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The Role of Oxygen and Peroxide Initiators in High-Pressure Polyethylene Production

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Abstract. *In this study, the effect of oxygen and initiator systems on LDPE properties under high-pressure conditions was investigated. Oxygen reduces molecular weight (MW) and increases chain branching, leading to reduced thermal stability; however, at optimal concentrations, it can contribute to the formation of a more stable polymer structure under controlled conditions. Peroxide systems improve control of molecular weight distribution (MWD) and increase mechanical strength by 15–20%. Di-tert-butyl peroxide (DTBP) regulates melt flow index (MFI) and molecular weight (MW) of the polymer by generating active radicals as a result of thermal decomposition and helps maintain product stability. Compared to oxygen-based systems, peroxide-based initiation increases mechanical strength by approximately 15–20% and elongation by 10–15%, while providing improved control of molecular weight distribution. In addition, peroxy-radical reactions occurring in the presence of oxygen can affect the composition of the radical pool in the system and change the course of the initiation phase under certain process conditions. However, such reactions also increase the likelihood of the formation of hydroperoxide and carbonyl-type oxidation products, which negatively affect quality parameters such as polymer stability, color indicators, and odor. The results of the conducted studies show that the type of initiator used and its concentration are among the main factors determining the physical and mechanical properties of the synthesized polymer. These findings provide practical guidance for optimizing initiator selection and dosage in high-pressure polyethylene production.*

Keywords: *polyethylene, initiator, polymerization, oxygen, di-tert-butyl peroxide (DTBP)*

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Yüksək təzyiqli polietilen istehsalında oksigen və peroksid inisiatorlarının rolu

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Xülasə. *Bu tədqiqatda yüksək təzyiq şəraitində oksigen və inisiator sistemlərinin aşağı sıxlıqlı polietilenin (LDPE) xassələrinə təsiri araşdırılmışdır. Oksigen molekulyar kütləni (MW) azaldır və zəncirlərin şaxələnməsini artırır ki, bu da termiki sabitliyin azalmasına səbəb olur. Bununla belə, optimal konsentrasiyalarda və nəzarət olunan şəraitdə oksigen daha sabit polimer strukturunun formalaşmasına töhfə verə bilər. Peroksid sistemləri molekulyar kütlə paylanmasına (MWD) nəzarəti yaxşılaşdırır və mexaniki möhkəmliyi 15–20 % artırır. Di-tert-butil peroksid (DTBP) termiki parçalanma nəticəsində aktiv radikallar əmələ gətirməklə polimerin ərinti axıcılıq indeksini (MFI) və molekulyar kütləsini (MW) tənzimləyir və məhsulun sabitliyinin qorunmasına kömək edir. Oksigen əsaslı sistemlərlə müqayisədə peroksid əsaslı inisiasiya mexaniki möhkəmliyi təxminən 15–20 %, nisbi uzanmanı isə 10–15 % artırmaqla yanaşı, molekulyar kütlə paylanmasına daha yaxşı nəzarəti təmin edir. Bundan əlavə, oksigenin iştirakı ilə baş verən peroksi-radikal reaksiyalar sistemdəki radikalların tərkibinə təsir göstərə və müəyyən proses şəraitində inisiasiya mərhələsinin gedişini dəyişə bilər. Lakin belə reaksiyalar hidroperoksid və karbonil tipli oksidləşmə məhsullarının əmələ gəlmə ehtimalını da artırır ki, bu da polimerin sabitliyi, rəng göstəriciləri və qoxusu kimi keyfiyyət parametrlərinə mənfi təsir göstərir. Aparılmış tədqiqatların nəticələri göstərir ki, istifadə olunan inisiatorun növü və onun konsentrasiyası sintez edilmiş polimerin fiziki-mexaniki xassələrini müəyyən edən əsas amillərdəndir. Bu nəticələr yüksək təzyiqli polietilen istehsalında inisiatorun seçilməsi və dozasının optimallaşdırılması üçün praktik istiqamətlər təqdim edir.*

Açar sözlər: *polietilen, inisiator, polimerləşmə, oksigen, di-tert-butil peroksid (DTBP)*

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Introduction

Polymeric materials occupy an important place in modern industrial production, and polyethylene is considered one of the leading materials in this direction due to its production volume, economic importance, and wide application areas. Polyethylene properties depend on initiator systems (Peacock, 2000; Baird & Collias, 2014). However, comparison of oxygen and peroxide systems remains insufficiently studied. In particular, there is limited systematic analysis of how oxygen- and peroxide-based initiator systems influence molecular weight distribution (MWD), chain branching, and thermal stability under high-pressure conditions. This research gap highlights the need for a comparative evaluation of initiator systems in terms of their impact on polymer structure and process stability.

Although oxygen- and peroxide-based initiators have been investigated in previous studies, their effects on polyethylene formation are often discussed separately and under different process conditions. In this context, the present study brings together available findings and evaluates these initiator systems from a comparative perspective. Particular attention is given to their influence on molecular weight distribution, chain branching behavior, thermal stability, and overall process performance under high-pressure polymerization conditions. Such an approach makes it possible to

identify common trends and differences that are not always evident when individual initiator systems are considered independently.

The main objective of this study is to scientifically analyze the polymerization technologies and initiator systems used in the production of polyethylene under high-pressure conditions. In particular, the production of low-density polyethylene (LDPE) by free-radical polymerization is of great industrial importance. Modern scientific studies show that process parameters directly affect the molecular structure of polymer chains and the quality indicators of the final product (Bocare et al., 2019; Zhu et al., 2019). As a result of the conducted research, the influence of different initiator systems on the high-pressure polymerization process was comprehensively investigated, and their effects on process kinetics were scientifically substantiated. This study provides a comparative evaluation of oxygen- and DTBP-based initiation systems under high-pressure LDPE production conditions. It was determined that polymer yield reaches 27–28% in peroxide-based systems, whereas in oxygen-based systems this value remains at 17–18%. This difference was attributed to the specific characteristics of the decomposition kinetics of the initiators.

Unlike previous studies that mainly focused on individual initiator systems, this work comparatively evaluates oxygen-and DTBP-based initiation under the same technological framework and relates radical generation mechanisms directly to polymer microstructure and product quality. The scientific novelty of this study lies in the comparative evaluation of oxygen- and di-tert-butyl peroxide-based initiator systems in high-pressure LDPE production. Particular attention is given to their influence on molecular weight distribution, crystallinity, thermal properties, and polymer conversion. The study provides an integrated assessment of the relationship between radical generation mechanisms and the resulting polymer characteristics.

Materials and Methods

Object and Subject of Research

The object of the study is the process of producing polyethylene by radical polymerization of ethylene monomer. This process, carried out under various technological conditions, provides the synthesis of materials with different structural properties, such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), and linear low-density polyethylene (LLDPE). LDPE is obtained mainly by high-pressure polymerization methods, while HDPE is produced by low-pressure polymerization methods. The technological parameters of these processes directly determine the properties of the final product.

The subject of the study is the interaction between the main technological parameters used in polyethylene production—temperature, pressure, type and concentration of the initiator, and catalyst amount—and the physical, chemical, and mechanical properties of the resulting polymer.

Polymerization Process and Initiators

Low-density polyethylene (LDPE) is mainly produced on an industrial scale by free-radical polymerization of ethylene under high pressure. The process is carried out at temperatures of 150–300°C and pressures of 1000–3000 bar. Oxygen and di-tert-butyl peroxide (DTBP) are used as initiator systems (Bocare et al., 2019; Zhu et al., 2019; Azmi & Aziz, 2016). The polymerization process begins with the introduction of ethylene into the reactor under high pressure. The initiator decomposes at elevated temperature, generating free radicals that initiate chain reactions. Polymer chains are formed through the sequential addition of ethylene molecules. Temperature and pressure are monitored throughout the process, and the final product is cooled and collected as LDPE.

Process Flow Diagram and Operating Principle

The technological scheme of high-pressure LDPE production consists of several interconnected stages, including ethylene purification, compression, polymerization, product separation, and final

processing. Initially, ethylene is purified to remove moisture, carbon dioxide, and other impurities that may negatively affect polymerization performance. The purified gas is then compressed to high pressure using multistage compressors before being introduced into the reactor.

In tubular reactors, initiator systems are injected at selected points along the reactor length. The decomposition kinetics of the initiator and the temperature profile determine the distribution of active radicals and consequently influence polymer chain formation. Due to the plug-flow characteristics of tubular reactors, temperature and conversion vary along the reactor axis, affecting reaction kinetics and polymer properties.

The reaction mixture leaving the reactor is directed to a separation unit, where unreacted ethylene is separated from the polymer and recycled back into the process. The polymer product is subsequently cooled, homogenized in an extruder, and converted into granules for further processing. Proper control of each technological stage is essential for obtaining polyethylene with the desired molecular weight distribution, branching degree, mechanical strength, and thermal stability.

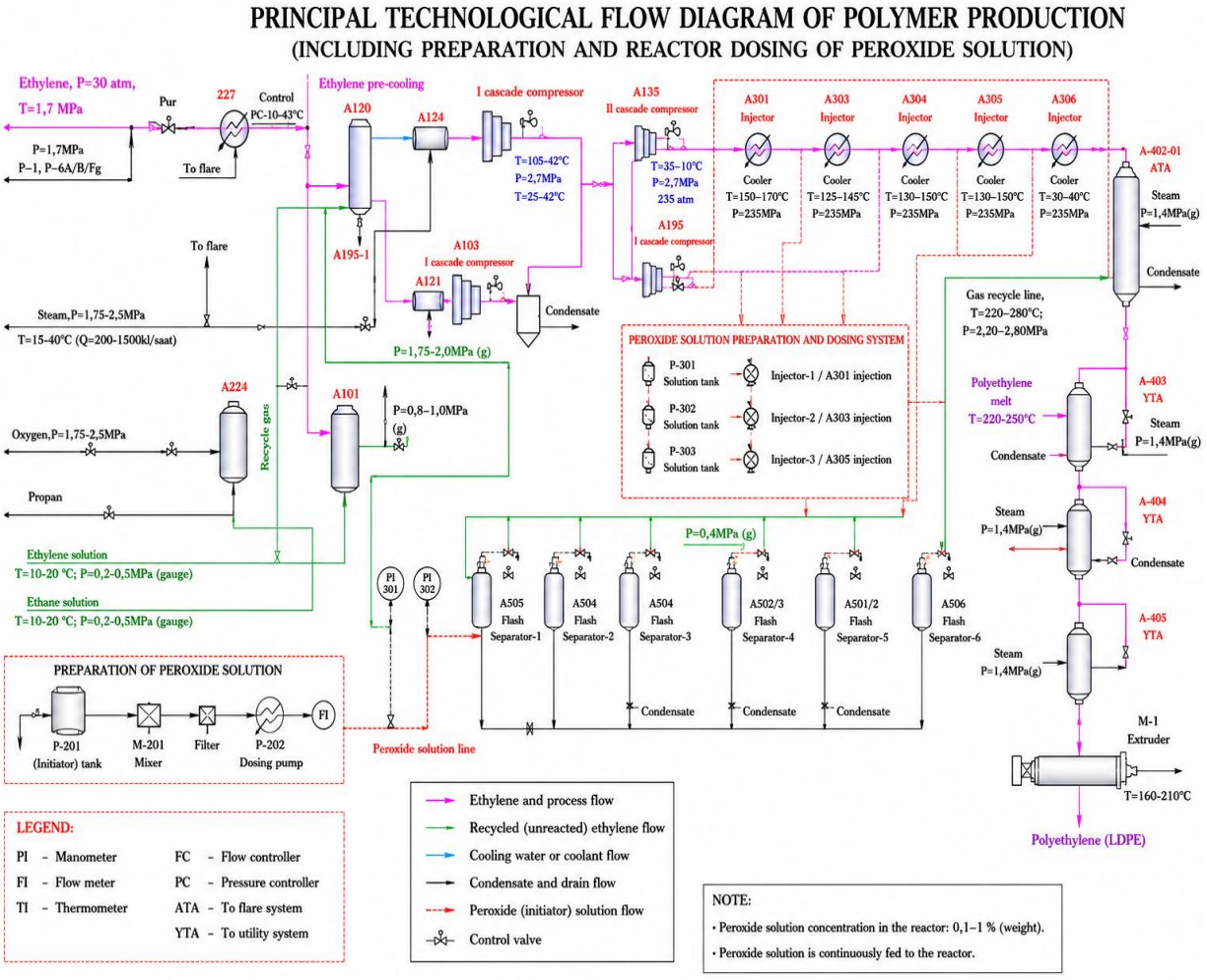


Figure 1

Principal technological flow diagram of high-pressure LDPE production including preparation and reactor dosing of the peroxide initiator solution

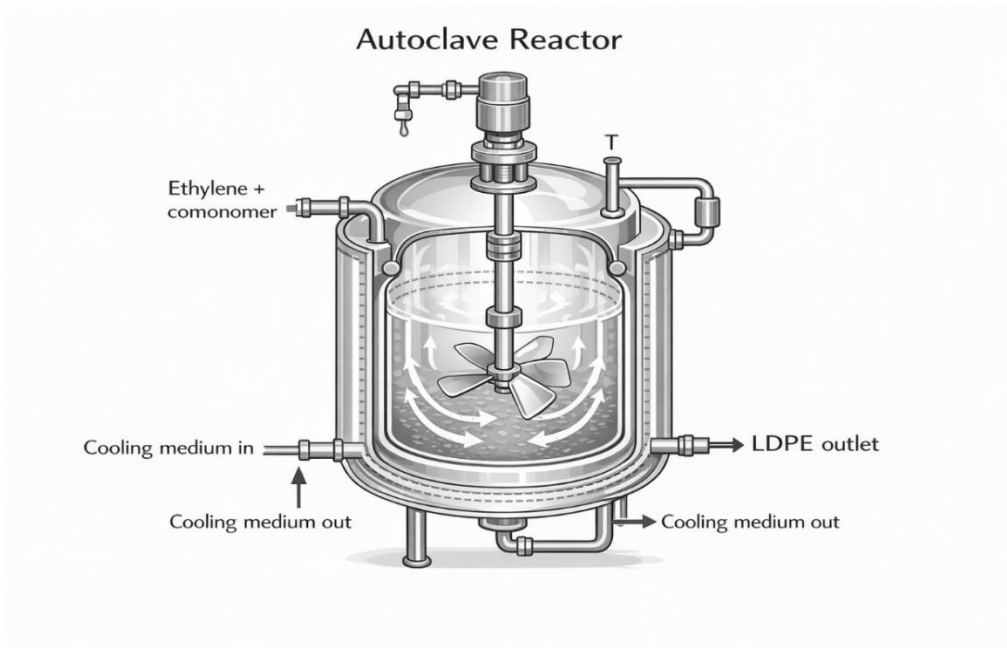
As shown in Figure 2, the high-pressure LDPE production process consists of ethylene purification, compression, peroxide initiator preparation and dosing, polymerization, separation of unreacted ethylene, recycle operations, and final polymer recovery. The methodological framework of this study is based on the examination and comparison of scientific data related to polyethylene production by

free-radical polymerization of ethylene. The research focuses on the technological conditions applied during LDPE synthesis and their influence on the characteristics of the resulting polymer. The study considers industrial polymerization processes carried out in high-pressure reactor systems, particularly tubular and autoclave reactors. Operating conditions reported in the literature, including temperatures ranging from 150 to 300°C and pressures between 1000 and 3000 bar, were analyzed to evaluate their effect on reaction behavior and product formation.

Special attention was given to the role of initiator systems, such as oxygen and di-tert-butyl peroxide, in the initiation and development of polymer chains. The analysis also included the influence of reactor design on heat transfer, mixing efficiency, residence time, and monomer conversion. To assess the relationship between process conditions and polymer properties, information obtained from published studies was organized and comparatively evaluated. Key parameters such as molecular weight distribution, degree of branching, polymer conversion, and product stability were examined as indicators of polymer quality. The interpretation of the results was carried out using principles of polymer reaction engineering and reactor analysis. Published experimental observations and modeling results were compared to identify common trends and determine the technological factors that have the greatest impact on polyethylene structure and performance.

In recent years, modeling of kinetics, heat transfer, and hydrodynamics in tubular and autoclave reactors has received significant attention (Van Steenberge et al., 2022; Zhang, 2021). Axial temperature and conversion variations in tubular reactors, as well as mixing intensity and residence time distribution (RTD) in autoclave reactors, are key factors influencing polymer microstructure. Modern approaches aim to predict key quality indicators such as molecular weight distribution (MWD/PDI), chain branching, and product stability (Kryven et al., 2022).

The formation of the internal structure of the polymer directly depends on the type of reactor used.



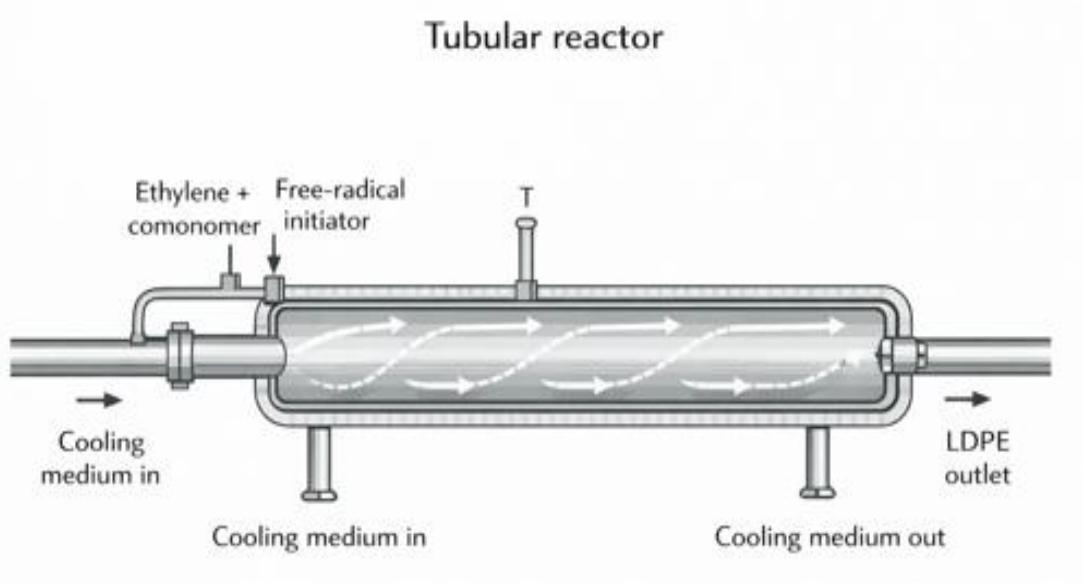


Figure 2
Schematic representation of autoclave and tubular reactors used in high-pressure LDPE production

Results

Studies have shown (Zhu et al., 2019; Michelsen & Møllerup, 2020; Alvarez et al., 2021; Gao et al., 2023) that in autoclave reactors, where intensive mixing is provided, the distribution of radicals is more homogeneous, resulting in a narrower molecular weight distribution (MWD). Compared to tubular reactors, the MWD is reduced by approximately 20–30%. This condition causes the polymerization to proceed in a more even kinetic environment. The even distribution of radicals results in more frequent activation and termination of chains, leading to polymers with relatively low average molecular weight.

In tubular reactors, the flow regime is mainly plug-flow, so the temperature and pressure are distributed unevenly throughout the reactor. Under these conditions, radical concentration and reaction rate vary along the axis, resulting in the formation of polymer chains under different kinetic conditions and a broader molecular weight distribution. Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC) analyses demonstrated that the type of initiator has a significant influence on the molecular and thermal properties of polyethylene. According to the GPC results, the weight-average molecular weight (Mw), number-average molecular weight (Mn), and polydispersity index (PDI) of the DTBP-based sample were 210,000 g/mol, 78,000 g/mol, and 2.7, respectively. For the oxygen-based sample, Mw, Mn, and PDI were determined to be 185,000 g/mol, 42,000 g/mol, and 4.4, respectively. DSC analysis revealed that the peroxide-based sample exhibited a melting temperature of 113°C and a crystallinity degree of 51%, whereas the oxygen-based sample showed corresponding values of 108°C and 42%, respectively.

Experimental results show that switching to peroxide-based initiation increases mechanical strength by 15–20% and elongation by 10–15%, while also improving the optical performance of the product (Brandão et al., 2020; Zhang et al., 2021; Sadeghi & Grady, 2024; Azmi & Aziz, 2016). The results presented in this study demonstrate that initiator type significantly affects the structural and thermal properties of LDPE. The peroxide-based system exhibited higher melting temperature and crystallinity compared with the oxygen-based system, indicating the formation of a more ordered polymer structure.

DSC (Differential Scanning Calorimetry) Analysis

Table 1
Thermal properties and degree of crystallinity of polyethylene samples

Initiator	Melting Temperature (°C)	Crystallinity (%)
Oxygen	108	42
DTBP (Peroxide)	113	51

Furthermore, peroxide initiation was associated with improved polymer conversion and enhanced control of polymer characteristics, confirming its advantages for high-pressure polyethylene production. As can be seen, the polyethylene sample produced using DTBP (peroxide) exhibited a higher melting temperature and degree of crystallinity than the oxygen-based sample. These results indicate the formation of a more ordered polymer structure with a higher degree of crystallinity in the peroxide-based system. The lower crystallinity observed in the oxygen-based sample may be attributed to a greater degree of structural irregularities within the polymer chains.

The experimental investigations performed within the framework of this study confirmed that the initiator system significantly influences both the kinetics of ethylene polymerization and the quality characteristics of the resulting polyethylene. The oxygen-based initiation system exhibited less controlled radical generation, which contributed to a broader molecular weight distribution and lower structural uniformity of the polymer. In contrast, the DTBP-based initiation system provided more stable and controlled radical formation throughout the polymerization process, resulting in improved regulation of chain growth and polymer structure development. GPC analysis revealed that the peroxide-based sample possessed a higher weight-average molecular weight (Mw = 210,000 g/mol) and number-average molecular weight (Mn = 78,000 g/mol) compared with the oxygen-based sample (Mw = 185,000 g/mol; Mn = 42,000 g/mol), while the polydispersity index decreased from 4.4 to 2.7, indicating a narrower molecular weight distribution. Thermal characterization by DSC further demonstrated that the peroxide-initiated polyethylene exhibited a higher melting temperature (113°C) and crystallinity degree (51%) than the oxygen-initiated sample (108°C and 42%, respectively). In addition, polymer conversion increased from approximately 17–18% in the oxygen-based system to 27–28% in the peroxide-based system. These results demonstrate that peroxide initiation provides more favorable conditions for obtaining polyethylene with enhanced structural homogeneity, improved thermal characteristics, and higher process efficiency under high-pressure polymerization conditions.

Discussion

To reduce this non-uniformity, multiperoxide initiator systems are widely used in tubular reactors. The stepwise introduction of peroxides with different decomposition temperatures makes radical generation more balanced, reduces the risk of local temperature maxima, and ultimately allows for more stable polymer structure formation.

In high-pressure polymerization technologies, the choice of initiator is one of the main factors that directly affects the process kinetics, reactor safety, and the physical and mechanical properties of the resulting polymer. In the early stages of industrial development, oxygen was a widely used initiator. Although its economic availability and the absence of the need for additional reagents provide certain advantages, its high reactivity makes it difficult to control the process stably and kinetic instability occurs. Oxygen leads to broader molecular weight distribution (MWD) and reduced thermal stability. In addition, reactions involving oxygen increase the likelihood of the formation of oxidized functional groups, which can lead to a decrease in the thermal stability of the material, deterioration of color properties, and weakening of mechanical strength. This behavior is associated with the uncontrolled radical generation and increased chain transfer reactions in oxygen-based systems, which lead to

broader molecular weight distribution and reduced thermal stability. Similar trends have been reported in previous studies (Bocare et al., 2019; Zhu et al., 2019). In contrast, peroxide systems provide controlled radical generation and improved process stability.

Peroxide-based initiation systems are widely used. The combination of peroxides with different decomposition temperatures allows for stepwise regulation of radical generation throughout the reactor. This approach leads to more balanced formation of polymer chains, narrowing of the molecular weight distribution, and increased structural homogeneity. Similar effects of peroxide-based systems on polymer structure, thermal properties, and material performance have also been reported in recent studies (Cardoso et al., 2021; Yolsal et al., 2024).

As a result, peroxide-based initiation systems are widely used in modern high-pressure polyethylene production. These systems not only improve the mechanical and thermal properties of the product, but also increase the safety and technological stability of the process. The obtained results demonstrated that the peroxide-based system produced polyethylene with higher molecular weight, narrower molecular weight distribution, and a higher degree of crystallinity. Therefore, the experimental findings confirmed that peroxide-based initiator systems provide more favorable technological performance and superior product characteristics in high-pressure polyethylene production. Overall, the differences between oxygen and peroxide initiator systems can be explained by their distinct radical generation mechanisms, which directly influence molecular weight distribution, chain branching, and thermal stability of LDPE.

The observed differences between oxygen- and peroxide-based initiation systems originate from their distinct radical generation pathways. Under high-pressure polymerization conditions, oxygen reacts rapidly with ethylene and intermediate radicals, producing highly reactive oxygen-containing species. These reactions may promote chain transfer and termination processes, resulting in greater variability in chain length and consequently a broader molecular weight distribution. Furthermore, oxygen-containing radicals can facilitate the formation of oxidized structures within the polymer matrix, which may negatively affect thermal stability and long-term material performance.

Peroxide initiators decompose thermally at predictable rates, generating radicals in a more controlled manner. When several peroxides with different decomposition temperatures are applied simultaneously, radical formation can be distributed throughout the reactor volume and over different stages of the polymerization process. Such behavior contributes to a more uniform chain-growth mechanism, improved control of branching reactions, and a narrower molecular weight distribution. Similar observations have been reported in studies investigating the relationship between initiator decomposition kinetics and polyethylene microstructure, where peroxide-based systems were associated with enhanced structural homogeneity and improved thermal and mechanical characteristics.

The discussion of the obtained results demonstrates that the differences between oxygen- and peroxide-based initiation systems originate from their distinct radical generation mechanisms. These mechanisms directly affect molecular weight distribution, branching behavior, crystallinity, and thermal stability of LDPE. The GPC and DSC results obtained in this study are consistent with literature data reported for peroxide-initiated high-pressure polyethylene production, confirming the ability of peroxide systems to provide more controlled polymerization kinetics and improved structural homogeneity. Therefore, the experimental findings support the theoretical understanding of radical polymerization processes and highlight the advantages of peroxide-based initiator systems for industrial LDPE production.

Conclusion

1. Differential Scanning Calorimetry (DSC) analysis revealed that the peroxide-initiated polyethylene exhibited a higher melting temperature (113°C) and crystallinity degree (51%) than the oxygen-initiated sample (108°C and 42%, respectively), indicating the formation of a more ordered polymer structure.
2. The experimental results confirm that peroxide-based initiation provides improved control of radical generation and polymerization kinetics, resulting in enhanced molecular uniformity, higher crystallinity, and improved material performance. Literature data further indicate that peroxide initiation may increase mechanical strength by approximately 15–20% and improve thermal stability.
3. From an industrial perspective, the application of peroxide-based initiator systems can contribute to increased process stability, improved product quality, reduced recycle flow, lower compressor loads, and higher reactor productivity. These advantages make peroxide initiation a promising approach for modern high-pressure LDPE production.
4. Future research should focus on optimization of initiator concentration, peroxide combinations, reactor operating conditions, and detailed investigation of molecular weight distribution and branching characteristics in order to further improve product performance and process efficiency.

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