Feedstock Recycling of Plastic Wastes

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Feedstock Recycling of Plastic Wastes
by J. Aguado, *Rey Juan Carlos University, Móstoles, Spain*; D.P. Serrano, *Complutense University of Madrid, Spain*

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Preface

The use of plastic materials in daily life has continuously increased over the last 30 years. The amount of plastic consumed per inhabitant in the industrialized countries has increased by a factor of 60 over this period, while the generation of plastic wastes has grown at a similar rate. Thus, over 17.5 million tonnes of plastic wastes are generated per year in Western Europe, their environmental impact being a matter of great public concern. The variation in properties and chemical composition between different types of plastic materials hinders the application of an integrated and general approach to handling these plastic wastes. The light weight of plastic goods, and the fact that plastic wastes are mainly found in MSW (municipal solid waste) mixed with other classes of residues, are factors that greatly limit their recycling. As a consequence, the primary destination of plastic wastes is landfill sites, where they remain for decades due to their slow degradation. In 1996, only around 10% of the plastic wastes generated in Europe were recycled, whereas over 70% were disposed of in landfills.

At present, there are three main alternatives for the management of plastic wastes in addition to landfilling: (i) mechanical recycling by melting and regranulation of the used plastics, (ii) feedstock recycling and (iii) energy recovery. Mechanical recycling is limited both by the low purity of the polymeric wastes and the limited market for the recycled products. Recycled polymers only have commercial applications when the plastic wastes have been subjected to a previous separation by resin; recycled mixed plastics can only be used in undemanding applications. On the other hand, energy recovery by incineration, although an efficient alternative for the removal of solid wastes, is the subject of great public concern due to the contribution of combustion gases to atmospheric pollution. There has also been some controversy in the past about the possible relationship between dioxin formation and the presence of Cl-containing plastics in the waste stream.

Consequently, feedstock recycling appears as a potentially interesting approach, based on the conversion of plastic wastes into valuable chemicals useful as fuels or as raw materials for the chemical industry. The cleavage and degradation of the polymer chains may be promoted by temperature, chemical agents, catalysts, *etc*.

The aim of this work is to describe and review the different alternatives developed for the feedstock recycling of plastic wastes, with emphasis on both the scientific and technical aspects. Due to the wide variety of plastic types, the work focuses on the major polymers present in household and industrial plastic wastes: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polyurethanes (PU) and polyamides (PA). These plastics account for more than 90% of total plastic wastes. Although elastomers are not usually considered as plastic materials, the book also covers the feedstock recycling of rubber wastes, mainly used tyres. This is supported by the fact that a number of degradation treatments have been developed which can be used for both plastic and rubber wastes.

Five main types of feedstock recycling processes have been considered: chemical depolymerization, gasification and partial oxidation, thermal degradation, catalytic cracking and reforming, and hydrogenation. Each of these alternatives is reviewed in an independent chapter, highlighting the most recent progress with extensive literature references. Besides conventional treatments (pyrolysis, gasification, *etc.*), the book includes new technological approaches for the degradation of plastics such as conversion under supercritical conditions and coprocessing with coal.

The first chapter gives a general introduction to the types and applications of polymeric materials, as well as to the various plastic waste management and recycling alternatives. Data are provided about the volume of plastic wastes generated, their origin and their composition. Previous separation and classification of the plastics is required in many feedstock recycling processes, and so the different methods available for plastic sorting are described: manual, density differences, selective dissolution, automated methods based on spectroscopic techniques, *etc.*

Chapter 2 discusses depolymerization processes based on the chemical cleavage of polymer molecules to convert them back into the raw monomers. The latter can be reused in the manufacture of new polymers, with properties similar to those of the virgin resins. However, this alternative is mainly used for condensation polymers, and is not successful for the degradation of most addition polymers. Glycolysis, methanolysis, hydrolysis and ammonolysis are the main treatments considered. Chemical depolymerization of polyesters, polyurethanes and polyamides is reviewed.

Chapter 3 deals mainly with gasification processes leading to synthesis gas, which is a mixture useful for the preparation of a variety of chemical products (ammonia, methanol, hydrocarbons, *etc.*). Gasification processes based on treatment with oxygen, air and steam are described. In many cases, gasification of plastic wastes takes place simultaneously with that of other organic residues, coal and petroleum fractions. In addition to gasification, other degradation alternatives based on partial oxidation methods are described in this chapter.

The degradation of plastic wastes by thermal treatments in the absence of oxygen is reviewed in Chapter 4. Depending on the raw polymer and the degradation conditions, a variety of thermal processes have been considered: thermal depolymerization into the raw monomers, thermal cracking, pyrolysis, steam cracking and thermal treatment in the presence of solvents. For each treatment both the products derived and the different types of reactors used are described.

Chapter 5 is devoted to catalytic processes for plastic waste recycling. Through selection of the right catalysts, the plastic degradation can be used to obtain a number of valuable products. The properties of the main types of catalysts are reviewed. Both direct catalytic cracking processes, and the combination of a previous thermal cracking of the plastic wastes with a catalytic reforming of the gases generated in the former are considered.

Chapter 6 deals with hydrogenation processes, usually based on the use of bifunctional catalysts. Plastic and rubber degradation in a hydrogen atmosphere is an effective treatment yielding highly saturated oils. Coliquefaction of plastics or rubber with coal is also considered.

The last chapter highlights the main conclusions and establishes a comparative study of the various alternatives for the feedstock recycling of plastic wastes. The final conclusion is that feedstock recycling of both plastic and rubber wastes has a high potential for growth in the next few years, although to be commercially successful a number of technical and economic aspects still have to be addressed.

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We are indebted to those who took the time to help us in drawing many of the figures and schemes in this book: Raul Sanz, José M. Escola, Rafael Garcia, Luis M. Garcia and Araceli Rodriguez. We also greatly appreciate the efforts and work of Prof. Rafael van Grieken, who patiently reviewed all the chapters. Finally, we would like to thank all those colleagues that gave permission for the reproduction of figures from their work.

To Maribel and to Juany

Contents

CHAPTER 1

Introduction

1 Significance of Plastic Materials in Today's Society

Plastics are not, as many people believe, new materials. Their origin can be traced to 1847 when Shönbein produced the first thermoplastic resin, celluloid, by reaction of cellulose with nitric acid. However, the general acceptance and commercialization of plastics began during the Second World War when natural polymers, such as natural rubber, were in short supply. Thus, polystyrene was developed in 1937, low density polyethylene in 1941, whereas other commodity plastics such as high density polyethylene and polypropylene were introduced in 1957.

Today, plastics are very important materials having widespread use in the manufacture of a variety of products including packaging, textiles, floor coverings, pipes, foams, and car and furniture components. Plastics are synthesized mainly from petroleum-derived chemicals, although only about 4% of total petroleum production is used in the manufacture of plastics.

The main reasons for the continuous increase in the demand for commodity plastics are as follows:

- Plastics are low density solids, which makes it possible to produce lightweight objects.
- Plastics have low thermal and electric conductivities, hence they are widely used for insulation purposes.
- Plastics are easily moulded into desired shapes.
- Plastics usually exhibit high corrosion resistance and low degradation rates and are highly durable materials.
- Plastics are low-cost materials.

Engineering plastics, particularly thermosets, are also used in composite materials. Their excellent technological properties make them suitable for applications in cars, ships, aircraft, telecommunications equipment, *etc.* In recent years, important new areas of application for plastics have emerged in medicine (fabrication of artificial organs, orthopaedic implants, and devices for the controlled release of drugs), electronics (development of conductive polymers for semiconductor circuits, conductive paints, and electronic shielding), and computer technology (use of polymers with non-linear optical properties for optical data storage).

The above paragraphs show that today plastic materials are used in almost all areas of daily life. Accordingly, the production and transformation of plastics are major worldwide industries. Consumption of plastics in Western Europe is forecast to grow from 24.9 million tonnes in 1995 up to about 37 million tonnes in 2006,[1] an annual growth rate of 4%. This prediction places plastics among the most important materials in the next century also.

Table 1.1 summarizes the changes in total plastic consumption in Western Europe from 1992 to 1996.[2] These data refer to the final market for plastic products consumed by end-users but they do not include sectors such as textile fibres, elastomers, coatings, or products in which plastics are present in small quantities, because these are not considered as plastic products. If non-plastic applications are also taken into account, the total plastic consumption in Western Europe in 1996 increases up to 33.4 million tonnes. By comparison, the consumption of plastics in the USA and Japan in 1995 were 33.9 and 11.3 million tonnes, respectively.[3]

The main sectors of plastic consumption in Western Europe are shown in Figure 1.1. The major field of plastic consumption is packaging, accounting for more than 40% of the total volume, followed by the building and automotive sectors. The most important uses of plastics in packaging are the production of films and sheets, sacks, bags, bottles and foams. In the building sector, plastics are used in a variety of applications: insulation, floor and wall coverings, window and door profiles, pipes, *etc.* The automotive sector is a good example of the continuous increase in the use of plastic materials. A car's weight can be reduced by 100–200 kg through the replacement of conventional metallic materials by plastics. Fuel tanks, bumpers, bonnets, insulation, seats, dashboards, textiles, batteries, *etc.* are examples of car components commonly manufactured with plastic materials. Plastics are used for a variety of applications in the agricultural sector such as greenhouses, tunnel and silage films, pipes for both drainage and irrigation, drums and tanks, *etc.*

Figure 1.2 illustrates plastic consumption in Western Europe by product for 1995,[4] confirming that plastics are versatile materials which can be found in a wide range of products. The production and consumption of plastics have continuously increased over recent decades. The plastic consumption per capita in Western Europe has increased from ~1 kg per inhabitant in 1960 to about 65 kg per inhabitant in 1995.

Table 1.1 *Total plastic consumption in Western Europe (based on reference 2)*

Year	1992	1993	1994	1995	1996
Plastic consumption (million tonnes)	24 730	24 360	26 260	24 909	25 905

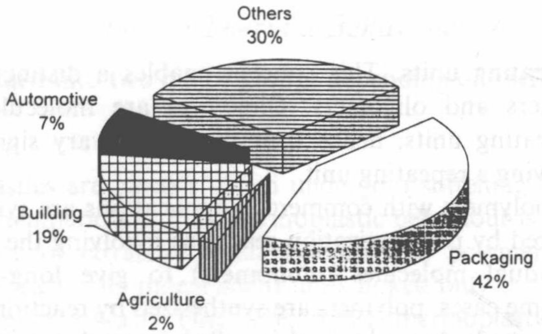

Figure 1.1 *Plastic consumption by sector in Western Europe (1996).*[2]

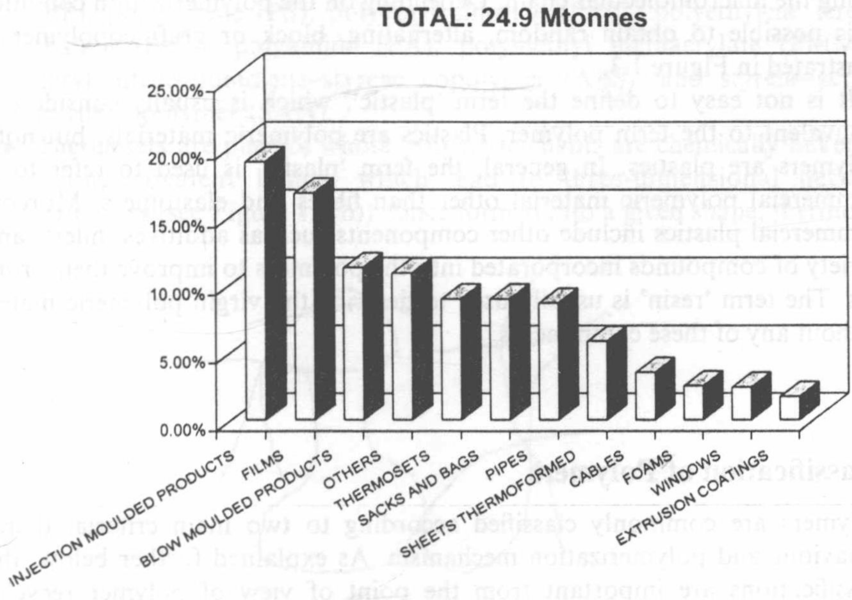

Figure 1.2 *Plastic consumption by product in Western Europe (1995).*[4]

2 Classes of Organic Polymers and their Main Applications

Polymers are long-chain molecules composed of a large number of identical units called repeating units. A polymer can be expressed as follows:

$$—(RU)_n—$$

where RU is the repeating unit and n the number of units present in the polymer molecule. The number of repeating units must be large enough that no variations in the polymer macroscopic properties occur by small changes in the number of repeating units. This concept enables a distinction to be made between polymers and oligomers. Oligomers are molecules with a small number of repeating units, hence their properties vary significantly by just adding or removing a repeating unit.

Most of the polymers with commercial applications are synthetic materials. They are prepared by polymerization reactions involving the chemical linkage of small individual molecules (monomers) to give long-chain polymeric molecules. In some cases, polymers are synthesized by reaction between several monomers. The product so obtained is called a copolymer while the starting molecules are known as comonomers. The structure of copolymers depends on both the relative proportion and the sequence of the different comonomers along the macromolecular chain. Depending on the polymerization conditions, it is possible to obtain random, alternating, block or graft copolymers, as illustrated in Figure 1.3.

It is not easy to define the term 'plastic', which is usually considered as equivalent to the term polymer. Plastics are polymeric materials, but not all polymers are plastics. In general, the term 'plastic' is used to refer to any commercial polymeric material other than fibres and elastomers. Moreover, commercial plastics include other components such as additives, fillers, and a variety of compounds incorporated into the polymers to improve their properties. The term 'resin' is usually used to describe the virgin polymeric material without any of these components.

Classification of Polymers

Polymers are commonly classified according to two main criteria: thermal behaviour and polymerization mechanism. As explained further below, these classifications are important from the point of view of polymer recycling, because the most suitable method for the degradation of a given polymer is closely related to both its thermal properties and its polymerization mechanism.

Figure 1.3 *Possible structures of copolymers containing A and B repeating units:* (a) *random,* (b) *alternating,* (c) *block,* (d) *graft.*