Chemical Recycling of bio-based and conventional polymers in the circular economy

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Research on polymer recycling at the lab of polymer chemistry and technology, Department of Chemistry, Aristotle University of Thessaloniki

- In our laboratory we have published research works on
- Chemical recycling of PET (hydrolysis, glycolysis, etc.)
- Thermochemical recycling by pyrolysis of polyolefins, PE, PP
- Thermochemical recycling with pyrolysis of PC
- Chemical recycling of PLA
- Use of microwave irradiation in the chemical recycling of polymers
- Limited works on solvent-based recycling

Necessity for plastics recycling

- The increase in plastics consumption led to increased amounts of plastic materials in the final recipients.

As much as 8.8 million metric tons of plastic trash is washed into oceans each year.

Small service life (approximately 40% have service life less than one month).

- Low biodegradation rates

It should be pointed out, that most plastics are non-toxic materials and do not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream and its high resistance to atmospheric and biological agents, they are seen as noxious materials.

The recycling of plastics do not only serve as a partial solution to the solid waste problem but also contributes to the conservation of raw petrochemical products and energy.

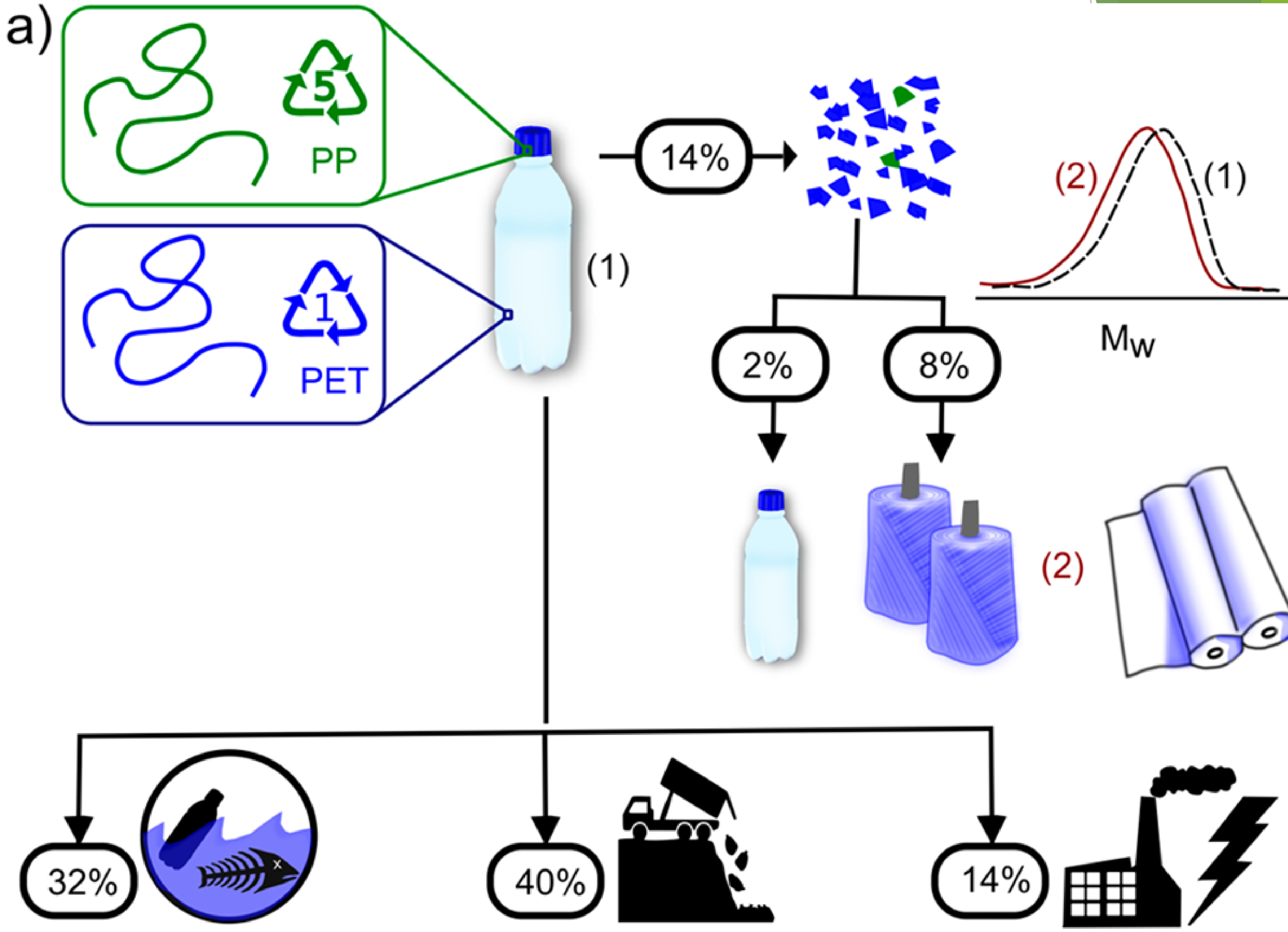
Key points in plastics recycling

- Constant feed
- Collection preferably in separate bins
- Adequate Sorting.
- Choose of a recycling method which should be environmentally friendly with economic benefits
- Applications of the products obtained after recycling (competitive price, confidence in their use by the consumers).

Some problems in polymer recycling

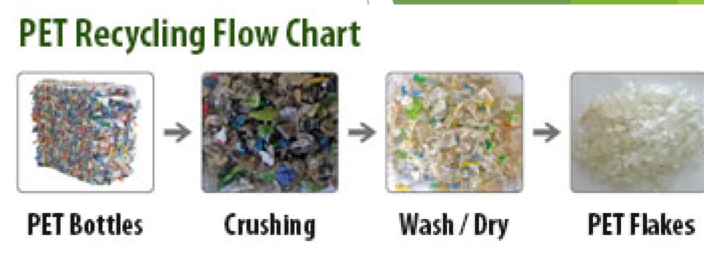
- **Different types of polymers with completely different properties** (PP has a melting temperature at 160 ^{o}C, whereas PET near 260 ^{o}C) .
- **Polymer mixtures** (blends, copolymers, composites, multilayer films).
- **Additives** (antioxidants, fillers, pigments, flame retardants, thermal stabilizers, UV stabilizers, etc.)
- **Admixtures from non-polymeric materials** (paper, glue, aluminum, food residues, etc).

Recycling of PET plastic bottles

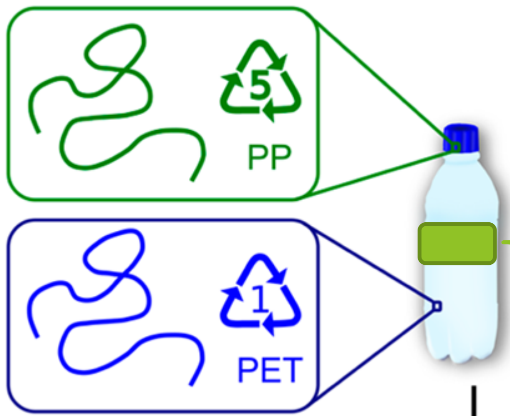


Deborah K. Schneiderman* and Marc A. Hillmyer, 50th Anniversary Perspective: There Is a Great Future in Sustainable Polymers, Macromolecules, 2018

PET bottle recycling
A common practice



Components of a PET plastic bottle



Label
(PE, PP)
Glue

Labels, caps
(PE, PP)

PET flakes

PET residue (frit)

Why mixtures of conventional with biodegradable polymers

- The increase in the production of plastics has resulted in large amounts of plastic wastes, creating a serious problem as far as their environmentally friendly disposal.
- Landfilling is not an adequate technique since most of the conventional plastics are non-biodegradable and accumulate in the final recipients for many years.
- Therefore, alternative materials were sought having similar properties though more environmentally friendly. This need gave birth to the production of biodegradable polymers used in the production of biodegradable plastics
- In 2019, the global production of bioplastics, was 2.11 million tons. Compared to the total production of plastics, i.e. 368 million tons in the same year, it can be postulated that the current production of bio-based plastics is still rather small, almost 1%

Definition of the word ‘bio’

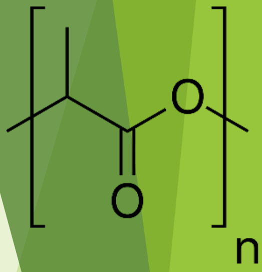
- According to *European Bioplastics,* bioplastics are those plastic materials that are biobased, biodegradable or both
- The term biobased refers only to the origin of the feedstock, i.e. the source from which the monomer(s) is produced, namely biomass. Thus, the biobased origin does not necessarily determine possible biodegradable properties. These are mainly dictated by the chemical structure of the polymer itself
- Poly(ethylene furanoate), PEF is a biobased polymer though not biodegradable.
- In contrast, petroleum-based polymers, such as polycaprolactone (PCL) are biodegradable.
- The degradation of a polymer is defined as the chain scission that a polymer undergoes resulting in a decrease of molar mass.

Definition of the word ‘bio’

- The term biodegradable polymer indicates that a material is able to be broken down into carbon dioxide, water, and biomass by the natural action of microorganisms.
- However, the term by itself does not define how quickly this process will occur, or a specific set of conditions that are required.
- Therefore, in several polymers it is advisable to use the term compostable instead of biodegradable.
- ‘Compostable’, in the context of plastics, means biodegradation under aerobic conditions into carbon dioxide, water, and biomass within a specific time frame of 6–12 weeks and under specific, controlled conditions, which are specified by the corresponding standard references (ISO 17088, EN 13432/14 995 or ASTM 6400 or 6868) and certification.
- Currently, most of the plastics with the biodegradable tag cannot decompose in conditions found in the natural environment

Poly(lactic acid) PLA

- Among the so-called biodegradable polymers, being actually a bio-based and compostable polymer, poly(lactic acid), PLA has received extensive attention in the last 20 years both in academia and in the industry.
- The biodegradability of PLA depends on the environmental conditions. For example a PLA bottle may take a few years to decompose in a landfill as opposed to a few months in industrial compost at $60^{o}C$ in the presence of digestive microbes.
- PLA is one of the most promising materials for commercially replacing nondegradable polymers such as poly(ethylene terephthalate) (PET) and polystyrene (PS) mainly in food packaging.
- Due to similar applications and the lack of an appropriate collection infrastructure, post-consumer PLA waste often contaminates other plastic waste streams (especially PET); thereby, necessitating an additional supplementary effort using advanced sorting technologies in order to achieve a satisfactory reduction.
- This disturbs the recycling strategies that have been developed for PET and destabilizes the economic balance of this sector.
- It has been proposed that, even trace contamination of PLA (about 1000 ppm) in conventional PET waste streams renders them unsuitable for mechanical recycling as it causes noticeable hazing and degradation of recycled PET.
- In some cases, this problem has aggravated to an extent that some organizations (viz. NAPCOR) have refused to introduce PLA contaminated PET streams in their existing recycling infrastructure.



Existence of PLA together with PET

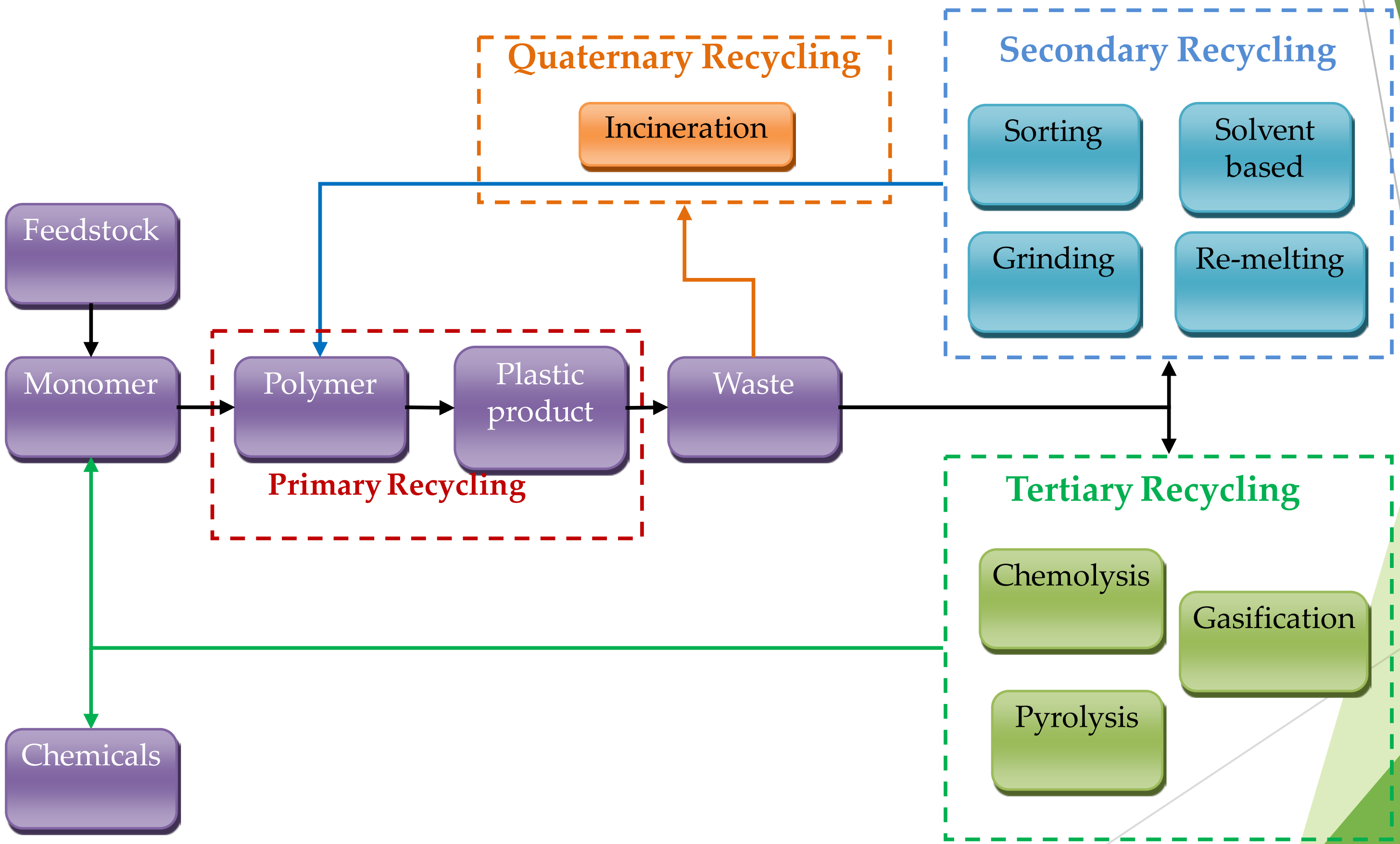
- The contamination of the PET waste stream by water bottles made of PLA has been pointed in literature and the existence of PLA as a contaminant was highlighted.
- Even if PLA was sorted using NIR spectroscopy an expensive investment is required which makes the process very costly.
- The difficulty of separating PLA from PET using differences in density and the sink-float method was also discussed since the density of PLA is similar to PET

	Density (kg/L)	Tg (°C)	Tm (°C)	Onset of degradation (°C)	Processing temperature
PET	1.35-1.39	69	255	410	270
PLA	1.20-1.45	45-60	155-165	320	180

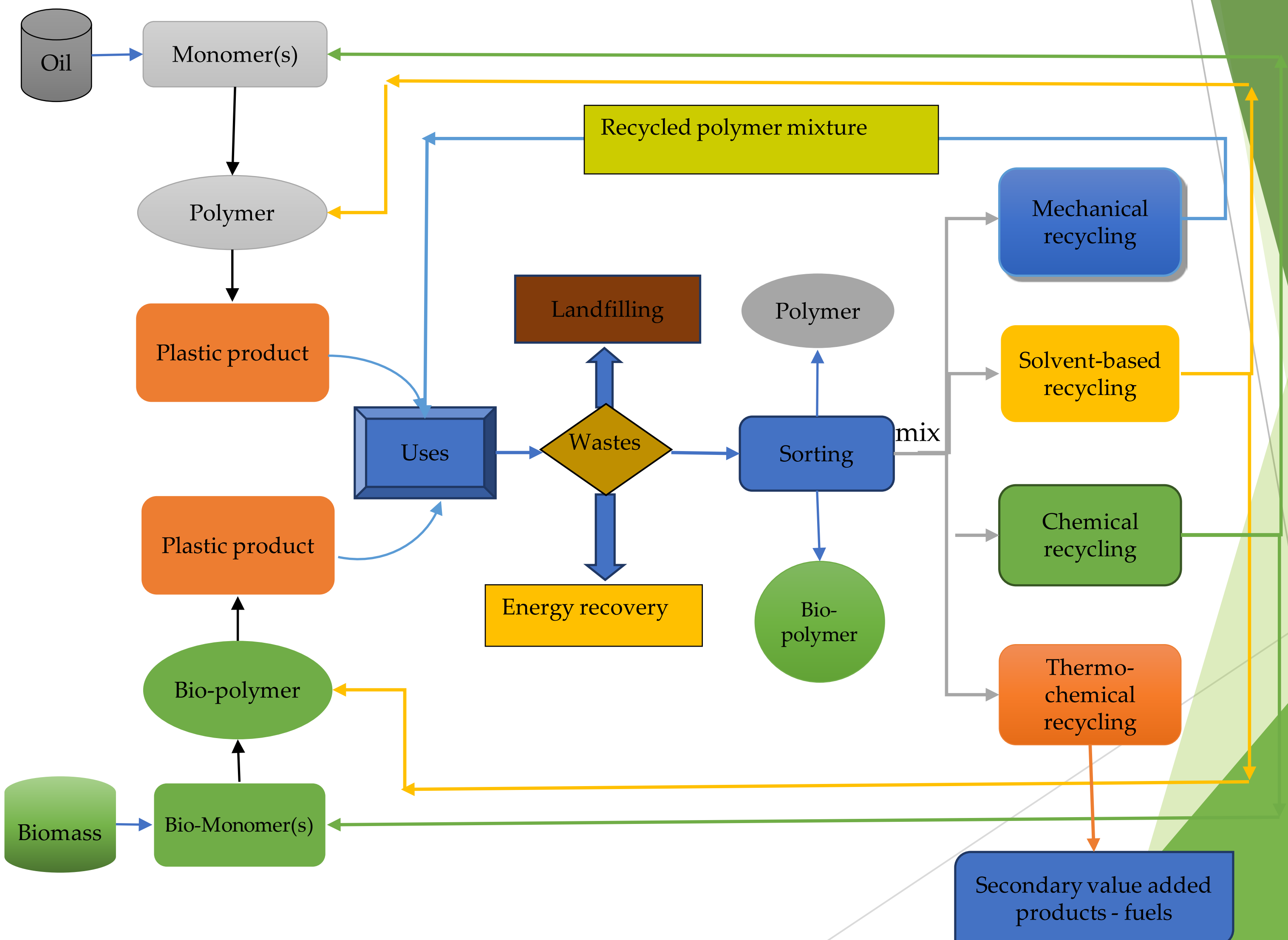
L. Alaerts, M. Augustinus, K. van Acker. Impact of Bio-based plastics on current recycling of plastics. Sustainability, 10 (2018), p. 1487. DOI: 10.3390/su10051487

- In 2015, the European Commission adopted the Circular Economy Action Plan which included goals to increase the recycling of the packaging waste and to reduce the landfill by 2030 and a more detailed strategy was laid on 2018
- However, what will be the impact of bioplastics in the recycling streams of conventional plastics is still under investigation.

Main recycling routes in plastic wastes

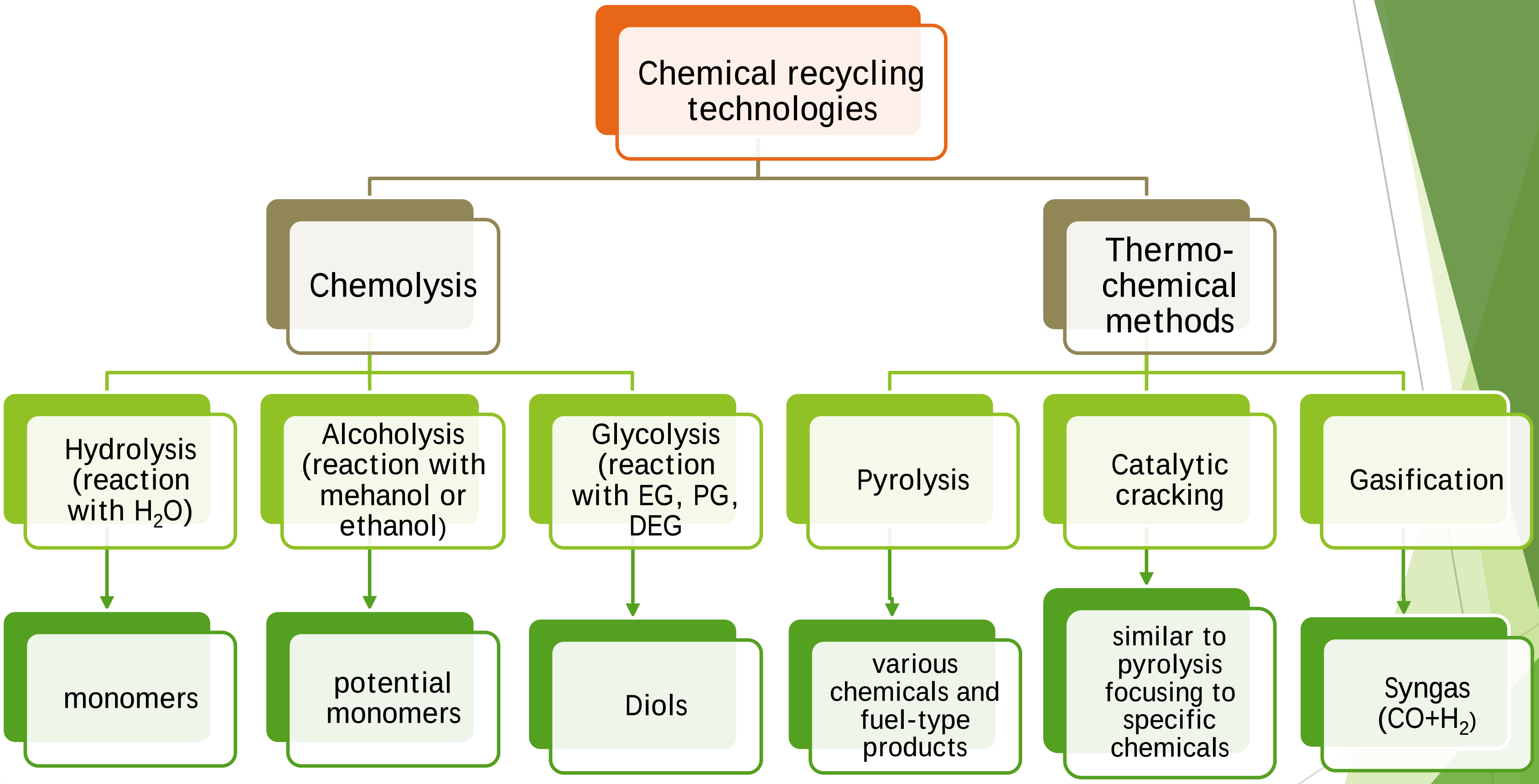


Recycling of petroleum-based plastics in the presence of bio-based plastics

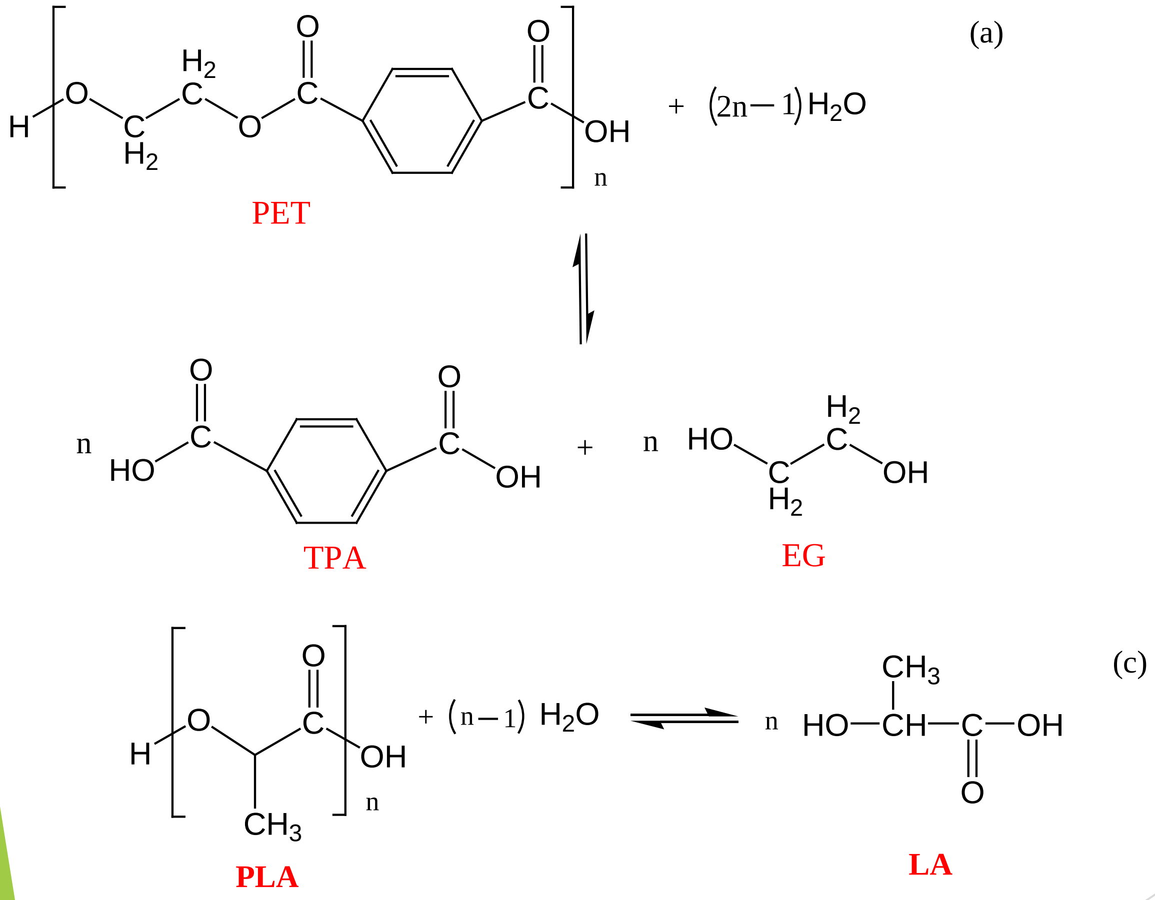


- In 2020, from the collected post-consumer plastic packaging (17.8 million tones), 42% was recycled 39.5% was used for energy recovery and 18.5 % was landfiled.
- Most of the waste was recycled mechanically, and only very limited volumes (less than 0.1 million tonnes) were treated by chemical recycling processes (PlasticEurope, 2019a; PlasticsEurope, 2020).
- To achieve the circular economy for plastics, zero landfilling is needed. Therefore, the amount of polymers recycled should be greatly increased

Chemical recycling methods

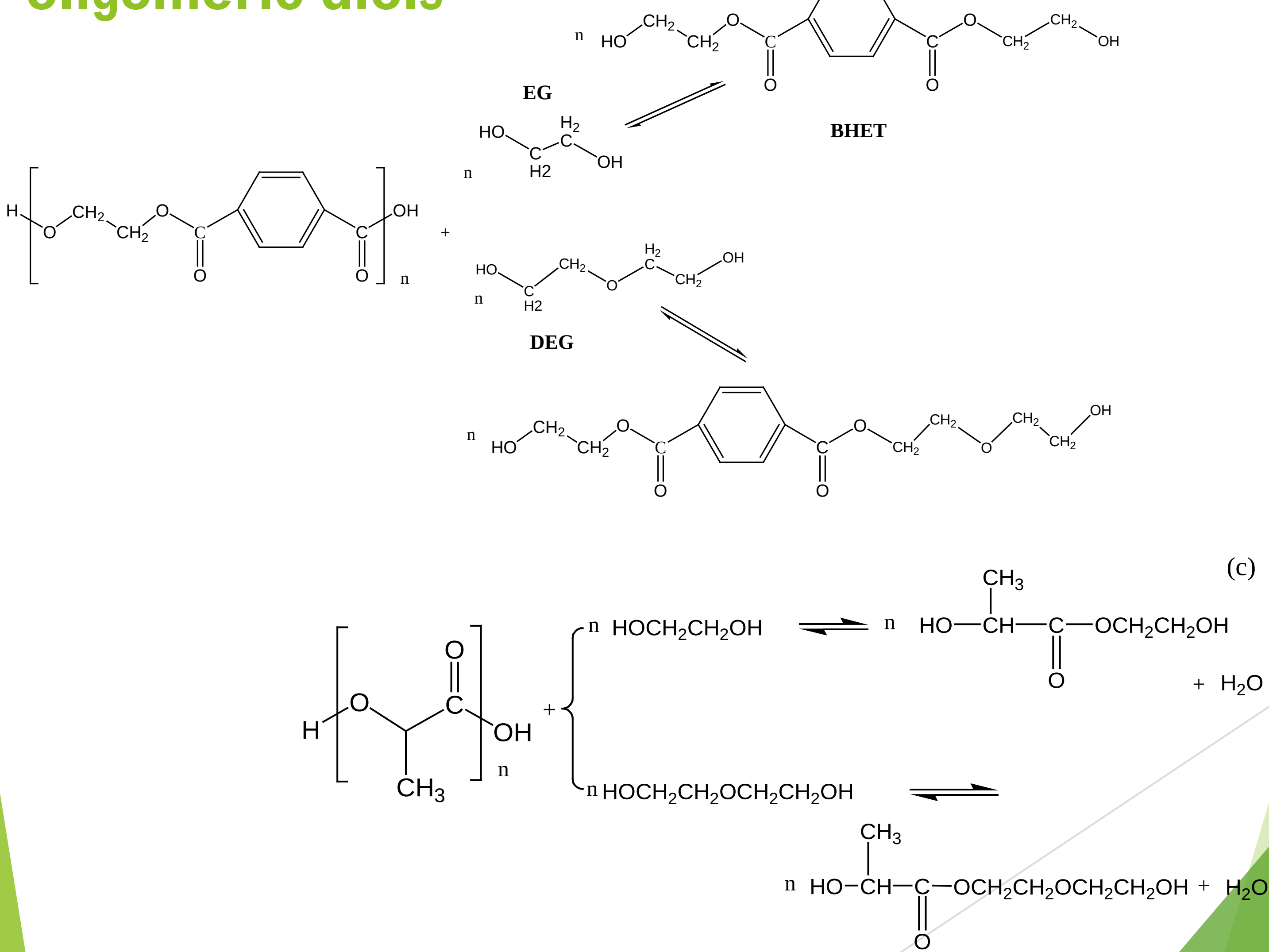


Overall chemical reactions taking place during neutral hydrolysis of PET (a), PLA (c)



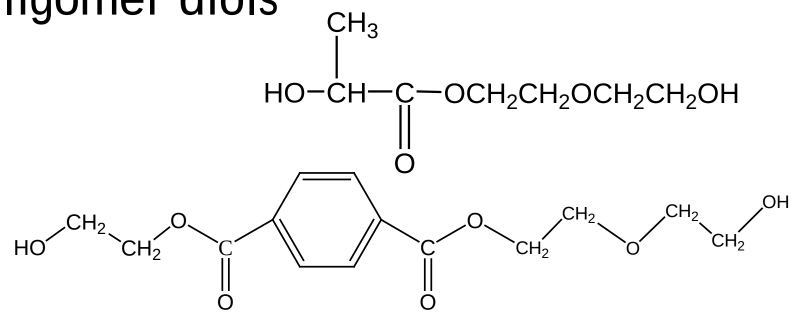
Overall chemical reactions taking place during glycolysis of PET and PLA with ethylene glycol or diethylene glycol to produce different oligomeric diols

(a)



Glycolysis of waste polyesters

Oligomer diols



Glycolysis

Waste
PET (and) PLA

Unsaturated Polyester resins
Alkyd resins

protective coatings with good weathering properties and important ingredients in many synthetic paints

Thermo-chemical polymer recycling techniques

Pyrolysis

- Production of monomers or other secondary value-added products
- Production of a liquid fraction with composition similar to liquid fuels

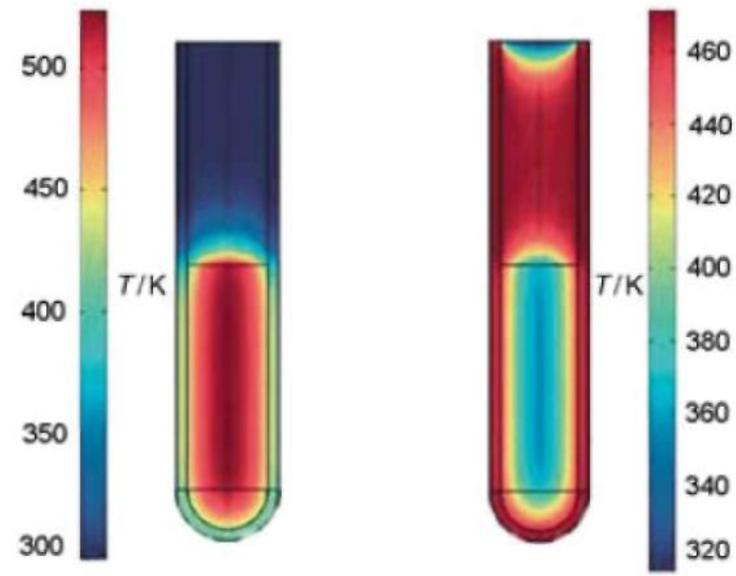
Use of Microwave irradiation

- Small degradation times
- Low consumption of energy

In accordance with the principles of sustainable development

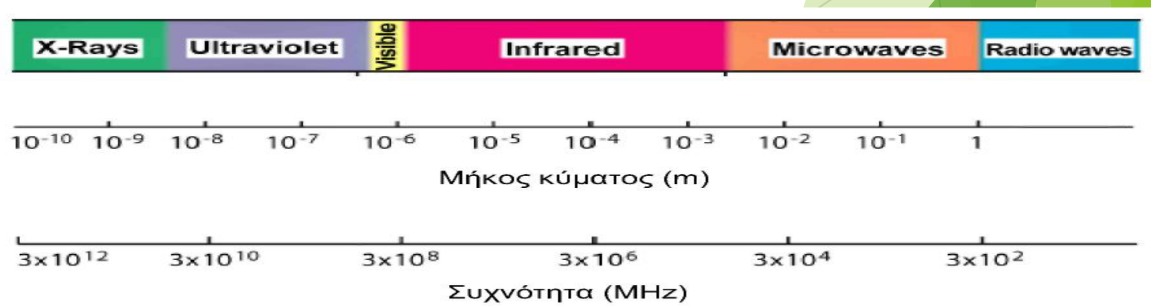
Microwave heating

- Heat transfer is taking place directly into the solution, since it has the ability to absorb the irradiated energy, through the vessel.
- Faster heating with no wasted energy
- It does not depend on factors such as the vessel thermal conductivity.
- The solution must have polar molecules

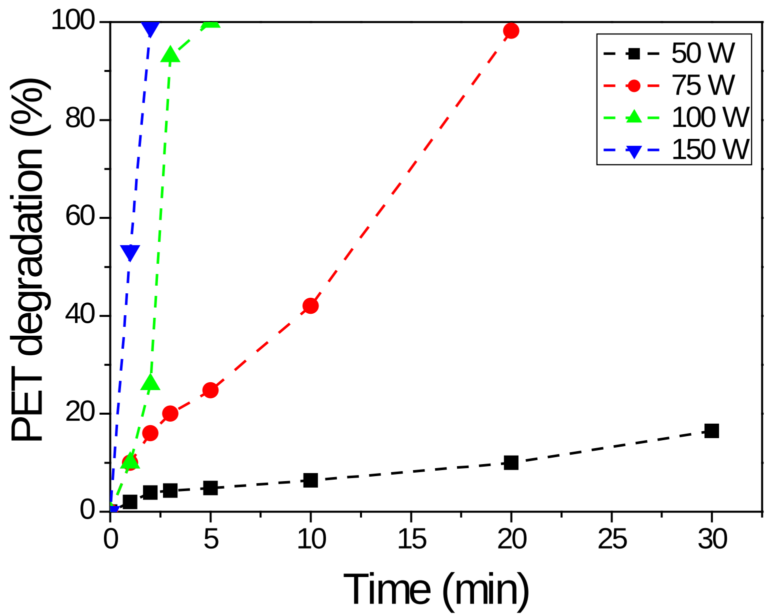


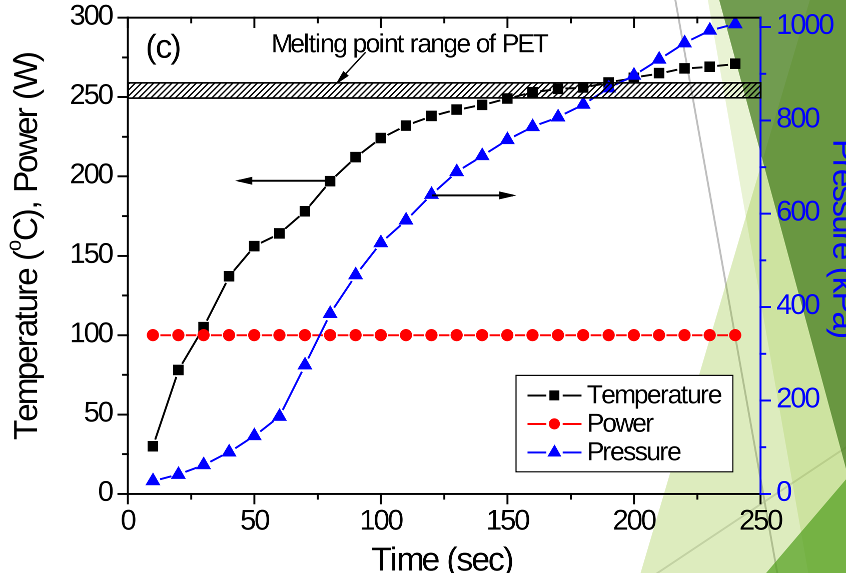
Microwave heating

Heating in an oil bath



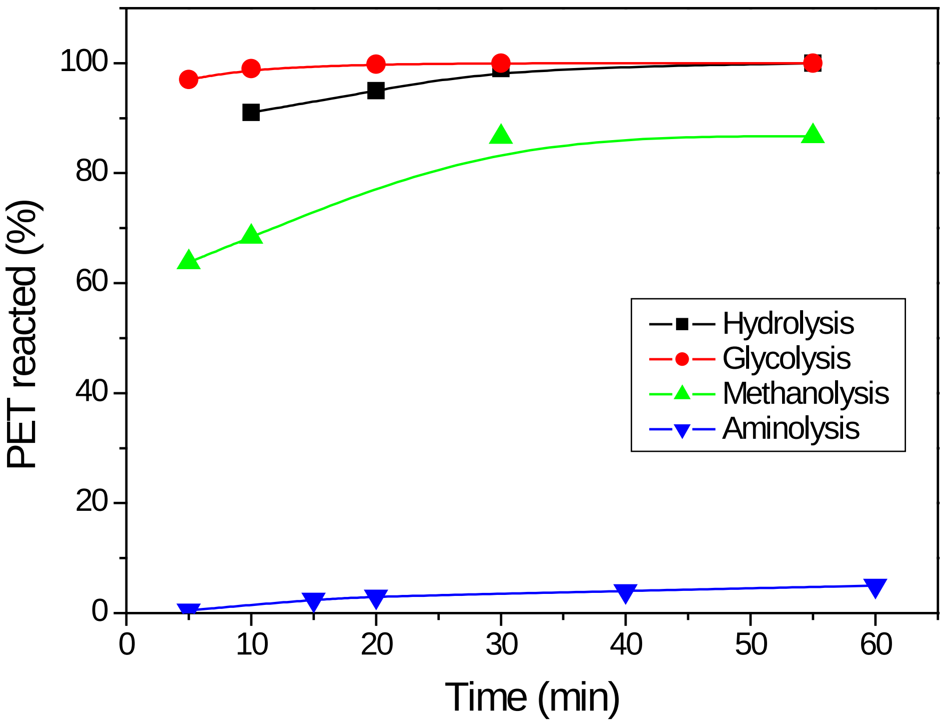
Alkaline hydrolysis of PET under microwave irradiation
Effect of microwave power





Effect of microwave power on the percentage of PET degradation with depolymerization time, during aminolysis of PET with ethanolamine under microwave irradiation. (from Achilias DS, Tsintzou GP, Nikolaidis AK, Bikiaris DN, Karayannidis GP (2011) Polym Int 60: 500–506

Variation of the amount of PET reacted with time during PET hydrolysis, glycolysis, aminolysis and methanolysis under microwave irradiation at 180 °C for 60 min.

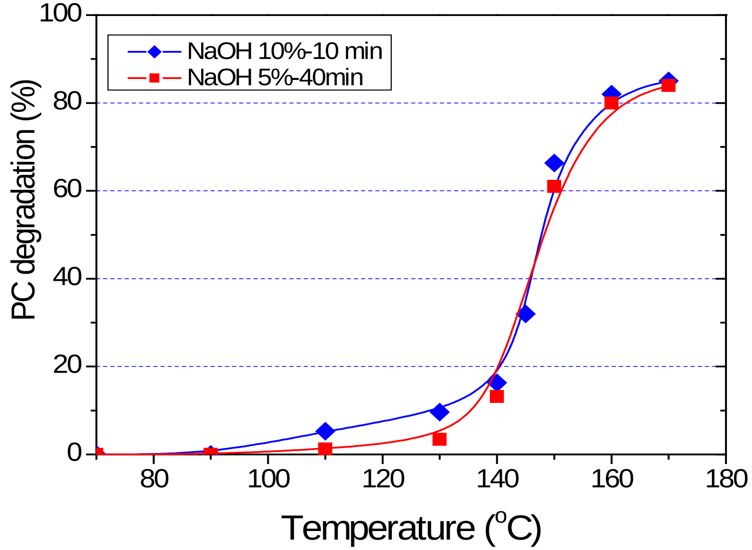


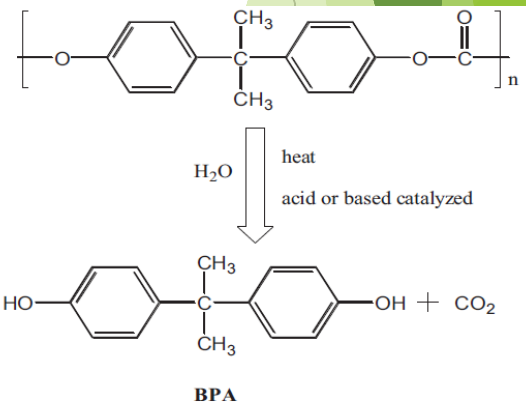
- **Project to Chemically Recycle PET Plastics Launched in Brussels**
- A new European project is to focus on the chemical recycling of PET with the aim of enabling de-polymerization at industrial scale based using a microwave-based process
- DEMETO, a new European project on the chemical recycling of PET has officially launched with the aim of enabling chemical de-polymerization of PET at industrial scale based on its microwave-based process intensification, focusing as a start on coloured bottles waste.
- The project has received funding from the European Union's Horizon 2020 research and innovation programme Oct 2017
- "DEMETO proposes the industrialisation and demonstration at full-scale of a new industrial process which allows to chemically recycle PET bottles, food containers and even textiles in a highly profitable and environmentally sustainable way," explained Maurizio Crippa, CEO of gr3n, during the event

Siddiqui MN, Achilias DS, Redhwi HH (2012) J Anal Appl Pyrol 98: 214–220

Microwave assisted recycling of Polycarbonate, PC

- Effect of depolymerization temperature on the amount of polycarbonate (PC) reacted during microwave-assisted PC alkaline hydrolysis after 40 min at 5% w/v NaOH, or **10 min** at 10% w/v NaOH

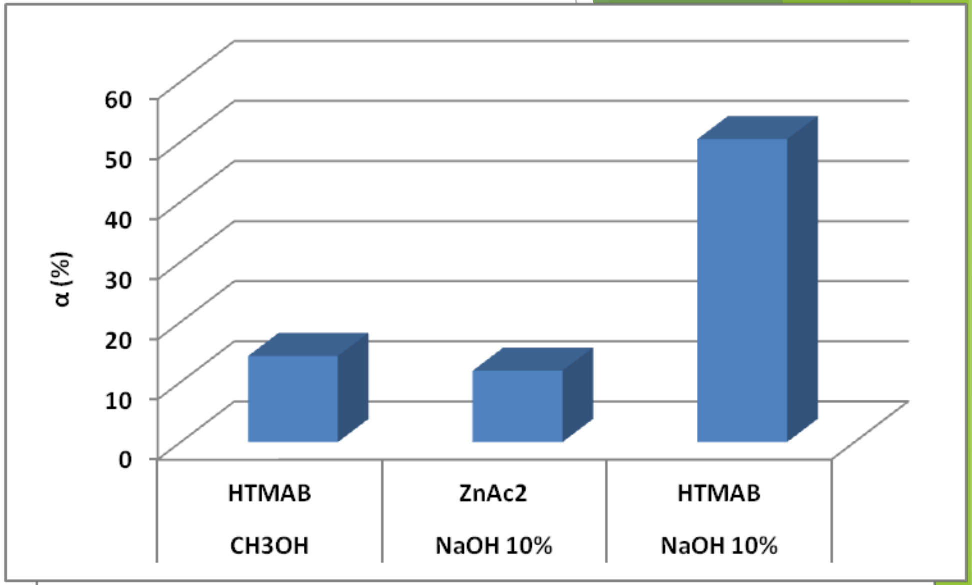




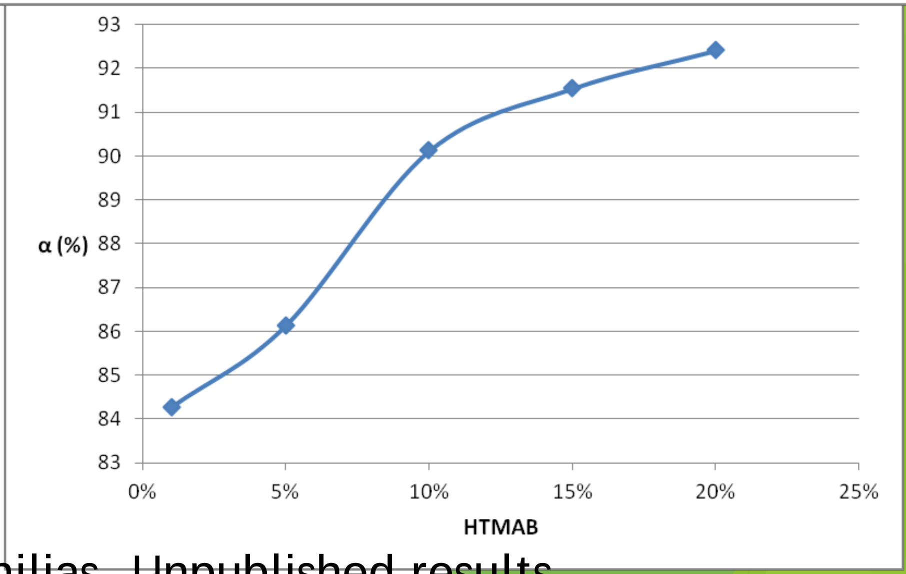
from Tsintzou GP, Antonakou EV, Achilias DS (2012) J Hazard Mater

Chemical recycling of PLA under microwave irradiation

- Irradiation time =10 min, Temperature =100 ^oC, microwave power p=100 W
- Alkaline hydrolysis in 10% NaOH, catalyst Hexyl trimethyl ammonium bromide 10%w/w
- Effect of solvent-catalyst



- Effect of the amount of the catalyst in alkaline hydrolysis

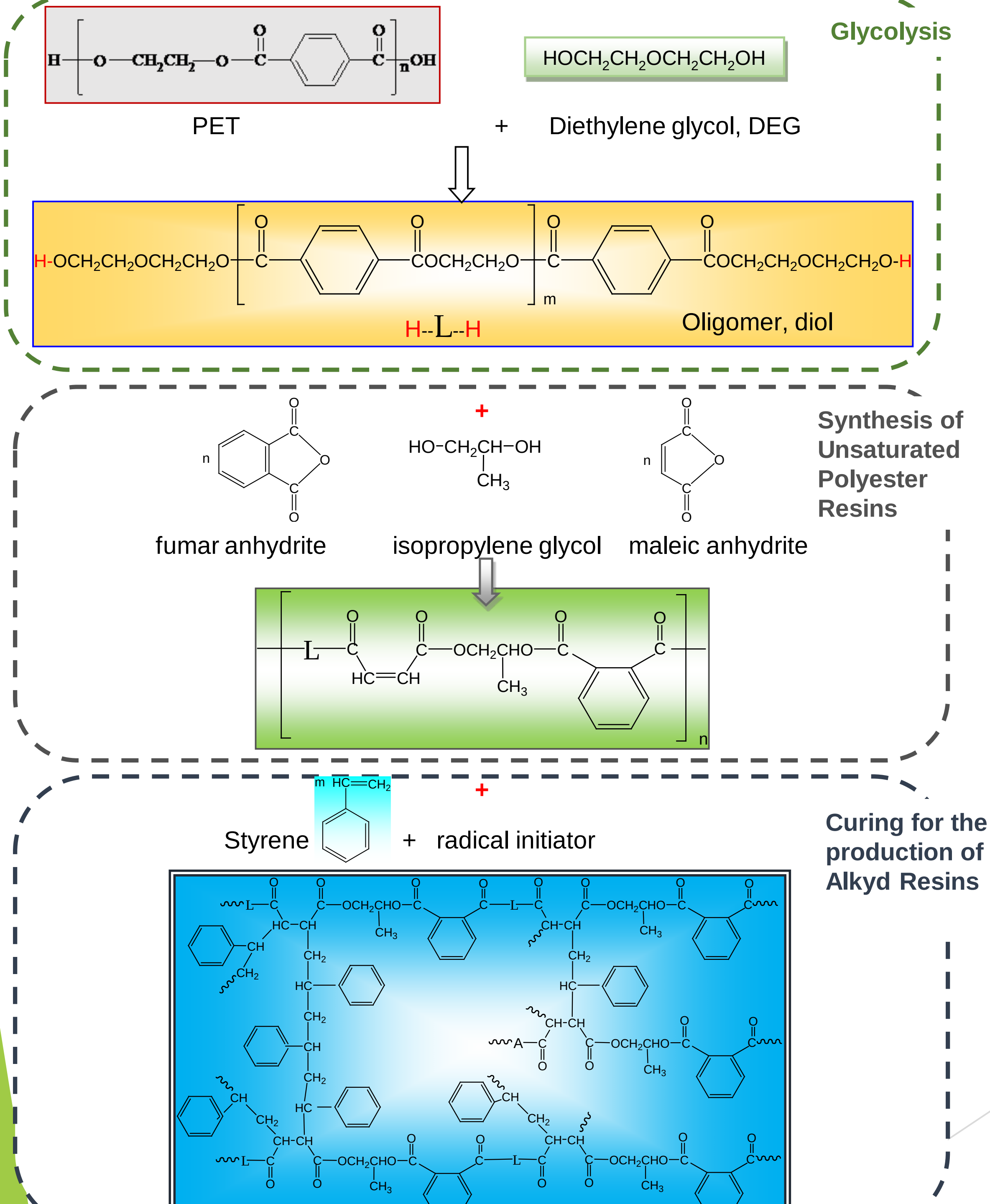


Kolokotsiou Lydia, Evangelia Vouvoudi, D. Achilias, Unpublished results

Effect of process parameters on the amount of polymer reacted (%) at 10 min reaction using different glycols

PET/PLA	Temperature (^oC)	DEG	EG	PG
90/10	120	71	72	73
90/10	150	86	86	86
90/10	180	99	98	98
95/5	120	68	72	73
95/5	150	85	79	79
95/5	180	97	97	96
98/2	120	72	71	69
98/2	150	81	84	82
98/2	180	98	96	97
100/0	150	76		
100/0	180	98		
0/100	150	95		

Synthesis of Alkyd resins from waste PET glycolysis



I would like to thank the organizers of the Conference

And you for your attention