Analysis Method

GPC-VIS-MALS study of EVA copolymers: Quantification and interactions of SCB and LCB

Inmaculada Suárez, Baudilio Coto*

Chemical and Energy Technology, Chemical and Environmental Technology, Mechanical Technology and Analytical Chemistry Department, ESCET, Universidad Rey Juan Carlos, c/ Tulipán s/n, 28933, Móstoles, Madrid, Spain

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ABSTRACT

Long-chain branching (LCB) is a structural phenomenon that affects important properties in polyethylene (PE) and some copolymers. Quantification of LCB frequency ($\lambda$) can be carried out by gel permeation chromatography dotted with detector for viscosity (GPC-VIS) or light scattering (GPC-MALS) by calculating branching indexes against a linear reference. In copolymers, interactions between LCB and SCB (short chain branching) have been described and lead to errors in quantification.

In this work, ethyl vinyl acetate (EVA) copolymers of composition ranging 3–20 wt% VA have been studied. A numerical method, developed for the reduction of GPC-VIS and GPC-MALS data of PE, was used for quantifying molecular weights, intrinsic viscosities and gyration radius, as well as the confident ranges. Reliable results were obtained despite the low LCB determined values.

A low density polyethylene was also included and compared. Discrepancies in the scaling laws for gyration radius and intrinsic viscosity reveal a strong effect of SCB which was confirmed by the structure factor and its dependence on molecular weight and comonomer content. However, the recently designed gpcBR index revealed to be nearly independent on the short chain branching and allowed detecting differences between apparently similar samples.

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1. Introduction

Vinyl acetate ethylene copolymers, often referred as EVA copolymers, are thermoplastic materials resulting from the copolymerization of ethylene and vinyl acetate (VA). These copolymers are generally produced in high pressure and temperature bulk polymerization processes similar to those employed for the conventional high pressure free radical low density polyethylene (LDPE) production [1].

Three structural attributes of EVA copolymers largely determine the properties of any particular copolymer grade [2]: 1) weight % of vinyl acetate, 2) average molecular weight and molecular weight distribution, and 3) long (LCB) and short (SCB) chain branching.

In EVA copolymers, the primary effect of short chain branches, acetoxyl groups from the vinyl acetate is to disrupt the crystallinity of the polyethylene (PE) segments. However, short chain branches have practically no impact on melt viscosity behaviour.

The long chain branching characterization is crucial to understand the viscoelastic behaviour of branched polymers in the melt flow, especially the viscosity at very low shear rate and the degree of shear thinning. Shear thinning is the phenomenon in which the viscosity decreases with increasing shear rate. The consequence of shear thinning is that the material exhibits lower viscosity and flows easier than expected when the flow rate is increased and branched materials require less pressure to be pumped at the same rate. 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 [3]. Higher viscosity at lower shear rate for a polymer with long chain branching can enable easier fabrication via processes like profile, blown film, or foam extrusion [4]. Consequently, LCB is fundamental for the prediction of the processing behaviour [5]. However, number of long chain branches in EVA is quite low, usually under 2 per 1000 carbon atoms [1], and detection of such low values is very difficult by usual techniques [6].

Nuclear magnetic resonance ($^{13}$C NMR) and Fourier Transform Infrared (FTIR) are used for the determination of overall short chain branching levels in LLDPE samples, while Temperature Rising
Elution Fractionation (TREF) and Crystallization Analysis Fractionation (CRYSTAF) are techniques widely used for the qualitative estimation of SCB distributions in semi crystalline copolymers [7–10].

Three methods allow LCB determination: rheology, nuclear magnetic resonance spectroscopy (NMR), and gel permeation chromatography (GPC) with triple detection (refractive index, DRI; viscometer, VIS; and a multi-angle laser light scattering, MALS) [11]. Rheology and NMR techniques determine the average LCB for the overall polymer sample while GPC technique allows determining the LCB distribution along the molecular weight distribution.

Combination of GPC-MALS allows determining both the molecular weight distribution and molecular dimension in solution in terms of the mean square radius of gyration \(R_g\) [12]. The branched polymer is more compact than linear polymer at any given molecular weight and consequently branches lead to smaller hydrodynamic volume, smaller radius of gyration and lower intrinsic viscosity \([\eta]\) [11,18].

Ratio of the intrinsic viscosities (determined by GPC-VIS) or of the radius of gyration (determined by GPC-MALS) of branched samples compared to a linear reference can be used [13,14].

The branching indexes, \(g\) and \(g'\), can be determined from \(R_g\) values by GPC-MALS and intrinsic viscosities by GPC-VIS, respectively, according to Equations (1) and (2):

\[
g' = \left( \frac{[\eta]}{[\eta]_l} \right)_M \tag{1}
\]

\[
g = \left( \frac{R_g^2}{R_g^2_{l, M}} \right)_M \tag{2}
\]

where the subscripts \(l\) refers to the corresponding value for a linear chain, and \(M\) represents that both values are taken at the same molecular weight. Values of \(g\) and \(g'\) are 1 for linear samples and can decrease to 0.1 when LCB is increasing in the sample.

Branching index \(g\), also called contraction factor [15], is related to the intrinsic viscosity index \(g'\) by Equation (3):

\[
g' = g^e \tag{3}
\]

where \(e\) is a structure factor that determines the type of branching [16] and can be used to correlate the structure of the polymer with the properties and rheological behaviour of the material [17].

The number of branching points per chain of polymer, \(B_{sw}\), for tri-functional chains as those in PE, can be related to \(g\) factor by using the Zimm and Stockmayer relation given by Equation (4) [11,18]:

\[
g = \frac{6}{B_{sw}^2} \left( \frac{2 + B_{sw}}{2 + B_{sw}} \right)^{1/2} \ln \left( \frac{(2 + B_{sw})^{1/2} + B_{sw}^{1/2}}{(2 + B_{sw})^{1/2} - B_{sw}^{1/2}} \right)^2 - 1 \tag{4}
\]

LCB frequency is usually given in terms of \(\lambda\) or the number of long chain branches per 1000 carbon atoms and can be calculated, for each slice of the chromatogram, from the Equation (5):

\[
\lambda = 1000 \frac{M_B}{M_w \cdot M_l} B_{sw} \tag{5}
\]

where \(M_0\) is the molecular weight of the repeating unit (14 for \(-\text{CH}_2-\) in polyethylene), \(B_{sw}\) is the number of branches per molecule and \(M_l\) is the molecular weight of the polymer at the slice \(i\).

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the magnitudes have to be simultaneously confident, final ranges are typically very restrictive.

Along such data analysis, each magnitude of interest is explained as a function of the retention time. The experimental data from the several detectors allow obtaining the mathematical fitting function for next magnitudes:

- \( \log(M)_{l, LS} \): \( M \) for a linear polymer determined by MALS
- \( \log(M)_{l, GPC} \): \( M \) for a linear polymer determined by GPC
- \( \log(R_g)_{l, GPC} \): \( R_g \) for a linear polymer determined by GPC and Universal Calibration
- \( \log(M)_{GPC} \): \( M \) for a linear polymer determined by GPC and Universal Calibration
- \( \log([\eta])_{l, GPC} \): \( [\eta] \) for a linear polymer determined by GPC on-line viscometer
- \( \log([\eta])_{on-line} \): \( [\eta] \) for each polymeric sample determined by GPC on-line viscometer

It is important to note that such functions are always obtained from experimental values. Linear polymers were used as reference and their functions obtained by the analysis of linear standard polyethylene samples. Such functions can be used to compute the corresponding magnitudes for a given retention time, number of repeating units, or molecular weight. According to the previous definitions, \( g \) and \( h \) values are involved in the calculation of \( g' \); \( c \) and \( d \) values are involved in the calculation of \( g \); \( c \), \( d \), \( g \) and \( h \) values are involved in the calculation of \( \epsilon \); and \( a \), \( f \), \( g \) and \( h \) values are involved in the calculation of \( gpcBR \).

Original formulation of \( gpcBR \) was carried out for average properties, in this work such index was formulated for being computed point by point, according to above definition and determined functions, \( gpcBR \) value for slice \( i \) is calculated according to

\[
gpcBR_i = \left( \frac{M_{l,LS}}{M_{l,GPC}} \right)^a \frac{[\eta]_i}{[\eta]_i} - 1
\]

Where the subscript \( i \) refers to slice \( i \), and the rest of subscripts have the same meaning as in Equation (6).

From the distribution of the different properties calculated (\( \lambda \), \( \epsilon \), \( gpcBR \)), an average value can be calculated. In this paper, weight average value was determined according to the next equation:

\[
y = \frac{\sum c_i y_i}{\sum c_i}
\]

where \( c_i \) is the concentration for each slice in the chromatogram, and \( y_i \) represents the involved magnitude (\( \lambda_i \), \( \epsilon_i \), \( gpcBR_i \)) determined for each slice.

In addition, listed magnitudes allow the determination of the dimension of the macromolecules in solution as a function of the molar mass. Accurate determination of the radius of gyration and of the intrinsic viscosity vs molar mass power law, generally known as Mark-Houwink-Sakurada (MHS), are of fundamental importance because molecular architectures of the polymers in solution are usually investigated with the scaling laws relating \( R_g \) and \( [\eta] \) with \( M_w \):

\[
R_g = Q \cdot M^\theta
\]

where \( q \) and \( q' \) are shape parameters which depend on the polymer, the solvent, and the temperature and reveals information about the polymer conformation in solution. Generally, \( q \) has a value of 0.33 for globular polymers, 0.5 for random coil polymers at theta conditions, and up to 0.6 for random coil polymers in good
solvents [14,25,26]. Typical values for q' are 0 for compact sphere, 0.65—0.85 for random coil or 1.8 for very stiff chain).

3. Results

3.1. Determination of EVA copolymers dn/dc

dn/dc values are required in any MALS study, and they are scarce properties for most copolymer systems. Most of the copolymer properties depend on its composition and consequently the dn/dc values have to be experimentally determined for EVA copolymers.
dn/dc values for EVA copolymers at 639 nm, 145 °C and different compositions are available in the literature [27]. New values were determined in this work by GPC at 810 nm and 145 °C. Table 1 list dn/dc values of EVA copolymers at a given λ, temperature and copolymer composition.

Dependence of dn/dc with composition and wavelength has been studied following a procedure developed in previous study for ethylene-propylene copolymers [21].

Both dependences can be expressed simultaneously by Equation (11):

\[
dn/dc = a + a'w + b + b'w/l^2
\]

where a, a', b and b' are considered fitting parameters that minimize the objective function:

\[
F = \sum [(dn/dc)_{exp} - (dn/dc)_{cal}]^2
\]

The fitted parameters were \(a = -1.303 \times 10^{-1}, a' = 4.179 \times 10^{-4}, b = 3.2010 \times 10^{-4}\) and \(b' = -3.809 \times 10^{-2}\) with a standard deviation between experimental and calculated dn/dc values of \(\sigma = 0.003\). As q value is similar to the experimental uncertainty, the equation can be used to extrapolate a confident dn/dc value for a copolymer at a given composition and wavelength.

Table 2 lists basic characterization of each EVA copolymer used in this study: VA comonomer content, calculated dn/dc values at λ = 690 nm, average molecular weight and polydispersity indexes for each injection.

3.2. Study of dimension of macromolecules in solution by GPC-VIS and GPC-MALS

Fig. 1a) plots radius of gyration and viscosity as a function of molecular weight for EVA14 sample obtained along 2 different injections. Similar results were obtained for the different samples and the reproducibility between the injections can be considered excellent.

Scaling laws given by Equations (9) and (10) were applied in the range of confident values both for \(R_g\) and \(\eta\). Obtained q and q' values for EVA copolymers in comparison with LDPE are plotted in Fig. 2 as a function of VA comonomer weight percent. A branched chain is more compact than a linear one and its dimension decreases as the degree of branching increases at constant molecular weight [28]. The q value was 0.22 for LDPE, representing a compact globular polymer, and increases to 0.42 for EVA20, showing how the second monomer favoured to adopt a random coil chain configuration that can be related with the size of VA comonomer and its polarity.

However, when similar study is carried out with GPC-VIS data, obtained q' values are nearly independent of the comonomer content and similar to that for LDPE (around 0.40) as can be seen in Fig. 2. These values confirm how the melt flow behaviour, especially the viscosity at very low shear rate and the degree of shear thinning behaviour, is affected by long chain branches while short chain branches have practically no impact.

Consequently, scaling law allows obtaining q values from GPC-MALS results is affected by comonomer size and polarity (SCB and LCB) but on the contrary intrinsic viscosity obtained by GPC-VIS is only affected by LCB.

3.3. Study of the branching index

Fig. 1b) compares the branching indexes (g' and g) calculated from Equations (1) and (2) as a function of molecular weight. High reproducibility can be checked for both magnitudes in two injections. Similar values were obtained for both parameters with the highest differences for the lower molecular weights.

The relation between branching indexes g and g' is given by Equation (3) through the ε factor. Different values of this factor have been described as a function of the LDPE synthesis method: a value
of $\epsilon = 0.5$ was obtained by Stockmayer for star branched molecules, Berry assumed $\epsilon = 1.5$ for comb shaped molecules with small branches, Kuhn and Kromert determined $\epsilon$ values of 1.2 and 2.0 for one zone autoclave and tubular LDPE, and Scholte found $\epsilon$ values ranging from 1.0 to 0.5 with increasing molecular weight for autoclave and tubular products [29]. In a previous work [30], the dependence of this parameter with molecular weight was studied for different LDPE samples and a clear decrease of $\epsilon$ towards a limit value of 1.0 was obtained when molecular weight was increased along a range similar to that covered in the present work.

In Fig. 3 $\epsilon$ values for all samples are plotted as a function of molecular weight. It can be observed a clear decrease of $\epsilon$ with the increase of molecular weight for all samples towards a limit value of 1. The values reached at low molecular weights are related with the comonomer content; similar behaviour was previously obtained when dimension of macromolecules in solution is studied.

3.4. Study of LCB

Fig. 1c) plot LCB distributions ($\lambda$ and $\lambda'$), determined using Equations (4) and (5), versus molecular weight for EVA14 sample. It can be seen how these samples present distributions where LCB increases with molecular weight. Small differences in $g$ or $g'$ lead to higher differences in the values for $\lambda$ and $\lambda'$, and values obtained by GPC-VIS are more reproducible than those obtained by GPC-MALS, with the highest deviations at low molecular weight.

In order to improve the quantification of the LCB, the new gpcBR LCB index has been determined following Equation (7). This new LCB index was created to allow a direct comparison with the LCB index used in the rheological tests [19]. The definition of gpcBR takes advantage of the most precisely measured parameters in the experiments i.e., the light scattering $M_{W,LS}$, the viscometer $[\eta]$, and the conventional GPC $M_{W,GPC}$ and $M_{G,GPC}$ values, where $M_{W,GPC}$, $[\eta]$ and $M_{G,GPC}$ are the weight-average molecular weight, intrinsic viscosity, and viscosity-average molecular weight, respectively. The theoretical value of gpcBR is 0.0 for linear polyethylene and it can range up to 4.0 for typical LDPE resins.

Fig. 4 plotted these values for each sample analysed as a function of molecular weight. The small error bars plotted represent a high reproducibility for this parameter when it is compared with previous values of $\lambda$ and $\lambda'$ calculated from $g$ and $g'$. From Fig. 4 it is possible to check how these branching indexes are increasing with molecular weight for all samples independent of the comonomer content. EVA copolymers and LDPE behaviour is similar and both present higher amounts of branches at high molecular weight, despite EVA copolymers show lower branching than LDPE in the whole molecular weight range.

In order to give a more quantitative sense to above results, average values have been determined. Fig. 5 plots together the slice concentration (left axis), and $\epsilon$, gpcBR and $\lambda$ (right axis) values versus molecular weight for EVA14 sample. The range plotted is that determined with confidence. This figure allows to confirm that average values can be considered confident because the concentration values are high enough in the covered range and because most properties fails to very small values when concentration increases.

From the distribution of $\lambda$, $\epsilon$ and gpcBR and the slice concentration obtained by GPC average values were calculated according to Equation (8). Obtained values are listed in Table 3 for each sample and injection. Fig. 6 shows the gpcBR and $\lambda$ for each injection as a function of the comonomer weight percent. A slightly and continuous dependence with comonomer content is found for $\lambda$ with a minimum value around 10 wt%. Reproducibility in $\lambda$ is reasonable but differences between injections increase with VA weight percent. However, a different plot is obtained for the gpcBR.
value higher than 2 is obtained for LDPE sample, but values lower than 1 are obtained for EVA samples and with very low VA percentage.

These results clearly show the higher dependence of λ with SCB in comparison with gpcBR.

Conclusions

Analysis of EVA copolymers has been carried out using GPC-VIS and GPC-MALS techniques following experimental and numerical procedures previously developed. The range of application of GPC-VIS covers lower molecular weights than GPC-MALS and the full analysis was limited to the region were all the experimental data were confident, i.e. log\(M_w\) ranging 4.5 to 6.

Scaling laws for \(R_g\) and \([\eta]\) vs. \(M_w\) were determined with very different values for \(q\) and \(q'\) parameters, thus confirming how MALS is sensitive to SCB while viscometer is not affected by such comonomer content. Branching indexes, \(g\) and \(g'\), and the branching frequencies, \(\lambda\) and \(\lambda'\), reveal the same difference, and lead to a structure factor, \(\epsilon\), highly dependent both in \(M_w\) and in the comonomer content, even considering that uncertainty is higher in the low \(M_w\) range.

\(\lambda\) and \(\epsilon\) average values were determined using the experimental slice concentration. Despite no confident values are available for the full range, the covered \(M_w\) range can be considered significant enough. Average \(\lambda\) values range from 0.15 to 0.29, thus describing very low branched samples but dependent of SCB. On the opposite, average \(\epsilon\) values range from 0.9 to 2.3, and they increase according to the increase of comonomer content, in agreement with the differences found between \(q\) and \(q'\) values.

Calculated values for gpcBR index are very low and few sensitive to comonomer content, according to the definition of that index. Average values range from 0.6 to 0.9 in agreement with low \(\lambda\) values.

For comparison purposes, a LDPE sample with similar \(M_w\) and synthesis procedure was included in the study. Despite similar \(q'\) values, that sample presented the lowest \(q\) value, and the highest \(\lambda\), \(\epsilon\) and gpcBR values. Value for gpcBR was about 2 and consistent with a long chain branching sample where SCB has no influence.

On the opposite, low LCB in EVA samples (with gpcBR lower than 1), has to be considered influenced by the content and nature of the polar SCB and consequently the real \(\lambda\) values should be even lower. However, gpcBR index is not affected by SCB and differs in samples that in principle should be expected very similar.

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References


