APPLICATION NOTE

MICROWAVE ENHANCED ALKALINE HYDROLYSIS OF POLYETHYLENE TEREPHTHALATE (PET)

PROBLEM

Many synthetic polymers are (relatively) chemically inert and break down very slowly in the environment. Consequently, plastic pollution has become an increasingly critical environmental problem since these materials came into everyday use in the last century. Both terrestrial landfills and natural aquatic environments are beginning to overflow with plastic waste that remains intact. Plastic waste in aquatic environments is especially problematic as it is an active killer of marine life. These factors have made it imperative that society find effective ways to either recycle or destroy plastic waste.

BACKGROUND

Plastics (polymers) are ubiquitous in modern society. Since the 1907 invention of the first synthetic polymer by the Belgian chemist, Leo Hendrik Baekeland (the phenolic resin polyoxybenzylmethyleneglycolanhydride, Bakelite), plastics have become the dominant material used in the manufacture of myriad useful artifacts. Figure 1 (left) displays a graph showing the remarkable increase in total global plastics manufacturing, with annual production growing from two million tonnes in 1950 to 460 million tonnes in 2019. Global plastics production has doubled in the last decade alone. The righthand graph in Figure 1 shows the cumulative global plastics production between 1950 and 2019. The cumulative mass of plastics produced by 2019 was 9.5 billion tonnes.

The intractable nature of plastics waste has become a significant issue in terms of environmental pollution. Figure 2 shows the fate of plastic waste, globally and regionally. While it appears that the more developed regions (Europe, USA) are handling plastics waste more efficiently (6% and 4% of plastic waste mismanaged, respectively) the numbers are misleading. Both Europe and the USA offshore much of their plastic waste disposal to the less developed regions. Within those regions, more than a third of the plastic waste is mismanaged and ends up as either terrestrial or marine pollution. These graphs suggest that the total plastic waste that was mismanaged on a global scale in 2019 is over 100 million tonnes.

Plastic waste undergoes physical, chemical, and biological changes in terrestrial and marine environments creating

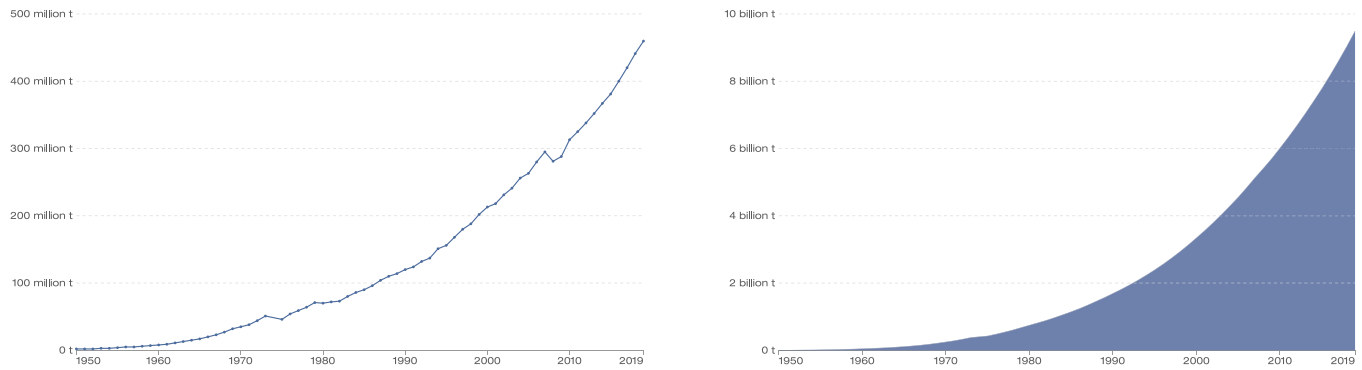

Figure 1 - Global plastic production, 1950-2019 (left); Cumulative global plastic production, 1950-2019 (right) [21].

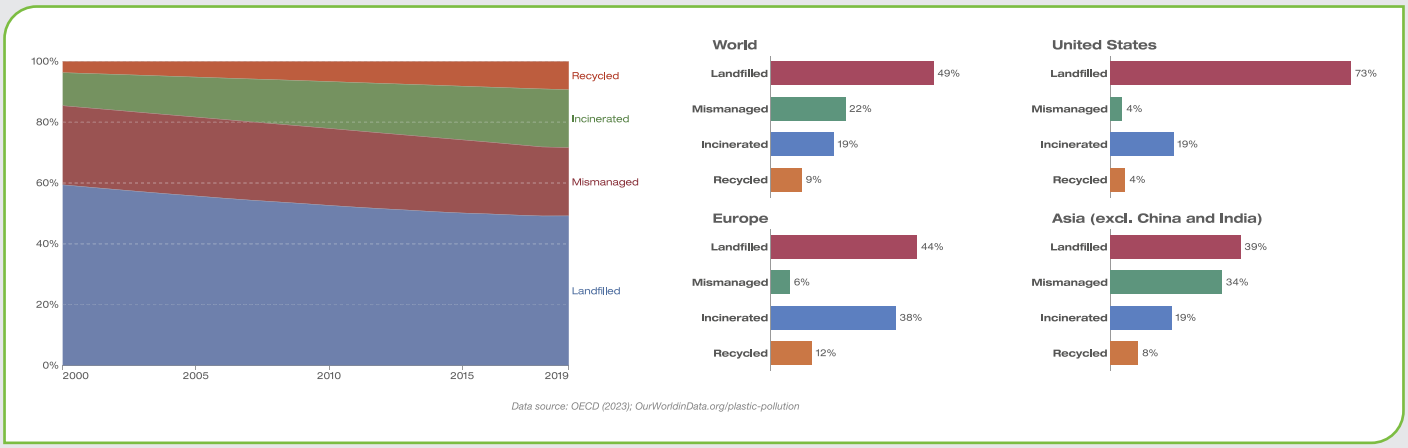

Figure 2 - The fate of plastic waste globally and regionally [21].

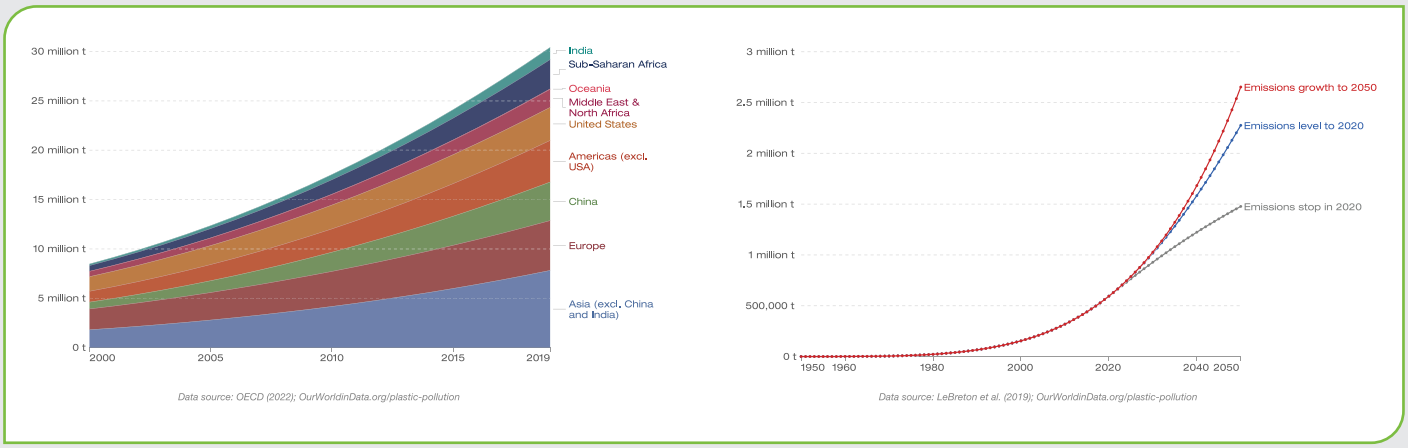

Figure 3 - Microplastic (<0.5 cm diameter) pollution in the surface ocean [21].

microplastic pollution that can produce physical, microbial, and toxicological effects that are hazardous to many species of plants and animals on land and in the ocean [1] [2]. Figure 3 shows the level of microplastic pollution currently in the World's oceans, along with a graph showing total (macro and micro) marine plastic pollution. Nearly 140 million tonnes of plastic waste are projected to be present in marine environments (rivers, lakes, and oceans) in 2019, with roughly 560,000 tonnes in the form of oceanic microplastics that are nearly impossible to remediate. This pollution will not disappear on its own. Figure 4 shows the long lifetimes, extending into hundreds of years, that various types of plastic waste have in marine environments.

Global recycling of polymers that prevents their introduction into natural environments is thus a critical priority for the future of environmental sustainability. Theoretically, recycling polymers such as polyolefins, polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET), can be accomplished using methods such as primary recycling, mechanical recycling, chemical recycling, and energy recovery. Recycling plastic waste for reuse is, however, a complex and often energy-intensive process. Primary and mechanical recycling of plastic waste must first sort the plastics in terms of their original use or their chemical nature. Then the waste must be cleaned and dried. Primary recycling then routes the waste to be reused for its original purpose, while mechanical recycling further processes it with grinding, re-granulation, and compounding that make it suitable as a raw material for plastic manufacturing.

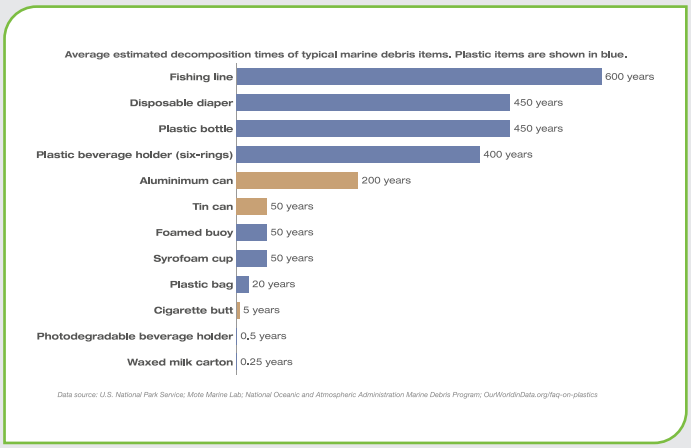

Figure 4 - Degradation rates of plastic items in marine environments [21]

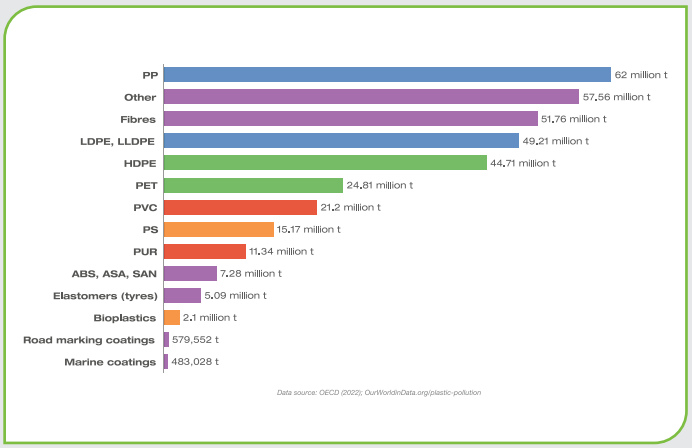

Figure 5 - Global plastic waste generation, by polymer, 2019 [21].

Chemical recycling further breaks down the plastic waste to recover the molecular species used to produce the original polymer. For instance, PET can be chemically recycled to recover the monomers mono-ethylene glycol (MEG) and parateraphthalic acid (pTPA). These then can be used to produce virgin PET. Finally, incineration of plastic waste can provide simple energy recovery (since the plastic waste is flammable and acts as a co-fuel in the incinerator). This is the simplest way to recycle plastic waste and between a quarter and a third of global plastic waste is incinerated, presumably with some form of energy recovery (see Figure 2). This latter route is, however, the least environmentally sound practice since it reduces a complex material with a high material and energy production cost into a polluting greenhouse gas. Furthermore, incineration of plastic waste often releases toxic contaminants such as dioxins, furans, mercury, and polychlorinated biphenyls into the atmosphere. Primary, mechanical, and chemical recycling of plastic waste are thus preferred as sustainable methods for plastic recycling. Chemical recycling is of particular interest since, once recovered, the monomers can be put to use as feedstock in different chemical manufacturing processes. However, chemical recycling requires long reaction times and high energy consumption. There is strong interest, therefore, in finding chemical recycling processes that operate more quickly and with a lower energy penalty.

SOLUTION

Polyethylene terephthalate, is a semi-crystalline thermoplastic polyester. It is widely used in applications ranging from its dominant use in single-use plastic bottles to lesser quantities employed in carpet and textile manufacturing. It accounts for a significant fraction of global plastic waste (~7%, Figure 5). There is a high demand for recycled polyethylene terephthalate (rPET) driven by an increase in environmental awareness, the application of more restrictive environmental legislations, and the magnitude of post-consumer PET plastic waste. This has resulted in an urgent need for efficient recycling processes. In this work, solvolysis is presented as a promising chemical recycling for the treatment of PET waste. MKS Industrial Microwave Generators (Figure 6) are compact, reliable microwave power sources for use in the microwave-assisted depolymerization of PET.

Chemical recycling of PET waste is currently the subject of a significant research effort [3] [4] owing to the relative ease with which polyesters can be depolymerized [5]. PET can be converted to the monomers, terephthalic acid (TPA), or dimethyl terephthalate (DMT), using common reagents such as water or methanol. One promising class of reactions currently being explored involves the depolymerization of the PET polymer through solvolysis reactions. Solvolysis is a sustainable approach that converts PET waste into oligomers and monomers [4]. The various solvolytic depolymerization reactions for PET are shown in Figure 7.

Figure 6 - MKS industrial microwave generators.

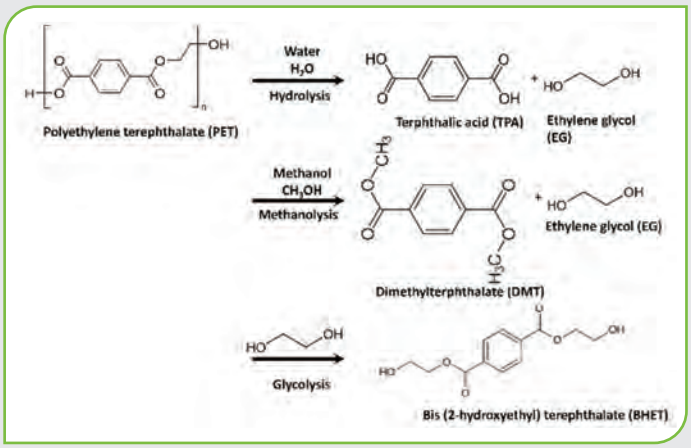

Figure 7 - Depolymerization reactions for PET.

Glycolysis, depolymerization in ethylene glycol (EG) solvent, is of particular interest for PET waste treatment since it requires relatively mild reaction conditions and produces bis (2-hydroxyethyl) terephthalate (BHET), the true monomer in PET polymerization processes. PET glycolysis is well-studied, with the first process patented in 1965 [6] and commercial processes in place in Europe and Japan. PET glycolysis processes have continued to be patented to the present day [7].

Conventional PET solvolysis processes suffer from certain drawbacks. Typically, all require long reaction times. Hydrolysis requires acid or alkaline solutions which can cause severe corrosion to equipment. Methanolysis requires high temperatures (>200°C), and high pressures (>2 MPa, 290 psi). Glycolysis, while it requires low reaction temperatures (<190°C) and is free of the need for corrosive catalysts, still requires a relatively long reaction time to produce relatively low BHET yields. These issues pose significant problems for the large-scale commercial application of PET glycolysis processes.

Long reaction times and dangerous or costly reaction requirements can be ameliorated using microwave energy. The use of microwaves does not alter the basic thermodynamics of chemical reactions. However, microwave irradiation enables more direct and controllable coupling of energy into the reaction system, increasing the efficiency and rate of reaction. Under microwave irradiation, the dipoles of polar molecules rotate as they align with the alternating electromagnetic field (915 or 2450 million times per second, depending on the frequency employed). Molecular collisions convert this rotational energy to translational energy which defines thermal energy (i.e., heat) contained within the system. The ability of a material to convert electromagnetic energy into heat (at a given frequency and temperature) is determined by its dielectric loss tangent ($\tan\delta = \varepsilon''/\varepsilon'$) [8]. Microwave promotion has been successfully employed in microwave-assisted pyrolysis of different plastic wastes [9] [10] [11] and microwave-assisted processes have exhibited unique advantages over conventional pyrolysis in terms of reduced reaction times, simplification of reaction mixtures, reaction control and product selectivity. The high $\tan\delta$ of ethylene glycol allows direct microwave heating of the solvent/reactant in the PET glycolysis process. This makes EG an ideal solvent for the microwave-assisted depolymerization of PET. Microwave-assisted depolymerization of PET has been the subject of various patents [12] [13] [14] and literature reports [15] [16] [17] [18]. As well, the microwave-assisted depolymerization processes are beginning to see commercial use in Europe and Japan with a demonstration-scale plant for PET recycling recently announced for Northern Italy [19]. As well, Asahi Kasei and Microwave Chemical in Japan have launched a joint demonstration project for chemical recycling of polyamide 66 using microwave-based technology [20]. Figure 8 shows a proposed process flowsheet for the microwave-assisted glycolysis of PET to produce BHET [16].

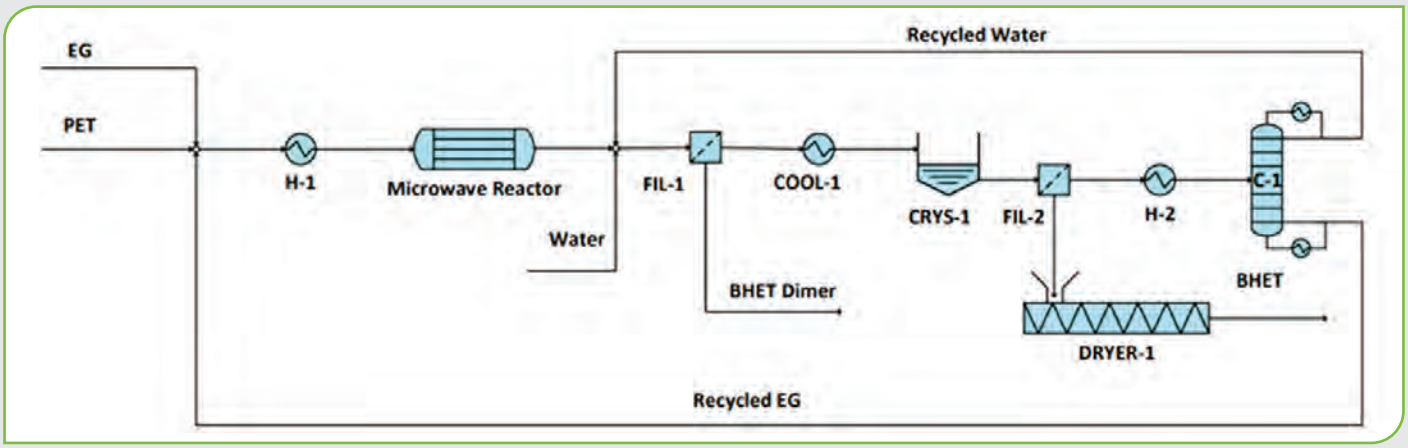

Figure 8 - Proposed process flowsheet for microwave-assisted glycolysis of PET waste [16].

MKS offers the 915 MHz GS Series and the 2450 MHz Industrial Microwave Generators. The 915 MHz GS Series generators provide 15 to 100 kW of microwave power, depending on the model. Power is delivered from a shielded cabinet with continuous powerline control, safety interlocks, various interface options, and optional remote control. The 2450 MHz generators are designed as rugged and reliable switch mode power supplies for demanding industrial applications. These are compact generators that deliver up to 15 kW of microwave power in a 19-inch standard rack with a remote head and integrated isolator. All MKS microwave generators are equipped with switch mode topology for all power ranges and support a variety of fieldbus communications protocols.

CONCLUSION

Plastic waste has become a critical problem for pollution control. Comprehensive studies have found that the ubiquitous presence of macro-, micro-, and nano-particles of plastic in our marine and terrestrial environments can cause significant harm to many plant and animal species through physical, biological, and toxicological effects. Consequently, processes for the recycling of plastic waste have become important contributors to efforts aimed at establishing sustainability in our civilization.

Microwave-assisted depolymerization processes are promising as sustainable technologies for recycling plastic waste. Literature reports have shown that polyethylene terephthalate, PET, can be readily depolymerized to useful monomers and oligomers using different microwave-assisted reactions. The most promising of these routes for microwave-assisted PET depolymerization is solvolysis in which water, methanol, or glycol, for example, can be reacted with PET to produce monomers and oligomers.

MKS industrial microwave generators are ideally suited for use in microwave-assisted depolymerization reactors. They provide the maximum achievable microwave power (up to 100 kW) for the large-scale depolymerization processes needed in plastic recycling systems. They are designed for rugged and reliable operation with the necessary interlocks and controls for service in industrial settings.

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APP NOTE - Alkaline Hydrolysis PET_03/25

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