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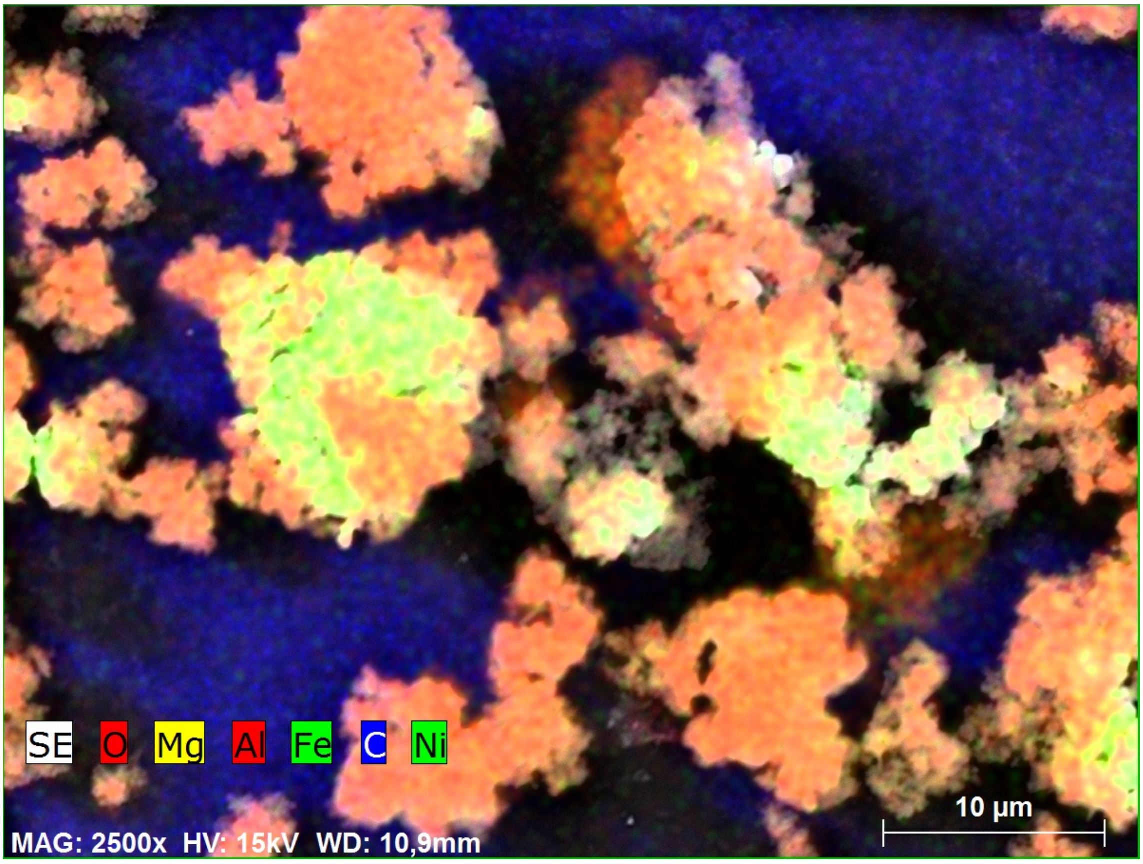

Synthesis of a Magnetic Catalyst for Depolymerisation of Polyester

-A magnetic Magnesium-Aluminium mixed Oxides Catalyst

Master's thesis in Materials Chemistry

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CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2016

Synthesis of a Magnetic Catalyst for Depolymerisation of Polyester

by

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Cover: Energy-dispersive X-ray spectroscopy picture of MgAl-O@Fe_3O_4 catalyst, x2500

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ABSTRACT

Polyester today is the most common textile fibre, and the large production and use leads to large amounts of waste. To handle the waste, chemical recycling can be used by depolymerise polyester into the monomer bis(2-hydroyethyl) terephthalate (BEHT), which is a intermediate product for polyethylene terephthalate (PET), the most common polyester. BHET can thereafter be used to produce new PET and therefore turn post-consumer waste to new valuable material.

To provide more gentle reaction conditions in glycolysis, a catalyst can be used, and lately magnesium-aluminium mixed oxides (MgAl-O) has gained attention, partly owing to its ability to convert PET to BHET with high yield and conversion, and partly because it is both a cheap and environmental friendly catalyst. In this project, a MgAl-O catalyst has been provided with magnetic properties by using a magnetic support of iron oxide (Fe_3O_4) to achieve an easy recovery of the catalyst. The synthesised catalyst showed high conversion of PET, up to 82%, and the catalyst could easily be recovered with a magnet.

The obtained product was analysed with Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanninng Calometry (DSC), and the catalyst was analysed with Scanning Electron Microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The results showed that the magnetic support was partly covered by the catalyst, and a magnet could recover the catalyst and XRD showed that the chemical composition of the catalyst changed with heat treatment, which imply that a chemical bond is formed between the magnetic support and the catalyst. However, only FTIR and DSC are not enough to prove that the wanted BHET is the only product formed, and further investigation is needed.

Keywords: polyester, polyethylene terephthalate, chemical recycling, glycolysis, magnetic catalyst, magnesium-aluminium mixed oxides, bis(2-hydroxyethyl)terephthalate

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Emma Hermansson, Gothenburg, June 2016

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1 INTRODUCTION

Polyester is the most common textile fibre today, and is most commonly made of polyethylene terephthalate (PET). The production of PET has increased in the last decades, and the total PET consumption year 2012 was over 28 million tons compared with 11.3 million tons year 2004, and the production is still growing. Out of this, about 65% goes to production of polyester fibres and 30 % to beverage bottle production.

PET is made of non-renewable resources, such as crude oil, and has a costly production due to high energy needs, which makes it of high economical and environmental interest to recycle PET. Today, two main categories of PET recycling are in use: mechanical and chemical recycling. In mechanical recycling, which is currently the most common, the PET is washed, cut, melted and remoulded into new materials. This recycling process has a negative impact on the properties of PET since the polymers degrades for each process cycle, giving the recycled PET poorer properties compared to virgin PET. By using chemical recycling, where PET is depolymerised into monomers and thereafter polymerised, properties equal to virgin PET can be achieved.

A common chemical recycling method is by the use of solvolysis such as hydrolysis, methanolysis or glycolysis. Of these, glycolysis has many advantages such as lower working temperature and pressure, and no need to remove the solvent after solvation. To achieve a better depolymerisation with higher yield of monomers in milder reacting conditions, a catalyst can be used. Amongst the catalysts available for glycolysis of PET, the magnesium-aluminium mixed oxide (MgAl-O) catalyst, which is a mineral low in cost and with low impact on the environment has gained interest lately. MgAl-O has been proven to have high conversion and selectivity for the monomers of BETH. The catalyst has also been proven to be recyclable.

When using a heterogenous catalyst, separation of the catalyst must be performed to purify the product. At industrial scales, where separation methods such as centrifugation is complicated to perform, a new, easy and energy efficient separation method is needed. By giving the catalyst magnetic properties, by using a magnetic support such as iron oxide (Fe_3O_4), an easy and efficient separation of the catalyst can be obtained by using a magnet.

1.1 Aim

The aim of this project is to develop a magnetic catalyst with high conversion and selectivity for depolymerising of polyethylene terephthalate (PET) into bis(2-hydroxyethyl)terephthalate (BHET) monomers. The catalyst should have good magnetic properties to enable efficient catalyst recovery. This was done by synthesising a magnesium-aluminium-oxide-catalyst (MgAl-O) with magnetic iron oxide (Fe_3O_4) core, which was tested and compared with other catalysts in regard to conversion of PET into BHET. By testing the recovery of the catalyst with a magnet, the recyclability of the magnetic catalyst was investigated. The optimal parameters such as time, temperature and ratio of ethylene glycol to polyethylene terephthalate were not evaluated. Also only one type of magnetic catalyst was tested regarding the recoverability by a magnet in this work.

2 THEORY

This chapter explains the theory behind polyester and how it is produced, used and recycled. Also recycling methods and how different catalysts can be used to achieve a faster and more efficient reaction with high conversion is explained.

2.1 Polyester

Polyester is a polymer with an ester group in its main chain, and usually refers to the textile fibre of polyethylene terephthalate (PET), which is what polyester will be referred to in this work. Polyester is the most common man-made fibre today, where PET is the most common polyester fibre. The production of polyester is bigger then the production of cotton, about twice as much per year [1, 2], making it the most common textile fibre. The polyester production has increased rapidly since its invention 1941, and has increased with over 100% during the time period 2000-2012, from 25 million tones to 55 million tones [3], most of it PET, and the forecast is that the production will continue to increase the coming centuries [4].

The popularity of polyester in the textile industry is owing to its attractive properties. It is very strong and durable, does not shrink or wrinkle and is easy to wash, and is also cheap to produce. This makes polyester useful in many applications, such as clothing where it is used for making anything from simple t-shirts to more advanced sporting, furniture filling and clothing, in automobiles, non-woven etc. [1, 5, 6]. Polyester can also be blended with other fibres to modify the properties of the final fabric. For example, it is common that cotton is mixed with polyester to create a stronger and wrinkle free material, or to blend polyester with other synthetic fibres to create tailored properties such as wind and water resistance [6].

2.2 Polyethylene Terephthalate

PET is one of the most common and important polymers today, being the forth most produced polymer after polyethylene, polypropylene and polystyrene. The popularity of PET comes from its good mechanical properties such as transparency, high strength, good thermal stability and good gas barrier properties, which makes PET suitable for several applications in addition to textiles. While the textile industry uses about 60% of the global PET production, around 30% goes to food and beverage packing industry [3, 7].

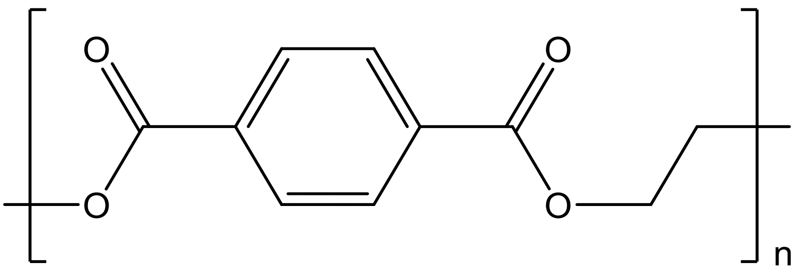


Figure 2.1: Chemical structure of polyethylene terephthalate (PET).

To produce PET, terephthalic acid (TPA) and ethylene glycol (EG), or dimethyl terephthalate (DMT) and EG, all three derived from crude oil, are used as starting materials. The production is carried out by a trans-esterification reaction between TPA and EG or between DMT and EG at elevated temperatures and pressures, which results in the monomer bis(2-hydroxyethyl) terephthalate (BHET), which thereafter is polymerised to create PET [7, 4].

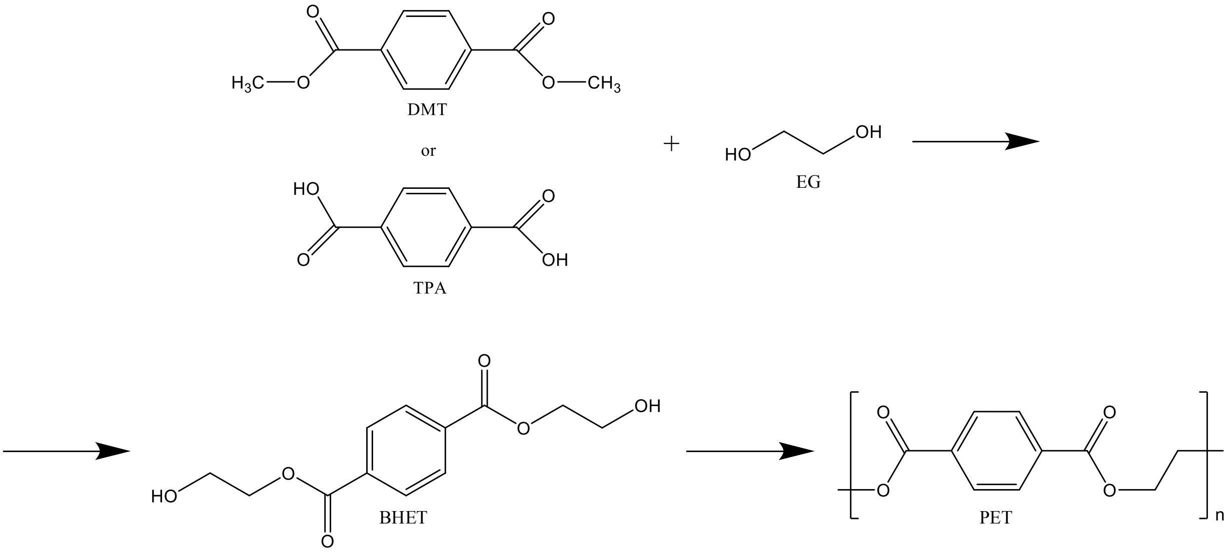


Figure 2.2: Reaction steps in the production of PET with DTA or TPA and EG as starting material and with BHET as middle product.

Depending on the molecular weight and the number of repetitive monomer units, PET has two classifications: fibre-graded PET which has a molecular weight of 15 000-20 000 g/mol that equals a repeating monomer unit of 80-100, and bottle-graded PET with a molecular weight of 24 000-36 000 g/mol, which equals a repeating monomer unit of 125-185 [3]. With higher molecular weight, stiffness and creep resistance increases due to longer chains.

2.3 Recycling

PET, like many other polymers, is not biodegradable, and due to the extent of PET used, a lot of waste is formed. Of the globally produced solid waste, PET accounts for 12% of the volume and 8% of the weight [4], and therefore a good waste management for PET that is needed. Since the price of virgin PET is low, a recycling method that is economical and efficient and that does not degrade the properties of the material is needed, and therefor chemical recycling is of interest [8, 9].

Today PET-recycling occurs in a cycle of four: the first recycling cycle includes non-contaminated PET-waste from industries, which is blended with virgin PET to achieve a high quality PET. In the second cycle PET-waste is mechanically processed to achieve a postconsumer-PET which, depending on its quality, can be used as for example beverage bottles or polyester fibre. In the third cycle, post consumer PET is chemical recycled where different monomers, oligomers or other compounds is obtained. In the fourth cycle, post consumer PET is incinerated to attain the energy content, which can be used in district heating for example [3, 7, 10].

2.3.1 Mechanical recycling

During mechanical recycling PET undergoes several steps such as contaminants removal, drying and melt processing. During contaminant removal, PET is separated from other polymers. Thereafter the PET is cut into smaller pieces, washed and grinded. The drying is an important step since water contamination during the melt processing leads to hydrolysis and decreases the molecular weight of PET. To prevent hydrolysis, the water contamination should be below 0,02%. The PET is thereafter melt processed by extrusion at around 280°C into granules. The melt processing, as mentioned before, causes hydrolysis especially at higher water contamination, but also thermal degradation, which likewise to hydrolysis decreases the molecular weight of PET, giving it poorer properties [10, 11, 12, 13, 14].

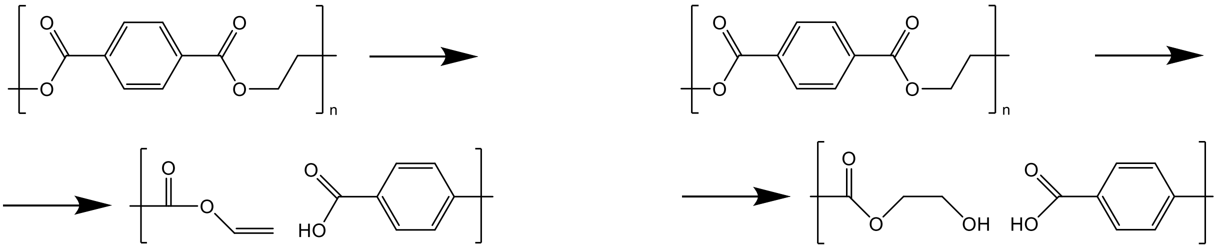


Figure 2.3: Thermal degradation reaction (left) and hydrolysis reaction (right) of polyethylene terephthalate (PET).

Hydrolysis and thermal degradation are the two biggest disadvantages of mechanical recycling, but other difficulties such as oxidation and crosslinking, which leads to discoloration, called yellowing, of PET is a big problem as well. Together, these disadvantages give PET poorer properties for each time it is mechanically recycled, and often the term “down cycle” is often used. But mechanical recycling has many advantages as well: it is relatively cost effective, simple and has low environmental impact [3, 7].

2.3.2 Chemical recycling

In chemical recycling, the polymer is depolymerised into monomers or into chain fragments, which then can be re-polymerised or used otherwise. Chemical recycling has the advantage of being able to reproduce the polymers starting material in the form of monomers, which then can be used to re-create the polymer with the same properties as the virgin material. There are two types of chemical recycling processes: pyrolysis, where PET is depolymerised by heating in vacuum or in an inert atmosphere, or by solvolysis, where a solvent is used instead. Within solvolysis, there are five methods: aminolysis, ammonolysis, glycolysis, hydrolysis and methanolysis [3, 7, 9, 15].

2.3.2.1 Glycolysis

Glycolysis is one of the oldest, easiest and cheapest ways to chemically recycle PET through a transesterfication catalyst. By using a glycol, usually ethylene glycol, which also is a starting material in the production of PET, and increased temperature, pressure and time, PET can be depolymerised into the monomer BHET and other oligomers. The BHET produced can then be blended with virgin BHET in a PET-plant to produce new PET with the properties of virgin PET [16, 17].

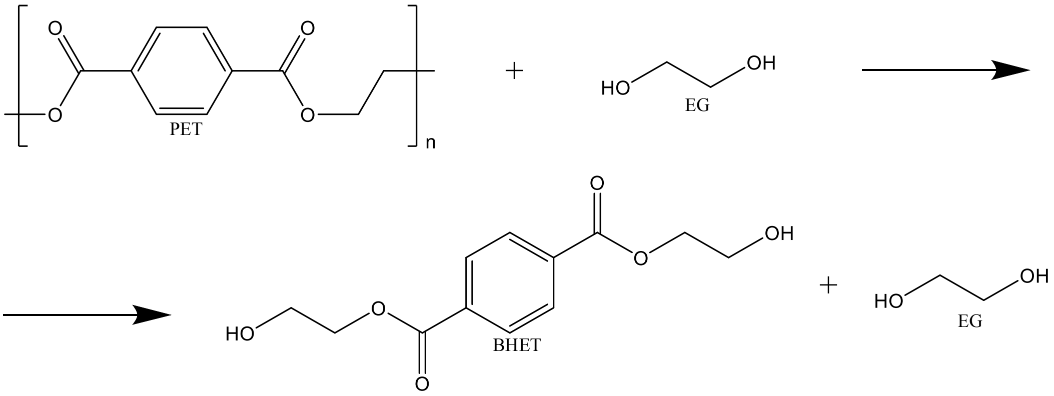


Figure 2.4: Glycolysis of PET to BHET.

2.3.3 Glycolysis with catalyst

Glycolysis is a slow and sluggish reaction and needs long reaction time to obtain high conversion. Therefore, a transesterfication catalyst is often used to lower reaction temperature, time and pressure. The catalyst works by breaking the linkage between the carbon chain and the tertiary carbon, replacing the carbon chain with an alcohol from the glycol consumed. A transesterfication catalyst used is glycolysis for chemical recycling of for example PET in an equilibrium reaction: it breaks the linkage and also founds it. Therefore, if the reaction is taken to far, the depolymerisation will stop and the monomers will be polymerised into longer chains again. Today ionic liquids, metal salts and magnesium-aluminium-oxides are the most common transesterfication catalysts for glycolysis of PET [3, 16, 18, 19].

2.3.3.1 Ionic liquids catalysts

An ionic liquid is a salt with a melting temperature lower than the boiling point of water, 100°C. The low melting temperature is inherent from the structure of the liquid ions, which consists of one ion, and one organic component, which prevents the formation of a stable crystal. Ionic liquids can be used as solvents as well as catalysts and electrolytes, and its popularity comes from their low volatility, which leads to lower emissions. Also, ionic liquids can be tailored to specific uses in form of solvents and catalysts. As a catalyst, ionic liquid has the advantage to be easily separated after reaction, and the final product therefore is easily purified [3, 19, 20].

2.3.3.2 Metal salts catalysts

Metal salts, which consist of a metal and an alkali metal, are the oldest known catalysts for depolymerisation of PET. The use of relatively heavy metals in the metal salts, forming compounds such as zinc acetate, which reaches a high conversion of PET, and manganese acetate, is an easy way to achieve an efficient catalyst, but is also environmentally harmful. To attain more environmental friendly metal salts, the use of alkali metals has increased with compounds such as sodium carbonate. Even if many metal salts reach a high conversion of PET, the reaction is slow and in need of high temperatures, and it is hard to separate the catalyst from the final product since most metal salts are soluble in ethylene glycol [3, 4, 19, 20].

2.3.3.3 Magnesium-Aluminium mixed oxide catalyst

A catalyst of magnesium-aluminium mixed oxide (MgAl-O) has been found to be an eco-friendly, cheap and efficient catalyst for the conversion of PET into BHET. The Mg/Al-ratio as well as calcination temperatures effects the efficiency of the catalyst, and the optimal parameters for the catalyst has been investigated many times. Chen et al. investigated the efficiency of the MgAl-O catalyst for depolymerisation of PET [21], and it was found that a conversion of PET to BHET of 81,3% was reached with the ratios EG/PET = 5 and catalyst/PET = 0,01 at 196°C for 50 min. One of the main advantages of the MgAl-O-catalyst compared to other eco-friendly catalysts is that it is heterogeneous and therefore easy to separate by filtration or centrifugation, making the catalyst reusable [16, 19, 20, 21].

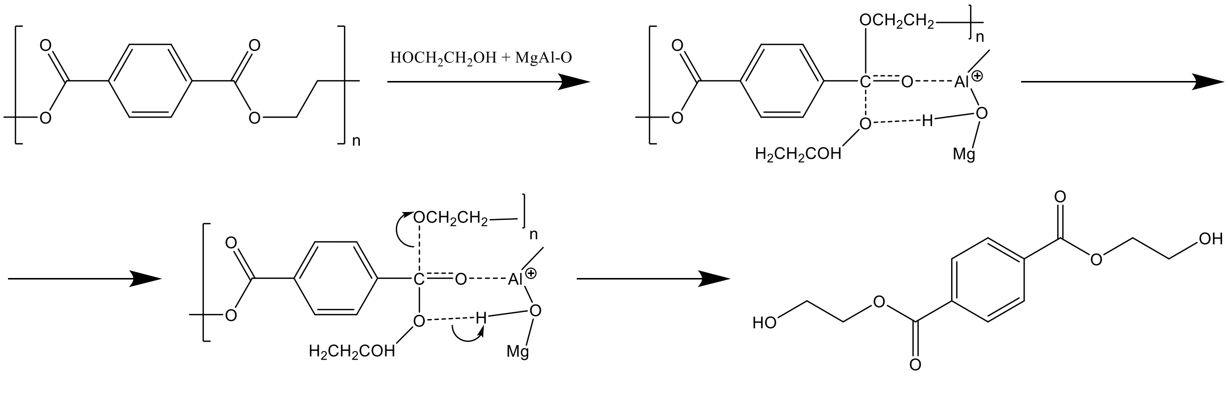


Figure 2.5: Glycolysis of PET with MgAl-O as catalyst to BHET [21].

2.3.4 Magnetic catalysts

One of the main problems using catalysts is to recover it. Among homogenous catalyst, the recovery of the catalyst is often hard, while for heterogeneous catalysts it is simpler even if methods like centrifugation is difficult to use at industrial level. One way to solve this problem is by giving the catalyst magnetic properties, which results in that he catalyst can be recovered by a simple magnet, and thereafter reused either directly or after reactivation.

One way to give catalysts magnetic properties is by using a magnetic catalyst support, where magnetite, Fe_3O_4, is a common support to use. Fe_3O_4 is an environmental friendly support with good ferromagnetic properties. To create a magnetic catalyst, the co-precipitation method is commonly used, where the Fe_3O_4 is solved into a basic solution with a pH around 10. This will put Fe_3O_4 above its iso electrical point (IEP = 6,35 in water, 25°C [22]), which will make the surface negatively charged. When adding positive ions to this solution, such as the ions of magnesium (Mg^{2+}) and aluminium (Al^{3+}), these will precipitate onto the surface of the Fe_3O_4, creating a layer of MgAl-O catalyst on top of the magnetic support [23, 24, 25, 26].

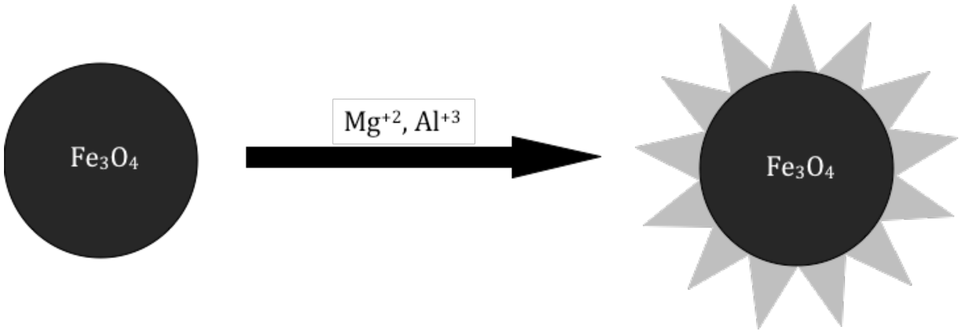


Figure 2.6: The mechanism of the formation of a MgAl-O-catalyst with a magnetic Fe_3O_4-core (MgAl-O@Fe_3O_4)

By burning the magnetic catalyst, the catalyst particles and the magnetic support can be burnt together to create more durable particle. After reaction, the catalyst can easily be removed with a magnet due to the magnetic properties [19, 27, 28].

3 EXPERIMENTAL

The experimental part was carried out in four steps: First the catalyst was synthesised and thereafter tested in glycolysis with EG of PET to monomers aside other catalysts. Then, the catalyst was recycled and thereafter tested again to see how the conversion changed and for how many times the catalyst could be reused. Thereafter the ability to press the catalyst into pellets was evaluated. Last, the catalyst and the obtained monomers were characterised.

3.1 Synthesis of catalyst

Table 3.1: The amount of chemicals for preparation of the catalyst.

Solution 1		Solution 2		Solution 3	
400 ml	distilled water	300 ml	distilled water	500 ml	distilled water
1,0058 g	Fe_3O_4	23,4598 g	$Mg(NO_2)_3$	8,0660 g	NaOH
		11,1950 g	$Al(NO_3)_3$	6,4603 g	Na_2CO_3

In order to synthesis the magnesium-aluminium mixed oxides on top of iron oxide (MgAl-O@Fe_3O_4), firstly, solution 1 was prepared by weighing the Fe_3O_4, which was added to a beaker filled with 400 ml distilled water. The beaker was the put in an ultrasonic bath for 10 minutes to disperse the Fe_3O_4.

Secondly solution 2 was prepared by weighing $Mg(NO_2)_3$ and $Al(NO_3)_3$, which was added to a beaker with 300 ml distilled water. Solution 3 was prepared by adding NaOH and Na_2CO_3 to another beaker with 500 ml distilled water.

Solution 1 was poured to a big beaker, which could fit all three solutions and was vigorously stirred with a magnetic stirrer for the rest of the procedure. The catalyst was then produced by precipitating Mg^{2+} and Al^{3+} on top of the magnetic core by adding solution 3 to solution 1 until pH 10 was obtained, and thereafter solution 3 was added to keep the pH at about 10 constantly during the rest of the procedure. Solution 2 was added drop wise to solution 1 until ended. Thereafter the magnetic stirrer was turned of, and the final solution was left to age for 24 h at 60°C.

Next, the solution was washed with deionized water six times and the magnetic catalyst was separated with a magnet. Thereafter the catalyst slurry was freeze dried for 24 h to remove water molecules. Thereafter the catalyst was heat treated at a “step-program” where the temperature was raised 5°C per minute until 1000°C, hold at 1000°C for 120 minutes and thereafter cooled with 5°C per minute. The catalyst was thereafter rehydrated in a ball mill with distilled water for 24 h before it was freeze granulated again.

To obtain a catalyst with a smaller size distribution, Fe_3O_4 was heat treated at 1200°C to sinter it harder and thereafter ball milled for 72 h, where the finer particles was decanted every 12 h. Thereafter, the Fe_3O_4 was sieved into +50 µm, 30-50 um, 10-30 µm, -30 µm and -10 µm and the -10 µm and -30 µm was sedimentated with the times 1 min, 5 min and 15 min. The -30 µm sedimentated for 1 min was then chosen as a magnetic support due to high amount and even size of the particles. The -30 µm sedimentated for 1 min was thereafter freeze dried, and the catalyst was synthesised with the same method as the first catalyst with Mg/Al-molar ratio 3:1 and Mg/Fe_3O_4-molar ratio 20:1 according to table 2.

Table 3.2: The amount of chemicals for preparation of the catalyst the second time.

Solution 1		Solution 2		Solution 3	
2200 ml	distilled water	2750 ml	distilled water	1650 ml	distilled water

11,0733 g	Fe_3O_4	88,7539 g	$Mg(NO_2)_3$	257,9830 g	NaOH
		71,3863 g	$Al(NO_3)_3$	123,1537 g	Na_2CO_3

The MgAl-O-catalyst and the FeMgAl-O-composite catalyst used was produced by the precipitation method and heat treated at 1000°C.

3.2 Depolymerisation of polyethylene terephthalate

For the experiment for depolymerisation of PET, 10 g PET and 50 ml ethylene glycol (EG/PET-ratio=5) were added into a reactor together with the catalyst. Ten silica balls were added to the reactor to benefit stirring. The reactor were then put into an oven at 240 °C for 2 h rotating one laps per minute. After 2 h the reactor were cooled in cold water. The solution within the reactor were dissolved with boiling water, and the resulting slurry were brought to boil and there after filtered four times or until clear to remove oligomers and unreacted PET. Thereafter the resulting liquid were cooled over night to crystallize the monomers.

The cooled solution were then filtered once, and the resulting monomers were dried at 60°C for four hours and thereafter conditioned for another four hours and thereafter weight. The conversion of PET to BHET were calculated by the following equation

$$\text{Yeild of BHET (\%)} = \frac{\frac{m_{\text{BHET monomer}}}{\text{M}_{\text{BHET}}}}{\frac{m_{initial\ PET}}{\text{M}_{\text{PET}}}} \cdot 100$$

Equation 3.1: Formula to calculate the conversion of PET to BHET [20].

Where M_{BHET} is 245g/mol and M_{PET} for the repeating unit is 192g/mol.

3.2.1 Different catalysts

To evaluate how efficient the MgAl-O@Fe_3O_4 catalyst is, it was tested together with other catalysts: no catalysts, Fe_3O_4 heat treated at 1000°C, MgAl-O with Mg:Al 3:1 heat treated at 1000°C and FeMgAl-O composite with Fe:Mg:Al 2:3:1 heat treated at 1000°C. Also, the MgAl-O@Fe_3O_4 catalyst was tested directly after heat treatment at 1000°C as well as after water treatment where the catalyst was put in water for 24 h. This to evaluate whether the presence of hydroxide groups affects the activity of the catalyst.

3.2.2 Process window

Since it is probable that a small amount of catalyst is lost for each recycling of the catalyst, and since it is hard to scale the recovered catalyst due to adsorbed monomers and oligomers, a process window was investigated. The process window was investigated by following the procedure for depolymerisation of PET, but with different amounts of catalyst. The process window was obtained by increasing and decreasing the amount of catalyst with catalyst to PET ratio of 1% as standard, until the conversion decreased.

3.2.3 Recycling of catalyst

For the first cycle, 0,5 g of catalyst together with 10 g of PET and 50 ml EG was measured and run in the reactor at 240°C for 2 h. The resulting solution was thereafter solved with 100 ml boiling water and the catalyst was recovered with a magnet, and the solution was filtered four times or until clear. The recovered catalyst was thereafter washed and freeze dried, and run again with the same amount of PET and EG until the conversion started to decrease.

3.2.4 Size of catalyst

To evaluate another technique to achieve an efficient recover of the catalyst, the FeMgAl-O composite was pressed into pellets as well as spray granulated into a powder. The powder was sieved into two different sizes: above 500 µm and below 125 µm. These three different sizes was thereafter tested at 240°C, 220°C and 200°C and compared with each other to evaluate how the size of the catalyst affects the conversion.

Table 3.3: The amount of catalyst used for the different sizes of catalyst.

Size of catalyst	Amount of catalyst
>125 µm	0,1 g
<500 µm	0,1 g
Pellet	1,3 g (5 units)

At higher temperatures, PET efficiently solves in the EG, which makes the PET able to penetrate the catalyst pellet. Since lower reaction temperature always is of interest for a cheaper process, pellet catalysts is only of interest if they are able to convert PET to monomer at lower temperatures.

3.3 Characterisation

The monomer formed after reaction as well as the catalysts at different composition and stages need to be analysed to characterise the true composition. It also makes it possible to investigate how different compositions within the catalysts affects the monomers and oligomers formed during the reaction.

3.3.1 Fourier Transform Infrared Spectroscopy

The formed monomers from the reaction were evaluated with FTIR (Tensor 27, Bruker) in solid state to evaluate the bonds within the samples and the obtained spectrum was compared with the FTIR spectrum for the references for BHET.

3.3.2 Differential Scanning Caloremitry

To evaluate the results from FTIR further, and to evaluate the purity of the obtained monomers, three different samples that were chosen from the FTIR-spectrum that were found representative for all the FTIR-analysis were chosen. These were examined with differential scanning calomitry (DSC) and composition and purity were evaluated.

DSC was preformed with a Mettler Toledo DSC1 STAR^e system with a nitrogen atmosphere with 80 ml N^2/min. The samples in the first cycle was heated 10°C/min, at the second cycle the sample was cooled with 5°C/min, and at the third cycle the sample was with 10°C/min. The temperature interval for PET was set to be 30°C to 280°C since the melting temperature for PET is 250-255°C [31], and for the other samples to be 30°C to 130°C due to the melting temperature for BHET is 106-110°C [33].

Table 3.4: the samples analysed with DSC.

	Sample	Weight [mg]
1	PET (reference)	4,19
2	PET (reference)	5,25
3	BHET Sigma Alderich (reference)	4,73
4	BHET Sigma alderich (reference)	4,16
5	Monomers from 0,025% MgAl-O@Fe_3O_4 catalyst	5,18
6	Monomers from 0,025% MgAl-O@Fe_3O_4 catalyst	4,72
7	Monomers from 0,1% MgAl-O@Fe_3O_4 catalyst	4,36
8	Monomers from0,1% MgAl-O@Fe_3O_4 catalyst	4,11
9	Monomers from 2,5% MgAl-O@Fe_3O_4 catalyst	5,35
10	Monomers from 2,5% MgAl-O@Fe_3O_4 catalyst	4,09

3.3.3 Scanning Electron Microscope

The topography, morphology and size of the magnetic catalyst was evaluated using Scanning Electron Microscope (SEM), and whether the MgAl-O had attached to the surface of Fe_3O_4, and therefore whether the preparation of the catalyst had succeeded, and how the catalyst is affected by being recycled was evaluated by SEM.

Table 3.5: The samples that were investigated with SEM in regard to topography and morphology.

Sample analysed
Fe_3O_4 burned at 1200°C
MgAl-O burned at 1000°C
MgAl-O@Fe_3O_4 catalyst burned at 1000°C
MgAl-O@Fe_3O_4 catalyst used five times, organic material burned of at 900°C

To investigate the magnetic catalyst further, a number of samples was casted in epoxy and thereafter grinded to obtain cross sections of the particles. The cross section was then investigated to confirm whether the MgAl-O actually had formed a layer around the magnetic core, and how the recycling had affected the MgAl-O-layer. The cross sections of Fe_3O_4 and MgAl-O were used as references.

Table 3.6: The samples analysed with SEM in regard to cross section.

Sample analysed
Fe_3O_4 burned at 1200°C
MgAl-O burned at 1000°C
MgAl-O@Fe_3O_4 catalyst burned at 1000°C
MgAl-O@Fe_3O_4 catalyst used five times, some organic material is present

MgAl-O@Fe_3O_4 catalyst used five times, organic material burned of at 900°C

3.3.4 Energy-dispersive X-ray spectroscopy

For the samples MgAl-O@Fe_3O_4 catalyst burned at 1000°C and MgAl-O@Fe_3O_4 catalyst used five times, organic material burned of at 900°C, Energy-dispersive X-ray spectroscopy (EDS) was preformed for elemental analysis to investigate whether the coating of the magnetic support had succeeded or not, and how the coating is affected by recycling.

3.3.5 X-ray diffraction

To evaluate the chemical composition of the catalyst and how it is affected by different treatments, samples of interest was analysed with X-ray diffraction, (XRD) (Bruker D8 advanced) with a chromium (Cr) electron source with the settings 25°-150° with step size 0,05°and step time 0,8s.

Table 3.7: The samples analysed by XRD.

Samples analysed
MgAl-O@ Fe_3O_4-catalyst burned at 1000°C
MgAl-O@ Fe_3O_4-catalyst burned at 1000°C, rehydrated
Fe_3O_4 magnetic support, burned at 1200°C
MgAl-O@Fe_3O_4 catalyst burned at 1000°C
MgAl-O@Fe_3O_4 catalyst burned at 1000°C and used one time
MgAl-O@Fe_3O_4 catalyst not burned
MgO burned at 1000°C
AlO burned at 1000°C

3.3.6 Recovery of Catalyst

To evaluate the recovery of the catalyst a magnet was used. The time it took for the magnet to fully recover the catalyst was measured.

4 RESULTS

This chapter presents the results from conversion as well as the recycling of the MgAl-O@Fe_3O_4. Also the results from characterisation of the MgAl-O@Fe_3O_4 catalyst and the obtained monomers are presented.

4.1 Monomers

The conversion of PET to monomers was calculated by using equation 3.1. The monomers obtained from the reaction was analysed with FTIR and DSC.

4.1.1 Conversion

The conversion of PET differs as seen below depending on the catalysts composition, amount of catalyst and the formation of catalyst as well as how many times the catalyst has been used.

4.1.1.1 Different catalysts

As seen in figure 4.1 the conversion of PET at 240°C for 2 hours without catalyst and with Fe_3O_4 is almost neglectable. With MgAl-O as catalyst, the conversion increased to around 75%. The FeMgAl-O catalyst, both the composite and the MgAl-O-covered magnetic core, gave the same conversion just above 80%. Also, the heat treated and watered MgAl-O@Fe_3O_4 gave the same conversion.

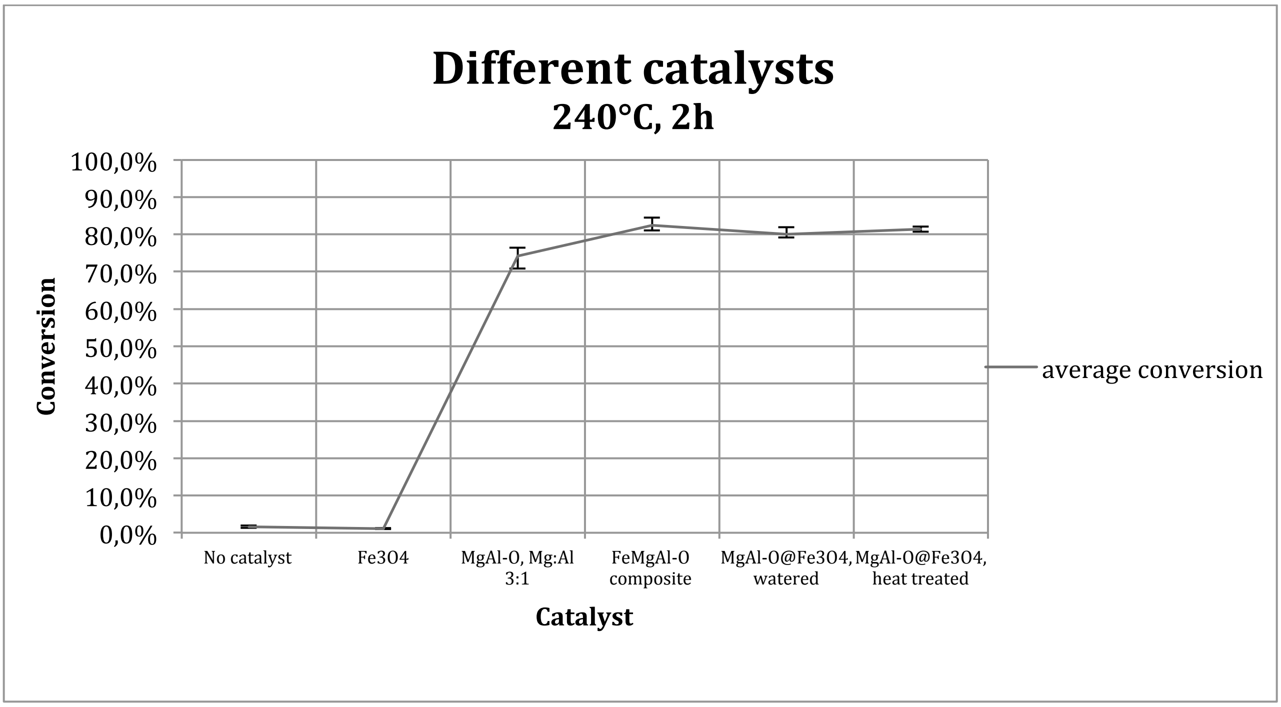


Figure 4.1: The conversion from polyethylene terephthalate (PET) to monomers for glycolysis with different catalysts.

4.1.1.2 Process window

Figure 4.2 shows that a small amount of catalyst gives a high conversion. Going above the ratio catalyst/PET of 1% makes the conversion decrease since it causes the reaction to go backwards and polymerise oligomers and monomers, and under 0.1% the conversion gets unstable and varies from trial to trial until it reaches a conversion of 0%.

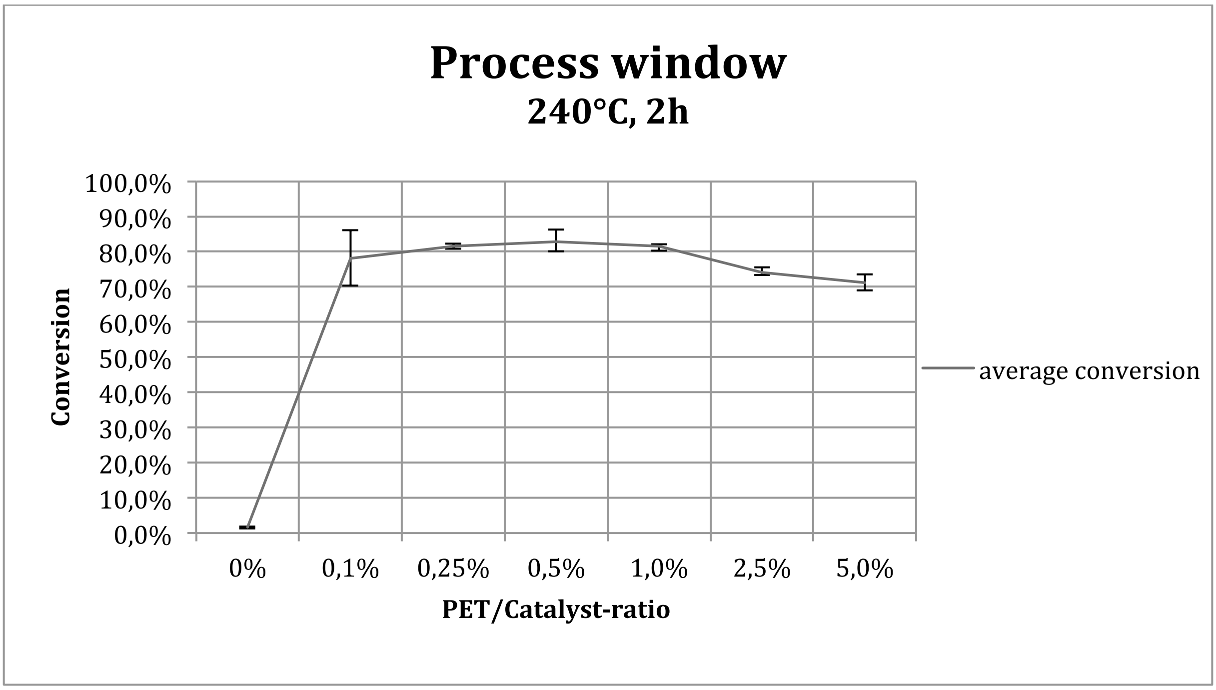


Figure 4.2: The conversion of polyethylene terephthalate (PET) to monomer for different amount of MgAl-O@Fe_3O_4 catalyst.

4.1.1.3 Recycling of catalyst

As seen in figure 4.3, the catalyst can be used three times without any treatment and still achieve a high conversion. The conversion for cycle four is relatively high for some trials, but the activity of the catalyst varies between trials. At the fifth run no conversion was recorded, and the catalyst is deactivated.

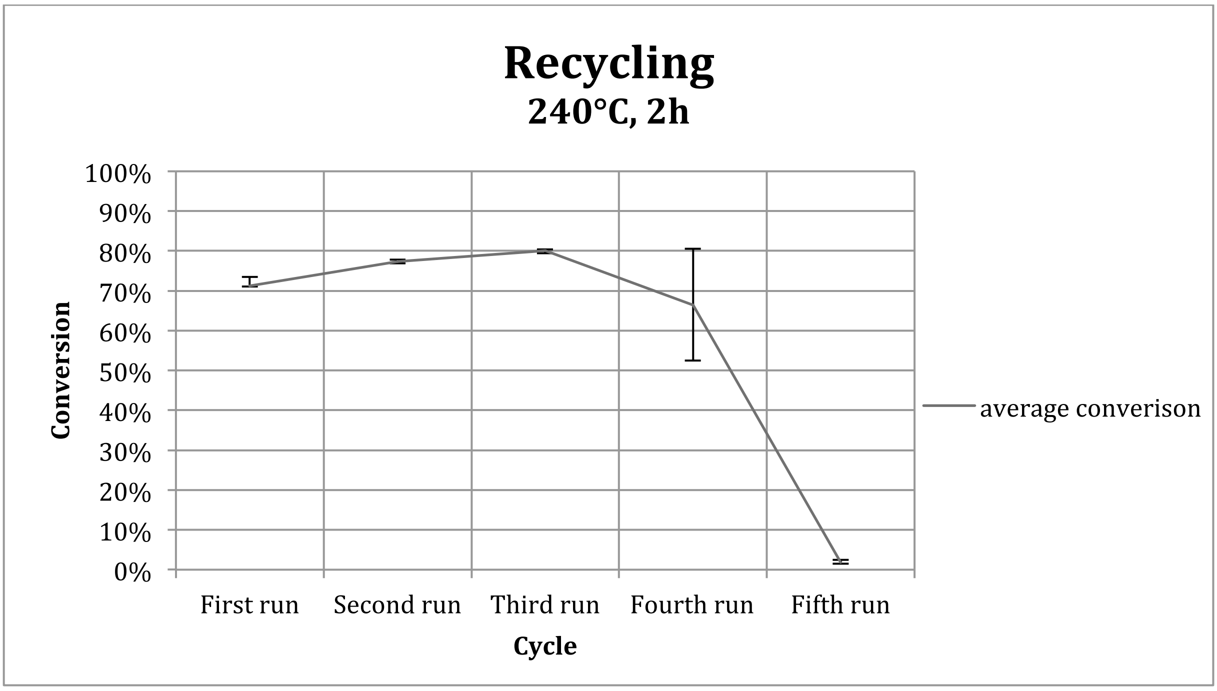


Figure 4.3: The conversion of polyethylene terephthalate (PET) to monomer with recycled catalyst. At the first cycle the catalyst is virgin, the second cycle it has been used once before etc.

4.1.1.4Shape of catalyst

From figure 4.4 it can be seen that neither the powder, granule nor pellet show any conversion of PET to BHET when carried out at 200°C. At 220°C the conversion for all three shapes increases, but for the pellet shape there was still unsolved PET pellets present after the reaction compared to the granule and powder, where all PET had been solved. At 240°C all three shapes gave equally high conversion.

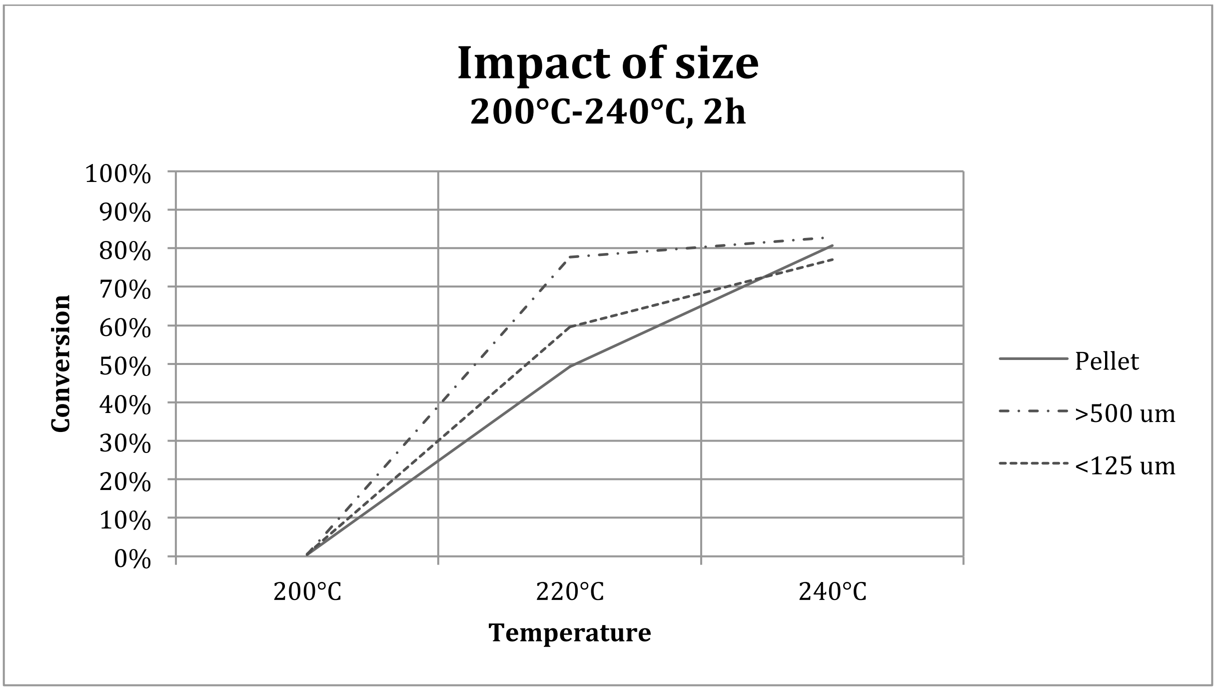


Figure 4.4: The impact of size of the catalyst depends on temperature. The conversion increases with the temperature for all shapes.

4.1.2 Fourier Transform Infrared Spectroscopy

FTIR spectrum gives information about the monomer structure could be obtained. The wanted monomer, BHET, and DMT, the monomer obtained from methanolysis and a starting material for PET, is used as references. The peak that can be found in all spectra's shown in this chapter at about 2350 cm^{-1} originates from carbon dioxide (CO_2) and can be disregarded. The peaks found at 3650-3700 cm^{-1} in figure 4.7 and 4.9 are most likely contamination and can be disregarded as well.

4.1.2.1 Catalyst/PET=1%

Figures 4.5, 4.6 and 4.7 present the FTIR spectrum for the obtained monomers from experiments (black) and for the reference for the wanted monomer BHET (red). As seen in figure 4.5 and 4.6, the spectrum for the obtained monomers follows the spectrum for BHET, indicating that the wanted monomers were formed during depolymerisation.

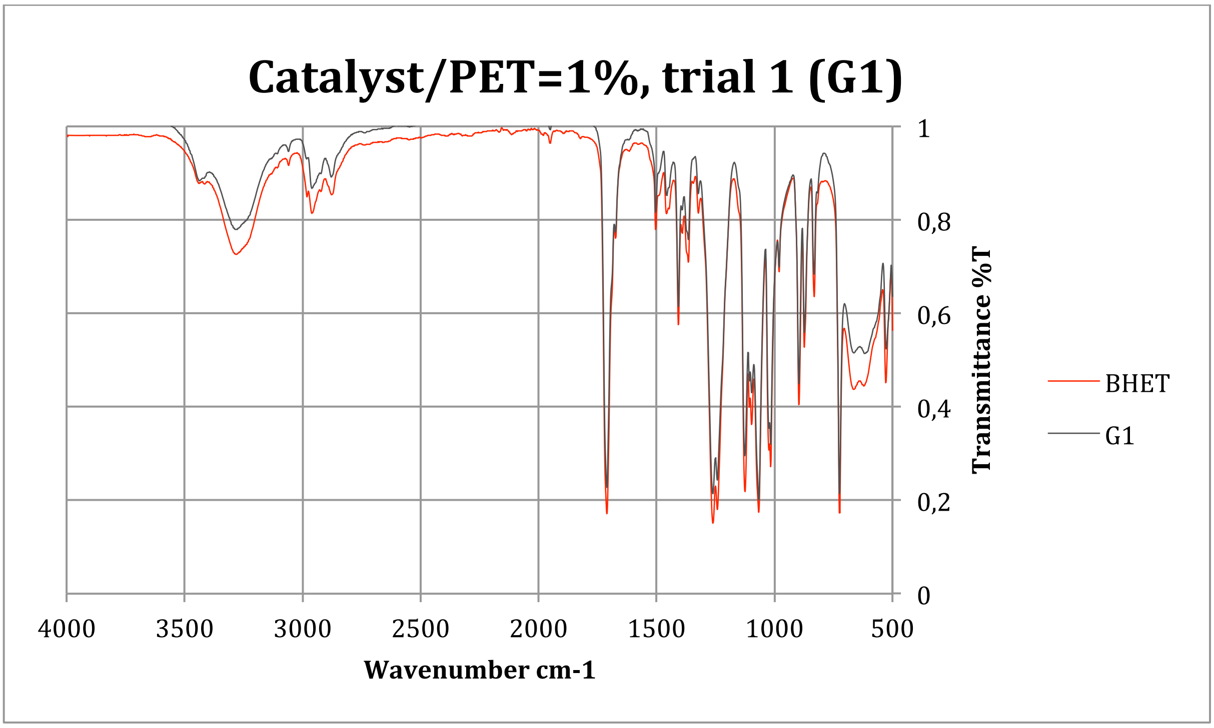


Figure 4.5: The FTIR spectrum for BHET (red) and the monomer obtained from a reaction with the ratio catalyst to PET =1% (G1, black).

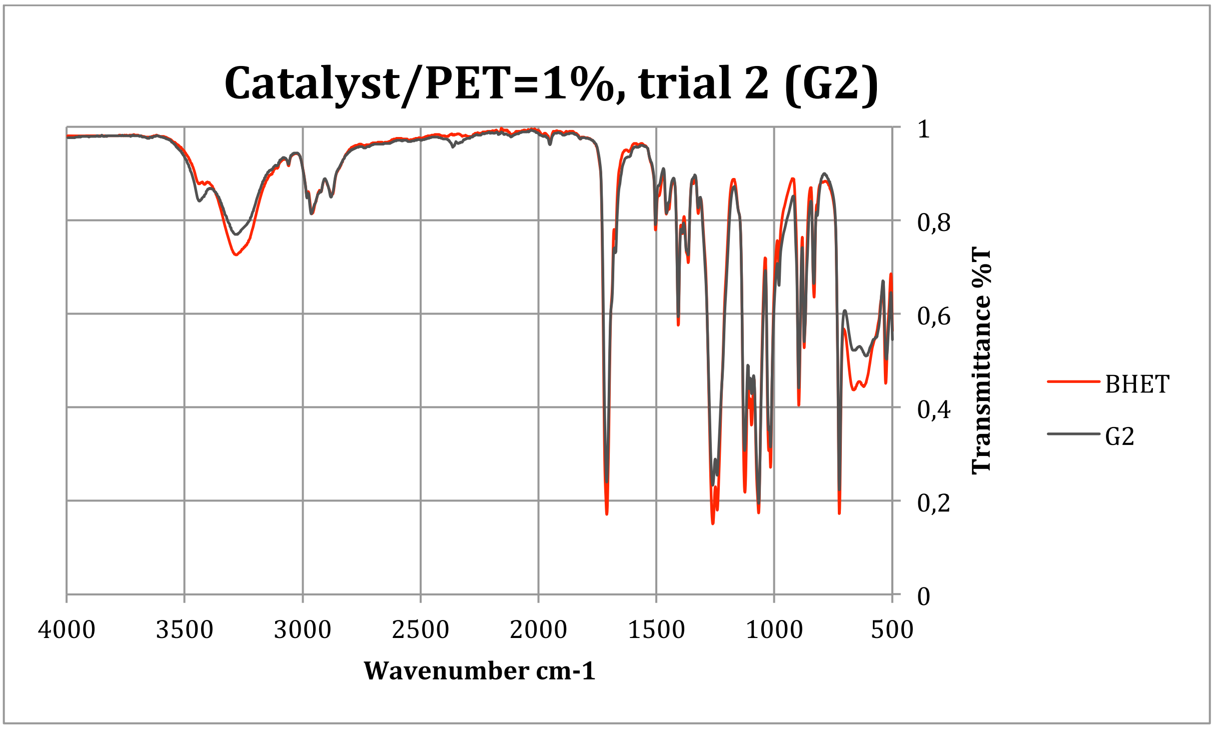


Figure 4.6: The FTIR spectrum for BHET (red) and the monomer obtained from a reaction with the ratio catalyst to PET =1% (G2, black).

In figure 4.7, the spectrum of the obtained monomers follows the spectrum for BHET partially, but has some difference. The peak at 3000 cm^{-1} has higher transmittance then for BHET, indicating that the formed monomer has more carbon-carbon bonds then BHET.

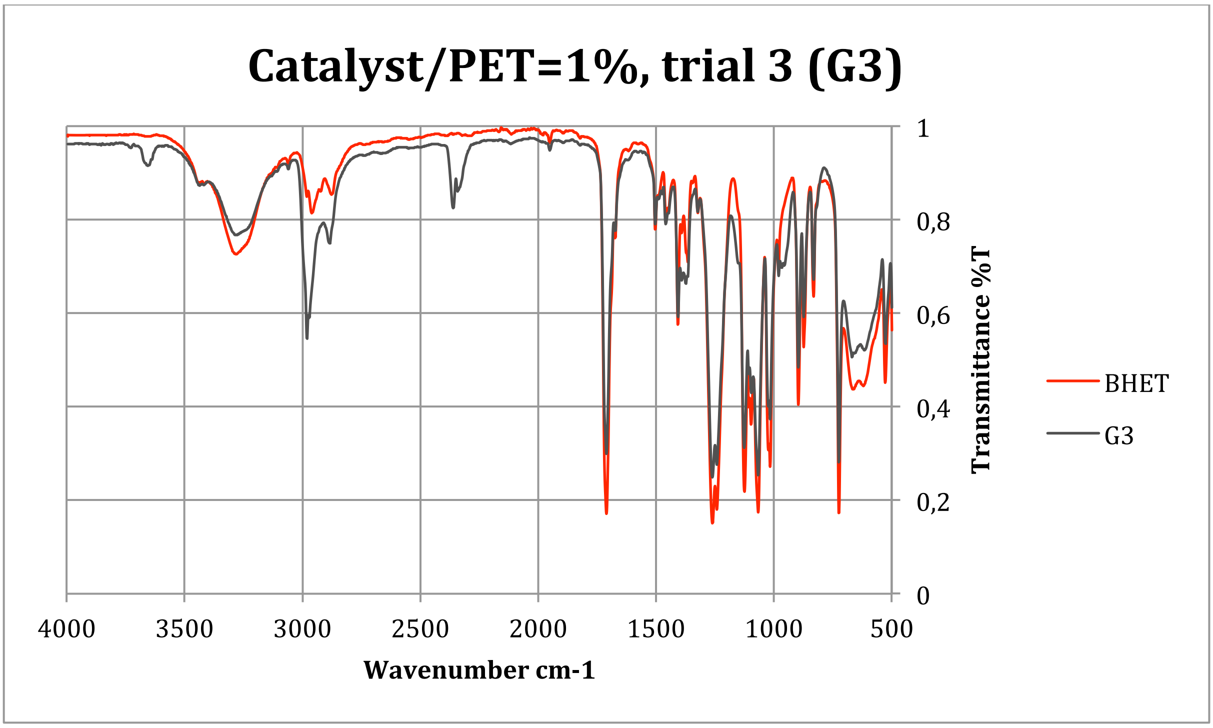


Figure 4.7: The FTIR spectrum for BHET (red) and the monomer obtained from a reaction with the ratio catalyst to PET =1% (G3, black).

4.1.2.2 Variance in spectrums

For the rest of the obtained monomers from the samples, the FTIR follows the same three patterns. Many of the obtained monomers follow the spectrum as for the one for BHET, indicating that the wanted monomers are formed, as seen in figure 4.8.

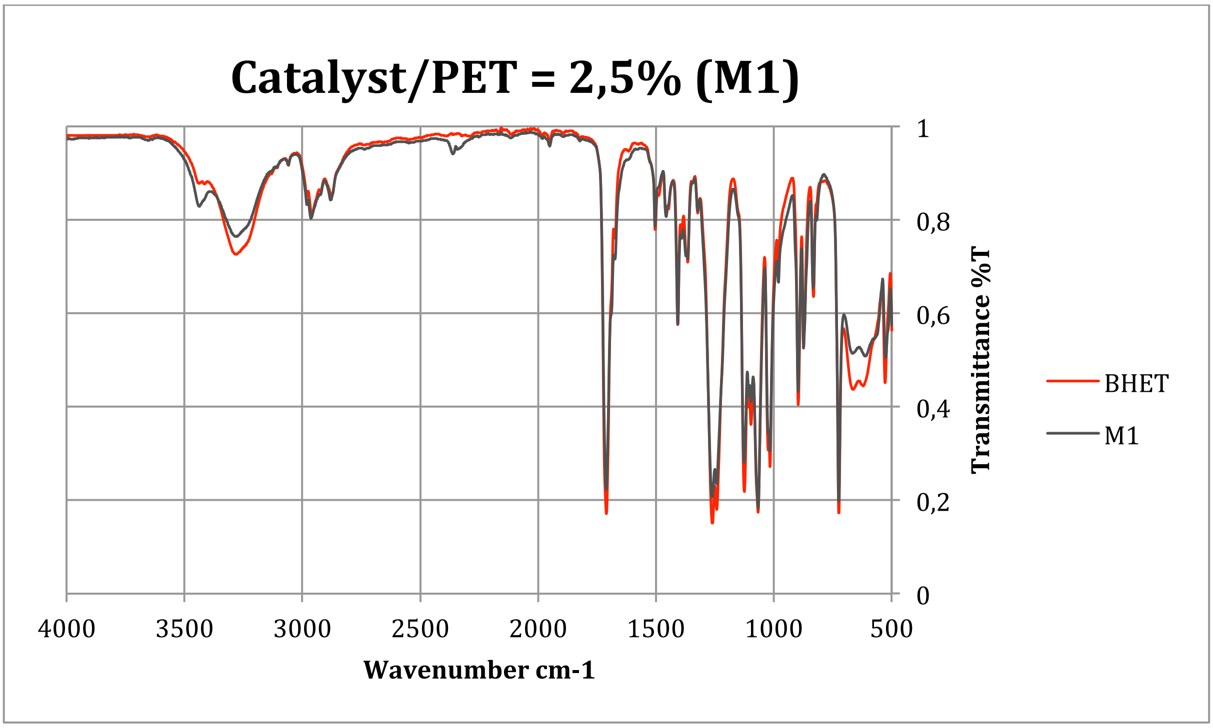


Figure 4.8: The FTIR spectrum for BHET (red) and the monomer obtained from a reaction with the ratio catalyst to PET =2,5% (M1, black).

In figure 4.9 the monomers obtained from the catalyst to PET ratio =0,25% (J2) is shown, which also is representative for many samples. The biggest difference for M1 compared to BHET is that the peak at 3450 cm^{-1} has higher transmittance then for BHET. At lower wavenumbers, the spectrum for the monomer and for BHET corresponds well.

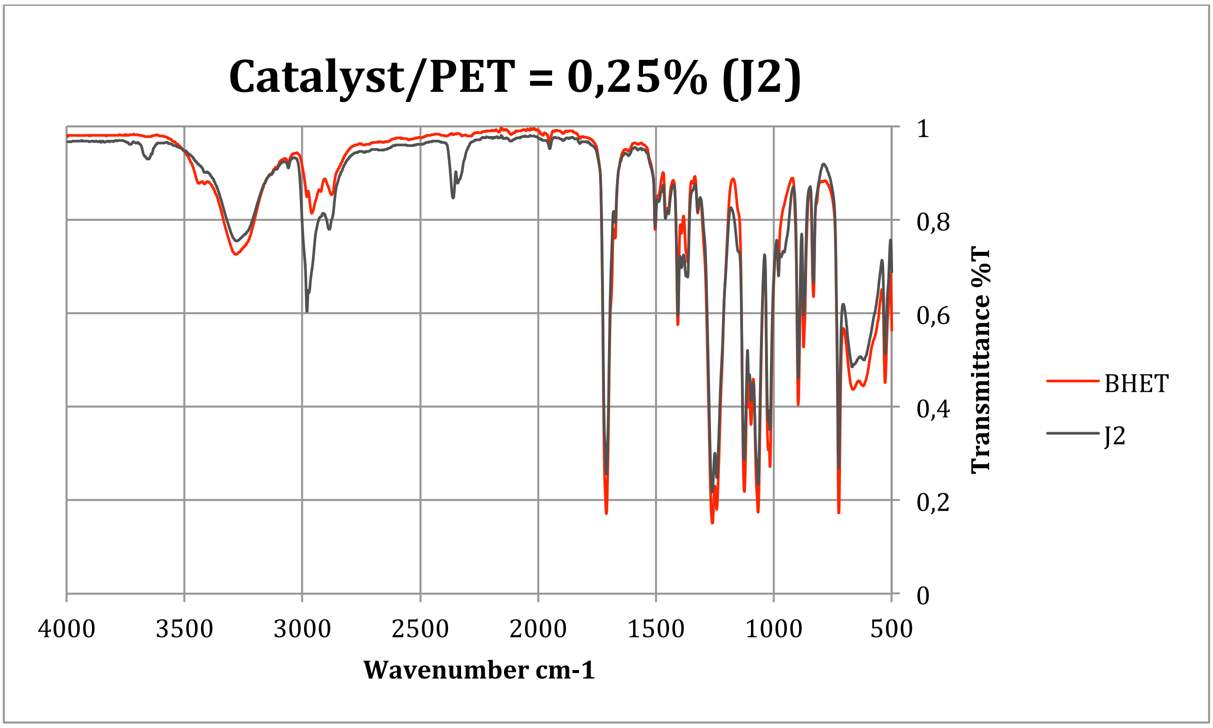


Figure 4.9: The FTIR spectrum for BHET (red) and the monomer obtained from a reaction with the ratio catalyst to PET =0,25% (J2, black).

For L2, shown in figure 4.10, which also is representative for many samples, the relatively broad peak that can be found for BHET at about 3300 cm^{-1} is instead found as a sharp peak at 3450 cm^{-1}. For BHET, a small peak can be found at this wavelength. Also the peak at about 1710 cm^{-1}, which corresponds to the carboxyl group, is divided into two peaks. The spectrum for J2 corresponds well to the reference spectrum for BHET at lower wavelengths except for the peak at 700 cm^{-1}.

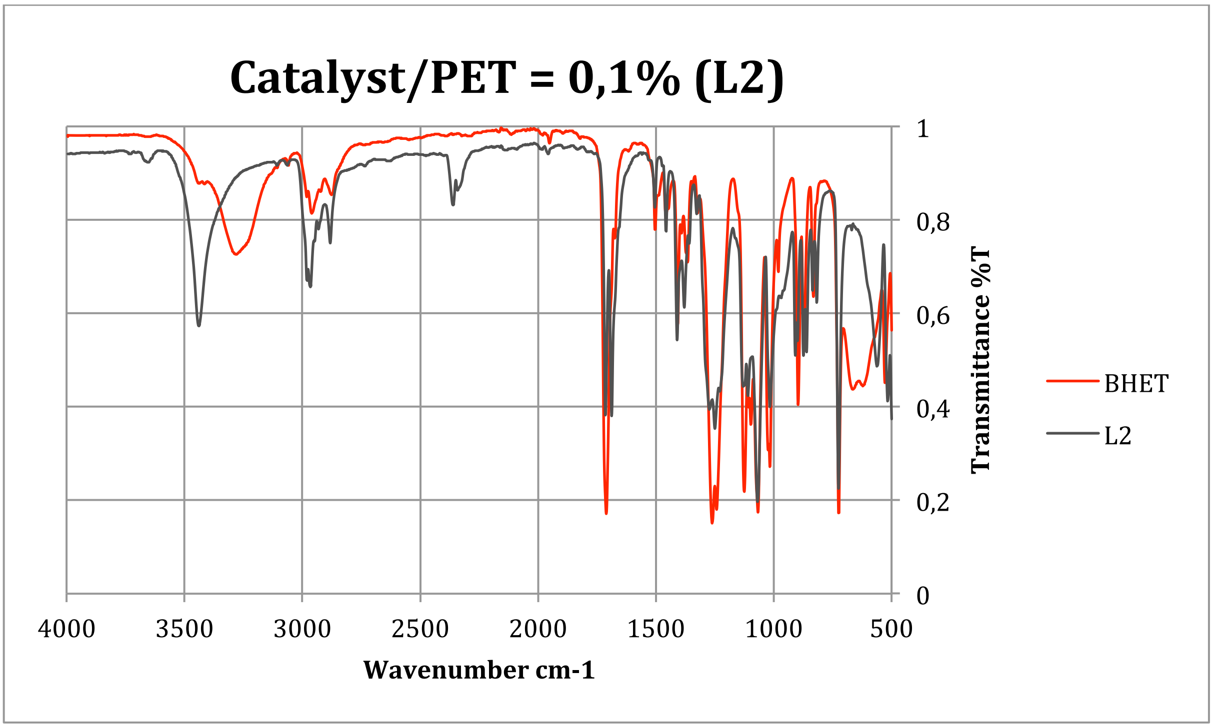


Figure 4.10: The FTIR spectrum for DMT (green), BHET (red) and the monomer obtained from a reaction with the ratio catalyst to PET =0,1% (L2, black).

4.1.3 Differential Scanning Caloremitry

In table 4.1 the samples analysed with DSC is presented along with the colour that represents them in figure 4.10 and 4.11, the enthalpy (J/g) for the melting and crystallization points, where the rate of melting is the highest and their melting point.

Table 4.1: The normalized integral, highest rate of melting (H.R) and peak of melting for samples analysed with DSC for the first and second increase of temperature.

Samples first run	Colour	Normalized integral [J/g]	H.R of melting [°C]	Peak of melting [°C]
Reference BHET a	Orange	-142,00	108,38	109,76
Reference BHET b	Turquoise	-146,52	109,07	109,75
J2 a	Brown	-146,86	107,88	110,08
J2 b	Purple	-144,57	108,32	110,05
L2 a	Green	-149,88	110,06	110,93
L2 b	Blue	-144,68	110,14	111,13
M1 a	Red	-151,28	108,54	110,95
M2 b	Black	-142,56	108,34	110,77
Samples second run	**Colour**	**Normalized integral [J/g]**	**H.R of melting [°C]**	**Peak of melting [°C]**
Reference BHET a	Orange	-118,39	99,63	108,02
Reference BHET b	Turquoise	-122,54	100,05	108,12
J2 a	Brown	-133,42	107,57	110,47
J2 b	Purple	-132,46	107,32	110,35
L2 a	Green	133,48	105,23	107,84
L2 b	Blue	-137,19	107,96	110,77
M1 a	Red	-138,45	108,03	110,52
M2 b	Black	-132,99	107,74	110,44

Figure 4.11 shows the DSC curve of the analysed samples shown in table 4.1. The first peaks show the melting temperatures and enthalpy of the samples at the first increase of temperature. It is seen in figure 4.12 (left) that the melting temperatures and the enthalpy from the melting is quite similar to each other in the first increase of temperature. The second sets of peak in figure 4.10 shows the enthalpy received when the samples start to crystallize. Here it can be seen that the peaks from the references BHET (orange and turquoise) has lower peaks and are shifted right compared to the other peaks, which are sharp and narrow and shifted to the left.

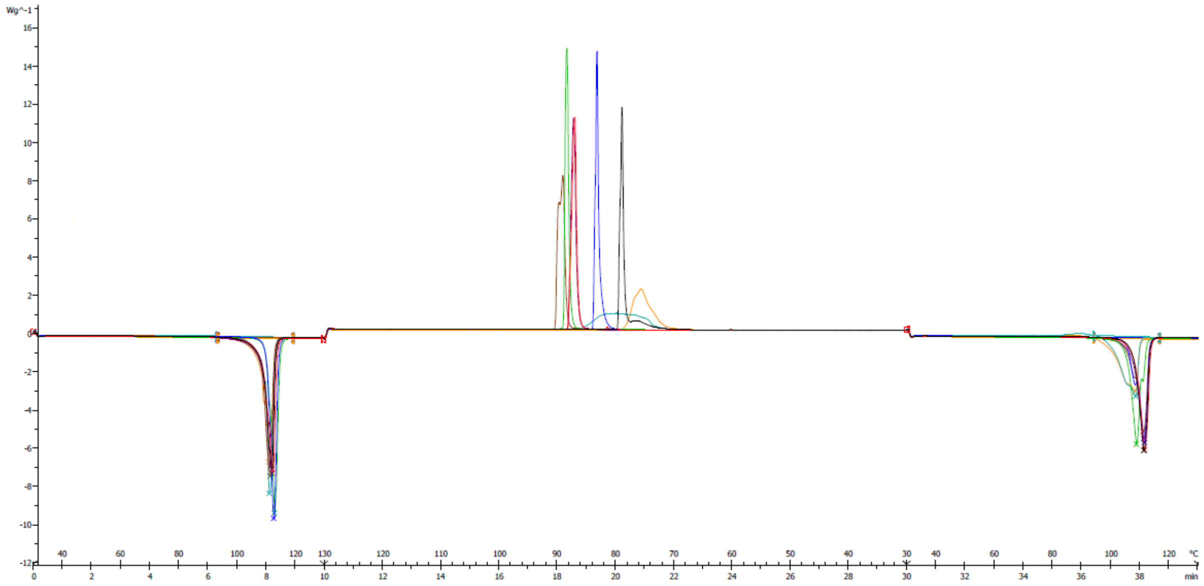


Figure 4.11: DSC-curve of BHET (orange and turquoise), J2 (brown and purple), L2 (green and blue) and M2 (red and black).

The third set of peaks, seen in figure 4.11 (right) shows the melting point and enthalpy achieved from the second temperature increase. Here it can be seen from table 4.1 that the melting temperatures for the obtained monomers are very similar, except for L2b, at about 110,5°C, whilst the melting temperature for the BHET reference is about 108°C. The enthalpy for all samples except for BHET is also quite alike.

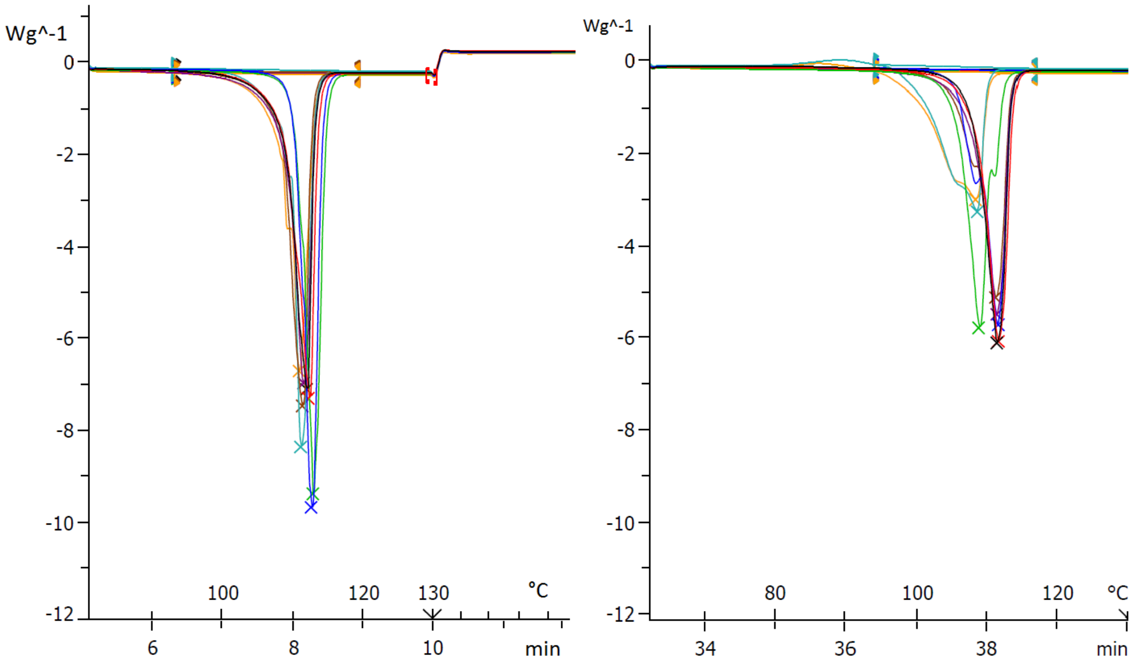


Figure 4.12: Zoom of DSC-curve of BHET (orange and turquoise), J2 (brown and purple), L2 (green and blue) and M2 (red and black).

4.2 Catalyst

To evaluate the MgAl-O@Fe_3O_4-catalyst and whether the coating of the magnetic support succeeded, as well as to evaluate the chemical composition of the catalyst and how it changed after use, the catalyst was analysed with SEM, EDS and XRD.

4.2.1 Scanning Electron Microscope

Figure 4.11 shows the SEM picture of a) Fe_3O_4, which is used as magnetic support for the MgAl-O-catalyst, and b) MgAl-O. The size distribution for Fe_3O_4 is quite large as seen in the left picture, and in figure 4.14 b) that shows the cross section of Fe_3O_4. The topology and morphology of Fe_3O_4 and MgAl-O is also different from each other: the Fe_3O_4 surface is rather smooth whereas the MgAl-O surface is more flaky and porous.

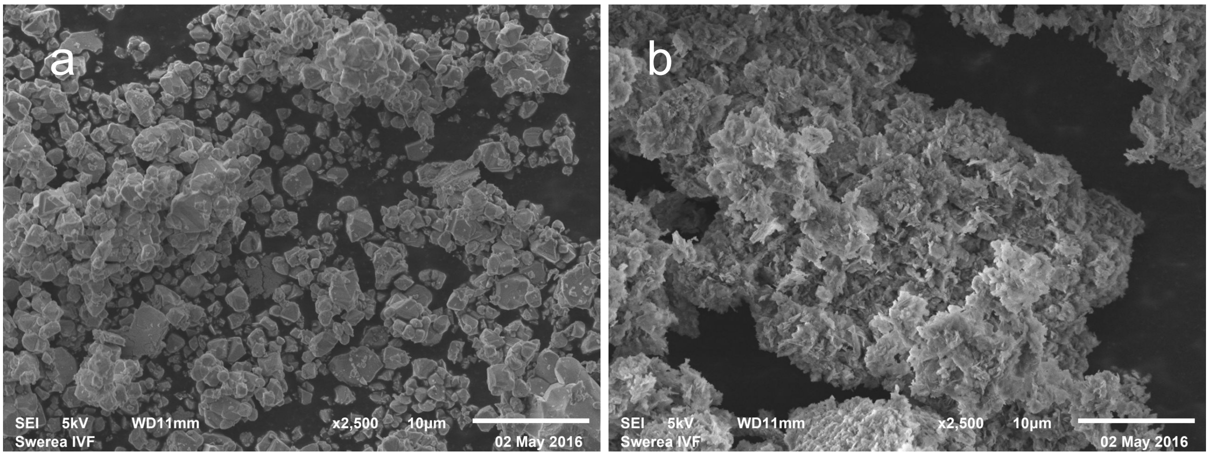


Figure 4.11: The secondary ion (SEI) scanning electron microscope (SEM) pictures showing a) Fe_3O_4 and b) MgAl-O.

Figure 4.12 shows the a) MgAl-O@Fe_3O_4 catalyst and b) the magnetic support Fe_3O_4, and it can be seen that the surface structure and morphology of MgAl-O@Fe_3O_4 is different from pure Fe_3O_4. The surface structure of MgAl-O@Fe_3O_4 is more porous than for Fe_3O_4 and corresponds to the surface structure for MgAl-O indicating that figure 4.12 a) shows Fe_3O_4 covered with MgAl-O. The left picture shows a size distribution alike the one from the right figure.

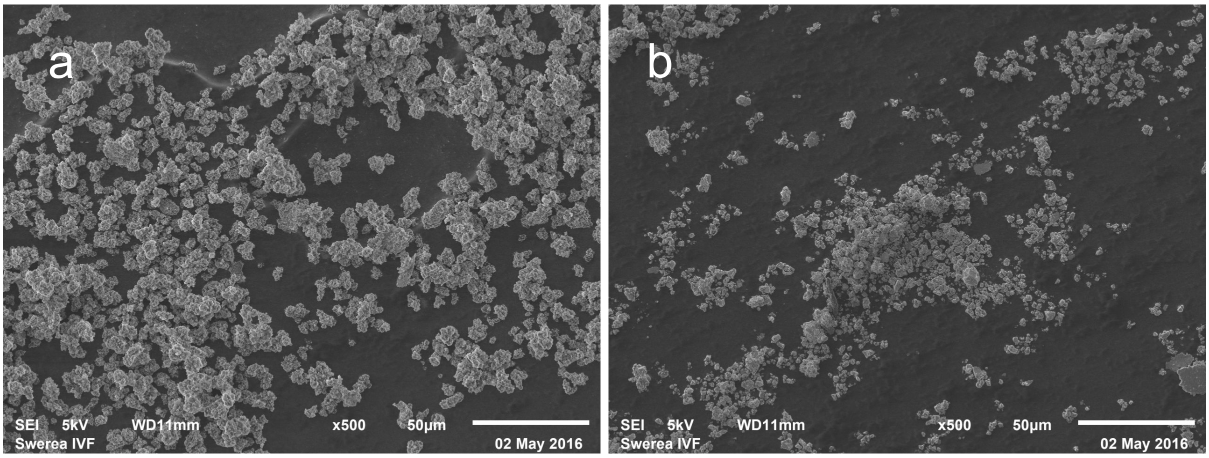


Figure 4.12: The secondary ion (SEI) scanning electron microscope (SEM) pictures of a) MgAl-O@Fe_3O_4 and b) Fe_3O_4.

In figure 4.13, which is a zoom in from 4.12, it is seen how MgAl-O partially is covering a Fe_3O_4 particle. The left figure using secondary electrons shows the differences in topology and surface structure, while the right picture using backscattered electrons, shows the difference in atoms. The light parts shown corresponds to Fe_3O_4 and the dark grey parts to MgAl-O, indicating that the coverage is partially completed.

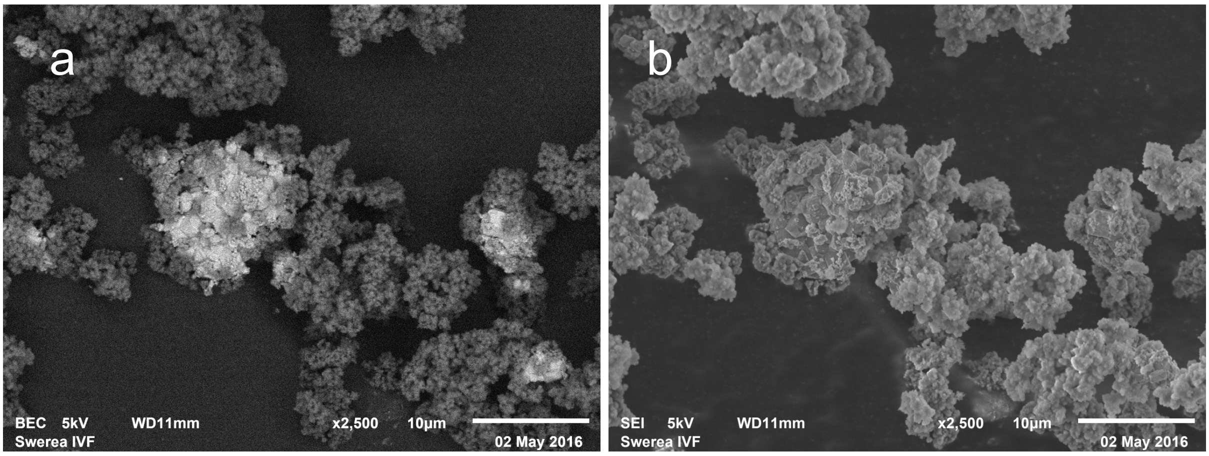


Figure 4.13: The scanning electron microscope (SEM) pictures of MgAl-O@Fe_3O_4: a) backscattering electron (BEC) and b) secondary ion (SEI).

When investigating figure 4.14, which is a) the cross section of the MgAl-O@Fe_3O_4 catalyst and b) Fe_3O_4, the covering of the magnetic support with MgAl-O is not as clear. Partially the MgAl-O is attached to the Fe_3O_4, but there is a lot of loose MgAl-O, and many of the Fe_3O_4 particles have no MgAl-O attached to its surface.

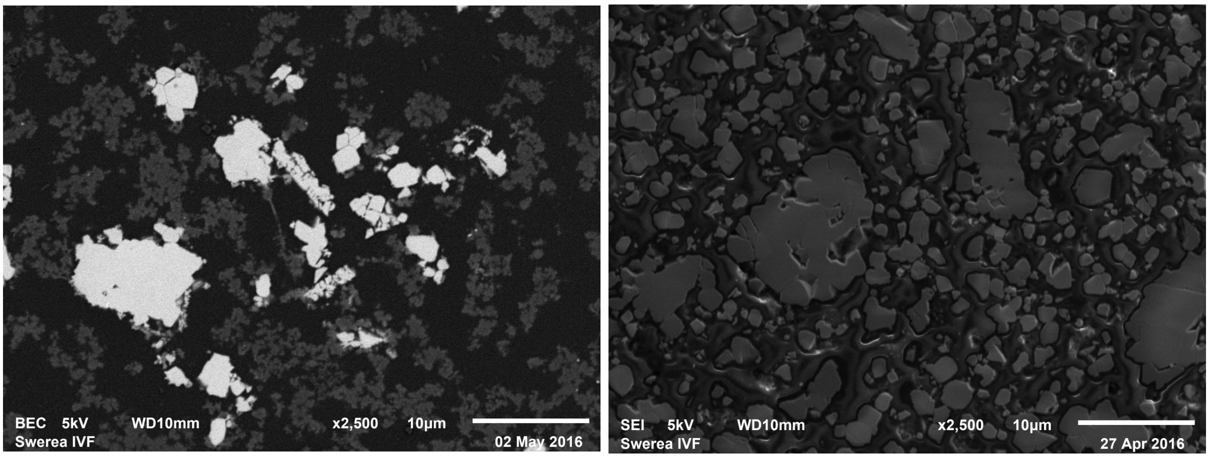


Figure 4.14: a) the secondary ion (SEI) scanning electron microscope (SEM) pictures of the cross section of MgAl-O@Fe_3O_4 *and b) the backscattering electron (BEC) SEM picture of the cross section of* Fe_3O_4*.*

Further more, figure 4.15 shows the MgAl-O@Fe_3O_4 catalyst used for five times and thereafter burned at 900°C, and it can be seen that there is still MgAl-O present on the Fe_3O_4, but the morphology differs from the unused catalyst as well as from pure Fe_3O_4, and the surface structure appear to be less porous.

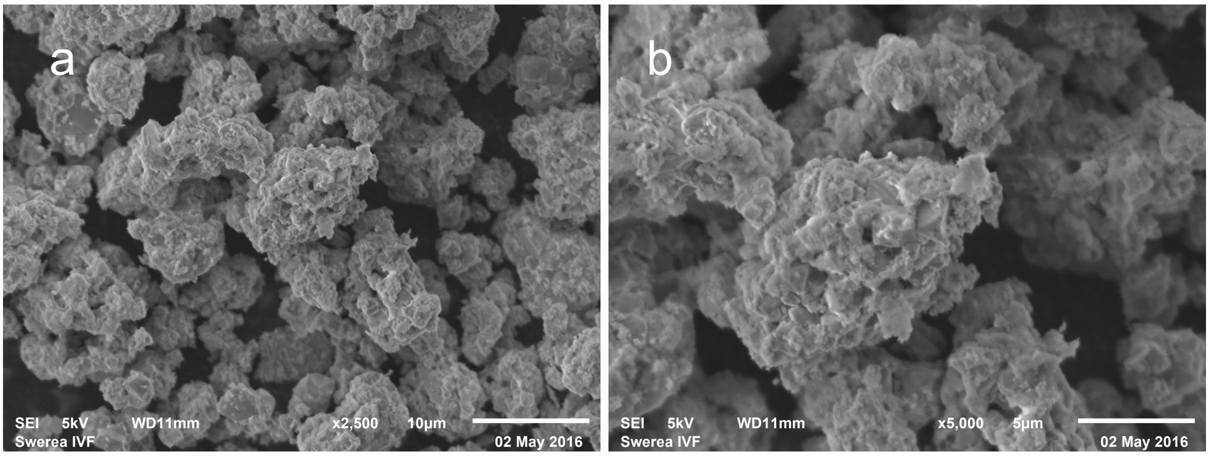


Figure 4.15: a) and b) the secondary ion (SEI) scanning electron microscope (SEM) pictures of MgAl-O@Fe_3O_4 *used 5 times.*

4.2.2 EDS

Looking at figure 4.16, which is an EDS mapping of MgAl-O@Fe_3O_4, all the compounds present is seen in the right picture, and the original picture on the left (SE). The carbon (C, blue) present comes from the carbon sputtering from the sample and can be disregarded. The oxygen present (O, red) appears both in Fe_3O_4 and in the MgAl-O. There is also nickel present (Ni, green), which is existent in Fe_3O_4 and is an impurity of the magnetic support.

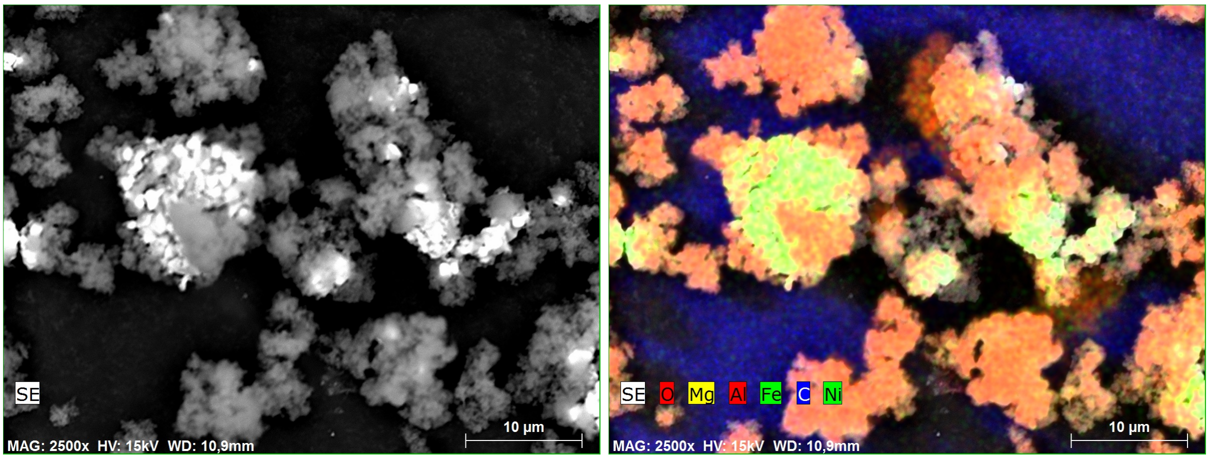


Figure 4.16: a) the EDS mapping of MgAl-O@Fe_3O_4*, with the original image (SE) and b) the mapping with all existent elements on the right on top of the original picture.*

Figure 4.17 shows the EDS mapping of MgAl-O@Fe_3O_4 as well, but here only iron (Fe, green), magnesium (Mg, yellow) and aluminium (Al, red) is mapped to achieve a clearer image. It is seen that Mg and Al partially covers a couple of particles, which is seen as orange around green. The particles that are completely orange can either be free MgAl-O or MgAl-O that completely cover Fe_3O_4 particles. On the right, the mapping is done with nickel marked as green as well, but without the underlying original picture (SE), and it is seen that Fe_3O_4 and nickel is present in most particles, indicating that the MgAl-O seen is covering the magnetic support.

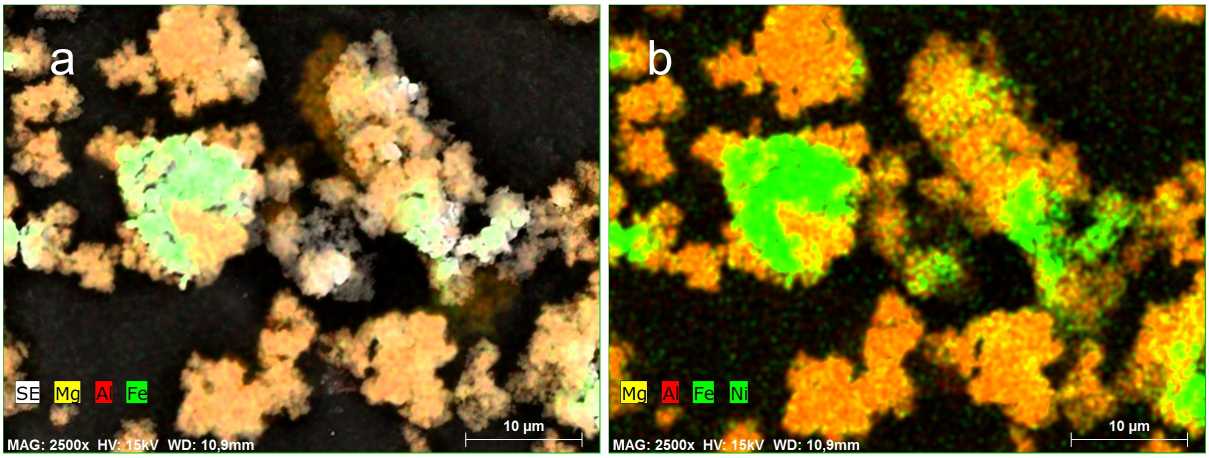


Figure 4.17: a) The EDS mapping of 4.17, showing Fe, Mg and Al and original photo (SE) and b) showing Fe, Ni, Mg and Al.

4.2.3 X-ray diffraction

Figure 4.18 shows the results from XRD for pure Al-O and Mg-O, and for MgAl-O and MgAl-O that has been put in water for 24 h. The pattern for Mg-O corresponds to the pattern of magnesium hydroxide ($Mg(OH)_2$). The pattern for Al-O corresponds to the pattern for k-

Al_2O_3. For MgAl-O, the pattern corresponds to the patterns of $Mg(OH)_2$, $(Mg_{0,80}Al_{0,18})(Al_{1,86}Mg_{0,14})O_4$ and $Mg_{0,97}Al_{0,03}O$.

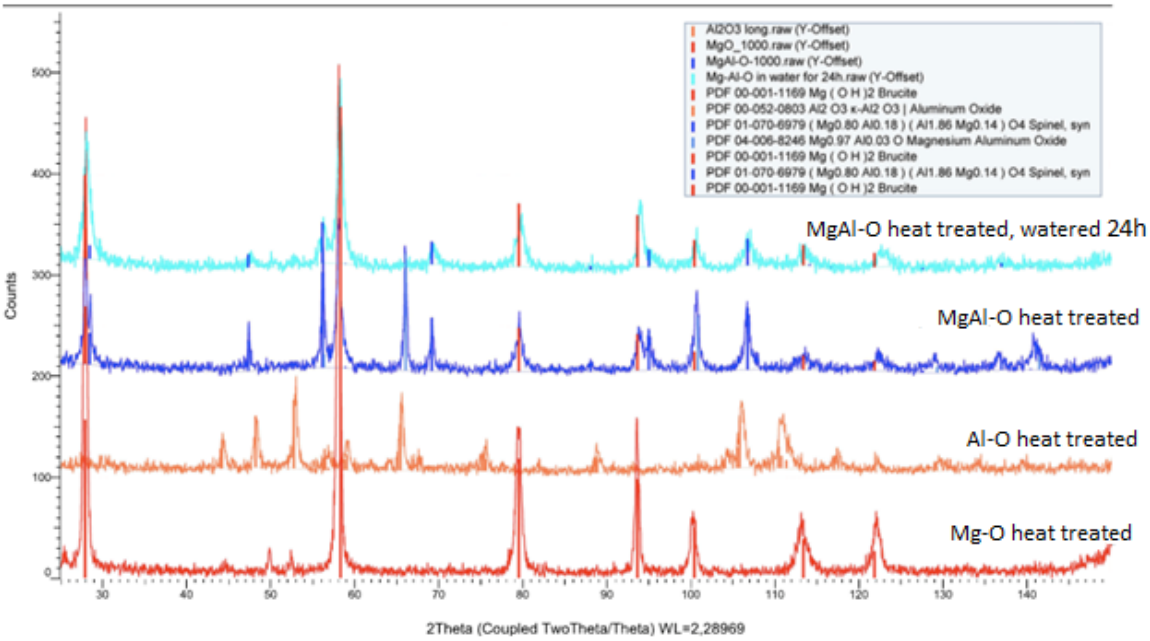
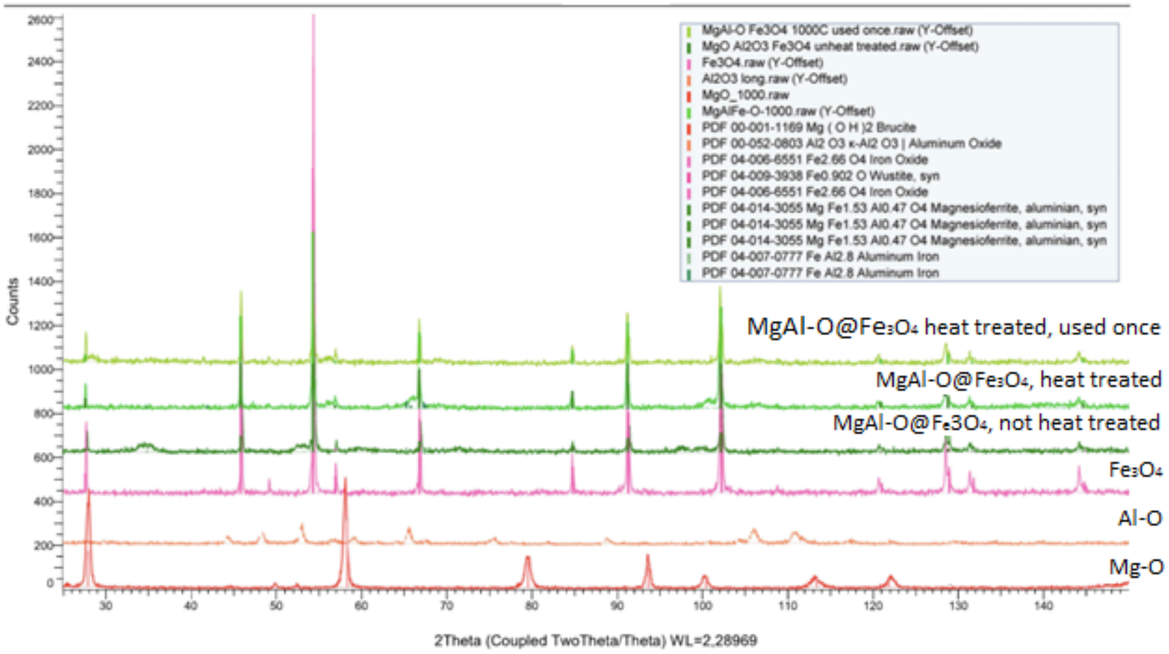


Figure 4.18: The XRD patterns for MgAl-O heat treated at 1000°C, MgAl-O heat treated at 1000°C and watered for 24 h, Al-O and Mg-O.

Figure 4.19 shows the results from XRD for Fe_3O_4, MgAl-O@Fe_3O_4 not heat treated, MgAl-O@Fe_3O_4 heat treated at 1000°C, MgAl-O@Fe_3O_4 heat treated at 1000°C and used once, Mg-O and Al-O. The pattern for Fe_3O_4 corresponds to the ones for $Fe_{2,66}O_4$ and $Fe_{0,902}O$ wurstite. The not heat treated MgAl-O@Fe_3O_4 corresponds to the patterns of $Fe_{2,66}O_4$, $MgFe_{1,53}Al_{0,47}O_4$ and $FeAl_{2,8}$, whilst the pattern for MgAl-O@Fe_3O_4 heat treated at 1000°C corresponds to the pattern for only $MgFe_{1,53}Al_{0,47}O_4$. MgAl-O@Fe_3O_4, heat treated at 1000°C and used once, also corresponds well to $MgFe_{1,53}Al_{0,47}O_4$ but has some changes such as the small peaks at 66° and 101°, that either shifted or disappeared, and a small peak at 28° that has appeared.



Figue 4.19: The XRD patterns for MgAl-O@Fe_3O_4 heat treated at 1000°C and used once, MgAl-O@Fe_3O_4 heat treated at 1000°C, MgAl-O@Fe_3O_4 not heat treated, Fe_3O_4, Al-O and Mg-O.

Figure 3 shows a ruff estimation of the distribution of the compounds found in non heat-treated and heat treated MgAl-O@Fe_3O_4, and it can be seen that no $Fe_{2,66}O_4$ is present in the heat treated catalyst compared to the not heat treated one, and that the ratio of $MgFe_{1,53}Al_{0,47}O_4$ has increased. The amount of $FeAl_{2,8}$ is about the same for both samples.

Figure 4.20: The distribution of different compositions in MgAl-O@Fe_3O_4 not heat treated (left) and heat treated at 1000°C (right).

4.2.4 Magnetic Recovery of Catalyst

Figure 4.21 shows how the separation of the catalyst with a magnet in water. At t=0 s the catalyst is dispersed in the water, and at t=15 s the catalyst is completly separated and is attatched to the magnet.

Figure 4.21: Separation of the catalyst with a magnet at three different stages from t=0 (left) and t=15s (right).

5 DISCUSSION

The MgAl-O@Fe_3O_4 catalyst has shown to have a good conversion of PET into monomers and the catalyst is easily separated by a magnet, as shown in figure 4.21. When it comes to the characterization of the monomers, it is uncertain whether the wanted BHET is formed in all experiments, and the amount of monomers formed compared to oligomers is not established.

5.1 Monomers

From the conversion in figure 4.1, it is seen that Fe_3O_4 on its own has no catalytic activity during the present reaction conditions, but that the combination of MgAl-O and Fe_3O_4 results in a slightly higher conversion than pure MgAl-O, indicating that the combination has a higher catalytic activity than MgAl-O itself. Also, no differences in conversion can be seen from the heat treated and the watered MgAl-O@Fe_3O_4, indicating that the activity of the catalyst does not depend on whether there are hydroxide or oxygen groups present in the catalyst.

Furthermore, the results from FTIR indicate that the formed monomers differ between different experiments. The differences, such as the sharp peak at 3450 cm^{-1} in figure 4.10 might come from a sterically hindered hydroxyl group (OH) or from leakage form the catalyst into the monomer. When the results from FTIR are compared to the results from DSC, it is seen that the melting temperature and the enthalpy for the first increase in temperature is relatively equal. In the second increase of the temperature, the enthalpy of the monomers received from the experiments differs from the reference but is quite equal to each other. The melting temperature among the monomers from experiments is about two degrees Celsius higher then the references, except for L2 a which is one degree lower, indicating that the monomers obtained is rather similar to each other, but might differ from the reference.

In figure 4.4, which shows the influence of the catalyst shape on the conversion, it can be seen that it has a small effect on the conversion with this catalyst, from micro scale up to pellets size, which can provide a new approach in terms of an easily recycled catalyst in the shape of pellets.

5.2 Catalyst

When observing the results from SEM, it can be seen in figure 4.12 that the topology and morphology of Fe_3O_4 has changed between the pure Fe_3O_4 and the MgAl-O@Fe_3O_4, which indicates that the covering of the magnetic support with catalyst has succeeded. When looking at the cross section in figure 4.14 on the other hand, the coverage seems to be non existing or inadequate. This might depend on the sample preparation with the embedment of catalyst particles into epoxy, or that the coverage of the particles are rather low and therefore can not be seen in cross section pictures. The results from EDS in picture 4.16 promote this theory since it can be seen that the magnetic support is only partially covered by the catalyst in most cases.

The results from XRD, (figure 4.18) show that the spectra for Mg-O corresponds to the pattern of magnesium hydroxide ($Mg(OH)_2$), which indicates that there is not only Mg-O but also Mg-OH in the sample. This is most likely because magnesium readily reacts with water forming MgOH, and reacts with the water in the atmosphere during storage. For MgAl-O, the pattern corresponds to the patterns of $Mg(OH)_2$, $(Mg_{0,80}Al_{0,18})(Al_{1,86}Mg_{0,14})O_4$ and $Mg_{0,97}Al_{0,03}O$, indicating that MgAl-O is a combination of these three, containing MgAl mixed oxides as well as $Mg(OH)_2$, but no k-Al_2O_3. The pattern for MgAl-O put in water for 24 h is quite similar to the one for MgAl-O, but does not correspond to $Mg_{0,97}Al_{0,03}O$, and has higher counts for $Mg(OH)_2$ then for $(Mg_{0,80}Al_{0,18})(Al_{1,86}Mg_{0,14})O_4$, indicating that the amount of $Mg(OH)_2$ has increased by the water treatment and therefore shows that the composition of MgAl-O changes when put in water to form hydroxides.

In figure 4.19, the pattern for the non heat treated MgAl-O@Fe_3O_4 and for MgAl-O@Fe_3O_4 heat treated at 1000°C differs, indicating that the heat treatment has changed the composition of the catalyst. This can be confirmed by figure 4.20 showing that the composition of the not heat treated and the heat treated catalyst has changed. Also, the peaks of MgAl-O@Fe_3O_4 heat treated at 1000°C is shifted slightly to the left compared with the not heat treated, indicating that the lattice parameters has increased and that ion diffusion of Mg^{+2} and Al^{+3} into the magnetic support has occurred. For MgAl-O@Fe_3O_4 heat treated at 1000°C and used once has some changes such as the small peak at 66° and 101° has either shifted or disappeared, and a small peak at 28° has appeared, indicating that a small change has occurred in the sample.

However, as seen in figure 4.19, there is no indication of separate MgAl-O in the catalysts in XRD, even if figure 4.20 shows an increase of $MgFe_{1,53}Al_{0,47}O_4$ in the catalyst during heat treatment, indicating that there must be some free MgAl-O to react with. This might be because the concentration of MgAl-O is much lower then the concentration of Fe_3O_4, leading to that the peaks of MgAl-O is so small in comparison with Fe_3O_4 that they are mistaken for noise.

As for the separation of the catalyst, it is easily done by a magnet. Yet, the amount of catalyst recovered by magnet and the possible leakage of catalyst is not determined. However, visually all of the catalyst seems to be recovered.

5.3 Recycling

Regarding the recycling of the catalyst, high conversion was recorded until the fifth use. For the first run, the conversion was about 10% lower then the conversion for catalyst/PET ratio = 1%, which is around 80%. This is probably because of the transesterfication reaction reaching an equilibrium, and that the amount of catalyst for the first run was so high that the depolymerised monomers started to polymerise again. For the fourth run, the conversion differed between the experiments. This is probably because of more loss of catalyst in one experiment while handling the catalyst. The SEM pictures (figure 4.15) shows that MgAl-O@Fe_3O_4 catalyst used five times compared to 4.12 b) that shows the unused MgAl-O@Fe_3O_4, no difference can be seen. Looking at figure 4.19 for MgAl-O@Fe_3O_4 unused and used once, some few differences can be seen. For example a small peak can be seen at 31°, and the small peak at 67° at MgAl-O@Fe_3O_4 unused is shifted slightly to the right to 69°, indicating that the catalyst has changed slightly during use.

6 CONCLUSION

The preparation of the MgAl-O@Fe_3O_4 catalyst appears to have succeeded, and from the SEM pictures it seems as if the MgAl-O covers the magnetic Fe_3O_4 support. Due to heat treatment, a more robust catalyst seems to have been formed due to bonding between MgAl-O and Fe_3O_4, which can be seen in the results from XRD. Also, the magnetic separation of the catalyst can be established, providing an easy method for separation of the catalyst.

The catalyst shows high conversion of PET into monomers, even if the chemical composition of the monomers cannot be fully determined with FTIR or DSC. From this work it cannot be stated whether it is the oxide or hydroxide groups that carries the catalytic effect since both heat-treated and watered catalyst carries out about the same conversion.

7 FUTURE WORK

The work presented here provides a magnetic MgAl-O catalyst for depolymerisation of polyester. The results confirm that the catalyst is magnetic with high conversion, but the selectivity of BHET is not stated. There exist several interesting aspects in this work that should need further investigation, such as:

- The true chemical composition of the monomers formed to ensure that the catalyst works as wanted. This can be done by H-NMR.
- The magnetic strength of the catalyst, which can be done by a magnetic hysteresis loop, and how it differs with the size of the support as well as the amount of catalyst participated on top of the magnetic support.
- The surface area of the catalyst and how it differs between size of catalyst and on the heat treatment/watering of the catalyst, which can be done by N^2-absorption.
- The leakage of catalyst into the monomers.
- The recycling of the catalyst after reactivation after the fourth usage, by heat treatment.
- The calcination temperatures effect of the durability and leakage of the catalyst together with its activity.

Further on, if the catalyst shows to be of further interest, optimal parameters such as calcination temperature, ratio of catalyst/PET and EG/PET, reaction time and temperature should be investigated.

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9 APPENDIX

9.1 Serial numbers of experiments

Table 9.1 shows all the experiments that have been used for the results. The type and amount of catalyst is shown together with the conversion. Each experiment has an unique serial number displayed under "Serial number". The reaction conditions for all experiments if nothing else is stated is 240°C for 2 h.

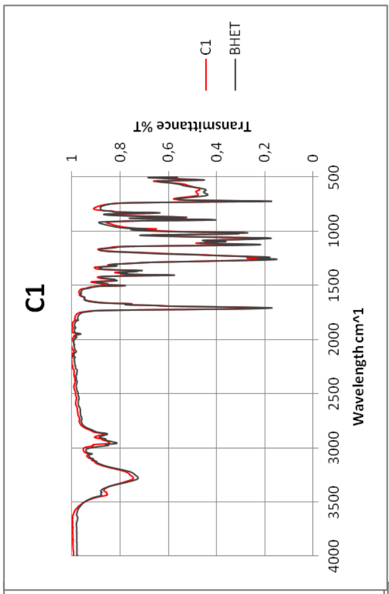
Table 9.1: Type and amount of catalyst for each series number used in the evaluation of results.

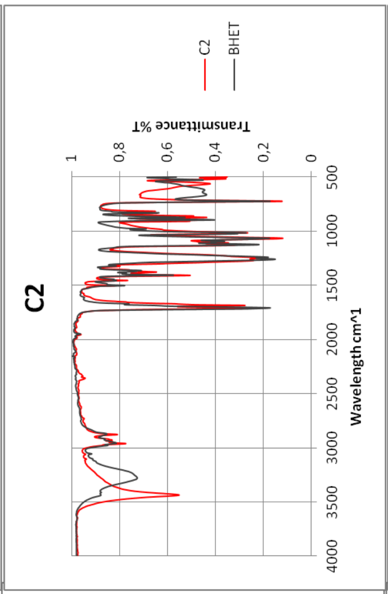
Type of catalyst	Serial number	catalyst [g]	conv [%]	cat/PET
MgAl-O@Fe_3O_4	T1	0,1000	78%	1,00%
MgAl-O@Fe_3O_4	T2	0,0479	-	1,01%
No catalyst	A1	0,0000	2%	0,00%
No catalyst	A2	0,0000	1%	0,00%
No catalyst	A3	0,0000	2%	0,00%
Fe_3O_4	B1	0,1003	1%	1,00%
Fe_3O_4	B3	0,0999	1%	1,00%
Fe_3O_4	B4	0,1003	1%	1,00%
MgAl-O@Fe_3O_4	C1	0,1000	82%	1,00%
MgAl-O@Fe_3O_4	C2	0,1000	79%	1,00%
MgAl-O@Fe_3O_4	C3	0,1133	79%	1,00%
MgAl-O@Fe_3O_4, watered	D1	0,1001	79%	1,00%
MgAl-O@Fe_3O_4, watered	D2	0,1001	81%	1,00%
MgAl-O@Fe_3O_4, watered	D3	0,1002	79%	1,00%
MgAl-O@Fe_3O_4, watered	D4	0,1002	80%	1,00%
MgAl-O 3:1	E4	0,1001	75%	1,00%
MgAl-O 3:1	E5	0,1001	76%	1,00%
MgAl 3:1	E6	0,1000	71%	1,00%
FeMgAl-O composite	F1	0,1001	84%	1,00%
FeMgAl-O composite	F2	0,1001	81%	1,00%
FeMgAl-O composite	F3	0,0999	82%	1,00%
1% MgAl-O@Fe_3O_4	G1	0,1000	82%	1,00%
1% MgAl-O@Fe_3O_4	G2	0,0997	82%	1,00%
1% MgAl-O@Fe_3O_4	G3	0,1000	80%	1,00%
5% MgAl-O@Fe_3O_4	R1	0,5001	71%	5,00%
5% MgAl-O@Fe_3O_4	R2	0,5000	69%	5,00%
5% MgAl-O@Fe_3O_4	R3	0,4998	74%	5,00%
0,5% MgAl-O@Fe_3O_4	I1	0,0501	86%	0,50%
0,5% MgAl-O@Fe_3O_4	I2	0,0500	82%	0,50%
0,5% MgAl-O@Fe_3O_4	I3	0,0500	80%	0,50%

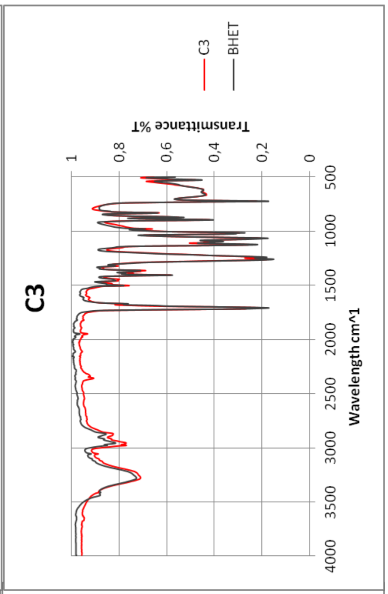
0,25% MgAl-O@Fe_3O_4	J1	0,0249	82%	0,25%
0,25% MgAl-O@Fe_3O_4	J2	0,0250	81%	0,25%
0,25% MgAl-O@Fe_3O_4	J3	0,0250	82%	0,25%
2,5% MgAl-O@Fe_3O_4	M1	0,2500	73%	2,50%
2,5% MgAl-O@Fe_3O_4	M2	0,2499	73%	2,50%
2,5% MgAl-O@Fe_3O_4	M3	0,2499	76%	2,50%
0,1% MgAl-O@Fe_3O_4	L1	0,0100	86%	0,10%
0,1% MgAl-O@Fe_3O_4	L2	0,0100	70%	0,10%
0,1% MgAl-O@Fe_3O_4	L3	0,0100	78%	0,10%
MgAl-O@Fe_3O_4 first recycling	R1-1	0,4994	77%	4,99%
MgAl-O@Fe_3O_4 first recycling	R2-1	0,6141	78%	6,14%
MgAl-O@Fe_3O_4 first recycling	R3-1	0,4911	77%	4,91%
MgAl-O@Fe_3O_4 second recycling	R1-2	0,3058	79%	3,06%
MgAl-O@Fe_3O_4 second recycling	R2-2	0,2816	80%	2,81%
MgAl-O@Fe_3O_4 second recycling	R3-2	0,3887	80%	3,89%
MgAl-O@Fe_3O_4 third recycling	R1-3	0,2376	53%	2,38%
MgAl-O@Fe_3O_4 third recycling	R2-3	0,2164	x	2,17%
MgAl-O@Fe_3O_4 third recycling	R3-3	0,1703	80%	1,70%
MgAl-O@Fe_3O_4 fourth recycling	R1-4	0,1220	2%	1,22%
MgAl-O@Fe_3O_4 fourth recycling	R2-4	0,1652	3%	1,65%
MgAl-O@Fe_3O_4 fourth recycling	R3-4	0,1425	1%	1,42%
FeMgAl-O composite pellets 240°C	P1-1	1,3549	81%	13,55%
FeMgAl-O composite pellets 220°C	P1-2	1,3093	49%	13,08%
FeMgAl-O composite pellets 200°C	P1-3	1,2862	0%	12,86%
FeMgAl-O composite powder 240°C	P2-1	0,1000	77%	1,00%
FeMgAl-O composite powder 220°C	P2-2	0,1000	60%	1,00%
FeMgAl-O composite powder 200°C	P2-3	0,1000	1%	1,00%
FeMgAl-O composite granul 240°C	P3-1	0,1000	83%	1,00%
FeMgAl-O composite granul 220°C	P3-2	0,1000	78%	1,00%
FeMgAl-O composite granul 200°C	P3-3	0,1000	0%	1,00%

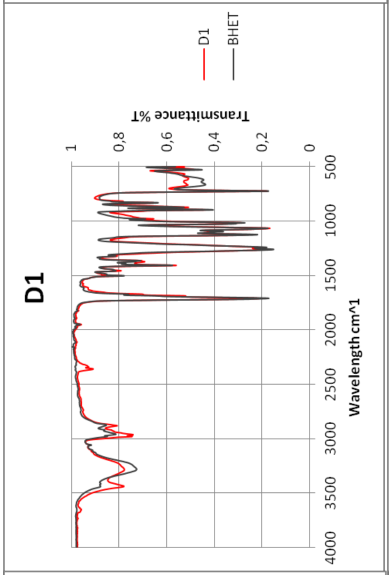
9.2 FTIR

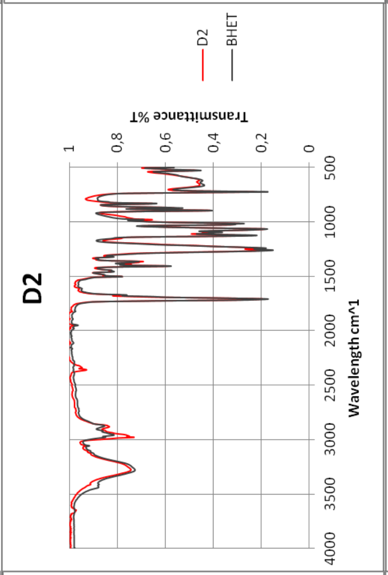
Here are all FTIR spectrums that have been used for the evaluation displayed

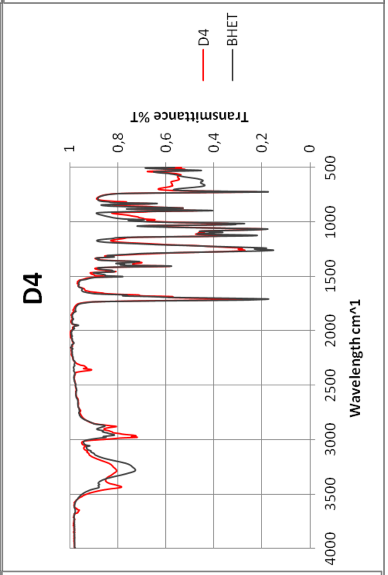


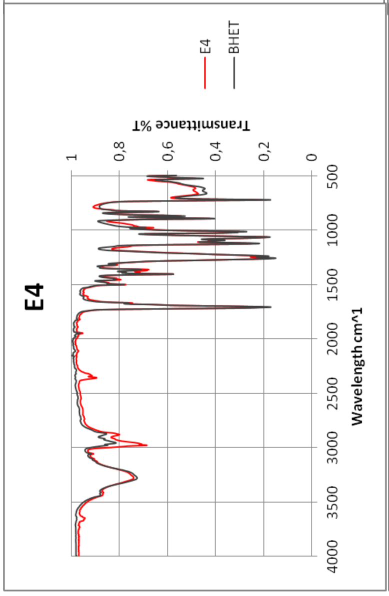


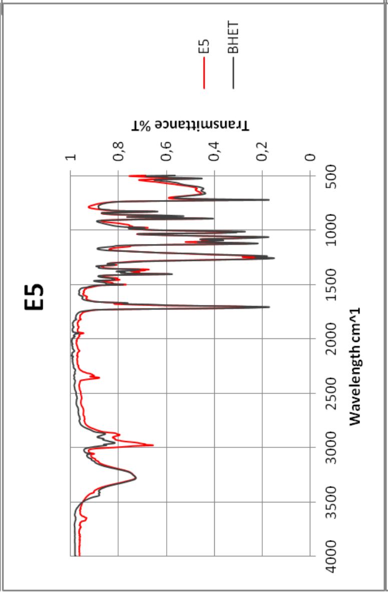


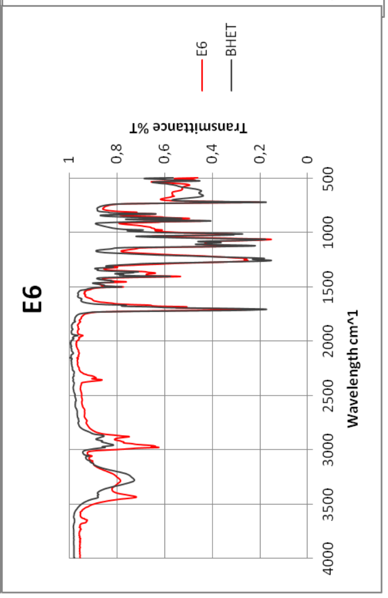


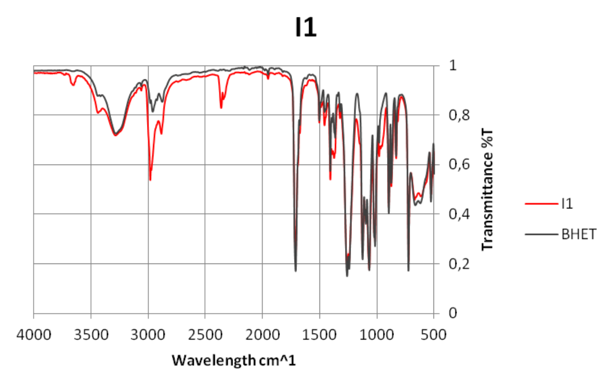








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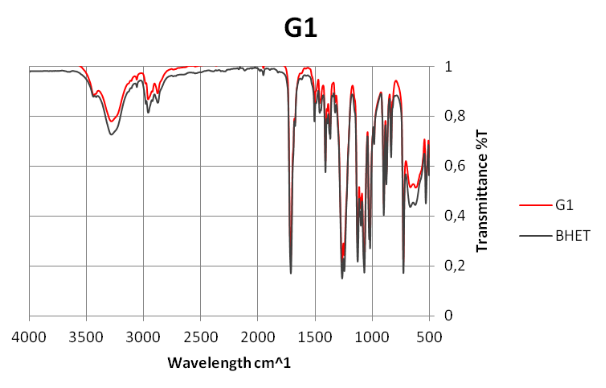
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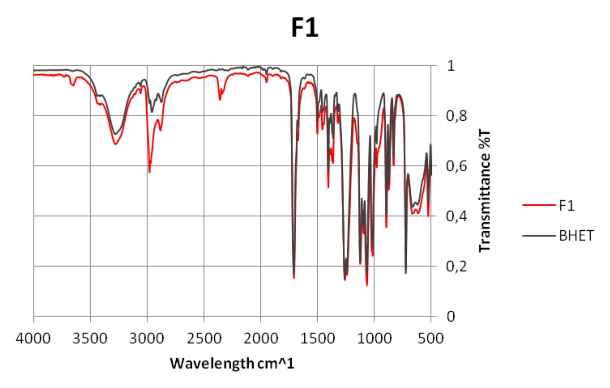
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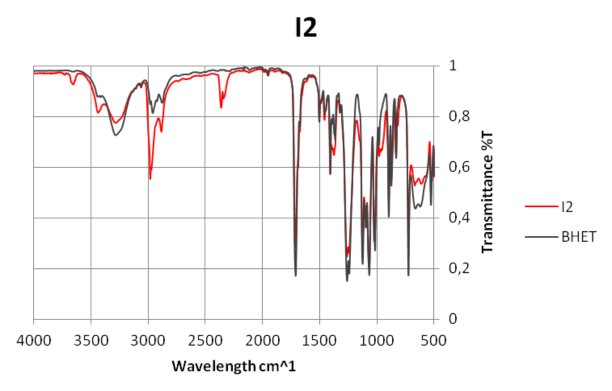
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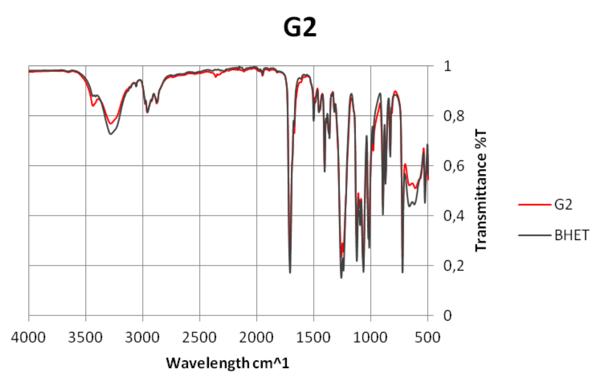
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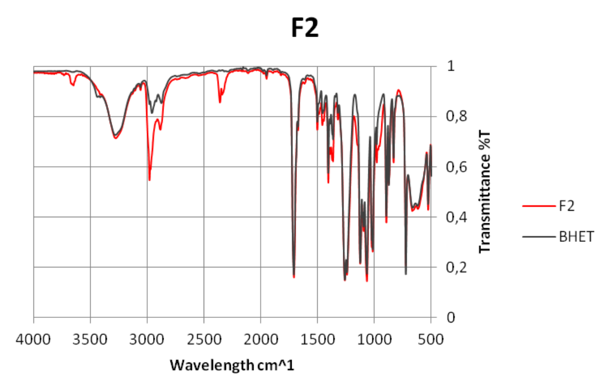
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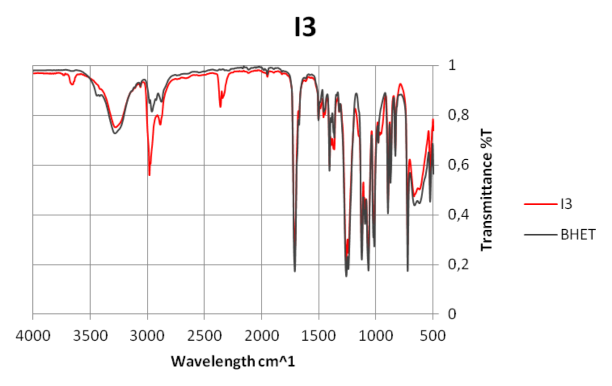
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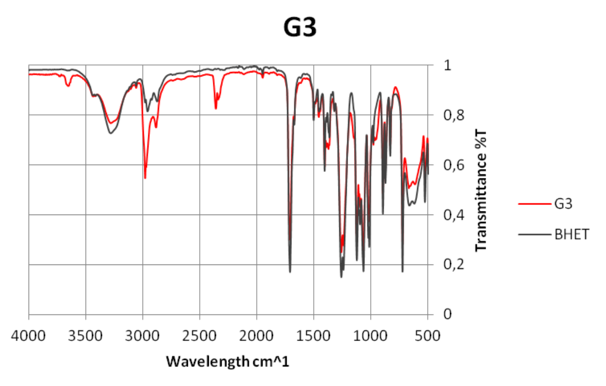
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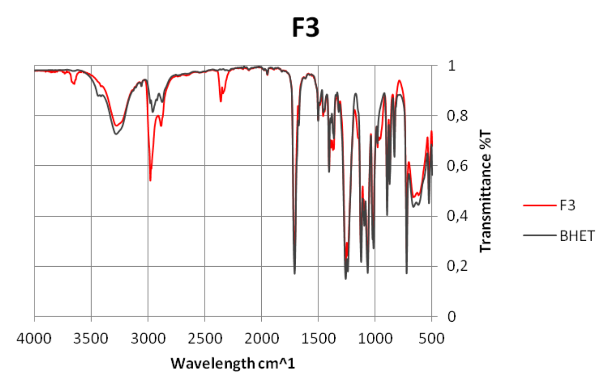
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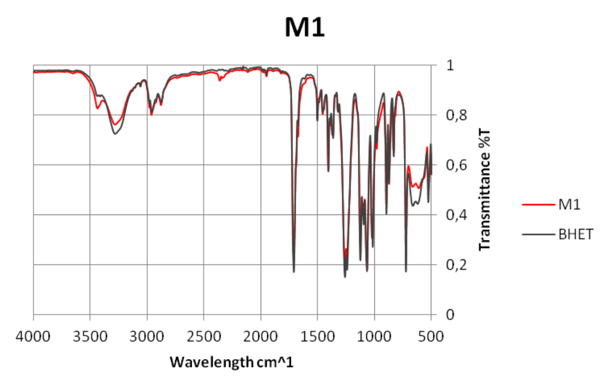
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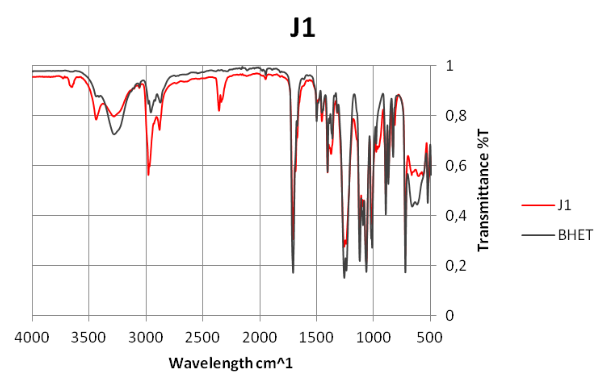
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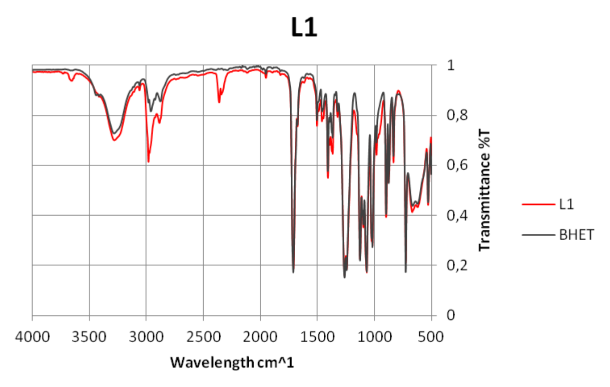
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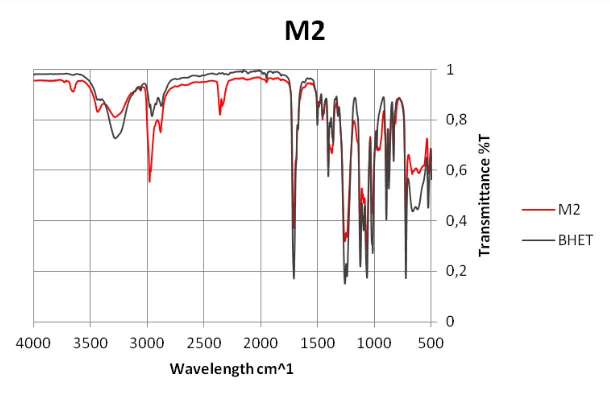
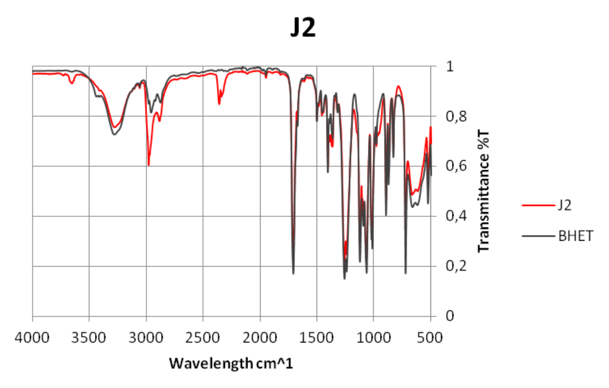
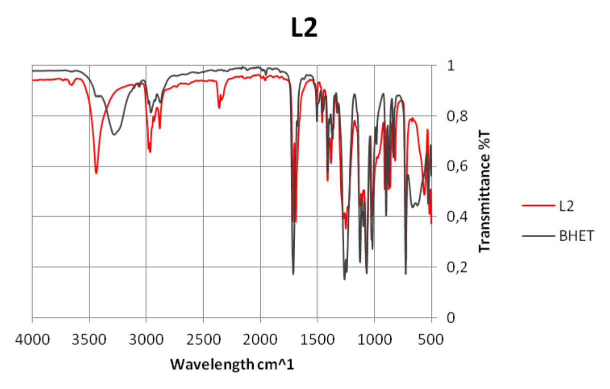
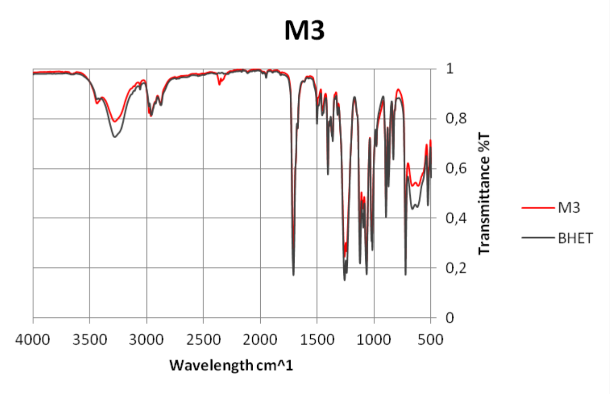
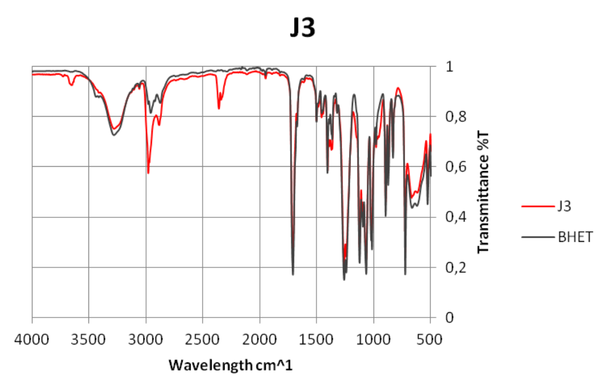
L1
BHET

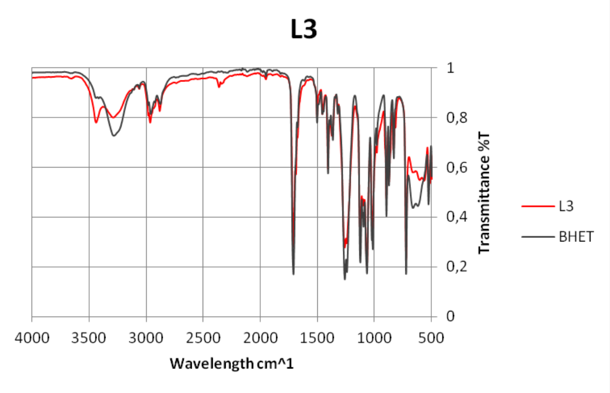

M2
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
M2
BHET

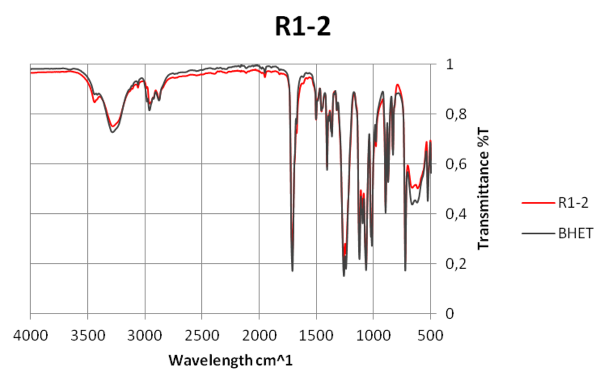

J2
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
J2
BHET

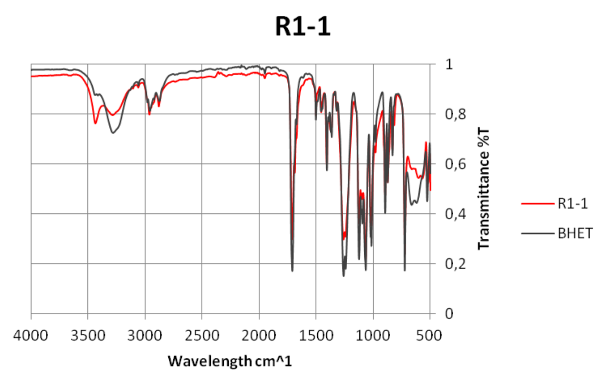

L2
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
L2
BHET

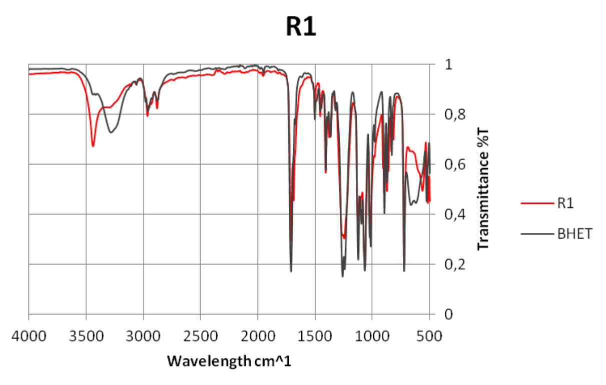

M3
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
M3
BHET

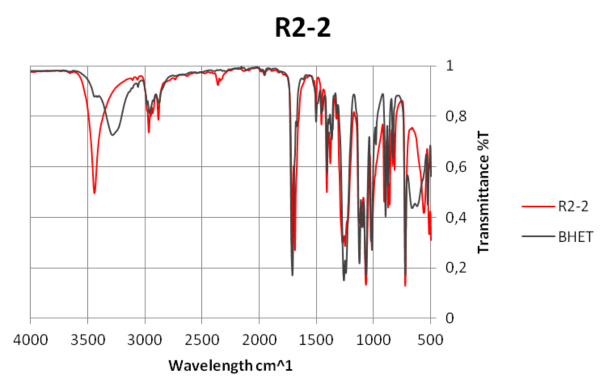

J3
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
J3
BHET

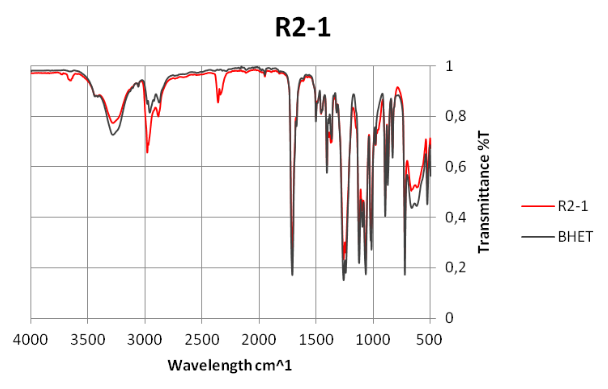

L3
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
L3
BHET

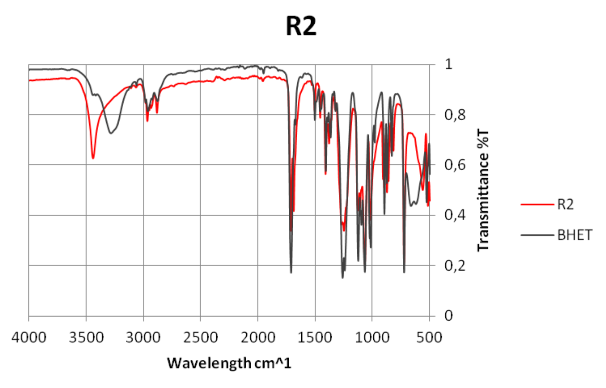

R1-2
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R1-2
BHET

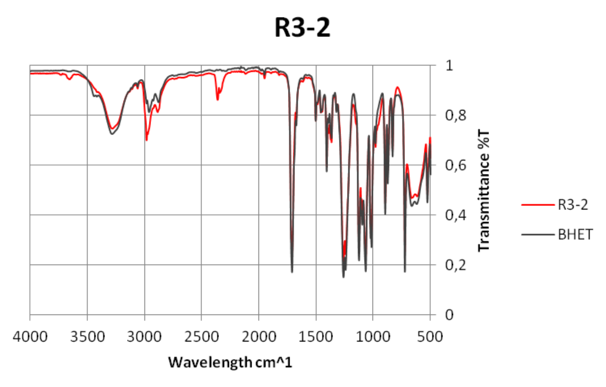

R1-1
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R1-1
BHET

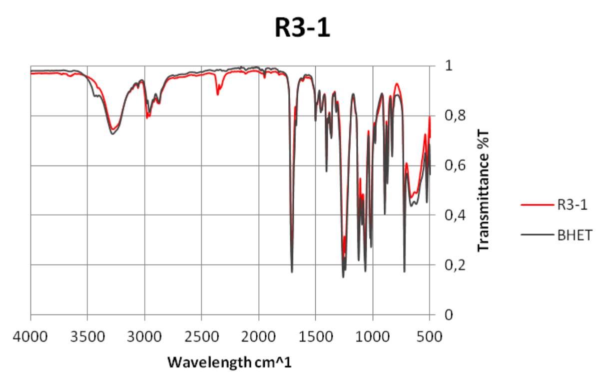

R1
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R1
BHET

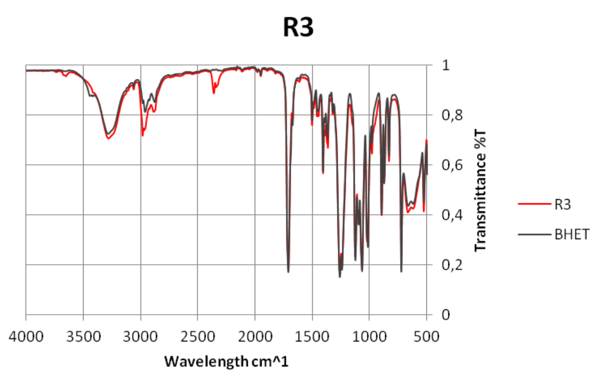

R2-2
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R2-2
BHET

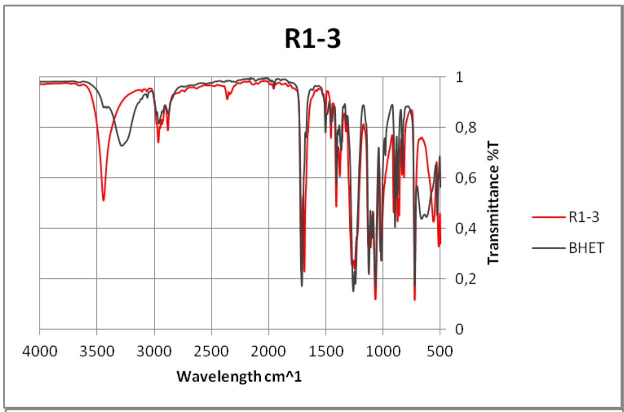

R2-1
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R2-1
BHET

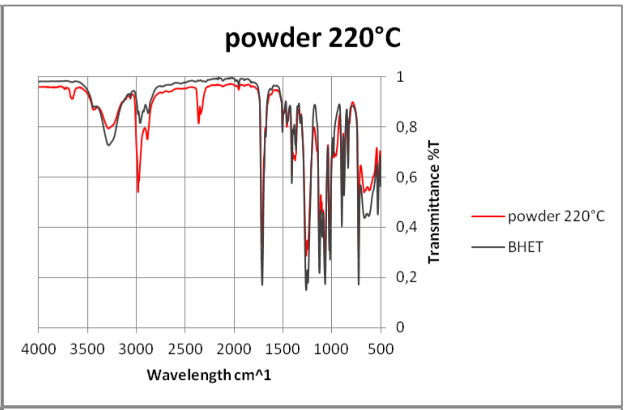

R2
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R2
BHET

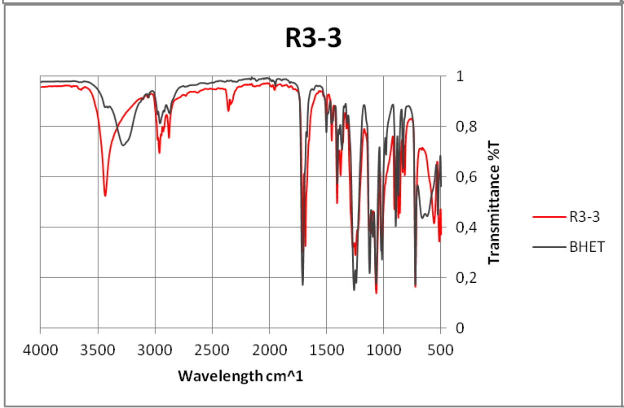

R3-2
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R3-2
BHET

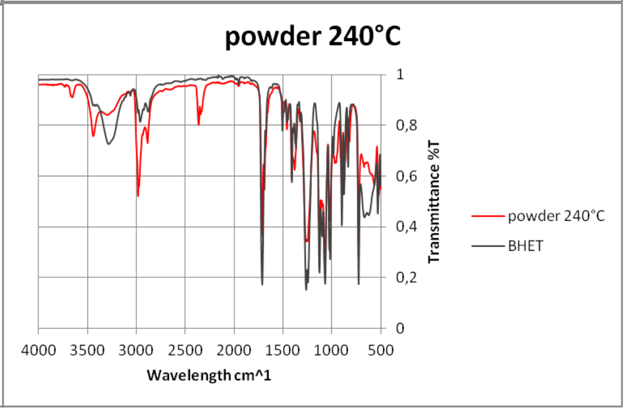

R3-1
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R3-1
BHET

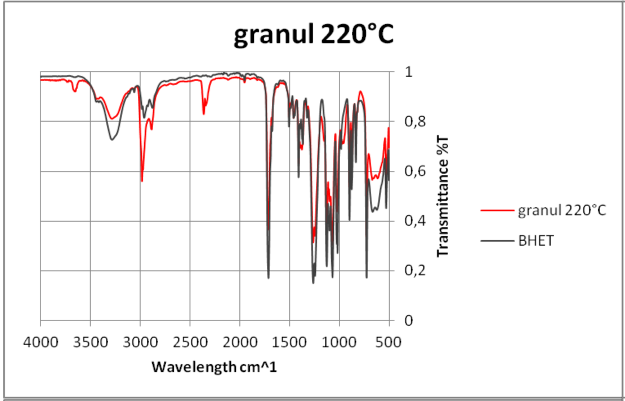

R3
1
0,8
0,6
0,4
0,2
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength cm^1
Transmittance %T
R3
BHET

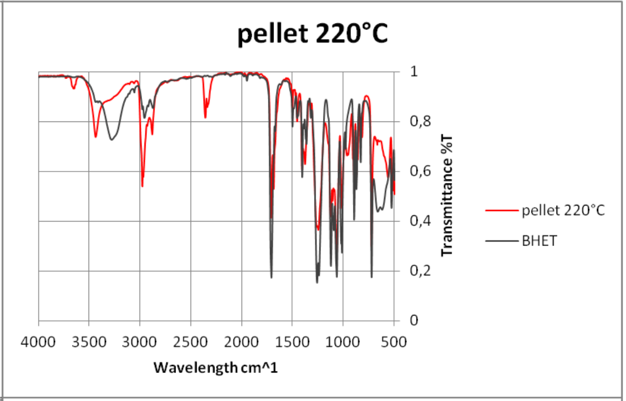

R1-3
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm^1
R1-3
BHET

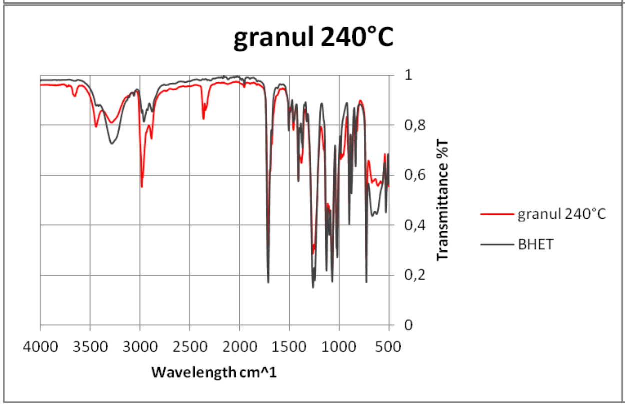

powder 220°C
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm^1
powder 220°C
BHET

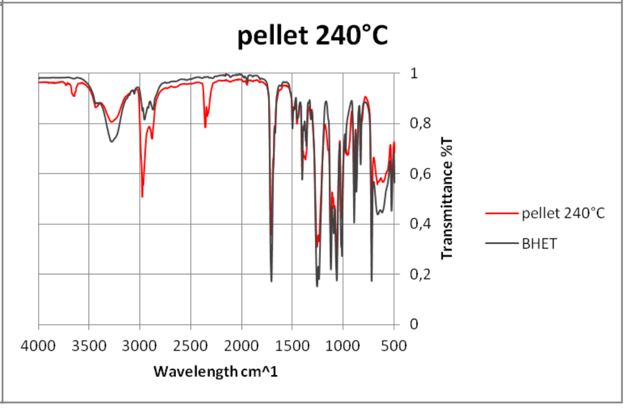

R3-3
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm^1
R3-3
BHET


powder 240°C
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm^1
powder 240°C
BHET


granul 220°C
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm^1
granul 220°C
BHET


pellet 220°C
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm^1
pellet 220°C
BHET


granul 240°C
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm^1
granul 240°C
BHET


pellet 240°C
1
0,8
0,6
0,4
0,2
0
Transmittance %T
4000 3500 3000 2500 2000 1500 1000 500
Wavelength cm^1
pellet 240°C
BHET