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Review

A review of clay-supported Ziegler–Natta catalysts for production of polyolefin/clay nanocomposites through in situ polymerization

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ABSTRACT

Polyolefin/clay nanocomposites are mainly prepared by melt mixing, solution, and in situ polymerization approaches. Among them, the last one is more attractive because the dispersion obtained through in situ polymerization is the most efficient, particularly, in the fully exfoliated polyolefin/clay nanocomposite formation. The clay-supported coordination catalysts, i.e. Ziegler–Natta, metallocene, and late transition metal catalysts, were applied to olefins polymerization in order to produce the polyolefin/clay nanocomposites. This review presents the studies reported on the use of the clay-supported Ziegler–Natta catalysts for polymerizing the olefins, which provided that detailed examples reported in the open literature. The emphasis is placed on the production of the polyolefin/clay nanocomposites via in situ polymerization.

Contents

1. Introduction

Polyolefins are the most important commercial thermoplastics which have the largest tonnage in the polymeric industries, more than 60% of the total worldwide polymer production, because of the abundance of the monomers and being easily molded by many

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different processes. In addition, these polymers enjoy the valuable physical and mechanical properties which lead to a variety of applications in different industries. However, such products suffer from some drawbacks including mechanical properties. These properties can outstandingly be further enhanced by adding the fillers and reinforcements. Many different types of materials including calcium carbonate, talc, carbon black, silica, etc. have been introduced into the polymers to provide a synergistic improvement for processibility and final product properties [1–4].

In the last few years, a great attention has been paid to the preparation of polyolefinic nanocomposites using nanoparticles due to the dramatic modification in the physical and mechanical properties of polymers. Such properties can be achieved by adding just a small fraction of nanoparticles including $CaCO_3$ [5–10], clay [11–15], talc [16–18], carbon nanotube [19–23], carbon black [24–28], silica [29–35], etc. to the polymer matrix. Totally, the nanocomposite technology offers superior mechanical, thermal and barrier properties which are not achievable in the conventional polymer composites [4,36–39].

The synthesis of the polymer/clay nanocomposites can be performed by three methods namely, melt processing, solution and in situ polymerization [4,36–41]. The melt processing of the polyolefins with nanofillers is often led to insufficient filler dispersion. It leads to the aggregation and intercalation which decrease the mechanical properties, especially at high filler contents. The solution method suffers from some drawbacks including the low solubility of polyolefin in the low boiling organic solvents. Another problem of both above methods is the hydrophilic nature of most inorganic fillers, the hydrophobic nature of the polyolefins including polyethylene (PE) and polypropylene (PP). The diverseness results in the weak interfacial adhesion between the filler and the polyolefin matrix and also the low mechanical properties. Therefore, the fillers must be modified by the surface active agents. These disadvantages can be solved by in situ polymerization [42,43]. Totally, the in situ polymerization is more effective method in the nanocomposite formation than the melt processing method according to the comparison of the silicate dispersion data [43,44]. In addition, an in situ polymerization is practiced by introducing an olefin polymerization catalyst into the interlayer galleries of the silicate layer of the clay where in situ olefin monomer polymerization will generate sufficient heat. This is combined with the physical expansion effect in the continuously growing polyolefin macromolecules to effectively promote the delamination into exfoliation state and homogeneous dispersion of the silicate layers in the polyolefin matrixes.

The in situ polymerization technique is generally believed to be the way to access to the polyolefin/clay nanocomposites due to the successful bypassing the rigorous thermodynamic requirement associated with the polymer intercalation process. In addition to an easy accomplishing a nano-scale dispersion, an in situ polymerization also allows the versatile molecular design of the polyolefin matrix. This paves a route to not only gaining different polyolefin nanocomposites with expanded property range by flexible tuning the matrix composition and structure, but also the rational designs of the interface between the nanoparticles and the polyolefin matrix. For example, by implanting polar functional groups into the chain of the polyolefins can lead to strong interfacial interaction with the nano-particles in order to enhance their nano-effects on polyolefin properties [45,46]

Metallocenes and Ziegler–Natta catalysts supported on the clay have been widely employed for the in situ polymerization of ethylene [47–54]. The clay-supported metallocenes have been comprehensively considered in reference [55]. In addition, the clay-supported late transition metal catalysts have been also reported in some papers used for the preparation of polyolefin/clay nanocomposites via in situ polymerization [56–61].

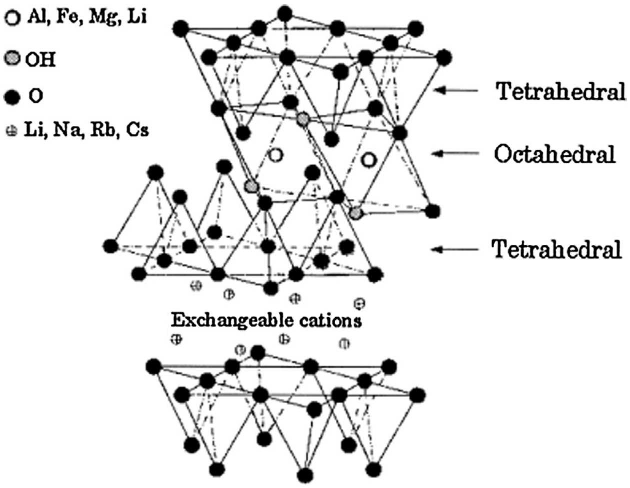

Fig. 1. Structure of 2:1 phyllosilicates [4].

The preparation of the polyolefin nanocomposites, using a typical Ziegler–Natta catalyst by in situ polymerization, has the advantage of using industrial catalysts. It is the most cost-effective one among the coordination catalysts.

The aim of this article is to provide a comprehensive review of the clay-supported Ziegler–Natta catalysts used to obtain polyolefin-layered silicate nanocomposites. In addition, the catalyst performance in the olefin polymerization and also the properties of the obtained nanocomposites has been considered.

2. Generalities

2.1. Structure and chemistry of layered silicates

The usual layered silicates used in nanocomposites, belong to the structural category, are known as the 2:1 layered or phyllosilicates (Fig. 1). Their crystal lattice consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either alumina or magnesia. The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 30 nm to several microns and even larger depending on the particular silicate. Stacking of the layers leads to a regular Van der Waals gap between them called the interlayer or gallery. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+}, or Mg^{2+} replaced by Li^{+}) generates negative charges which are counterbalanced by alkali or alkaline earth cations situated inside the layers.

Montmorillonite (MMT), hectorite and saponite are the most commonly used layered silicates. Their chemical structures are shown in Table 1.

2.2. Types of nanocomposites

Layered silicates have a general thickness in the order of 1 nm and very high aspect ratios (typically, 10–1000). A few weight percentages of layered silicates, when fully dispersed in the polymer

Table 1
Chemistry formula and characteristic parameter of phyllosilicates[a] [4].

2:1 Phyllosilicates	Chemical formula	Particle length (nm)
Montmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	100–150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	200–300
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	50–60

[a] *M*, monovalent cation; *x*, degree of isomorphous substitution (between 0.5 and 1.3).