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investigating the Impact of Crystalline Structure on the Physical Properties of Polyethylene Using TREF Analysis

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دراسة تأثير التركيب البلوري على الخصائص الفيزيائية للبولي إثلين باستخدام تحليل تقنية TREF

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Abstract

The structure–property relationships of two linear low-density polyethylene (LLDPE) plastomers, ethylene/1-octene (PE1) and ethylene/1-hexene (PE2), were investigated using preparative temperature rising elution fractionation (TREF). Fractionated and bulk materials were characterized by differential scanning calorimetry (DSC), density-based crystallinity, and Vickers microhardness measurements. TREF revealed distinct elution behaviors, with PE2 exhibiting broader and higher-temperature fractions, indicating longer ethylene sequence lengths and enhanced crystallizability. DSC results showed consistently higher melting and crystallization temperatures for PE2, reflecting thicker and more perfect lamellae. Increasing short-chain branching was found to reduce melting temperature, crystallinity, and microhardness, confirming a strong dependence of thermal and mechanical properties on comonomer distribution. Fraction removal experiments further demonstrated that eliminating low-crystallinity fractions increases melting temperature and hardness, while removal of highly crystalline fractions leads to their reduction. These findings highlight the critical role of comonomer type and distribution in tailoring the thermal and mechanical performance of LLDPE plastomers.

Our findings demonstrate that strategic modification of polymer architecture at the molecular level can lead to significant improvements in performance, paving the way for the development of more efficient, durable, and application-specific polyethylene materials. This research contributes to the growing field of advanced polymer design and offers practical pathways for enhancing material performance through targeted structural engineering.

Keywords: crystallinity, Linear low-density polyethylene (LLDPE), TREF, crystalline structure, CRYSTAF, mechanical properties.

العلاقة بين التركيب البنائي والخواص في نوعين من البولي إيثيلين منخفض الكثافة (LLDPE)، وهما إيثيلين/1-أوكتين (PE1) وإيثلين/1-هكسين(PE2) ، حيث تمت دراستهما باستخدام تقنية الفصل (TREF). حيث تم فصل الجزيئات بحسب نسبة التبلور وتم قياس الخواص الحرارية بواسطة (DSC)، وقياس درجة التبلور اعتمادًا على الكثافة، واختبار الصلادة المجهرية بطريقة فيكرز. أظهرت نتائج الفصل بواسطة TREF سلوكيات مختلفة، حيث أبدى البوليمر PE2 نطاقًا أوسع ودرجات حرارة أعلى، مما يشير إلى طول سلاسل (الإيثيلين) وقدرة أعلى على التبلور. كما بينت نتائج DSC درجات انصهار وتبلور أعلى للبوليمر PE2، وهو ما يعكس وجود صفائح بلورية أكثر سماكة وكمالًا. وقد وُجد أن زيادة التفرعات قصيرة السلسلة تؤدي إلى انخفاض درجة الانصهار ونسبة التبلور والصلادة المجهرية، مما يؤكد الاعتماد القوي للخواص الحرارية والميكانيكية على توزيع comonmer. وأظهرت تجارب إزالة الجزيئات منخفضة التبلور يؤدي إلى زيادة درجة الانصهار والصلادة، في حين أن إزالة الجزيئات عالية التبلور يؤدي إلى انخفاضهما. وتؤكد هذه النتائج الدور الحاسم لنوع اcomonmer وتوزيعه في ضبط الخواص الحرارية والميكانيكية ل.LLDPE .

الدراسة أظهرت أن التعديل التركيب البنائي للبوليمر على المستوى الجزيئي يمكن أن يؤدي إلى تحسينات كبيرة في الأداء، مما يمهّد الطريق لتطوير مواد بولي إيثيلين أكثر كفاءة ومتانة ومصممة لتلبية تطبيقات محددة. وتسهم هذه الدراسة في تعزيز وتوسيع مجال تصميم البوليمرات المتقدمة.

الكلمات الدالة:. البولي إثلين – البلورة- الخصائص الميكانيكية

Introduction:

Plastic materials play a crucial role in various industries due to their adaptability, affordability, and extensive range of applications [1]. Polyethylene (PE) is one of the most widely used plastics, known for its excellent mechanical properties and chemical resistance [1,2,3]. Within the category of PE, plastomers - a type of linear low-density polyethylene (LLDPE) - have garnered significant attention which attributed to their distinctive blend of characteristics, which includes not only elastomeric behavior but also exceptional processability. These properties enable plastics to be easily molded and shaped into various forms, making them suitable for a wide array of applications. The combination of flexibility, durability, and the ability to be processed using different manufacturing techniques further enhances their utility across multiple industries. Understanding the structure-property relationships of plastomers is critically important for customizing their characteristics to meet the demands of specific applications. This understanding allows for the manipulation of molecular structures to achieve desired physical and mechanical properties, thereby optimizing performance in various industrial contexts. By examining how structural variations influence properties, researchers and manufacturers can effectively design plastomers that fulfil particular functional requirements [4].

The relationship among molecular structure, morphology, and mechanical properties of polymers is a multifaceted and intricate area of study. This interplay encompasses numerous factors that determine how the arrangement and configuration of polymer chains influence their physical characteristics and overall performance. The mechanical properties of polymers are influenced by several key elements, including the arrangement of monomers, side group presence, polymerization degree, and the interactions between polymer chains [5,6].

Molecular structure refers to the specific configuration of atoms and chemical bonds within a polymer. This includes the type and sequence of monomers, branching or cross-linking, and the overall chain architecture. The molecular structure plays a crucial role in defining the mechanical properties of polymers, influencing their strength, elasticity, and durability.

Understanding these relationships is essential for the development of tailored materials with desired performance characteristics for various applications [7,8].

As a result, the morphology of a polymer significantly influences its mechanical properties. Factors such as chain arrangement, crystallinity, and phase separation can all affect how the material behaves under stress. For instance, a well-ordered crystalline structure typically contributes to higher strength and stiffness, while amorphous regions can enhance toughness and flexibility.

Moreover, the distribution of different phases within the polymer can lead to variations in performance. Understanding these morphological characteristics allows for the optimization of polymers for specific applications, ensuring that they meet the desired mechanical requirements. This knowledge is vital for innovations in fields such as packaging, automotive, and biomedical materials, where customized performance is essential.

Experimental

Two different polymers of (LLDPE) were utilized in this study. The first, designated as PE1, consists of ethylene with octane as the comonomer, featuring a comonomer content of 4.5%. The second polymer, identified as PE2, is composed of ethylene and hexene, with a comonomer content of 3.4%.

These polymers were chosen to explore the effects of different types of comonomers (octane versus hexene) and varying comonomer levels on the properties and behaviors of the LLDPE materials. The specific physical characteristics of both plastomers are detailed in Table 1.

Table 1. polymer physical properties

Sample	MFI (g/10ml)	Density (g/cc)	Melting temperature T_m (°C)	Crystallinity temperature Tc (°C)	Crystallinity (%)
PE1	1	0.9035	100	82	26
PE2	1.3	0.927	120	110	35

Using Preparative temperature rising elution fractionation (TREF) which is a powerful analytical technique for separating polymer samples based on crystallizability, providing detailed insights into their structural characteristics. This method allows researchers to perform cross fractionation, which is particularly useful for characterizing linear low-density polyethylene (LLDPE) by examining the interplay between comonomer composition and the degree of branching.

TREF was employed to separate polymer fractions based on their crystallizability. The method consisted of the following steps:

1. Dissolution: Approximately 2 g of polymer was dissolved in 200 mL of xylene containing 3 mg of antioxidant at 135 °C.
2. Inert Support: A heated inert support is introduced into the mixture.
3. Crystallization: The hot solution was poured over ~2–3 kg of pre-heated inert support (sea sand) and allowed to cool slowly to room temperature. This induced crystallization based on chain regularity.
4. Crystallinity Measurement: Lower crystallinity corresponds to a lower crystallization temperature.
5. Elution: The crystallized polymer mixture was transferred into a TREF column. Xylene solvent was passed through the column while the temperature was gradually increased from 60 °C to 140 °C. Fractions were collected at

regular intervals (e.g., every 10 °C), corresponding to chains of increasing crystallinity.

6. Collection: A total of twelve fractions were isolated for each copolymer and dried for subsequent analysis.

When applying TREF to LLDPE samples, specific fractions can be isolated, each exhibiting unique crystallization behaviors and branching features. The comonomer composition is crucial; different comonomers like hexene or octene can markedly influence crystallization kinetics, leading to variations in crystalline morphology. For example, the incorporation of larger comonomers may hinder crystallization, resulting in a more amorphous structure.

Moreover, the degree of branching—defined by the number and length of short-chain branches—significantly impacts crystallizability. A higher degree of branching typically disrupts the orderly packing of polymer chains, leading to lower crystallinity and altered mechanical properties. Understanding these relationships not only aids in elucidating the material's performance but also informs the design of LLDPE formulations for specific applications, such as packaging, where tailored mechanical and thermal properties are essential.

The crystallinity of the polymers was evaluated through density measurements, based on the assumption of a two-phase system comprising amorphous and crystalline phases, each with constant and uniform densities. This method operates under the premise that the polyethylene samples maintain a two-phase morphology, where the densities are consistent not only within each sample but also across different samples.

To calculate crystallinity, the density of each sample is measured, and the known densities of the amorphous and crystalline phases are utilized. The crystallinity is determined using the equation:

Crystallinity present $=\frac{(\text{density of the sample}) - (\text{density of fully amorphous PE})}{(\text{density of fully crystalline PE}) - (\text{density of fully amorphous PE}}$) [9].

The density values used for the calculation of crystallinity in polyethylene (PE) are 0.855 g/cm³ for fully amorphous PE and 1.0 g/cm³ for fully crystalline PE. These values are essential for determining the crystallinity of a sample by measuring its density and applying the appropriate equation, which assumes a two-phase system with consistent densities for both the amorphous and crystalline phases [10].

DSC was used to evaluate the Tm and Tc behaviour of the samples. A heating/cooling cycle of 10 °C/min was applied between −40 °C and 200 °C. The second heating run was used for analysis. For Figures 1–3, the reported measurements showed high reproducibility with negligible variation between repeated runs. As such, the results are presented as representative datasets without error bars. For subsequent analyses where variability was more critical to interpretation, error bars are included to explicitly indicate data scatter.

- Microhardness Testing

Microhardness is a critical parameter that quantifies a material's resistance to localized deformation or indentation on a microscopic scale .Vickers microhardness testing was performed using a calibrated microindenter under standardized load and dwell time conditions. Each sample was tested at multiple points, and the average value was recorded.

In this analysis, a Vickers hardness tester, equipped with a diamond indenter, was employed to evaluate the hardness of the polymer samples. A load of 10 gf was applied to create an indentation, allowing for the observation of the deformation pattern.

The Vickers hardness test is particularly useful because it provides a continuous scale of hardness measurements, making it suitable for thin films or small samples. Each measurement reflects the average of at least five individual readings, which enhances the reliability of the data by accounting for variability in the material.

The resulting hardness values offer insights into the mechanical properties of the polymers, such as their resistance to wear and indentation. Higher microhardness typically indicates greater resistance to deformation, which can correlate with enhanced durability and performance in applications where mechanical stress is a factor.

Understanding microhardness is essential for material selection and design, particularly in industries such as automotive, aerospace, and packaging, where the mechanical integrity of materials directly impacts functionality and longevity. By characterizing microhardness, researchers can better predict how polymers will perform under various conditions, facilitating the development of tailored materials for specific applications.

Results and Discussion

The TREF results shown in the figure 1, indicate that the elution distribution for PE1 occurs within a temperature range of 50-100°C. This relatively narrow range suggests that the copolymer demonstrates a more defined crystallization behavior, highlighting a specific temperature interval where the polymer chains effectively separate from the solvent. Such a narrow elution distribution implies a more homogeneous composition and a uniform crystalline structure for PE, reflecting consistent molecular arrangements within the material.

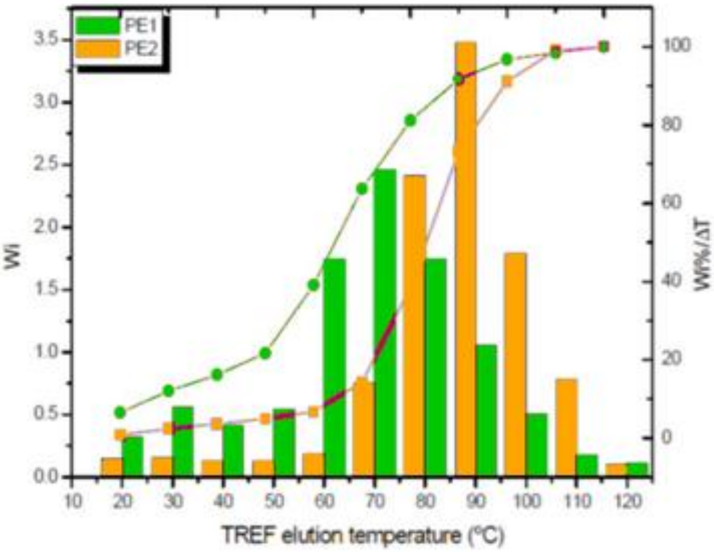

Figure 1 TREF elution curve of PE1 and PE2.

In contrast, PE2 exhibited a broader elution distribution spanning 60-120°C. This wider range suggests a greater variation in crystallization temperatures and a less defined crystallization behavior compared to PE1. The broader elution distribution points to a more heterogeneous composition and a less uniform crystalline structure for PE2, indicating that the polymer chains exhibit more variability in their arrangements and interactions.

Differences in the elution curves between PE1 and PE2 are primarily influenced by the type of comonomers used—specifically, 1-octene versus 1-hexene—and their impact on crystallization kinetics. Variations in comonomer structure and concentration directly affect the copolymer’s ability to develop crystalline domains, which is reflected in distinct elution patterns during fractionation. Because of the minimal content in fractions eluting below 50 °C, these were collectively grouped as a single "soluble fraction" (SF). Each resulting fraction was then analyzed for its thermal properties, including crystallization temperature (Tc) and melting temperature (T_m), using Differential Scanning Calorimetry (DSC).

DSC provides critical complementary data on the molecular structure and crystallization behavior of linear low-density polyethylene (LLDPE) copolymers, utilizing a thermal-based mechanism distinct from physical separation techniques like TREF. While TREF separates polymer chains based on their overall crystallizability, DSC analyzes the thermal response of polymer segments based on lamellar thickness and methylene sequence length. This allows DSC to detect both inter- and intramolecular structural differences. In the case of PE1 and PE2, both copolymers display similar crystallization exotherms, yet PE2 exhibits a higher crystallization temperature, suggesting the presence of longer, more linear segments that crystallize more efficiently. The figure 2 shows the melting behavior further distinguishes the two: PE1 presents a lower melting peak at 98°C, while PE2 shows a higher melting peak at 123°C, indicating more perfect and thicker lamellae in PE2.

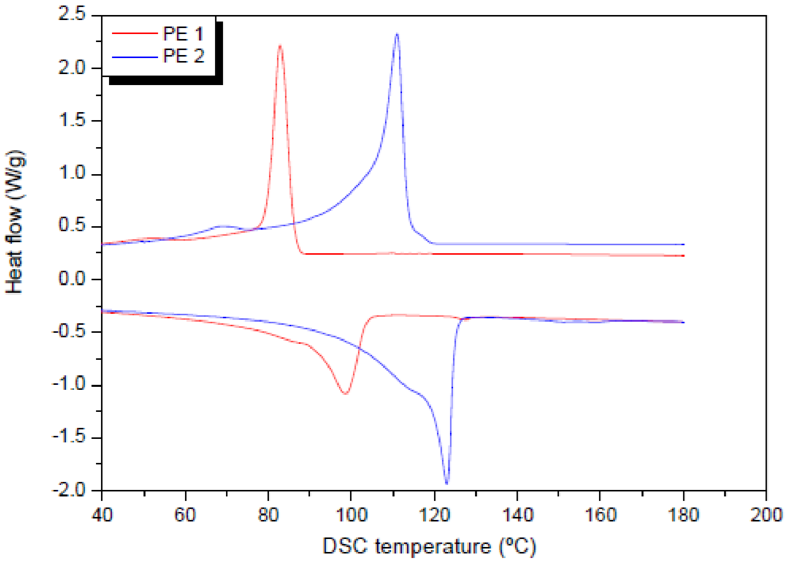

Figure 2 DSC crystallization and melting endotherms of PE1and PE2.

Despite this increased crystallinity in PE2, both polymers show complex melting profiles with secondary peaks and extended tails, which reflect heterogeneous lamellar distributions and internal structural irregularities. These features are more pronounced in PE2, suggesting that while it contains more crystalline regions, it also exhibits significant intra-molecular variation likely due to uneven comonomer incorporation. This duality in thermal behavior implies a balance between ordered and disordered domains within the same molecule. The DSC results are in good agreement with TREF and CRYSTAF analyses, reinforcing the conclusion that PE2, though structurally more capable of forming well-ordered crystals, still possesses a heterogeneous composition. These findings underscore the utility of DSC in revealing the morphological and molecular intricacies that influence the performance and processing characteristics of LLDPE materials.

Table 2. Properties of TREF fractions

Fraction Temperature (°C)	**T_m (°C) PE1**	**T_m (°C) PE2**	**Tc (°C) PE1**	**Tc (°C) PE2**	**Comonomer Content (%) PE1**	**Comonomer Content (%) PE2**
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	114.8	81.3	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 illustrates the relationship between melting temperature and increasing elution temperature. This phenomenon is well-documented and results from the impact of decreasing short-chain branching (SCB) content on the melting temperature of both copolymers [11]. Zhang et al [12], also noted changes in the melting temperature of ethylene-butene copolymer as the elution temperature increased.

Additionally, it is observed that with rising elution temperatures, the melting peaks become significantly narrower. This narrowing may stem from various factors, as reported by Simanke et al [13]. They suggested that the broadening of DSC endotherms could be attributed to different thermal histories of the polymers, broader molecular weight distributions, and varying crystal sizes present in the fractions.

Since the DSC analysis of both copolymers was conducted under identical conditions, the influence of thermal history and crystallization methods can be discounted as factors contributing to broadening. Instead, the broadening of the endotherms is likely due to differences in crystal sizes and the degree of their perfection, which are directly affected by increasing amounts of the comonomer in the PE chain. Specifically, a higher comonomer content reduces the sequence length between comonomer points, resulting in thinner lamellae, which in turn lowers the crystallization temperature.

Both copolymers exhibited similar behavior; all fractions displayed a single melting peak as it illustrated in figures 3,4. The peak temperature increased with higher fractionation temperatures. However, the melting temperature of PE2 was consistently higher than that of PE1 across all fractions, aligning with the findings from TREF and CRYSTAF analyses.

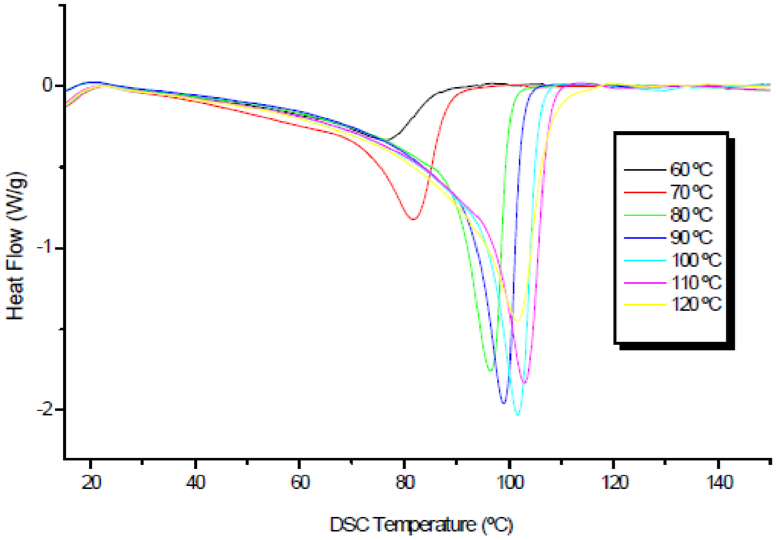

Figure 3 The DSC melting endotherms for the PE1 fractions

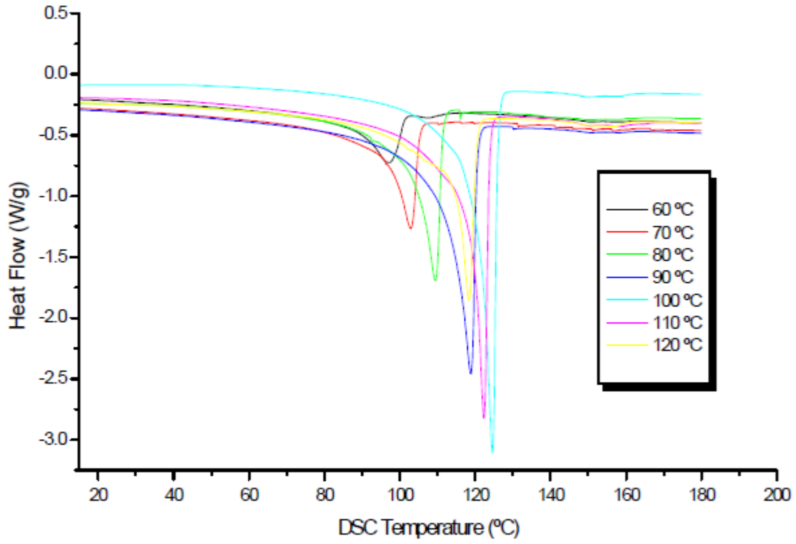

Figure 4 The DSC melting endotherms for the PE2 fractions

The comonomer content across TREF fractions shows a close similarity at any given temperature for both copolymers as it shown in figure 5. However, a significant difference arises in the soluble fraction (SF), where PE1, the octane copolymer, has a notably higher comonomer content compared to PE2.

Despite these relatively comparable comonomer contents, there is a clear variation in lamellar thickness, as evidenced by the melting temperatures of each fraction. This difference could be linked to the distribution of short-chain branching (SCB) in the two copolymers. The variation in SCB distribution could lead to differences in crystallization behavior and lamellar structure, ultimately affecting the melting characteristics of the fractions.

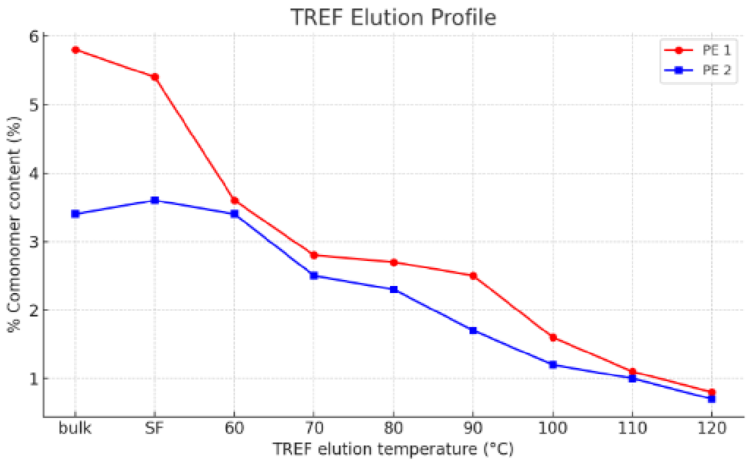

Figure 5 Comonomer content of TREF fractions of PE1 and PE2 and bulk copolymers.

Hosoda's [14] work on the estimation of short-chain branching (SCB) in linear low-density polyethylene (LLDPE) copolymers provides significant insights into the relationship between molecular structure and material properties. The equations developed for estimating SCB based on the copolymers' melting points are crucial for understanding how branching affects crystallinity.

The equations presented, specifically for 1-hexene and 1-octene copolymers, demonstrate a clear inverse relationship between melting temperature (T_m) and SCB [15] :

For 1-hexene copolymers:

$T_m = -1.69\ \mathrm{SCB} + 133$(2)

For 1-octene copolymers:

$T_m = -2.18\ \mathrm{SCB} + 134$(3)

These equations indicate that as the SCB increases, the melting temperature decreases, suggesting that higher branching leads to disruptions in the crystalline structure of the polymer.

Table 3 further illustrates this trend by providing data on percentage crystallinity alongside SCB values for various fractions of both copolymers. Notably, in the case of PE2, an increase in SCB correlates with a dramatic reduction in crystallinity, with losses of up to 50%. This observation underscores the significant impact of branching on the polymer's physical properties.

Table 3: crystallinity and SCB values for all fractions of both copolymers

Fraction temperature (°C)	Crystallinity % (DSC) PE1 | PE2	Crystallinity % (Density) PE1 | PE2	SCB CH_3/1000C PE1 (c)	SCB CH_3/1000C PE2 (d)
SF	12.06 | 16.56	13.4 | 18.4	28.2	17.92
60	13.95 | 17.19	15.5 | 19.1	26.6	17.0
70	25.10 | 23.67	27.9 | 26.7	20.1	14.1
80	25.72 | 30.33	28.5 | 33.7	17.2	11.2
90	27.30 | 32.48	30.9 | 35.6	15.0	9.4
100	29.38 | 44.55	32.6 | 45.0	14.7	7.3
110	30.91 | 45.72	34.3 | 45.4	14.3	7.2
120	29.43 | 44.47	32.7 | 38.3	14.6	7.2

a) Where: $\Delta H°f$ × % 100 crystallinity for PE is 293.6 J/g
b) Crystallinity from equation (1)
c) Short-chain branching as calculated from equation (2)
d) Short-chain branching as calculated from equation (3)

The mechanism behind this reduction in crystallinity can be attributed to the presence of branch points caused by the comonomer content. As the comonomer content increases, the average number of consecutive ethylene units decreases. This structural change impedes the formation of long ethylene segments that are essential for creating chain folds. As a result, the crystallizable portion of the copolymer diminishes, leading to decreased overall crystallinity.

An increase in comonomer content in LLDPE copolymers leads to a decline in both melting temperature (T_m) and crystallinity percentage. This trend occurs because a higher comonomer content reduces the average number of consecutive ethylene units, resulting in a decreased crystallizable portion of the copolymer. As a result, there is a notable reduction in crystallinity, accompanied by an increase in amorphous and interfacial regions.

Similar observations were made by Hongrui Yang et al. [16] in their studies of ethylene copolymers that included 1-hexene and 1-octene as comonomers.

Furthermore, it is significant to note that the melting temperatures of the PE2 fractions are generally higher than those of the PE1 fractions. This difference is evident in the calculated SCB values, where the PE2 series shows a lower degree of SCB for each fraction [17]. This variation can be attributed to differences in sequence length distribution between the two copolymer series, despite having comparable branching content.

It is essential to recognize that the calculated SCB values, which are derived from T_m, represent single estimates based on the assumption of a uniform distribution of branching within the materials. This simplification may overlook the complexities of actual branching distributions present in the copolymers.

Calculating the degree of crystallinity using density is beneficial due to its simplicity, accuracy, and applicability to nearly any sample shape. This method reveals the crystallinity of each TREF fraction through two distinct measurements, with both approaches yielding similar results. However, the density-based method tends to provide slightly higher values. Consequently, all crystallinity data presented in this study rely on density measurements as it shown in figure 6. As previously noted, this approach not only circumvents potential challenges associated with DSC measurements but also allows PALS measurements to be conducted at room temperature.

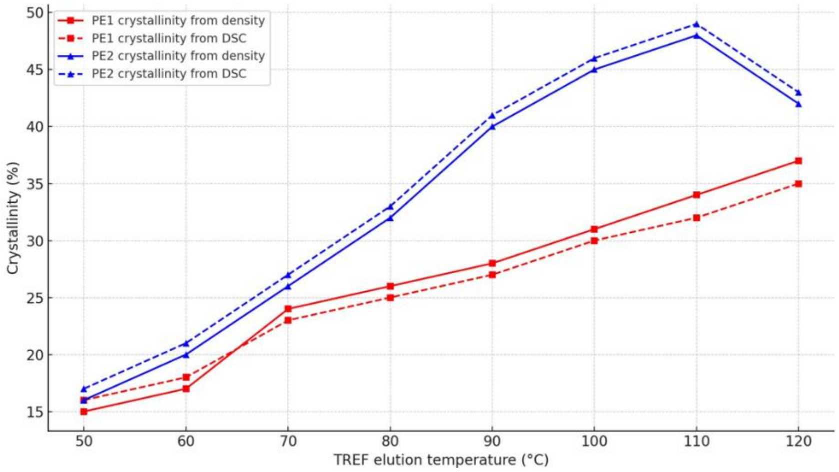

Figure 6 Crystallinity measurement from DSC and density for both polymers.

The microhardness values for the fractions of both copolymers showed a strong correlation with the percentage of crystallinity, as illustrated in Figure 7. An increase in microhardness was observed alongside rising crystallinity percentages. At lower levels of crystallinity, the steric hindrance and compaction of disordered molecular regions likely contribute to plastic deformation. In contrast, at higher crystallinity levels, the deformation mechanisms of the microcrystals become more dominant. The microhardness is influenced by the distribution and proportion of crystalline and amorphous phases within the polymer.

The elevated microhardness values associated with the higher TREF temperature fractions can be linked to their increased crystallinity when compared to the lower TREF temperature fractions as illustrated in figure 7. This enhancement in microhardness is likely related to an increase in the thickness of the lamellae [18].

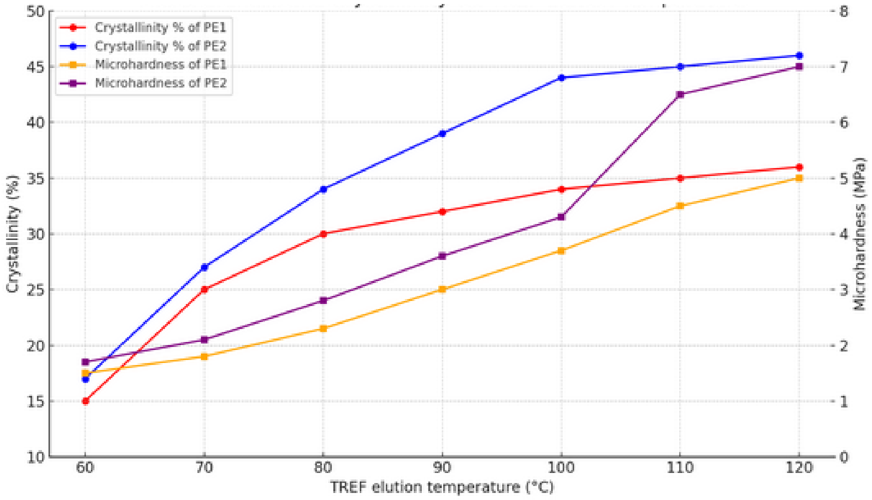

Figure 7 Microhardness and crystallinity of the fractions

Removal of a polymer fractions

There are multiple methods for extracting fractions from bulk polymer. Fraction removal can be based on either the extraction of homogeneous molar mass fractions or the removal of fractions that can crystallize uniformly. In this study, the focus was on removing crystallizable fractions, as this approach significantly influences crystal morphology and allows for the creation of sample series with varying types and degrees of crystallinity. In each instance, a single fraction was extracted from the bulk copolymers using the TREF process, as described below

Description of the process

1- The amorphous fraction of the copolymer is removed by heating within the range of 20–60 °C. After this step, the remaining copolymer, which has not been subjected to temperatures below 60 °C, is collected for further analysis. This process helps isolate the crystalline regions for a more accurate assessment of the material's properties.

2- The fraction of the copolymer between 70–80 °C is removed, excluding the material at 80 °C. This step allows for the isolation of specific components for further analysis, focusing on the characteristics of the remaining copolymer.
3- The fraction of the copolymer between 90–100 °C is removed, excluding the material at 100 °C. This process enables the isolation of specific components for further analysis, concentrating on the properties of the remaining copolymer.
4- The fraction of the copolymer between 110–120 °C is removed, excluding the material at 120 °C. This step allows for the isolation of specific components for further analysis, focusing on the characteristics of the remaining copolymer.

Effect of the removal of TREF fractions on the melting, crystallization and microhardness properties of PE1 and PE2

The effect of removing specific TREF fractions on the melting temperature (T_m) of the samples is illustrated in the figure. In this representation, the size of each data point indicates the relative quantity of material removed in that fraction; thus, larger data points correspond to a greater amount of material extracted. The observed trend indicates that the removal of lower crystalline material results in an increase in melting temperature [19]. This pattern was consistent for both copolymers, where the melting temperature rose as the amorphous fraction was eliminated. This is anticipated, as the removal of the amorphous fraction leaves behind a more ideal crystalline structure, given that the amorphous fraction contains highly branched chains with higher comonomer content, as previously mentioned. Consequently, this leads to an elevation in melting temperature.

Conversely, as higher temperature fractions are removed, the melting temperature decreases compared to the bulk copolymers as it shown in figure 8. This decrease is expected, as a greater amount of crystalline material is being extracted (specifically, fractions with lower short-chain branching or comonomer content). While the differences in melting points between the two copolymers have been addressed earlier, it's important to highlight that the amorphous fraction, which has lower crystallizability, represents a larger portion of the PE1 material compared to the PE2 material.

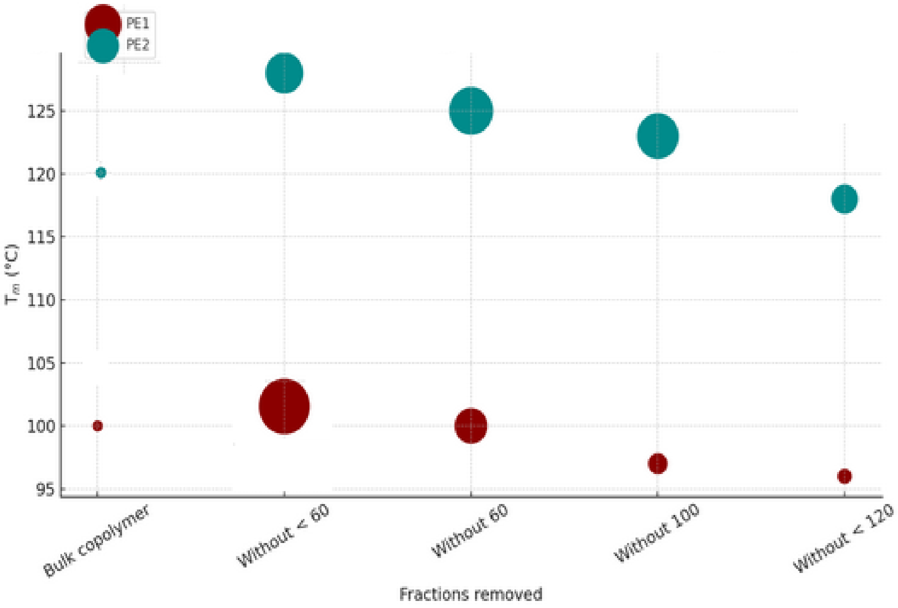

Figure 8 Melting temperature of the bulk and remaining material of PE1 and PE2.

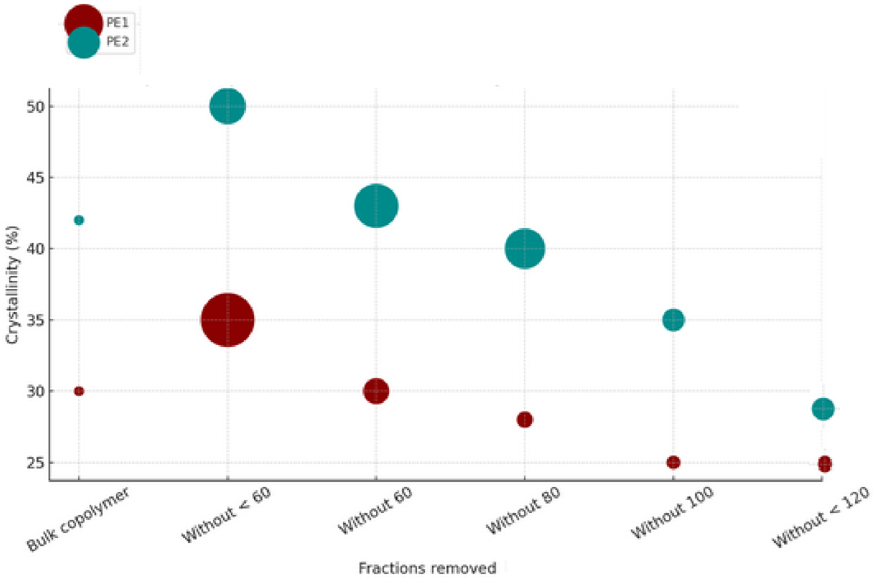

Figure 9 Crystallinity % of the bulk and remaining material of PE1 and PE2.

Figure 9 depicts how the removal of TREF fractions impacts the degree of crystallinity. The observed trend indicates that as the temperature of the removed fractions increases, the crystallinity of the remaining material decreases. This phenomenon can be explained by noting that the removal of lower temperature fractions leads to the extraction of a greater amount of amorphous and short-chain branched materials. Consequently, the crystallinity of the remaining material is higher compared to scenarios where, for example, the 100 °C fraction is removed, which results in the loss of more crystalline material and thus a lower crystallinity in the remaining sample. Additionally, it is noteworthy that the PE2 copolymer consistently exhibits a higher degree of crystallinity.

Figure 10 illustrates the microhardness of the materials, revealing a trend akin to that of crystallinity. Overall, microhardness tends to decrease as the temperature of the removed fraction increases.

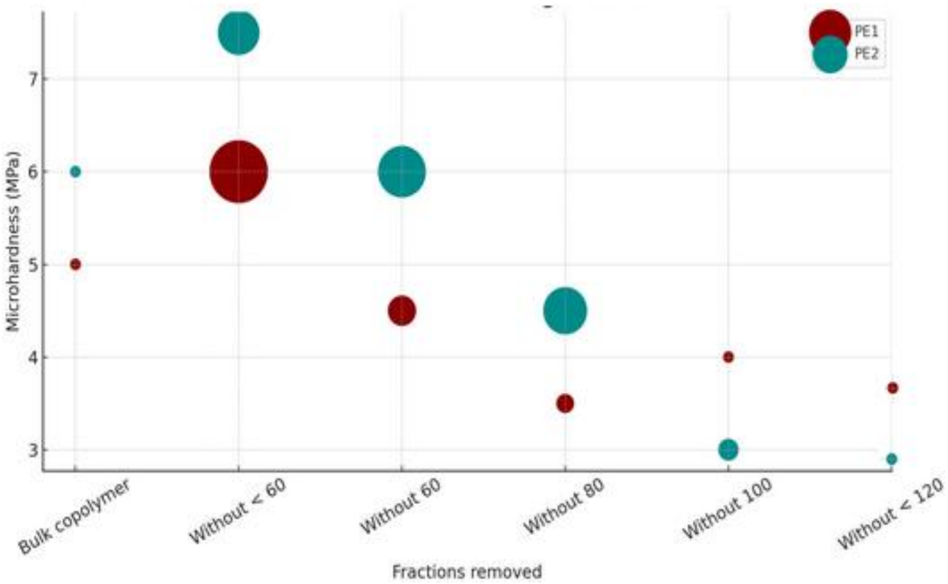

Figure 10 Microhardness values of the bulk and remaining material of PE1 and PE2.

the preceding discussion highlights that the fraction removal method significantly impacts crystal morphology and the associated physical properties.

Conclusion

This study examined the fractionation and characterization of two LLDPE copolymers to understand the influence of comonomer distribution on their structural and thermal properties. Fractionation based on crystallizability produced distinct samples with varying comonomer contents and crystallinity, which were subsequently analyzed using DSC, NMR, and CRYSTAF.

The results confirm that chain branching strongly affects molecular packing, which governs both the density and crystalline structure of the material. An increase in comonomer incorporation reduces the average length of ethylene sequences, thereby limiting the ability to form crystalline regions. This leads to a noticeable decrease in overall crystallinity and a corresponding increase in amorphous and interfacial components, Joshua and others has recently observed similar results [20].

These observations emphasize the fundamental relationship between comonomer content and the microstructural organization of LLDPE copolymers. Understanding this correlation is essential for tailoring material properties for specific applications, particularly where mechanical performance and thermal stability are influenced by crystallinity.

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