactured. However, chemical recycling is a nice alternative but it isn’t used in large scale because there are some processes that have to be studied so they can be optimized. Mostly is used in a complementary way of the mechanical recycling.

Chemical recycling can be done with several different chemical processes. Depending on the chemical agent used for the PET chain scission we can distinguish glycolysis, methanolysis, hydrolysis, hydrogenation, gasification, pyrolysis, chemical depolymerization, photodegradation, ultrasound degradation or degradation in the microwave reactor. Nevertheless, the most used are the first three ones [18].

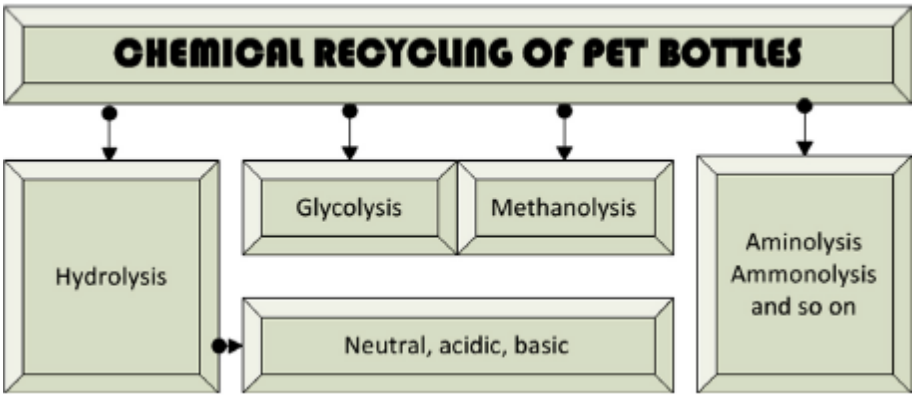

Figure 5: Main chemical recycling processes

4.3.1 Glycolysis

Glycolysis is the simplest and oldest method of PET depolymerization and mostly is used when the PET that we want to recycle is high valued. It is a slow chemical process in which, at temperatures between 180 and 250 ºC, the reaction of polyethylene terephthalate (PET) with glycols (commonly used ethylene glycol EG) happens, and gives as products PET oligomers, Bis(2-hydroxyethyl) Terephthalate (BHET), BHET Dimer and Ethylene Glycol. However, the reaction can be carried and several different glycols like such as diethylene glycol (DEG), propylene glycol (PG), polyethylene glycol (PEG) or 1,4-butanediol and hexylene glycol. In order to increase the speed of the chemical reaction, a catalyst is used [19 - 20].

It is consider as a versatile and important method because, during the process, the obtained products can be used as plasticizers, crosslinking agents, chain extenders, corrosion inhibitors, and precursors in the generation of value-added products. Furthermore, produced PET oligomers can be used later in the synthesis of other polymers like unsaturated polyesters, polyurethanes, vinyl esters, epoxy resins, textile dyes or antibacterial drugs, among others.

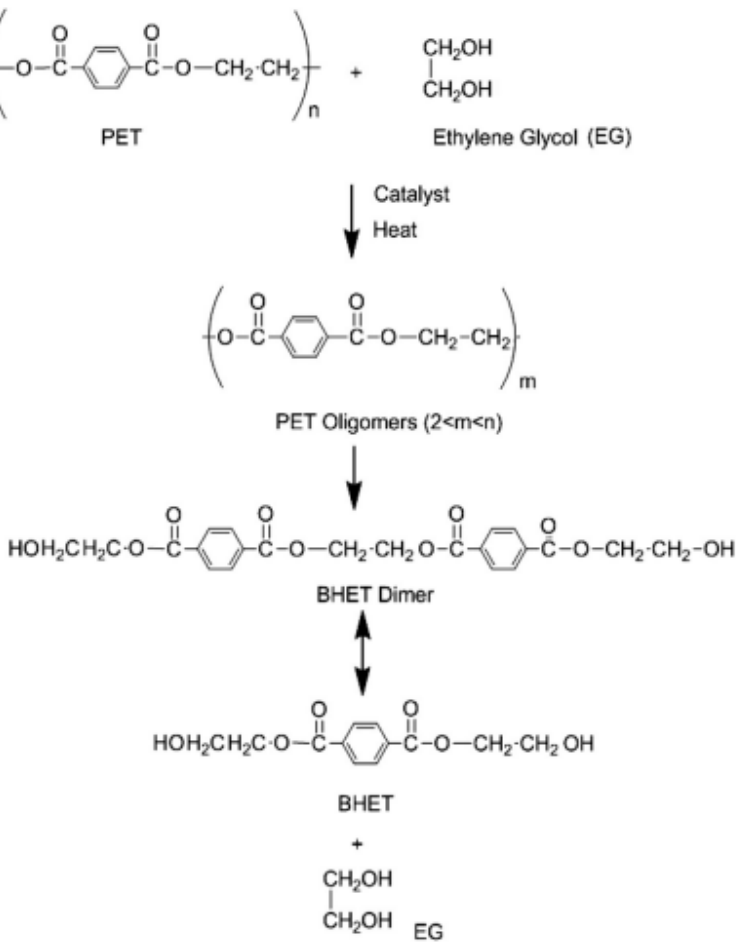

Figure 6: Glycolysis process

4.3.2 Methanolysis

Methanolysis is the second technique included in the most used ones. It is a PET depolymerization process based in making react this material with methanol (CH_3OH), a light, volatile, colourless and flammable liquid with a distinctive odour (similar to the ethanol's one). It is a methyl group with a hydroxyl group that makes it one of the simples alcohols [21].

Work conditions are stablished and, in order to make the reaction happen, temperatures from 180 to 280 ºC are needed. Talking about pressure, the range of values is from 20 to 40 bar. The reaction has a catalyst and it has to be done without water presence if we don't want to pollute the catalyst [22]. The chemical reaction that we have in this case is:

The obtained products are Dimethyl terephthalate (DMT) and Ethylene glycol (EG). Despite is a high performance reaction, the separation and refinement of the obtained products limit the use of this technique [23].

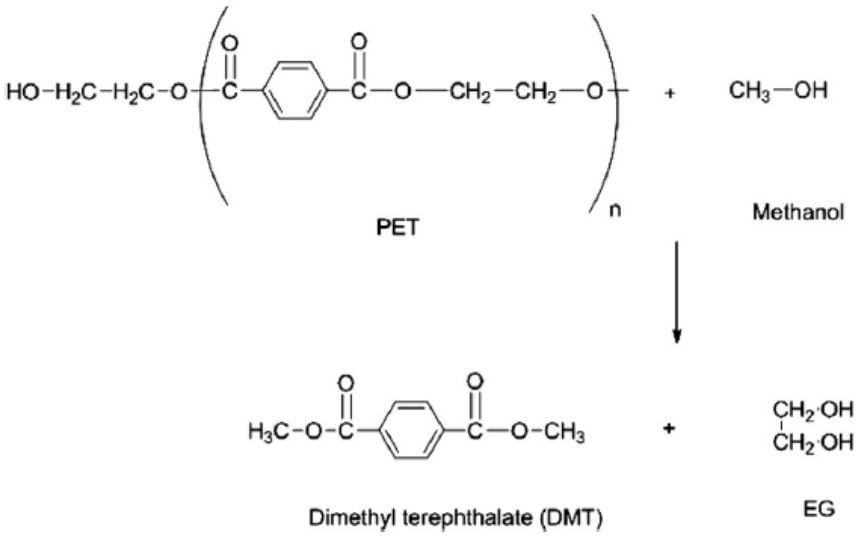

Figure 7: Methanolysis process

4.3.3 Hydrolysis

Hydrolysis is another way of depolymerization of PET. The main goal of this chemical process is the obtention of terephthalate acid (TPA) that can be used to produce new plastics. Despite it can be done under neutral conditions, acid conditions and alkaline conditions the main drawback is the low purity obtained TPA. This process is characterised for not being fast due to water is a weak nucleophile. The main scheme for all different kinds of hydrolysis could be summarized in [24]:

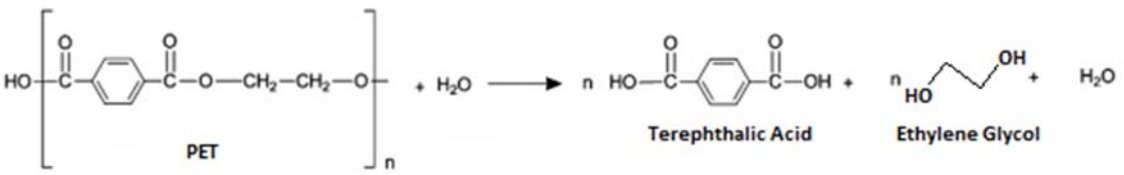

Figure 8: Hydrolysis process

4.3.3.1 Neutral Hydrolysis

Neutral hydrolysis means making react the PET only with water. The needed work conditions (pressure and temperature) for making PET depolymerization happen are stablished and they are 40 bar and 250 ºC. Under these conditions the chemical reaction we have is:

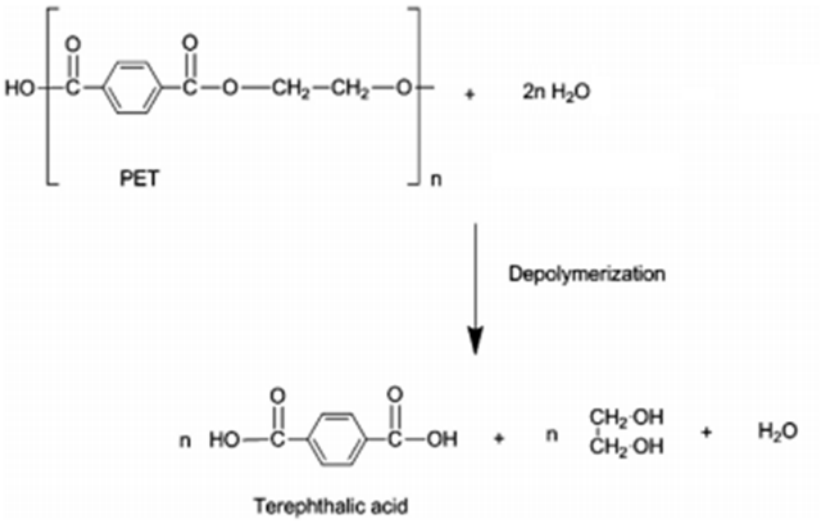

Figure 9: Neutral hydrolysis process

As we can see on the chemical reaction, we obtain as product a mixture of Terephthalic acid (TPA), Ethylene glycol (EG) and water. The first one is not soluble in water so the way of obtaining this component is by filtration. The second one is soluble in water, so the way of separating ethylene glycol is by distillation.

4.3.3.2 Acid Hydrolysis

This chemical process is similar to the previous one but the reaction is carried out with sulphuric acid (H_2SO_4) and water. Work conditions are also the same and the chemical reaction we have is:

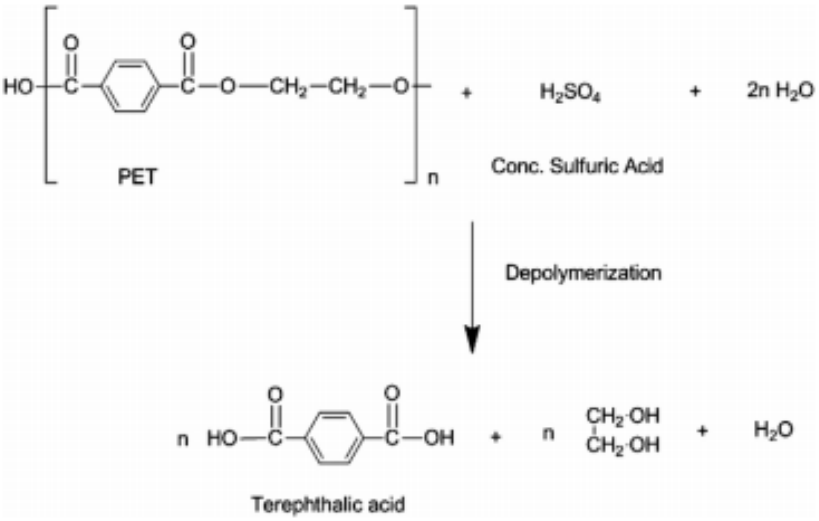

Figure 10: Acid hydrolysis process

The obtained results still being the same (Terephthalic acid (TPA), Ethylene glycol (EG) and water) and the obtaining techniques are also the same.

4.3.3.3 Alkaline Hydrolysis

This chemical process is similar to the two previous ones again but the reaction is carried out with an alkaline compound (e.g., sodium hydroxide). Work conditions are also 250 ºC and 40 bar of pressure. The chemical reaction we have in this case is:

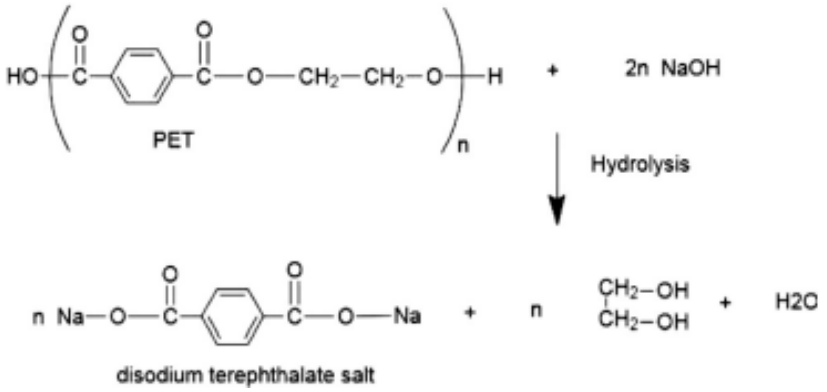

Figure 11: Alkaline hydrolysis process

Finally, the obtained products and the way of separating them, still being the same again.

4.4 Quaternary recycling or ''Energy Recovery''

This solution can be a good alternative for plastics that can't be sustainable recycled due to factors like the huge amount, low purity or the heterogeneous composition. For this kind of plastics classifying process is complicated and expensive and it's complicated to obtain a high valued recycled plastic.

For this reason, best choice is energy recovery carried out by incineration, instead throwing to landfills. Cogeneration installations recover heat and energy from plastic and some other combustibles. These installations are characterised for being efficient, safe and environmentally friendly [25].

5 WHY FUNCTIONALISED PET IN FOOD PACKAGING. CHITOSAN PROPERTIES

When we talk about food packaging, we are not only talking about transportation and storage functions. We need to take into account some other issues like microbes, because they are a problem for human health. For that reason, it's necessary to introduce the term 'antimicrobial packaging', which mainly consists in adding some chemical substances to the packages or directly use antimicrobial polymers, in order to prevent pathogenic microorganisms. As we have already said, PET is one of the most used material in food packaging so, when it is coated with some antimicrobial compound is known as 'functionalised PET'. These pathogenic microorganisms can shorter the time that food is conserved optimally, what is a risk for human health. For that reason, the main functions of this kind of packaging are microbicidal (reduction of the infectivity of microbes) and microbiostatic (inhibition of microorganisms growth), in order to ensure safety. The way they work is when a microbial growth happens, a lag phase is extended reducing that growth rate.

Chitosan is one of the most used materials in antimicrobial packaging. It is a natural compound that belongs to the non-migratory bioactive polymers and it is the second most abundant polymer in the world. It is obtained from the deacetylation of chitin and its name includes a wide range of different types based on the different molecular weights, viscosities and the degree of deacetylation (number of D-glucosamine units in the main chain). Chitosan's antimicrobial activity is mainly due to the amino functional groups which, diluted in acids form ammonium salts that reduce growth of microorganisms, like bacteria, yeast or filamentous fungi. However, this activity it depends on some other factors like the kind of chitosan, the degree of chitosan polymerisation, chemical or nutrient composition or environmental conditions, among others. Chitosan can be added directly to the food or it can be also used in a coating process. However, it is proved in several experiments that the best option is a combination of both techniques. Because of its properties, chitosan is viable for preserving food, specially of oxidation process, due to a water vapour permeability that don't allow oxygen to penetrate [26].

6 LABORATORY WORK. EXPERIMENTAL PART

Lab work consists in making a research in the field of the environmental engineering related with the chemical recycling of PET sheets. This succession of experiments will allow us to study and to understand how preparation of functionalised PET is done and how is possible to recycle it chemically. Chemical recycling will be carried out applying hydrolysis technique.

We will do it for some non-treated polyethylene terephthalate (PET) sheets and some others treated with a recovery of a 1 % solution of chitosan. This way, we will be able to do a comparation between both cases and see how the properties of each case are modified. We will focus on composition and differences in obtained products so we will set some conclusions about how it works and comment the best recycling option for each case.

Lab work can be divided into two big blocks. The first one consists in doing the neutral hydrolysis and the second one the alkaline hydrolysis. At the beginning of both cases, we will do the preparation of the plastics, cleaning and coating steps.

During all the lab work we will do several times IR spectrometry to see how the composition properties are modified. We will use the FT-IR (Fourier Transform Infrared) spectrometer. The usefulness of infrared spectroscopy is because each compound consists in different molecules that produce a different spectral fingerprints.

6.1 Instrumentation and materials

6.1.1 Laboratory instruments

- Reactor: 1 L stainless steel high pressure reactor from Ecom, Slovenija.
- Spectrometer: ATR FT-IR spectra were recorded on a Perkin Elmer Spectrum GX spectrometer. The ATR accessory (supplied by Specac Ltd.,UK) contained a diamond crystal.
- Glass instruments like trays, test tubes or pipettes among others.

6.1.2 Materials

- PET material $(C_{10}H_8O_4)_n$, obtained from a thin PET roll available in the lab
- Distilled water
- Chemicals:
    - 1 % solution of chitosan, prepared in the lab and obtained after deacetylation of chiting in an aqueous solution of sodium hydroxide, rinsing of resulting precipitate with water, dissolving the obtained mass acetic acid and neutralization with sodium hydroxide.
    - Commercial chitosan, brand Sigma-Aldrich.
    - Sodium hydroxide (NaOH) in pellets, commercial brand Sigma-Aldrich.
    - Sodium hydroxide (NaOH) granulated, commercial brand GRAM-MOL, Zagreb.
    - Terephthalic acid (TPA, $C_8H_6O_4$) in dust, commercial brand Sigma-Aldrich.
    - 37 % hydrochloric acid (HCl) solution, commercial brand GRAM-MOL, Zagreb.

6.2 Coating process preparation

First of all, we decided to do the experiment with 12.5g of PET. Once we had it decided, we cut two packs of six sheets each one from a PET roll and we measured to see if we had the desired weight. Once we did it, we proceed to clean them. We put each pack in a bowl with ethanol and we waited for some minutes. Later, we used some ultrasounds and then we left the sheets drying for more than half an hour.

Figure 12:Cleaning with ultrasounds step

Figure 13: Drying process

After that, we took one of the packs and we recovered PET sheets with 1 % solution of chitosan. We left them for some minutes and then they were drying for some days.

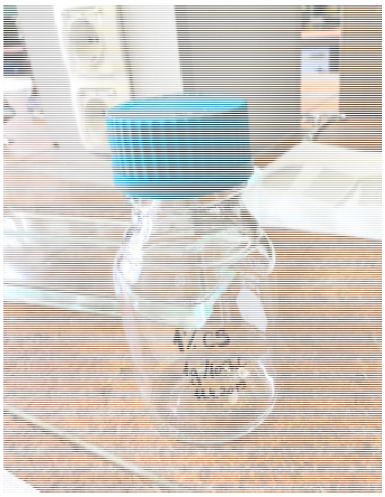

Figure 14: 1 % solution of chitosan

Figure 15: Coated sheets drying

6.3 Composition study with the spectrometer

Once we had the coating process ended, we studied the composition of both type of sheets with a FT-IR spectrometer. The operating principle of the FT-IR spectrometer consists in radiating with infrared a sample. Some of the radiation is transmitted through the sample and some other is absorbed. A detector placed in the spectrometer interprets the transmitted signal and represents a molecular fingerprint of the sample. The detector's output is translated by the Fourier Transform and it creates the spectrum that give us information that can be used to quantify or identify materials [27]. Using a software called "Spectrum v5.3.1", it is possible to translate spectrometer's info and graph them. The program represents the wavenumber on the abscissa axis and transmittance on the ordinate axis. Wave number is understood as the spatial frequency of a wave [cm^{-1}] and the transmittance of the surface of a material is its effectiveness in transmitting radiant energy [%]. A total of 16 scans were taken for each sample with a resolution of 4 cm^{-1}. All spectra were recorded at ambient temperature over a wavelength interval between 4 000 and 650 cm^{-1}.

Figure 16: FT-IR spectrometer

We did PET sheet spectrum, commercial chitosan spectrum and coated sheets spectrum separately in order to make a comparation and have some conclusions. Some considerations we had while we were measuring were that in the case of covered sheets, the chitosan coating could not be spread evenly on the sheet's surface. For that reason, in each sheet we did one measure in both sides (in total twelve different measures) so at the end we could choose a valid or better scan. The final obtained results were:

Date: 4/15/2019

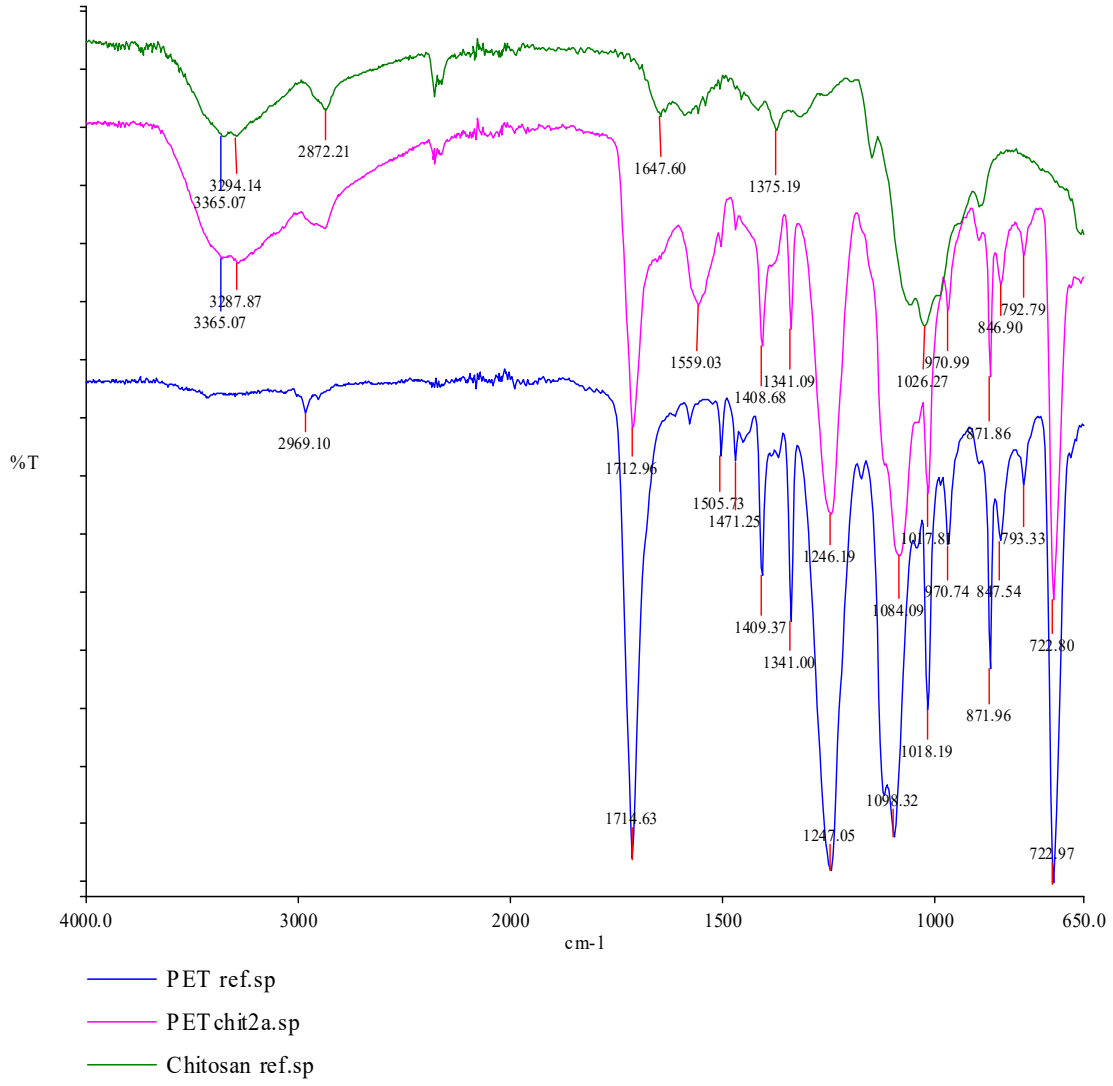

Figure 17: PET, PET + chitosan and chitosan spectra

As we can see in Figure 17, we have three spectra, blue spectrum is PET reference, pink spectrum is PET + chitosan and green spectrum is spectrum of chitosan. In the case of PET + chitosan spectrum (pink), we can conclude that we obtain successful coating of chitosan on PET foil. In PET + chitosan spectrum we can see typical signals for chitosan (signals in the range from 3370 to 3280 cm^{-1}, and signal at 1560 cm^{-1}) as well as signals for PET foil (signal at 1714 cm^{-1}).

6.4 Neutral hydrolysis in the reactor

Next step it was carrying out the neutral hydrolysis in the reactor. We did it for the PET sheets and for the coated ones. The technique for both cases it was similar. We put inside the reactor the sheets cut into small pieces (in both cases were around 12.5 g as we said before) and we also put 250 mL of distilled water. The reached pressures and temperatures (work conditions) in order to allow the process be completed must be 40 bar and 250 °C, what means that they have to go from 0 bar to 40 bar and from environment temperature (20 - 25 °C~~ºC~~) to 250 °C. Once we connected the reactor we started taking some data every 15 minutes about pressure and temperature until the stablished temperature was reached. Once we had it we had to wait 10 min more so the experiment could have some equilibrium and the reached pressure could be more near to the 40 bar. The reason for taking these data it wasn't only for seeing if the experiment was developing properly, it was also for making some graphs (for both cases) and see how the process vary.

Figure 18: Reactor

For the PET sheets case we have:

Table 6: Neutral hydrolysis of PET sheets

PET amount (g)	12.29
Amount distilled water (mL)	250
Terephthalic Acid amount obtained (g)	8.6

Table 7: Temperatures and relative pressures measured during the neutral hydrolysis of PET sheets

Clock (h:min)	Time (min)	T (ºC)	Relative pressure (bar)
9:23	**0**	24	0
9:38	**15**	95.4	0-0.5
9:53	**30**	140.5	3
10:08	**45**	188.3	11.5
10:23	**60**	233.6	29
10:38	**75**	248.3	38
10:42	**79**	250	39
10:52	**89**	251.1	40

For the coated sheets:

Table 8: Neutral hydrolysis of PET + chitosan sheets

PET amount (g)	12.42
PET + chitosan amount (g)	12.55
Amount distilled water (mL)	250
Terephthalic Acid amount obtained (g)	8.7 after first filtration
	0.48 after second filtration

Table 9: Temperatures and relative pressures measured during the neutral hydrolysis of PET + chitosan sheets

Clock (h:min)	Time (min)	T (ºC)	Relative pressure (bar)
9:00	**0**	23.7	0
9:15	**15**	93	0-0.2
9:30	**30**	130.6	2
9:45	**45**	186.6	11
10:00	**60**	234.5	29.1
10:15	**75**	249.4	37
10:17	**77**	250	38
10:27	**87**	250.9	38.9

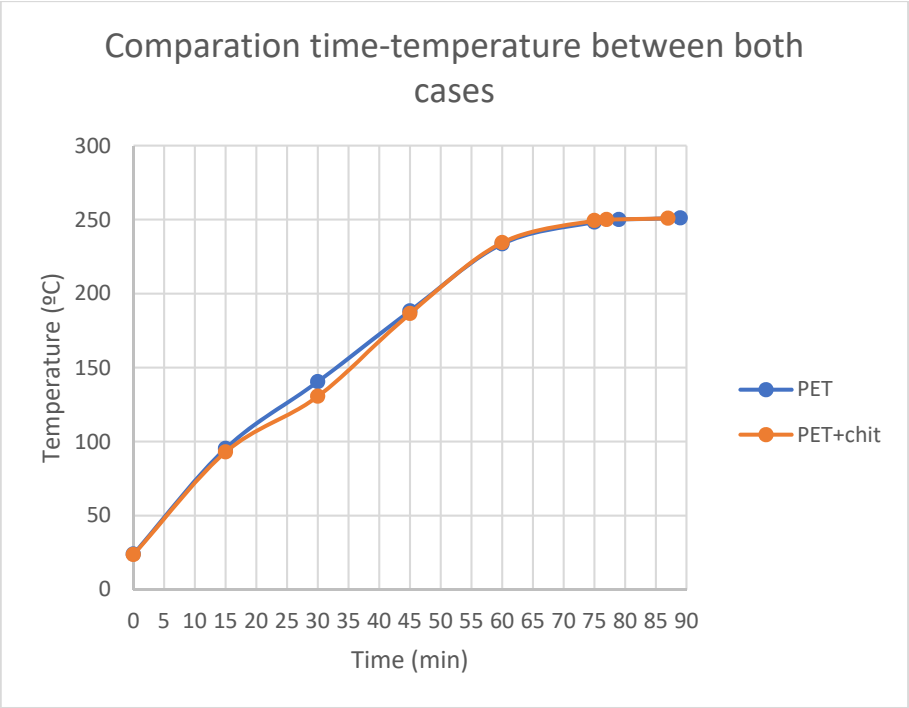

Figure 19: Comparation time - temperature between both cases (neutral hydrolysis)

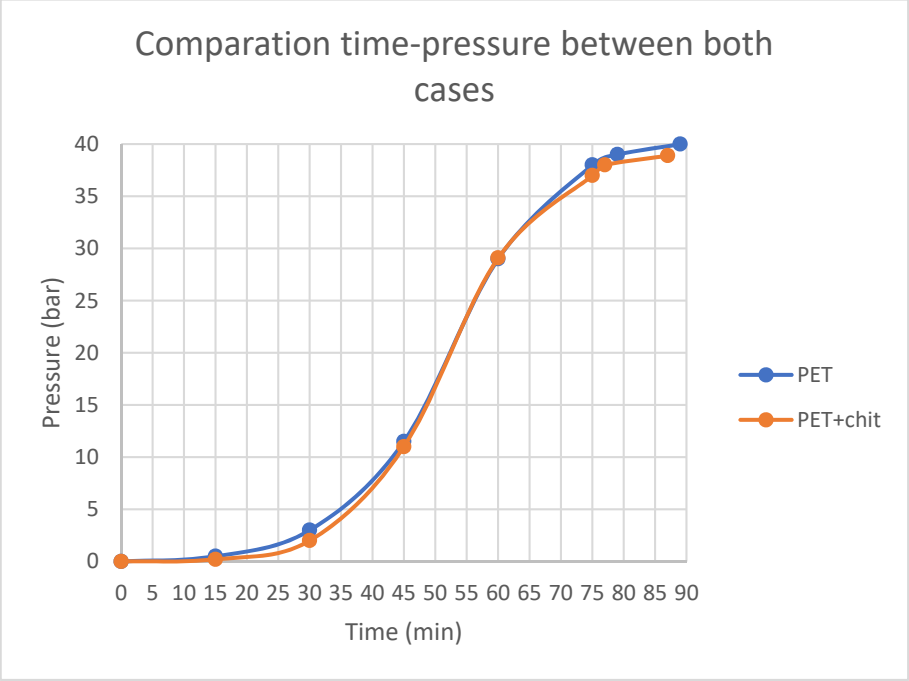

Figure 20: Comparation time - pressure between both cases (neutral hydrolysis)

Having a look at Figure 19 and Figure 20, we can conclude that both cases were carried out almost in an equal way because the addition of 1% solution of chitosan it doesn't modify apparently the process.

6.5 Separation of Terephthalic Acid (TPA)

Despite the hydrolysis for both cases its very similar, attending to the obtained products they look very different. For the PET sheets we obtain a non-coloured or white product while for the coated one the obtained product is orange-brown.

As we said in the theoretical part, the obtained products from the hydrolysis is a mixture of terephthalic acid, ethylene glycol and water. In order to obtain the terephthalic acid, which is not soluble in water, we used the filtration technique. This was the most interesting part because for the PET sheets case it looked white and homogeneous while for the coated case looked more heterogenous, with some black particles that made us think they were carbon because reached temperatures may have burnt the chitosan.

Figure 21: Filtration process and TPA of PET sheets (neutral hydrolysis)

Figure 22: Filtration process and TPA of PET + chitosan sheets (neutral hydrolysis)

For the coated sheets we did a second filtration. The reason why we did two times this process was that the solution of ethylene glycol and water still having some solid particles that made the liquid doesn't look transparent.

Next step it was analysing both products with the IR spectrometer and make a comparative with the commercial terephthalic acid. The obtained results were:

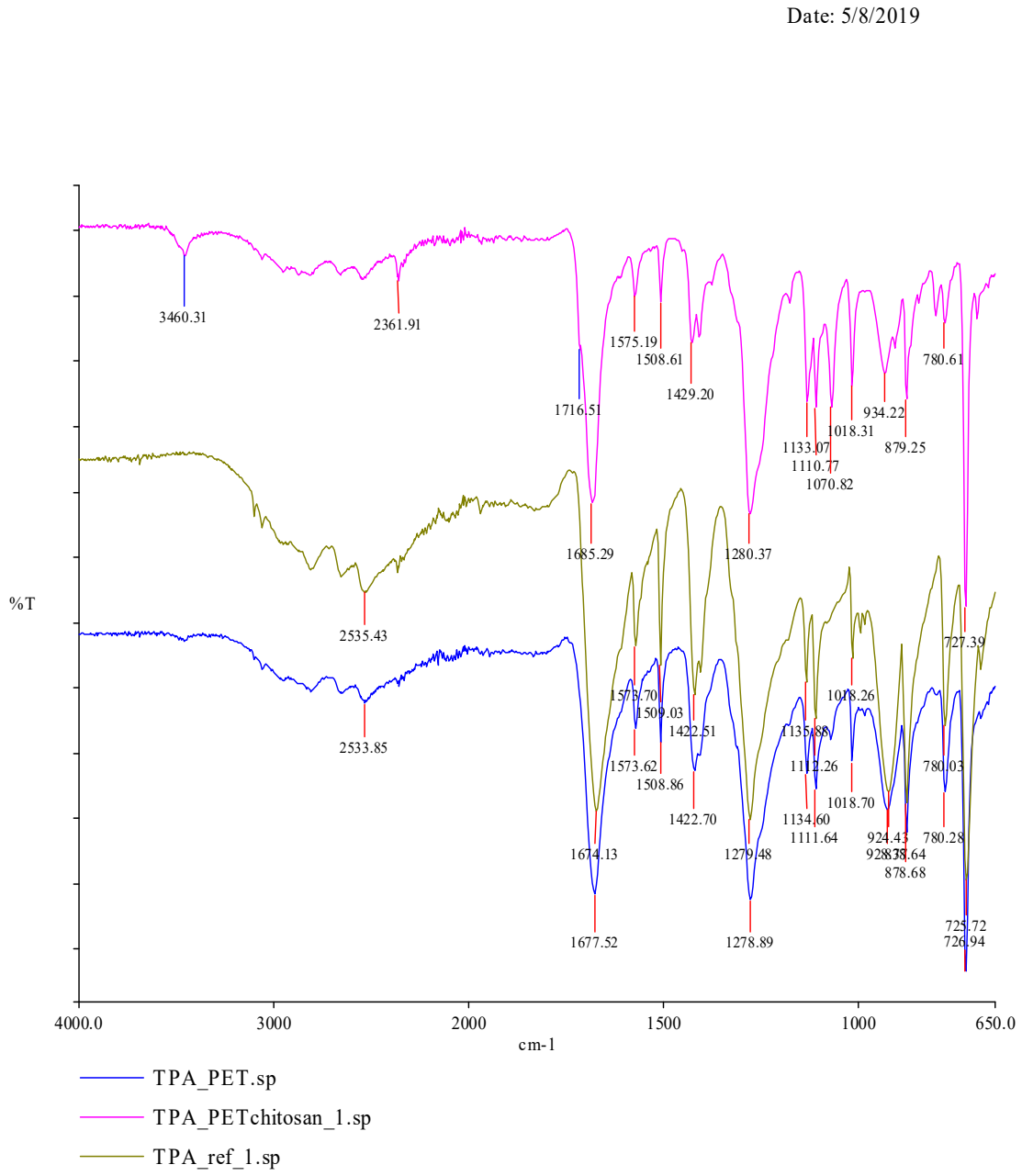

Figure 23: TPA spectrum of PET sheets, TPA spectrum of PET + chitosan sheets and TPA reference spectrum (neutral hydrolysis)

As we can see in Figure 23, for the first case (the blue spectrum) the curve looks similar, what makes us think the depolymerization has been done properly. However, for the second case (pink spectrum) we have some different signals. The first one it may be related with the presence of chitosan but the most interesting part is the one in the characteristic peak that have every PET (which corresponds to the ester group). Having a look we see a smaller signal, a small second peak at the wavenumber 1716 cm^{-1}, that corresponds to a ester bond. It may indicate that the depolymerization is not completed.

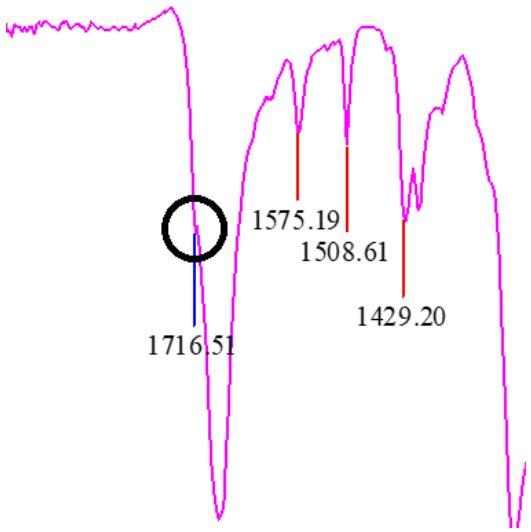

Figure 24: Ester bond peak in PET + chitosan case (neutral hydrolysis)

We also did the IR spectroscopy for the TPA obtained after the second filtration and we obtained the same result, as it was expected. Both spectra had the same shape and in both was visible the problem of the uncompleted depolymerization.

6.6 Improving purity of the TPA from depolymerized product

This process is stablished and consists in making react TPA molecules with solution of sodium hydroxide (NaOH) in order to obtain an organic salt of TPA, which is soluble in water, and some insoluble residue.

The removing of the residue will be done by filtration technique and we will add to the solution, hydrochloric acid (HCl). This way it's going to happen a recombination that will give as a result a TPA molecules.

As we said, stoichiometry is stablished, what means that we have to calculate the needed amounts given the initial one. Anyway, the experiment would happen wrong.

STEPS:

1. Initial amount of terephthalic acid (TPA): 5 g
2. We have to calculate the number of TPA moles

   Molecular mass of TPA: 166.13 g/mol

   TPA moles = 5/166.13 = 0.0301 mol
3. Stoichiometry says the number of NaOH is double

   NaOH moles = 2 x 0.0301 = 0.0602 mol
4. Now we can calculate the required mass of NaOH

   Molecular mass of NaOH: 40 g/mol

   Mass NaOH = 0.0602 x 40 = 2.407 g

With this calculated values we have to prepare a solution of 2.407 g of NaOH in 50 mL of distilled water:

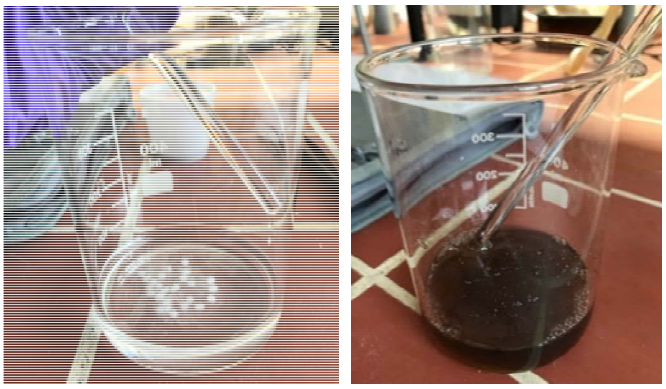

Figure 25: Preparation of NaOH solution and addition of TPA (purification step)

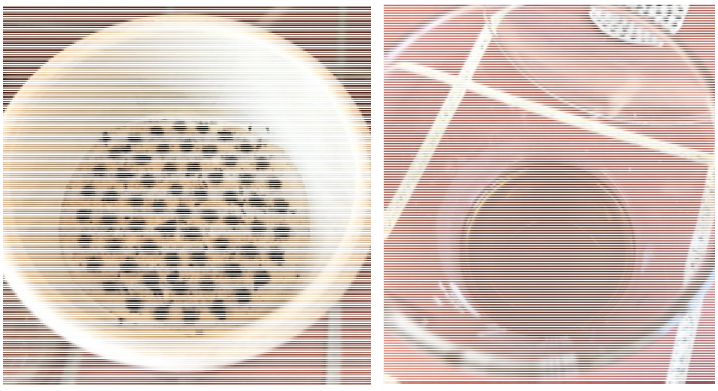

Figure 26: Filtration of impurities (purification step)

Next is calculating amount of HCl we have to add. It has to be the same number of NaOH moles. We will add a commercial solution of HCl, specially we will use the concentrated HCl (37% solution), so we have to do calculations according to this concentration.

STEPS:

1. HCl moles = 0.0602 mol

   Molar mass HCl = 36.5 g/mol

   Mass HCl = 2.19 g

2. Applying proportionality:

   100g 37 % HCl ---------- 37g 100 % HCl

   X g 37 % HCl ---------- 2.19 g 100 % HCl

   So we have: X = 100 x 2.19 / 37 = 5.9 g

3. Knowing mass and density of the 37 % HCl solution, which is 1.18 g/ml [28], we can finally calculate the volume we have to add:

   V = 5.9 / 1.18 = 5 mL of HCl solution

Figure 27: Addition of HCl solution (purification step)

Last step in improving purity process is filtering once again in order to obtain the TPA:

Figure 28: Purified TPA

After this process, the obtained amount of TPA was 3.42 g and 0.02 g of impurities. Now, we have to check (doing the IR analysis) if we remove impurities from obtained product after depolymerisation. Impurities were degradation product of chitosan and products of incomplete depolymerisation (oligomers). We did it and the results were:

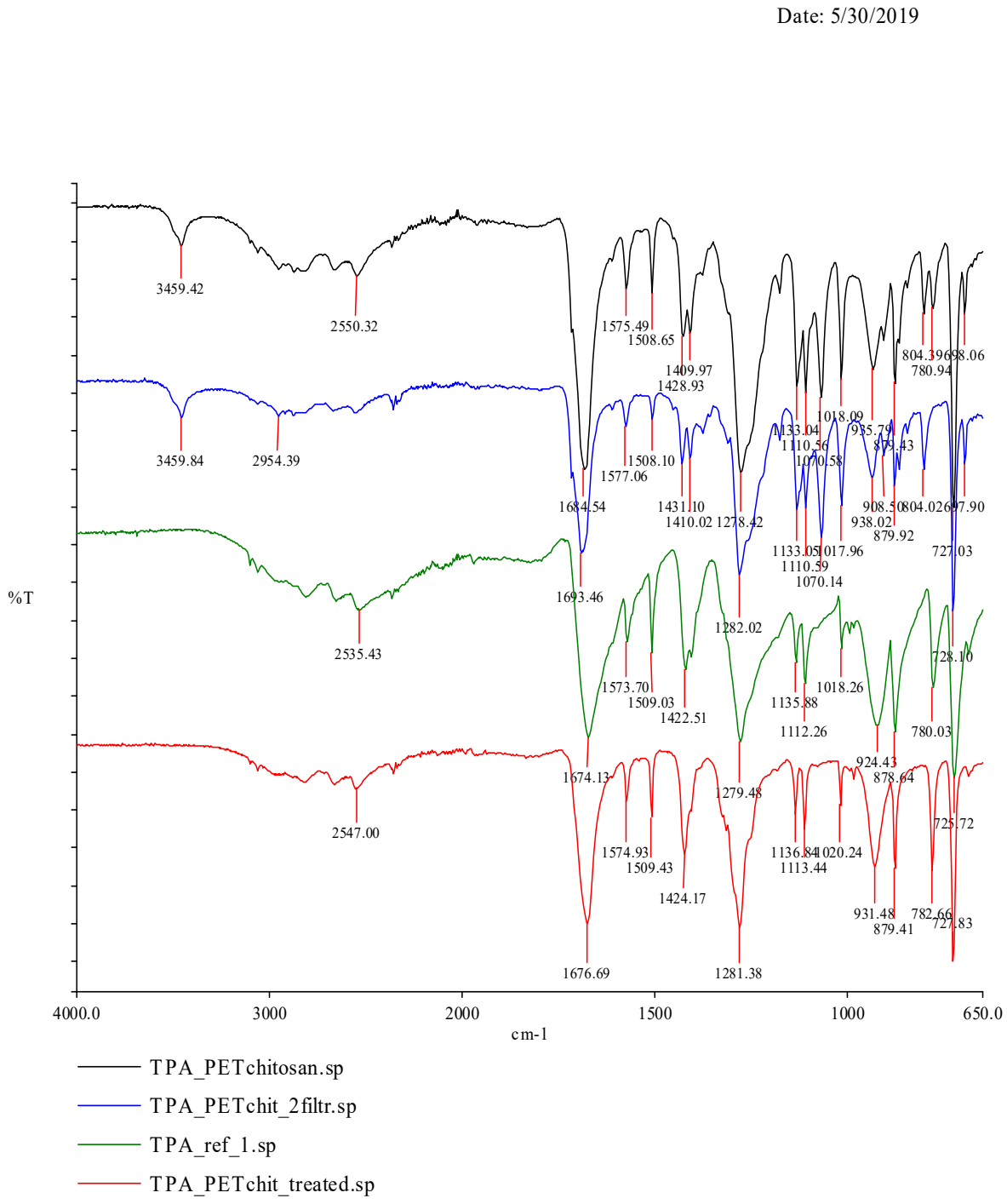

Figure 29: TPA spectra after first and second filtration (neutral hydrolysis), Treated TPA spectrum and TPA reference spectrum

From the Figure29, we can conclude that the obtained product after the first (black spectrum) and second (blue spectrum) filtration it's the same. Moreover, we can compare the obtained TPA after neutral hydrolysis (black spectrum) and the TPA after improving the purity (red spectrum). From the FT-IR spectra we can conclude that the purification was successful. Furthermore, we can compare all of them with the commercial TPA and conclude they all are the same product. It should be noted that in the obtained products after neutral hydrolysis (black and blue spectra) it appears other signals at the beginning that are probably due to the presence of water. This was because the product wasn't completely dry.

6.7 Considerations of this method

This method works perfectly for the case of non-treated sheets. However, for the case of PET + chitosan, the neutral hydrolysis is not enough and an additional process to improve purity has to be done.

This process not only makes longer the degradation process, it also makes it more expensive (more chemical compounds and chemical processes are needed) and the final amount and the purity of terephthalic acid is lower because in each step some amount of material is lost.

Furthermore, this process is quite similar to the alkaline hydrolysis. For that reason, we are going to carry out it because, if it works properly, the depolymerization process for PET + chitosan sheets it would be much faster.

6.8 Alkaline Hydrolysis

As we have already said, now it’s the turn for the alkaline hydrolysis. In this case, we only did this kind of hydrolysis for the coated sheets. First step it was repeating coating process like in the other case. Once we had it all done, we carried out the alkaline hydrolysis in the reactor, which is similar to the neutral hydrolysis but instead of distilled water, we use a solution of NaOH in water.

Second step is calculating the solution that we have to put inside the reactor with the sheets cut into small pieces (12.67 g). The needed pressures and temperatures (work conditions) are again 40 bar and 250 °C. In order to get that value of pressure we have to make a solution of 250 mL.

We know that the needed amount of NaOH for alkaline hydrolysis when we work with 25 g of PET and 250 mL of water it's 10.5 g. In or case we work with 12.5 g so we can calculate the amount of NaOH applying proportionality:

25 g PET ---------- 10.5 g NaOH

12.5 g PET ---------- X g NaOH

X = (10.5 x 12.5) / 25 = 5.25 g NaOH

However, we can also calculate it applying stoichiometry and see that both results are similar. Knowing that chemical reaction is: PET + 2 NaOH → TPA (salt) + H_2O + impurities

STEPS:

1. PET mass = 12.67 g

   Molar mass PET ($C_{10}H_8O_4$) = 192 g/mol

   PET moles = 12.67/192 = 0.066 mol PET

2. Moles of NaOH = 2 x 0.066 = 0.132 mol NaOH

   Molar mass NaOH = 40 g/mol

   NaOH mass = 0.132 x 40 = 5.28 g

Figure 30: Preparation of NaOH solution for alkaline hydrolysis

After preparing the NaOH solution and putting it into the reactor we connected it. We did like in the other cases, we started taking some data every 15 minutes about pressure and temperature until the stablished temperature was reached. Once we had it we had to wait 10 min more so the experiment could have some equilibrium and the reached pressure could be more near to the 40 bar.

For this PET + chitosan sheets we have:

Table 10: Alkaline hydrolysis of PET + chitosan sheets

PET amount (g)	12.67
PET + chitosan amount (g)	12.84
Amount distilled water (mL)	250
Terephthalic Acid amount obtained (g)	10.21

Table 11:Temperatures and relative pressures measured during the alkaline hydrolysis of PET + chitosan sheets

Clock (h:min)	**Time (min)**	**T (ºC)**	**Relative pressure (bar)**	
9:25	**0**	20.8	0	
9:40	**15**	71	0.1	
9:55	**30**	91.5	0.2	**During the process there was a valve open that didn't allow to continue the process, so it stayed in equilibrium. However, when we closed it, the experiment continue in a normal way and the depolymerization process wasn't disturbed.**
10:10	**45**	96.3	0.2	
10:25	**60**	96.6	0.2	
10:40	**75**	160.3	5	
10:55	**90**	216	20	
11:10	**105**	244.9	35	
11:17	**112**	250	38	
11:27	**122**	250.8	39	**Cooling**

With the obtained data from Table 11, we can graph some results and see how temperatures and pressures have been in equilibrium during some minutes until the problem was solved. We can also graph how it would have been without the equilibrium.

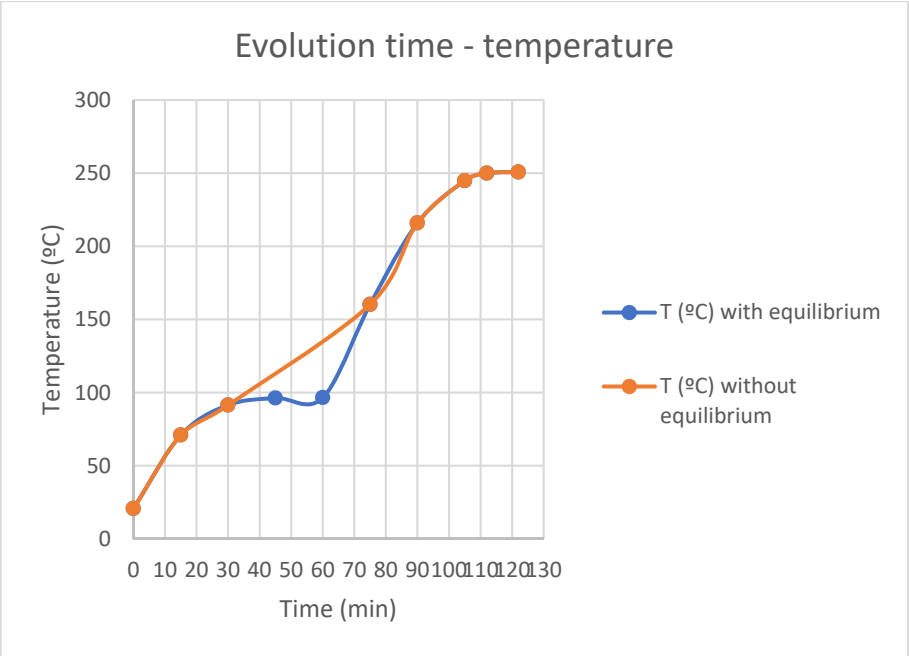

Figure 31: Comparation time - temperature between both cases (alkaline hydrolysis)

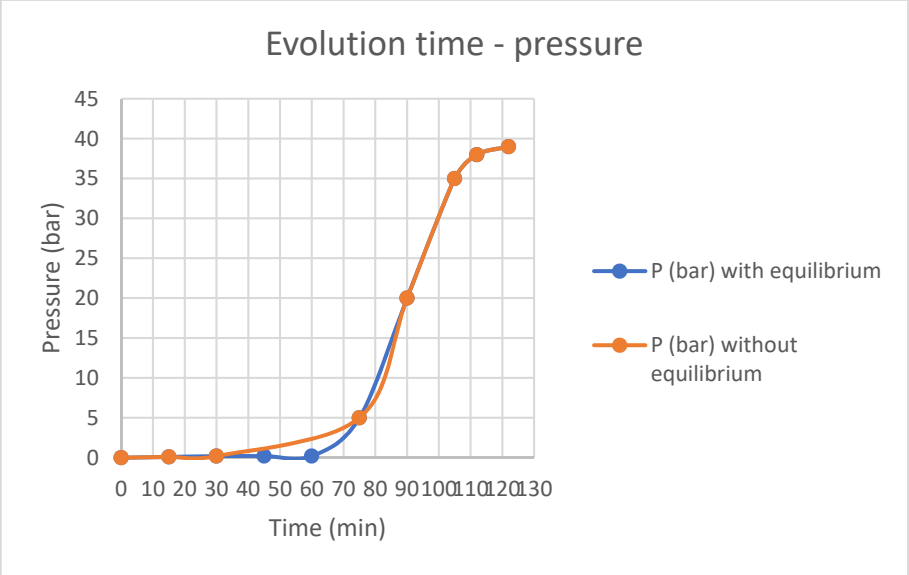

Figure 32:Comparation time - pressure between both cases (alkaline hydrolysis)

Once we took out the product from the reactor, we had the solution of the organic TPA salt, water and impurities. As we did in the purification step, we have to filter of to remove impurities and then we have to add hydrochloric acid (HCl) to obtain TPA.

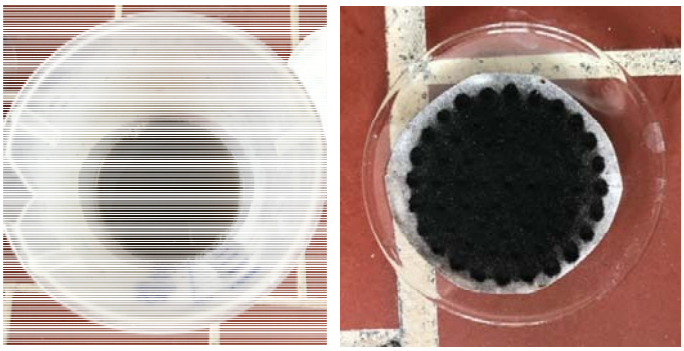

Figure 33: Filtration of impurities (alkaline hydrolysis)

Despite it doesn't matter if we add hydrochloric acid in excess, we have to calculate the amount of solution of HCl. As in the other case, it has to be the same number of NaOH moles and we will add a commercial 37 % HCl solution.

STEPS:

1. HCl moles = 0.132 mol (it's the same of NaOH, twice the number of PET moles)
   Molar mass HCl = 36.5 g/mol
   Mass HCl = 0.132 x 36.5 = 4.818 g HCl
2. Applying proportionality:
   100 g 37% HCl ---------- 37 g 100%HCl
   X g 37% HCl ---------- 4.818 g 100%HCl
   So we have: X = 100 x 4.818 / 37 = 13.02 g
3. Knowing mass and density of the 37 % HCl solution, which is 1.18 g/ml [29], we can finally calculate the volume we have to add:
   V = 13.02 / 1.18 = 11.03 mL of HCl solution

Finally, we add it and filter it off to obtain the TPA:

Figure 34: Addition of HCl solution and obtention of TPA (alkaline hydrolysis)

Last step is to analyze the terephthalic acid (TPA) in the spectrometer to see if the depolymerization has been complited:

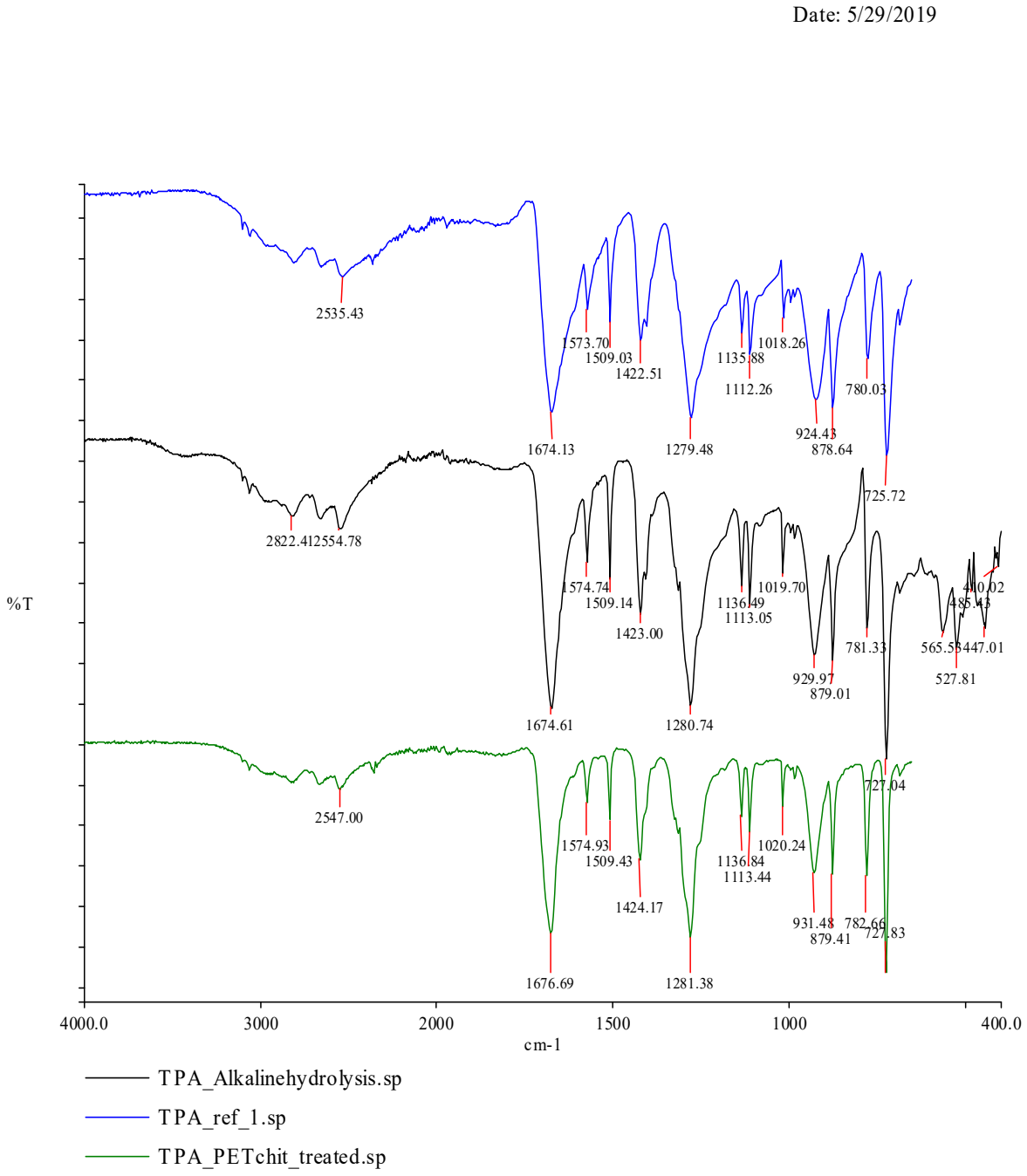

Figure 35:TPA spectrum after alkaline hydrolysis, TPA treated spectrum and TPA reference spectrum

As we can see (Figure 35) in the obtained product after alkaline hydrolysis (black spectrum), depolymerization is completed. Comparing it with the TPA improved purity (green spectrum) and the commercial one (blue spectrum) we can conclude that for the three cases we have almost the same product.

6.9 Analysis of the impurities

Finally, we can make a comparation between the impurities that we obtained during the purification step and the ones obtained during the alkaline hydrolysis. In order to make it we analysed them in the spectrometer and the results were:

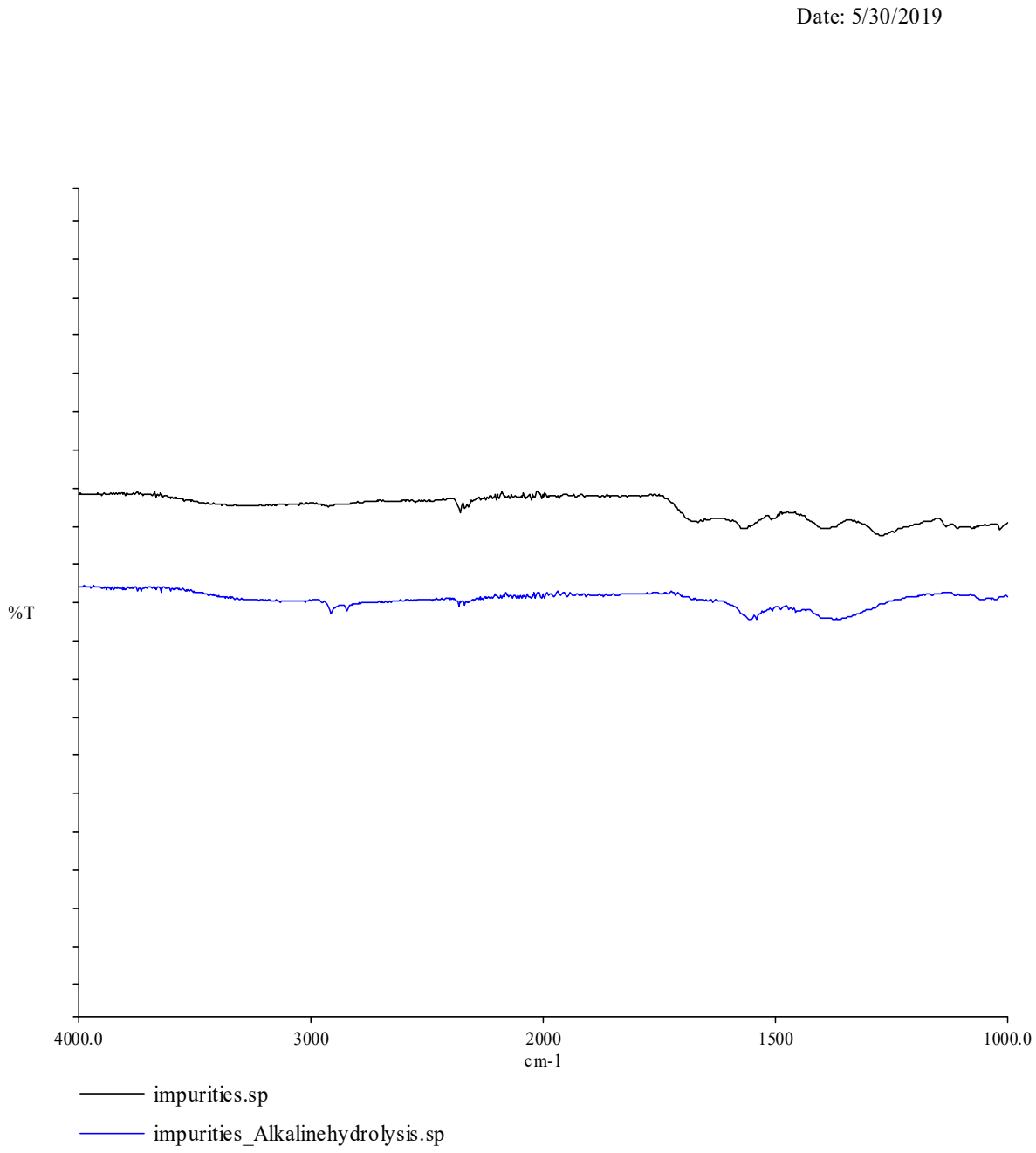

Figure 36: Impurities spectra

In Figure 36, we can see the black spectrum, that correspond to the purification step impurities, and the blue spectrum that is from alkaline hydrolysis impurities. Despite spectra have some different details (probably because products weren't dried at all), they are almost the same shape, what makes us think what we had already said. Impurities come from burnt chitosan and not from contamination in the reactor due to other experiments.

This impurities can be used as bio-charcoal or in the soil as a humus enhancer. However, this is something innovative that needs to be researched, but it exists the potential. A nice starting point for the research it could be the elemental analysis of Carbon (C) and Nitrogen (N).

7 RESULTS

With the different amount of terephthalic acid (TPA) during the different chemical processes, we can calculate the yield of the chemical reactions that have been carried out in order to make a comparation and decide which method is the best. To calculate them, first we have to know the molecular mass of PET and TPA and the amount of used reagent and obtained product.

Table 12: Molecular weight of PET and TPA. Amounts of introduced PET in the reactor and obtained product from the reactor

Molecular Mass PET ($C_{10}H_8O_4$)	**Molecular Mass TPA**
192 g/mol	166.13 g/mol

PET sheets case – Neutral Hydrolysis	
PET	**TPA**
12.29 g	8.6 g
PET + chitosan sheets – Neutral Hydrolysis	
PET	**TPA***
12.42 g	9.18 g
TPA*	**TPA**
5 g	3.42 g
PET + chitosan sheets – Alkaline Hydrolysis	
PET	**TPA**
12.67 g	10.21 g
*Amount of non-completed depolymerized PET	

- Yield of PET sheets – Neutral Hydrolysis
  1. Number of PET moles = 12.29 / 192 = 0.064
  2. Number of TPA moles = 8.6 / 166.13 = 0.0518
  3. **Yield =** 100 x (0.0518 / 0.064) **= 80.87%**

- Yield of PET+chitosan sheets – Neutral Hydrolysis

1. Number of PET moles = 12.42 / 192 = 0.065
2. Knowing that with 5 g of TPA* we obtain 3.42 g of TPA, applying proportionality we have:

   5 g of TPA* ---------- 3.42 g of TPA

   9.18 g of TPA*---------- X g of TPA

   So we have: X = (3.42 x 9.18) / 5 = 6.28 g of TPA
3. Number of TPA moles = 6.28 / 166.13 = 0.0378
4. **Yield =** 100 x (0.0378 / 0.065) **= 58.15%**

- <u>Yield of PET+chitosan sheets – Alkaline Hydrolysis</u>
  1. Number of PET moles = 12.67 / 192 = 0.066
  2. Number of TPA moles = 10.21 / 166.13 = 0.0614
  3. **Yield =** 100 x (0.0614 / 0.066) **= 93.03%**

Differences on the yield are the expected ones. During the process, there is a huge amount of material that can't be used because it remains in the containers. For that reason, the longer is the process is, means that more containers are used and more material is wasted. Based on this, the second case is the longest, so we can justify its low yield.

For that reason, we can conclude that if we want to do the chemical recycling of PET, we can do it with both techniques. If we decide to use neutral hydrolysis it would be cheaper because you only need water to carry it out but it has lower yield than the alkaline one. However, for coated sheets it's much better to use directly the alkaline hydrolisis so we can obtain more amount of TPA (higher yield) and make it faster and cheaper.

8 CONCLUSIONS

On the one hand, to conclude the work we will evaluate the level of scope of the proposed objectives, indicating that by using the two techniques (neutral and alkaline hydrolysis), satisfactory results have been achieved, such as the obtaining of terephthalic acid (TPA). This way, we can conclude that we have successfully completed the depolymerization of PET and PET with a chitosan coating.

On the other hand, the theoretical approaches that were made before the beginning of the practice, made us hope that the way to carry out the chemical recycling only depended on the technique used. On the contrary, with the development of the experimental work, we realized that it was also conditioned by the characteristics of the used materials.

For the evaluation of the design of the practice that allows reaching the objectives, we will highlight that the use of two different techniques to carry out and compare, allows us to obtain two different justifications for the results that are exposed. This makes a greater certainty that they have been developed correctly. In addition, this allows showing the possible effects or considerations that must be taken into account to minimize inaccuracies during the development of the method.

Collecting all these exposed reasons, it is considered that the work has achieved the objectives that were proposed and, the way in which it was thought, is the right one.

Finally, we can conclude that biodegradability, biocompatibility, antimicrobial activity, non-toxicity and versatile chemical an physical properties ~~make~~ of chitosan makes it a viable option for using as functionalised PET. Furthermore, its mechanical properties also need to be highlighted because they can be compared with the ones of medium-solid polymers.

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