

# CHAPTER I

## INTRODUCTION



Introduced in the early 1990s, metallocene catalysts were engineered to radically change the molecular structure of polyolefins and create new application markets. This new catalysts system was estimated to have the same impact on the polymers industry as the discovery of Ziegler-Natta (ZN) catalysts in the 1950s [1]. ZN catalysts are still the workhorse of the global polyethylene (PE) and polypropylene (PP) industries. The course of this revolution would draw on the unique characteristics offered by metallocenes:

- The ability to polymerize almost any vinyl unsaturated monomer
- Inherent ability to produce extremely uniform homopolymers and copolymers of very narrow molecular weight distribution (MWD) and composition distribution
- Capability to control stereoselectivity of the catalysts and produce new molecular structures such as highly syndiotactic polymers
- Unprecedented precision in assembling polymers of predictable structure and properties as if each metallocene holds the genetic code for a specific family of polymers

The metallocene catalyst technologies became a “must do” R&D objective for many global polyolefins companies. The development field soon broadened to include systems that were not true metallocenes. However these catalysts have the same characteristics derived from single active site or species (SSC). The early expectations of SSC usage for low-density PEs has been met well and exceeded for some resin types such as for linear low-density polyethylene (LLDPE) large volume applications.

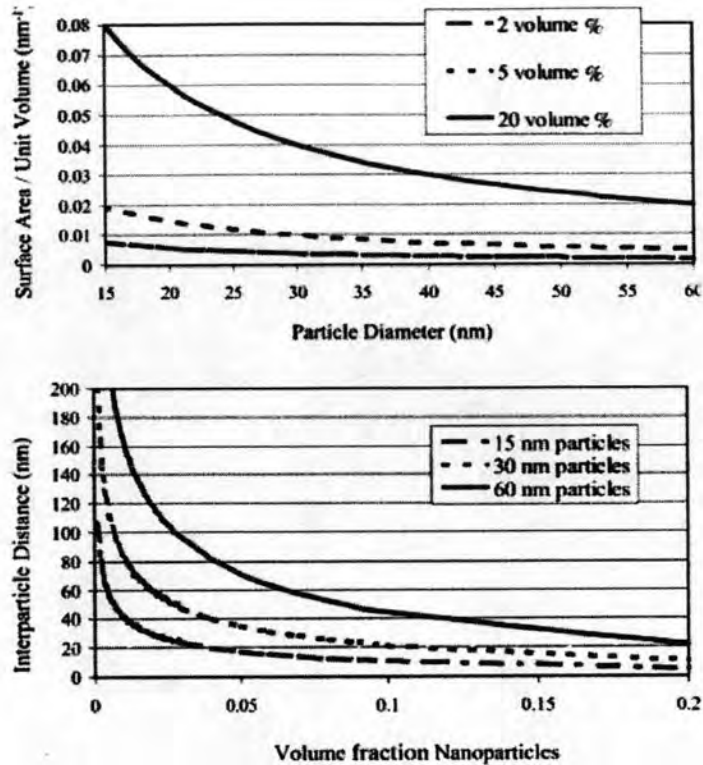
It is known that the copolymerization of ethylene with higher 1-olefins is a commercial importance for productions of LLDPE. LLDPE (density 0.920 to 0.940) is one of the most widely used polyolefins in many applications, especially, for plastic films.

However, in some cases, the use of polyolefins or LLDPE is limited by their drawbacks such as low mechanical strength, low thermal resistance, poor optical properties and so on. Thus, in order to improve the specific properties of these polymers, some additives need to be blended with them.

It has been known that blending polymer with inorganic materials is recognized as a powerful method to produce new materials called polymer composites or filled polymers. However, due to the significant development in nanotechnologies in the recent years, nano-inorganic materials such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  have brought much attention to this research field.

There are several reasons for many researchers to consider the nano-material replace the traditional micro-material. One of the important reasons is the effect of size on particle properties[2], the small size of the filler leads to an exceptionally large interfacial area in the composites. Figure 1a shows the surface area per unit volume as a function of particle size for spherical particles that are ideally dispersed. The increase in surface area below 100 nm is dramatic.

As defined in traditional composites, the interfacial region is the region of altered chemistry, altered polymer chain mobility, altered degree of cure, and altered crystallinity. Interface size has been reported to be as small as 2 nm and as large as about 50 nm. Figure 1b shows interparticle spacing as a function of particle size for an ideally dispersed nanoparticle composite: at low volume fractions the entire matrix is essentially part of the interfacial region. Even if the interfacial region is only a few nanometers, very quickly the entire polymer matrix has a different behavior than the bulk. If the interfacial region is more extended, then the polymer matrix behavior can be altered at much smaller loadings. Therefore, by controlling the degree of interaction between the polymer and the nanofiller, the properties of the entire matrix can be controlled.



**Figure 1.1**

- (a) Surface area per unit volume vs. particle size for spherical particles that are ideally dispersed.
- (b) Interparticle distance for spherical that are ideally dispersed.[2]

The polymer composites filled with nano-inorganic materials are well recognized as polymer nano-composites. Basically, there are probably three methods used to produce the filled polymer; (i) melt blending, (ii) solution blending, and (iii) *in situ* polymerization. Due to the direct synthesis via polymerization along with the presence of nano materials, the *in situ* polymerization is perhaps considered to be the most powerful techniques to produce polymer nano-composites with good dispersion of the nanoparticles into polymer matrix. Although, LLDPE composites have been investigated by many authors [3-8], no such a study has been done on synthesizing polymer nano-composites via the *in situ* polymerization.

In the present study, LLDPE-Al<sub>2</sub>O<sub>3</sub> polymer nanocomposites synthesized via *in situ* polymerization with methylaluminoxane (MMAO)/zirconocene catalyst was

investigated for the first time. The nano- $\text{Al}_2\text{O}_3$  was commercially obtained from Aldrich. The amounts of nanomaterials filled were also varied. Yields, activities, and polymer morphologies were discussed.

### 1.1. Objective of the Thesis

- To synthesize and characterize of the LLDPE / nano-alumina composites using *in situ* polymerization with a zirconocene catalyst.
- To study effects of various alumina fillers on properties of the LLDPE nanocomposites produced.

### 1.2. Scope of the Thesis

- Synthesize LLDPE nano-alumina composites by *in situ* polymerization of ethylene/1-hexene with [*rac*-ethylene bis-(indenyl)] zirconium (IV) dichloride with d-MMAO.
- Characterize the nano-alumina fillers and catalyst precursors using X-Ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM),
- Characterize the obtained LLDPE nano-alumina composites using scanning electron microscopy (SEM), energy-dispersive X-ray spectrometer (EDX), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and  $^{13}\text{C}$ -nuclear magnetic resonance ( $^{13}\text{C}$ -NMR ).