

Manufacturing, structure, and properties of crosslinked polyethylene induced by peroxides

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Abstract

Crosslinking of polyethylene induced by peroxides can greatly improve some of its properties such as stability and impact strength. The underlying material science is well-known yet provides great potential for process optimization as well as product amelioration. In this review, the structure-processing-property relationship of crosslinked polyethylene is introduced with a focus on the chemical reaction mechanisms involved.

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1. Introduction

Polyethylene (PE) is widely used as commodity plastics in various fields such as cable insulation, packaging materials, and medical products, processed at a temperature range between 150°C and 250°C [1-3]. To make PE suitable for more applications, some improvements in its chemical resistance, crack tolerance, modulus, and service temperature can be achieved via crosslinking with peroxides at elevated temperatures [1-3]. Crosslinking PE would induce structural changes since it produces a thermoset material and forms a three-dimensional molecular network, and in turn, alters the gel content as well as the crystallinity. [1-5] Crosslinked PE (XLPE) can be processed by injection molding, extruding, or foaming [1, 3].

The major reactants involved in the reaction include PE as the raw material and peroxides, often being dicumyl peroxide (DCP) as the crosslinking agent. In some cases, especially when less effective peroxides are used, coagents or activators, such as triallyl isocyanurate (TAIC), can be added to the reaction system. The coagents may act to increase the crosslinking efficiency or prevent premature crosslinking, or scorching [5-7]. It was found that two competing mechanisms, chain coupling (crosslinking), and chain scission (disproportionation) favor different reaction environments, and adding coagents or adjusting the temperature can prevent

the unwanted mechanism from happening to some degree [2, 5].

2. Manufacturing of XLPE

2.1. Mechanisms

Using DCP as the exemplary crosslinking agent, Akbariaian et al. gave a detailed explanation of the crosslinking reaction of PE [3]. The well-known serial process begins with the breaking of the O-O bond upon heat or light within the DCP molecule, producing principle radicals. By hydrogen extraction, the radicals can attack the PE molecules, inducing the recombination of them, forming a three-dimensional network. This mechanism would yield α -cumyl alcohol as the byproduct, which may dehydrate and become methyl styrene and water as the impurity. It was also shown that the principle radicals may undergo β -scission before attacking the PE molecules, leaving acetophenone, methane, and XLPE as the products of the reaction [3].

Chain scission, including β -scission at branch points and interchain scission, may occur during the free-radical initiated reaction. These mechanisms favor more elevated temperatures compared to the formation of the crosslinking network structure which is desirable. Therefore, to avoid the unfavorable chain scission mechanism and thus increase the

crosslinking efficiency, the reaction temperature acts as a critical consideration when manufacturing the XLPE [2].

2.2. Processing parameters

Temperature is a primary point of concern in the manufacturing process of XLPE, various temperatures have been tested for crosslinking PE with peroxides, ranged between 140 to 247 °C [2-7]. However, the optimal crosslinking temperature of the DCP-PE system has been determined to be around 500K (227°C), above which the efficiency starts to decrease due to competitive reactions such as hydrogen transfer among the radicals[3]. It was also noted that temperature is a primary concern due to the decomposition rate of the peroxides, and DCP has the advantage among most of the peroxides because of its high decomposition rate within the processing temperature range of PE (a half-life of only 538.8 seconds at 155°C) [2]. Byproduct formation is also greatly influenced by the reaction temperature, in conclusion, the amount of α -cumyl alcohol does not depend on the temperature beyond 140°C, whereas acetophenone and methane production is more significant at elevated temperatures [3]. As mentioned previously, the temperature has a direct effect on the chain scission mechanism which should be avoided, making it a critical concern in the manufacturing process of XLPE.

Coagents are usually added to the peroxide-PE system to achieve one or more of the following goals: increasing the crosslinking efficiency by preventing chain scission, or prevent premature crosslinking, also called scorching of the material [5-7]. Some coagents, such as triallyl cyanurate, triallyl isocyanurate, quinone dioxime, diallyl phthalate, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, N,N'-m-phenylene bismaleimide, 1,2-polybutadiene, are added to increase the crosslinking efficiency by providing more reactive sites [1, 6, 7]. Others, such as nitrites, 2-mercaptobenzothiazole, and hydroquinones, can act as scorch inhibitors, maintaining the processability and rheological properties of PE during the crosslinking process[6, 7]. The two functions often require different chemical properties of the coagents, but studies have shown that the addition of 2,4-diphenyl-4-methyl-1-pentene (MSD) can fulfill both needs as the reaction mechanism of MSD would change as the reaction proceeds [6, 7]. It was noticed that one coagent, pentaerythritol triacrylate (PETA), can substitute for the role of peroxides in the crosslinking reaction, inducing crosslinking on its own with PE [5].

3. Structure of XLPE

The microstructure of XLPE is a three-dimensional network made with polymeric chains. Within this amorphous structure, crosslinking sites are local defects, decreasing the overall crystallinity of the material. However, these sites can improve the local packing efficiency if the density is kept relatively low, by restricting molecular motion, and thus increase the crystallinity[1, 3-5]. The gel content shows a significant

correlation to the dose of the peroxide, as the peroxides in a low-amount usage greatly increase the gel content and no longer significantly affect it after passing a certain amount [2].

4. Properties of XLPE

Mechanical properties of PE can change significantly upon crosslinking. While the hardness and yield strength can slightly increase due to crosslinking, the flexural modulus and impact strength of PE can get enhanced [1, 5]. The processability decreases as the flowability of the material decreases due to the formation of the network structure [5]. The formation of the inert network also induces a reduction in the elongation at break and strengthens the creep resistance by being inhibitive to crack propagation. The maximum service temperature of XLPE is also higher than regular PE because of its more stable thermoset structure at higher temperatures. Besides, the inert structure also allows for better chemical resistance [1]. According to Akbarian et al., byproducts generated from the peroxide-induced crosslinking process are always found in XLPE in great amounts, which may induce space charge accumulation within the insulating material, affecting its applications [3].

5. Conclusions

The manufacturing process, structure, and properties of crosslinked polyethylene are introduced with explanations on the chemical reaction mechanisms and effects of various processing parameters. The structure-processing-property relationship of crosslinked polyethylene induced by peroxides is established and emphasized. In conclusion, peroxide-induced chemical crosslinking of polyethylene has shown its effectiveness in improving the performance in various applications of polyethylene and can be enhanced by the addition of coagents. As a point of interest for future research, the discovery of multipurpose coagents is certainly beneficial for the advancement of plastics technology.

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Conflict of Interest

The author declares no conflict of interest.

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