

New recycling approaches for non-recycled plastic fractions PET, PE, PP

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Packaging is the main plastic waste fraction representing about 63% of the total plastic waste generated in Europe (PlasticsEurope, 2018). Thus, it is necessary to develop new processes for recycling the currently not valorised plastics, especially: **Multilayer packaging** (PET/PE & PET/PP), **post-consumer PET trays & Clamshell containers** and **microplastics** present in wastewater. Since mechanical recycling is not always an option or leads to down-grading of the material, e.g. for multilayer and plastic mixes, biochemical or enzymatic recycling of recalcitrant plastic fractions might form a powerful alternative. The use of enzymes for plastics recycling benefits from their extremely high substrate specificity, a high catalytic power, as well as their sustainability, due to enzymes operate under mild conditions of temperature, pH and pressure and often in aqueous media. The European project **ENZYCLE** (<https://www.enzykle.eu/>), will encompass the plastic enzymatic recycling from a holistic point, approaching all the development stages from the identification and selection of new enzymes, through the development of new systems for continuous enzyme production, to the development of recycling and valorisation processes (**Figure 1**).

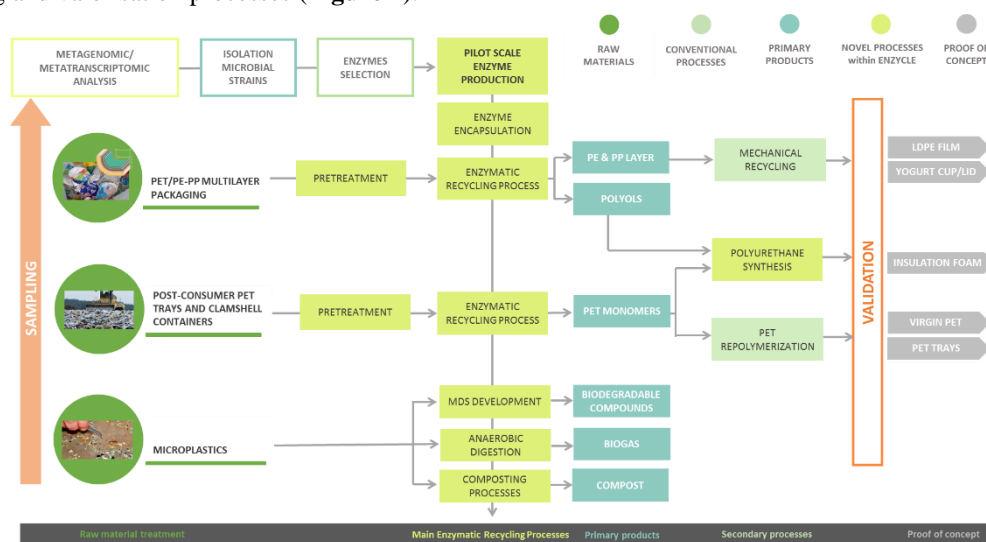


Figure 1. Overview of ENZYCLE in terms of processes and targeted markets.

In this sense, and to improve the efficiency of enzymatic depolymerization protocols have been designed for this purpose (chemical oxidation, photooxidation, decreasing crystallinity of materials). The polymer structure and increase of the plastic depolymerization efficiency rates of post-consumer polyester (PET) and polyolefins (PE and PP) in a mono- and different multilayer thickness packaging by new versatile and robust pre-treatment methodologies have been evaluated for subsequent enzymatic degradation. Different chemical-physical treatments have been selected to decrease the crystallinity for polyesters and to increase the degree of oxidation of polyolefins due to their rigid C-C structures. For this purpose, different strong and mild pre-treatments of the material have been developed and compared (**Table I**).

Basically, these pre-treatments are based on alkaline treatments with methanol as solvent, strong and organic acids, mild and more aggressive detergents, ammonium persulfate, different salt in a base medium reaction and the well-known Fenton reaction. In addition, different physical treatments were tested such as sonication, different temperatures and UV light. Although these oxidative pre-treatments are different, they all induce the appearance or disappearance of practically the same functional groups in each type of plastic, PET, PE or PP. Fundamentally, these functional groups are carbon dioxide groups, alkane groups, hydroxyl groups, alcohol groups, and nitrogen compounds (only for those involving a nitrogen-containing oxidant). In general terms, treatments such as acidic and alkaline compounds in methanol as a solvent are very efficient in the complete degradation of PET and the partial degradation of polyolefins in both mono- and multilayer. However, these pre-treatments are very aggressive and are not aligned with an environmentally efficient methodology. In contrast, pre-treatments with water at high temperatures, ammonium persulfate or metal salts in an alkaline medium are surprisingly efficient in terms of oxidation and partial degradation of all materials tested in both mono- and multilayer. Moreover, such efficiency

is carried out under mild temperature conditions and at short times for most of these treatments which is in line with such energy and environmental efficiency methodologies, avoiding the generation and release of toxic pollutants.

Table 1. Comparative table of all treatments for the different materials. In the case of multilayer materials the first character before the / equals PET and the second character refers to PE or PP. Legend: X (oxidation induced), Y (decrease in crystallinity induced), Z (increase in crystallinity induced), D (complete degraded material).

Group and Type		Treatment	Material				
			PE	PP	PET	PET/PE_1	PET/PP
1) Water		1	X	X, Z	X	D/X	X/X
		2	X, Y	X, Y	X	X, Z/X	X/X
2) pH	Alkaline	3				X/	
		4			X, Y	D/X	D/X
		5	Z	Z		X/	/X
		6	X	X	X	X, Z/X	X/X
		7		Y	X	D/X, Z	D/X
	Alkaline in metanol solvent	8	X	X	D	D/Z	D/X
		9	Y		X	D/X, Z	D/X
		10	X	X	D	D/X, Z	D/X
		11		Y		Z/	/X
	Acid	12				X, Z/X	D/X
		13	X	X	Y	D/X, Z	D/X
		14		X, Z	Y		D/X
		15	Z			X	/X
		16	X		X	Z/	D/X
		17	X			Z/X	
		18				Z	
	Organic acids	19			Z		
		20			Z		
		21				Z	
		22	X		Z	Z	
		23			Z		
		24		Y		X/X	X/X
	3) Detergents	Aggressive	25		X	X	D/X
26				Y		X/X	X
Mild		27			X	Z/X	D/X
		28					
		29			Z		
		30			Z		
		31			Z	X/	D/X
4) Amonnia persulfate	32			Y	X, Z/	/X	
	33	Y	Y		X/	X/, Y	
	34	Y		Z	X, Y/X, Y	/X	
	35	Y			D/X, Z	/X, Z	
	36					/X	
5) Salts in a base medium	37	X	X, Y	X			

	38	Y	Y			/X
	39	Y	X	Y		/X
	40		Y	Z	D/X , Z	
6) Fenton reaction + UV light	41	Y	X			/X

As a summary of all the physicochemical pre-treatments performed, it can be concluded that treatments with nitric acid (T11-T14) induce important structural changes in the FTIR spectra of polyolefins and PET in both mono- and multilayer due to the appearance of oxidation groups in their structures oxidative groups such as carbon dioxide, hydroxyl groups, nitro groups and alcohol groups, as well as a decrease in the percentage of crystallinity measured by DSC. Additionally, methanol treatments induce the almost total degradation of PET as can be seen in the tests derived from FTIR and DSC analysis which are not able to detect PET after these treatments (T7, T9, T8 and T10). However, these pre-treatments are very aggressive with the material and highly polluting due to the concentrations used which is not in line with an environmentally efficient methodology, these treatments were therefore discarded.

In contrast, pre-treatments with sudden changes in water temperature, ammonium persulphate or metal salts in an alkaline medium are surprisingly efficient in terms of partial oxidation and crystallinity decrease of all materials tested in both mono- and multilayer format. Moreover, this efficiency is achieved under mild temperature conditions and at short reaction times for these treatments which is in line with such energy and environmental efficiency methodologies, avoiding the generation and release of toxic pollutants. Specifically, the best pre-treatments for polyolefins (both PE and PP) due to an induction of oxidative groups such as carbon dioxide, hydroxyl groups and alcohol groups measured by FTIR, as well as a decrease in the percentage of crystallinity measured by DSC are the treatment with water at high temperatures (T1 and T2), the treatment with $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{Na}_2\text{S}_2\text{O}_5$ (T33), with $\text{ZnCl}_2 + \text{NaOH}$ (T37) and the Fenton reaction ($\text{H}_2\text{O}_2 + \text{FeSO}_4$) + UV light (T41). However, less clear is the pre-treatment of PET. Of all those tested, it seems that the most effective due to the decrease in the percentage of crystallinity that they induce in this material are the treatment with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (T32), the treatment with $\text{CuCl} + \text{NaOH}$ (T39) and the treatment with enzyme compatible detergents such as Tween-80(T26).

On the other hand, when determining the degree of crystallinity of the multilayer plastics, it is observed that it is very low for both layers. It is found that the PET layer has between 8-12.42% compared to the previously evaluated monolayer PET (27.94%), and the polyolefin side (both PE and PP) has between 1-5% compared to monolayer polyolefins (28-32%). Therefore, one thing that could be considered in the light of these results is that due to the low crystallinity observed in multilayer plastics, a pre-treatment as in monolayer plastics may not be necessary prior to enzymatic degradation. However, there are certain pre-treatments that induce either a partial oxidation of the multilayer materials, especially on the polyolefin side, such as the treatment with water at high temperatures of (T1 and T2) with the induction of the hydroxyl groups mentioned above, or a decrease in the degree of crystallinity of the material, such as the treatment with $(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{NaOH}$ (T34) and the treatment with $\text{FeCl}_3 + \text{NaOH}$ (T36).

Finally, the real effectiveness of these pre-treatments on the above-mentioned materials will be confirmed by enzymatic degradation tests. In this sense, and for these enzymatic tests to work, the correct washing and drying of the samples after the physico-chemical pre-treatments must be considered so that the products do not inhibit the action of the different enzymes.

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References

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