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Review

#### An overview of present treatment and valorification methods used for plastic waste

#### FLORENTA DANIELA CONSTANTINOV\*, MIRELA ALINA CONSTANTIN

National Research and Development Institute for Industrial Ecology- ECOIND, Bucharest, Street Drumul Podu Dambovitei 57-73, 60652, Romania \*Corresponding author: daniela.constantinov@ecoind.ro

Corresponding author: adnieta.constantinov@ecoina.ro

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#### Abstract

Most freequent used methods for recycling and treating plastic waste, with their advantages and disadvantages were analysed and investigated. Plastic waste present a slow degradation rate in nature, almost one thousand years, therefore it is important to adress this type of pollution, by finding the most sustainable methods in reducing the percentage of plastic that ends up in landfills or in the ocean. The negative impact of plastic waste include bioacumulation in organisms by exposure to micro and nanoplastics that end up in the environment from degrading macroplastics or directly from products that contain microplastic, like exfoliating personal care products.

*Keywords:* plastic waste, recycling plastic, plastic waste valorification, waste management, circular economy

### INTRODUCTION

Plastic materials are present in almost everyday activity; their use varies from packaging materials, construction materials (polyvinyl chloride pipes, window profiles), electrical, automotive, medical equipment, to textile industry.

Nowadays legislation requires more responsability in protecting the environment and health of people while developing new methods for economical growth, which is knowned as green economy. These goals aim to reduce emissions (minimum 55% greenhouse gases by 2030), reduce external energy dependency, finding sustainable energy resources and developing renewable sources of energy while reducing fossil fuel energy consumption. By achiving these goals European Union (EU) aims to become the first climate-neutral continent by 2050 [1].

The discovery of plastic is dated since 1907 by Leo Baekeland, who sintetized the polymer named bakelite (that was used as insulation material) from phenol and formaldehyde [2].

Plastics are usually synthetic or semi-synthetic materials of organic or anorganic nature, which can be molded into different shapes, with or without heat and pressure. Depending on their properties, they can be classified as thermoplastics meaning they can be re-melted and processed by extrusion, injection moulding or thermoforming and therefore re-used many times, without showing significant changes in their chemical properties [3]. The other category is represented by thermoset plastics - usually in liquid form at room temperature, they become hard after heating or by using chemical addition, therefore they present better resistance to heat and chemicals [4].

The production of plastic materials is rising every year because they are relatively cheap to produce and due to their well-known properties like high mechanical resistance compared with their weight, resistance to both physical and chemical degradation, and their high non-permeability towards liquids [5].

Plastics are not biodegradable in nature; they usually decompose in around  $100\div1000$  years. Taking into consideration the waste management used nowadays, the municipal solid waste generated by weight contains about  $7\%\div12\%$  plastic [5], while another study shows the sectors in which plastics are most used are: packaging (146 million metric tons), building & construction (65 million metric tons) and textiles (59 million metric tons). Since 2015, the amount of generated plastic waste was

around 6300 Mt (million metric tons), from which around 9% was recycled, 12% was subjected to incineration, while the majority, around 79% was managed by landfilling or randomly thrown into the environment. Based on this trends it is estimated that by year 2050 there will be 12,000 Mt of plastic waste in landfills or environment [6].

The incineration method is widely used for energy recovery while reducing the plastic waste, but it has some disadvantages, they generate toxic gases in the process, like dioxins, furans, carbon monoxide, carbon dioxide, hydrogen sulphide, sulfur oxides and nitrogen oxides. Other pollutants resulted from incineration include fly ash and coke [7].

European Union (EU) proposed a frame-work directive for waste management, in which the focus is established on prevention and preparing for re-use, followed by recycling, recovery and last sollution should be disposal of waste. The main objective of european countries is to increase the recycling rate and preparing for re-use of municipal waste to a minimum of 55% until 2025, 60% until 2030 and 65% until 2035 [8].

Currently, the plastic waste management include methods like incineration, and recycling by mechanical, biological, or thermochemical methods. Although researchers find new techniques for treating or recycling plastic waste, 80% of the global plastic waste is managed through landfilling or discarded into the environment, while only 9% of the plastic waste is recycled [9].



Fig. 1. Treatment methods in waste management

Data collected in a study from Europe in 2020 showed the importance of separate waste collection, and the results showed a growth in the amount of recycled plastic from 5% (currently) up to 65%, when the waste was collected separately [12].



Fig. 2. The percentage of recycled plastic for separate waste collection versus mixed waste collection

# Classification of plastics

The resin identification codes are used to identify the type of resin from which the plastic product was created. Codes 1 and 2 can usually be recycled, while products marked with code 3 aren't collected from households and for this reason the recyclability rate is decreasing. Code 4 and 5 can be recycled, while code 6 is not recyclable. Number 7 is not recyclable because these products usually contain a mixture of other materials, some of them very toxic [7, 13].

Table 1 presents the identification code for every polymer type, along with the global producation of plastic and the plastic demand in Europe; other useful information include properties and use for every type of polymer [7, 12, 13].

Table 1. Classification, properties, production and demand of plastics						
Plastic Type	Resin identification code	Europe plastic demand (%)	Global plastic production 2022 (%)	Density (g/cm <sup>3</sup> )	Melting point (°C)	Uses
Polyethylene terephthalate	L PET	7.1	6.2	1.38	>250	Soft drink bottles, furniture, carpet & clothing fibers, food containers,
High-density polyethylene	2 HDPE	12.1	12.5	0.941 ÷ 0.96	130	Bottle caps, milk bottles, insulation cable, pipes, recycling bins, grocery bags, car stops, 3D printer filament
Polyvinyl chloride	3 PVC	10.1	12.3	1.38	100 ÷260	Vinyl records, non-food bottles, credit cards, window&door frames, toys, pipes, ceiling tailes, fencing, flooring

# Table 1. Classification, properties, production and demand of plastics

Low-density polyethylene	LDPE	17.3	14.4	$\begin{array}{ccc} 0.91 & \div \\ 0.925 & 115 \end{array}$	Oil containers, shampoo & detergent bottles, pipes used for irrigation, bubble wrap, grocery & packaging bags
Popypropylene	25 PP	19.1	19.3	0.855 130 ÷171	Auto parts, bottle caps, plant pots, furniture, drinking straws, tarpaulin, boxes, industrial fibers, medicine bottles
Polystyrene	6 PS	6.9	5.3	0.96 ÷ 240 1.04	Polystyrene foam, food trays, clothing hangers, egg boxes, single-use tableware, cups, toys, insulation materials, video tapes,
Others: polybutylene terephthalate, polycarbonate, polylactic acid, acrylic, acrylonitrile butadiene styrene, multilayered mixed polymers and nylon	OTHER	19.9	14.2	Difficult to recycle	Nylon, acrylic, polycarbonate, polylactic acid, multilayer plastics, compact-discs, auto & aircraft parts, lumber, safety glasses, safety shields, baby bottles,

## Mechanical treatment

This method is the most simple available and consists in sorting the plastic waste based on the polymer type, washing and drying, then melting the material for obtaining flakes or another new product. The finished product presented lower quality (mechanical properties, thermal stability) than the original one because of thermomechanical degradation, therefore the new product has limited applicability (non-food). As a result mechanical treatment of plastic waste is considered a short-term solution firstly due to the loss in mechanical properties (downcycling) and because of limited number of reprocessing cycles and cannot be applied to all plastic materials (e.g. PU cannot be recycled mechanically) [14, 15]. For instance, the virgin PET has a strain-at-break of 42% which after five cycles of extrusion reduces dramatically to only 0.7% [14].

# Biodegradation as treatment method

Biodegradation is described as the process of decomposing the polymer chain under the enzymatic activity of microorganisms and specific environmental conditions (temperature, pH, UV radiation, humidity); microorganisms use the polymer as energy source and break it into smaller molecules and monomers until they reduce to  $CO_2$ ,  $CH_4$  and  $H_2O$  [11, 16].

The degradation of plastic waste in the environment begins when exposed to solar radiation; the UV radiation favours the oxidation process to break down the polymers [17].

Based on the scientific information available in the present moment, there are two paths for the biodegradation of plastic waste:

- Finding the most suitable microorganisms for the degradation of plastic;
- Developing polymers sensitive to biodegradation.

To this date, researchers found out more than twenty species of bacteria that present affinity for plastic biodegradation [10].

The continuous development of industry and economy areas has a direct influence on the amount of generated waste. From this perspective, biodegradable plastics represents an eco-friendly solution in

managing plastic waste due to their lower environmental impact during the production process [18]. But there are some challenges also, like the difficulty in degrading mixed plastic waste and high production cost, finding the most suitable microbial strains for biodegradation and focus on enzyme characterization. Another drawback could be the lack of studies about all polymer types, the majority of plastic biodegradation studies are concentrated mostly on PET, LDPE, PP polymers. When refering to biodegradable plastic its necessary to take into consideration the presence of additivies in the polymers that can give a wrong result about the biodegradation rate, because the bacteria consumes first the additive and then the polymer [11, 19, 20]. The most common biodegradable bioplastics available on the market are polybutylene adipate terephthalate (PBAT), polylactic acid (PLA), polyvinyl alcohol (PVA), polybutylene succinate (PBS), starch based compounds, cellulose films and polyhydroxyalcanoates (PHAs). In some cases the biodegradability is evaluated on the pellets instead of the final product, neglecting the impact of temperature on the crystallinity of the materials [21].

In order to measure the biodegradation of plastic there are some techniques available, listed in the table below.

Table 2. Methods for measuring the biodegradation of plastic				
Method	Description	Polymer	References	
Clear zone method	The polymer is degraded with extracelular enzymes placed in agar plates; the appearance of a clear zone on the plate suggest the polymer was degraded.		[17], [22]	
Gravimetric determination of weight loss	Using anaerobic conditions, after seven months incubation with specific microbial species, the polymer is degraded and the weight loss was calculated as a percentage of the initial weight.	PVC	[22], [23]	
Fourier Transform Infrared Spectroscopy (FTIR)	Microbial degradation causes changes in the chemical structure of polymers (indicated by the presence of O-H, C-O and C=O groups), which is measured using FTIR spectroscopy.	PE, PVC, PHA	[22], [23], [24], [25]	
Scanning Electron Microscopy (SEM)	Microbes adhere to the polymeric surface by forming a biolfilm and generating morphological changes (cracks, cavities) that indicate the surface destruction; the structural changes are observed using SEM.	PE, LDPE, PVC, PHA	[9], [17], [20], [22],[23]	
Gel Permeation Chromatography (GPC)	The bacterial strains break the polymeric chain and starts to consume it; after incubation the molecular weight is determined with GPC. The decrease of molecular weight demostrates the biodegradation occured.	PVC	[17], [22]	
Nuclear Magnetic Resonance (NMR) Spectroscopy	NMR spectroscopy is suitable to analyze the molecular changes produced by microorganisms in the biodegradation process. The NMR method can reveal the degraded products and secondhand products from the biodegradation process.	PVC	[17], [22]	
pH variation	Alkaline pH values of the aqueous media can influence the activity and growth of bacterial culture and as a result it can improve the biodegradation rate of the polymer.	РР	[17], [20]	
ADP/ATP ratio	By measuring the ADP/ATP content it is possible to determine the activity of microbial cultures. Lower ADP/ATP ratio suggest higher metabolic activity of the bacteria in the presence of different polymers	PP, PE	[17], [22]	

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## **Chemical Treatment**

This treatment method implies chemical processes in order to recover the monomers from plastis waste or transform them into other useful materials, making the transition to a circular economy possible [12]. A report from World Economic Forum's platform presented some initiave regarding the economical growth and minimizing environmental impact; actions like recycling 10% of the current plastic waste can reduce the amount of plastic in the oceans up to 50% [26].

### Solvolysis

Solvolysis represents a chemical treatment process in which the depolimerization takes place using a solvent and temperature between 80-280°C. The resulted monomers can be used for making new plastic products or to produce other value-added products. Based on the type of solvent used in the reaction, several types of solvolysis are presented in table 3 [12, 13].

Name of		Suitable Plastic Polymer /	Yields in	
solvolysis	Description Reaction products resulted		reaction	References
method	_	from solvolysis	products	
Alcoholysis	Depolymerization is realised with exces alcohol, for example methanol (methanolysis) at high temperature (180÷280 °C) and pressure (2÷4 Mpa)	$\begin{array}{rcl} \mbox{PET} & \rightarrow & \mbox{dimethyl} \\ \mbox{terephthalate} & (DMT) & + \\ \mbox{ethylene glycol} (EG) \\ \mbox{PLA} & \rightarrow & \mbox{alkyl} & \mbox{lactate} \\ \mbox{PC} & \rightarrow & \mbox{Bisphenol} & \mbox{A} & + \\ \mbox{dimethyl} & \mbox{carbonate} \end{array}$	DMT (97.8÷100%) PLA (81÷96%)	[13], [17], [27]
Hydrolysis	Depolymerization with a aqueous solution in different media: Acidic – using H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> , or H <sub>3</sub> PO <sub>4</sub> Neutral – H <sub>2</sub> O or water vapors Alkaline – KOH or NaOH solution	PET + NaOH $\rightarrow$ terephthalic acid (TPA) + ethylene glycol (EG) $\rightarrow$ BHET PLA $\rightarrow$ alkyl lactate, lactic acid PHB $\rightarrow$ Crotonic acid (CA), 3-hydroxybutyric acid (3- HBA)	TPA (98.31%)	[17], [28], [29]
Glicolysis	reaction realized with a diol, most often is used ethylene glycol in excess; can be assited by microwave, catalyst or supercritical conditions	$PET \rightarrow bis (2-hydroxyethyl)$ terephthalate + ethylene glycol	BHET (77÷100%)	[17], [28], [29]
Ammonolysis	Depolimerization reaction realised using ammonia	$PET \rightarrow terephthaldiamide + ethylene glycol \rightarrow Oxalic acid$	TPA (90%)	[17]
Aminolysis	The polymer is degraded using a methylamine or ethylenediamine solution	$PET \rightarrow bis (2-hydroxylethyl)$ terephthalamide + EG $\rightarrow$ bis (2-hydroxylethyl) terephthalat. PET $\rightarrow$ bis (2-aminoethyl) terephthalamide (BAET)	BHETA (91%) BAET (75%)	[17], [29]

### Table 3. Solvolysis methods available for plastic waste treatment

# Thermo-Chemical Treatment

Pyrolysis, incineration and co-incineration are some of the most eligible thermo-chemical methods knowned for treating plastic waste.

## Pyrolysis

When the valorification or energy recovery methods aren't possible to implement, pyrolysis is very useful because this technology is capable to process different plastic polymers and raw materials. As a result is beneficial for protecting the environment while promoting economy growth by reducing the amount of landfilled plastic and green house gases emmited into the atmosphere or to produce electricity [30]. Through pyrolysis, plastic waste can be transformed into valuble products such as oils, gas and wax. Studies have demonstrated that these products have calorific value similar with classic fuels, so they represent an valuable alternative to the emerging problem regarding petroleum resources [31, 32]. Using pyrolysis products as an altenative for burning fossil fuel or gas prevents  $CO_2$  to be emitted into the atmosphere by 30% wt [15].

Pyrolysis can be classified according to the media conditions as followed in table 4.

Type of pyrolysis	Description	Reaction products	Yields in reaction products	References
Thermal pyrolysis	Simple and advantageous method, using temperatures between 300÷900°C and inert atmosphere	$C_1$ - $C_4$ paraffins, $C_2$ - $C_4$ olefins,lighthydrocarbons( $C_2$ - $C_4$ ),valuableoils( $C_8$ - $C_{12}$ ),graphite	Liquid fuel (74%)	[13], [33], [34]
Catalytic pyrolysis	Developed to improve the selectivity of the method by using a catalyst (e.g. sludge, nitric acid, zeolites, activated carbon, red mud, amorphous $SiO_2-Al_2O_3$ ) at milder temperatures.	Terephthalic acid, ethylene, polycyclic hydrocarbon, hydrocarbon oil, dicarboxylic acids, biphenyl derivatives.	Ethylene (22÷25%), PET (34÷84%), dicarboxylic acids (71%) PP, LDPE and HDPE (80%)	[33], [35]
Co- pyrolysis	Represents the synergy reaction between plastic polymer and biomass (sugarcane bagasse, pinewood)	Alcohol, hydrocarbons, aromatics	Syngas (incresed by 27%), H <sub>2</sub> (increased by 80%), CO (increased by 63%)	[13], [33], [36]

Table 4. Valuable products and yields obtained for diffent pyrolysis methods

# Incineration

Represents a frequently encountered method used for minimizing the amount of waste before they are landfilled and to generate energy [37]. Basically the waste undergoes a termical degradation using exces oxygen, while maintaining a temperature between 900 and 1100°C [38]; the final products resulted after incineration are carbon dioxide, carbon monoxide, nitrogen oxides and an inert solid residuu which represents only 10% weight of the pre-treated waste [39].

# Valorification methods of plastic waste

### Gasification

This technology is used to transform plastic waste into gases with high calorific value like carbon monoxide, hydrogen and methane. The steps involved in this process include waste drying, pyrolysis, cracking, reformation, followed by carbon gasification. An experimental study conducted

by [40], showed that by introducing different polymer types (co-gasification) improves the efficiency up to 89%, while the results obtained for each individual polymer were smaller (59.03% for PE, 62.73% for PP and 73.13% for PS. In a study it was found that when performing the gasification under optimal conditions, using supercritical water and temperatures between  $500 \div 800$  °C and pressure of  $22 \div 25$  Mpa for about 60 minutes, the gasification achieves a carbon conversion of 94.48 wt% from plastic waste [41].

The primal benefit of this method compared to the steam gasification method is its simplicity, since it does not require external energy and the resulting gas has lower tar content [42].

## Adsorbent materials

PET plastic waste can be converted into porous carbon, a valuable product which has a well-defined pore structure and a high surface area and thus posses the capacity to adsorb tetrafluoromethane (CF<sub>4</sub>), a gas with global-warming potential much more harmful than CO<sub>2</sub>, having an atmospheric retention time of almost 50.000 years [43]. Using this method the mass of plastic waste was reduced by 80.2% in the range between room temperature and 600°C, while after 600 °C to 1000 °C the mass loss was less significant. CF<sub>4</sub> is a pollutant included in the Kyoto Protocol of the United Nations Framework Convention on Climate Change, therefore the adsorbtion method offers an economical solution for reducing the environmental pollution and plastic waste [43, 44].

### Nanoparticles (C-dots)

Studies have suggested a recycling method that transforms plastic waste into carbon dots (smaller particles under 10nm) with photoluminescent properties. These C-dots can be used in biomedicine, as sensors in solar cells, or as photocatalyst for treating evironmental pollutants. The experiment was realised by simply heating the PP plastic bags for almost 20 minutes at specific temperatures (200 °C, 250 °C, and 300 °C) afterwards was added ethanol for the purpose of dispersing the C-dots nanoparticles. Increasing the temperature favors the formation of many C-dots but has a negative influence on the photoluminescence. The photoluminescence was observed by exposing the polymer to ultra-violet (UV) light and finally confirmed by measuring the absorption using a spectrofluorometer UV-Vis in the range of 340÷550 nm spectra [45, 46].

### **3D** Printing

A simple method for converting plastic waste into new valuable products using 3D printing. The process implies on the first hand sorting the plastic waste based on the polymer type, secondly they are washed & dried, followed by shredding the plastic into smaller pieces called flakes. These flakes are then melted and pressed into a filament which is then inserted to the 3D printer and the machine prints a new product. A dutch company (Better Future Factory) developed a series of solutions for recycling the plastic waste into new valuable products such as: lamps, toys, furniture, trofies made from fishing nets, old fridges or plane parts. Another example was the transformation of plastic waste collected from water canals in Amsterdam into flower pots or making plant trellises from used digipasses [47].

# Plastic-cement composite materials

Considering that the wast majority of plastic is used globally in the packaging and construction sector [6] recent studies sugested plastic-cement composites as a sustainable plastic recycling method. Recycled PET was treated with sodium hydroxide solution, ethanol solution (95% ethanol and 5% water) and two silane binding products like (3-Aminopropyl) trimethoxysilane (APTES) and 3-(Trimethoxysilyl) propyl methacrylate (MPS) to improve the adhesion with the matrix of the composite. The treatment improved the frictional bond between PET fibers and the cement matrix from 0.64 MPa to 0.80 MPa. Then the PET samples were dried in the furnace for twelve hours at 60°C. These composites showed improved mechanical strength and good resistance to environmental factors similar to Strain-Hardening Cementitious Composites, with the observation that recycled PET fibers are cheaper than polyethylene (PE) or polyvinyl alcohol (PVA) which are

normally used in the fabrication of these composites. After a period of eighteen months PET fibers were extracted from both cement composite (the one with virgin fibers and the other one with recycled PET fibers) and tested their resistance to alkali. They examined the surface morphology using SEM and it was observed that pure PET fibers presented higher degradation rate than the treated fibers, therefore the treated fibers exibited reasonable stability to be considered as a feasible method for construction application and recycling plastic waste [48, 49]. Similar studies were made for testing mechanical properties of classic concrete and fiber-reinforced cementitious composite high-strength, high-ductility concrete (HSHDC). These composite materials have showned a compressive strength greater than 150 MPa, an average tensile strength of 14.5 MPa and tensile ductility greater than 3%, which can be translated as improvment in strenght and ductility for construction application [49÷52].

#### Plastic-wood composite materials

Another method that uses plastic waste was studied in the making of poplar-HDPE composite as environmental friendly alternative in construction and automotive sector, or furniture manufacturing. Usually this type of composite consist in combining a polymer matrix (PP, PE, HDPE, PVC or ABS) and biomass (wood or bamboo) using thermo-mechanical technique (extrusion, injection, moulding) [53÷55]. In order to produce a stable bond between the matrix and biomass, there must be used a coupling agent to ensure a strong adhesion for example sodium hydroxide, silane, acetic acid, acrylic acid, peroxide [55]. A small amount of HDPE powder (0.3g) was laid on five poplar tablets than they were hot molded at 185 °C and 78.7 MPa for 65 min with a mold. After 30 minutes cooling the composite was ready and had the following dimensions: 50 mm × 8 mm × 3 mm. Tests were made for the characterisation of the composite using thermogravimetry analysis and scanning electron microscope, followed by resistance to corrosion test with H<sub>2</sub>SO<sub>4</sub> 72% and NaOH 50%. The results showed that poplar/HDPE composite has superior mechanical strenght (tensile strength 198.9 MPa) than untreated poplar and posses high resistance to corrosion and flame, while maintaining an eco-friendly aproach since this method did not used any adhesive [53, 55].

#### Synthesis gas

Used tires were transformed into syngas and the efficiency of the process was studied. After optimizing the operation conditions was observed that a higher temperature ( $625^{\circ}C$ ) leads to a better yield for H<sub>2</sub> (14.4 mmol/g) and carbon gasification efficiency (42.6%) by using only 5% raw materials in just 60 minute reaction time [56]. Tires present a higher calorific value ( $34 \div 40 \text{ J/kg}$ ) [56, 57] than coal ( $12.56 \div 35 \text{ J/kg}$ ) [58] which means these type of waste can be converted to energy as a feasible alternative to classic fuels [7]. The study was performed by combining the pyrolysis with gasification at a temperature between  $500^{\circ} \div 800^{\circ}C$  in the presence of a catalyst (Ni-Mg-Al) [59]. In another study was found that by using steam gasification of waste tyres can produce approximate 86% high-quality syngas in a temperature range of 850°C to 1000°C [60]. Recent studies promoted a recycling method which consists in dissolution of HDPE, PP and PS plastic waste assisted by microwave and a catalyst (Titanium aluminum carbide – Ti<sub>3</sub>AlC<sub>2</sub>) [61] to produce H<sub>2</sub> gas and carbon fibers [62]. The selectivity and efficiency of this method are presented in table 5.

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Type of polymer	H <sub>2</sub> selectivity (%)	Hydrogen extraction efficiency (%)			
LDPE	75	96			
HDPE	78	99			
PP	78	92			

Table 5. H<sub>2</sub> selectivity and extraction efficiency through microwave catalytic process

It was found that co-gasification of mixed plastic (PE, PP and PS) recorded a higher efficiency (89%) compared to each individual plastic (59.03% for PE, 62.73% for PP and 73.13% for PS) therefore high quality gases were obtained (H<sub>2</sub>, CO and CH<sub>4</sub>) [40]. Another feasible approach for

gas production was investigated through a pyrolysis/gasification process using a mixture of 80% biomass and 20% plastic (PE, HDPE, PS and a mixture of those three polymer). The results showed improved gas yield (56.9%) when 20% PP was mixed with biomass, furthermore by adding Ni/Al<sub>2</sub>O<sub>3</sub> catalyst improves gas yield while generating only a small amount of coke (less than 1%) [63].

## Carbon nanotubes

Carbon nanotubes represent represent a promising alternative for recycling plastic waste. Organic materials with solid-liquid phase change (PCM) are able to store and stably release latent heat energy in a narrow temperature range, during melting and solidification. It has proven to be an efficient method of thermal management, due to their high heat storage capacity, as well as low operating costs, but also due to their durability - they maintain their properties after several successive cycles of use [64]. Another study shows that by adding only 10% plastic waste into the phase change material increases the thermal conductivity and thermal diffusivity of the composite more than two times compared to the commercial composite. This can be explained by the presence of metal catalyst residues in the composition of carbon nanotubes obtained from plastic waste, which improve thermal conductivity. Based on the resulting data, the carbon nanotube-phase change material composite shows a high application potential as a conductive filler in battery thermal management systems [65, 66]. These studies sustain the efficiency of these materials obtained from plastic waste due to their high heat storage capacity and low operating costs, showing a promising practice for plastic recycling

## Alternative fuels

The quaternary treatment of plastic waste, through energy recovery, is a good solution when other types of treatment are not possible. Plastic materials are derived from unrefined petroleum and they have a high calorific value. There are multiple studies that suggest the application of plastic waste as alternative fuels [34] obtained diesel like fuel (74% yield) from HDPE plastic bags through the process of pyrolysis using a batch reactor at  $420^{\circ}$ ÷ $440^{\circ}$ C; the analysis showed the composition of the oil resulted contains ethane and ethene (52%), C<sub>4</sub> compounds (32%) and a solid residue (almost 17%). By adding a catalyst (ZSM-5) the efficiency of the pyrolysis process can be increased which resulted in better yields for gases (5.1% to 12.2%), gasoline (from 18.2% to 34.5%) and light oil (from 17.9% to 24.1%) [67]. These valuable products can be utilized as alternative fuels in automotive industry by adding a fine modification to the engine or other application that requires thermal energy (boilers, heaters) [30, 68, 69].

In table 6 are presented the calorific value for the most common polymers, by comparison with the calorific value of petroleum [70].

Substance name	Calorific value (MJ kg <sup>-1</sup> )	
PET	24.13	
HDPE	49.40	
LDPE	37.4 - 46.60	
PP	45.3 - 46.40	
PS	37.7 - 42.10	
PVC	18.0	
Diesel fuel	43.0	
Gasoline	46.8	
Household mixed plastic waste	31.80	

<b>Calorific value of different p</b>	polymer types and classic fuels
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### Textile materials

The textile industry occupies an important role in the economy and trade market, with a global growth observed especially in developing countries. Studies have showed that recycled plastic can

be used in the production of textile materials [71], since the textile industry uses fabrics which contain 63% derivatives from petroleum and only 24% cotton fibers [72]. A lot of reasearch studies are focused mainly on fiber recycling (57%), while 37% focus on polymer recycling and less on fabric recycling [72]. Considering these aspects, recycling plastic waste into textile can save both raw materials (ethylene glycol and terephthalic acid) and energy, while contributing to the reduction of air pollution (resulting from incineration), water and soil (through landfill). Also it was demonstrated the difference between recycled polyester fibres and the pure polyester fibers; the recycled fibers presented higher rigidity and lower cristallinity than pure fibers which can limit their use [71]. At the same time an incovenient emerges regarding the difficulty in recycling these mixed textile (PET-cotton) consequently they might end up landfilled [73]. But nowadays companies found solutions in recycling mixed plastic waste at industrial level [74] in return contributing to pollution prevention and recovering pure materials to create new value added products.

### Energy storage

Some studies focused on using plastic waste for battery application. Sodium terephthalate recycled from PET plastic waste was subjected to a process of ultra-fast microwave irradiation for two minutes followed by X-ray diffraction, IR Fourier spectroscopy and nuclear magnetic resonance spectroscopy analysis in order to validate the purity of synthesized disodium terephthalate. It was also studied the electrochemical properties of PET waste in the structure of Li-ion and Na-ion batteries. Its a fair assumption to say that PET waste can be used as filler for batteries [65, 75].

## Synthethic graphite

Synthetic graphite can be obtained through pyrolysis at 900°C followed by a graphitization technique conducted at 2400°C in the presence of boron catalyst. The conclusion drawn from this study states that a high crystallinity can be correlated with electrochemical performances. This new product can be used as material for rechargeable lithium-ion batteries, as a filler in composite materials [76] or can be transformed into graphene [77, 78].

### CONCLUSIONS

Regardless of the field of activity, a responsible approach is necessary in terms of waste management by taking into account both benefits and drawbacks of the recycling / treatment methods, in order to choose the optimal route which best fulfills the requirements regarding the circular economy, environmental protection and human health.

Thermochemical recovery of plastic waste is undeniable if we take into account the degree of accumulation both on the ground and in the water sources (oceans and sea), as well as the potential it presents in minimizing fossil fuel by creating clean alternative fuels while increasing energy security.

Plastic waste represents an increased risk for the environment as well as for human health . In the COVID-19 period the amount of waste from medical units has drastically increased. Through degradation of these medical waste resulted small plastic particles, microplastics and nanoplastics which represents a risk for ecosystems, human health and professional safety because they can adsorb chemical and microbial pollutants. Both plastic products, as well as their unregulated release during the coronavirus pandemic, influenced the objectives of sustainable development due to their ecotoxicity, which negatively contributed in blocking the wastewater treatment plants. Therefore, it is necessary to evaluate the potential impact of plastic medical waste in the environment, using life cycle analysis methods, in order to better understand the impact it presents on sustainability objectives.

Life cycle assessment methods have shown that anaerobic digestion, storage and incineration of waste are not sustainable approaches and could contaminate the environment with chemical substances, microbes and genetic material resistant to antibiotics.

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## REFERENCES

[1] European Commission, https://ec.europa.eu/info/strategy/priorities-2019-2024\_en. [17.12.2022]

[2] Science History Institute, https://www.sciencehistory.org/historical-profile/leo-hendrik-baekeland. [25.04.2023].

[3] TWI Global, https://www.twi-global.com/technical-knowledge/faqs/what-is-a-thermoplastic. [20.03.2023]

[4] TWI Global, https://www.twi-global.com/technical-knowledge/faqs/thermoset-vs-thermoplastic#Thermoplastics. [20.03.2023]

[5] BABAREMU, K.O., OKOYA, S.A., HUGHES, E., TIJANI, B., TEIDI, D., AKPAN, A., IGWE, J., KARERA, S., OYINLOLA, M., AKINLABI, E.T., HELIYON, **8**, no. 7, 2022, https://doi.org/10.1016/j.heliyon.2022.e09984.

[6] GEYER, R., JAMBECK J.R., LAW, K.L, Sci. Adv, **3**, no. 7, 2017, https:// 10.1126/sciadv.1700782.

[7] NANDA, S., BERRUTI, F., Environ. Chem. Lett., 19, no. 1, 2021, p. 123.

[8] European Commission, https://environment.ec.europa.eu/topics/waste-and-recycling/waste-framework-directive\_en. [28.03.2023].

[9] LAZORENKO, G., KASPRZHITSKII, A., FINI, E.H., Constr Build Mater., **324**, 2022, https://doi.org/10.1016/j.conbuildmat.2022.126697.

[10] GHATGE, S., YANG, Y., AHN, J.-H., HUR, H.-G., Appl. Biol. Chem., **63**, no. 1, 2020, https://doi.org/10.1186/s13765-020-00511-3.

[11] IACOVIDOU, E., VELENTURF, A.P., PURNELL, P., Sci. Total Environ., 647, 2019, p. 441.

[12] JIANG, J., SHI, K., ZHANG, X., YU, K., ZHANG, H., HE, J., J. Environ. Chem. Eng., **10**, no. 1, 2022, https://doi.org/10.1016/j.jece.2021.106867.

[13] AMOBONYE, A., BHAGWAT P., SINGH S., PILLAI S., Sci. Total Environ, **759**, 2021, https: 10.1016/j.scitotenv.2020.143536.

[14] VOLLMER, I., JENKS, M.J, ROELANDS, M.C.P, WHITE, R.J., WILD, P.D, PAUL DE WILD, VAN DER LANN, G.P, MEIRER F., KEURENTJES, T.F, WECKHUYSEN, B.M., Angew. Chem. Int. Ed., **59**, no. 36, 2020, p. 15402, <u>https://doi.org/10.1002/anie.201915651</u>.

[15] HAHLADAKIS, J.N., IACOVIDOU, E., J. Hazard. Mater., **380**, 2019, https://doi.org/10.1016/j.jhazmat.2019.120887.

[16] PALARIE, D.L., CHIRIGIU, L., Notions of waste management and the chemistry of materials, Edit. Universitaria, Craiova, 2016, p. 8-10.

[17] OLIVEIRA, J., BELCHIOR, A., DA SILVA, V.D., ROTTER, A., PETROVSKI, Z., ALMEIDA, P. L., LOURENCO, N.D., GAUDENCIO, S.P., Front. Mar. Sci., **7**, 2020, https://doi.org/10.3389/fmars.2020.567126.

[18] PLOS BIOLOGY, https://journals.plos.org/plosbiology/article?id=10.1371/journal.pbio. 3002045. [27.04.2023].

[19] RADDADI, N., FAVA, F., Sci. Total Environ, **679**, 2019, p. 148.

[20] ER THEW, C.X., LEE, Z.S., SRINOPHAKUN, P., OOI, C.W., Bioresour. Technol., **374**, 2023, https://doi.org/10.1016/j.biortech.2023.128772.

[21] FILICIOTTO, L., ROTHENBERG, G., ChemSusChem, 14, no. 1, 2021, p. 56.

[22] THIOUNN, T., SMITH, R.C., J. Polym. Sci., 58, no. 10, 2020, p. 1347.

[23] GIACOMUCCI, L., RADDADI, N., SOCCIO, M., LOTTI, N., FAVA, F., N Biotechnol., **52**, 2019, p.35.

[24] SUN, Y., REN, X., RENE, E.R., WANG, Z., ZHOU, L., ZHANG, Z., WANG, Q., Bioresour. Technol., **332**, 2021, https://doi.org/10.1016/j.biortech.2021.125133.

[25] MUHAMMAD, I.A., SAFIA, A., GEOFF, R., JAVED, I., NAEEM, A., NAIMA, A.,

HAMEED, A., J. Basic Microbiol., 54, no. 1, 2014, p.18.

[26] World Economic Forum, https://www.weforum.org/reports/future-of-reusable-consumption-models/. [13.05.2023].

[27] LAMBERTI, F., ROMAN-RAMIREZ, L.A, MCKEOWN, P., JONES, M.D., WOOD, J., Environ. Green Process., **8**, 2020, https://doi.org/10.3390/pr8060738.

[28] AGUADO, A., MARTINEZ, L., BECERRA, L., ARIETA-ARAUNABENA, M., ARNAIZ, S., ASUETA, A., ROBERTSON, I., J. Mater. Cycles Waste Manag., **16**, 2014, p. 201.

[29] WANG, Y., ZHANG, Y., SONG, H., WANG, Y., DENG, T., HOU, X., J. Clean. Prod, **208**, 2019, p. 1469.

[30] SASIKUMAR, C., KANNAN, R., SENTHILKUMAR, C., SARWESWARAN, R., NAGARAJA, M., SUNDARESAN, R., Mater. Today., **64**, no. 5, 2022, p. 1679.

[31] CONSTANTINESCU, M., BUCURA, F., IONETE, R.E., NICULESCU, V.C., IONETE, E.I., ZAHARIOIU, A., OANCEA, S., MIRICIOIU, M.G., Mater. Plast., **56**, no. 1, 2019, p. 41.

[32] HARUSSANI, M.M., SAPUAN, S.M., RASHID, U., KHALINA, A., ILYAS, R.A., Sci. Total Environ., **803**, 2022, https://doi.org/10.1016/j.scitotenv.2021.149911.

[33] ZHAO, D., WANG, X., MILLER, J.B., HUBER, G.W., ChemSusChem, 13, no. 7, 2020, p. 1764.

[34] SHARMA, B.K., MOSER, B.R., VERMILLION, K.E., DOLL, K.M., RAJAGOPALAN, N., Fuel Process. Technol., **122**, 2014, p. 79.

[35] DOGU, O., PELUCCHI, M., VAN DE VIJVER, R., VAN STEENBERGE, P.H.M., D'HOOGE, D.R, CUOCI, A., MEHL, M., FRASSOLDATI, A., FARAVELLI, T., VAN GEEM, K.M., Prog. Energy Combust. Sci., **84**, 2021, https://doi.org/10.1016/j.pecs.2020.100901.

[36] HASSAN, H., HAMEED, B.H., LIM, J.K., Energy, **191**, 2020, https://doi.org/10.1016/j.energy.2019.116545.

[37] LI, X., ZHANG, C., LI, Y., ZHI, Q., Energy Procedia, **104**, 2016, p. 498.

[38] NUNES, L.J.R., MATIAS, J.C.O, CATALAO, J.P.S, Appl. Energy, **127**, 2014, p. 135.

[39] VANAPALLI, K.R., SAMAL, B., DUBEY, B.K., BHATTACHARYA, J., Plas. to Energy, no. 12, 2019, p. 313, https://doi.org/10.1016/B978-0-12-813140-4.00012-1.

[40] JANAJREH, I., ADEYEMI, I., ELAGROUDY, S., Sustain. Energy Technol. Assess., **39**, 2020, https://doi.org/10.1016/j.seta.2020.100684.

[41] BAI, B., LIU, Y., WANG, Q., ZOU, J., ZHANG, H., JIN, H., LI, X., Renew. Energ., **135**, 2019, p. 32.

[42] LOPEZ, G., ARTETXE, M., AMUTIO, M., ALVAREZ, J., BILBAO J., OLAZAR, M., Renew. Sust. Energ. Rev, 82, part 1, 2018, p. 576.

[43] YUAN, X., CHO, M-K., LEE, J.G., CHOI, S.W., LEE, K.B., Environ. Pollut., **265**, 2020, https://doi.org/10.1016/j.envpol.2020.114868.

[44] CHO, D.-W., KIM, W.S., CHANG, H., JUNG, T.S., PARK, J., PARK, J.-H., Korean J Chem Eng, **34**, 2017, p. 2922.

[45] PRASETYA AJI, M., WATI, A.L., PRIYANTO, A., KARUNAWAN, J., NURYADIN, B.W., WIBOWO, E., MARWOTO, P., SULHADI, **9**, 2018, p. 136.

[46] ZHOU, Y., SHARMA, S.K., PENG, Z., LEBLANC, R.M., Polymers, **9**, 2017, p.1, https://doi.org/10.3390/polym9020067.

[47] Better Future Factory, https://betterfuturefactory.com/our-work/. [19.12.2022].

[48] LIN, X., YU, J., LI, H., LAM, J.I.K., SHIH, K., SHAM, I.M.L., LEUNG, C.K.I., J. Hazard. Mater., **357**, 2018, p. 40.

[49] YU, J., YAO, J., LIN, X., LI, H., LAM, J.Y.K., LEUNG, C.K.I., SHAM, I.M.L, SHIH, K., Cem. Concr. Res., **107**, 2018, p. 110.

[50] RANADE, R., LI, V.C., STULTS, M.D., HEARD, W.F., RUSHING, T.S., ACI Mater. J., **110**, no. 4, 2013, p. 413.

[51] LI, Q., HUANG, B., XU, S., ZHOU, B., YU, R.C., Cem. Concr. Res, 90, 2016, p. 174.

[52] CUROSU, I., LIEBSCHER, M., MECHTCHERINE, V., BELLMANN, C., MICHEL, C., Cem. Concr. Res, 98, 2017, p. 71.

[53] XIAO, R., YU, Q., YE, H., SHI, Y., SHENG, Y., ZHANG, M., NOURANI, P., GE, S., J. Build. Eng., **63**, 2023, https://doi.org/10.1016/j.jobe.2022.105445.

[54] KLYOSOV, A.A., Wood-Plastic Composites, John Wiley & Sons, New Jersey, 2007, p. 2-25.

[55] ASHORI, A., Bioresour. Technol., 99, no. 11, 2008, p. 4661.

[56] NANDA, S., REDDY, S.N., HUNTER, H.N., Vo, D-V. N., KOZINSKI, J.A., GOKALP, I., J Supercrit. Fluids, **154**, 2019, https://doi.org/10.1016/j.supflu.2019.104627.

[57] DIEZ, C., MARTINEZ, O., CALVO, L.F., CARA, J., MORAN, A., J. Waste Manag., **24**, no.5, 2004, p. 463.

[58] ZHANG, L., YAN, K., GAO, J-M., CHENG, F., WANG, M., ZHANG, X., GUO, M., ZHANG, M., Constr. Build. Mater., **375**, 2023, https://doi.org/10.1016/j.conbuildmat.2023.130973.

[59] ELBABA, I.F., WU, C., WILLIAMS, P.T., Energy Fuels, **24**, no. 7, 2010, https://doi.org/10.1021/ef100317b.

[60] PORTOFINO, S., DONATELLI, A., IOVANE, P., INNELLA, C., CIVITA, R., MARTINO, M., MATERA, D.A., RUSSO, A., CORNACCHIA, G., GALVAGNO, S., Waste Manag., **33**, no. 3, 2013, p. 672.

[61] CAO, Q., DAI, H.-C., HE, J.-H., WANG, C.-L., ZHOU, C., CHENG, X.-F., LU, J.-M., Appl. Catal. B: Envir., **318**, 2022, https://doi.org/10.1016/j.apcatb.2022.121828.

[62] JIE, X., LI, W., SLOCOMBE, D., GAO, Y., BANERJEE, I., GONZALEZ-CORTES, S., YAO, B., ALMEGREN, H., ALSHIHRI, S., DILWORTH, J., THOMAS, J., XIAO, T., EDWARDS, P., Nat. Catal, **3**, 2020, p. 912.

[63] ALVAREZ, J., KUMAGAI, S., WU, C., YOSHIOKA, T., BILBAO, J., OLAZAR, M., WILLIAMS, P.T., Int. J. Hydrog. Energy, **39**, no. 21, 2014, p.10883.

[64] ZHIJIE, B., NAICI, B., HU-RONG, Y., ZHANG, Y., HUAQING, X., WEI, Y., ACS Appl. Energy Mater., **4**, no. 8, 2021, p.7710, https://doi.org/10.1021/acsaem.1c01061.

[65] WANG, Y., BAILEY, J., ZHU, Y., ZHANG, Y., BOETCHER, S.K.S., YONGLIANG, L., CHUNFEI, W., Waste Manag., **154**, 2022, p. 96.

[66] IANNICIELLO, L., BIWOLE, P.H., ACHARD, P., J. Power Sources, **378**, 2018, p. 383, https://doi.org/10.1016/j.jpowsour.2017.12.071.

[67] MISKOLCZI, N., ANGYAL, A., BARTHA, L., VALKAI, I., Fuel Process. Technol., **90**, no. 7-8, 2009, p. 1032.

[68] LEE, S., YOSHIDA, K., YOSHIKAWA, K., Energy Environ. Sci., **5**, no. 1, 2015, http://doi.org/10.5539/eer.v5n1p18.

[69] MOHAN, R.K., SAROJINI, J., AGBULUT, U., RAJAK, U., VERMA, T.N., REDDY, K.T., Energy, **275**, 2023, https://doi.org/10.1016/j.energy.2023.127374.

[70] MIRKARIMI, S.M.R., BENSAID, S., CHIARAMONTI, D., Appl. Energy, **327**, 2022, https://doi.org/10.1016/j.apenergy.2022.120040.

[71] ABHIJIT, M., SANDEEP, S., SINGH, A.A., ARORA, S., Resour. Conserv. Recycl., 161, 2020, https://doi.org/10.1016/j.resconrec.2020.104915.

[72] SANDID, G., PETERS, G.M., J. Clean. Prod., **184**, 2018, p. 353, https://doi.org/10.1016/j.jclepro.2018.02.266.

[73] RAMAMOORTHY, S.K., SKRIFVARS, M., ALAGAR, R., AKHTAR, N., J. Polym. Environ., **26**, 2018, p. 487.

[74] Saperatec, https://www.saperatec.de/en/. [27.04 2023].

[75] GHOSH, S., MAKEEV, M.A., ZHIMIN, Q., WANG, H., R., RAJPUT, N.N., SURENDRA, K.M., VILAS, G.P., ACS Sustain. Chem. Eng., **8**, no. 16, 2020, p. 6252, https://doi.org/10.1021/acssuschemeng.9b07684.

[76] KO, S., KWON, Y.J., LEE, J.U., JEON, Y.-P., J. Ind. Eng. Chem., 83, 2020, p. 449.

[77] KAMALI, A.R., YANG, J., SUN, Q., Appl. Surf. Sci., 476, 2019, p. 539.

[78] EL ESSAWY, N.A., SAFA M.A., FARAG, H.A., KONSOWA, A.H., ELNOUBY, M., HAMAD, H.A., Ecotoxicol. Environ. Saf., **145**, 2017, p. 57.

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