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**Degradation of Polypropylene Random Copolymer in Aqueous Solution of Chlorine
Dioxide: Effect of Crystalline Structure and Morphology**

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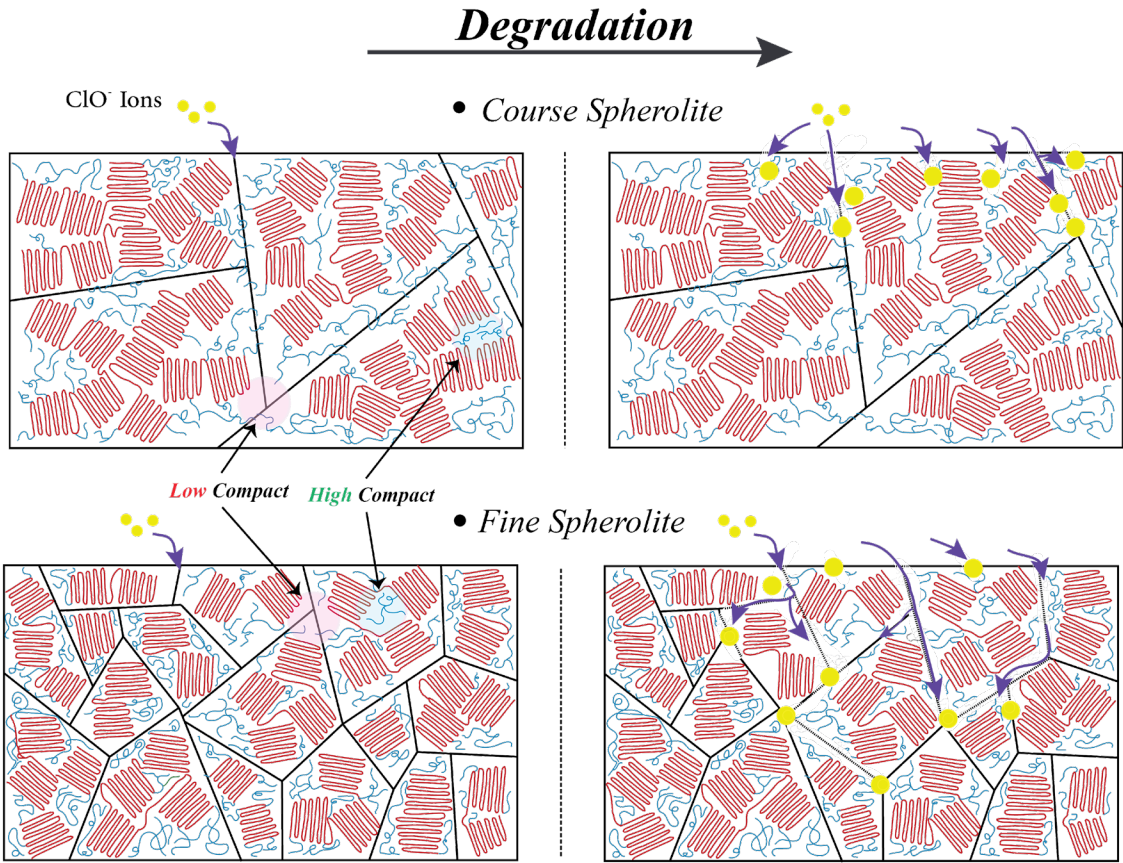
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Abstract

The effect of different crystalline phases and spherulite diameter (D_s) on polypropylene random copolymer (PP-R) aging behavior in chlorine dioxide (ClO_2) was investigated. Three samples were prepared, a sample without a nucleating agent (P) and two samples containing α (A) and β (B) phase nucleating agents. The aging process was conducted in 20 ppm ClO_2 aqueous solution at 60 °C for up to 1440 h. For initial (unaged) samples, X-ray Diffraction (XRD) and Optical Microscope (OM) analysis showed that they were composed of different crystalline phases (P: $\alpha + \gamma + \beta$, A: $\gamma + \alpha$, and B: $\beta + \alpha$) and different D_s ($P > B > A$). The extent of chemical degradation was monitored by Carbonyl Index (CI) obtained from Fourier Transform Infrared Spectroscopy (FTIR). After 1440 h of aging, A sample had the highest, and P sample had the lowest CI values. Elongation at break (ϵ_b) values from a tensile test showed that A and B samples reached 50% of their initial ϵ_b after 700 and 800 h, respectively. In contrast, ϵ_b for P decreased only 25% after 1440 h pointing out the less chain scission and degradation. Rheological experiments and isothermal and non-isothermal Differential Scanning Calorimetry (DSC) were conducted to study the characteristics of degraded chains in melt state and their crystallization behavior, respectively. Finally, summarizing the test data concluded that the spherulite size controls the chemical stability of PP-R in water containing ClO_2 , and samples with smaller spherulite sizes are more susceptible to chemical degradation.

Keywords: Polypropylene random copolymer, Crystalline Structure, Morphology, Spherulite size, Chemical Degradation, Chlorine Dioxide

Graphical Abstract



1. Introduction

The chemical degradation of polypropylene random copolymer (PP-R) in chlorinated water presents a critical challenge for manufacturers and users of plastic piping systems, as it directly impacts the longevity and safety of water infrastructure [1], [2]. While PP-R has become the material of choice for hot and cold water distribution networks due to its excellent thermal stability and mechanical properties [3], its susceptibility to oxidative degradation when exposed to disinfectants like chlorine dioxide and sodium hypochlorite threatens its long-term performance [4]. This vulnerability is particularly concerning given that water disinfection is essential for preventing waterborne diseases [5], creating an unavoidable tension between maintaining water safety and preserving pipe integrity. Understanding the degradation mechanisms and developing strategies to enhance PP-R's resistance to chlorinated water is therefore crucial for ensuring the reliability of modern plumbing systems [6].

Previous researches have extensively documented the general degradation behavior of PP-R in chlorinated water environments. Studies have shown that exposure to chlorine-based disinfectants leads to chain scission, reduction in molecular weight, and eventual embrittlement of the polymer [7], [8], [9]. Multiple analytical approaches have been employed to track this degradation process: infrared microscopy has revealed the spatial distribution of oxidation products and antioxidant depletion across pipe walls [4], while rheological measurements have demonstrated significant changes in molecular weight distribution and melt behavior [10], [11]. Time-resolved studies have shown that the degradation progresses from the pipe surface inward, with a complex interplay between diffusion and reaction kinetics [12]. However, these investigations have primarily focused

on bulk property changes without considering the fundamental role of polymer microstructure in the degradation mechanism.

The crystalline structure of PP-R, which can exist in multiple polymorphic forms (α , β , and γ), significantly influences its mechanical and thermal properties [13]. The α -form, characterized by a monoclinic unit cell, is the most common structure, while the β -form with its hexagonal arrangement offers improved impact strength and toughness [14], [15]. The γ -form, typically induced under high pressure or in copolymers, exhibits unique chain packing that affects mechanical properties [16], [17]. Recent studies have demonstrated that β -nucleated PP-R exhibits enhanced mechanical properties and thermal stability compared to conventional α -form materials [7], [18]. The morphological characteristics of these different forms, including spherulite size and lamellae arrangement, can be controlled through nucleating agents and processing conditions [19], [20]. Nevertheless, the relationship between these different crystalline forms and their resistance to chemical degradation by chlorine dioxide remains largely unexplored. This gap is particularly significant given that chlorine dioxide's degradation mechanism may differ from other oxidizing agents due to its unique molecular structure and reactivity [21], [22].

Furthermore, while the importance of polymer morphology in photooxidative and thermal degradation has been established [15], [23], [24], [25], [26], [27], [28], [29], [30], [31], its role in chemical degradation by chlorine dioxide is not well understood. The complex hierarchical structure of PP-R, from molecular to macroscopic scales, includes various interfaces between crystalline and amorphous regions that could influence degradation patterns [32], [33]. Studies on other degradation modes have shown that the initial attack often occurs in the amorphous regions, followed by progressive deterioration of the crystalline domains [34], [35]. The spherulitic

structure's role in degradation has been particularly highlighted in thermal oxidation studies, where the spherulite boundaries act as preferred oxidation sites [28]. However, the specific influence of morphological parameters such as crystallite size, lamellae thickness, and amorphous region distribution on chlorine dioxide-induced degradation remains unclear. Advances in understanding polymer oxidation mechanisms [36], [37] suggest that the spatial arrangement of crystalline and amorphous regions could significantly affect both the diffusion pathways and reaction kinetics of oxidizing species. The lack of comprehensive studies connecting crystalline structure, morphology, and degradation kinetics has limited our ability to design more resistant PP-R materials for water distribution applications.

To address these knowledge gaps regarding the influence of crystalline structure and morphology on PP-R degradation in chlorine dioxide environments, we designed a comparative study using three PP-R formulations: one without nucleating agents and two containing α and β phase nucleating agents, respectively. Through controlled exposure to 20 ppm chlorine dioxide solution at 60°C, we systematically investigated how different crystalline phases (α , β , and γ) and spherulite sizes affect the degradation process. Our analysis focused on two primary outcomes: (1) establishing the relationship between initial crystalline structure/morphology and degradation resistance through combined XRD and POM analysis, and (2) determining the mechanistic pathway of degradation in different crystalline phases through correlation of chemical (FTIR), mechanical (tensile), thermal, and rheological measurements. This approach directly addresses the identified gap in understanding how polymer microstructure influences chlorine dioxide-induced degradation, providing insights essential for developing more resistant PP-R materials.

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