Determination of long chain branching in EVA copolymers by GPC-MALS and GPC-VIS: comparison and uncertainties.

Baudilio Coto, Inmaculada Suárez

Universidad Rey Juan Carlos (Spain)

Vinyl acetate ethylene copolymers, often referred as EVA, are thermoplastic materials resulting from the co-polymerization of ethylene and vinyl acetate. As it is well known these copolymers are generally produced by a high pressure, high temperature, bulk polymerization process similar to that employed for conventional high pressure, free radical, low density polyethylene (LDPE) [1].

Long-chain branching (LCB) is a well-known structural phenomenon in polyethylene (PE). Unlike short-chain branching (SCB), LCB in PE can significantly influence the processability and properties of polyethylene resins, even at very low concentrations. LCB governs swell, melt strength, and environmental stress crack resistance in blow molding operations, bubble stability and lamellae orientation in film, sag resistance in pipe and geomembrane, and shear thinning and melt fracture in all extrusion processes [2].

GPC-VIS-MALS equipment is a gel permeation chromatograph (GPC, Waters Alliance 2000) equipped with refractive index and viscometer detectors combined with a multi-angle light scattering (MALS, DAWN EOS Wyatt Technology).

Direct analysis of experimental R_g vs. M_w data is difficult because the extremely disperse data usually obtained by MALS technique. In order to avoid such difficulty, in this work, the numerical method previously developed [3] is used. In this method both M_w and R_g experimentally obtained from MALS are considered functions of elution time and three order polynomials are used in the correlation procedure. During the fit procedure both parameters of the polynomial function and the range where experimental data appears to be confident are obtained. An iterative procedure carried out in four steps is used that automatically increases/decreases the involved data points according to well established statistical conditions and independent on the user.

In this work, such procedure is also applied to the analysis of experimental M_w and □ data obtained by GPC-VIS obtaining good results for the fitting equations and the confident ranges.

References:

1. Peón, J.; Vega, J. F.; Aroca, M.; Martínez-Salazar, J. Rheological behaviour of LDPE/EVA-c blends. On the effect of vinyl acetate comonomer in EVA copolymers. Polymer, 2001; 42: 8093-8101.
2. Yang, Q.; Jensen, M. D.; McDaniel M. P. Alternative View of Long Chain Branch Formation by Metallocene Catalysts. Macromolecules, 2010; 43: 8836–8852.
3. Suárez, I.; Coto, B. Quantification of uncertainties involved in the conformational study of polymers by light scattering. European Polymer Journal, 2011; 47: 2331–2341.