

GPC and TREF, complementary techniques for complete analysis of polyethylene resins

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Abstract

In function of the catalyst, different structures of polyethylene resins are obtained, with relatively complex distributions of molecular weight, short chain and long chain branches. The analytical methods of choice to characterize these chemical structures are gel permeation chromatography (GPC) and temperature rising elution fractionation (TREF). The application of these techniques, implemented at Certech in a collaboration with Agilent Technologies, are explained for different types of polyethylene resins.

Keywords

GPC, TREF, LDPE, HDPE, metallocene PE

1. Introduction

Although the chemical composition of polyethylene (PE) is an array of $-\text{CH}_2-$ groups, the infinite possibilities to add short and long chain branches on the main chain generate complex structures. These structures can be classified in function of the catalyst used for synthesis of PE:

- When the radical polymerization of ethylene is initiated by minute concentrations of oxygen or peroxides, a complex PE structure with long and short chain branches is obtained due to inter and intra chain transfer reactions. The branches impede the crystallization thus generating a PE with low density (LDPE).
- Using catalysts based on chromium (Phillips) or titanium (Ziegler-Natta) it is possible to obtain PE

with a much lower number of short chain branches, having a high density (HDPE).

- Recently, metallocene catalysts provided a way to obtain more controlled PE structures (mPE), thus displacing from the market the previous LDPE and HDPE resins.

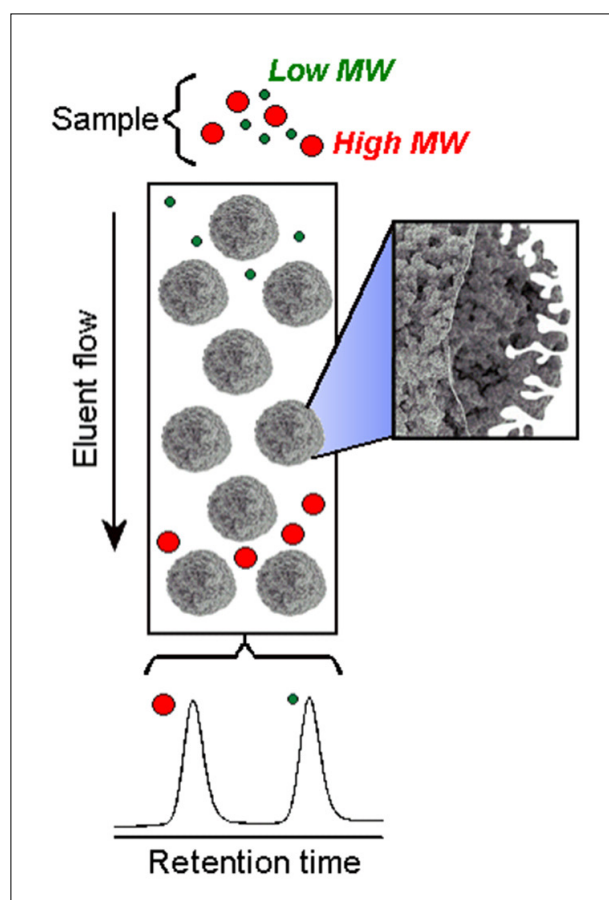


Figure 1: GPC separation mechanism

The methods of choice to analyze these complex PE structures are gel permeation chromatography (GPC) with triple detection and temperature rising elution fractionation (TREF).

In GPC, the polymer is prepared as a dilute solution and injected into the column packed with porous beads of controlled porosity. Large molecules are not able to permeate all of the pores and have a shorter residence time in the column. Small molecules permeate deep into the porous matrix and have a long residence time in the column. Therefore, polymer molecules are separated according to molecular size, eluting largest first, smallest last as presented in Figure 1. The concentration of eluted species from the column is usually measured with a differential refractive index detector.

To calculate the molecular weight of an unknown sample, the column has to be calibrated by injecting narrow standards with known molecular weights as presented in Figure 2:

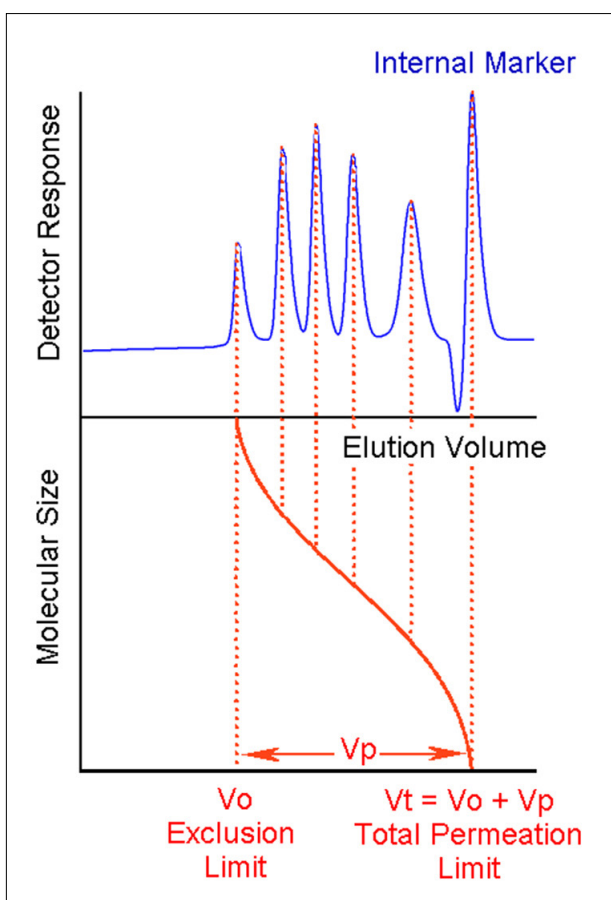


Figure 2: GPC column calibration

When supplementary to the concentration detector, other on-line detectors are available such as viscometer (VS) and light scattering (LS), the GPC with triple detection allows direct measurement of the true molecular weight of the sample without the necessity to calibrate the column. By plotting the measured viscosity in function of calculated molecular weight it is also possible to evaluate Mark-Houwink parameters, which are related to the presence of long chain branches.

However, GPC cannot ascertain the number of short chain branches, the parameter regulating the density of PE. This can be done separately by measuring the melting point in the presence of a solvent by TREF. For this analysis, polymers are dissolved in a solvent and injected in a stainless steel column containing metal beads. An oven is used to properly control the temperature of the column. The polymer solution is introduced into the column at 160°C and undergoes a temperature cycle:

- 1) Cooling at a slow rate (usually 0.1°C/min) during which the polymer chains crystallize around metallic beads at different temperatures depending on their amount of short chain branching (SCB). The first fractions that crystallize are linear polymers without short chain branches. At lower temperatures, the fractions with higher concentrations of branches crystallize onto the first layer. Therefore, crystallized polymer layers form around the metallic beads with increased short chain branching.
- 2) Heating at a rate of 1°C/min during which the polymer fractions are eluting, first the amorphous ones, and after that the highly crystalline ones. The amount of eluted species is detected with an infrared detector set to the wavelengths corresponding to the vibrations CH_2 and CH_3 .

The choice of cooling and heating rates in these two stages defines the accuracy of the results. However, the use of very slow crystallization and heating rates induces very long analysis time. A compromise between the accuracy and duration of analysis must be found.

The results of the analysis are reported as an IR absorption curve as a function of elution temperature, as presented in Figure 3 for a mixture of mPE resins.

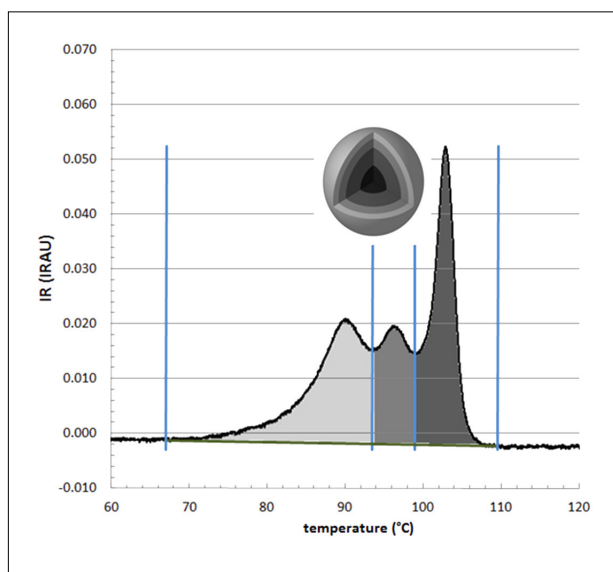


Figure 3: TREF mechanism and the chromatograms obtained for a mixture of 3 mPE resins with different densities

These two methods, GPC and TREF, were implemented at Certech in a collaboration with Agilent Technologies. The developments on polyolefin characterization realized with these techniques were reported in recent papers, providing details on the following topics:

- Triple detection GPC of polyolefin resins using an alternative environmentally friendly (non-chlorinated) solvent [1-4];
- Fast TREF of polyethylene and propylene samples [5-8];
- Correlation between GPC, TREF and DSC for linear polymers [9].

2. Experimental

The study was done on 10 commercially available polyethylene resins having the following characteristics, listed in the Table below.

Sample	Type	Density (g/cm ³):
LDPE 1	Radical PE with LCB and SCB	0.921
LDPE 2	Radical PE with LCB and SCB	0.9225
LDPE 3	Radical PE with LCB and SCB	0.923
LDPE 4	Radical PE with LCB and SCB	0.925
LDPE 5	Radical PE with LCB and SCB	0.930
mPE 1	Metallocene PE with SCB	0.923
mPE 2	Metallocene PE with SCB	0.934
mPE 3	Metallocene PE with SCB	0.947
mPE 4	Metallocene PE with SCB	0.955
HDPE	Linear Ziegler Natta PE	0.978

These samples were analyzed using the Agilent PL-GPC 220 High Temperature GPC System equipped with a differential refractive index (DRI) detector, viscometer (VS) and dual angle light scattering detector (LS). Agilent GPC software (v2.1) was used for data interpretation. The method had the following parameters:

- Column set: 3 x PLgel Mixed B (300 x 7.5 mm) columns.
- Injection Volume: 200 μ l.
- Eluent: 1,2,4-trichlorobenzene (TCB) at 160°C.
- Flow rate: 1.0 ml/min
- Calibrants: Polystyrene
- Samples were dissolved in TCB eluent at approximately 2 mg/ml.

Furthermore, the polyethylene resins were also analyzed using a TREF-CRYSTAF instrument (Polymer Char, Valencia, Spain). Each sample was dissolved in TCB at 160°C to obtain a 2 mg/ml solution. The hot solution was injected at 160°C in the ATREF column (100 mm length, 0.25 in diameter) filled with metallic beads. The column filled with solution was rapidly cooled to 100°C and then was further cooled to 30°C with a cooling rate of 0.1°C/min. After the cooling step, the polymer was eluted from the column, using a heating rate of 1°C/min between 30°C to 160°C, and a flow rate of 0.5 mL/min. The concentrations of the eluted polymer fractions were measured with the built-in infrared detector.

3. Results and discussion

3.1. GPC results

The chromatograms obtained with the differential refractive index detector can be converted in molecular weight distributions using a calibration

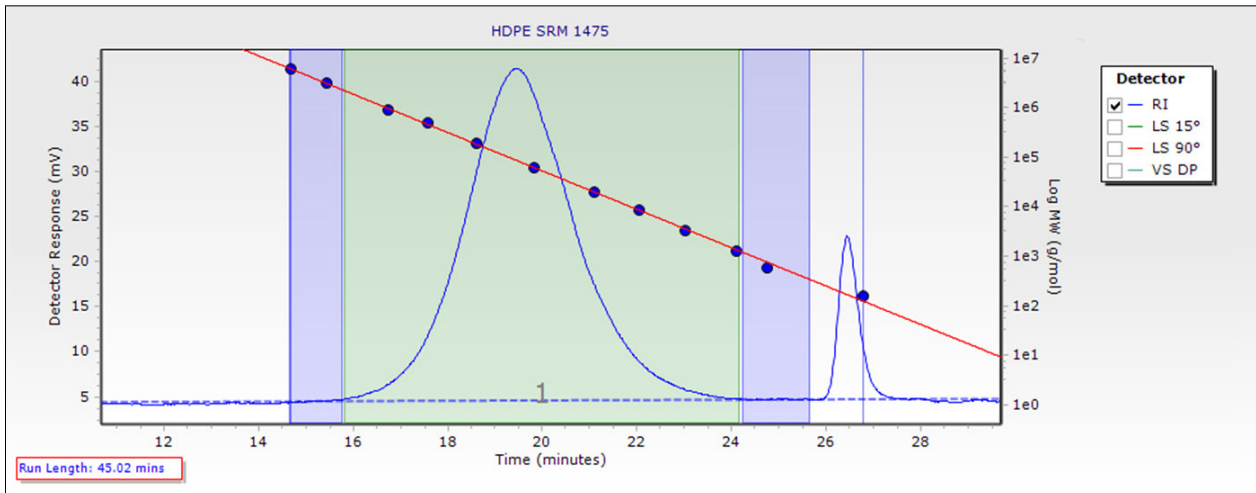


Figure 4: GPC chromatogram and calibration curve for HDPE sample

determined with polystyrene standards. The obtained curve for polystyrene:

$$\log(\text{MW}) = f(\text{elution time})$$

is translated in a curve for PE on the fact that a polymer which passes through the column is eluted in function of its hydrodynamic volume. The hydrodynamic volume of a certain polymer fraction is proportional with the product between its molecular weight and its intrinsic viscosity. Therefore, at each elution time, the following relationship holds:

$$M_{\text{PS}} [\eta]_{\text{PS}} = M_{\text{PE}} [\eta]_{\text{PE}}$$

For a certain combination of solvent-polymer, the intrinsic viscosity can be evaluated using the empirical Mark Houwink Sakurada relationship:

$$[\eta] = K M^\alpha$$

where K and α are parameters which depend on the polymer, solvent and temperature.

For PS and PE in TCB the recommended values for K and α parameters are provided by ASTM D 6474 [10]:

- $K_{\text{PS}} = 19 * 10^{-5}$ (dL/g)
- $\alpha_{\text{PS}} = 0.655$
- $K_{\text{PE}} = 39 * 10^{-5}$ (dL/g)
- $\alpha_{\text{PE}} = 0.725$

With these values, the chromatogram provided in Figure 4 for HDPE sample is converted in a molecular weight distribution curve in Figure 5.

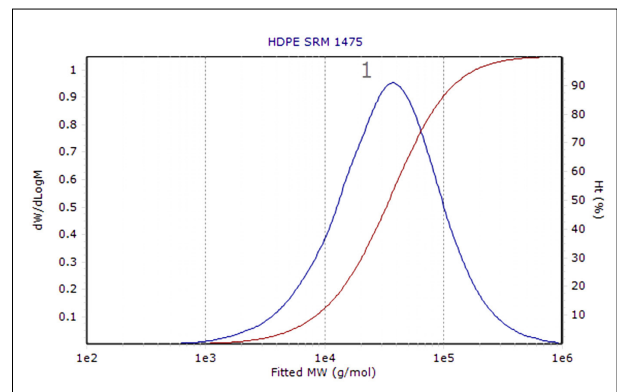


Figure 5: Molecular weight distribution of HDPE sample

Although conventional GPC, using a single concentration detector, can be sufficient for relative comparison of the molecular weight distributions of the samples, by adding on-line LS and VS detectors it is possible to directly measure true molecular weights and to evaluate the long chain branching distribution. Details for instrument calibration by injecting a PS standard with a molecular weight between 100 and 200 kg/mol were given in our previous works [2, 3]. An example of chromatograms obtained for the HDPE is given in Figure 6.

The triple detection procedure also allows measurement of the viscosity, and hence the Mark-Houwink parameters for PE samples can be calculated, by plotting the measured intrinsic viscosity as a function of the molecular weight. The results are provided in Figure 7, where a clear distinction is observed between α values for linear PE (0.72 - 0.73), and the branched LDPE which have much lower α values (0.56 - 0.58).

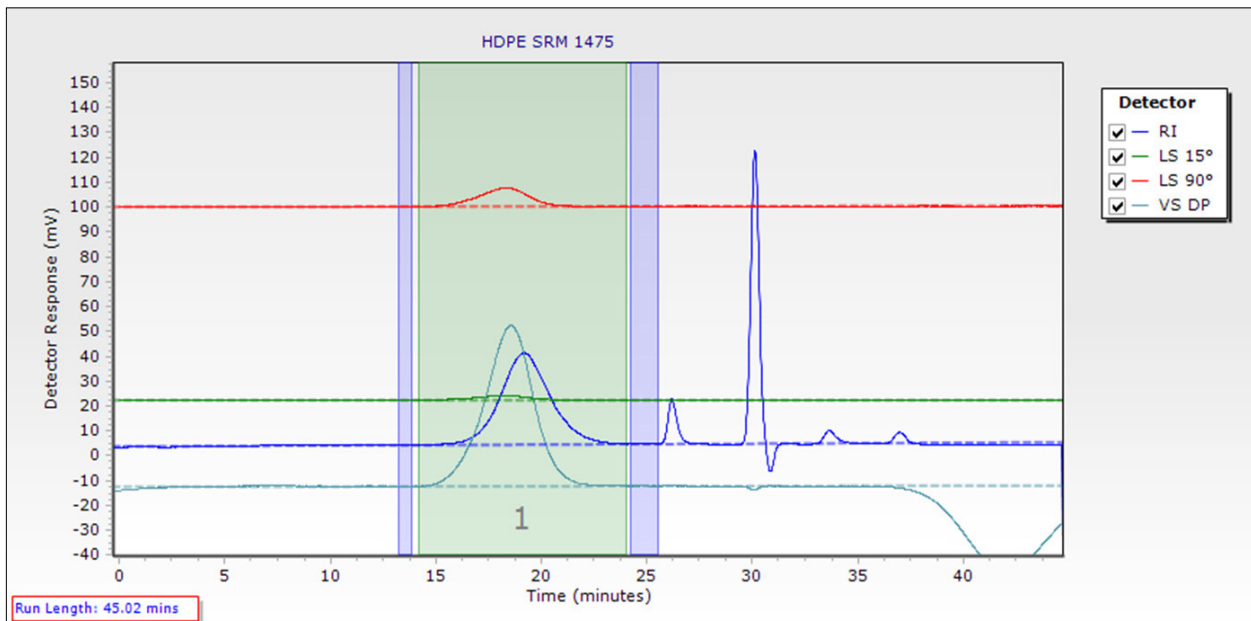


Figure 6: Triple detection GPC chromatograms for HDPE sample

Although the mPE samples have different densities, their α values are comparable to the value provided by ASTM 6474 for linear HDPE (0.725). Therefore, we can conclude that triple detection GPC is very sensitive to long chain branching, but it also has

difficulties to distinguish between samples having different distributions of short chain branching, which is the major parameter controlling the density of the PE resins.

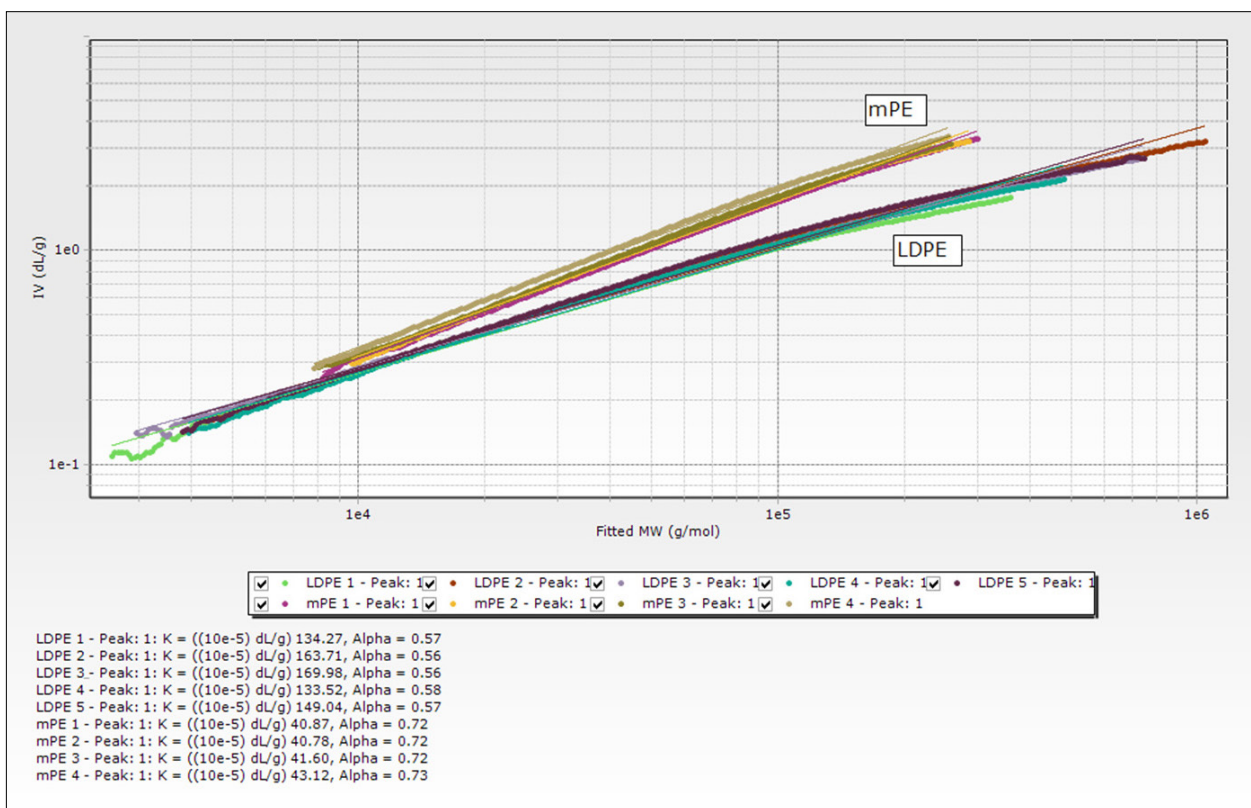


Figure 7: Overlay of Mark Houwink plots for PE samples

Figure 8: Overlay of TREF curves for mPE samples

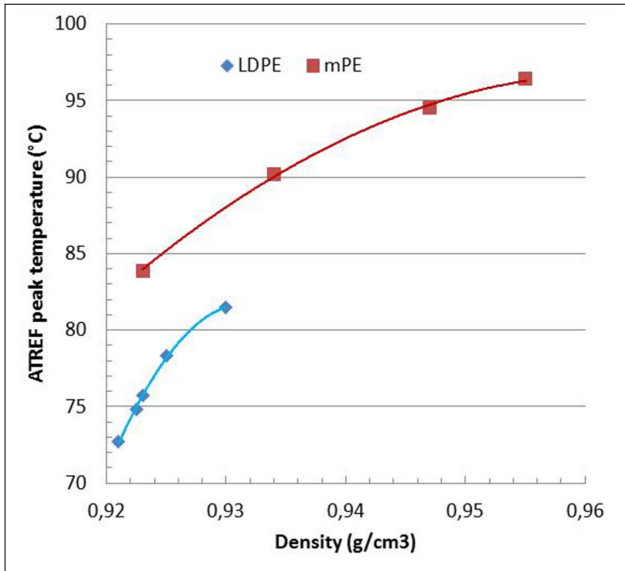
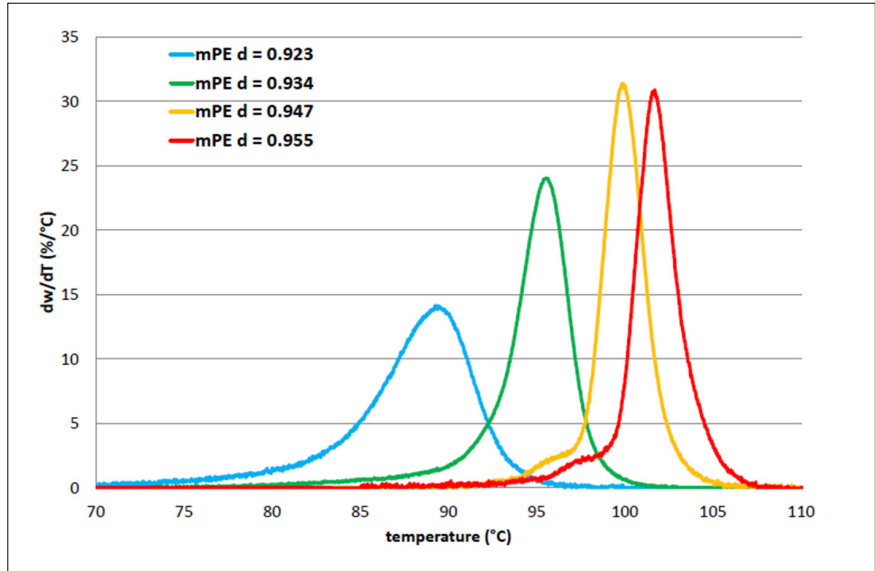
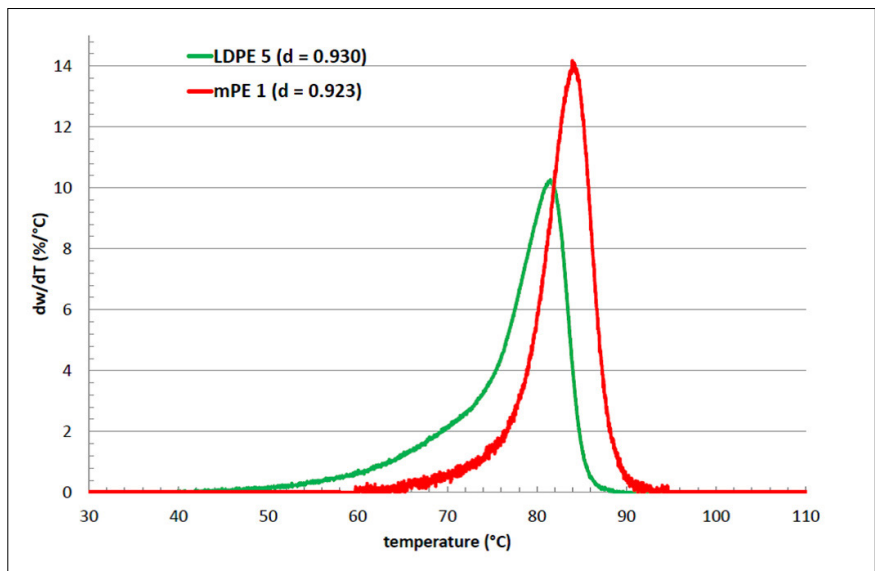


Figure 9: Correlation between density and TREF peak temperature for different types of PE

Figure 10: Overlay of ATREF curves obtained for LDPE 5 and mPE 1, which clearly shows that the metallocene PE presents a higher peak temperature than a LDPE, even when the metallocene PE has a lower density than LDPE.



3.2. TREF results

The TREF technique is very sensitive to identifying differences in short chain distribution, as presented in Figure 8.

When the type of the PE can be identified with triple detection GPC, the elution temperature in TREF can then be easily correlated with the sample density, as shown in Figure 9.

But analytical TREF alone is not enough to evaluate the density of an unknown sample of PE. This is clearly presented in Figure 10 where the LDPE 5 ($d = 0.930 \text{ g/cm}^3$) has a lower eluting temperature than mPE 1 ($d = 0.923 \text{ g/cm}^3$):

Therefore, only when the two techniques, triple detection GPC and TREF, are applied together on an unknown PE sample is it possible to extract comprehensive information regarding its structure such as:

- the existence or not of long chain branches using the viscometer,
- the true molecular weight given by light scattering, and
- the distribution of short chain branches by TREF.

4. Conclusions

Our study confirms that triple detection GPC is a reliable method to evaluate the type of PE, by measuring the α parameters of the Mark Houwink plots. For metallocenes, these parameters were found to be comparable to the values recommended by ASTM 6474 for linear HDPE ($\alpha = 0.725$), and they do not depend on the density of PE. Due to the long chain branching, the molecular coil cannot freely extend in TCB, and the values for the α parameters of LDPE samples are close to the value corresponding to a theta solvent ($\alpha = 0.5$).

Supplementary TREF analyses can complete the information for an unknown PE sample, by providing the short chain distribution, which is the most important parameter controlling the density of PE resins.

Therefore, only by applying both techniques, GPC and TREF, it is possible to reach a complete description of the chemical structure of an unknown PE sample.

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