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PEX Synthesized via Peroxide for Oil Pipes, Starting from Different Commercial Polyethylenes: Influence of Comonomer and Catalyst Type

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Summary: In the present work, crosslinked polyethylene (PEX) was obtained by adding dicumyl peroxide (DCP) to polyethylene. High-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) were used as starting polymers, synthesized by Ziegler-Natta or metallocene catalysts. Also, the effect of the comonomer type (butene or hexane) in the LLDPE was investigated. Materials were processed with increasing amounts of dicumyl peroxide (DCP). Samples were pressed with suitable amounts of these components. The efficiency of the crosslinking reaction was evaluated by gel content and thermal properties, and the melting temperature and degree of crystallinity were evaluated using differential scanning calorimetry (DSC). The microstructure of the starting polyethylene was correlated with the effectiveness of crosslinking and the resultant thermal and mechanical properties of the PEX. A new crosslinking coagent was also evaluated, along with the resistance of PEX samples in oil.

Keywords: crosslinked polyethylene; degree of crystallinity; dicumyl peroxide; gel content; melting temperature

Introduction

Crosslinked polyethylene has become commonly used for a number of industrial applications which require withstanding high temperatures. Examples of such applications include wire and cable coating, hot water tubing and steam resistant food packaging. There are many ways to achieve the crosslinking of polyethylene. Polyethylene has no functional groups to provide crosslinking capability. Therefore, the main reaction under consideration involves the free radical mechanism.[1]

Two main methods to achieve crosslinking of polyethylene are employed: by means of radiation (physical crosslinking) or through the use of peroxide or peroxide/silane (chemical crosslinking).[2] The main differences between physical and chemical crosslinking are the time and temperature at which they occur. Physical crosslinking has an immediate effect, because the breaking of bonds with a high energy beam and the subsequent combination of macroradicals occur immediately at a relatively low temperature. In turn, chemical crosslinking takes place in the presence of heat, which breaks down the crosslinking agent. The initiator and crosslinking kinetics parameters are essential to determine the required initiator concentration, reaction time and process temperature.[3]

The crosslinking of polyethylene by organic peroxides has attracted substantial attention in the literature and is becoming a widely accepted and studied method of altering polymer structures and properties. As a result of peroxide addition and heating, intermolecular bonds are formed by reaction between macroradicals, which are first obtained by thermal decomposition

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of peroxide, followed by removal of hydrogen from the polyethylene main chain.[4] One of the most employed substances for this process is dicumyl peroxide (DCP), which is fairly stable at temperatures ranging from 130 to 150 °C.[5,6] This substance has been selected because its decomposition rate is favorable under the melt processing temperatures of polyethylene. DCP has been shown to be effective in introducing long chain branching in linear polyethylene, and low concentrations favorably alter the original molar mass distribution. On the other hand, at high concentrations of DCP, crosslinked polyethylene is obtained.[1]

Polyethylene grades found in the market[7] that can undergo crosslinking were used in the present work: high-density polyethylene obtained with Ziegler-Natta catalyst (ZN-HDPE), with virtually no branching and high melting temperature (although the impact resistance is relatively low); and linear low-density polyethylene, also produced by Ziegler-Natta catalyst (with 1-butene or 1-hexene as comonomer, ZN-LLDPE) or metallocene (ethylene-1-hexene copolymer, m-LLDPE). Thus, short chain branching is present in the main chain of PE, reaching intermediate properties between HDPE and LDPE (low-density polyethylene).

The aim of this work is to evaluate the synthesis of PEX obtained from different starting polyethylenes using dicumyl peroxide, to compare the influence of PE microstructure on the gel content and thermal and mechanical properties of the final product.

Experimental Part

Materials and Methods

High-density polyethylene, ZN-HDPE (MFI = 7.0; density = 0.960) and linear low-density polyethylenes: ZN-LLDPE 1 (butene as comonomer, MFI = 1.0; density = 0.922); ZN-LLDPE 2 (hexene, MFI = 0.7; density = 0.922), and m-LLDPE 3 (hexene, MFI = 0.6; density = 0.928), were kindly donated in pellets by Quattor S.A., Brazil. Dicumyl peroxide, DCP 98% was purchased from Aldrich Co. Ltd., USA. A new crosslinking coagent (CC), hydroxylated liquid polybutadiene (HLPB), was purchase from Petroflex Ltd., Brazil, and used as received.

Sample Preparation

Initially, the pellets in contact with liquid nitrogen were ground using an IKA-MF10 mill. Then, solutions of DCP in 5 ml of methanol were prepared and added to the polymers, as shown in Table 1. For the experiments with the crosslinking coagent (CC), the material was introduced

Table 1.
Conditions of polyethylene crosslinking and sample identification.

Sample	Starting PE	Original thermal properties	DCP (wt%)	Code
LLDPE 1	Ziegler-Natta catalyst, 3.1 mol% butene	$T_m = 121.9$	0	BF0
		$X_c = 41$	1.0	BF1
			2.5	BF25
			5.0	BF5
LLDPE 2	Ziegler-Natta catalyst, 3.8 mol% hexene	$T_m = 123.9$	0	HF0
		$X_c = 36$	1.0	HF1
			2.5	HF25
			5.0	HF5
LLDPE 3	Metallocene catalyst, 1.7 mol% hexene	$T_m = 119.5$	0	MF0
		$X_c = 57$	1.0	MF1
			2.5	MF25
			5.0	MF5
HDPE	Ziegler-Natta catalyst	$T_m = 132.2$	0	EI0
		$X_c = 65$	1.0	EI1
			2.5	EI25
			5.0	EI5

with the polymer and subsequently, the DCP methanol solution was added. After removal of excess methanol by passing a nitrogen gas flow, the samples were pressed at 180 °C and 10 MPa for 30 minutes in a Carver press, for the crosslinking reaction. Afterwards, the samples were water-cooled for 10 minutes under pressure.

Gel Content

This method allows for quantification of the fraction of material that can be extracted by a solvent. Through the gel content, the degree of crosslinking of a polymer can be estimated.[8] The pressed specimens were weighed (initial mass) and placed in an extractor. The extraction process was carried out using 100 ml of xylene at reflux for 8 hours. Then, the samples were dried at 60 °C to constant weight (final mass). The gel content was calculated with the relation between the final mass and the initial one, in percentage.

Differential Scanning Calorimetry

Samples with masses ranging from 3.0 – 4.5 mg were weighed in an aluminum holder and heated at a rate of 10 °C/min over a temperature range between 25–170 °C in a DSC-TA instrument, model Q–1000. The degree of crystallinity was calculated according to Equation 1.

$$X_c = \frac{\Delta H_m^a}{\Delta H_m^{100}} \tag{1}$$

Where X_c = degree of crystallinity (%); ΔH_m^a = melting enthalpy of the sample (J/g); ΔH_m^{100} = melting enthalpy of 100% crystalline polyethylene (J/g), which was considered to be 292 J/g.[2]

Thermogravimetric Analysis

The thermogravimetric analysis (TGA) was carried out by heating the samples from room temperature to 700 °C at a heating rate of 10 °C/min under air. The initial temperature of degradation (T_{onset}) and the temperature of maximum degradation rate (T_{max}) were measured.

Mechanical Properties

The procedures for the tensile test followed ASTM D638-5. The deformation of the specimens was performed at a rate of 50.0 mm/min. The dimensions of the specimens used for mechanical tests were approximately 6.0 × 3.0 × 1.2 mm (length × width × thickness). For each sample, six specimens were tested for reproducibility of the results and standard deviations were determined. The tensile and elongation at yield and at break were also obtained, as well as the modulus of elasticity.

Swelling Properties

For this test, samples of the obtained premolded PEX were left in contact with an intermediate fraction of oil (Petrobras S.A., 21.2° API) at room temperature over a period of seven days. After this time, the weight gain of each sample and its deformation were analyzed.

Results and Discussion

The gel content results are shown in Table 2 and Figure 1. An increasing concentration of peroxide increased the degree of crosslinking, reaching maximum values when the concentration of DCP was 2.5% for all polyethylenes, with the exception of samples from crosslinked LLDPE 1 (butene as comonomer), whose degree of crosslinking achieved its maximum only when the concentration of peroxide was 5.0%. As the chosen ZN-LLDPE grades have the same density and about the same MFI, we believe this effect occurred due to the differences in the distribution of ethylene sequence lengths in the polymer chain. In other words, LLDPE 1 (with butene) has shorter ethylene sequences (and hence lower T_m and X_c than those of LLDPE2), and consequently better distribution of tertiary carbons in the polymer backbone, which assists the formation of macroradicals in the presence of peroxide.

Analyzing the maximum degree of crosslinking, PEX obtained from HDPE showed better performance compared to

Table 2.
Gel content and thermal properties of PEX samples.

Sample	Gel Content (%)	X_c (%)	T_m (°C)
BF0	0	46	121.9
BF1	78.2	30	116.5
BF25	94.0	30	111.5
BF5	96.0	22	112.0
HF0	0	36	123.9
HF1	68.6	37	119.1
HF25	93.4	26	111.4
HF5	90.4	28	104.7
MF0	0	57	119.5
MF1	86.3	41	116.7
MF25	95.9	32	107.4
MF5	90.6	36	111.6
EI0	0	65	132.2
EI1	78.9	65	129.9
EI25	99.3	56	128.0
EI5	92.3	57	125.5

other materials, reaching 99% crosslinking, possibly because of the closer intramolecular entanglements in polyethylene resulting from the linearity of HDPE chains compared to those from LLDPE. Another possible explanation of this behavior could be that we have employed a grade of HDPE with higher MFI than those of LLDPE and therefore, lower molar mass, which would make the melt viscosity to be lower. This would facilitate the combination of macroradicals of HDPE.

When we compared the results with metallocene-LLDPE and Ziegler-Natta-LLDPE, there was a slightly higher degree of crosslinking achieved for m-LLDPE. Thus, it seems that the more homogenous the distribution of short chain branching in LLDPE is, the higher the gel content will be for the same amount of peroxide in PEX. Finally, the decrease of gel content when the amount of DCP added was 5.0% for most of the polyethylene can be related to a reduction in molar mass.

From Figure 2, it can be seen that the degree of crystallinity (X_c) decreased with increasing peroxide concentration, reaching a minimum value when the peroxide concentration of peroxide was 2.5%. Moreover, the variation of X_c with DCP concentration in both HDPE and LLDPE 2 samples was very similar, as well as that of the samples from LLDPE 1 and LLDPE 3. This is perfectly understandable since the microstructures of the first two and the last two samples are similar, where both first polymers have long ethylene sequences. This hinders the formation of macroradicals, and therefore, the crosslinking reactions, the opposite behavior of the last two samples.

In the polymers synthesized with metallocene catalyst, the comonomer is more

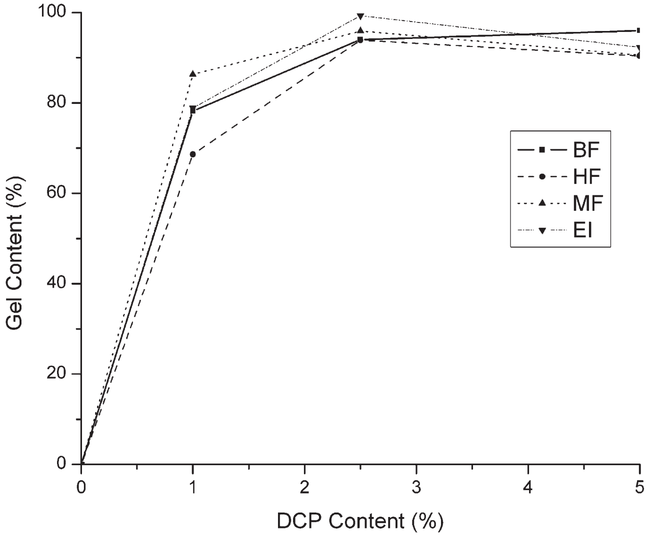

Figure 1.
Gel content of crosslinked samples BF = LLDPE 1; HF = LLDPE 2; MF = LLDPE 3; EI = HDPE.

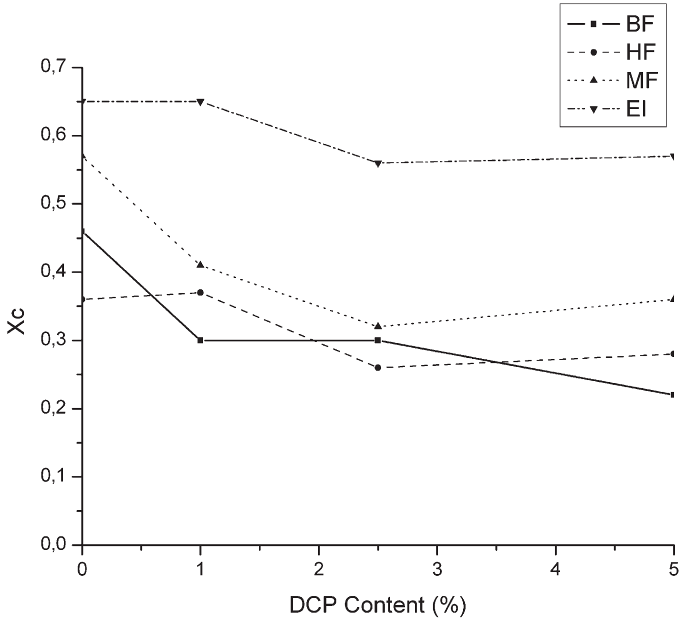

Figure 2.
Degree of crystallinity of crosslinked samples BF = LLDPE 1; HF = LLDPE 2; MF = LLDPE 3; EI = HDPE.

evenly distributed in all chains, which makes networking more homogeneous, causing a smaller loss of crystallinity. In all the LLDPE samples, an increase in DCP content up to 5.0% caused a slight increase of the X_c. As already noted, the loss of molar mass with excess DCP leads to an increase of the X_c, since smaller polymer chains crystallize easier. In HDPE, the X_c is well above that of LLDPE polymers, as expected, and the decrease of the X_c with the crosslinking was not very sharp.

Similar behavior can be observed in Figure 3, which relates the melting temperature of the materials (T_m) with the concentration of DCP. However, the samples of LLDPE 1 and 3 showed a greater decrease in T_m when employing 2.5% of DCP.

Furthermore, it can be noticed that the polymer LLDPE3 has its T_m increased with the addition of 5% of DCP. The excess of peroxide could be diminished the copolymer molar mass, causing an easier rearrangement of the chains and therefore, the polymer crystals were more perfect, increasing the material melting temperature.

Regarding only HDPE, a new crosslinking coagent (CC) at concentrations of 1.0%, 5.0% and 10.0% wt, was employed in the formulations aiming to produce PEX with improved mechanical properties. The resulting tensile properties are shown in Table 3 and Figure 4, where comparison can be seen of this new PEX with the starting material (HDPE) and also with PEX obtained without addition of CC.

The modulus of elasticity of PEX was lower than that of HDPE, mainly due to the decrease in the degree of crystallinity of this starting material. Moreover, the elongation at break also decreased in PEX, due to the increased crosslinking. Also, the tensile at the yield point tended to decrease (relaxation behavior).

The incorporation of CC, along with the increase of its concentration, had a tendency to increase the modulus of PEX. Possibly this occurred because CC acted as an inner plasticizer, delivering the best points for crosslinking, thus making the

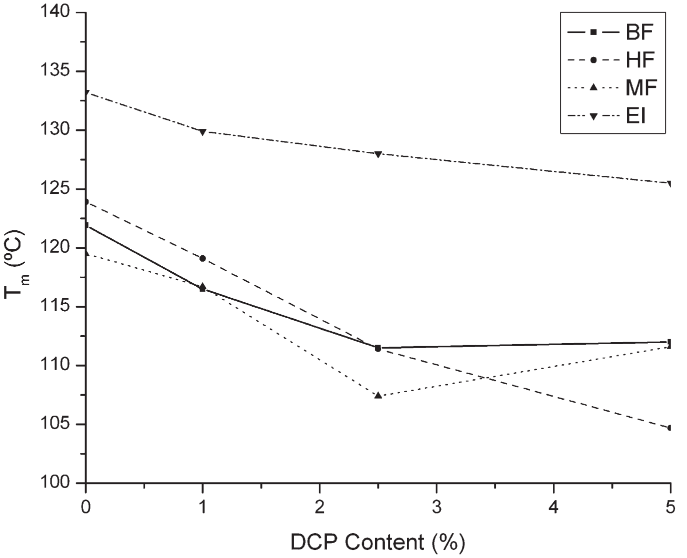

Figure 3.
Melting temperature of crosslinked samples BF = LLDPE 1; HF = LLDPE 2; MF = LLDPE 3; EI = HDPE.

Table 3.
Mechanical properties of PEX samples obtained.

Sample	Tensile Stress at Yield (MPa)	Elongation at Yield (%)	Modulus (MPa)	Tensile Stress at Break (MPa)	Elongation at Break (%)
EI0	23.56 ± 1.65	7.76 ± 1.09	605.37 ± 72.15	11.97 ± 4.02	103.67 ± 86.66
EI25	13.78 ± 0.26	14.17 ± 0.67	194.97 ± 8.09	10.97 ± 1.33	42.06 ± 16.29
ECC1	13.86 ± 0.61	11.48 ± 0.01	257.25 ± 29.94	7.67 ± 2.42	31.49 ± 11.09
ECC5	15.73 ± 1.13	10.99 ± 0.23	279.41 ± 30.03	12.33 ± 1.80	25.13 ± 7.36
ECC10	17.10 ± 1.44	10.33 ± 1.02	340.57 ± 34.26	12.13 ± 0.78	54.00 ± 35.35

EI0 = HDPE, ZN; EI25 = HDPE with 2.5% of DCP; ECC 1, 5 and 10 = EI25 with 1 to 10% w/w of CC.

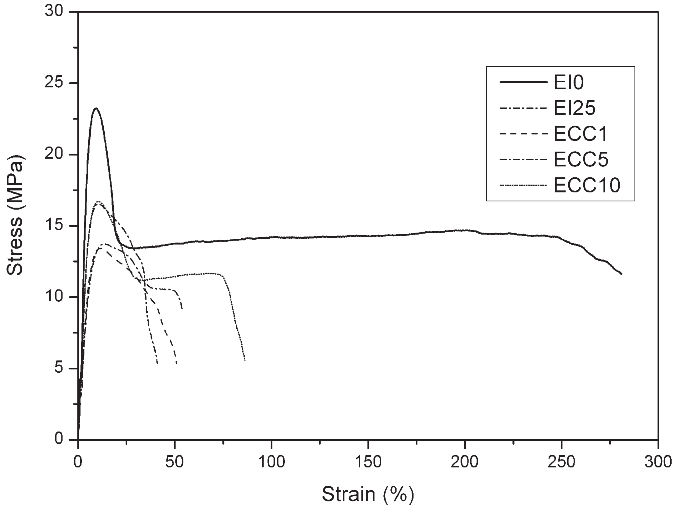

Figure 4.
Stress-strain curves of the crosslinked samples.

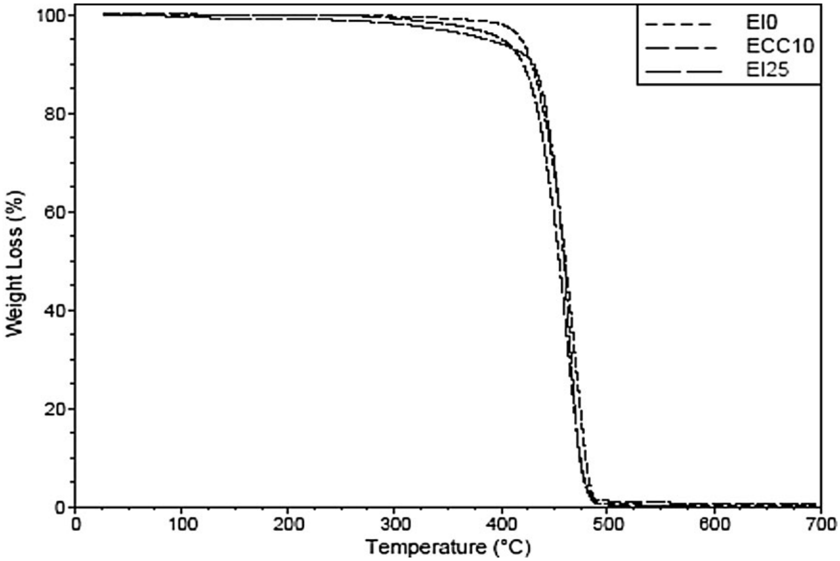

Figure 5.
Profiles of thermogravimetric analysis of the crosslinked samples.

Table 4.
Swelling properties of PEX's samples.

Sample	Gel Content (%)	X_c (%)	T_m (°C)	Swelling in oil (%)
EI0	0	65	132.2	4.09
EI25	99.3	56	128.0	3.76
ECC10	73.6	67	131.0	2.44

material more homogeneous, increasing the moduli. The addition of 10% CC in PEX caused the tensile strength at break to increase in comparison to PEX without CC.

Figure 5 illustrates the thermal degradation behavior (TGA) of the samples: HDPE (EI0); PEX (EI25); and PEX/CC (ECC10), where only a small variation can be observed. It is worth noting the lower temperature of the maximum degradation rate of PEX/CC, which may be related to its low gel content compared to the other samples discussed above.

In relation to oil resistance, the degree of swelling in the same series of samples subjected to TGA is reported in Table 4. Sample PEX/CC (ECC10) showed a significantly lower degree of swelling, suggesting that this material can be an interesting alternative for use in oil pipelines. Another important finding is that for polyethylene, the most important factor regarding oil resistance is the high degree of crystallinity of PEX, and not the high gel content, as can be shown in Table 4.

Conclusion

The peroxide method employed in the synthesis of PEX starting from various grades of polyethylene under the conditions studied proved to be feasible. We also observed that the more homogeneous the comonomer distribution in the polyethylene chains is, the higher the gel content is in the PEX obtained. Among the polyethylenes studied in this work, the most efficient for crosslinking was the one obtained through metallocene catalyst, although the use of HDPE with higher MFI caused a good network performance.

The incorporation of a new crosslinking coagent for the preparation of PEX led to better mechanical properties, with increased modulus, along with outstanding oil resistance properties.

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