

The effect of chain branching on the free volume properties of polyethylene

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ABSTRACT

The effects of the length of the chain branching on free volume properties of polyethylene studied by Positron annihilation lifetime spectroscopy (PALS). Because of its sensitivity to the microstructural changes in the polymer matrix this technique can be used as a novel method to study of polymers at a molecular level.

The variations in the physical properties of polyethylene polymer are governed by the microstructure of the chains constituting the polymer, in particular, the amount, length and placement of the alkyl branches along the chain. The length of the chain branching constitutes the most important factor affecting both structure and properties of the PEs[1]. A significant decrease in crystallinity and increase in the free volume as the comonomer content increases is expected [2]

In this study free volume of the polymers can be correlated to many properties, such as crystallinity, comonomer content, and comonomer length. Therefore, the behaviour of the copolymer will depend largely on the microstructure free volume

KEYWORDS

Polyethylene, Free volume, Positron annihilation

1-Introduction

The physical properties of polyethylenes (PEs) can be broadly differed by controlling their microstructural parameters, specifically, the position, length and amount, of the alkyl branches along the chain. The comonomer substance establishes the most significant factor influencing both structure and properties of the PEs, in spite of the fact that the length of the comonomer may likewise be significant [3]. An impressive decreasing in crystallinity and increase in the free volume as the comonomer substance increments is predictable. The incorporation of the comonomer into an otherwise crystalline copolymer will normally reduce the crystallinity and reduce the melting point in a continuous manner. This is because of fuse of the comonomer as deformities, and these imperfections decline the melting point and heat of fusion by upsetting the intermolecular bonding inside the crystalline cross section [4].

In this study m- LLDPE was selected because all metallocene sites produce polymer chains with nearly the same architectures compared to using Ziegler-Natta catalyst, and also the material is expected to provide homogeneous fractions. The degree of chain branching plays a major role in preventing the polymer chains from packing along in a very frequently and closely packed structure, which will have an effect on the density and crystallinity as well as the free volume properties, and hence the final properties of the copolymer.

Studies were carried out to determine the influence of the comonomer length on the free volume properties of LLDPE [5-8].

In this study, Two different types of polymers (LLDPE), with different comonomer lengths, were fractionated by temperature rising elution fractionation (TREF), and then characterized by Positron lifetime spectroscopy (PALS).

The estimation of parameters relating to free volume inside polymer systems is an critical viewpoint of their characterization. Free volume can be related to numerous properties, such as crystallinity, comonomer substance, and comonomer length. In this manner, the behaviour of the copolymer will depend generally on the microstructure free volume.

Yang and others [9-10], reported PALS measurements for a LDPE and several ethylene-1-hexene copolymers synthesized with metallocene catalysts. They found a linear relationship between the location of the β relaxation and the free volume fraction: the higher the relaxation temperature is the lower the free volume value will be.

2- Experimental

2.1 Materials

As mentioned before, two different types of polymers (LLDPE), with different comonomer lengths (hexene and octene), were used in this study.

The first plastomer (PE1) was from the Affinity range of DOW Chemicals PL1881. The plastomer consisted of ethylene and octane, as comonomer. The percentage comonomer content was 4.8 % as determined by ^{13}C NMR. The physical properties are tabulated in Table 1.

The second plastomer (PE2) used was Exceed 1327CA produced by ExxonMobil Chemicals. The plastomer consisted of ethylene and hexene, as comonomer. The percentage comonomer content was 3.2 % as determined from the ^{13}C NMR.

Table 1 Physical properties of the two copolymers

Sample	MFI (g/10ml)	Density (g/cc)	T_m^a ($^{\circ}\text{C}$)	T_c^a	Crystallinity ^b (%)
PE1	1	0.9035	100	82	26
PE2	1.3	0.927	120	110	35

a) Melting and crystallization temperature from DSC.

b) Crystallinity according to density.

2.2 Calculation of the comonomer content

The percentage of comonomer was calculated using the following equation

$$\text{Comonomer content} = \frac{(\alpha \text{ Br carbon} / 2) + \text{Br carbon}}{\text{Total number of backbone carbons}} \dots (1)$$

By using the integration of the peaks associated with the backbone carbons and relating this to the peaks associated with backbone carbons at the branch points, the comonomer content was determined, and then using equation 1 to determine the comonomer content. The percentage of the carbons α to branching was divided by two; because there are two carbons α to the branching and the percentage of the branching carbons are added together.

2.3 Free volume Measurement

To determine the free volume properties in both copolymers and their fractions PALS measurements were used. The measured lifetime spectra were resolved into four lifetime components with the help of the computer program PATFIT-88.

3- Results and discussion

In this paper first we will study the measured positron annihilation parameters as a function of the nature and degree of short chain branching in semi-crystalline polymers, where we used two different LLDPEs with different branch length.

The first part of this section summarizes the results of fractionation by TREF and subsequent characterization of the two LLDPEs. The free volume of the fractions was determined by PALS. Results of the measured positron annihilation parameters analysis were used to create correlation between the comonomer lengths and free volume properties.

3.1- Fractionation

It is well known that in LLDPE it is not only the average molecular mass and the number of short-chain branches, but also their distributions, that have a significant effect on the end-use properties of the material. There are many ways to characterize LLDPE including the use of cross fractionation. In this study LLDPE is fractionated by crystallizability (comonomer composition and degree of branching).

Preparative temperature rising elution fractionation (prepTREF) is utilized as a essential strategy for fractionation of the copolymers were it involve slow crystallization and elution steps. This strategy isolates semi-crystalline macromolecules concurring to their crystallizability due to the chemical compositions of the polymeric chains (molecules). The more comonomer content or greater amounts of SCB results in an almost linear depression of the melting or elution temperature [11]. In this study both of the copolymers were fractionated by TREF into eleven fractions.

To get more understanding to the properties of the bulk copolymers, Crystallization Analysis Fractionation (CRYSTAF) were used to understand the crystallization behavior of each copolymers. Figure 1 shows the CRYSTAF profiles for both bulk copolymers PE1 and PE2. Two crystallization peaks were observed for PE1 at 32°C and 55°C. The first crystallization peak represents the highly branched polymer chains and the second crystallization peak is attributed to lower branched polymers chains. Similar results were later observed from TREF analysis.

Two crystallization peaks was also observed for PE2 at 80°C and 88°C. This is due to broad and bimodal short-chain branch distributions, which occur due to either non-homogeneous active sites in the metallocene catalysts or the presence of more than one type of active site. Soga *et al.* [12] observed a similar profile for m-LLDPE. This bimodality was attributed to the types of active sites present in the metallocene catalysts.

The higher crystallization temperature of PE2 compared to PE1 is due to a lesser degree of branching in PE2, as a result of its lower comonomer content (4.8% for PE1 and 3.2% for PE2).

The CRYSTAF profiles and the presence of the two distinct peaks are illustrative of the complexity of the molecular structure of the commercial samples and resulting limitation of previous PALS studies on these types of commercial samples.

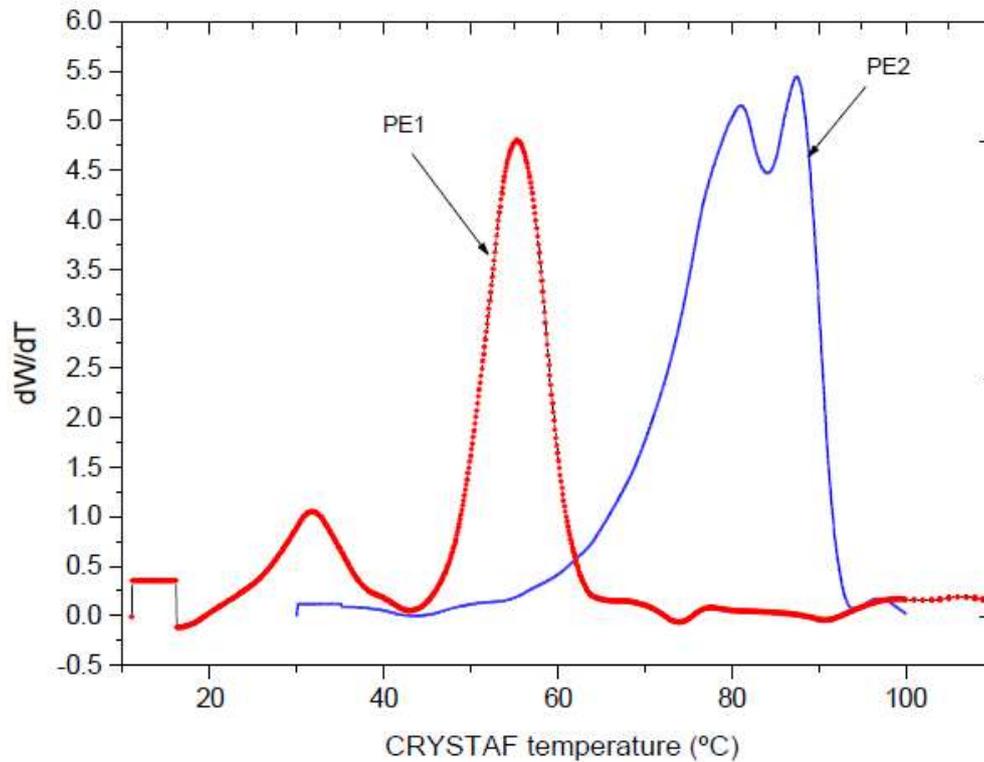


Figure 1 CRYSTAF traces for bulk copolymers PE1 and PE2.

Figure 2 shows the distributions of eluted material of the TREF fractionation of PE1 and PE2. The elution profiles for PE2 are much broader than PE1. This demonstrates a much broader distribution in the chemical composition of the chains in the ethylene/1-hexene copolymer (PE2) compared to the ethylene/1-octene copolymer (PE1).

The octene copolymer (PE1) showed an elution distribution in the temperature range 50-100°C, while the hexene copolymer (PE2) showed a relatively wide elution distribution in the range 60-120°C. As was the case on the CRYSTAF profiles, this difference is due to the difference in the comonomer content: 4.8% in 1-octene compared to 3.2% for the 1-hexene copolymer.

PE1 showed a broad crystallization peak with a smaller at 30 °C and a maximum peak at 70 °C. This is consistent with the bimodal peak observed in the CRYSTAF analysis. PE2 showed only one peak at a higher temperature (87 °C), which suggests that PE2 has less chain heterogeneity than PE1 [13]. It is also illustrative from the figure that the TREF profile of PE1 shift to lower values, compared to PE2 as was the case in the CRYSTAF analysis. This may be explained by the difference in the short chain branch distributions, but as well may be due to the fact that as the length of the branches increases, the branches become more effective at disruption of regular packing and thus decrease the melting point of the crystalline regions.

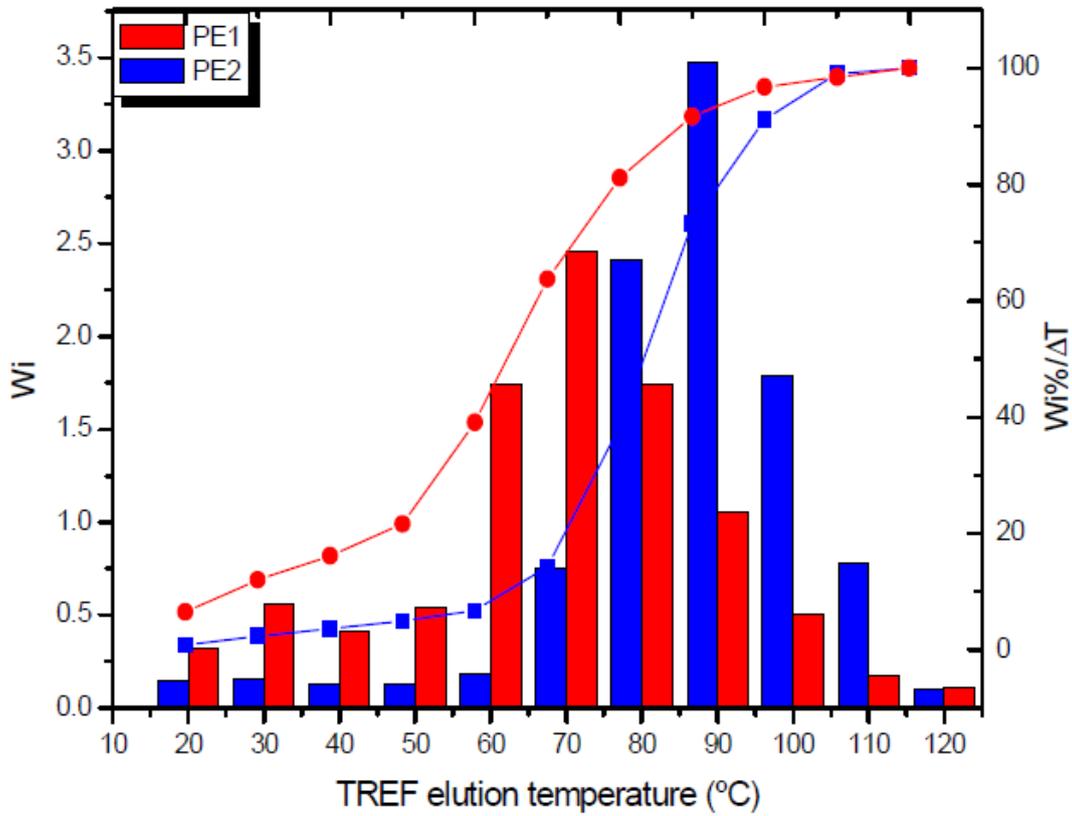


Figure 2 Prep TREF profiles of PE1 and PE2.

There is a considerable variation in terms of the peak maxima for CRYSTAF profile and TREF profile for the higher temperature peaks which clearly shows much higher in the case of prep-TREF (70 °C), compared to CRYSTAF (60 °C). This shift is a result of the under-cooling effect. A comparable result was reported by Britto *et al.* [14] and Gabriel and Lilge [15]. They pointed out that the shift between CRYSTAF and TREF profiles is due to the “super cooling effect” because CRYSTAF profiles are measured during crystallization, while TREF data is measured during the melting/dissolution process

3.2- Characterization of copolymer fractions

Table 2 summarises the melting, crystalline temperature and comonomer content for each fraction of both copolymers PE1 and PE2, after fractionation by prep TREF. Limited amount of material in the soluble fractions was collected in each experiment, because of this it was decided to combine all the fractions below 50 °C into one fraction, which is designated as the soluble fraction (SF). The soluble fraction (SF) plays an undeniable role in the final properties of the copolymer. Table 2 shows the melting temperatures (T_m), DSC crystallization (T_c) and of the fractions as well as the peak maximum temperature of the CRYSTAF analysis of each fraction ($T_{CRYSTAF}$). As is expected, as the TREF elution temperature increases, the T_c , T_m and $T_{CRYSTAF}$ all increase. The melting temperature increases from 26°C to 60°C for PE1 and from 64°C to 88°C for PE2.

Table 2 Properties of TREF fractions of PE1 and PE2.

Fraction temperature (°C)	T_m^a (°C)		T_c^a (°C)		$T_{CRYSTAF}^b$ (°C)		Comonomer content (%) ^c	
	PE1	PE2	PE1	PE2	PE1	PE2	PE1	PE2
SF	72.4	93.2	62.9	85.7	-	-	5.60	3.50
60	76.2	96.1	65.4	89.1	26.3	62.8	3.52	3.46
70	81.5	102.7	68.2	90.4	34.4	64.0	2.64	2.60
80	96.1	109.8	77.6	97.3	45.1	75.1	2.77	2.55
90	98.4	118.4	81.8	106.4	54.8	82.5	2.61	1.91
100	101.4	118.6	85.4	110.4	58.1	88.4	1.61	1.20
110	103.3	122.7	86.9	111.6	58.6	87.6	1.20	1.15
120	103.4	124.9	87.7	107.4	60.4	87.7	0.90	0.62

a) Melting and crystallization temperature from DSC

b) CRYSTAF peak maximum temperature

c) Comonomer content as calculated from ¹³C NMR and equation 4.2

As it shown in Figure 2, both TREF profiles have a quite broad distribution which indicates that there is a broad distribution in the chemical composition of the chains. This broadness is due to chain defects, or comonomers preventing the crystallization of the copolymer chain and usually leading to broadening and decreasing of the melting temperature. The effect of chain defects can be obviously seen in the crystallization and melting behavior as it shown in Table 1. The exact depression of the melting point depends on the amount, type and distribution of defects and the crystallization conditions. [16].

Figure 3 shows that the comonomer content of each TREF fraction is very similar at any given temperature for both copolymers. The exception is the soluble fraction (SF) where the PE1 (octane copolymer) has a much higher comonomer content than the PE2 copolymer.

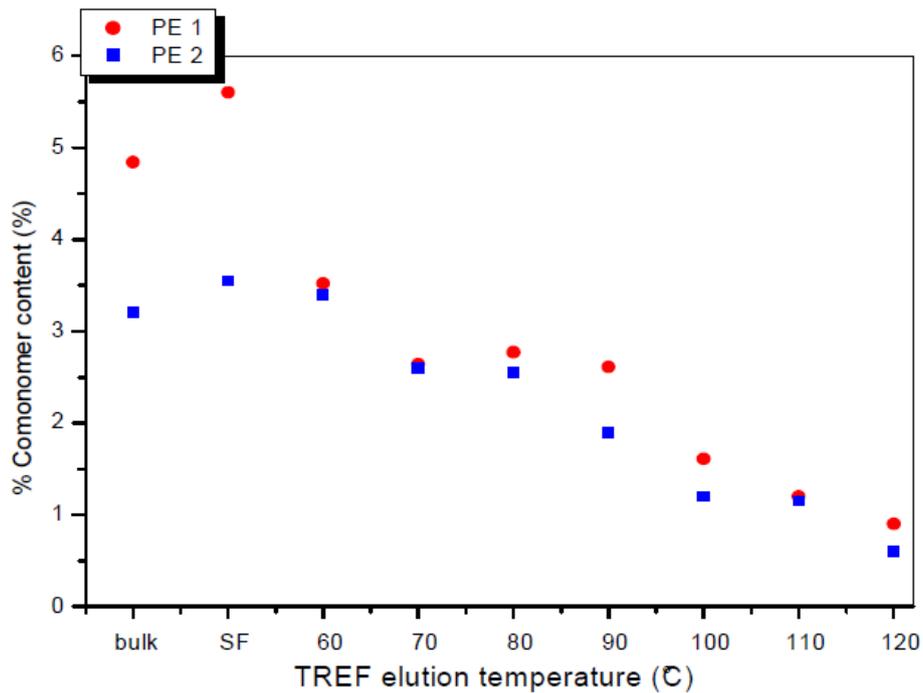


Figure 3 Comonomer content of bulk copolymers and TREF fractions of PE1 and PE2.

3.3 Measurement of positron annihilation parameters.

The primary objective of this part of the study is to determine how the measured parameters of positron annihilation change due to variations in the length of the comonomer length. Positron Annihilation Lifetime Spectroscopy (PALS) which is non-destructive spectroscopy technique that allows studying a variety of phenomena and material properties on an atomic scale is used for both the bulk and fractionated copolymers.

In all cases investigated, it was found that a four lifetime component fit gave the best fitting to the raw positron lifetime data. τ_1 which the shortest lived component, is usually attributed to para-positronium (p-Ps) annihilation. The intermediate component, τ_2 , describes the annihilation of the free positrons.

The two longest lifetime components designated as τ_3 and τ_4 represent the annihilation of the longer lived o-Ps localized within the open spaces in the polymer which mainly due to the positrons trapped in the defects of the crystalline regions or trapped in crystalline-amorphous interface region

In a typical amorphous material, only one o-Ps lifetime is detected. The fact that in the copolymer samples studied here an additional lifetime is detected is reflective of the complex morphology of the semicrystalline sample. In previously reported studies [5-8], the third component, τ_3 , has been attributed to the “pick-off” annihilation of the o-Ps in the crystalline regions (interface and/or defects) of the polymer. The longest lived component, τ_4 , has been attributed to the pick-off annihilation of o-Ps in the amorphous regions of the polymer [17].

Table 3. Value of o-Ps lifetimes τ_3 , and intensities I_3 obtained for the bulk and fractionated copolymers PE1 and PE2

Fraction temperature (°C)	τ_3 (ns)		I_3 (%)		τ_4 (ns)		I_4 (%)	
	PE1	PE2	PE1	PE2	PE1	PE2	PE1	PE2
bulk	0.68±0.04	0.61±0.01	6.45±1.80	9.88±0.52	2.77±0.01	2.72±0.01	27.27±0.2	19.32±0.10
SF	0.49±0.02	0.51±0.02	5.84±1.15	7.87±1.81	2.79±0.01	2.78±0.01	28.38±0.2	23.67±0.10
60	0.53±0.03	0.56±0.03	9.51±2.53	9.93±1.61	2.76±0.01	2.70±0.01	27.26±0.2	22.95±0.20
70	0.54±0.03	0.59±0.03	6.72±0.87	11.09±2.14	2.73±0.02	2.67±0.01	27.23±0.2	22.45±0.20
80	0.55±0.03	0.59±0.03	9.56±2.47	6.80±0.73	2.71±0.02	2.68±0.01	27.39±0.2	21.39±0.20
90	0.57±0.04	0.62±0.03	9.69±1.16	9.87±1.69	2.68±0.02	2.66±0.01	24.95±0.2	21.21±0.30
100	0.65±0.05	0.72±0.05	9.89±0.90	9.08±1.31	2.65±0.02	2.63±0.01	24.22±0.3	19.14±0.30
110	0.67±0.01	0.76±0.03	10.15±0.83	11.37±2.31	2.62±0.02	2.57±0.01	23.24±0.1	17.14±0.20
120	0.68±0.04	0.77±0.11	10.19±1.35	11.80±2.23	2.63±0.05	2.54±0.02	21.11±0.2	15.70±0.60

Figure 4 shows a graphical illustration of the τ_3 and τ_4 lifetimes as a function of the TREF elution temperature. The value of τ_4 (which is attributed to the pick-off annihilation of o-Ps in the amorphous regions of the polymer) shows a slight decrease as the fractionation temperature increases while the τ_3 values show the opposite trend where the value increases at higher elution temperature. The decrease in the τ_4 value (and corresponding decrease in the mean free volume hole size in the amorphous parts of the polymer) can be explained by the fact that in the higher temperature fractions, the chains in the amorphous areas of the copolymer have fewer short chain branches than the lower temperature fractions (as shown in the previous sections).

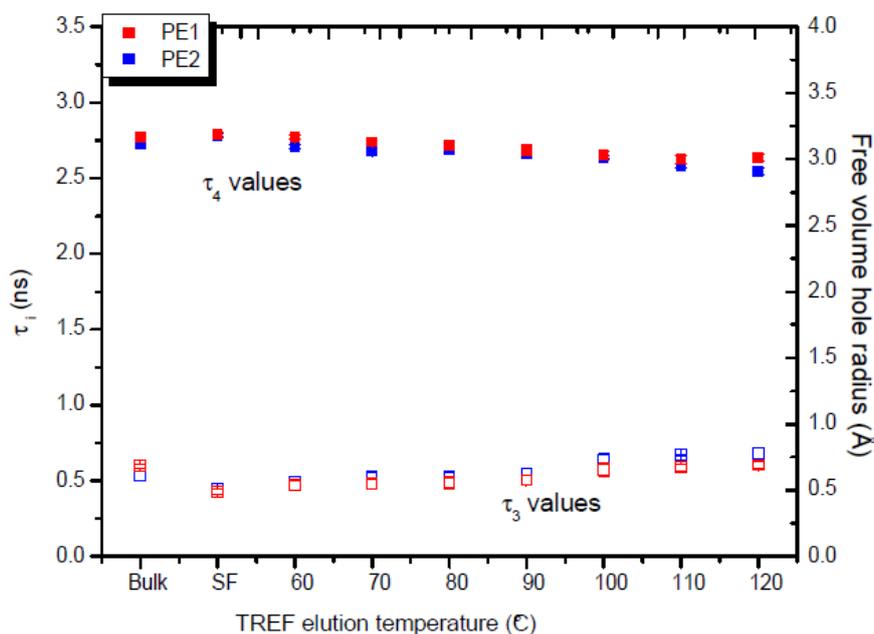


Figure 4 τ_3 (open symbols) and τ_4 (closed symbols) lifetimes for the bulk and TREF fractions of PE1 and PE2.

This effectively leads to a slightly smaller average free volume hole size within these amorphous areas and a decrease in τ_4 lifetime due to a higher “packing density” of the chain in the amorphous region. The average hole size in the amorphous region may also be decreased due to the very high crystallinity of the sample. Since the amorphous areas are “connected” to the crystalline areas, the increase in crystallinity will affect the chains segmented mobility in the amorphous region to a small degree

which may contribute to the overall decrease in the measured values.

In all cases the τ_4 value for all the fractions of PE1 compared to PE2 are slightly higher. This is explained by the difference in the nature of the comonomer. PE1 has an octane comonomer which has a longer carbon side chain than the hexene comonomer in PE2.

The results also suggest that there is a correlation between τ_3 and the TREF fractionation temperature. The τ_3 value increases as the fractionation temperature increases.

The increase of τ_3 (which is attributed to the pick-off annihilation of o-Ps in the crystalline regions or crystalline interface) can be correlated to the increase in the crystalline region as the fractionation temperature increases. The increase is most likely reflective of the greater degree of crystalline defects as well as the increasing amount of interfacial area as the amount of crystallinity increases. It is also interesting to note that the PE2 copolymer with the hexane comonomer shows slightly higher values than the PE1 octene copolymer.

4- Conclusion:

Series of copolymer samples of differing degree of comonomer content and consequently crystallinity were successfully produced by fractionated the copolymers according to crystallizability

Each fraction was characterized by PALS.

As has been extensively reported in literature, the chain branching plays a major role in preventing the polymer chains from packing together regularly and closely and has a predominant effect on the density and crystallinity of the copolymer. The results showed that as the comonomer content increases, the average number of consecutive ethylene units decreases and the crystallizable part of the copolymer becomes smaller. As a consequence, the crystallinity decreases and the amorphous and interfacial contents increase. Variations in the free volume size of LLDPE with varying comonomer contents were observed by means of PALS measurements. A correlation between the relative free volume of the amorphous phase, and comonomer length was also established. It was found that the size of the free volume holes in the amorphous phase increases with increasing comonomer content and related decreasing crystallinity. Therefore, these factors also affect the physical properties by dictating the molecular motions possible in the amorphous domains, which can be important, especially for low temperature properties.

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