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### Molecular Characterisation of Rubbers

Size exclusion chromatography (SEC) is an analytical method that is frequently used to characterise a polymer. To analyse a polyolefin, a high temperature system is necessary, which is called HT-SEC. HT-SEC yields information about the molecular weight distribution of the polymer, as well as information about its structure (e.g. linear, long chain branched, star-shaped) and chemical composition (short chain branched) as a function of its molecular weight.

#### What we can do for you

Using HT-SEC, we can carry out an in-depth analysis of a polymer (rubber) before vulcanisation and determine its molecular weight distribution and molecular weight averages, defined as  $M_n$ ,  $M_w$  and  $M_z$ .

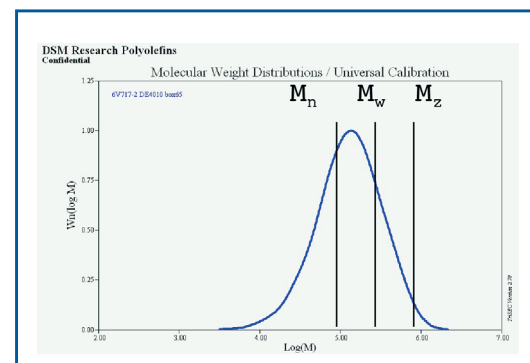


Figure 1:  
*The molecular weight distribution and its averages*

This distribution and its averages can help us determine important physical properties of your polymer:

- $M_n$  is the number average molecular weight. It is related to the impact

properties of the polymer: the higher the  $M_n$  value, the lower the amount of chain-ends there are and the higher the impact resistance of the polymer.

- $M_w$  is the weight average molecular weight. It is related to the Melt Flow Index (MFI) or reciprocal viscosity at low shearing rate. The higher the  $M_w$  value, the lower the MFI.
- $M_z$  is the z average molecular weight. It is related to 'die swell' and melt fracture (consequence of elastic recovery). The higher the  $M_z$  value, the higher the change of 'die swell'.
- $M_w/M_n$  and  $M_z/M_w$  are the polydispersity indices. It is related to shear thinning (deviation of Newton's behaviour). The higher the polydispersity, the higher the deviation of Newton's behaviour and the lower the viscosity at higher shearing rate.

#### How HT-SEC works

The polymer is first dissolved in an appropriate solvent at a high temperature (about 140-160°C). The polymer solution is then injected into a SEC column. The columns are filled with porous beads. The pores are characterized by a certain pore size distribution (PSD). The PSD must be selected in such a way that the large molecules of the sample can only move into the larger pores while small molecules can move in almost all pores. When flowing over the column, the larger polymer molecules will be retarded more than the smaller molecules. Separation is according to their size or hydrodynamic volume. For linear molecules this volume is directly related to the molecular weight. For branched molecules with a certain molecular weight, the size will always be less than for the linear molecules having the same molecular weight. As a consequence these branched molecules will elute later than the corresponding linear ones.

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To determine the concentration of all separated fractions and obtain detailed information on molecular weight, structure and branching, several detectors must be coupled to the columns. For molecular characterization of elastomers preferably following detectors are used: refractive index detection (RI), infrared detection (IR), viscosity detection (DV) and light scattering detection (LS).

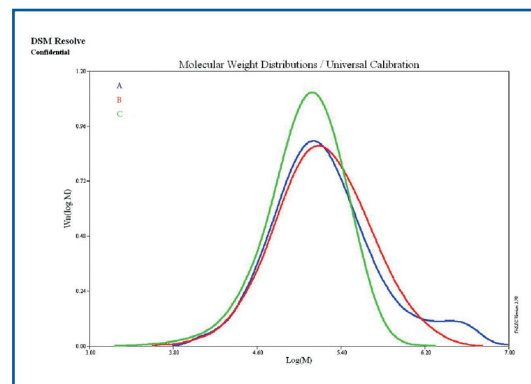
**Sample size and preparation**

The HT-SEC analysis is performed on virgin EPDM material (10-20 milligrams of sample is required). The measurement cannot be performed on compounds because these will not dissolve in the solvent, due to the cross linking.

**Example of HT-SEC analysis of an EPDM sample**

Figure 2 shows the molecular weight distribution of 3 samples:

Looking at the molecular weight distribution (and averages), sample A shows the highest molecular weight with the broadest distribution (blue graph). For this sample there is a clear presence of a fraction of high molecular weight material. Sample C shows the lowest molecular weight with the narrowest distribution (green graph).

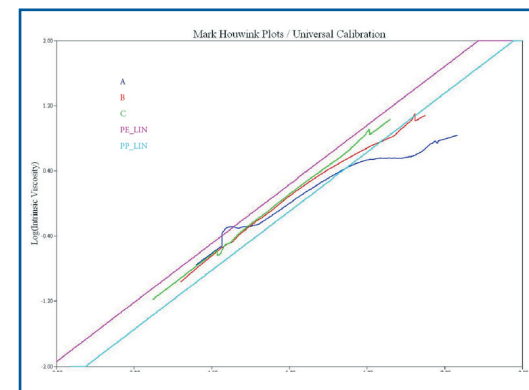


**Figure 2:** Overlay of molecular weight distributions of different keltan EPDM samples.

For dissolved polymers the relationship between molecular weight and intrinsic viscosity is the so called Mark-Houwink equation, as shown in Figure 3. It is clear that this information can only be obtained by using in addition to a concentration detector (RI and/or IR) also a viscometer and preferably a light scattering detector.

In a good solvent, the slope of this plot is close to 0.7 for linear molecules. When the slope is less than this value, there is good evidence for branching. At a certain molecular mass, the intrinsic viscosity of a branched molecule will be less than for the corresponding linear molecule. The intercept of the Mark Houwink plot is related to the composition of the material. The higher the intercept, the higher the ethylene content (the pink line is for pure linear PE). The lower the intercept, the higher the propylene content (the blue line is for pure linear PP). Based on the result below, sample A shows a lower amount of PE compared to samples B and C.

The deflection of the Mark Houwink plot (reduction of slope at high molar masses) indicates the presence of long chain branching which is the case for B and A at a higher molar mass.



**Figure 3:** Overlay of Mark-Houwink plots of different EPDM samples and 2 reference samples (PE and PP).

The molecular weight averages, polydispersity indices (Mw/Mn and Mz/Mw) and intrinsic viscosity of these samples are shown in the table below.

**Table 1. Universal typical values calibration**

Sample	Mn	Mw	Mz	Mw/Mn	Mz/Mw	[η]
A	96	420	2300	4.4	5.5	1.64
B	96	295	800	3.1	2.7	2.08
C	73	160	280	2.2	1.7	1.71

\* Molecular mass in kg/mol. Viscosities in dl/g.

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