Calibration of a thermal fractionation technique for polyolefin characterization

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Introduction

The thermal fractionation technique CRYSTAF (CRYSTallization Analysis Fractionation) was invented by Benjamin Monrabal in 1991, in order to separate the compounds according to their crystallinity. This technique is used to determine the structure of polyethylene. Polyethylene is a semi crystalline polymer which has numerous applications according to its degree of crystallinity. It is also well used to make plastic bags as well as to make bulletproof vests. So it is very important to control its structure following its different utilities. The incorporation of comonomer in the polyethylene, like hexene, changes the structure of polyethylene to get different applications. We need to control the structure of polyolefins including their chain length which is measured by size exclusion chromatography and their short chain branching (SCB) rate which is determined using CRYSTAF. This method is recent. It is necessary to calibrate it to quantify the SCB. To do so, we use a range of polyolefins which has been incorporated with hexene at different rates during the polymerization process. These polyolefins have a narrow distribution of mass and are homogeneous in composition. Then SCB can be measured by NMR, We create a calibration curve which represents the rate of branches (measured by NMR) depending on the temperature of crystallinity.

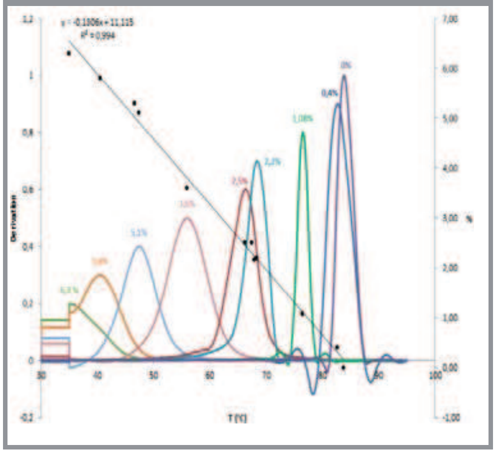
Experimental conditions

The separation of chain occurs in a stirred vessel during the crystallization step, About 40 g of polyolefin is completely dissolved in a solvent (1,2,4-TCB) at high temperature (150°C) and then we gradually reduce the temperature to 35°C to produce a recrystallization of the polymer. During this temperature reduction, the dissolved polymer concentration decreases and it is measured at regular intervals using an infrared detector

Results and discussion

The concentration profile is derived, and we obtain the composition distribution shown on the figure. The top of the peak corresponds to the temperature of crystallinity of the polymer and the square area at 30 to 35°C is the polymer that has not crystallized. The black line represents the calibration curve, which has a correlation coefficient of 0.994. Therefore we can use this calibration to determine the composition of ethylene-hexene copolymer. This method allows measuring an incorporation up to 6.3%.

CRYSTAF Calibration of PE-Hexene polyolefins



Conclusion

Knowing the composition of ethylene copolymer is essential and CRYSTAF gives unique information on its structure (short chain branching). This separation technique allows getting the complete chemical composition distribution as opposed to NMR which only gives us an average composition. To increase the range of calibration other separation techniques are actually developed such as TREF (Temperature Rising Elution Fractionation) or adsorption liquid chromatography.

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