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Correlation Between Crystallinity and Microhardness of Linear Low-Density Polyethylene (LLDPE)

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ABSTRACT

This study investigates the relationship between crystallinity and microhardness in linear low-density polyethylene (LLDPE) to gain insights into how changes in crystalline structure affect the material's strength. Different types of linear low-density polyethylene (LLDPE) were fractionated using Temperature Rising Elution Fractionation (TREF) to obtain distinct fractions based on their crystallizability, to investigate the relationship between the crystallinity and microhardness of each fraction. This study aimed to understand how changes in crystallinity affect the microhardness of LLDPE, providing valuable insights for the design and optimization of LLDPE materials for various applications where it allows for the production of tailored polymer fractions and provides valuable information about their thermal behavior. This knowledge is crucial for understanding the relationship between polymer structure, morphology, and properties, as well as for designing polymers with specific characteristics for various applications. The results illustrate, a decrease in crystallinity leads to enhanced molecular mobility in the amorphous domains, which can have implications for the material's mechanical behavior, thermal properties, processing characteristics, and other relevant physical attributes.

Keywords: Linear low-density polyethylene (LLDPE), crystallinity, microhardness, crystalline structure, mechanical properties, processing conditions, annealing

العلاقة بين التبلور والصلابة في البولي ايثيلين (LLDPE)

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ملخص البحث

تبحث هذه الدراسة العلاقة بين كمية التبلور **(crystallinity)** والصلابة في البولي إيثلين **(LLDPE)** وذلك لمعرفة تأثير التغيرات في البنية البلورية على قوة المادة. في هذه الدراسة تم اخذ عينات مختلفة من البولي إيثلين **(LLDPE)** بحيث تم فصلها بواسطة تقنية تسمى **(TREF)** للحصول على عينات مختلفة في نسب التبلور، لدراسة العلاقة بين التبلور والصلابة تهدف هذه الدراسة إلى فهم كيفية تأثير نسب البلورة على الصلابة لي بولي ايثلين، مما يوفر فرصة تحسين مواصفات **LLDPE** لمختلف التطبيقات حيث يسمح بإنتاج أجزاء بوليمر مخصصة، أيضا معلومات قيمة حول سلوكها الحراري .

تعتبر هذه المعرفة ضرورية لفهم العلاقة بين بنية البوليمر، وشكله، وخصائصه، وكذلك لتصميم بوليمرات ذات خصائص محددة لمختلف التطبيقات. وتوضح النتائج أن انخفاض التبلور يؤدي إلى تعزيز الحركة الجزيئية، مما قد يكون له آثار على السلوك الميكانيكي للمادة، والخصائص الحرارية، وخصائص المعالجة، والصفات الفيزيائية الأخرى ذات الصلة.

الكلمات المفتاحية: البولي إثيلين، التبلور، الصلابة، الخواص الميكانيكية

1. Introduction

Plastic materials have become integral to a multitude of industries owing to their remarkable versatility, cost-effectiveness, and extensive range of applications [1, 2]. Among the various types of plastics, polyethylene (PE) stands out as one of the most widely utilized, thanks to its excellent mechanical properties and resistance to chemical degradation [1, 3]. Specifically, linear low-density polyethylene (LLDPE) has attracted considerable attention, particularly in the form of plastomers, due to its unique combination of elastomeric behavior and favorable processability. This distinct blend of properties makes LLDPE particularly suitable for applications requiring flexibility and durability, such as packaging materials, automotive components, and consumer products.

Understanding the structure property relationships inherent in plastomers is essential for optimizing their performance across specific applications [4]. These relationships encompass a wide variety of factors, including molecular structure, morphology, and the resulting mechanical properties of the polymer. The mechanical properties of polymers are influenced by numerous factors, such as the arrangement of monomers, the presence and nature of side groups, the degree of polymerization, and the interactions between polymer chains [6]. Therefore, a comprehensive understanding of how these factors intertwine is very important for tailoring the properties of LLDPE to meet the demands of diverse applications.

Molecular structure refers to the specific arrangement of atoms and chemical bonds within a polymer molecule. It encompasses various parameters, including the type and sequence of monomers used in synthesis, the nature of branching or cross-linking present in the structure, and the overall architecture of the polymer chain. Each of these factors significantly influences the mechanical properties of polymers, such as tensile strength, elasticity, and thermal stability [7, 8].

For instance, a higher degree of crystallinity generally correlates with improved strength and stiffness, while increased amorphous regions may enhance flexibility and impact resistance. The concept of crystallinity is particularly important in the context of LLDPE, as it plays a pivotal role in defining the material's mechanical behavior. Crystallinity refers to the degree to which the polymer chains are ordered and packed closely together in a crystalline structure. A higher crystallinity typically results in a more rigid material, while lower crystallinity often leads to increased ductility and toughness. This balance between crystalline and amorphous regions is crucial for ensuring that LLDPE meets the performance requirements of specific applications [8].

Moreover, the morphology of a polymer significantly impacts its mechanical properties. The arrangement and distribution of polymer chains at various length scales can greatly affect the overall strength, stiffness, toughness, and other mechanical characteristics of the material [8]. For instance, the presence of crystalline regions can act as reinforcements, enhancing the material's ability to withstand mechanical stresses. Conversely, amorphous regions contribute to the material's ability to deform and absorb energy, which is particularly beneficial in applications where impact resistance is critical.

Investigating the correlation between crystallinity and microhardness in LLDPE is particularly relevant for advancing the understanding of how these structural features influence the material's performance. Microhardness, a measure of a material's resistance to localized plastic deformation, is a key indicator of the mechanical integrity of polymers. It is influenced by the degree of crystallinity, as more crystalline regions generally exhibit higher hardness values due to their ordered structure and strong intermolecular forces [9].

Therefore, the interplay between crystallinity and microhardness in LLDPE offers valuable insights into the material's mechanical behavior and performance. Understanding these correlations is vital for optimizing the properties of LLDPE for specific applications, ultimately paving the way for advancements in materials science and engineering. By delving into the nuances of molecular structure, morphology, and mechanical properties, this research aims to elucidate the fundamental principles governing the behavior of LLDPE, contributing to the ongoing efforts to enhance the performance of plastic materials in various industrial applications.

2. Experimental work

Two different plastomers (LLDPE) were used, the first plastomer, is referred to as PE1. This plastomer was composed of ethylene and octane as the comonomer. The comonomer content is 4.5%.

The second plastomer, labeled as PE2, was composed of ethylene and hexene as the comonomer. The comonomer content of PE2 is 3.4%.

These two plastomers were selected to investigate the influence of different comonomer types (octane vs. hexene) and comonomer content on various properties and behaviors of the LLDPE materials. Both PE1 and PE2 are prepared and obtained from the polyolefin lab at Stellenbosch university. The specific physical properties of both plastomers, as outlined in Table 1.

Table 1. Physical properties of both plastomers

Sample	MFI (g/10ml)	Density	T_m (ºC)	T_c (ºC)	Crystallinity (%)
PE1	1	0.9035	100	82	26
PE2	1.3	0.927	120	110	35

Preparative temperature rising elution fractionation (TREF) is a technique used to isolate polymer samples based on their crystallizability, by employ cross fractionation to characterize LLDPE based on its crystallizability, taking into account both comonomer composition and the degree of branching. By fractionating LLDPE samples using this approach, we can isolate specific fractions with distinct crystallization behavior and branching characteristics.

The comonomer composition plays a significant role in determining the crystallizability of LLDPE. The presence of different comonomers, such as hexene, or octene, can influence the crystallization kinetics and the resulting crystalline structure. Additionally, the degree of branching, which refers to the number and length of short-chain branches, also impacts the polymer's crystallizability and overall properties

The crystallinity of PE1 and PE2 was determined using the density measurements to calculate the crystallinity. It assumed a two-phase system with constant densities for the amorphous and crystalline phases. The method is based on the assumption that the PE samples have a two-phase morphology and that the density of each phase is uniform within the sample and consistent across different samples. By measuring the densities of the samples, the crystallinity (X) can be calculated based on measured densities of the amorphous and crystalline phases as follows:

$$X = (\rho - \rho a) / (\rho c - \rho a) \quad (1)$$

where X is the crystallinity present in the sample, ρ is the density of the sample, ρc is the density of fully crystalline PE, ρa is the density of fully amorphous PE.

The density values used in the calculation are 0.855 g/cm³ for fully amorphous PE and 1.0 g/cm³ for fully crystalline PE [10].

By measuring the density of the sample and applying the above equation, the crystallinity of the sample can be determined. This method assumes a two-phase system with uniform densities for the amorphous and crystalline phases.

Microhardness commonly defined as the material's ability to resist localized plastic deformation. To determine microhardness, a Vickers hardness tester with a diamond indenter was utilized, applying a load of 10 gf to observe the resulting deformation pattern. The recorded measurements represent the average of at least five individual measurements

3. Results and Discussion

TREF results shows that the elution distribution for PE1, was observed in the temperature range of 50-100°C. This relatively narrow range indicates that the copolymer exhibits a more defined crystallization behavior, with a specific temperature range at which the polymer chains separate from the solvent. The narrower elution distribution suggests more homogeneous composition and a more uniform crystalline structure for PE.

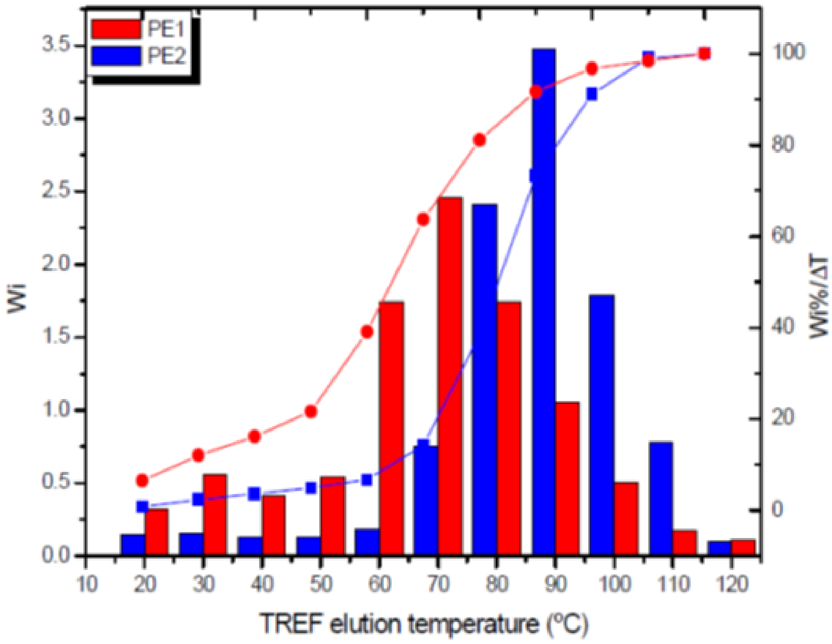

Figure 1. TREF profiles of PE1 and PE2.

On the other hand, PE2 displayed a broader elution distribution in the range of 60-120°C. This broader range suggests a wider distribution of crystallization temperatures and a less defined crystallization behavior compared to PE1. The broader elution distribution indicates a more heterogeneous composition and a less uniform crystalline structure for PE2.

The observed differences in elution distributions between PE1 and PE2 can be attributed to various factors, including the nature of the comonomers (1-octene vs. 1-hexene) and their influence on the crystallization kinetics. The comonomer type and content affect the copolymer's ability to crystallize and form ordered structures, leading to variations in the elution behavior during fractionation process.

This fact has been extensively studied by other researchers [11, 12] and our results are in agreement with their conclusions.

Due to limited material in the soluble fractions below 50 ºC, these fractions were combined into one fraction called the soluble fraction (SF). The properties of each fraction, including DSC crystallization temperature (Tc), and melting temperature (Tm).

Table 2. Properties of TREF fractions

Fraction temperature (°C)	**T_m (ºC)**		**T_c (ºC)**		**Commoner content (%)**	
SF	72.4	93.2	62.9	85.7	5.60	3.50
60	76.2	96.1	65.4	89.1	3.52	3.46
70	81.5	102.7	68.2	90.4	2.64	2.60
80	96.1	109.8	77.6	97.3	2.77	2.55
90	98.4	118.4	81.8	106.4	2.61	1.91
100	101.4	118.6	85.4	110.4	1.61	1.20
110	103.3	122.7	86.9	111.6	1.20	1.15
120	103.4	124.9	87.7	107.4	0.90	0.62

Table 2 provides a summary of the properties of the fractions obtained from TREF fractionation. It is observed that the Tc, Tm, increase with increasing TREF elution temperature, which indicates a correlation between elution temperature and crystallization/melting behavior. For PE1, the Tm temperature ranges from 26 ºC to 60 ºC, while for PE2, it ranges from 64 ºC to 88 ºC. This suggests that higher elution temperatures result in higher melting temperatures, indicating increased thermal stability and ordered crystalline structures.

The results show that these properties increase with higher TREF elution temperatures. The soluble fraction (SF) is highlighted as a crucial component influencing the ultimate properties of the copolymers.

Figure2 illustrates that the comonomer content of each TREF fraction is comparable at any given temperature for both copolymers, except for the soluble fraction (SF). In the case of PE1 (octane copolymer), the SF exhibits a substantially higher comonomer content compared to the PE2 copolymer.

It is intriguing to observe that despite the relatively similar comonomer contents, there is a noticeable difference in lamellar thickness, as indicated by the melting temperatures of each fraction. This discrepancy suggests that factors other than comonomer content alone influence the crystalline structure and properties of the copolymers. One possible contributing factor is the distribution of the short-chain branches (SCB) within both copolymers.

The distribution of SCB refers to the arrangement and placement of the comonomer units along the polymer chain. Variations in the distribution of SCB can affect the packing efficiency and arrangement of the polymer chains in the crystalline regions, subsequently influencing the lamellar thickness and melting behavior of the fractions. Therefore, the observed differences in lamellar thickness between the fractions of PE1 and PE2 may be attributable to variations in the distribution of SCB within the copolymer chains.

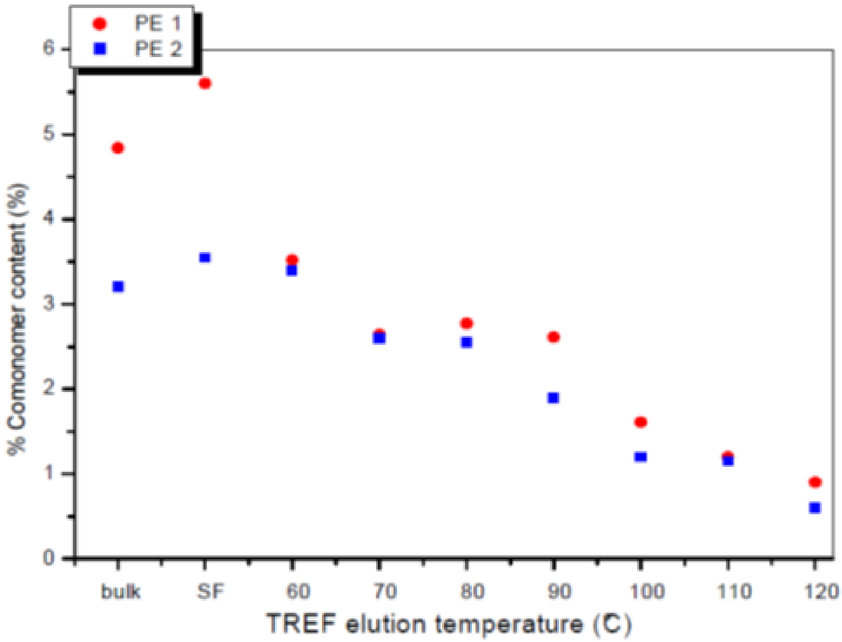

Figure 2. Comonomer content of bulk copolymers and TREF fractions of PE1 and PE2

This suggests that while comonomer content plays a role in the overall properties of the copolymers, other factors such as the distribution of SCB can significantly impact the crystalline structure and subsequent properties. Understanding and controlling the distribution of SCB can be crucial in tailoring the properties of the copolymers for specific applications.

Figure 3 shows the crystallinity of each of the TREF fractions, as it shown as TREF fractionation temperature increase the crystalline percentages increase.

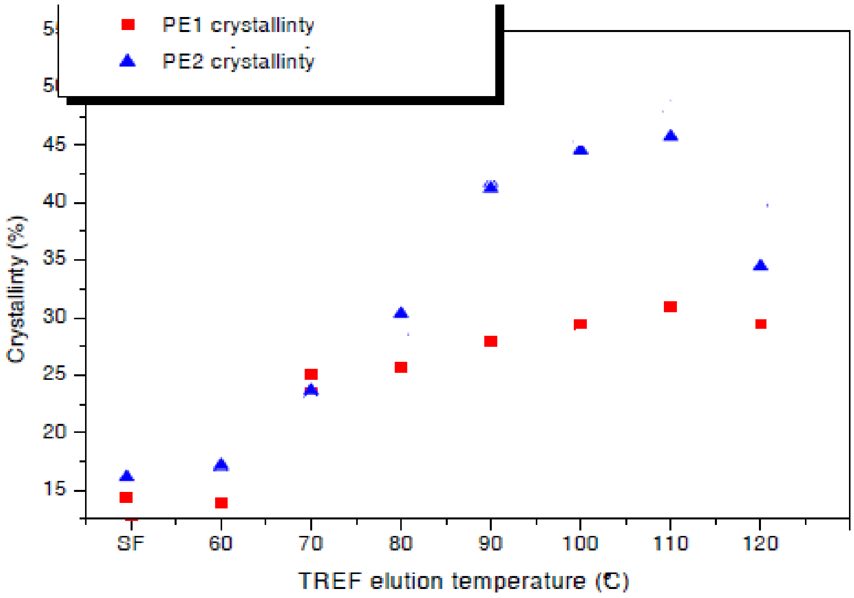

Figure 3. Crystallinity % of PE1 and PE2

The variations in crystalline structure significantly influence the mechanical behavior of the copolymers as it shown in Figure 4, which shows that the higher microhardness values observed in the higher TREF temperature fractions can be attributed to their higher crystallinity compared to the lower TREF temperature fractions. Crystallinity refers to the degree of structural order and organization in a polymer, particularly in its crystalline regions. Higher crystallinity generally leads to increased stiffness and hardness in polymers.

The correlation between microhardness and crystallinity can be attributed to the presence of larger and more defined crystalline regions. These crystalline regions contribute to higher overall crystallinity, which consequently leads to increased microhardness of the material. Similar results were obtained by Santa and his coworker [13] for polyethylene terephthalate. They found that the correlation between microhardness and crystallinity can be attributed to the presence of larger and more defined crystalline regions. These crystalline regions contribute to higher overall crystallinity, which consequently leads to increased microhardness of the material. This relationship highlights the significance of crystalline structure in influencing the mechanical properties of polymers.

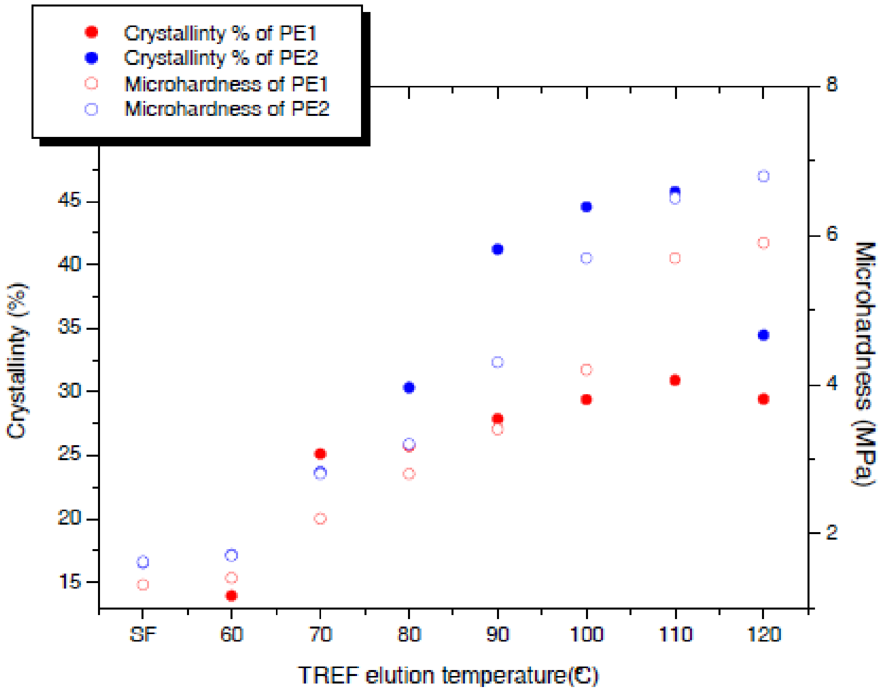

Figure 4. Microhardness (open symbols) and crystallinity

4. Conclusions

The crystallinity and the microhardness of copolymers of LLDPE has been investigated in this paper and the following conclusion are obtained:

- Chain branching significantly affects the packing and arrangement of polymer chains.

- Side chains hinder orderly alignment, impacting density and crystallinity of copolymers.

- Increasing comonomer content reduces the average number of consecutive ethylene units. Shorter chains decrease the crystallizable portion of the copolymer, leading to lower overall crystallinity and increased amorphous regions.

- The decrease in crystallinity influences the copolymer's physical properties. Molecular motions in amorphous regions become more significant, affecting behavior at lower temperatures. Properties such as flexibility, impact resistance, and low-temperature performance are influenced by these molecular changes.

- Microhardness results show that reduced crystallinity and increased amorphous content lower hardness. A decrease in ordered crystalline regions correlates with lower hardness values.

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