POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

Master of Science Course

in Chemical and Sustainable Processes Engineering

Master of Science Thesis

Innovative microwave PET degradation and recycle

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March 2020

To my parents, Gilda and Paolo

and to my sister Petra

Abstract

Polyethylene terephthalate (PET) is a widely used polyester material which dominates the global plastics market thanks to its excellent tensile and impact strength and chemical resistance. It also plays a major role in building a sustainable future, since it is fully recyclable.

The purpose of this study is to investigate the chemical recyclability of PET under microwave irradiation through three different chemical reactions: glycolysis, hydrolysis and aminolysis.

The goal is to chemically depolymerize the PET polymer chains. The microwave treatment has many advantages over conventional heating methods: it is faster, requires less energy and assures a higher reaction efficiency.

In this work neat PET from a wasted bottle was analyzed with different techniques such as Fourier transform infrared spectroscopy (ATR-FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), proton nuclear magnetic resonance (H-NMR) and carbon-13 nuclear magnetic resonance (C-NMR), in order to fully characterize the starting polymer.

The depolymerization reaction was carried out in a sealed microwave reactor. It was possible to control different reaction parameters such as temperature, PET:reagent ratio and microwave irradiation power. The reaction time influence on the final products was also investigated. The reagents used were ethylene glycol, water, ethanolamine and glycerol.

The products of the degradation were analyzed NMR, size-exclusion chromatography (SEC) and ATR-FTIR analysis. The use of microwave radiations proved to be extremely effective since it was possible to obtain a complete depolymerization after 5 minutes in the reactions performed with ethanolamine.

In order to create a new thermosetmaterial, the obtained products were subsequently methacrylated by a reaction performed into the microwave. The success of the reaction was confirmed by the NMR and ATR-FTIR analysis.

Both the UV-curing and thermal curing on the modified molecules were performed using Polyethylene Glycol Dimethacrylate as co-reagent.

This work leads to highly interesting and valuable results which suggest further investigations.

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Sommario

Il polietilene tereftalato (PET) è un poliestere ampiamente utilizzato nel mercato globale della plastica grazie alla sua eccellente resistenza a trazione e agli urti e alla sua resistenza chimica. Il PET inoltre svolge un ruolo cruciale nel fornire un futuro più sostenibile attraverso il suo riciclaggio.

Lo scopo di questa tesi è quello di studiare il riciclo chimico del PET mediante glicolisi, idrolisi e aminolisi sotto irraggiamento a microonde: attraverso queste reazioni è resa possibile la depolimerizzazione delle catene del PET. L'irraggiamento a microonde permette di ottenere un'alta resa di reazione in tempi minori rispetto al riscaldamento convenzionale comportando un notevole risparmio energetico.

Il primo capitolo è rivolto ad introdurre il tema trattato iniziando con una panoramica sulle principali categorie di plastica esistenti e con alcuni dati circa la crescente produzione globale di plastica, smaltimento della stessa e alcune considerazioni riguardanti l'esigenza sempre maggiore di riciclare questo materiale. Questo lavoro di tesi, infatti, tratterà il riciclaggio in particolare si focalizzerà sul riciclaggio chimico di uno dei polimeri maggiormente diffusi su scala globale: il polietilene tereftalato.

Il capitolo si sviluppa con una presentazione del PET, un polimero termoplastico appartenente alla famiglia dei poliesteri. La sua trasparenza e flessibilità unite al suo essere un materiale inerte e chimicamente resistente lo rendono perfetto per numerose applicazioni quali fibre per vestiti e contenitori per cibo e bevande. Per questo motivo è molto importante il suo riciclaggio il quale comincia con il riuso unito a una corretta raccolta differenziata da parte del consumatore e termina con il riciclaggio chimico o fisico.

I più importanti metodi di riciclaggio chimico che vengono analizzati in questo studio sono i seguenti:

- **Idrolisi** in cui la depolimerizzazione del PET viene effettuata con acqua dando origine a etilene glicole e acido tereftalico; essa può essere di tipo acido, basico o neutro;
- **Glicolisi** in cui la degradazione si effettua generalmente con etilene glicole dando origine a etilene glicole e monomeri o oligomeri costituenti il PET
- **Aminolisi** in cui la depolimerizzazione si effettua con etanolammina originando monomeri o oligomeri del polimero di partenza

Il capitolo prosegue con una breve presentazione della tecnologia alle microonde utilizzata per la degradazione. L'innovazione di tale metodo risiede nella capacità di rompere i legami chimici con l'irradiazione a microonde senza utilizzo di catalizzatori e soprattutto riducendo notevolmente i tempi di reazione con conseguente risparmio energetico.

L'introduzione termina, infine, con una presentazione dei metodi di reticolazione testati ovvero la reticolazione UV e la reticolazione termica.

Il secondo capitolo di questo elaborato introduce i materiali utilizzati nel lavoro sperimentale e le procedure seguite per gli esperimenti.

Il materiale da degradare scelto proveniva da una bottiglia usata.

Esso è stato dapprima analizzato con analisi di spettroscopia infrarossa in riflettanza totale attenuata (ATR-FTIR), calorimetria differenziale a scansione (DSC), analisi termogravimetrica (TGA), risonanza magnetica protonica (H-NMR) e risonanza magnetica carbonica (C-NMR), al fine di avere una completa caratterizzazione del polimero.

Viene successivamente illustrato il protocollo di degradazione del materiale di partenza. La bottiglia di acqua, la quale è stata tagliata in piccoli pezzi, è stata processata all'interno del forno a microonde Milestone FlexiWAVE disponibile presso i laboratori del KTH di Stoccolma, controllando i seguenti parametri operativi:

- Rapporto PET: reagente
- Temperatura di reazione
- Tempo di reazione

Per ogni esperimento è stato utilizzato 1 g di PET. Non è stato utilizzato nessun catalizzatore nelle reazioni eseguite.
I reagenti che si sono voluti testare sono l'etilene glicole (EG), il glicerolo (GLY), l'acqua (H_2O) e l'etanolammina (EA).

Di seguito vengono riportate delle tabelle (Tabella 1, 2, 3 e 4) riassuntive di tutti gli esperimenti condotti nel forno a microonde e le relative fotografie di alcuni dei campioni ottenuti.

Rapporto PET:EG	Temperatura [°C]	Tempo [minuti]
1:2	160	30
1:2	200	30
1:5	160	30
1:5	160	60
1:5	200	30
1:5	200	60
1:10	200	120
1:10	200	180
1:10	200	240

Tabella 1: Esperimenti condotti con glicole etilenico

Rapporto PET:GLY	Temperatura [°C]	Tempo [minuti]
1:5	200	30
1:5	200	60
1:5	200	120

Tabella 2: Esperimenti condotti con glicerolo

Rapporto PET: H_2O	Temperatura [°C]	Tempo [minuti]
1:10	200	60
1:10	200	120
1:10	200	240

Tabella 3: Esperimenti condotti con acqua

Rapporto PET:EA	Temperatura [°C]	Tempo [minuti]
1:10	200	5
1:10	200	10
1:10	200	30
1:10	200	60
1:10	200	120

Tabella 4: Esperimenti condotti con etanolammina

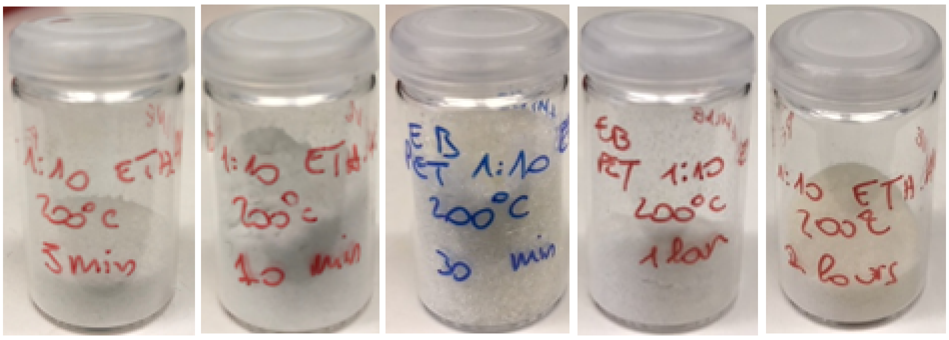


Figura 1: Alcuni dei campioni ottenuti dalla depolimerizzazione con irradiazione a microonde

Vengono poi presentati i protocolli di funzionalizzazione dei prodotti di degradazione. In particolare si è scelto di processare i campioni ottenuti da reazioni con etilene glicole e etanolammina. La reazione condotta è un'esterificazione con anidride metacrilica sotto irraggiamento a microonde. Una quantità di 0.5 g di prodotto degradato e 10 ml di anidride metacrilica (rapporto 1:18 circa) sono stati mescolati e infornati per 5 minuti a 150°C.

In tabella 5 vengono riassunti i campioni funzionalizzati mediante la procedura appena descritta.

Prodotto di degradazione	Quantità
PET 1:10 EG 200°C 3h	0,5 g
PET 1:5 EA 150°C 15 min	0,5g
PET 1:10 EA 150°C 5 min	0,5g
PET 1:10 EA 200°C 10 min	0,5g

Tabella 5: Prodotti di degradazione scelti per la metacrilazione

Il secondo capitolo si conclude con le metodologie utilizzate per la reticolazione. Il prodotto di degradazione scelto per quest'ultima fase è quello processato con etilene glicole.

Inizialmente si è effettuato un test di dissoluzione con acetato di butile, dimetil solfossido (DMSO) e cloroformio ($CHCl_3$). Quest'ultimo è stato scelto per dissolvere il prodotto di interesse il quale è stato mescolato con 50 %w di polietilene glicole dimetacrilato e 2%w di fotoiniziatore IRGACURE 819 (BAPO). La soluzione è stata quindi riversata su un vetro Petri e irraddiata per 15 minuti con una lampada UV di potenza pari a 36W.

La reticolazione termica è stata invece eseguita mescolando PET 1:10 EA con 92 %w di polietilene glicole dimetacrilato e 3%w di iniziatore perossido di benzoile (BPO). La soluzione è stata riversata in stampi circolari e deposta in un essiccatore a 90°C per 2 ore per poi portarla a 120°C per altre 2 ore. L'operazione è stata svolta in atmosfera di azoto per evitare problemi di inibizione dell'ossigeno.

Il terzo capitolo di questo studio descrive le tecniche di caratterizzazione che sono state utilizzate per:

- Caratterizzazione del PET di partenza
- Caratterizzazione dei prodotti di degradazione
- Caratterizzazione dei prodotti di degradazione metacrilati

La risonanza magnetica protonica (H-NMR) e carbonica (C-NMR), entrambe eseguite con lo strumento Avance 400 (400.13 MHz-Bruker USA) sui campioni disciolti in cloroformio deuterato e dimetil solfossido (entrambi in quantità di 10 mg/ml), hanno consentito di individuare i δ-shift dei vari spettri analizzati, permettendo inoltre di verificare l'efficacia delle funzionalizzazioni grazie alle variazioni dell'intorno chimico degli atomi di idrogeno e carbonio ad esse annesse nelle estremità terminali.

La spettroscopia infrarossa in riflettanza totale attenuata (ATR-FTIR) è stata eseguita utilizzando lo spettrometro Perkin-Elmer Spectrum 2000 (risoluzione 2 cm^{-1}) con l'intenzione di identificare la presenza dei gruppi ossidrili e metacrilici nelle reazioni di degradazione e metacrilazione. Per queste analisi è stato eseguito un background preventivo del macchinario, al fine di rimuovere le possibili interferenze. Per la registrazione degli spettri sono state effettuate 16 scansioni in un range di lunghezze d'onda compreso tra 4000 e 650 cm^{-1}.

La calorimetria a scansione differenziale (DSC) ha consentito di valutare la temperatura di fusione (T_m) e la temperatura di transizione vetrosa (T_g) del campione di PET iniziale. L'analisi è stata effettuata sotto flusso costante di azoto su campioni di 5 mg utilizzando una DSC/TGA (Mettler Toledo) ed impostando una rampa termica da -50 a 300°C.

L'analisi termogravimetrica (TGA) è stata invece utilizzata per valutare la stabilità termica del PET di partenza. Le misure sono state eseguite con una TGA Mettler Toledo sotto flusso costante di azoto con temperature che variavano da 0 a 600°C.

La cromatografia ad esclusione dimensionale (SEC), eseguita sugli oligomeri derivanti dalla degradazione del PET con etilene glicole, è servita ad avere un'indicazione sui pesi molecolari medi di queste catene.

Nel quarto capitolo sono riportati e discussi i risultati delle prove di caratterizzazione. Esso è strutturato in quattro sezioni:

1. Caratterizzazione del PET di partenza
2. Caratterizzazione dei prodotti derivanti dalla degradazione
3. Caratterizzazione dei prodotti funzionalizzati
4. Presentazione dei risultati dell'indurimento UV e dell'indurimento termico

Gli spettri ATR-FTIR, H-NMR e C-NMR del PET di partenza si sono rivelati coerenti con la struttura della molecola. La calorimetria a scansione differenziale (DSC) ha fornito una temperatura di fusione (T_m) pari a 240°C e una temperatura di transizione vetrosa (T_g) pari a 75°C, risultati compatibili con i valori trovati in letteratura. La temperatura di degradazione trovata con l'analisi termogravimetrica (TGA) è di 350°C circa. Tali risultati si sono rivelati coerenti alle aspettative.

Dall'analisi dello spettro ATR-FTIR dei prodotti di degradazione fatti reagire con il glicole etilenico, è emerso l'ottenimento sempre del medesimo prodotto fatta eccezione per le dimensioni del picco del gruppo -OH attorno a 3500 cm^{-1} il quale cresce aumentando il tempo di reazione come mostrato in Figura 2.

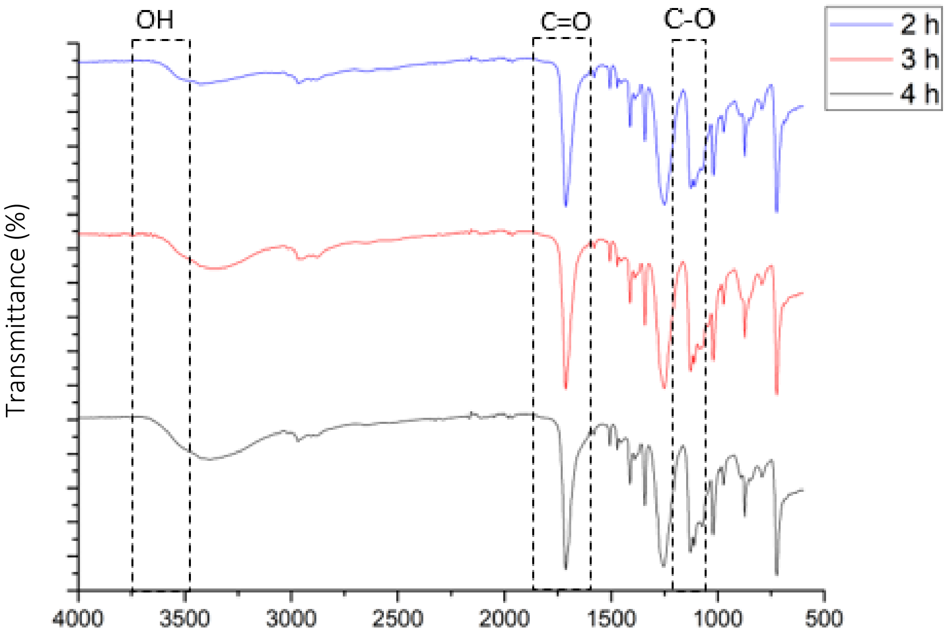


Figura 2: analisi ATR-FTIR sui campioni PET 1:10 EG

Il fenomeno è compatibile con quanto atteso, poiché maggiore è il tempo di reazione, maggiore sarà la degradazione del polimero di partenza nei rispettivi oligomeri e quindi la concentrazione dei gruppi -OH terminali. I restanti picchi dello spettro individuati sono compatibili con la struttura degli oligomeri del PET: si nota infatti la vibrazione del legame C=O a 1723 cm^{-1} e la vibrazione del legame C-O attorno 1094 cm^{-1}. Anche il picco a 1243 cm^{-1} testimonia la presenza del gruppo tereftalico riscontrato anche nelle strutture della letteratura [33].

La cromatografia ad esclusione dimensionale (SEC) effettuata sul prodotto ha permesso di trovare dei valori indicativi di peso molecolare medio numerico (M_n), peso molecolare medio ponderale (M_w) e indice di polidispersità riportati in Tabella 6.

Materiale	Pick RV [mL]	M_n [Da]	M_w [Da]	PDI
PET 1:10 EG 200°C 3 hours	18,183	312	457	1,465
PET 1:10 EG 200°C 4 hours	18,108	344	495	1,439

Tabella 6: Risultati evidenziati dall'analisi SEC

Dalle analisi effettuate sul campione PET 1:10 EG si è ipotizzata la struttura mostrata in Figura 3.

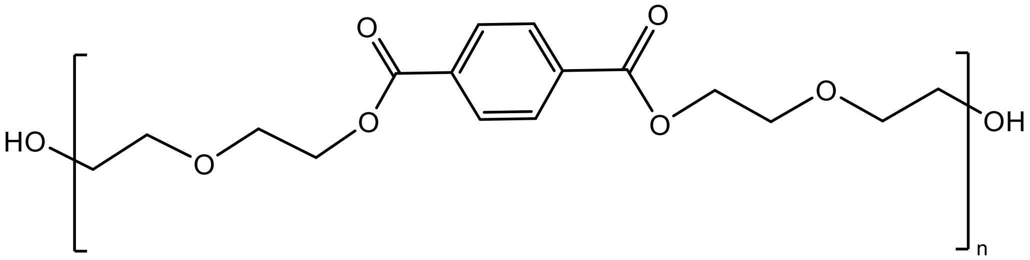


Figura 3: possibile oligomero ottenuto

Dall'analisi degli spettri ATR-FTIR del campione processato con glicerolo è emersa la comparsa del picco del gruppo -OH attorno a 3500 cm^{-1} segno del fatto che la depolimerizzazione è andata a buon fine. Tuttavia non si è proceduto con altre analisi sul prodotto in quanto la presenza di tre gruppi terminali del co-reagente glicerolo ha reso difficile l'interpretazione dei risultati che non è stata quindi terminata per mancanza di tempo.

Considerazione analoghe a quelle appena descritte valgono per il campione processato con acqua, in cui dallo spettro ATR-FTIR vi è il sospetto che la depolimerizzazione non sia riuscita come voluto vista la mancanza del picco del gruppo -OH attorno a 3500 cm^{-1}. Per questo motivo l'intenzione per uno studio futuro è quella di provare ad effettuare la reazione con l'ausilio di un catalizzatore.

Infine, il prodotto di degradazione processato con etanolammina, è stato analizzato con le tecniche di risonanza magnetica nucleare protonica e carbonica (H-NMR e C-NMR) di cui si riportano gli spettri analizzati in Figura 4 e Figura 5.

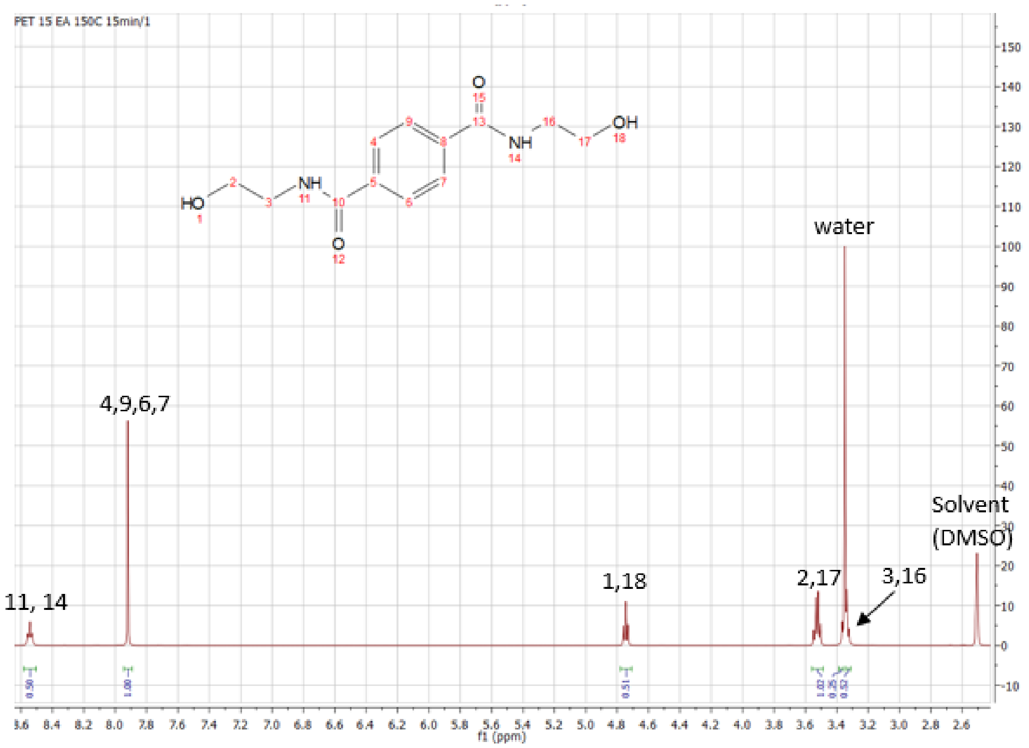


Figura 4: Spettro H-NMR del campione PET 1:5 EA

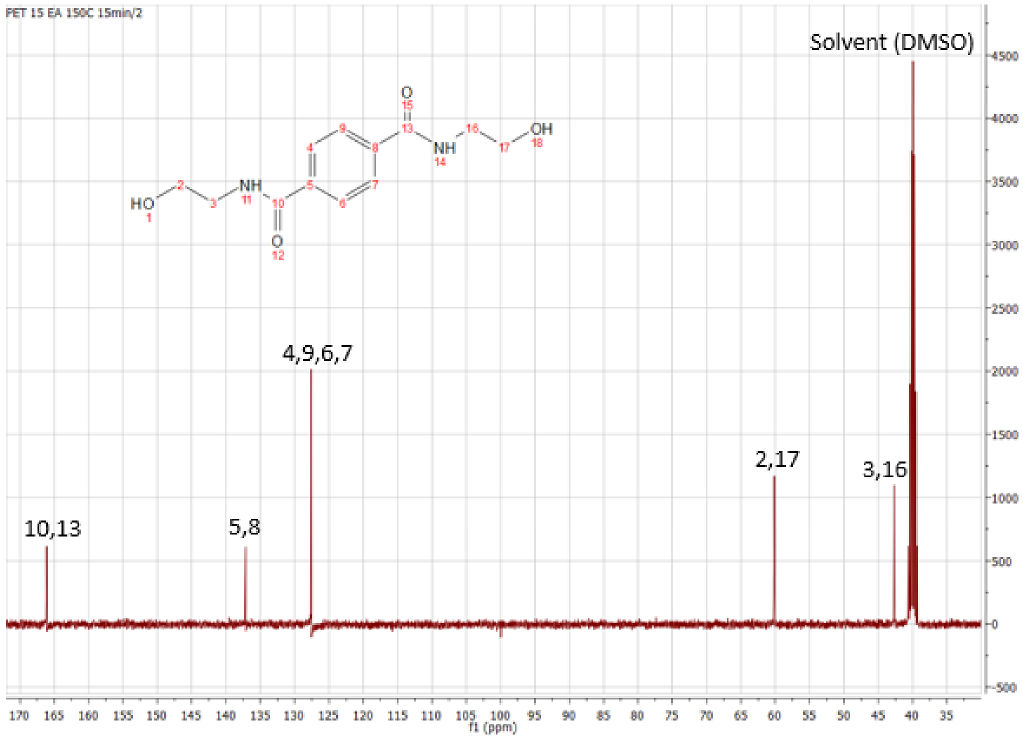


Figura 5: Spettro C-NMR del campione PET 1:5 EA

Risultati compatibili con la struttura del monomero ipotizzato sono emersi anche dall'analisi dello spettro ATR-FTIR. Tale struttura è riportata in Figura 6.

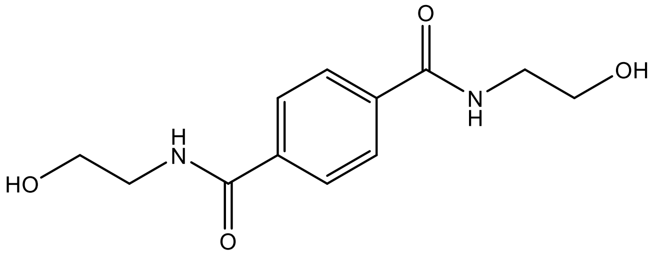


Figura 6: possibile monomero ottenuto

Dall'analisi dei vari spettri degli esperimenti condotti con etanolammina come co-reagente è emerso l'ottenimento sempre del medesimo prodotto al variare dei vari tempi di reazione. Di conseguenza si è potuto concludere che questa reazione di degradazione è stata la più efficace in quanto ha portato alla depolimerizzazione completa del polimero di partenza anche dopo soli 5 minuti.

La sezione successiva del quarto capitolo dei risultati riguarda l'analisi dei prodotti funzionalizzati tramite la reazione di metacrilazione con anidride metacrilica.

Lo spettro H-NMR del prodotto PET 1:10 EG funzionalizzato è riportato in Figura 7.

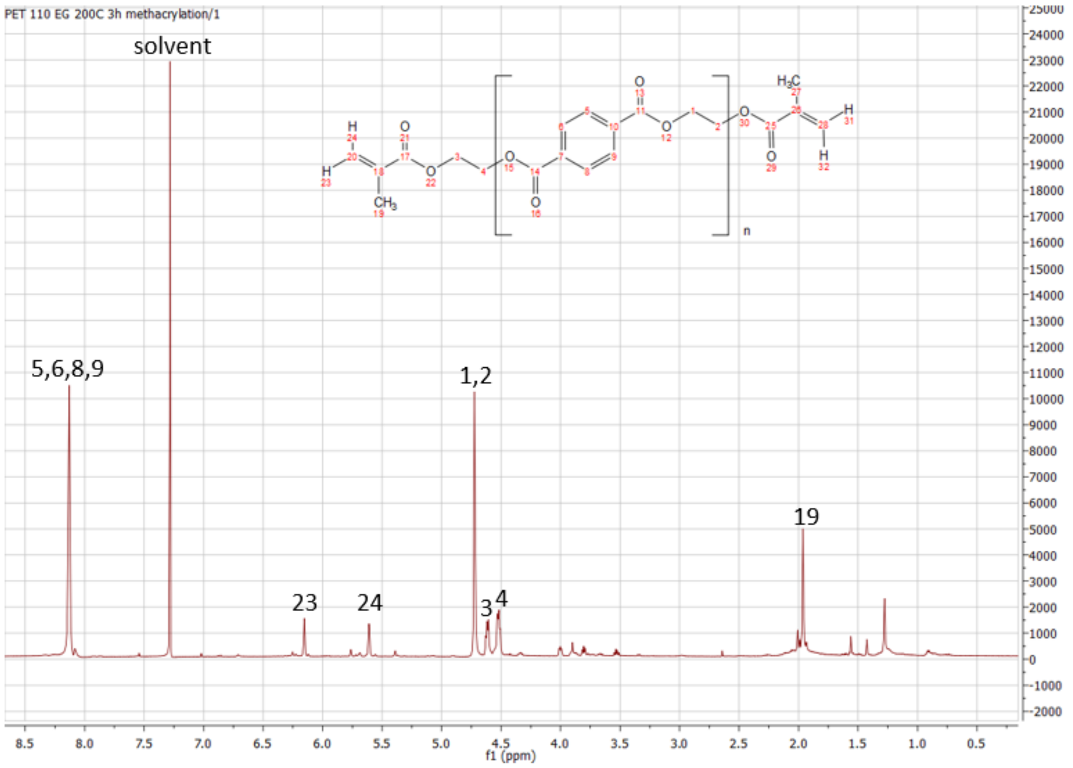


Figura 7: Spettro H-NMR del campione PET 1:10 EG dopo la funzionalizzazione

Emerge l'apparizione del gruppo metacrilico a δ 6.11, 5.56 e 1.95. Si può notare anche la presenza di un'impurezza a δ 1.27.

Il successo della metacrilazione è stato confermato anche dal confronto dello spettro ATR-FTIR del prodotto prima e dopo la funzionalizzazione riportato in Figura 8.

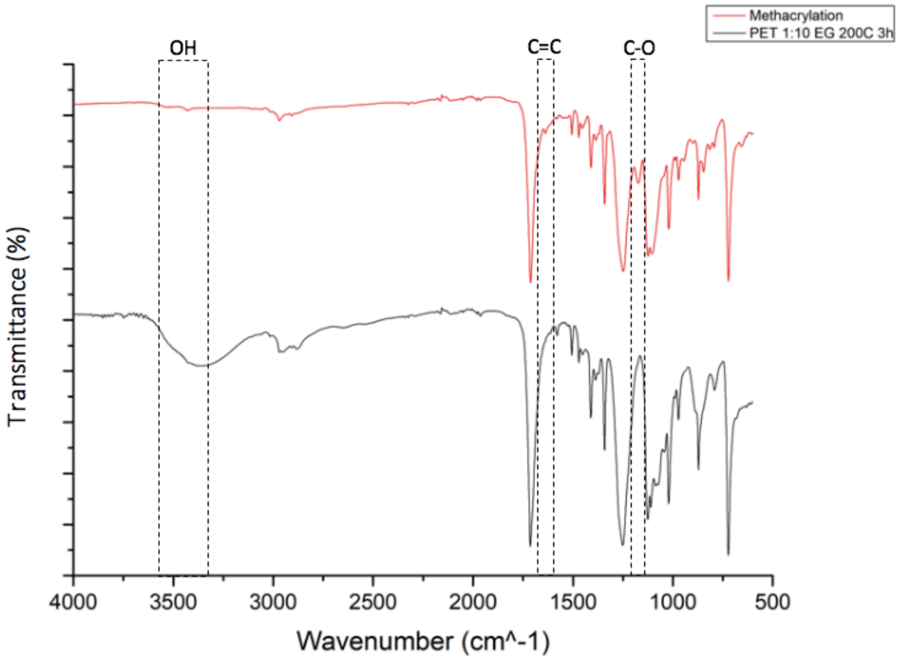


Figura 8: Spettro ATR-FTIR del campione PET 1:10 EG prima e dopo la funzionalizzazione

Risulta evidente la scomparsa del picco del gruppo -OH attorno a 3500 cm^{-1}. Meno evidente ma comunque presente la comparsa dello stretching del legame C=C a 1637 cm^{-1} e del legame C-O a 1173 cm^{-1}.

Lo spettro H-NMR del prodotto PET 1:5 EA funzionalizzato è riportato in Figura 9.

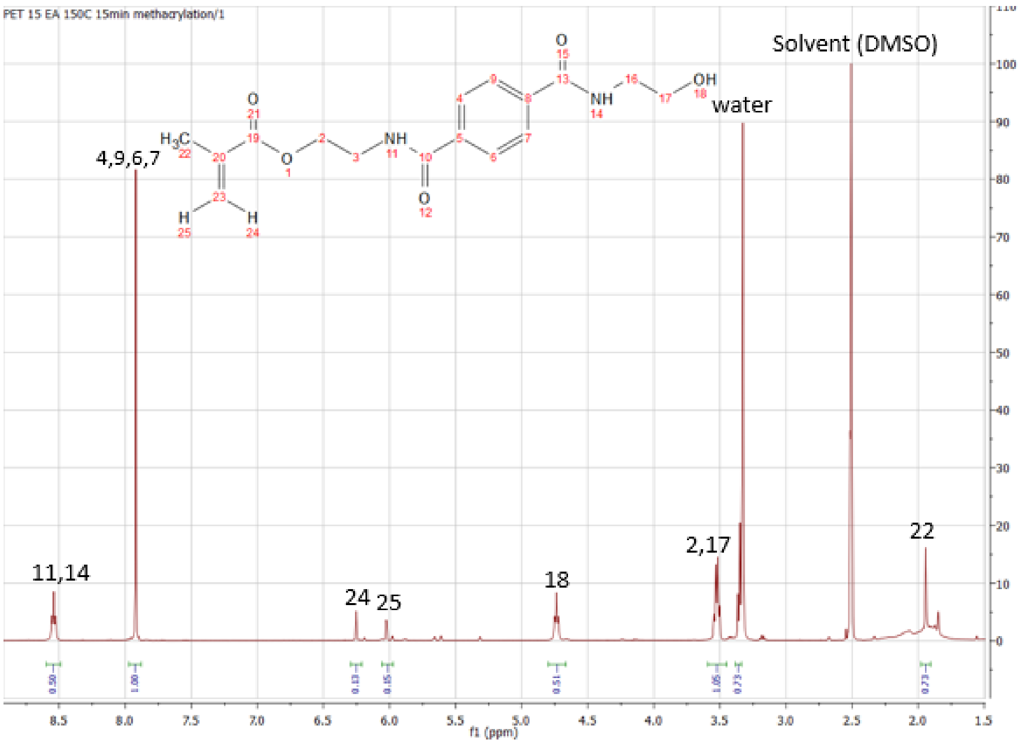


Figura 9: Spettro H-NMR del campione PET 1:5 EA dopo la funzionalizzazione

Dall’analisi si evince che la funzionalizzazione non è stata effettuata per entrambe le estremità del monomero in quanto si rileva il picco del gruppo -OH a δ 4.73. Emerge comunque l’apparizione del gruppo metacrilico a δ 6.11, 5.56 e 1.95.

Considerazioni analoghe sono state possibili dall’analisi dello spettro ATR-FTIR riportato in Figura 10, assieme a quello del prodotto pre-metacrilazione.

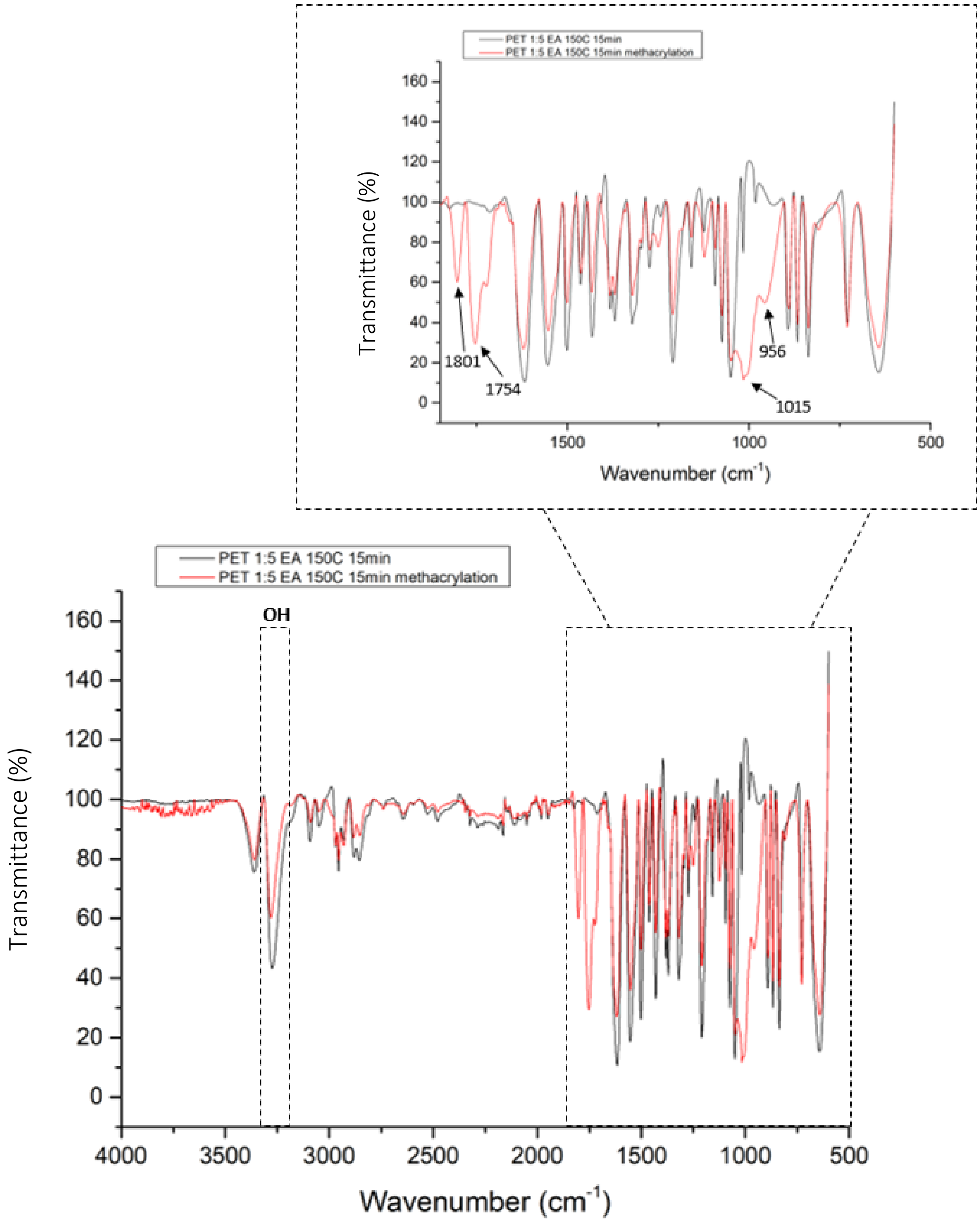


Figura 10: Spettro ATR-FTIR del campione PET 1:5 EA prima e dopo la funzionalizzazione

Risulta evidente la scomparsa del picco del gruppo -OH attorno a 3500 cm^{-1}. Meno evidente ma comunque presente la comparsa del picco rappresentante lo stretching del legame C=O a 1754 cm^{-1} e 1801 cm^{-1}. Compaiono inoltre i picchi dello stretching del legame C-O a 1015 cm^{-1} e la vibrazione del gruppo $C=CH_2$ a 956 cm^{-1}, mostrati nello zoom di Figura 10.

Nell'ultima sezione sono presentati i risultati della reticolazione UV e della reticolazione termica riportati in Figura 11 e in Figura 12.

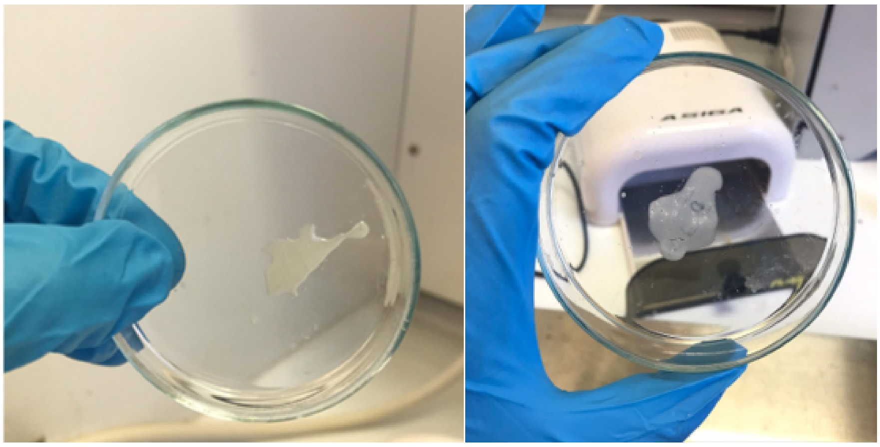


Figura 11: Reticolazione UV del prodotto di degradazione PET 1:10 EG

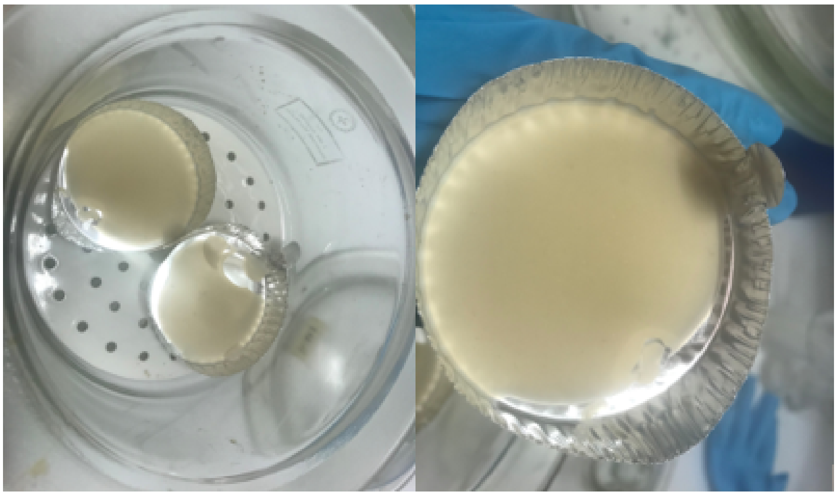


Figura 12: Reticolazione termica del prodotto di degradazione PET 1:10 EG

Risulta evidente che entrambi i casi la reticolazione ha funzionato. Sfortunatamente il tempo non è stato sufficiente per svolgere ulteriori analisi su questi prodotti.

In conclusione, sono stati ottenuti quattro diversi prodotti di degradazione tramite l'utilizzo della tecnologia alle microonde. Due di questi (quello ottenuto tramite depolimerizzazione con glicole etilenico e quello con etanolammina) sono stati funzionalizzati con una reazione di metacrilazione con anidride metacrilica effettuata sotto irraggiamento a microonde.

La funzionalizzazione è andata a buon fine su entrambi i prodotti scelti, anche se è risultata maggiormente efficace nel caso di PET 1:10 EG. Per questo motivo si è scelto quest'ultimo prodotto per l'applicazione delle tecniche di reticolazione UV e di reticolazione termica, effettuate con l'ausilio di opportuni iniziatori.

I risultati ottenuti risultano promettenti e incoraggiano studi futuri di questa metodologia innovativa di riciclo chimico del polietilene tereftalato.

1. Introduction

“Plastic” is a term derived from the Latin word “*plasticus*” that was used to describe something able to be moulded. This word was actually already used in the 16th century, long before the first plastic material (Parkesine) was developed in 1907.

Today the term “plastic” is used to describe a wide range of materials with different features, properties and uses.

Nowadays, plastic products have completely revolutionized the way we live since plastic is present in the clothes we wear, in the houses we live in, in the cars we travel on. The list is endless.

It has gained huge economic and technological importance with an estimated global plastic production of 381 million tonnes/year (in 2015) [1].

The plastic’s family includes a great variety of materials designed to meet the different needs of thousands of end products. The two main categories are:

- Thermoplastics which can be melted several times and reshaped by the application of heat.
- Thermosets that undergo an irreversible chemical change when heated, creating a three-dimensional network.

Below a table which lists the main types of thermoplastics and thermosets.

THERMOPLASTICS	THERMOSETS
Polyethylene (PE)	Polyurethane (PUR)
Polypropylene (PP)	Unsaturated polyester
Polyvinyl-chloride (PVC)	Epoxy resins
Polyethylene Terephthalate (PET)	Melamine resins
Polystyrene (PS)	Vinyl ester
Expanded Polystyrene (EPS)	Silicone
ABS	Phenol-formaldehyde
SAN	Urea-formaldehyde
Polyamides (PA)	Phenolic resins
Polycarbonate (PC)	Acrylic resins
Poly Methyl Methacrylate (PMMA)	Etc.
Thermoplastic elastomers (TPE)	
Polyarylsulfone (PSU)	
Fluoropolymers	
POM	
PBT	
Etc.	

Table 1.1: main types of thermoplastics and thermosets

In Figure 1.1 is reported the annual global polymer resin and fiber production (plastic production), measured in tonnes per year, from 1950 to 2015. The short downturn in annual production in 2009 and 2010 was the result of the 2008 global financial crisis [1].

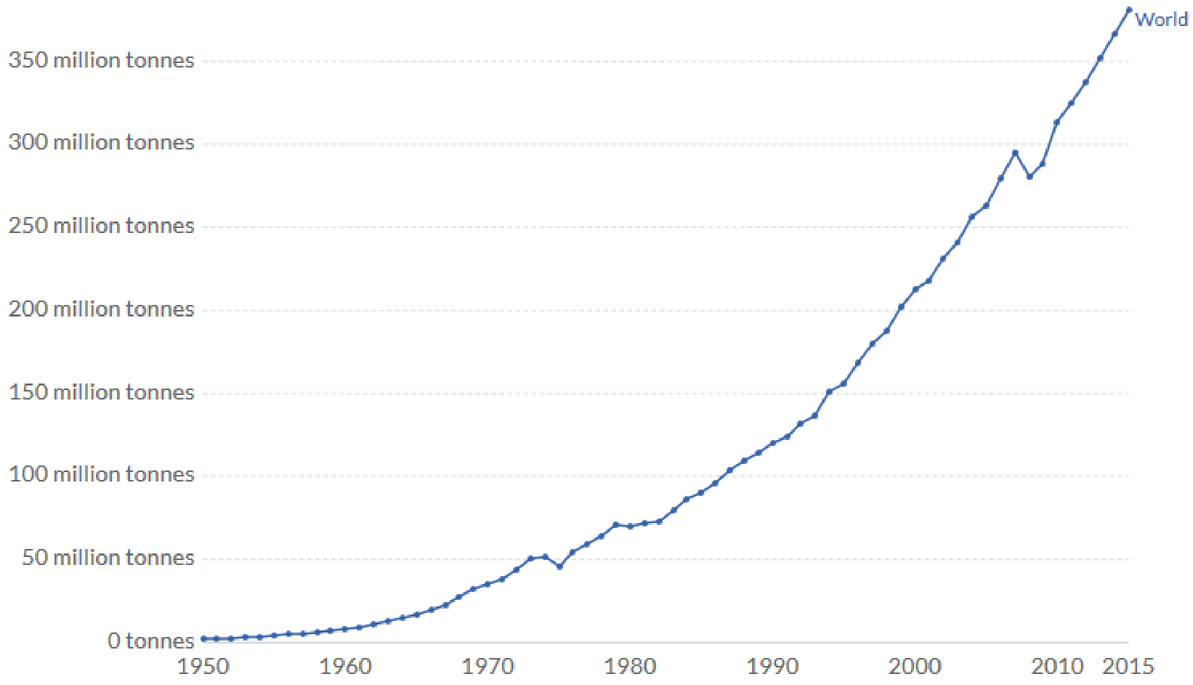


Figure 1.1: Global plastics production measured in metric tonnes per year [1]

The first critical factor related to the huge use of this material is that plastic is everywhere and it is difficult to replace it.

The second is that it is almost indestructible: objects deteriorate, but plastic remains, because most of the polymers are not biodegradable, or they are only over a thousand years, accumulating in the meantime in the oceans and seas, where they arrive via the rivers.

The phenomenon affects different areas of the world, where we can see more and more the formation of the so-called "plastic islands" or large piles of floating garbage scattered around the world.

In Figure 1.2 we see the share of global plastic waste that has been discarded, recycled or incinerated from 1980 to 2015: prior to 1980, recycling and incineration of plastic was negligible; from 1980 when it comes to incineration, and 1990 when it comes to recycling, rates have increased on average by about 0.7 percent per year.

In 2015, an estimated 55 percent of global plastic waste was discarded, 25 percent was incinerated, and 20 percent recycled [1].

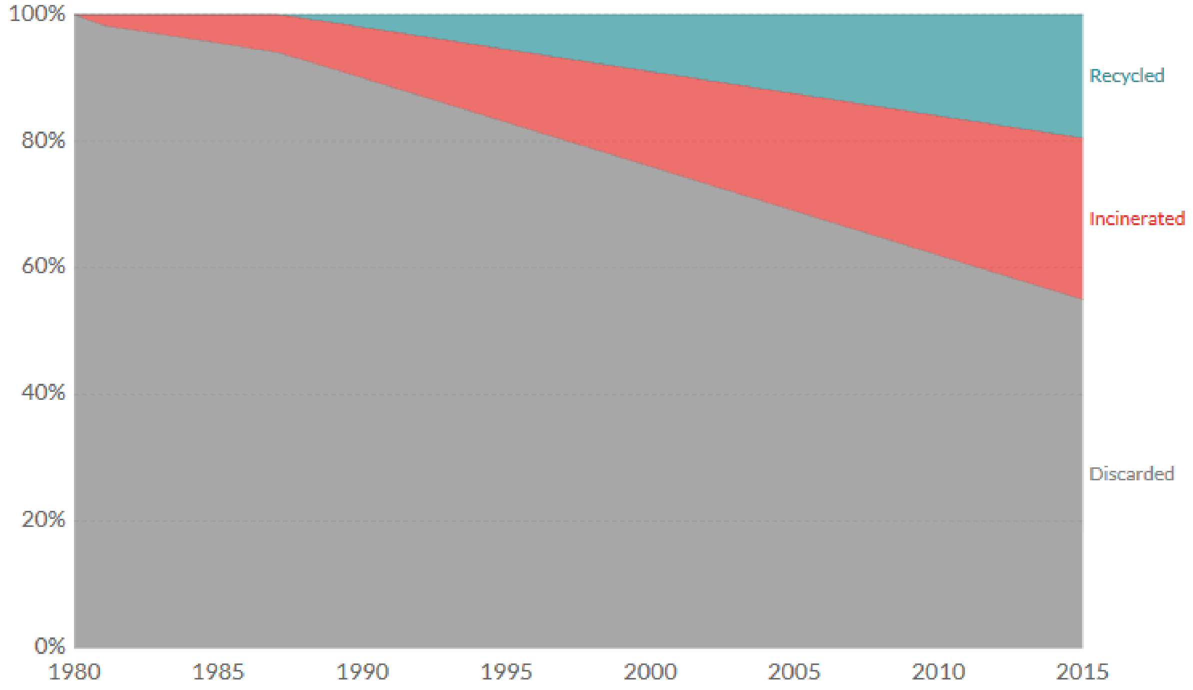


Figure 1.2: Global plastic waste by disposal [1]

In order to decrease the rate of plastic which is discarded and incinerated, there are two possible solutions: (i) the use of "bioplastic" materials, made out of renewable raw materials that are biodegradable in few months, or (ii) recycle.

This work is about recycle, being it focused in particular on chemical recycle of plastic. The plastic material studied is Polyethylene terephthalate (PET), one of the most diffused polymers in the world.

In the next chapters of this study, PET will be firstly investigated in terms of structure, properties and applications.

Afterwards, PET recycling process will be presented, focusing the attention on chemical methods.

Lastly, a presentation of the microwave-assisted methods will be reported, followed by a brief overview of UV curing and thermal curing techniques.

1.1 PET

PET is the common abbreviation of Polyethylene terephthalate, a thermoplastic polymer resin belonging to the polyester family.

It was first synthetized by John Rex Whinfield and James Tennant Dickson in 1941, after advancing the previous research of Wallace Carothers (the inventor of Nylon resin).

PET is a colourless, highly flexible and inert material. This is the reason why its applications include fibres for clothing, containers for both liquids and foods. This is also due to its chemical resistance, its high strength-to-weight ratio (which means that it is very lightweight), its transmissivity (so that it is possible to see through it) and its being shatterproof.

Nowadays, PET has become one of the most widely used and versatile materials on the market. Some examples are given in Figure 1.3 below.

The most interesting aspect is that PET is recyclable in many different ways, which start from the re-use of a bottle by the consumer, to the chemical breaking down of the material to make new PET resin.

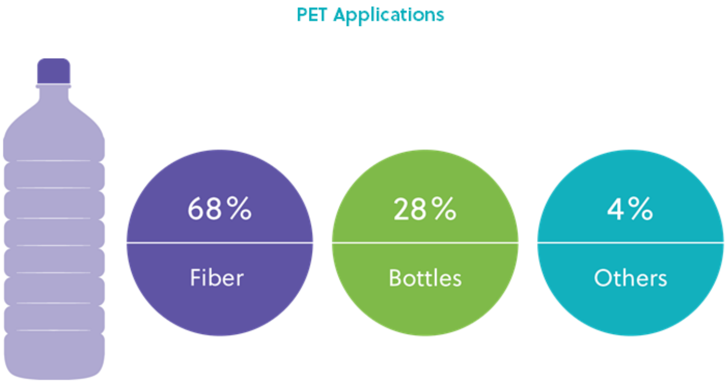


Figure 1.3: PET main applications

The repeating unit of PET (also abbreviated as PETE) is reported in Figure 1.4. Its chemical formula is :$(C_{10}H_8O_4)_n$. Since PET is one of the most recyclable thermoplastic, it is identified with a resin identification code (RIC), which is the number 1 (Figure 1.5).

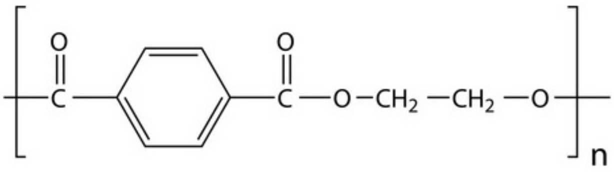


Figure 1.4: PET molecular structure

Figure 1.5: PET resin identification code

The monomer bis(2-hydroxyethyl) terephthalate is the PET intermediate product. It can be synthesized by an esterification reaction between ethylene glycol and terephthalic acid with water as by-product. This reaction is shown in Figure 1.6 [2].

Terephthalic acid is a crystalline solid (it can be found either in white crystals or in powder) and it is obtained from xylene; while ethylene glycol is a colourless liquid obtained from ethylene. Pictures 1.7 and 1.8 report the PET starting materials.

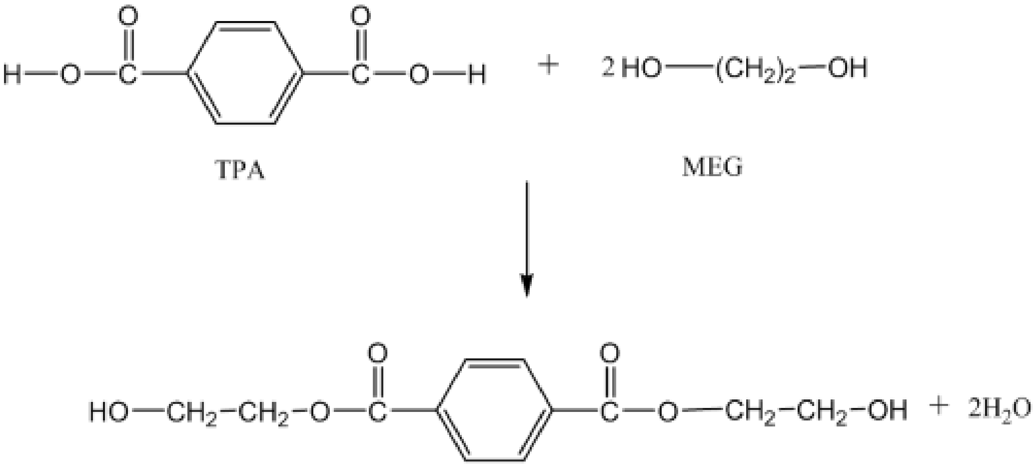


Figure 1.6: Synthesis of bis(2-hydroxyethyl) terephthalate *via* esterification reaction

Figure 1.7: Terephthalic acid

Figure 1.8: Ethylene glycol

The monomer bis(2-hydroxyethyl) terephthalate can also be synthesized by the transesterification reaction between ethylene glycol and dimethyl terephthalate (DMT) with methanol as by-product [2]. The reaction is shown in Figure 1.9.

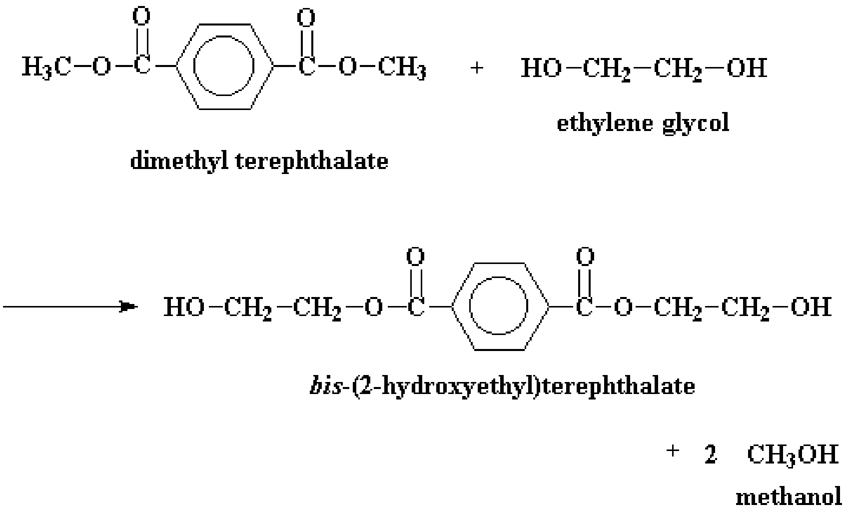
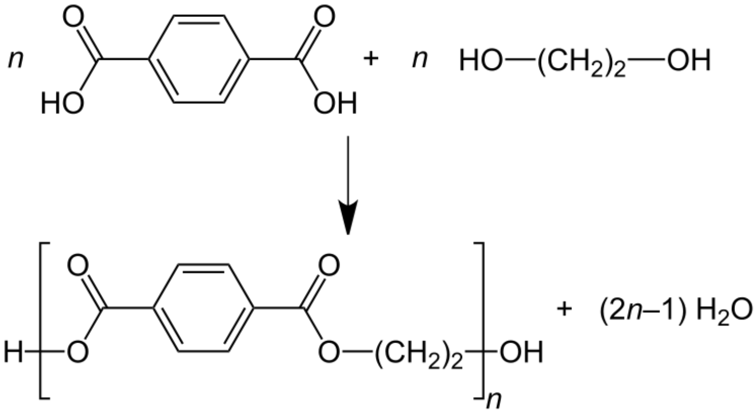


Figure 1.9: Synthesis of bis(2-hydroxyethyl) terephthalate *via* transesterification reaction.

Dimethyl terephthalate is an organic compound formed from terephthalic acid and methanol. It is a white solid (Figure 1.10) that melts to give a distillable colourless liquid.

Figure 1.10: Dimethyl terephthalate

The PET polymerization is subsequently performed through a polycondensation reaction of the monomers, with water as byproduct. The reaction is shown in Figure 1.11.



Picture 1.11: PET polymerization through polycondensation

1.1.1 Properties

Virgin PET has excellent tensile and impact strength, resistance, clarity and chemical resistance.

The PET chain has low flexibility, thanks to the presence of the p-phenylene groups and the nature of the short ethylene groups. This characteristic markedly affects its structural properties.

The physical and chemical properties of commercial PET are listed in Table 1.2.

Property	Test method	Value [unit]
Molecular weight (of repeating unit)	-	192 [g/mol]
Weight-average MW	-	30.000-80.000 [g/mol]
Density	-	1.41 [g/cm^3]
Glass transition temperature	DSC	69-115 [°C]
Melting temperature	DSC	265 [°C]
Heat of fusion	DSC	166 [J/g]
Breaking strength	Tensile	50 [MPa]
Tensile Strength (Young's modulus)	-	1700 [MPa]
Yield strain	Tensile	4 [%]
Impact strength	ASTM D256-86	90 [J/m]
Water absorption (after 24 h)	-	0.5 [%]

Table 1.2: physical and chemical properties of PET [2]

Depending on its thermal history and processing, PET can be either semi-crystalline (white-opaque) or amorphous (transparent). The first one can also be transparent if the particle size is less than 500 nm. The semi-crystalline status confers PET excellent gas-barrier and chemical resistance properties and it also entails a slower water absorption.

Both the glass transition temperature and the melting temperature increase as the crystallization percentage increases.

Virgin PET, like all the polymers, has a crystallization rate which depends greatly on temperature, molecular weight, the presence of nucleating agents and on the degree of chain orientation.

Another characteristic of PET is its intrinsic viscosity [3] which is measured in decilitres per gram. This property depends on the length of the polymer chains and on the numbers of entanglements.

1.1.2 Applications

The PET global consumption is estimated to amount to billions and billions of dollars per year.

PET resin is widely used due to its advantages and of the key properties of its resins. The most important ones are:

- It has higher strength and stiffness;
- It is very strong and lightweight and hence easy and efficient to transport;
- It is known for its good gas (oxygen, carbon dioxide) and moisture-barrier properties;
- It shows excellent electrical insulating properties;
- It has a broad range-of-use temperature, from -60°C to 130°C;
- It has higher heat distortion temperature (HDT);
- It has low gas permeability, in particular with carbon dioxide;
- It is suitable for transparent applications, when quenching during processing;
- It does not break or fracture. It is practically shatter-resistant and, hence, a suitable glass-replacement in some applications;
- It is recyclable and transparent to microwave radiation;
- It is approved as safe for contact with foods and beverages by the FDA, Health Canada, EFSA & other health agencies;
- It is low cost and readily available.

PET also has some important chemical properties:

- Excellent resistance to alcohols, aliphatic hydrocarbons, oils, greases and diluted acids;
- Moderate resistance to diluted alkalis, aromatic & halogenated hydrocarbons.

As all materials, it also has some limitations that need to be mentioned:

- Lower impact strength compared to other polymers;
- Lower moldability compared to other polymers, due to its slow crystallization rate;
- It is affected by boiling water;
- It can be attacked by alkalis and strong bases;
- It can be affected by hydrolytic degradation. Hence, it must be dried using a dehumidifier before processing;
- It can be attacked at high temperatures (>60°C) by ketones, aromatic and chlorinated hydrocarbons and diluted acids and bases;
- Poor burning behaviour;
- It is not a carbon neutral material. It is made from hydrocarbons and hence it is fossil fuel dependent. It is also affected by the price of the oil;
- It can be recyclable, but it is not bio-degradable. Hence, there is always the issue of accumulation of big amounts of it;
- It can at times be susceptible to oxidation. If a food item such as wine is stored in a PET bottle/container, then the oxidation might actually alter the taste of the beverage. This is the reason why it is not recommended to store food/drink item into PET containers for a very long time.

PET resin is used in many different fields of application, PET films and fibres being its oldest forms of usage. PET films are produced by biaxial orientation through heat and drawing; they are used in photographic applications, X-ray sheets and in food packaging. PET films are also used as electrical insulator and for recording tapes. PET fibres are another important field of application of PET; they are produced by forcing molten PET through small holes in a die. Their strength is achieved by applying tension to align the chains through uniaxial stretching [2].

PET resin is also used in the food industry, such as in beverage bottles, food containers and food trays. This is due both to its inherent properties and its lightweight, large capacity and shatter-resistance. It also provides an excellent barrier against oxygen, nitrogen, water and carbon dioxide [5].

Figure 1.12: PET uses

The main processes on PET are extrusion, blow moulding and injection moulding [2]:

- Extrusion is the process used to produce PET foam where a lot of modifiers are added (for example pyromellitic dianhydride, 2,2'-bis(oxazoline), triphenyl phosphate and dodiepoxides [1]) in order to achieve highly branched, high MW PET, enabling manufactures to produce PET foam by the extrusion process.
- Blow-moulding is used to produce bottles. The process starts with the injection of PET into a cold mould to produce an amorphous preform. This is then transferred directly into an air-blowing unit with a single stage injection blow moulding where the preform is stretched and blown into a bottle mould. In a two-stage injection blow moulding, PET is re-heated to about 10 °C above glass transition temperature and finally blown into a bottle mould in a different air blowing unit. If the preform appears transparent and clear, it means that the injection blow moulding process has been successful.
- Injection moulding, that consists of high-pressure injection of the raw material into a mould which shapes the polymer into the desired shape. When PET is moulded there

is a cooling phase, where the material solidifies. In the final phase the mould is opened in order to extract the PET piece.

These bottles and thin films become waste material after usage; post-consumer PET bottles are collected and processed through a series of special washing processes or by a chemical treatment to break down the PET into its raw materials or intermediates which are further used to produce recycled PET flakes. Consequently, PET recycling by physical or chemical methods are essential to make it usable. They are discussed in the following chapter.

1.2 PET recycles

Some plastic products have a shelf life of less than one year, some have a lifespan of more than 15 years and some others have a service life of 50 years or even more. Thus, from production to waste, different plastic products have different life cycles, and this is why the volume of collected waste cannot match, in a single year, the volume of production or consumption.
Figure 1.13 shows the global share of mismanaged plastic waste of a given country.
Mismanaged waste is the sum of littered or inadequately disposed waste. Inadequately disposed waste is not formally managed and includes disposal in dumps or open, uncontrolled landfills, where it is not fully contained. Mismanaged waste could eventually enter the ocean via inland waterways, wastewater outflows, and transport by wind or tides [1].

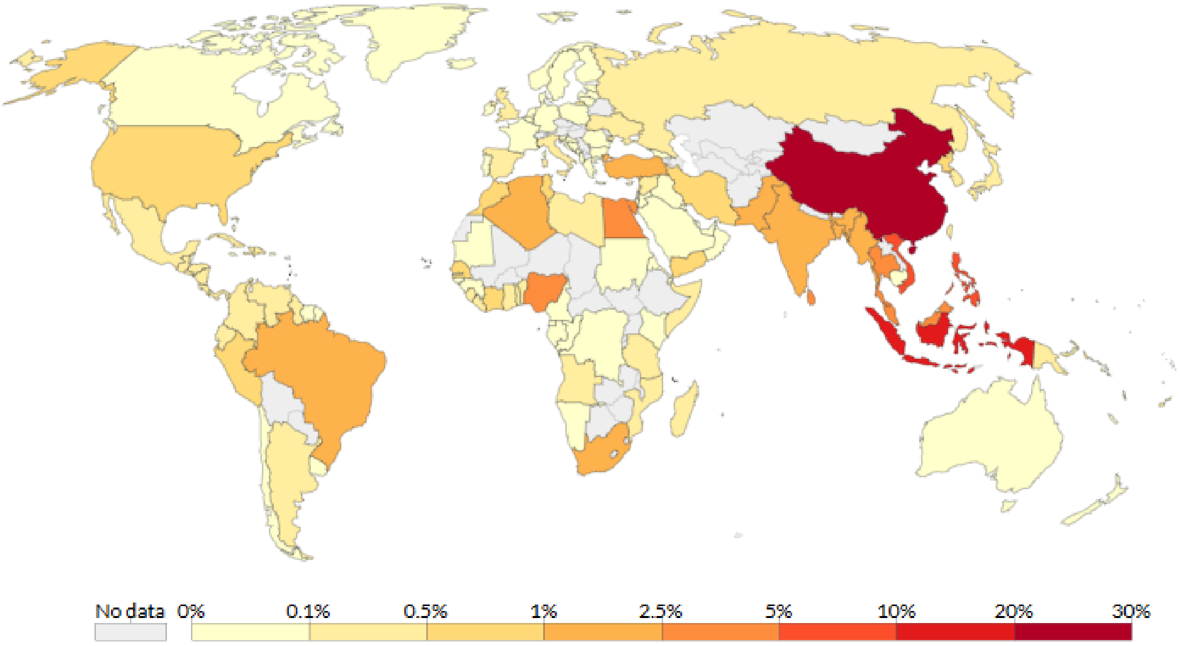


Figure 1.13: Share of global mismanaged waste (in 2010) [1]

PET is one of the most used plastic materials: wide-spread application of PET creates huge amounts of waste that need to be recycled in order to avoid environmental pollution due to the clogging of landfills. A driving force for PET recycling is its non-biodegradability: indeed, PET products have a slow rate of natural decomposition due to the fact that there is no known organism that can consume their large molecules [6].

Polymer recycled materials can be classified into four categories [7]:

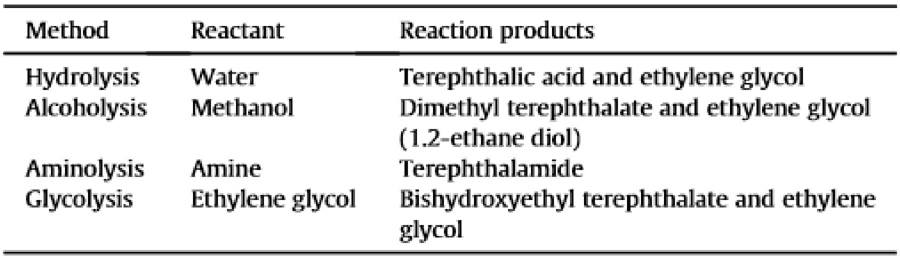
- Pre-consumer scrap (primary recycling): it is the recycling of clean, uncontaminated single-type waste which remains the most popular, as it ensures simplicity and low cost; the recycled scrap is either mixed with virgin material or used as second grade material.
- Physical Reprocessing (secondary recycling): it involves melting, grinding and reforming of plastic packaging material. The basic polymer is not altered during the process.
- Chemical Reprocessing (tertiary recycling): it may involve depolymerization of the used packaging material with subsequent regeneration and purification of resulting monomers (or oligomers). The monomers are then re-polymerized, and a new reconstituted polymer can be formed. Even in this case the new material may be blended with virgin materials.
- Incineration/combustion (quaternary recycling): it allows the recovery of the energy content of plastic waste and it helps reducing the volume of organic material. However, this method has environmental issues, as toxic substances are released in the air during plastic burning and this causes potential health risks for all living beings.

This work will focus on chemical recycling.

1.2.1 Chemical methods of PET recycling

Chemical recycling fundamentally entails converting polymer chains into monomers units along with oligomers (low molecular weight polymers comprising a small number of repeated units whose physical properties depend on the length of the chain) with related release of gas products. Chemical recycling is carried out by solvolysis which means using different kinds of solvents in order to perform depolymerization of PET.

Below is a table of the most important chemical recycling processes of PET:



Method	Reactant	Reaction products
Hydrolysis	Water	Terephthalic acid and ethylene glycol
Alcoholysis	Methanol	Dimethyl terephthalate and ethylene glycol (1.2-ethane diol)
Aminolysis	Amine	Terephthalamide
Glycolysis	Ethylene glycol	Bishydroxyethyl terephthalate and ethylene glycol

Table 1.3: Methods of chemical recycling of PET [8]

Many studies have been carried out on aminolysis [9], [10], [11] and alcoholysis [12].

This study will be focused on hydrolysis, glycolysis and aminolysis of PET.

Hydrolysis

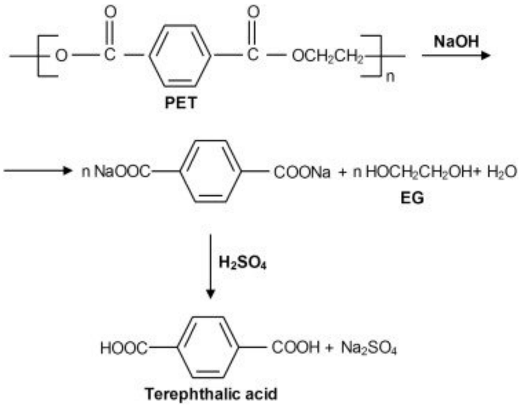
Hydrolysis involves the depolymerization of the post-consumed PET bottles into ethylene glycol (EG) and terephthalic acid (TPA). It can be performed both in alkaline, acid and neutral conditions [13].

It is typically carried out at a pressure of 1-4 MPa and temperatures of 200°C-300°C. Because hydrolysis reaction is faster in the molten state than in the solid state, it is better to perform it at a temperature above the melting point of PET. The main products formed are terephthalic acid (TPA) and ethylene glycol (EG). Even if this can seem a simple process, the basic mechanism of the reaction is not fully understood. It is considered as a non-diffusion controlled process characterized by a constant water concentration.

Figure 1.14: Schematic diagram of PET hydrolysis [14]

Two different kinetic models have been proposed for describing the process, summarized as follows [14]:

- Half-order kinetic model, assuming autocatalytic reaction mechanism, a catalytic effect of the carboxyl-end groups and a specific chain-end process.
- Classic second-order model, considering the absence of autocatalysis and crystallinity and hydrophilicity changes induced by chain scission.



Picture 1.15: Alkaline hydrolysis of PET

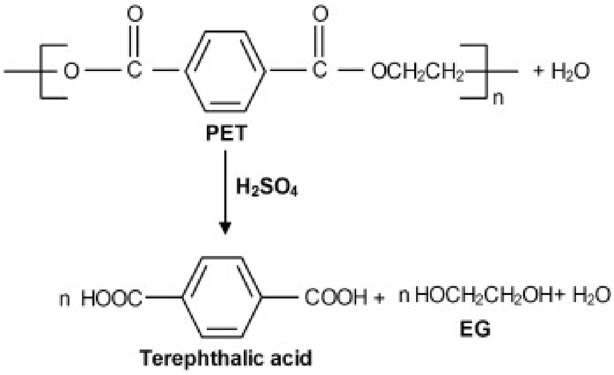


Figure 1.16: Acid hydrolysis of PET

PET is a semi-crystalline polyester, which means it has both amorphous and crystalline regions. Water absorption and thus chain scission occurs only in the amorphous phase, due to the water resistance of crystals. Therefore, the drastic increase in the crystallinity must be taken into account.

Glycolysis

Glycolysis is conducted by putting PET scrap into contact with EG in a wide range of temperatures (180°C-250°C) and pressure (0.1-0.6 MPa) during a time period of 0,5-8 hours [14]. The main products formed are bishydroxyethyl terephthalate (BHET), oligomers and ethylene glycol (EG).

Figure 1.17: Schematic diagram of PET glycolysis [14]

Two different kinetic models have been proposed for glycolysis by EG [14]:

- The rate of depolymerization is proportional to the square of EG concentration. These results suggest that EG acts as both a reactant and a catalyst in the glycolysis reaction.
- Kinetic model of first order in both EG and ethylene di-ester concentrations, for small reaction times. These results suggest that EG does not play a significant role as an internal catalyst in the glycolysis reaction.

The mechanism of pressurized depolymerization of PET can be divided in two steps [14]:

1. PET+EG → BHET + oligomer (chain scission)
2. BHET ↔ oligomers + EG (equilibrium)

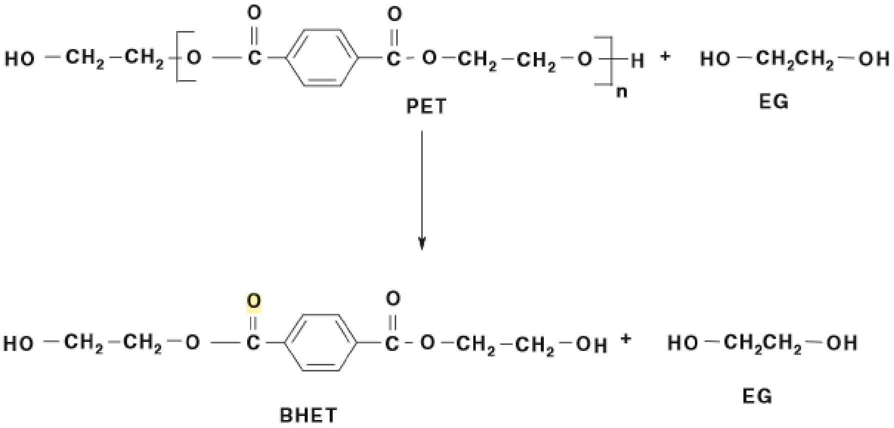


Figure 1.18: Glycolysis of PET

In addition, subcritical and supercritical glycolysis were employed to decompose PET into its monomer BHTE [15].

Glycolysis has the highest efficiency and quality when a catalyst is used. There are various catalysts that can be used, each of them having its own performance under different conditions of temperature and pressure. The most common catalysts are ionic liquids, metal salts (zinc acetate is the best one), hydrotalcites and enzymes [16].

Organic catalysts were discovered to be attractive alternatives to traditional organometallic reaction promoters: for example, glycolysis of PET catalysed by TBD (Triazabicyclodecene) was investigated [17].

Aminolysis

Aminolysis has been carried out using different kinds of amine such as ethanolamine, benzylamine, hexamethylenediamine, aniline, methylamine, hydrazinemonohydrate and some polyamines [18].

This study is focused on aminolysis carried out with ethanolamine (EA), where the main product is bis(2-hydroxyethyl) terephthalamide (BHETA). Below the mechanism of the reaction is shown:

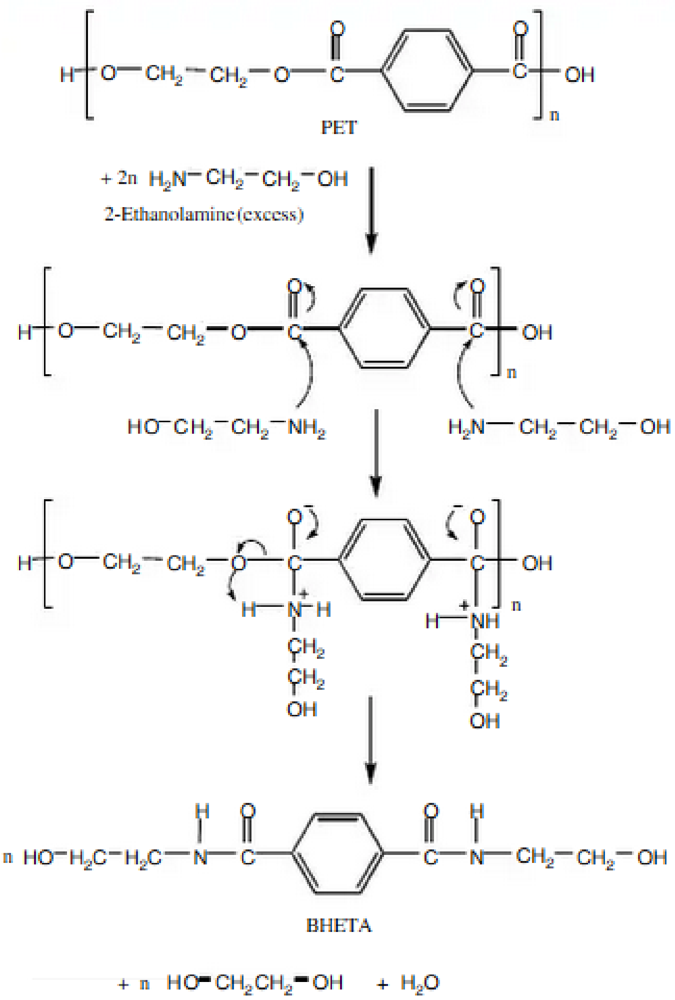


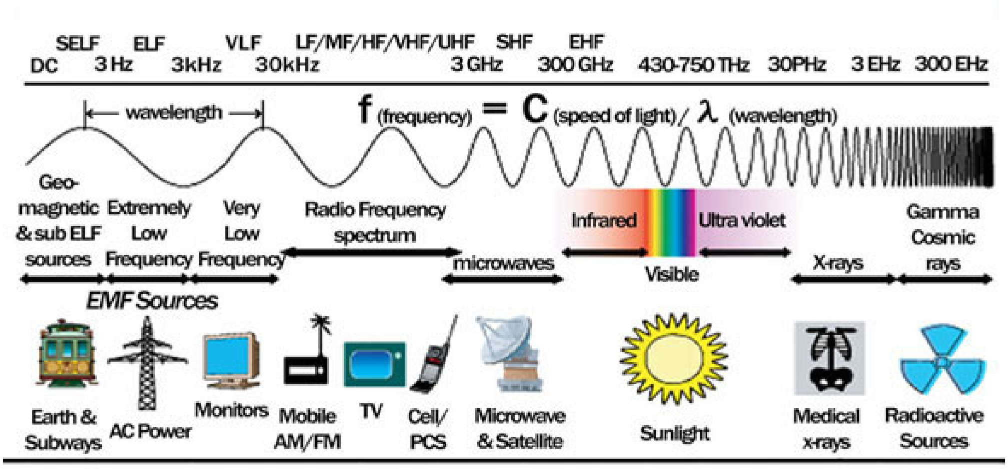
Figure 1.19: Mechanism of PET aminolysis with ethanolamine [18]

Catalysts such as lead acetate, glacial acetic acid, sodium acetate and potassium sulphate are usually used to facilitate the reaction [18].

Aminolysis has been little explored, when compared to other techniques.

1.3 Microwave assisted processes

Microwave electromagnetic radiation is an energy source adaptable to various applications. The frequency range covered by this type of radiation is extended from 30 GHz to 300 MHz and corresponds to wavelengths from 1 cm to 1 m. For industrial and domestic applications only, the use of some specific frequencies (between 0.4 and 24 GHz) is allowed; normal microwave ovens work with 2.45 GHz [19].

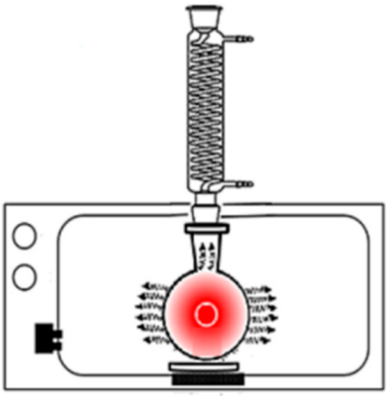


Picture 1.20: The electromagnetic spectrum

In gaseous phases, microwaves are absorbed selectively by small molecules. In condensed, liquid and solid systems the absorption is characterized by a very wide band of frequencies, depending on the irradiated material.

Since the 1980s, microwaves (“MW”) have been used in chemical laboratories for heating reaction mixtures as an alternative to conventional heating (such as oil baths, flames, heating plates) thanks to its rapid heating without contact with the material being heated. Surprisingly, MW heating has a very favourable influence on the course of a large number of reactions. Indeed, MW irradiation is highly effective in completing the depolymerization reaction of PET waste. The use of MW offers extremely short reaction time as compared to the conventional heating, without adversely affecting the products yield; at the same time, it allows substantial energy conservation. This happens because MW heat the reaction mixture essentially by oscillating the molecular dipoles or charged particles; part of the energy of the radiation is then transferred to the surrounding environment, which hinders these movements causing the so-called "dielectric loss" [19]. In the absence of electric dipoles and charged particles, the medium is transparent to MW. This is how this technology is able to penetrate and simultaneously heat the bulk of the material: the heating realized with the MW proceeds starts from points distributed throughout the volume of the irradiated sample; it is therefore very fast and easily involves phenomena of overheating. Heating can also be selective, if the reaction mixture is heterogeneous, since different materials have different dielectric losses; hot spots can therefore be created, also due to inhomogeneity of the MW field [19].

The main advantage of this kind of technology is related to the volumetric and specific absorption that particular materials present to MW and also to the possibility of avoiding the need of a catalyst (especially a metallic one), making the reaction more sustainable.



Picture 1.21: Microwave irradiation of a sample

Another advantage is that MW technology, with its system of irradiation, can perform more reactions in parallel by mixing homogeneous phases easily. This accelerates processes and prepares the ground for the creation of new bonds or for the break of bonds. Moving to MW reactions, we can promote reactions that would otherwise be extremely slow, thanks to the strong and selective heating.

This technology can find applications in a lot of different fields of chemistry, ranging from organic chemistry, inorganic chemistry, environmental chemistry, pharmaceutical chemistry, medical chemistry and even certain fields of biology.

The ease, speed and flexibility of the MW method make it ideal for laboratory investigations of polymer degradation reactions which are traditionally cumbersome and slow. Both hydrolytic depolymerization [20], aminolytic [18] and glycolysis depolymerization [21] have been studied under MW irradiation, achieving complete PET solubilization and shorter reaction times. Some researchers use this technique for preparing thermally stable and flame-retardant polyurethane foam (PUF) [22].

In KTH laboratory I was given the opportunity to use the Milestone flexiWAVE microwave oven, a flexible and powerful system typically used for high pressure and classic glassware synthesis, which offers functionality of first-class solid phase reactor. It is characterized by a cavity that has a volume of 70 litres, that allows the chemist to easily configure many different reactions setup in a very flexible environment.

The flexiWAVE microwave actually acts as a relatively small fume hood, as it incorporates a powerful exhaust system, which cools the outer surface of the reactors and provides a safe removal of vapours from microwave cavity. Temperature can be monitored by fibre optic and infrared sensors. When performing parallel reactions, a contactless sensor is used to control each vessel and the temperature can be checked on the instrument control terminal. The system is equipped with a rotating diffuser that distributes the MW throughout the cavity. The diffuser coupled with high power enables very homogeneous heating of samples. A magnetic stirrer is also present, designed to ensure vigorous stirring of the solutions in all vessels.

Picture 1.22: The Milestone flexiWAVE microwave oven

1.4 UV curable and thermal curable polymer-based materials

"Curing" is the chemical process employed in polymer chemistry and process engineering that produces the hardening of a polymer material by cross-linking of polymer chains. This method is used in all the processes where there is a liquid solution in the beginning from which a solid product is obtained.

Curing can be performed in a lot of different ways. The main ones are thermal curing and UV curing.

The resins involved are the same. What changes are the initiators involved to cure those resins. UV curing resins have distinct advantages over heat-cured resins, as they:

- Are not temperature-sensitive
- Cure faster
- Store longer

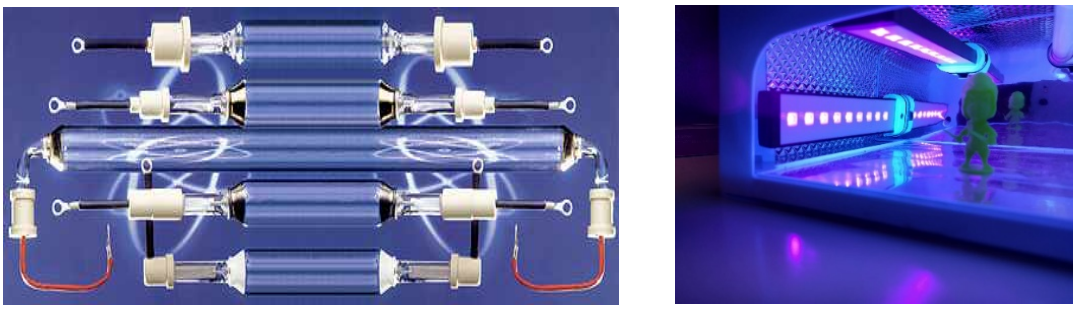
Interest has increased towards developing UV curing based technologies, due to their fast curing properties at room temperature (the process takes only few minutes or seconds), space and energy efficiency, solvent-free formulations and high-resolution methods [23].

Below a presentation of the UV curing and thermal curing methods, in which the oligomers realized by microwave-assisted processes can be used in future works.

1.4.1 UV curing and photopolymerization

The basic principle that occurs by using UV light is photocuring. Photocuring is a process of rapid conversion of specially formulated liquid solvent less compositions into solid films by ultraviolet irradiation.

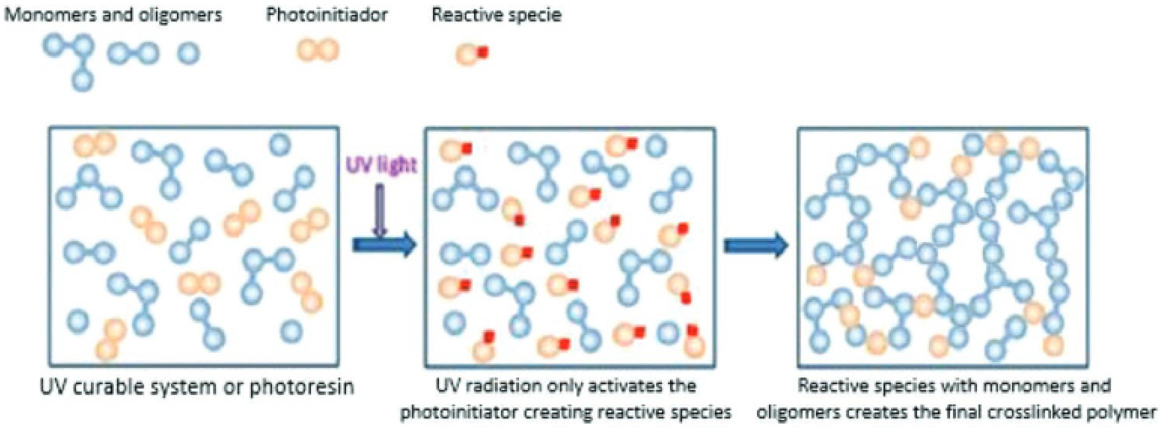
These reactions promote the creation of a crosslinked network of polymers that can be used in different fields such as printing, coating and stereolithography. It can be performed with different kinds of ultraviolet lamps, such as mercury vapor lamp (also in presence of additive), fluorescent lamps and LEDs, as shown in the picture below:



Picture 1.23: UV curing lamps: mercury vapour lamp and LEDs lamp

Photopolymerization is a synthesis of polymers by chain reactions that are initiated upon the adsorption of light by a polymerizable system (light is used only for initiating reactions, it does not interfere with propagation and termination stages).

It is an exothermic reaction that uses prepolymers or oligomers mixtures combined with polyfunctional monomers and photoinitiators as reactants: the photoinitiator produces a free radical, thanks to the light irradiation; the free radical is then able to catalyse the polymerization process. It is necessary to use a sufficiently high radiation power to avoid the redissolution into liquid monomers of the polymeric chain. Below a schematic representation of the photopolymerization process.



Picture 1.24: Schematic representation of the photopolymerization process [23]

1.4.2 Thermal curing

Thermal curing is the process of temperature-induced chemical change in a material, such as polymerization of a polymeric resin. That means that this process produces the hardening of a polymer material by cross-linking of polymer chains. During the curing process, single monomers and oligomers, mixed with a thermal initiator, react to form a tridimensional polymeric network. The reaction is initiated by heat and the methodology depends on the resin and the application.

Thermal curing is one of the most popular curing methods and it is characterized by a great variety of thermal heating: according to the heating mechanism, they can be categorized into radiation heating (infrared, laser and microwave), convection & conduction heating (hot gas, flame, oven, and hot shoe), induction heating, ultrasonic heating, resistance heating and thermal additive-based heating [24].

This study is focused on convection heating, that is based on the transfer of heat by temperature gradient.

A scheme of the working principle is presented in Figure 1.24.

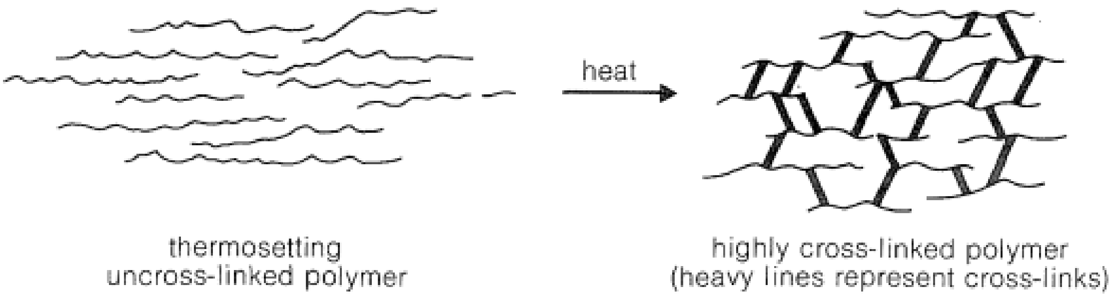


Figure 1.24: Thermal curing working principle

Compared to UV irradiation process, the reaction times of thermal curing are longer, so the energy expenses are higher.

1.5 Purpose of the study

The purpose of this study is to investigate the chemical recycle of PET by glycolysis under microwave irradiation: we will use this chemical recycling method to perform a depolymerization on PET into oligomers. Microwave irradiation is expected to be highly effective in completing the reaction using shorter reaction time, if compared to the conventional heating, allowing at the same time substantial energy conservation [26].

The idea is to use these recycled oligomers as raw materials that can be crosslinked by 3D printing or UV-curing in order to create new useful materials.

In order to reach this objective, I spent five months in Stockholm, Sweden, at KTH Royal Institute of Technology, where I carried out all the necessary experiments.

The main steps that I followed are:

- Step 1

Characterize the neat PET (both PET waste and general PET) by FTIR, DSC, TGA and NMR analysis.

- Step 2

Depolymerize the PET by microwave irradiation into oligomers by using ethylene glycol (EG), glycerol (GLY), water and ethanolamine (EA); characterize by NMR and SEC analysis. Optimize the depolymerization process regarding molecular weight by controlling the time, temperature and PET: solvent ratio.

- Step 3

Functionalize the oligomers with methacrylic anhydride directly in the microwave. Characterization of the functionalized product by FTIR and NMR analysis.

- Step 4

UV-curing and thermal curing of the functionalized oligomers.

2. Materials

2.1 Depolymerization

The first step was PET bottle cutting, which entailed reducing it into small flakes (rectangles of 5*6 mm^2 area). Pieces that could have had impurities (for example glue residues from the label) were discarded. This step is shown in Figure 2.1.

Figure 2.1: PET bottle cutting

Depolymerization was performed by controlling:

- PET : reagent ratio
- Temperature
- Time

No catalyst was used for the reactions. In all the experiment 1g of PET flakes were used for each batch. The co-reagent was then added with different PET : reagent ratio in small vessels. Stirring bars were also added. The small batches are shown in figure 2.2.

Figure 2.2: Preparation of the microwave oven batches

2.1.1 Ethylene Glycol (EG)

The experiments performed are summarized in Table 2.1.

PET:EG ratio	Temperature [C°]	Time [minutes]
1:2	160	30
1:2	200	30
1:5	160	30
1:5	160	60
1:5	200	30
1:5	200	60
1:10	200	120
1:10	200	180
1:10	200	240

Table 2.1: Ethylene Glycol experiments

The obtained solutions were placed into the fridge for one night. They were then filtered by using a filter paper. The liquid phase remained in the fridge while the solid phase was put into the vacuum oven for being dried for one night. The dry solid phases obtained are shown in Figure 2.3.

Figure 2.3: Depolymerization samples with EG

The samples that contained too many flakes were discarded because it was evident that the molar ratio was not high enough. Only the PET 1:10 EG 120 minutes, 180 minutes and 240 minutes were kept.

2.1.2 Glycerol (GLY)

The experiments performed are summarized in Table 2.2.

PET:GLY ratio	Temperature [C°]	Time [minutes]
1:5	200	30
1:5	200	60
1:5	200	120

Table 2.2: Glycerol experiments

The obtained solutions were placed into the fridge for one night. Then, they were filtered by using a filter paper. The liquid phase remained in the fridge while the solid phase was put into the vacuum oven for being dried for one night. The dry solid phases obtained are shown in Figure 2.4.

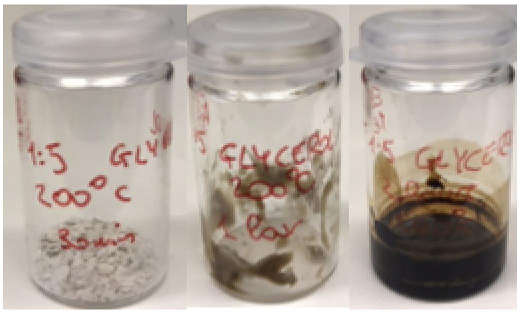


Figure 2.4: Depolymerization samples with GLY

The samples that appeared to be too sticky were discarded. Only the PET 1:5 GLY 30 minutes was kept.

2.1.3 Water (H_2O)

The experiments performed are summarized in Table 2.3.

PET: H_2O ratio	Temperature [C°]	Time [minutes]
1:10	200	60
1:10	200	120
1:10	200	240

Table 2.3: Water experiments

The obtained solutions were placed into the fridge for one night. They were then filtered by using a filter paper. The liquid phase remained in the fridge while the solid phase was put into the vacuum oven for being dried for one night.
The dry solid phases obtained are shown in Figure 2.5.

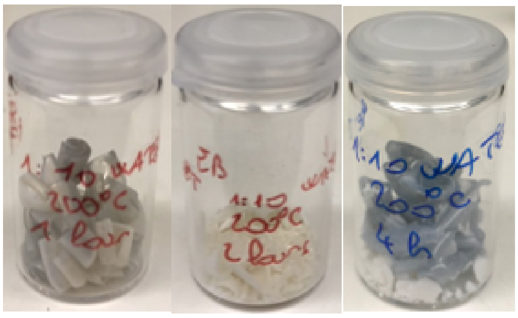


Figure 2.5: Depolymerization samples with H_2O

The samples that contained too many flakes were discarded, since it was evident that the reaction time was not high enough. Only PET 1:10 H_2O 120 minutes and 240 minutes were kept.

2.1.4 Ethanolamine (EA)

The experiments performed are summarized in Table 2.6.

PET:EA ratio	Temperature [C°]	Time [minutes]
1:10	200	5
1:10	200	10
1:10	200	30
1:10	200	60
1:10	200	120

Table 2.4: Ethanolamine experiments

The obtained solutions were placed into the fridge for one night. They were then filtered by using a filter paper. The liquid phase was kept in the fridge while the solid phase was put into the vacuum oven for being dried for one night. The dry solid phases obtained are shown in Figure 2.6.

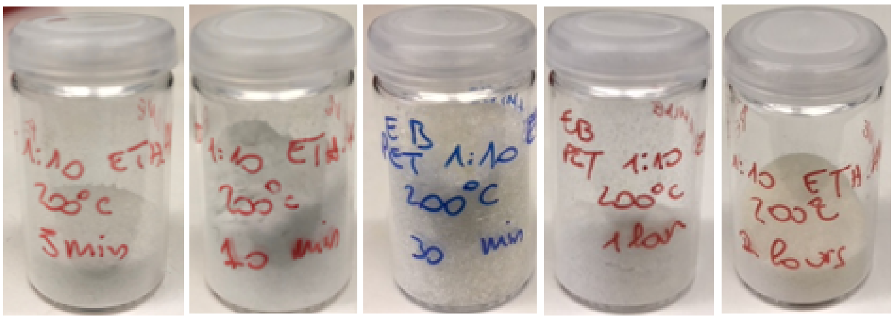


Figure 2.6: Depolymerization samples with EA

H-NMR analysis was performed on the samples, in order to determine the structure of the molecule.

2.2 Functionalization

PET oligomers need to be functionalized, since otherwise they cannot be crosslinked by UV-curing techniques.

The process of functionalization that was performed on the oligomers relied on the esterification reaction of the microwaved PET with Methacrylic Anhydride. The reaction was conducted into the microwave that allowed to use significantly shorter reaction times compared to conventional heating. Methacrylic Anhydride is shown in Figure 2.7.

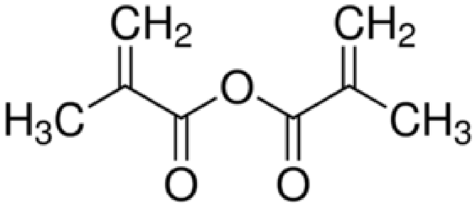


Figure 2.7: Methacrylic Anhydride

An amount of 0,5 g of the product was mixed with 10 ml of Methacrylic Anhydride into the microwave vessel adding the stirring bars. The reaction was conducted at 110°C for 5 minutes only. After cooling, the product was precipitated in ethanol, and the powder thus obtained was subsequently dried in a vacuum oven at 25°C for 24 hours.

The degradation product used to perform the procedure are summarized in Table 2.5.

Degradation product	Amount
PET 1:10 EG 200°C 3h	0,5 g
PET 1:5 EA 150°C 15 minutes	0,5g
PET 1:10 EA 150°C 5 minutes	0,5g
PET 1:10 EA 200°C 10 minutes	0,5g

Table 2.5: Degradation products used for methacrylation

2.3 Curing

Curing was performed on PET 1:10 EG 200°C 3h, in order to transform the liquid functionalized product into a solid three-dimensional network in which polymer chains cross-link and form a rigid material.

Curing was performed through two different ways:

- UV-curing by a radical photopolymerization reaction with the use of Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) as photoinitiator, as shown in Figure 2.8.

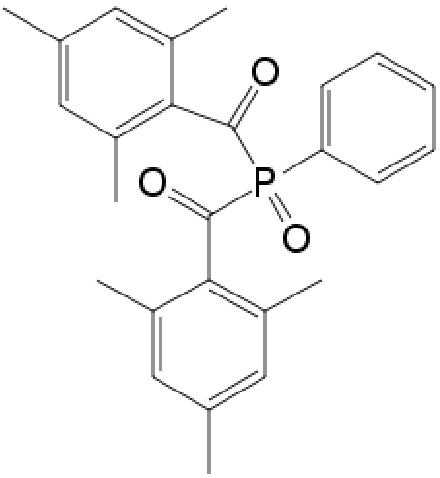


Figure 2.8: BAPO molecular structure

- Thermal curing by a radical polymerization reaction temperature-induced with the use of BPO (Benzoyl peroxide) as initiator, as shown in Figure 2.9.

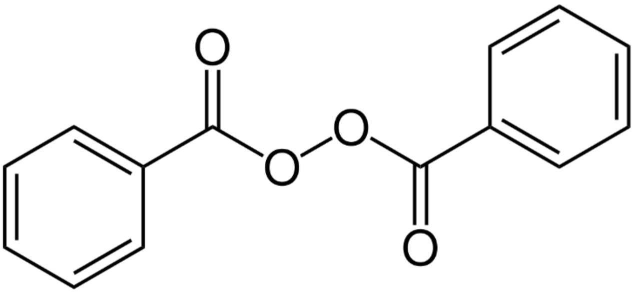


Figure 2.9: BPO molecular structure

Because of the small amount of product available for the reaction, in both cases Polyethylene Glycol dimethacrylate was added as co-reagent, which is shown in Figure 2.10.

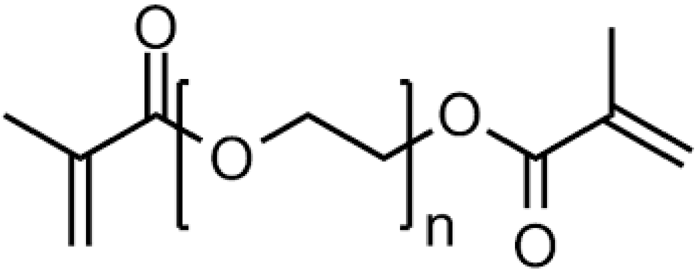


Figure 2.10: Polyethylene Glycol dimethacrylate molecular structure

2.3.1 UV-curing

The first step was the dissolution test, in order to obtain a homogeneous solution. The PET 1:10 EG sample was tested in three different solvents:

- Butyl Acetate
- Dimethyl sulfoxide (DMSO)
- Chloroform ($CHCl_3$)

The degradation product concentration was first set at 5% wt in all the solvents. Buthyl Acetate did not work and that is why it was discarded.

The concentration was increased at 50% wt in DMSO, the stirring bars were added and the samples were left on a shaking table at 35°C for an hour to let them be dissolved in the solvent.

Chloroform was then tested with a concentration of 50% wt in $CHCl_3$. while stirring, reducing the dissolution time to 30 minutes.

Later the solution was mixed with 50 wt% of Polyethylene Glycol dimethacrylate.

Finally, 2% of photoinitiator Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) was added while stirring in dark conditions for 3 minutes.

The solution was then poured in a Petri glass and irradiated for 15 min using a UV-lamp.

The UV-curing apparatus is shown in Figure 2.10.

Figure 2.10: UV-curing apparatus used for the photopolymerization

2.3.2 Thermal curing

The first step was the dissolution in chloroform of PET 1:10 EG sample, in order to obtain a homogeneous solution.

PET 1:10 EG 200C 3h sample was mixed with 92 wt% of Polyethylene Glycol dimethacrylate and with 3 wt% of BPO (Benzoyl peroxide) initiator. The solution was then poured in small circular moulds and put under Nitrogen flux in a desiccator at 90°C for 2 hours. Subsequently the temperature was increased to 120°C for 2 more hours. The thermal curing desiccator is shown in Figure 2.11.

Figure 2.11: Thermal curing desiccator

Nitrogen flux was used in order to avoid oxygen inhibition of the reaction, which is a common problem of radical polymerization.

3. Methods

3.1 Proton nuclear magnetic resonance (H-NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy is an instrumental analytical technique that allows the researcher to obtain detailed information on the structure of molecules by observing the behavior of atomic nuclei in a magnetic field.

Each nucleus has a proper spin: protons and neutrons, having spin ½, behave similarly to electrons and are housed in orbitals within the nucleus which, by the Pauli exclusion principle, cannot contain more than two protons or two neutrons with opposite spins (+1/2, -1/2). Therefore, two spin states exist: α (+1/2) and β (-1/2).

Some nuclei are charged and some others are neutral. The charged ones are able to create a nuclear magnetic moment (μ) proportional to the spin. Nuclear spins are randomly oriented in absence of an external magnetic field; when an external magnetic field (B_{0}) is applied the α state, which has lower energy, tends to align parallel to the external magnetic field, while the β state, which has higher energy, tends to align with an antiparallel configuration. The following Figure 3.1 shows the energy difference between the two spin states.

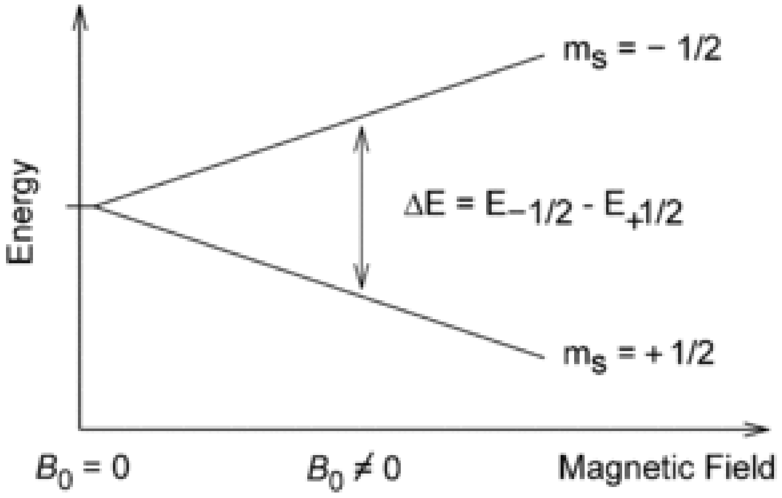


Figure 3.1: Difference between the two spin states and the external magnetic field

When looking at Figure 3.1, it is clear that when the external magnetic field is equal to zero the energy difference between the two states (ΔE) tends to zero.

For H-NMR measurements ΔE, commonly given in terms of frequency (ν), varies from 20 to 900 MHz, the typical radio frequencies, depending on the nucleus that has to be investigated. The correlation between frequency and nucleus momentum is expressed by equation 3.1

$$\nu = \mu \frac{B_0}{hI} \qquad \text{(equation 3.1)}$$

where ν is the frequency [Hz], h is the Plank's constant (h=6.626 *10-34 [J*s]) and I is the spin (+1/2 or -1/2).

The difference between two energetic levels is given by equation 3.2

$$\Delta E = h\nu \qquad \text{(equation 3.2)}$$

where again ν is the frequency [Hz] and h is the Plank's constant. As the applied external magnetic field increases, the frequency increases and, therefore, the difference between the two levels increases.

Generally speaking, all nuclei feel the influence of three different magnetic fields: the one generated by the Earth, the NMR one and the ones created by the other nuclei. Only the last two fields are taken into account for NMR measurements, especially the one generated by other nuclei. This is the reason why protons 1H are non-equivalent in many compounds, since protons within a compound create diverse magnetic fields thus giving different signal in H-NMR spectra.

After immersing the molecule that needs to be analyzed in a strong magnetic field, radio frequency radiations (from 100 to 1000 MHz) are sent into the specimen through a coil and the absorption of their emissions is measured by means of a second coil that transmits the signal to a computer. The emitted energy, in the radio frequency region, produces an NMR signal. This signal is reported in a graph, where on the horizontal axis the chemical shifts δ (measured in ppm) are given, which are calculated using a proton of tetramethylsilane (CH3)4Si, set at 0.00 ppm [27], as a reference.

In Figure 3.2 the scheme of the process is reported. In Figure 3.3 the NMR apparatus and the samples tube used to perform the analysis are shown.

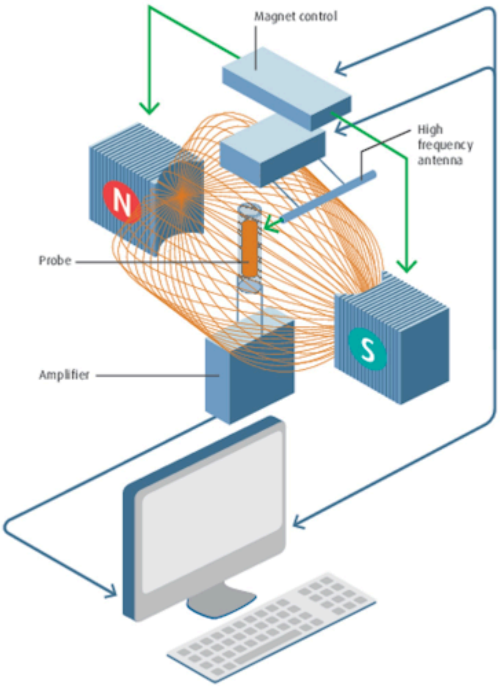


Figure 3.2: Scheme of NMR working principle

Figure 3.3: NMR apparatus [28] and sample tubes used for this analysis

In this work, H-NMR was used to characterize both the degradation products and the functionalized oligomers. The measurements were performed by means of Avance 400 (400.13 MHz - Bruker, USA) spectrometer at room temperature.

Ethylene Glycol and Glycerol samples were dissolved in Deuterochloroform ($CDCl_3$). In some cases +5% of 1,1,1,3,3,3-Hexafluoropropane (HEFP) was added in order to favour the dissolution. For Ethanolamine samples Dimethyl Sulfoxide (DMSO) was used.

The H-NMR glass tubes were filled with about 10 mg/mL of solution.

3.2 Carbon nuclear magnetic resonance (C-NMR)

The power and usefulness of H-NMR spectroscopy as a tool for structural analysis should be evident from the previous discussion. Unfortunately, when numerous C-H groups are present, an unambiguous interpretation of a H-NMR spectrum may not be possible.

This problem would be largely resolved if the carbon atoms of a molecule could be probed by NMR in the same manner as the hydrogen atoms. Since the major isotope of carbon (^{12}C) has no spin, ^{13}C is used, which represents the 1.1% of elemental carbon. This isotope has spin ½, so it is possible to conduct a carbon NMR experiment. The problem here is that, as noted, the abundance of ^{13}C in a sample is very low, so higher sample concentrations are needed and that ^{13}C nucleus is over fifty times less sensitive than a proton in the NMR experiment.

The most important operational technique that has led to successful and routine C-NMR spectroscopy is the use of high-field pulse technology, coupled with broad-band heteronuclear decoupling of all protons. The results of repeated pulse sequences are accumulated to provide improved signal strength. This signal, as for H-NMR, reported in a graph where on the horizontal axis the chemical shifts δ (measured in ppm) are given.

Unlike H-NMR spectroscopy, the relative strength of C-NMR signals is not normally proportional to the number of atoms generated by each one. Due to this circumstance, the number of discrete signals and their chemical shifts are the most important pieces of evidence delivered by a carbon spectrum [27].

In Figure 3.3 the NMR apparatus and the samples tube used to perform the analysis are shown, the same of the H-NMR analysis.

In this work, C-NMR was used to characterize both the degradation products and the functionalized oligomers. The measurements were performed by means of Avance 400 (400.13 MHz - Bruker, USA) spectrometer at room temperature.

Ethylene Glycol and Glycerol samples were dissolved in Deuterochloroform ($CDCl_3$). In some cases, + 5% of 1,1,1,3,3,3-Hexafluoropropane (HEFP) was added in order to favour the dissolution. For Ethanolamine samples Dimethyl Sulfoxide (DMSO) was used.

The C-NMR glass tubes were filled with about 10 mg/mL of solution.

3.3 Attenuated Total Reflectance – Fourier transform infrared (ATR-FTIR) spectroscopy

The Attenuated Total Reflection Fourier Transform IR Spectroscopy (ATR-FTIR) is a typical spectroscopic technique, which allows the examination of solid and liquid samples without complicated preparation techniques.

In this technique the sample is placed in contact with an optical element called internal reflection element, consisting of a crystal with a high refractive index. Subsequently, an IR beam is sent to the crystal surface with a certain angle: it enters the crystal, it is reflected through the crystal and penetrates inside the sample for few microns, being partially absorbed. After some reflections, the attenuation of the intensity of the IR beam is enough to be detected by the spectrophotometer, giving an ATR-FTIR spectrum. These spectra are uniquely dependent on the type of material, because the absorption regions are related to its chemical structure. Therefore, the recorded spectra, which are considered as the fingerprints of the chemical species, are evaluated to identify the composition of the sample. In Figure 3.4 the schematic working principle of ATR-FTIR is presented.

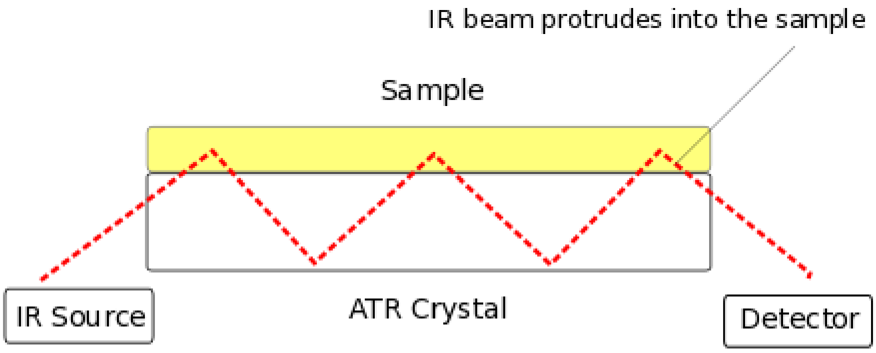


Figure 3.4: Schematic representation of ATR-FTIT working principle

In this work, ATR-FTIR was used to characterize both the neat PET and the degradation products. It was also used to prove the success of functionalization on the oligomers. The tests were performed using a Perkin-Elmer Spectrum 2000 (16 scans, resolution 2 cm^{-1}). The ATR-FTIR apparatus used for the characterization of the oligomers is shown in Figure 3.5.

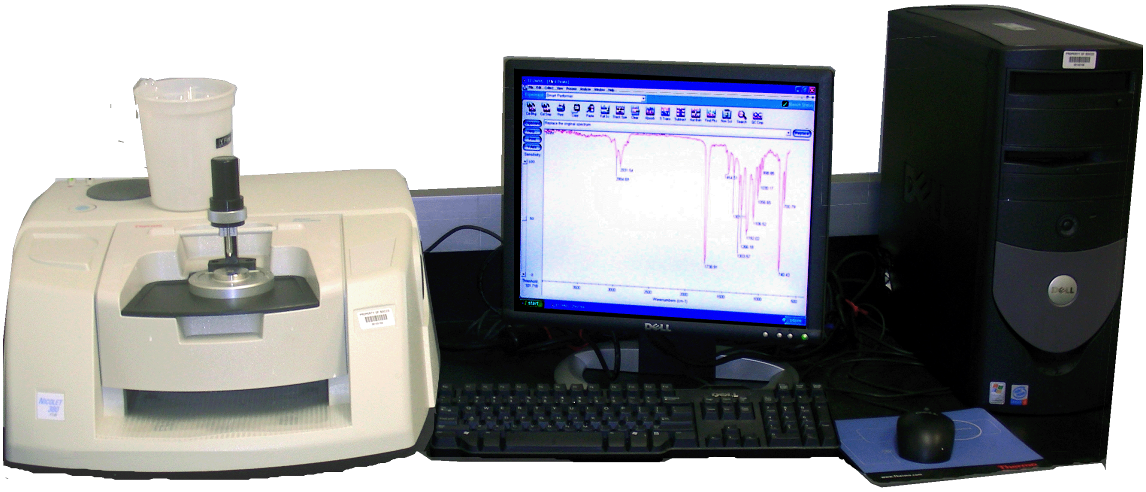


Figure 3.5: ATR-FTIR instrumental apparatus

3.4 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a thermal analysis technique that can be used to measure the temperature and heat flow associated with the transitions that occur in a sample, the melting enthalpies, the glass transitions and the crystallization kinetics of polymeric materials. The basic principle of this technique consists in obtaining information about the material by heating or cooling it in a controlled way. In particular, DSC is based on the measurement of the difference in thermal flow between the sample under examination and a reference: during the whole test both the sample and the reference are kept at the same temperature that is set to increase linearly over time. Usually, the crucibles caps present holes in the middle, allowing the penetration of a controlled atmosphere during the test.

The physical transitions are recorded and plotted in a thermogram in which we have the heat flow variations on y-axis, and the temperature on x-axis. This graph can be analysed with the tools of the program in order to evaluate the enthalpies of transitions. In Figure 3.6 the schematic working principle of DSC is presented.

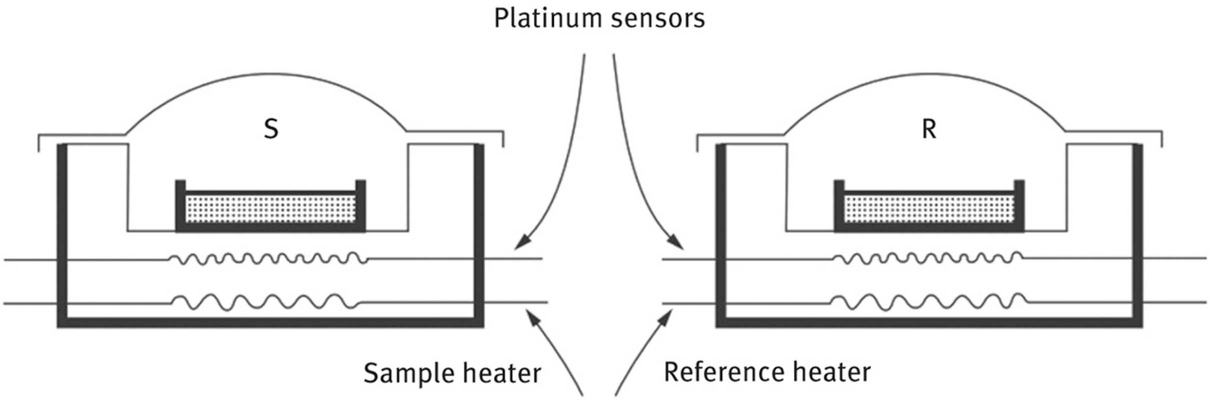


Figure 3.6: Scheme of a DSC measurement chamber [29]

DSC was used in this work to evaluate the thermal transition of the neat PET and of some of the degradation products. The measurements were carried out at a heating rate of 10 °C/min with a DSC Mettler Toledo DSC 820 using 100µL aluminium crucibles.

The DSC apparatus used for the characterization of neat PET and of the degradation products is shown in Figure 3.7.

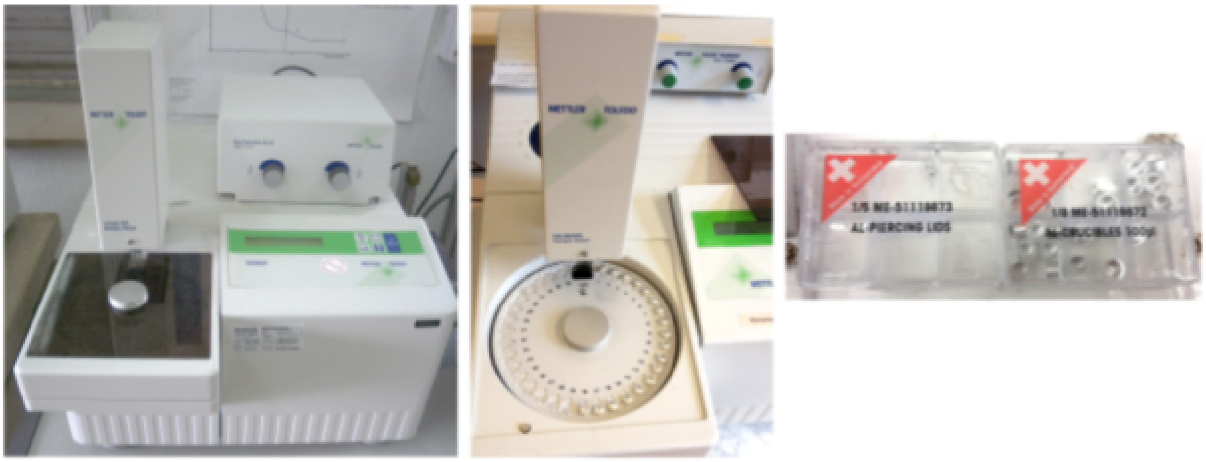


Figure 3.7: DSC Mettler Toledo 820 and crucibles used in DSC analysis

3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a technique used to determine materials weight losses upon heating, which can be the result of different physical processes induced by high temperature, such as oxidation and degradation.

The sample is inserted within a crucible that is positioned onto a precision micro-balance. The heating rate and the atmosphere are precisely controlled during the whole experiment.

From this analysis we obtain graphs in which there is the weight loss % on the y-axis and the temperature on the x-axis: these graphs are called thermogravimetric curves.

In Figure 3.8 below, a scheme of the TGA chamber is represented.

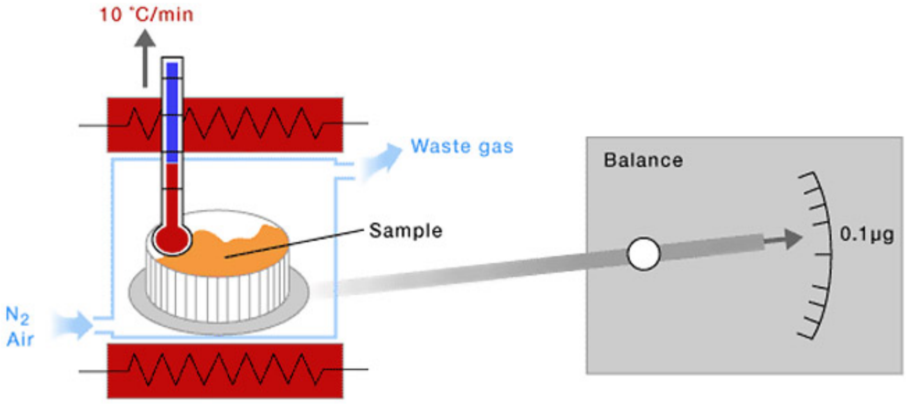


Figure 3.8: Schematic representation of TGA measurement chamber [30]

TGA was used in this study to investigate the thermal stability of neat PET. The samples were placed in alumina crucibles (70 µL) that were used without lids. The tests were run up to 800°C under Nitrogen flux, using a TGA Mettler Toledo (USA) and the results were analysed using STARe software.

The TGA apparatus used for the characterization of neat PET is shown in Figure 3.9.

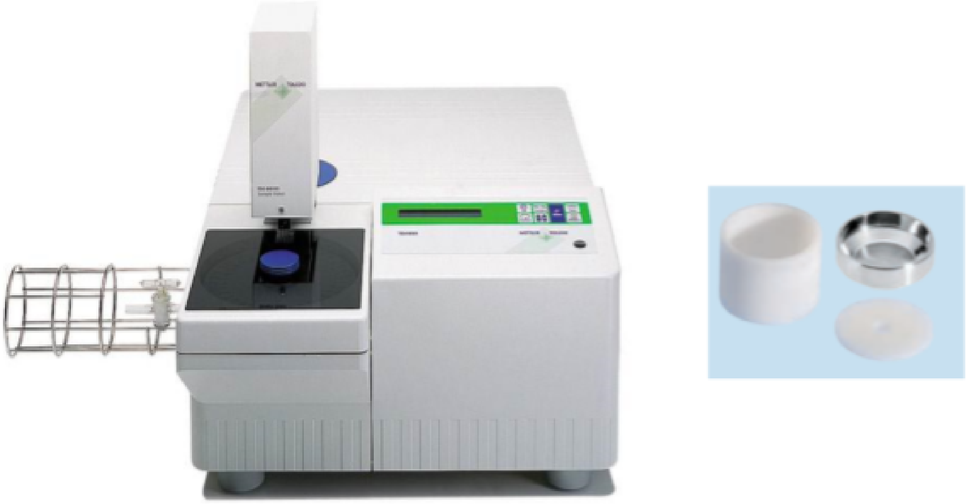


Figure 3.9: TGA apparatus and crucible used in the analysis

3.6 Size-exclusion chromatography (SEC)

Size-exclusion chromatography (SEC) is a chromatography technique which separates the components of a sample based on their molecular size. The exclusion or differential inclusion of the molecules is achieved via filtration through a gel that contains the spherical pearls. These pearls have pores of a specific size distribution to include or exclude molecules of different sizes when they pass through the gel contained into a column. This gel, also known as matrix, needs to be physically and chemically stable.

In Figure 3.10 below, the schematic working principle of SEC chromatography is represented.

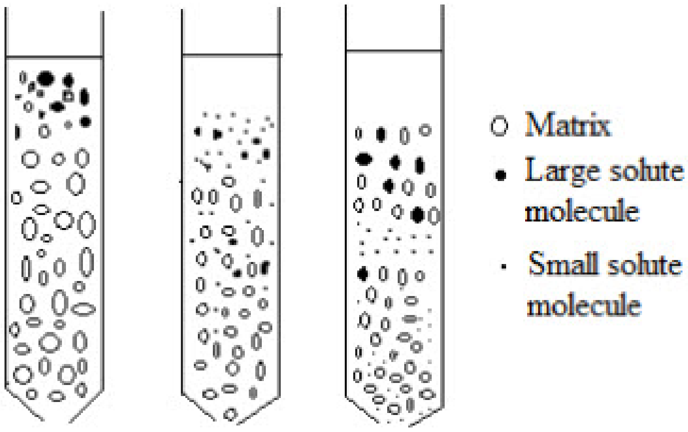


Figure 3.10: Schematic representation of SEC working principle [31]

Smaller molecules can enter the matrix pores and have a higher residence time compared to the one measured with bigger molecules. Therefore, particles with the same size are supposed to exit together. The times of elution are reported as peaks into the chromatogram. It is important to notice that the molecules' volume estimated by this technique is different from the real analyte volume: it just provides an indication of the hydration volume of the sample.

Equation 3.3 and 3.4 allow the estimation of respectively the number average molecular weight (M_n) and the weight average molecular weight (M_w).

(equation 3.3) $$M_n = \Sigma n_i M_i$$

(equation 3.4) $$M_w = \Sigma w_i M_i$$

where n_i is the number fraction $n_i = \frac{N_i}{\Sigma N_i}$ (N_i is the number of molecules i) and w_i is weight fraction: $w_i = \frac{W_i}{\Sigma W_i}$, (W_i is the weight of molecules i) [32].

SEC was used in this study to obtain an estimation of the molecular weight of some of the degradation products.

The measurements were carried out using a Malvern apparatus coupled with Viscotek viscometer, RI detector, light scattering and temperature-controlled system shown in Figure 3.11. Before the tests, the samples were opportunely dissolved in Dimethylformamide (DMF) solvent in a concentration of 1 mg/mL for ethanolamine samples and in Chloroform ($CHCl_3$) solvent in a concentration of 1 mg/mL for the ethylene glycol samples.

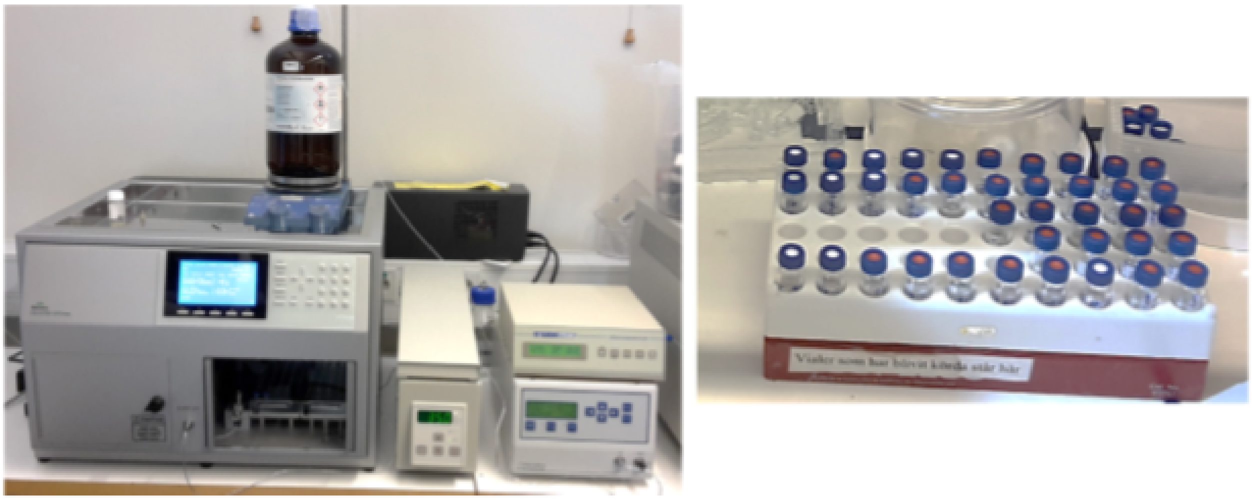


Figure 3.11: SEC apparatus and sample tubes used in this technique

4. Results and discussion

Here below all the analysis performed on the PET characterization.

4.1 PET characterization

4.1.1 FTIR analysis

A FTIR analysis was performed on the PET sample, in order to determine the structure of the molecule. The results are shown in Figure 4.1:

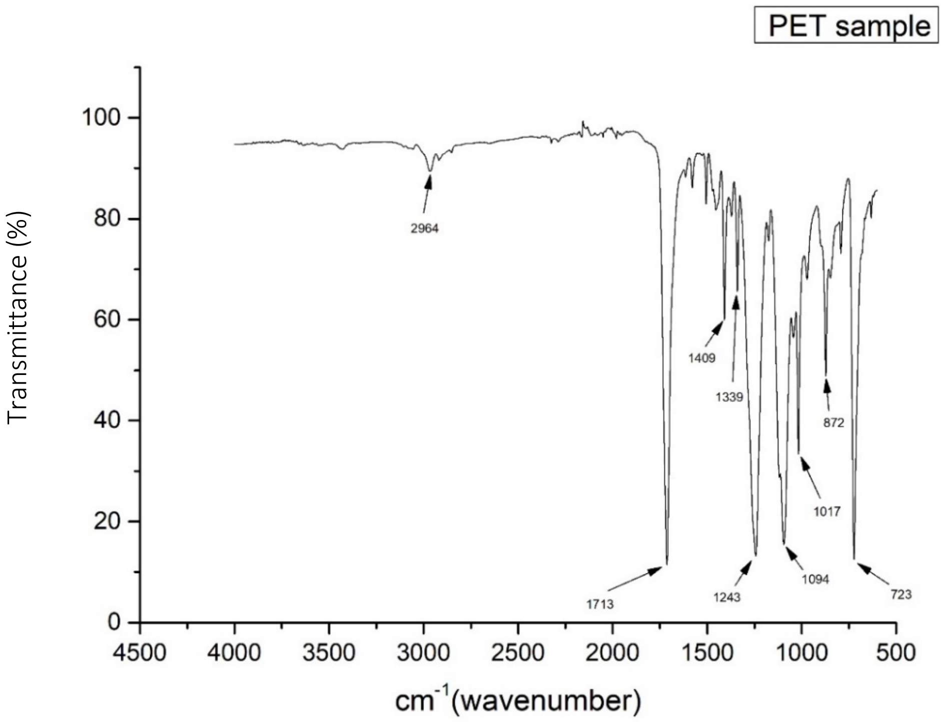


Figure 4.1: FTIR spectrum of the PET sample

The main groups characterized by the wavenumbers in the spectrum are summarized in Table 1.

ABSORPTION PEAK [cm^{-1}]	GROUP
723	Interaction of polar ester group and benzene ring
872	C=C aromatic ring vibration
1017	H aromatic vibration
1094	C-O
1243	$OOCC_6H_4$-COO terephthalate group [33]
1339	C-H bending of aliphatic chain
1409	C-H bending of aliphatic chain
1713	C=O carboxylic group
2964	C-H stretching of aromatic ring

Table 4.1: Absorption peaks of the main functional groups

The results are consistent with the PET structure that is reported in Figure 4.2.

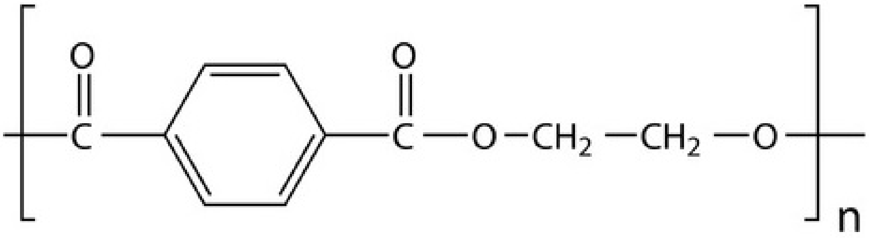


Figure 4.2: PET repeated unit

4.1.2 DSC analysis

DSC analysis was performed on the PET sample, in order to determine the glass transition temperature and the melting temperature.

The results are shown in Figure 4.3 and Table 4.2.

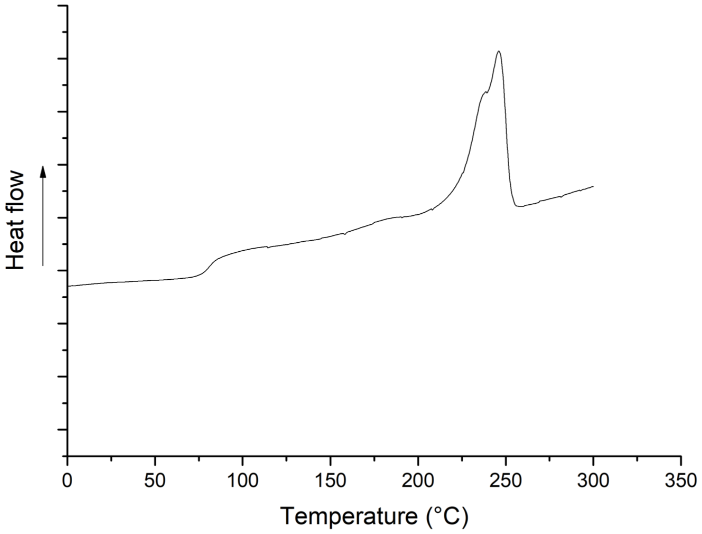


Figure 4.3: DSC analysis on PET sample

GLASS TRANSITION TEMPERATURE [°C]	75
MELTING TEMPERATURE [°C]	240

Table 4.2: DSC results

The results are consistent with the ones found in literature [2].

4.1.3 TGA analysis

TGA analysis was performed on the PET sample, in order to determine the degradation temperature. The results are shown in Figure 4.4.

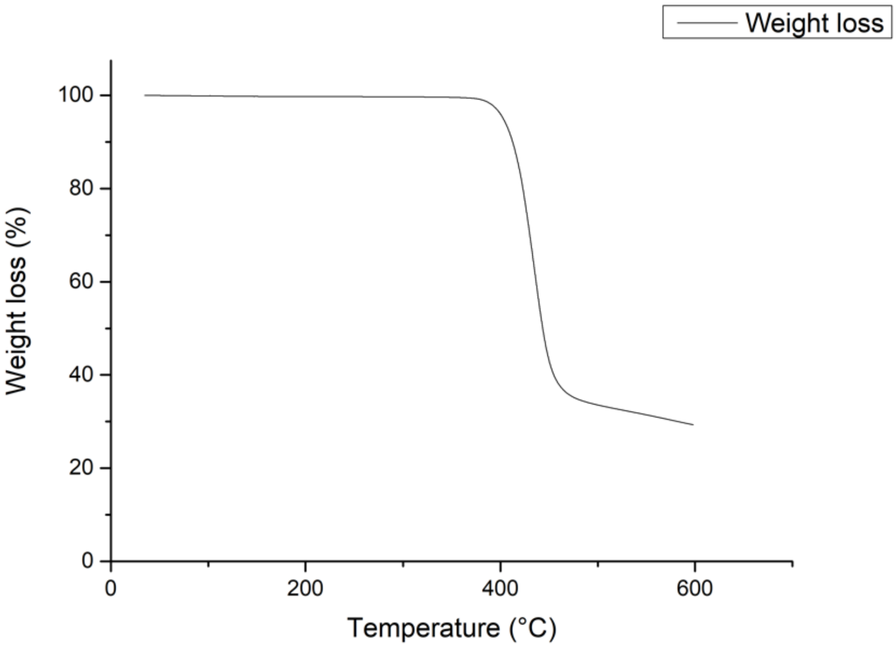


Figure 4.4: TGA analysis on PET sample

The degradation temperature is around 350°C, that is consistent with the value found in literature [2].

4.1.4 NMR analysis

H-NMR and C-NMR analysis were both performed on PET sample, in order to determine the structure of the molecule. The solvent for NMR analysis was prepared by mixing 0.5 ml of 1,1,1,3,3,3-HEXAFLUORPROPAN-2d (HEFP) with 4.5 ml of Chloroform-d (1:9 ratio).

After that, 20 g of PET were dissolved into the solvent using a shaking table.

The results are shown in Figure 4.5 and Figure 4.6.

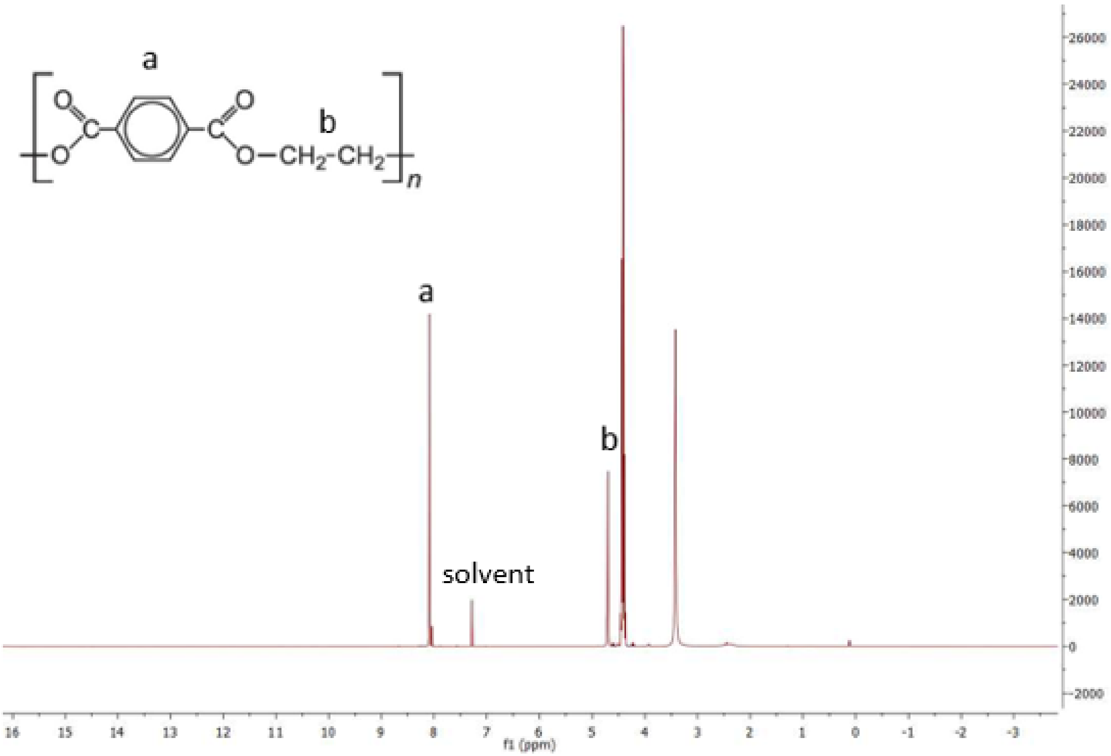


Figure 4.5: H-NMR analysis on PET sample

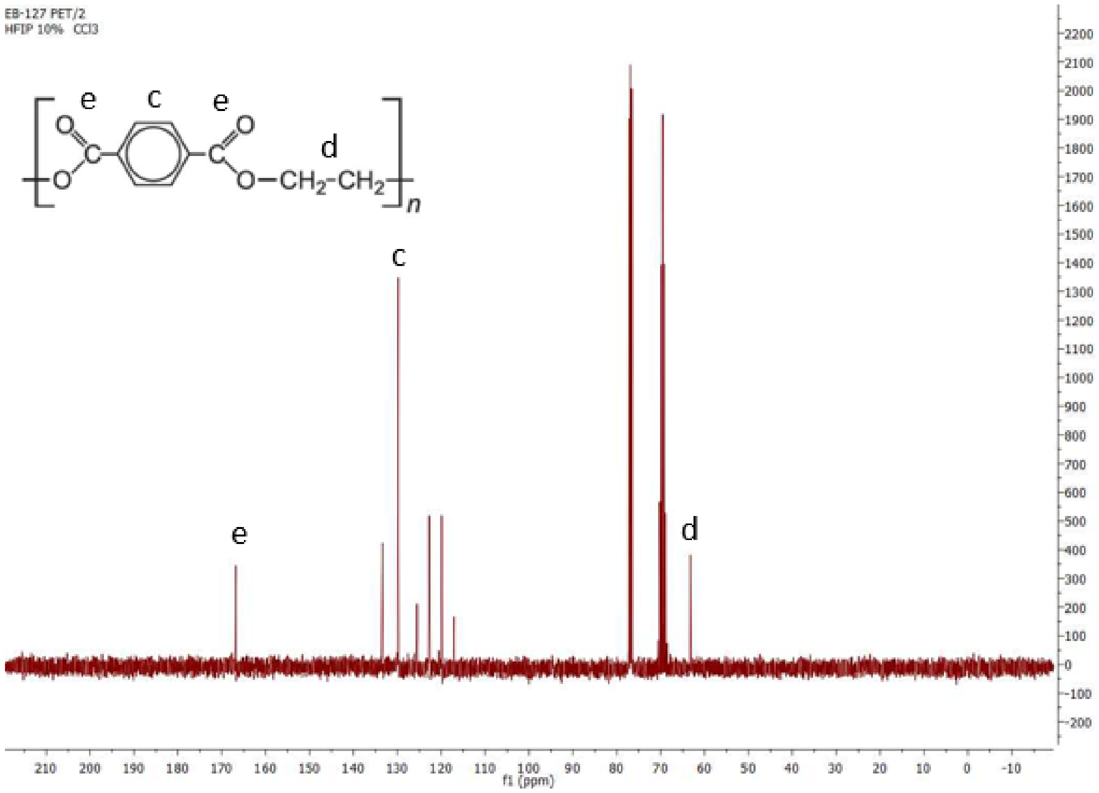


Figure 4.6: C-NMR analysis on PET sample

The results are consistent with the PET structure.

4.2 Degradation products characterization

4.2.1 Ethylene Glycol (EG)

ATR-FTIR analysis was performed on the samples, in order to determine the structure of the molecule. The results are shown in Figure 4.8.

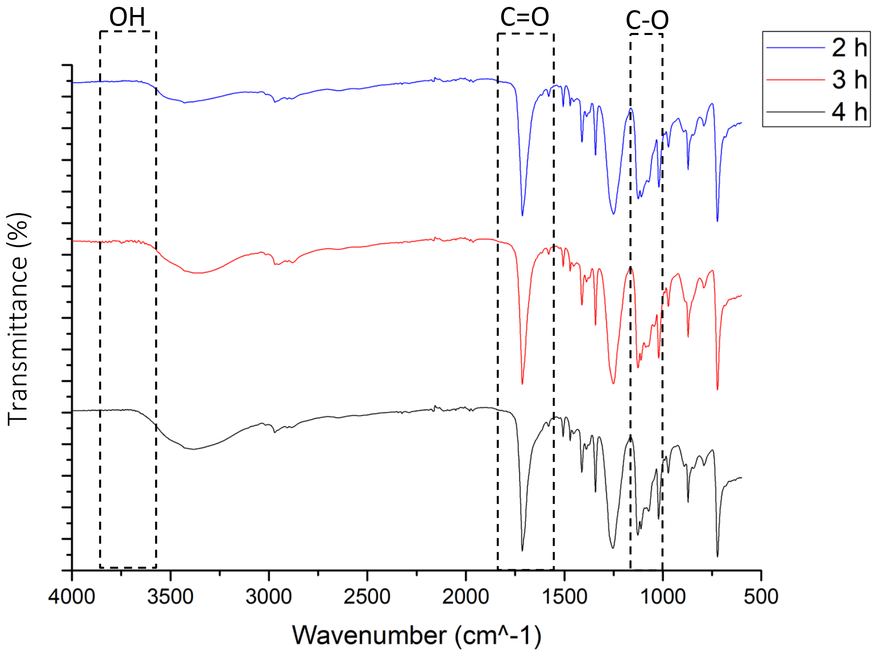


Figure 4.8: ATR-FTIR analysis on PET 1:10 EG samples

As we can see in Figure 4.8, the recorded spectra of the PET 1:10 EG samples are very similar, differing for the -OH broad peaks at around 3500 cm^{-1} if compared with the neat PET spectrum (Figure 4.1) which does not show a peak in correspondence of this wavenumber. This is due to the longer carbon chains that make the ending groups difficult to be detected.

All of the spectra show the typical peaks of C=O vibration at 1723 cm^{-1} and C-O vibration at around 1094 cm^{-1}. The peak at 1243 cm^{-1} prove the presence of the terephthalate group [33].

The time was not sufficient to complete the whole interpretation of the NMR spectra, which is why they are not reported in this thesis.

The molecular weights of the degradation PET 1:10 EG products are evaluated by means of size exclusion chromatography (SEC) measurements.

Figure 4.9 shows the volume, known as retention volume, at which the solute elutes from the column.

Figure 4.10 gives an estimation of the molecular weights. It is important to note that this instrument is able to measure only the hydrodynamic volume that strongly depends on the affinity between sample and solvent.

Therefore, it is not accurate but it can be quite precise, so it is only useful for comparative purposes.

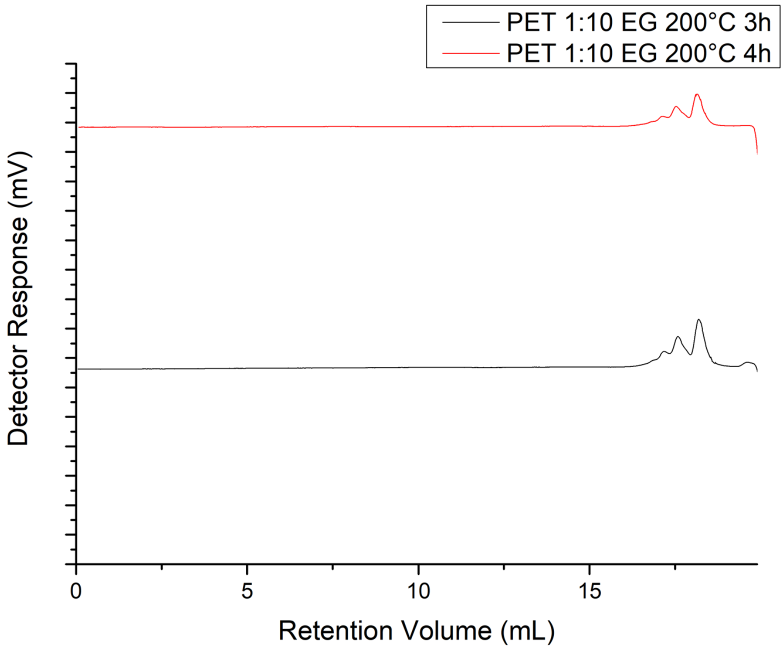


Figure 4.9: SEC retention volume plots of PET 1:10 EG 200°C 3 hours and PET 1:10 EG 200°C 4 hours

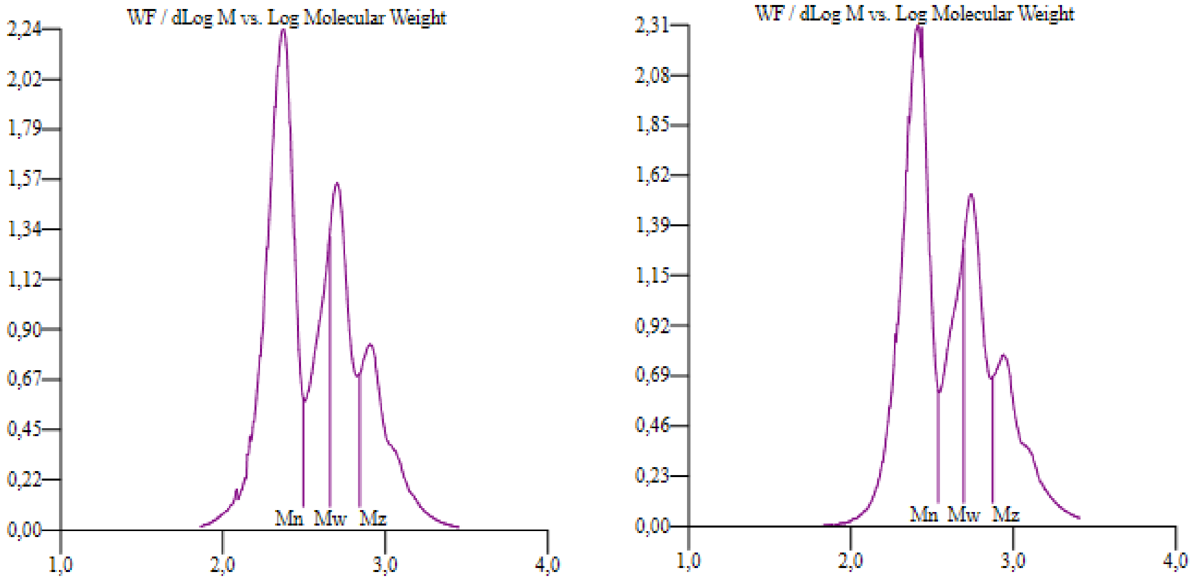


Figure 4.10: SEC molecular weights plots of PET 1:10 EG 200°C 3 hours (on the left) and PET 1:10 EG 200°C 4 hours (on the right)

In Table 4.3 the number average molecular weight (M_n), the weight average molecular weight (M_w), the retention volume and the polydispersity index ($PDI = \frac{M_n}{M_w}$) are summarized.

Material	Pick RV [mL]	M_n [Da]	M_w [Da]	PDI
PET 1:10 EG 200°C 3 hours	18,183	312	457	1,465
PET 1:10 EG 200°C 4 hours	18,108	344	495	1,439

Table 4.3: highlights results from SEC graphs

The results are consistent with the oligomer structure that is reported in Figure 4.11.

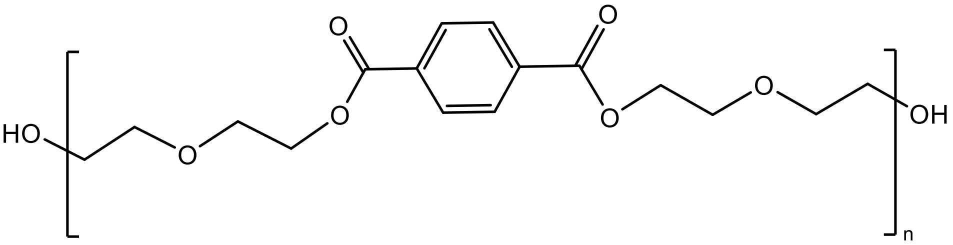


Figure 4.11: oligomer supposed

4.2.2 Glycerol (GLY)

ATR-FTIR analysis was performed on the sample, in order to determine the structure of the molecule. The results are shown in Figure 4.12.

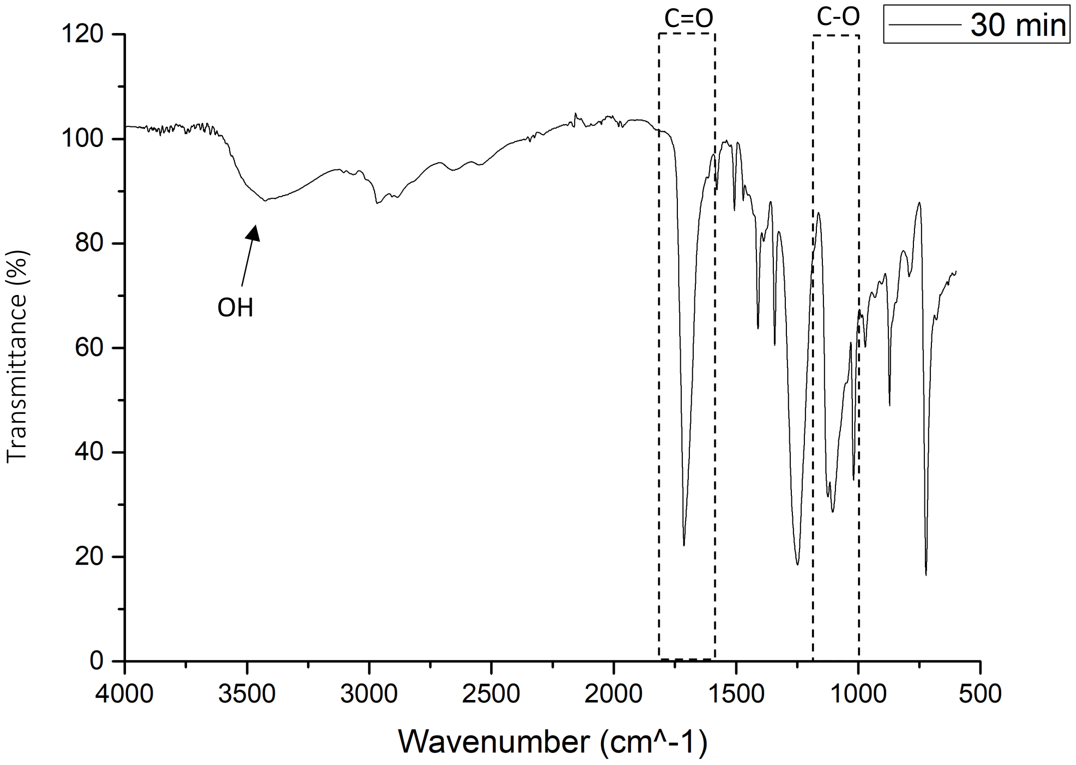


Figure 4.12: ATR-FTIR analysis on PET 1:5 GLY sample

As we can see from Figure 4.12 the recorded spectrum of the PET 1:10 GLY sample differs for the -OH broad peaks at around 3500 cm^{-1} if compared with the neat PET spectrum (Figure 4.1) which does not show a peak in correspondence of this wavenumber. This is due to the longer carbon chains that make the ending groups difficult to be detected. All of the spectra show the typical peaks of C=O vibration at 1723 cm^{-1} and C-O vibration at around 1094 cm^{-1}. The peak at 1243 cm^{-1} proves the presence of the terephthalate group [33].

The time was not sufficient to complete the whole interpretation of the NMR spectra, which is why they are not reported in this thesis.

It was difficult to determine a structure for this oligomer, due to the fact that Glycerol has three end groups. The time was not sufficient to perform deeper analysis on these samples.

4.2.3 Water (H_2O)

ATR-FTIR analysis was performed on the samples, in order to determine the structure of the molecule. The results are shown in Figure 4.13.

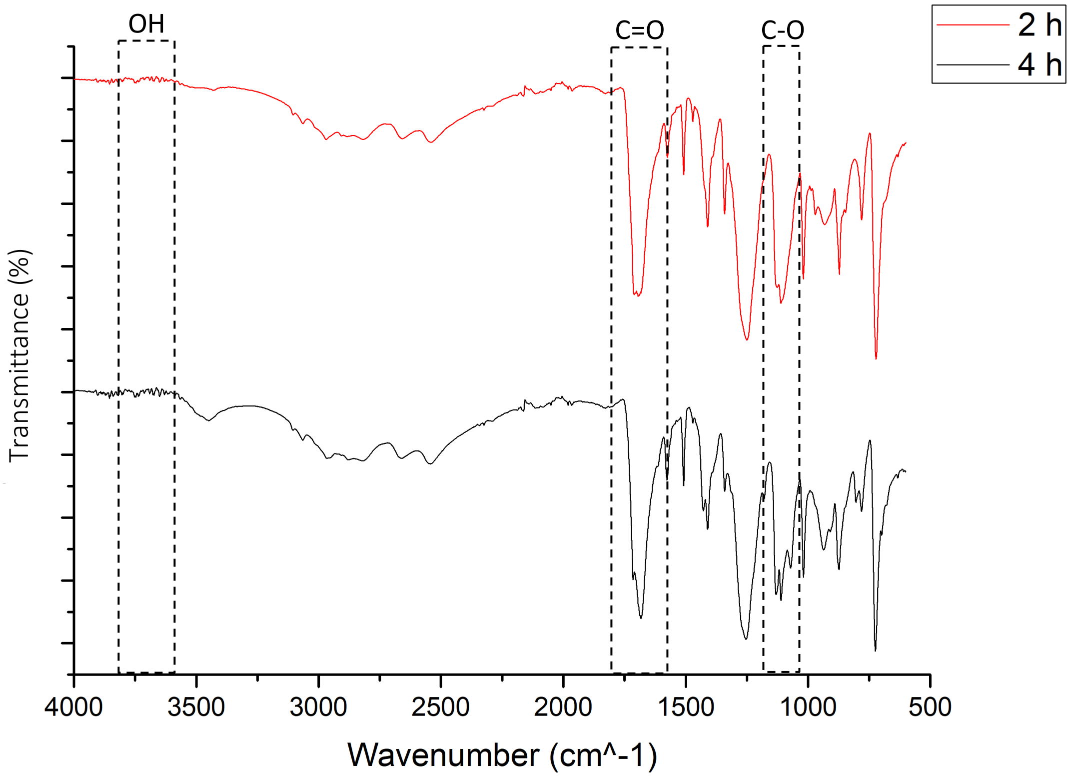


Figure 4.13: ATR-FTIR analysis on PET 1:10 H_2O samples

As we can see from Figure 4.13, the recorded spectrum of the PET 1:10 H_2O does not show an -OH broad peak at around 3500 cm^{-1}. This is due to the longer carbon chains that make the ending groups difficult to be detected. All of the spectra show the typical peaks of C=O vibration at 1723 cm^{-1} and C-O vibration at around 1094 cm^{-1}. The peak at 1243 cm^{-1} proves the presence of the terephthalate group [33]. This means that the depolymerization did not work properly.

The time was not sufficient to complete the whole interpretation of the NMR spectra, which is why they are not reported in this thesis.

4.2.4 Ethanolamine (EA)

H-NMR analysis was performed on the samples, in order to determine the structure of the molecule. The solvent for NMR analysis was Dimethylsulfoxide (DMSO).

The results are shown in Figure 4.14.

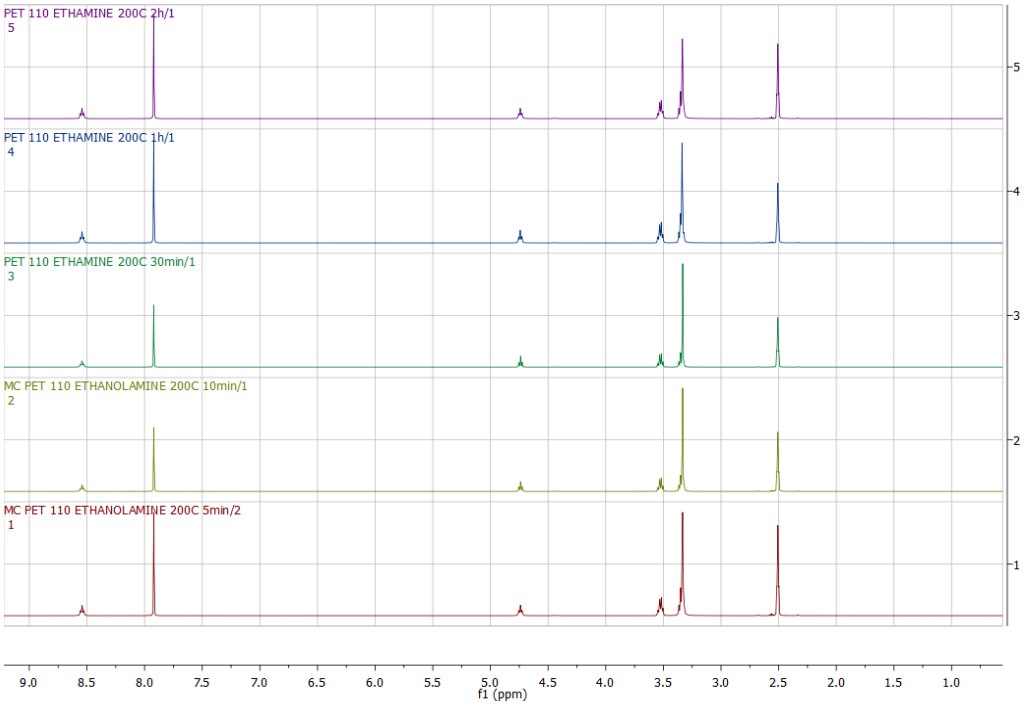


Figure 4.14: H-NMR analysis on PET 1:10 EA samples

The peaks can be found in the same position in each sample. The analysed spectrum is shown in Figure 4.15.

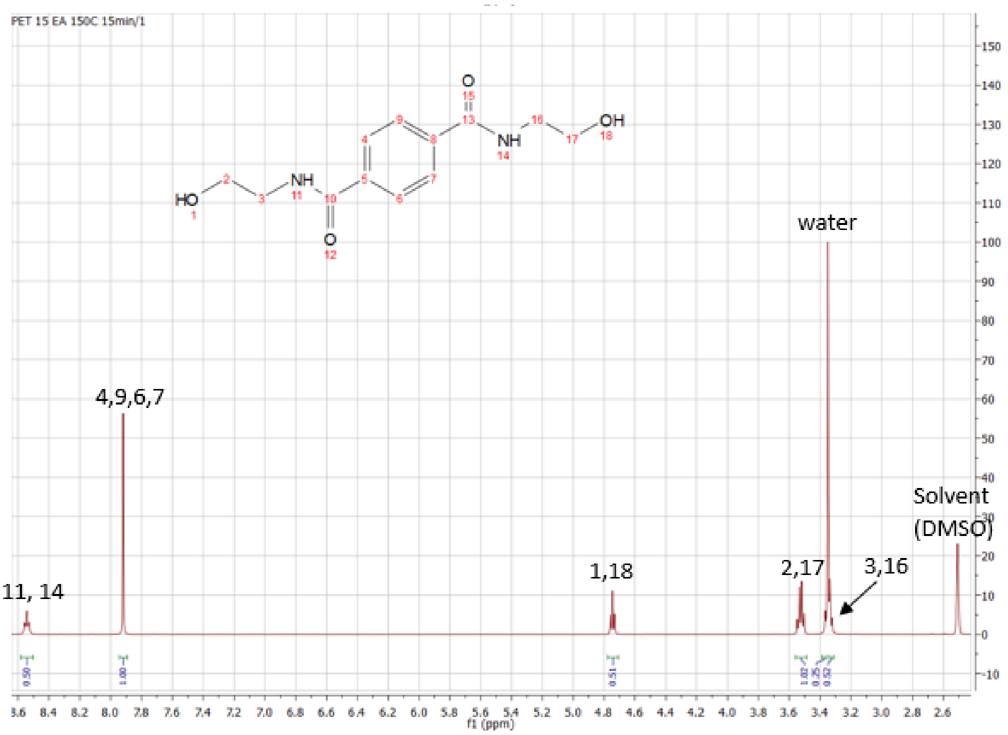


Figure 4.15: H-NMR spectrum on PET 1:10 EA sample

The structure identified is confirmed by the C-NMR analysis shown in Figure 4.16.

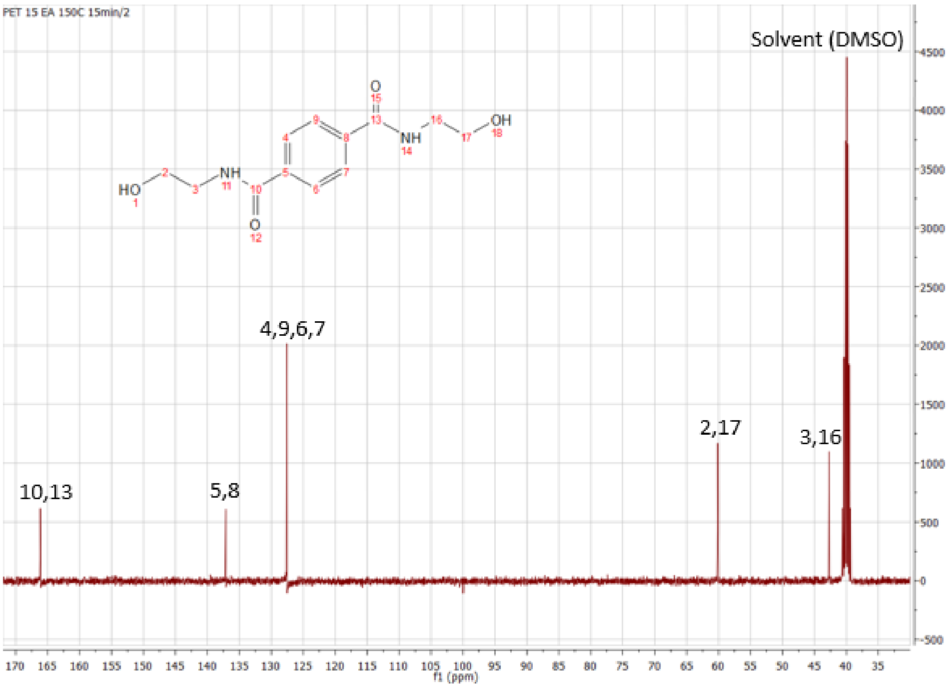


Figure 4.16: C-NMR spectrum on PET 1:5 EA sample

ATR-FTIR analysis was performed on the samples, in order to determine the structure of the molecule. The results are shown in Figure 4.17.

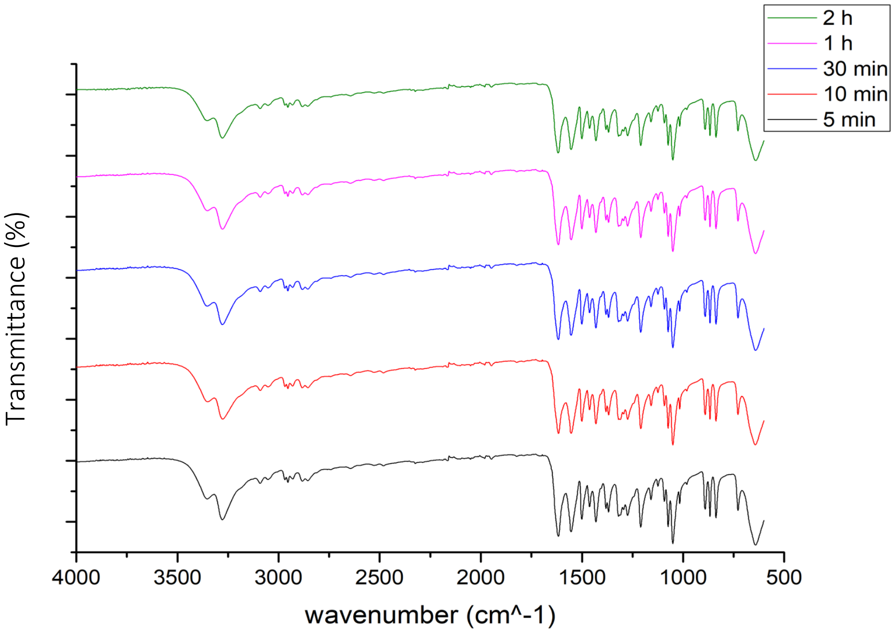


Figure 4.17: ATR-FTIR analysis on PET 1:5 EA sample

The peaks can be found in the same position in each sample. The analysed spectrum is shown in Figure 4.18.

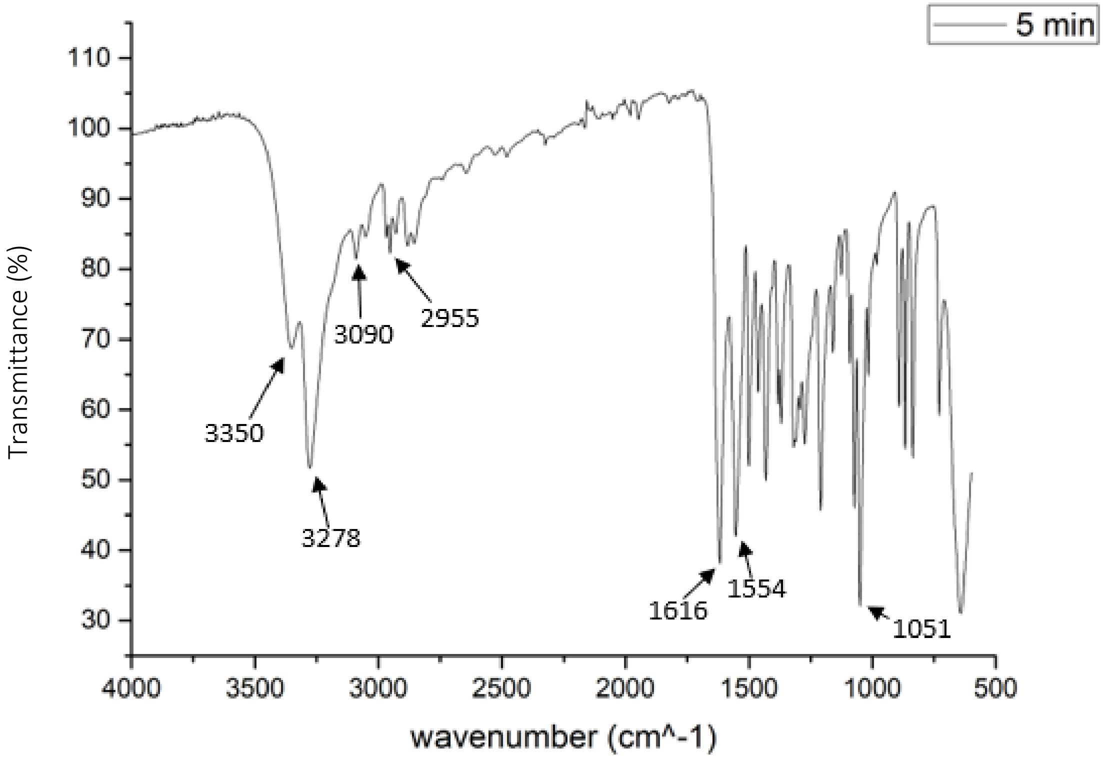


Figure 4.18: ATR-FTIR spectrum on PET 1:10 EA sample

The main groups characterized by the wavenumbers in the spectrum are summarized in Table 4.4.

ABSORPTION PEAK [cm^{-1}]	GROUP
1051	O-H
1554	Secondary amide stretching
1616	Aromatic amide stretching [3]
2955	CH_2-CH_2 stretching
3090	Aromatic amide stretching [3]
3278	O-H
3350	Secondary amide stretching

Table 4.4: Absorption peaks of the main functional groups

The results are consistent with the oligomer structure that is reported in Figure 4.19.

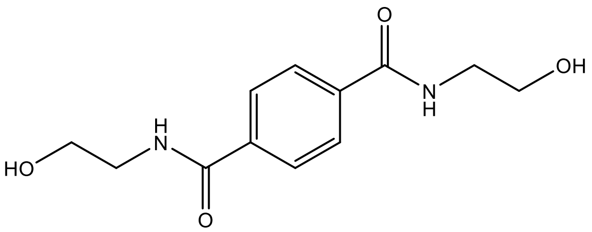


Figure 4.19: monomer supposed

4.3 Functionalized oligomers characterization

4.3.1 Ethylene Glycole

H-NMR analysis was performed on the samples, in order to determine the structure of the molecule. The solvent for NMR analysis was Deuterated chloroform ($CDCl_3$).
The results are shown in Figure 4.20.

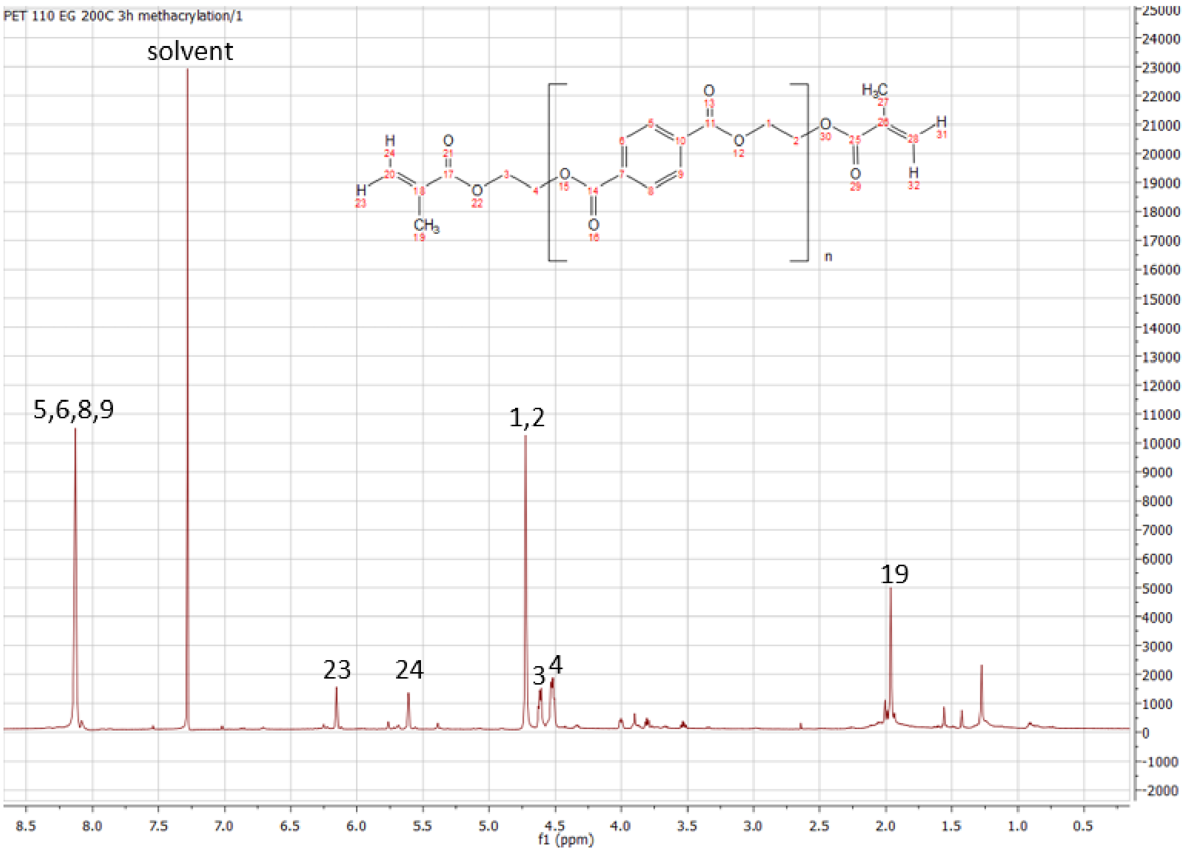


Figure 4.20: H-NMR spectrum of PET 1:10 EG after functionalized sample

The methacrylic group appeared in δ 6.11, 5.56 and 1.95.

It can be noted the presence of an impurity at δ=1.27 in the functionalized material.

ATR-FTIR analysis was performed on the samples, in order to determine the structure of the molecule. The results are shown in Figure 4.21.

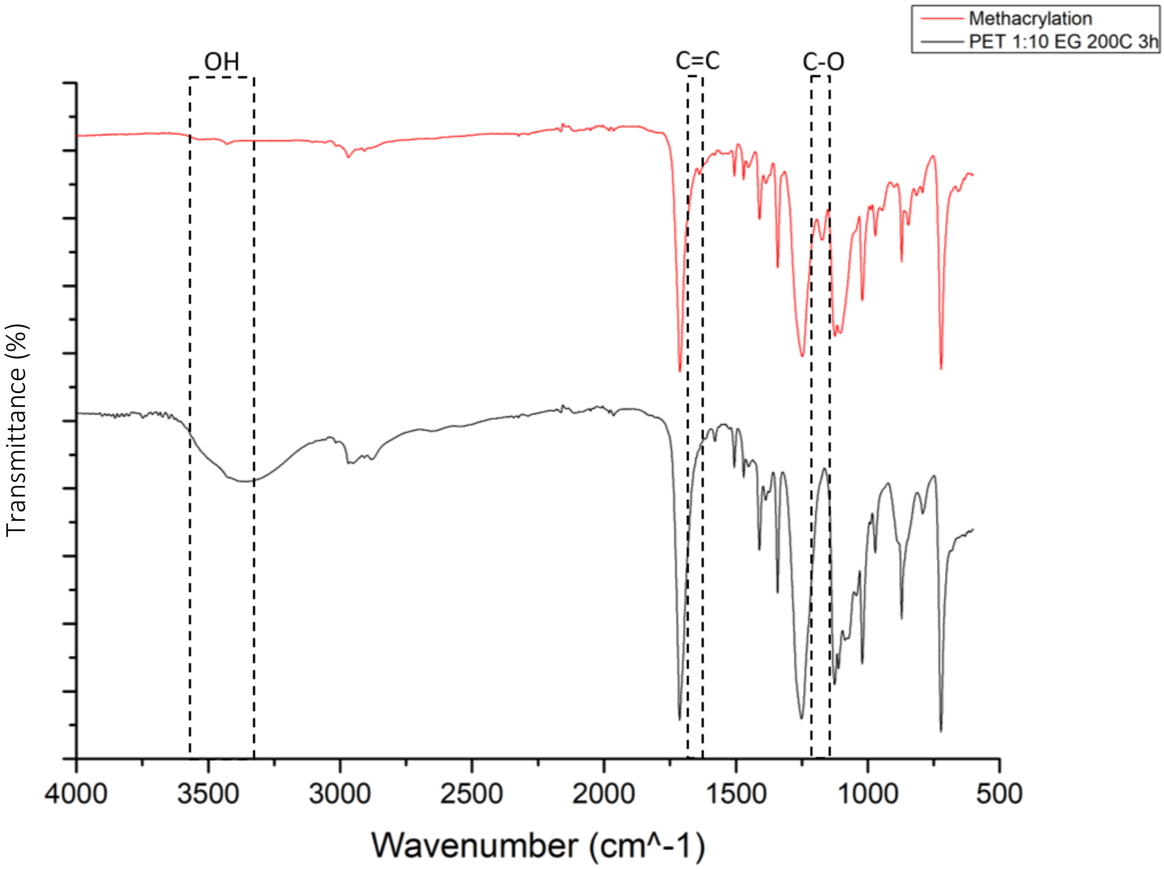


Figure 4.21: ATR-FTIR spectra of PET 1:10 EG before and after methacrylation

The success of the reaction was confirmed both by the presence of C=C stretching peak at 1637 cm^{-1}, by the C-O stretching peak at 1173 cm^{-1} and by the disappearance of the OH vibrational peak at around 3500 cm^{-1}. These results are summarized in Table 4.5.

ABSORPTION PEAK [cm^{-1}]	GROUP
3500	OH stretching
1637	C=C stretching
1173	C-O stretching

Table 4.5: Absorption peaks of the main functional groups

4.3.2 Ethanolamine

H-NMR analysis was performed on the samples, in order to determine the structure of the molecule. The solvent for NMR analysis was Dimethyl sulfoxide (DMSO).
The results are shown in Figure 4.22.

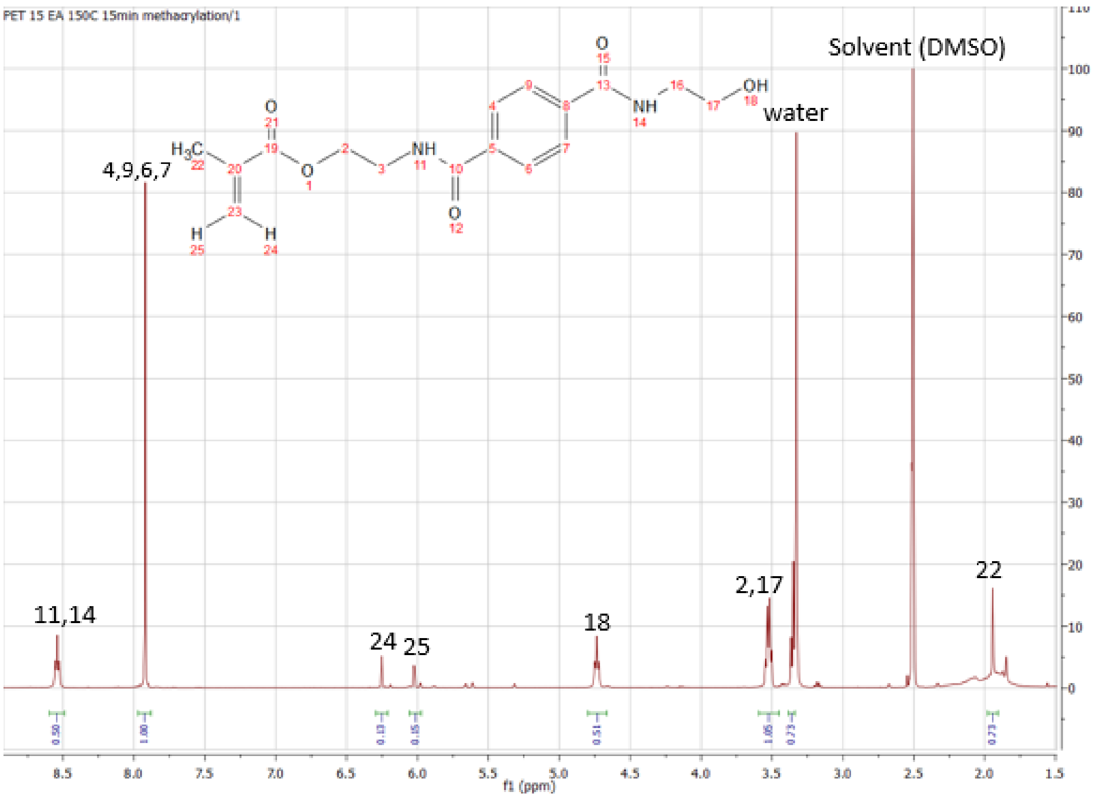


Figure 4.22: H-NMR spectrum of PET 1:5 EA after functionalized sample

The methacrylic group appeared in δ 6.11, 5.56 and 1.95.

It can be noted that in this case the functionalization reaction was less effective compared to the previous case: indeed, here it is still visible the -OH group peak in δ 4.73 that proves that methacrylation did not occur on both terminal groups.

The same results were obtained from the ATR-FTIR analysis shown in Figure 4.23 and Table 4.6.
From the comparison between the degradation product with EA before and after the functionalization reaction, the reduction of the peak of the -OH group around 3500 cm^{-1} is evident.
This peak, however, does not disappear, a symptom of an incomplete functionalization on both terminal groups.
The success of the reaction on some of the terminal groups was confirmed by both the presence of C=O stretching peak at 1754 cm^{-1} and 1801 cm^{-1} and by the C-O stretching peak at 1015 cm^{-1}. A small peak at 956 cm^{-1} also appeared, corresponding to the $C=CH_2$ vibration.

ABSORPTION PEAK [cm^{-1}]	GROUP
956	C=CH$_2$ vibration
1015	C-O stretching
1754	C=O stretching
1801	C=O stretching

Table 4.6: Absorption peaks of the main functional groups

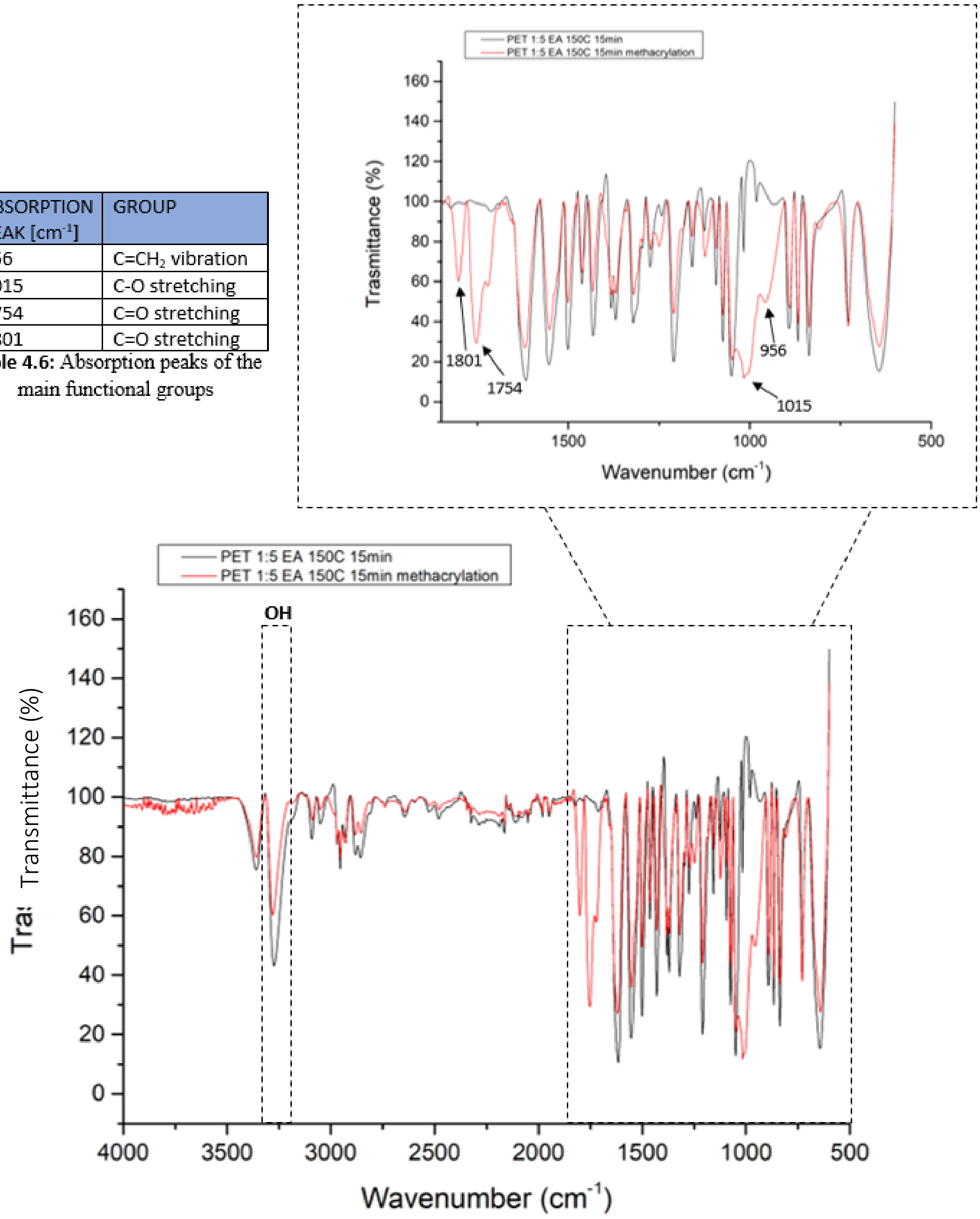


Figure 4.23: FTIR spectrum comparison between the PET 1:5 EA and the product obtained after the methacrylation reaction

4.4 Curing

As already described in Chapter 2, curing was performed on the methacrylated PET 1:10 EG 200°C 3h, in order to transform the liquid functionalized product into a solid three-dimensional network in which polymer chains cross-link and form a rigid material.

Both UV-curing and thermal curing were tested on the sample.

4.4.1 UV-curing

After the dissolution of the degradation product in chloroform, the solution was mixed with 50 wt% of Polyethylene Glycol dimethacrylate.

Later, 2% of photoinitiator Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) was added while stirring in dark conditions for 3 minutes. The solution was then poured in a Petri glass and irradiated for 15 min using a UV-lamp with a power of 36W.

The result of the UV-curing is shown in Figure 4.

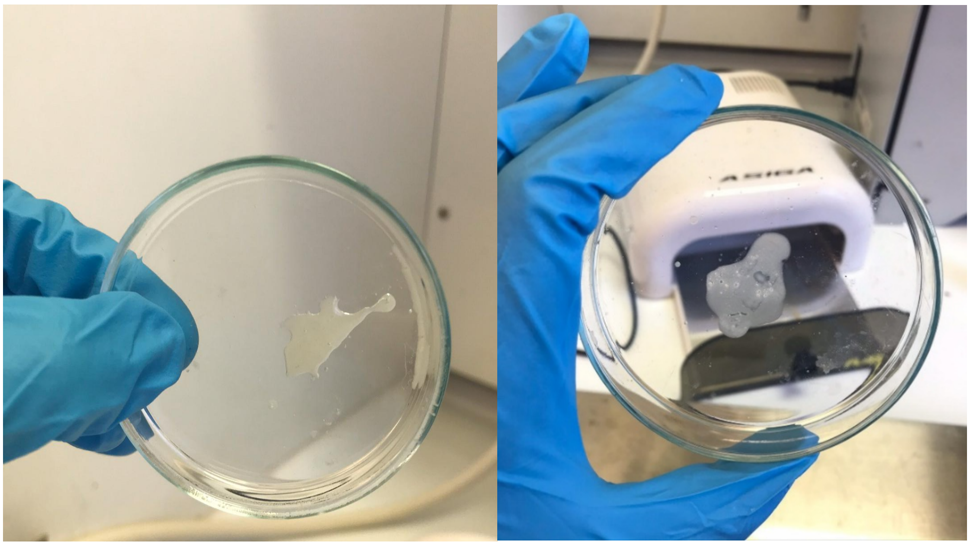


Figure 4: UV-curing of PET 1:10 EG degradation product

The cross-linking of the polymer solution can be clearly observed.
The time was not enough to perform any kind of analysis on this product.

4.4.2 Thermal curing

After the dissolution of the degradation product in chloroform, the solution was mixed with 92 wt% of Polyethylene Glycol dimethacrylate and with 3 wt% of BPO (Benzoyl peroxide) initiator. The solution was then poured in small circular moulds and put under Nitrogen flux in a desiccator at 90°C for 2 hours. Subsequently the temperature was increased to 120°C for 2 more hours.

The results are shown in Figure 4.

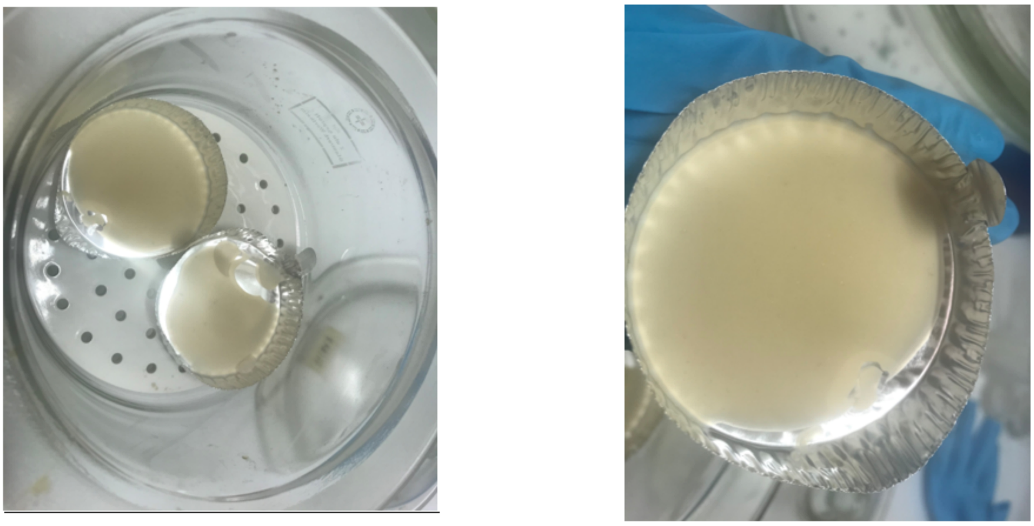


Figure 4: thermal curing of PET 1:10 EG degradation product

The cross-linking of the polymer solution can be clearly observed. The product had a fragile consistency.

The time was not enough to perform any kind of analysis on this product.

5. Conclusion and future works

In this study, the degradation of Polyethylene Terephthalate (PET) was performed, testing different reagents and finding super effective depolymerization reactions always under microwave irradiation.

Reactions with ethanolamine, in particular, brought us to a very efficient degradation even after 5 minutes only. The reactions with ethylene glycol revealed to be interesting, even if they have longer reaction time. That is why they were chosen for the functionalization reaction with methacrylic anhydride that was achieved successfully.
The main problem with these methacrylated products was finding a suitable solvent able to dissolve them properly. The ones found were toxic or too hard to be removed from the solution.
A purpose for the future could be testing more solvents, in order to find the one that is able to dissolve the products in shorter times and that is easy to remove avoiding toxicity problems.
The curable products obtained seemed to work but with a too low amount of functionalized degradation product inside that was caused by the low availability of it.
A purpose for future works is the optimization of the process in order to decrease the reaction time for energy recovery and the use of different operative conditions able to provide a higher quantity of product.

More complex issues were faced with the degradation reaction with water only, that lead us to discharge the samples. A purpose for future works is to use some kind of catalyst for this hydrolysis reactions, in order to favour the degradation into the microwave.

Glycerol also revealed to be problematic because of its three terminal groups that let difficult the interpretation of the spectra of the degradation products. A purpose for future works is to complete the interpretation of the degradation products spectra in order to understand if they are suitable for the functionalization and consequently for the curing.

Both UV-curing and thermal curing gave good results. A purpose for future works is to carry out more analysis on the cured samples in order to understand if they are suitable for 3D-printing applications.

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Acknowledgements

First, I would like to thank my Relator Marco Sangermano for the great opportunity that he gave me with this project. He really captured me with his enthusiasm and with his ability to create a real partnership with his students. It was an honour and a pleasure to work with him.

I would like to extend my sincere gratitude to Minna Hakkarainen and Eva Bäckström for their patience and assistance during all my period at KTH. I feel honoured to have been given the chance to work with them.

I would like to thank all the Department of Fiber and Polymer Technology of KTH for helping me during my project, especially Karin for always making me feel comfortable there.

I would like to thank my mother Gilda who has always believed in me since I was a little girl. I would never be here without her. She taught me how to be a strong person and how to face any hard times.

I would like to thank my sister Petra who has always inspired me in doing my best and in reaching my goals. In every period of her life she has always found time for giving me the best advice and for helping me with my choices.

I would like to thank my father Paolo for his capacity of making jokes even in the worst situations, helping me to go beyond stressing moments with a laugh. And I would like to thank him also for his delicious spaghetti.

I would like to thank my boyfriend Alessio. With his personal support I grew a lot, evolving from a girl to a woman. Everything was better if shared with him.

I would like to give a special thanks to Camilla for being the best office mate ever and for all the help that she gave me. I feel very lucky to have met this girl during this experience.

I would like to thank my Stockholm flatmates Eva and Virginie for all their support and guidance during these months.

Last but not least, I would like to thank all my friends in Udine, Trieste and Turin. I thank them for helping me getting through all the stress of these last two years. They helped me in not giving up, even if we were far from each other. Sharing with them this period of my life has been the best part of this life trip.

Finally, I want to make a reflection on the Covid-19 pandemic that is involving my country, Italy. I had imagined this conclusion of my course of study after five years of hard sacrifices and efforts in a completely different way. What has been going on in these weeks is almost surreal and I can't wait for the Italians to win this fight against Coronavirus. Because we will win, everything will be fine. For this I wanted to thank the government currently in office for how it is managing the situation: if I succeed to complete this work, it is also thanks to how Prime Minister Giuseppe Conte is managing the situation.

Let’s be strong for our country: we are far from each other today to embrace each other with greater joy tomorrow.