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REVIEWS

Gas Phase Ethylene Polymerization: Production Processes, Polymer Properties, and Reactor Modeling

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A review of relevant macroscopic and microscopic processes of gas phase ethylene polymerization, both chemical and physical, is given. The commercial technology development of gas-phase ethylene polymerization processes is illustrated through a selective survey of the patent literature. Both advantages and disadvantages of gas phase polymerization processes are addressed, and the challenges of laboratory studies of gas phase polymerization are also outlined. Physicochemical phenomena of ethylene polymerization using heterogeneous catalysts are discussed, including examination of catalyst preparation, polymer morphological development, and elementary chemical reactions. Metallocene-based catalysts and their kinetic performance for olefin polymerizations are also discussed. The current state of the art for reactor modeling of polymerization rate, molecular weight development, reactor dynamics, and resin grade transition strategies is illustrated on the basis of the most recent academic studies. Finally, relationships between resin properties and polymer microstructures as well as characterization methods are described briefly. In particular, temperature-rising elution fractionation technology is emphasized for characterization of ethylene copolymers. The fundamental issues involved in gas phase ethylene polymerization and their interrelationships are also discussed in some detail.

Contents

1. Introduction

Polyethylene (PE) is the largest synthetic commodity polymer in terms of annual production and is widely used throughout the world due to its versatile physical and chemical properties. The American Society for Testing and Materials (ASTM) has classified PE into four groups: I (low density) at 0.910–0.925 g/cm^3, II (also low density) at 0.926–0.940 g/cm^3, III (high-density copolymers) at 0.941–0.959 g/cm^3, and IV (high-density homopolymer) at 0.960 g/cm^3 and above (Redman, 1991). In the literature, however, PE is normally classified as low density (LDPE) at 0.910–0.930 g/cm^3 and high density (HDPE) at 0.931–0.970 g/cm^3. Low-density polyethylene is further classified as low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) based on polymer chain microstructure and synthesis processes. According to the figures reported in *Mod. Plast.* (1993), polyethylene production in the United States alone was over 10 million tons in 1992. The annual production of PE in Europe is about 9 million tons (Redman, 1991). The current annual worldwide capacity for PE production is over 30 million tons. Figure 1 shows the U.S. PE production profile over the past-decade. Although the annual rate of increase slowed down slightly at the end of the 1980s, the average annual increase rate is about 8% for HDPE and about 5% for LDPE and LLDPE for the past decade. Consumption of PE is still rising through the 1990s with development of synthesis and processing technology. The main markets and applications of LLDPE and HDPE are summarized in Figure 2 after James (1986) and Foster (1991).

Polyethylene is commercially produced exclusively by continuous processes. On the basis of polymerization mechanisms and reactor operating conditions, PE production processes can be classified into at least five process categories as shown in Table 1. Among them, the gas phase polymerization process is the most recently developed and also the most versatile. Since its emergence, this process has been challenging other existing processes for market share, particularly, for production of LLDPE, due to its economic and technological advantages. Many excellent reviews of ethylene polymerization processes have been published (Vandenberg and Perka, 1977; Short, 1981; Choi and Ray, 1985a; Nowlin, 1985; James, 1986; Beach and Kissin, 1986). However, the fundamental issues involved

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