POLYMERIZATION REACTORS

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Contents

Summary

This chapter focuses on the reaction engineering aspects of the production of polymers. This includes an overview of the historical developments in this field and a description of the wide variety of applications of polymeric products. Also, the different types of polymerization mechanisms are discussed. Based on this, the types of reactors used for polymerizations are described, including a number of important phenomena that determine the performance, such as mixing effects and heat control. A distinction is made between reactors for homogeneous polymerization, emulsion polymerization and polycondensations. Finally, potential future directions are given, with emphasis on product-inspired polymer reaction engineering.

1. Polymers

Synthetic polymers can be denoted as the materials of the 20th century. Since World War II the production volume of polymers has increased by a factor of 50 to a current value of more than 120 million tons annually (Figure 1). Also the consumption per capita has increased over the years to a worldwide average of approximately 20 kg/annum in the year 2000. In terms of volumetric output, the production of polymers exceeds that of iron and steel. The enormous growth of synthetic polymers is due tot the fact that they are light-weight materials, act as insulators for electricity and heat, cover a wide range of properties, from soft packaging materials to fibers stronger than steel, and allow for relatively easy processing. Moreover, parts with complex shapes can be made at low cost and at high speed by shaping polymers or monomers in the liquid state.

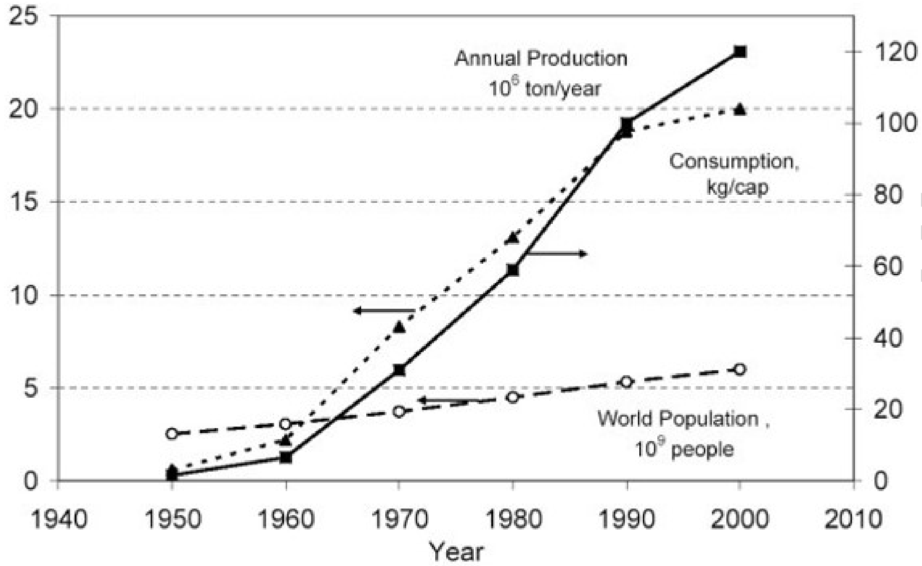

Figure 1. Polymer production and the evolution of the population during the last 50 years.

The polymer market can be divided into thermoplastics and thermosets. The major thermoplastics include high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene terephtalate (PET), polypropylene (PP), polystyrene (PS and EPS), polyvinyl chloride (PVC), polyamide (PA), polymethylmethacrylate (PMMA) and styrene copolymers (ABS, SAN). The most important applications of thermoplastics are summarized in Table 1. The total Western Europe demand for thermoplastics has been 37.4 million tons in 2002, a growth of about 9% as compared to 2001. Thermoplastics are not only used in the manufacture of many typical plastics applications such as packaging and automotive parts, but also in non-plastic applications such as textile fibers and coatings. These non-plastic applications account for about 14% of all thermoplastics consumed.

Thermoplastic	**Market $*10^3$ tons)**	**Applications**
LDPE	7935	pallet and agricultural film, bags, toys, coatings, containers, pipes
PP	7803	film, battery cases, microwave-proof containers, crates, automotive parts, electrical components
PVC	5792	window frames, pipes, flooring, wallpaper,

		bottles, cling film, toys, guttering, cable insulation, credit cards, medical products
HDPE	5269	containers, toys, housewares, industrial wrappings and films, pipes
PET	3234	bottles, textile fibers, film food packaging
PS/EPS	3279	electrical appliances, thermal insulation, tape cassettes, cups and plates, toys
PA	1399	film for food packaging (oil, cheese, "boil-in-bag"), high-temperature engineering applications, textile fibers
ABS/SAN	788	general appliance moldings
PMMA	317	transparent all-weather sheet, electrical insulators, bathroom units, automotive parts

Table 1. Applications and 2002 Western European markets for the major thermoplastics.

The major thermosets include epoxy resins, phenolics and polyurethanes (PU), for which the major applications are summarized in Table 2. It has to be noted, however, that about one third of the market for thermosets is for relatively small-scale specialty products. The total Western European market for thermosets has been 10.4 million tons in 2002, about 1% below the 2001 value.

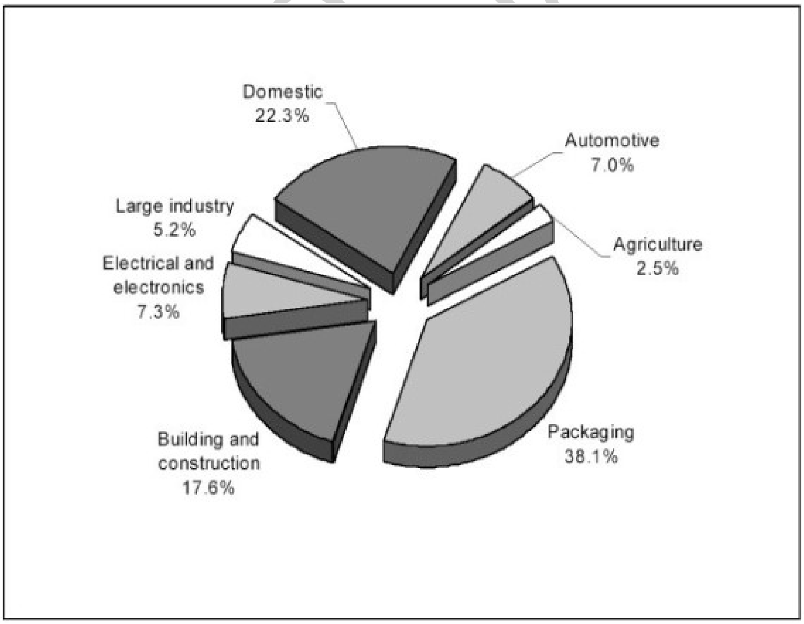

Figure 2. Plastic consumption in 2002 by industry sectors in Western Europe.

Thermoset	**Market $*10^3$ tons)**	**Applications**
PU	3089	coatings, finishes, cushions, mattresses, vehicle seats

Phenolics	912	general appliance moldingsadhesives, appliances, automotive parts, electrical component
Epoxy resins	420	adhesives, automotive components, E&E components, sports equipment, boat

Table 2. Applications and 2002 Western European markets for the major thermosets.

The major application areas of polymers can be defined as follows (Figure 2).

Automotive. Motorists want high-performing cars combined with reliability, safety, comfort, competitive pricing, fuel efficiency and, increasingly, reassurance about the impact on the environment. Lightweight polymeric materials are increasingly used in this sector (Daimler Benz' Smart is a nice example), also contributing to a 10% reduction in passenger fuel consumption across Europe.

Building and construction. Polymeric materials are used in the building and construction sector e.g. for insulation, piping and window frames. In 2002 this sector accounts for 17.6% of the total polymer consumption.

Electrical and electronic. Many applications in this field arise from newly designed polymeric materials, e.g. for polymeric solar cells and holographic films. It is interesting to note, that while the number of applications in this field is increasing, the weight of the polymers used per unit decreases.

Packaging. The packaging sector remains the largest consumer of synthetic polymers, approximately 38% of the total market. This is mainly due to the fact that these materials are lightweight, flexible and easy to process, thereby increasingly substituting other materials. Although polymer packaging ranks first in terms of units sold, they are only third if judged on weight.

Agriculture. As agricultural applications account for about 2.5% of the total of synthetic polymers consumed in Europe, they only play a marginal role. Irrigation and drainage systems provide effective solutions to crop growing, and polymeric films and greenhouses can increase horticultural production substantially. The use of so-called "super absorbers" for increased irrigation efficiency in arid areas can be considered an important emerging market.

2. A Short History of Polymer Reaction Engineering

In Table 3 a comprehensive overview of the major developments in the polymer industry is given. In the 19th century, polymers produced by nature like cellulose, *Hevea brasiliensis* latex (= natural rubber), and starch, are processed to manufacture useful products. This was often based on experimental discoveries. As an example, in 1839 Goodyear discovered by mistake the sulfur vulcanization of natural rubber allowing Ford to develop the automotive market. By those times no polymers were produced synthetically.

19th century	**Natural polymer and derivatives (vulcanized rubber, celluloid)**
1920	Concept of macromolecules postulated by Staudinger
1930-1940	First systematic synthesis of polymers Polyamides (Nylon) by Carothers at DuPont Discovery of polyethylene at ICI (Fawcett and Gibson)
1940-1950	Synthetic rubbers and synthetic fibers
1950-1960	Stereospecific polymerizations by Ziegler and Natta, the birth of polypropylene Discovery of polymer single crystals (Keller, Fischer, Till) Development of polycarbonate
1960-1970	Discovery of PPO at GE by Hay and commercialization of PPO/PS blends (Noryl)
1970-1980	Liquid crystalline polymers
1980-1990	Superstrong fibers (Aramid, Polyethylene) Functional polymers (conductive, light-emitting)
1990-2000	Metallocene-based catalysts; novel polyolefins Hybrid systems (polymer/ceramic, polymer/metals)
2000-	Nature-inspired catalysts Synthesis of polymers by bacteria and plants

Table 3. The history of polymers in brief

In the beginning of 20th century, the first empirical description of macromolecules is developed by Staudinger in 1920. At the same time, new methods are developed to determine the specific characteristics of these materials. Since the 1930s many research groups (e.g. those of Kuhn, Chalmers, Mark, Schulz and Flory) have developed models for the chain length distribution in batch reactors resulting from different polymer chemistries, a methodology that has been further developed in the 1940s leading to more complex and comprehensive models, some still being used today.

Around 1940, partly inspired by the Second World War, a more systematic search for new synthetic polymer materials as a replacement for scarce natural materials leads to the development of nylon (DuPont) and polyethylene (ICI). This was followed by the development of synthetic rubbers and synthetic fibers. In the same period, Denbigh was one of the first to introduce chemical reaction engineering concepts in polymer science by considering polymerization reactions both at the chemical and at the process level. A classification of processes in homocontinuous and heterocontinuous was made, depending on the mixing level. This pioneer approach also acted as a catalyst for the further development of polymer reaction engineering.

The development of transition-state-metal based catalysts by Ziegler and Natta has allowed for the development of stereospecific propylene polymerization processes and ethylene polymerization in the fifties. Several process schemes were developed at that time, of which some are still in use. The major problem in the process development has been to deal with the heat of polymerization, an issue that was solved e.g. by using an inert solvent as a heat sink or by flashing monomer followed by condensation outside the reactor. In the same period, polycarbonate and (somewhat later) polypropylene oxide (PPO) were developed. The main characteristic of the polymers developed so far is that they are bulk materials, to be produced in extremely large quantities.

In the seventies, a paradigm shift can be observed when polymers with more specific properties start to be produced. This includes various liquid crystalline polymers, e.g. leading to the production of superstrong fibers like Aramid®/Kevlar® . Also the development of functional polymers for the conduction of light and electricity and optical switches now starts. In the near future this will probably lead to highly effective and flexible polymer solar cells.

In the nineties, metallocene catalysts are developed for polyolefin production that surpasses the Ziegler-Natta catalysts in terms of selectivity and reactivity. Also, various hybrid materials are combining properties of both the polymer (lightweight, flexible) and a solid material, which can be metal (conductive) or ceramic (insulator), leading to materials with specific properties, e.g. as protective coatings.

Current developments include the mimicking of nature (enzymes) for the synthesis of rather complex polymers like natural silk. Also, bacteria and plants are being modified to produce polymers of interest. However, it can be anticipated that this will require polymer reaction engineering developments that are yet difficult to oversee.

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Biographical Sketches

Thierry Meyer, born 1961 in Geneva, obtained his MSc at the Swiss Federal Institute of Technology in Lausanne (EPFL) in 1985 followed by a PhD in 1989 in chemical engineering in 1989. He joined Ciba-Geigy in 1994 as a development chemist in the pigment division, then was head of development a.i. and became production manager in 1998. In 1999 he switched to the Institute of Chemical Sciences and Engineering at EPFL, heading the polymer reaction engineering unit. Since 2002, he also serves as the chairman of the working party on polymer reaction engineering of the European Federation of Chemical Engineering.

Jos Keurentjes (1963) did his MSc at the Wageningen Agricultural University, followed by a PhD in food engineering at the same university (1991). Subsequently, he joined Akzo Nobel Central Research as a researcher in the department of chemical and physical technology, followed by a position heading separation technology. In 1997 he switched to the Eindhoven University of Technology holding the chair on process development. Starting 2002, he also serves as scientific secretary of the working party on polymer reaction engineering of the European Federation of Chemical Engineering.