Theoretical Foundations for the Development of Active Organometallic Additives for Polyethylene

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Abstract

This article investigates the theoretical and practical foundations of obtaining active organometallic additives for modifying the polyethylene (PE) matrix. The chemical inertness of polyethylene and existing problems regarding the direct attachment of metal centers are analyzed, highlighting the shortcomings of traditional two-stage schemes. To reduce processing stages and ensure strong bonding of the metal to the polymer chain, the research proposes a technology for the direct incorporation of active organometallic compounds during the crosslinking process. Furthermore, physical and chemical crosslinking methods (Daoplast, Engel, Pont a Mousson, UHF) are comparatively examined, and the significance of organometallic (ionic) crosslinks in polymer recyclability is substantiated.

Keywords: Polyethylene (PE), organometallic additives, crosslinking, maleic anhydride (MAH), ionic bridges, peroxide crosslinking, recyclability, PEXa, functional polymers.

Introduction

This article presents the theoretical foundations, properties, advantages, disadvantages, and application areas of obtaining active organometallic additives for polyethylene. The significance of organometallic additives for polyethylene, and polymers in general, is remarkably extensive. Specifically, polyethylene (PE) is a high-molecular-weight saturated hydrocarbon according to its chemical structure. Its macromolecular chain consists exclusively of strong C-C and C-H sigma (σ) bonds, containing no polar functional groups or unsaturated double bonds. This unique "closed" structure ensures the thermodynamic stability of the polymer but, at the same time, results in its extreme chemical inertness. Consequently, the polyethylene matrix lacks the ability to chemically interact with other active substances, particularly organometallic compounds.

Research in the field of organometallic compounds for polyethylene (PE) is divided into two major periods: catalyst synthesis (for PE production) and polymer modification (to alter the properties of finished PE). The history of modifying polyethylene with organometallic compounds primarily began in the 1950s and 60s with the works of K. Ziegler and G. Natta. Initially, organometallic compounds (aluminum-alkyls, titanium chlorides) were viewed solely as catalysts for polymer synthesis. By the 1970s–1990s, researchers began working on "Ionomers" (polymers bonded with metal ions) to change the properties of the finished polymer. In this process, maleic anhydride (MAH) or acrylic acid was grafted onto the polyethylene chain, followed by treatment with zinc (Zn), magnesium (Mg), or sodium (Na) salts.

Current research shows that the chemical inertness of polyethylene prevents the direct attachment of organometallic centers. In most cases, researchers have utilized a two-stage “grafting → ion exchange” scheme.

Key Problem: In existing technologies, the organometallic compound is either unevenly distributed within the polymer matrix or degrades the rheological (flow) properties of the polymer. Furthermore, many organometallic compounds have been observed to be unstable and decompose at polymer processing temperatures (150–200°C).

To overcome the aforementioned shortcomings, the work we intend to pursue proposes a technology for the "synthesis of active organometallic compounds and their direct incorporation during the cross-linking process." This method:

- Reduces the number of processing stages;
- Ensures strong covalent or coordination bonding of the metal with the polymer chain;
- Imparts new functional (catalytic, magnetic, or antiseptic) properties to the polymer.

Below, we briefly review prior studies and analyze their achievements and limitations.

According to Hibal Ahmad and Denis Rodrigue [1] in their review article “Crosslinked Polyethylene: A Review of Preparation Methods, Applications, and Recycling” the following perspectives are presented:

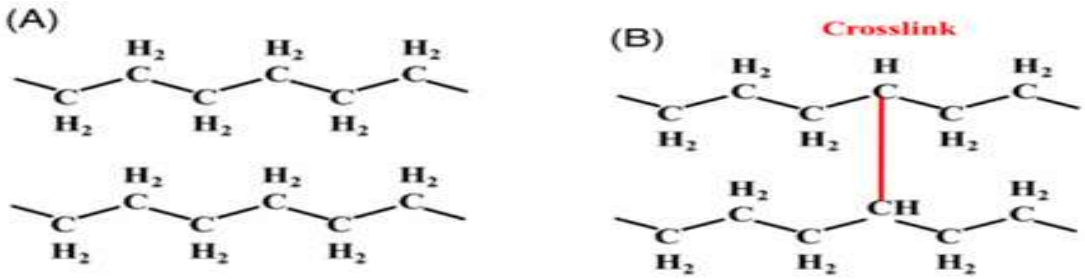
Polyethylene (PE) is one of the most widely used resins in the plastics industry. Although polyethylene possesses good impact resistance and plasticity, its low maximum operating temperature and insufficient mechanical strength limit its use in certain commercial projects, particularly in load-bearing structures. To improve overall performance, a cross-linking process is carried out to enhance the chemical, mechanical, and thermal properties of polyethylene. Although polyethylene can be cross-linked through various chemical and physical methods, the resulting three-dimensional (3D) network structure makes it difficult to recycle the obtained polymers.

Cross-linking refers to the intermolecular or intramolecular chemical bonding between polymer chains. The reaction mechanism involves the breaking of C-H bonds and the formation of radicals as a result of absorbing high-energy radiation or the action of cross-linking reagents, which in turn leads to the formation of C-C cross-links (bonds). During the reaction, small aliphatic molecules in gaseous form are also released. The three-dimensional network structure formed by cross-links in polyethylene (PE) results in cross-linked polyethylene (XLPE). The first report on the cross-linking of PE was provided by Gilbert and Precopio in the early 1930s. The fundamental idea of PE cross-linking is to improve its chemical, mechanical, and thermal properties. As described below, PE cross-linking can be carried out in two main ways:

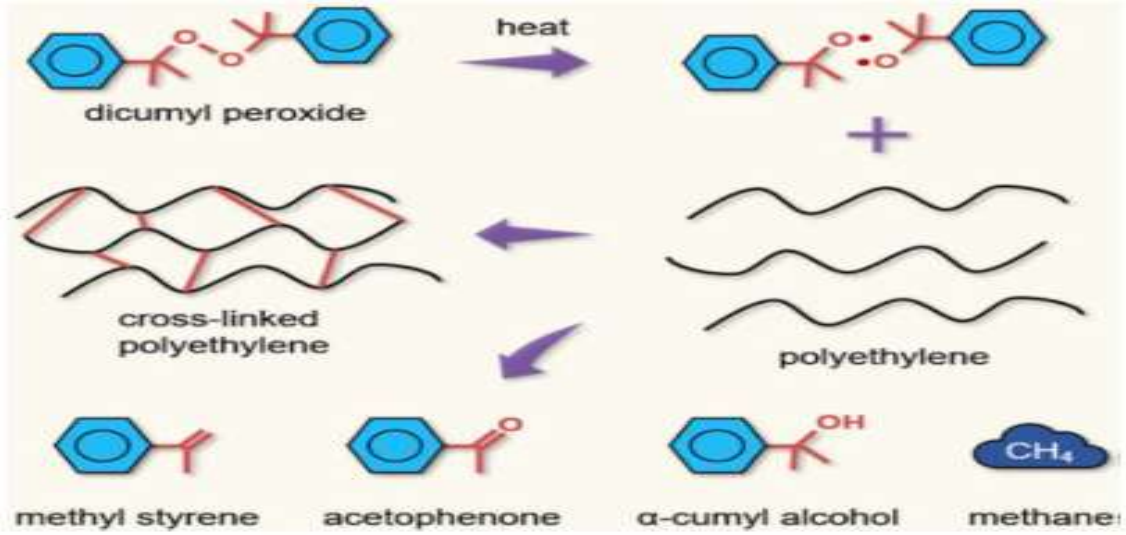
(a) physical cross-linking; (b) chemical cross-linking.

Physical cross-linking is also referred to as the radiation method, as polyethylene (PE) molecules are exposed to high-energy radiation sources such as microwaves and high-energy electrons. Primarily non-corpuscular (non-particulate) radiation types, such as ultraviolet (UV), X-ray, ultra-high frequency (UHF), gamma (γ), and electron beams (e-beam), are used to generate active free radicals in the PE chains.

Today, electron beams (e-beam) are the most common method used in physical



cross-linking. The process mechanism involves the absorption of high-energy radiation, which leads to the breaking of C-H bonds within the PE structure and the formation of hydrogen and polymer radicals; these radicals subsequently form C-C bonds (cross-links) between different polymer chains.



However, during this process, certain small aliphatic molecules, such as hydrogen and methane, are released in gaseous form. Therefore, it is essential to utilize an effective ventilation or gas extraction system during the process. Major focus is directed toward the mechanical recycling of XLPE and de-crosslinking techniques to produce recycled XLPE (r-XLPE). Finally, a conclusion is provided regarding the current state and the scientific gaps that need to be addressed through future research. The breaking of C-H bonds and the formation of C-C bonds described in the text represent static (irreversible) cross-linking.

As noted above, chemical cross-linking involves the addition of cross-linking agents (chemical substances) to generate free radicals. Chemical cross-linking can be categorized into three types: (a) the peroxide method; (b) the silane method; and (c) the azo-compound method.

In this article, the author reviews the latest achievements and developments in the field of cross-linked polyethylene (XLPE). It is emphasized that XLPE is attracting significant interest because it offers several advantages over ordinary polyethylene (PE), such as improved chemical, mechanical, and electrical durability.

These technologies encompass both physical and chemical recycling. Chemical recycling primarily utilizes supercritical fluids and pyrolysis to obtain valuable molecules (gases and liquids) that can be used as fuel by de-crosslinking (breaking the bonds of) the PE macromolecular network. This opens new directions for future developments using this material; however, several critical aspects must be considered for industrial solutions. This is precisely where the significance of our research emerges: why are organometallic bonds necessary? Because standard XLPE is difficult to recycle (an environmental issue), whereas the organometallic (ionic) cross-links we propose possess a “reversible” character, enabling the recycling of the polymer (zero-waste production).

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