Supplementary Information

Expanding Plastics Recycling Technologies: Chemical Aspects, Technology Status and Challenges

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KEYWORDS: Plastics, waste, recycling, decomposition, energy, commercial

SI 1.0 Manufacture of Plastics and the Environmental Footprint of Plastics Disposal

From the discovery of vulcanization by Charles Goodyear in 1839, to the production of Bakelite, the first synthetic polymer, by Leo Hendrik Baekeland in 1907, to the production of HDPE in 1953 through the combined research of Karl Ziegler and Giuglio Natta, the history, knowledge, and application of plastics in our daily lives is only a fraction of our human history, yet they comprise some of the most well-known and utilized materials to date. Table 1 contains common commercial polymers and illustrates the gaps between their discovery and industrial production. As our technologies advance, and our knowledge regarding material science and polymer behavior expands, the gaps between the first laboratory synthesis of a polymeric material and its industrial production and application has closed.
{Canevarolo, 2020 #5}

Table S1. Primary occurrence and industrial production of some commercial polymers.[1]

Polymer	Resin Classification Code	Discovery	1st Industrial Production
Polystyrene (PS)	6	1839	1936/37
Polyvinyl Chloride (PVC)	3	1835	1933
Polyamide (PA)	7	1930	1940
Low-density Polyethylene (LDPE)	4	1933	1939
High-density Polyethylene (HDPE)	2	1953	1955
Polycarbonate (PC)	7	1953	1958
Polypropylene (PP)	5	1954	1959

When the feedstock is ethane, the initiation occurs by bond fission of a C_2H_6 molecule into two CH_3 free radicals:[2]

$$C_2H_6 \rightarrow CH_3 \cdot + CH_3 \cdot$$

Then a chain of reactions occurs as follows:

$$CH_3 \cdot + C_2H_6 \rightarrow CH_4 + C_2H_5 \cdot$$

$$C_2H_5 \cdot \rightarrow C_2H_4 + H \cdot$$

$$H \cdot + C_2H_6 \rightarrow H_2 + C_2H_5 \cdot$$

$$2C_2H_5 \cdot \rightarrow C_4H_{10}$$

$$C_2H_5 \cdot + C_2H_4 \rightarrow C_3H_6 + CH_3 \cdot$$

$$H \cdot + C_2H_4 \rightarrow C_2H_5 \cdot$$

In 2021, there were 35 steam cracking facilities located in the US. Most steam crackers are located in the Gulf region. In the US, total ethylene production capacity is 45 million tons/yr. Meanwhile, an additional five crackers with combined ethylene capacity of 9.1 million tons are under construction or planned. More than 22 power plants are responsible for providing electricity for these steam crackers; the total CO_2 emission of these power plants and steam crackers is up to 70 million tons/yr. Much of the ethylene produced in US is exported. A total of 3.4 million tons of ethylene are shipped to Asia and Europe by ships and 3.2 million tons are sent to Canada and Mexico through pipelines. Nearly half of the plastic resins produced in the US are exported (25 million tons/yr).[3]

Figure S1 shows the number of plastic industry employees for the top 10 states in the US. Among these states, Texas has the highest plastic industry employments (77,000). Access to raw materials is an essential requirement for the plastic industry. Given the reliable natural gas supply, Texas has witnessed an increase in plastics manufacturing in recent years.[4] In addition to the market availability of natural gas, the site must also have a direct connection to the transmission pipelines in the region. It is estimated that the freight transportation network moves approximately 130 million tons of plastic resins annually, which corresponds to 37 percent of total resin shipped. Meanwhile, trucks move approximately 53 percent of plastic resins.[4] Therefore, access to transportation (railway, highway, pipeline) also plays a key role in the plastic industry.

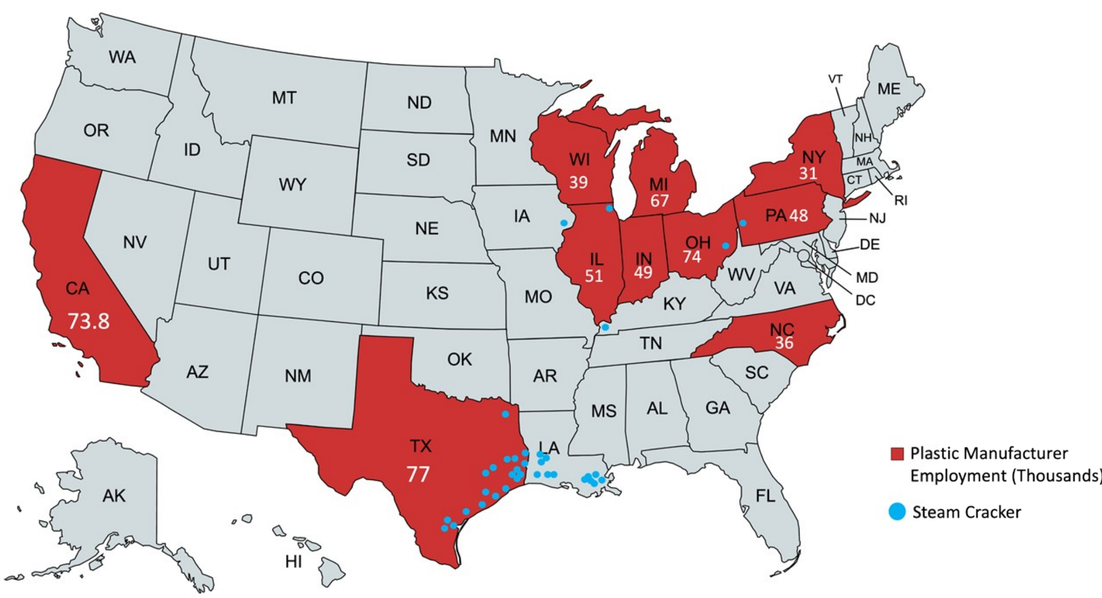

Fig. S1. Number of plastic industry employees and cracking facilities in US.[3-4]

SI 2.0 Mechanical Recycling

SI 2.1 Injection Molding

The main components of the extrusion machine[5] are shown in Figure S2. In terms of extruder design, there are two main types: single-screw extruder and twin-screw extruder. A single screw extruder is preferred in homogeneous recycled plastic extrusion where compounding is not required. Compounding is needed when additional compounds, such as fillers and additives, are introduced into the molten plastic to maintain a desirable quality product. Single-screw extruders can produce many products, including film, foam, and fibers. Twin-screw extruders are used by industry where product processing occurs with less heat friction, uniform shearing, and more controlled extrusion. The screw rotation of twin-screw extruders can be counter-rotating and co-rotating. Different kinds of twin-screw extruders with variable screw designs are used to optimize mixing efficiency and generate different heat generation profiles. For example, they can produce different plastic blends with various plastic viscosities, melting points, and glass transition temperature characteristics. Single-screw extruders are desirable to reprocess post-industrial waste, but twin-screw extruders are chosen over single-screw extruders where multiple materials are run by adding secondary substances (e.g., plasticizer).[6] For example, Erema's 'Corema' technology uses a tailored twin-screw extruder in combination with a single-screw extruder for recycling in a single, continuous step.[7] Their recycling process involves plasticizing and filtering using a single-screw extruder, and the processed plastic melt proceeds with compounding in a twin-screw extruder.[8]

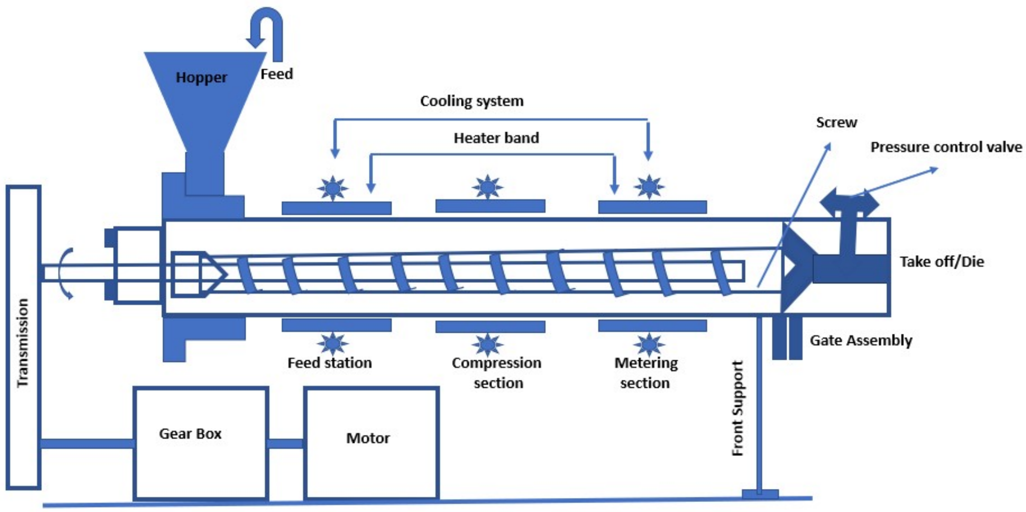

Fig. S2: Single screw extruder.[5, 9]

SI 2.2 Injection Molding

Injection molding produces the desired product from the melted recycled plastic by injecting it into a mold.[10] This technology is similar to the extrusion system except the melted plastic enters a temperature-controlled mold through a nozzle. The amount of plastic entering the mold is controlled by a moving screw. This technique generates desirable final products with complex shapes and high-quality surfaces. Typically, the recycled material comes to the companies after being pelletized at another facility to create the feedstock material for injection molding.[11]

SI 2.3 Blow Molding

Blow molding differs from injection molding or extrusion as it blows the molten plastic against the mold's cavity wall using pressurized air to manufacture parts with a hollow center. The extrusion or injection molded plastic (tube shape) is clamped and then placed into an enclosed split die. Compressed air forces the molten plastic into the mold surface.[10]

SI 2.4 Film Blowing

Blown films extrusion is a polymer manufacturing process that requires high-quality raw material. This technique blows compressed air into a thin polymer tube, forcing expansion to make a thin film tube.[10] This technique is mainly applied in plastic bags, film for food packaging, and other thin film applications.

SI 2.5 Fiber

The processed post-consumer plastic flakes or pellets are melt-processed through a spinneret (a type of extrusion die) to produce filament fiber.[12] The speed of the melt-spinning can generate different grades of fiber, low-oriented yarn is produced at 500-1500 m/min speed, and fully-oriented yam is produced at 6000 m/min speed.[13]

Extrusion temperature and screw speed play an important role in product formation. Extrusion temperatures are important for the flow properties of the material. Excessively high screw speeds causes improper melting while low speeds results in over melting of the plastic.[14] Thermo-oxidative chain scission occurs in the plastic from thermal conduction and shear stress in the presence of oxygen during extrusion. Plastics each possess drastically different oxygen solubility properties and saturation levels [15]. Such chain scission events reduce processability and functionality of the plastic by decreasing the polymer chain length and altering the molecular weight and molecular weight distribution.[16-17] Extrusion conditions such as temperature and screw speed are the controllable influential factors in the chain degradation mechanism.[14] Thermally-induced hydrogen abstraction from oxygen-centered radicals is mainly responsible for the β-scissions of chains.[16]

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