Analysis of Polybutadiene using Gel Permeation Chromatography

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Abstract

Polybutadiene is used as homo- and co-polymers for the production of tyres (70 %), moving belts and soles of shoes. In 1989 1.1 Mio.t. were used worldwide.

For example, the performance of tyres depends strongly on the molecular weight (MW) of the polybutadiene used and its additives. To ensure highest quality and consequently highest safety MW data need to be evaluated for each batch of produced polymer. Gel Permeation Chromatography (GPC) is an analytical tool used to characterize polymers which are soluble in organic solvents. In general an isocratic pump is sufficient for GPC analysis, however for ease of solvent change and rinsing, a pump with two or more channels would be advantageous. The pump should be able to pump the selected flow rate with a precision of typically < 0.15 %. Solvent degassing is recommended either offline or even better online with vacuum degassing. For high sample throughput the use of an autosampler would be beneficial. The temperature of the column oven needs to be very stable to avoid retention time shift and therefore MW errors—a peltier controlled thermostat is ideal for highest temperature stability especially at and below ambient temperatures

For detection a UV detector and/or a refractive index detector can be used. In this example we used both detectors to demonstrate, that results can be quite different, depending on the detection system used. The use of a diode array system enables the taking of spectra as an additional identification tool. This can help to identify for example remaining monomers (figure 1).

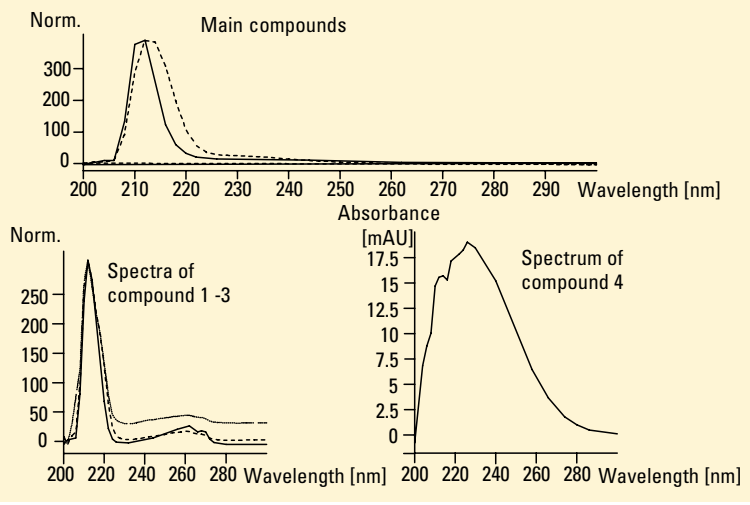

Figure 1
Spectra of oligomers and monomers

Method Performance

In figure 2 the different signal traces of UV-DAD and refractive index detection are shown. It can be seen that the calculated MW data differ significantly. In addition to MW data like Mw and Mn, GPC evaluation software also calculates molecular weight distribution curves (MWD),

which offer information about the relation between for example height percentage and log molecular weight or cumulative height percentage versus log molecular weight. (figure 3).

Method performance

Precision of weight: average molecular weight (rsd of Mw) = < 1 %
Precision of number weight average: molecular weight (rsd of Mn) = < 2 %

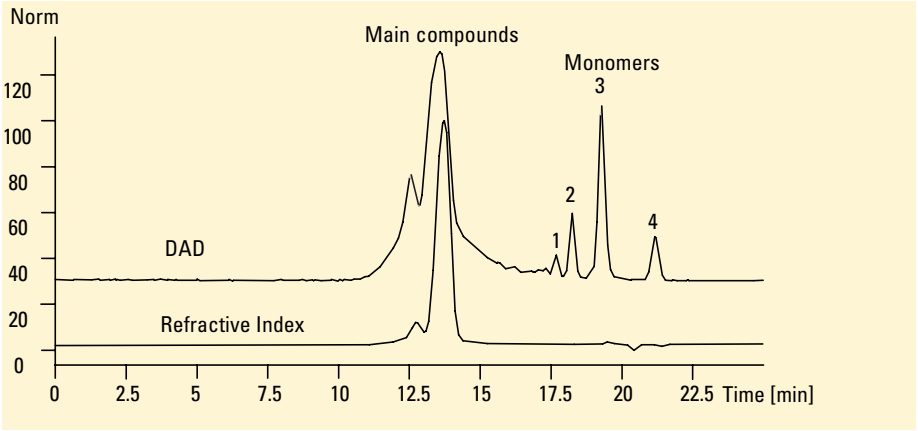

Figure 2
Analysis of polybutadiene using UV and refractive index

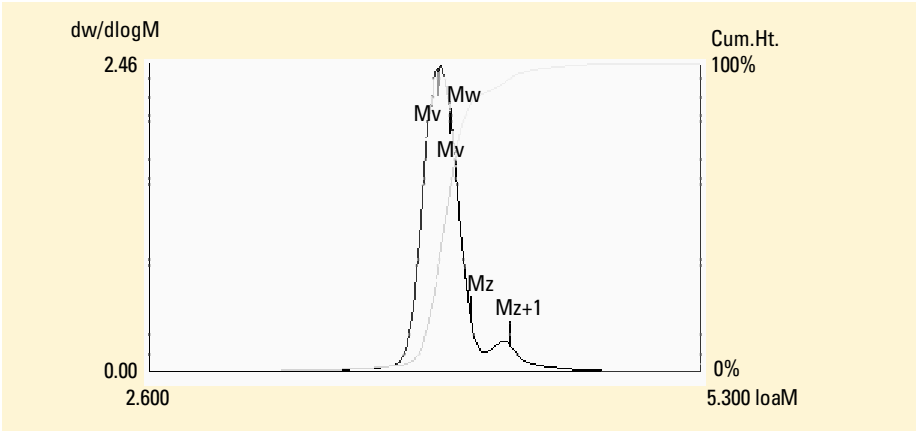

Figure 3
Molecular weight data based on refractive index detection

MW data	Refractive index	UV Detection
Mp	10283	10000
Mn	10543	6567
Mw	12054	13565
Polydispersity	1.143	2.066
Mz	14804	22037
Mz + 1	21860	35784
Mv	11780	12579

Table 1
Molecular weight data refactive index versus UV detection

Conditions

Column 2 × PLgel mixed-D, 7.5 × 300 mm, 5 µm
Mobile phase
Tetrahydrofurane (THF)
Flow rate 1 ml/min
Oven Temp 20 °C
Injection vol 20 µl
UV detector DAD 254/100 nm, reference 360/100 nm
Refractive index detector
Sample preparation
33 mg sample dissolved in 1 ml THF; Polystyrene standards from PSS were used for narrow standard calibration

Equipment

Agilent1100 Series:
- isocratic pump
- degasser (recommended)
- autosampler
- thermostatted column compartment
- diode array detector and/or HP 1047A refractive index detector

Agilent ChemStation + software + polymer labs GPC software

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