GPC/SEC of Compositionally Complex Natural Polymers with Agilent PLgel MIXED Columns

Application Note

Materials Testing & Research

Author

Graham Cleaver

Agilent Technologies, Inc.

Introduction

Many synthetic polymers used in applications such as packaging and construction are well-understood, consisting of homopolymers or co-polymers of chemically simple monomers. Analysis of these materials by gel permeation chromatography (GPC) yields useful molecular weight distributional information that can be used to predict the physical properties of the material and, therefore, end-use application. In contrast, many naturally occurring polymeric materials are chemically complex and even today are poorly understood. Nevertheless, many of these materials have important and wide ranging usage in the modern world, and analysis by GPC forms an integral part of investigations in the end-use suitability of such materials in key applications.

This application note describes the analysis of a series of rosins or colophonic resins and bitumens. Both materials are used in a wide range of applications that rely on their physical properties, and so GPC plays a key role in the assessment of these materials for end use.

Rosin resins are produced by the evaporative removal of low molecular weight terpene components from the resin of certain coniferous trees such as the Scotch Pine. Typically a solid material ranging in color from yellow to black, rosin consists of complex mixtures of aromatic resin acids such as abietic acid. Applications of the material include use as varnishes, adhesives, soap, as a friction increasing agent for players of stringed instruments, as a pill coating in the pharmaceutical industry, and as an ingredient in chewing gum. Molecular weight analysis can be used to characterize the source of the resin used in the manufacture of the rosin, and to indicate the toughness and melting point of the material.

Bitumens (often referred to as asphalts) are complex polyaromatic materials. Black, sticky, and viscous, bitumens are present in nearly all crude petroleum deposits. They are very complex materials, and their exact composition is still the source of debate. Despite the lack of clear understanding of their nature, bitumens find extremely wide usage as binders of aggregate used in road surfaces (asphalt concrete), and as water-proof sealing for flat roofs. Molecular weight distribution is one of the properties that can be used to distinguish bitumen from different sources and the melt properties of the material.

Colophonic Resin

The aim of this experiment was to determine the suitability of Agilent PLgel 10 µm MIXED-B columns for analysis of rosin resin.

Materials and methods

A sample of colophonic resin was prepared as nominally 0.2% (w/v) solution. The system was calibrated with narrow Agilent EasiCal PS-1 polystyrene standards and, therefore, all molecular weight values quoted were relative to polystyrene. Toluene was added to act as a flow-rate marker.

Conditions

Column(s):	3 × Agilent PLgel MIXED-B, 7.5 × 300 mm, 10 µm (p/n PL1110-6100)
Calibrants:	Agilent EasiCal PS-1 (polystyrene)
Eluent:	THF (stabilized)
Injection volume:	100 µL
Flow rate:	1.0 mL/min
Flow rate marker:	Toluene
Temperature:	Ambient
Pressure:	4.0 MPa
Sample concentration:	0.2% (w/v)
Detector:	Refractive index

Results and discussion

The column set was calibrated with polystyrene standards prepared at 0.25% (w/v). Calibration data are shown in Figure 1.

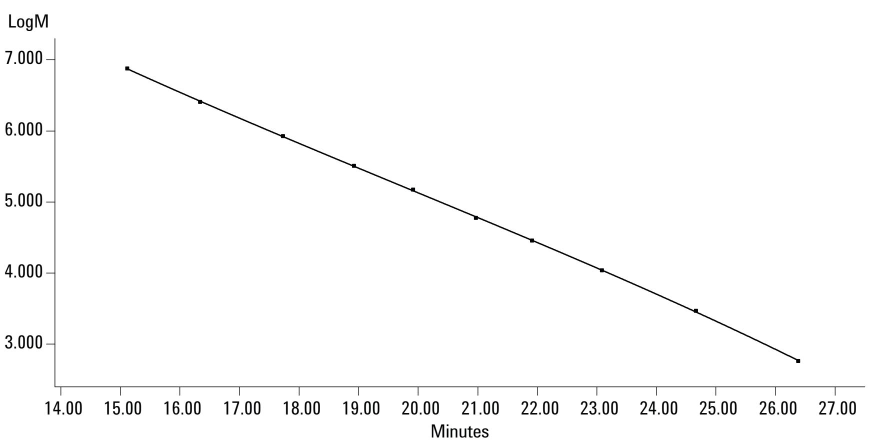

Figure 1. Calibrating an Agilent PLgel 10 µm MIXED-B column using Agilent EasiCal PS-1 standards.

Similar elution profiles were obtained for all 7 injections, with the toluene eluting as a tall sharp peak. The molecular weight distribution plots and calculated molecular weight averages of one of the repeat injections are illustrated in Figure 2 and Table 1.

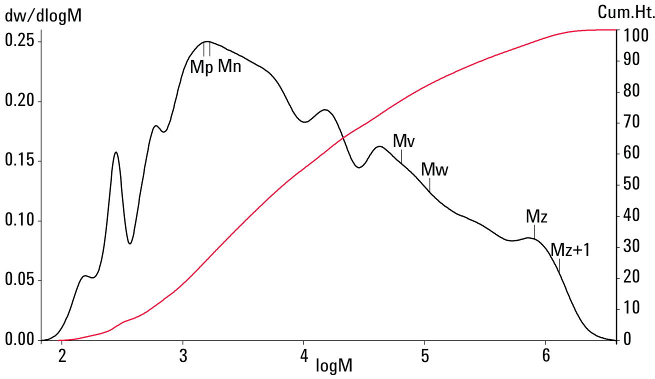

Figure 2. Molecular weight averages calculated for the first injection of rosin.

Table 1. Molecular weight characteristics of the first injection of rosin.

Mz+1	1,292,797
Mz	809,462
Mw	109,480
Mp	1477
Mn	1656
Polydispersity	66.104
Peak area	108,235

Several repeat injections were performed and typical overlaid raw data chromatograms are shown in Figure 3.

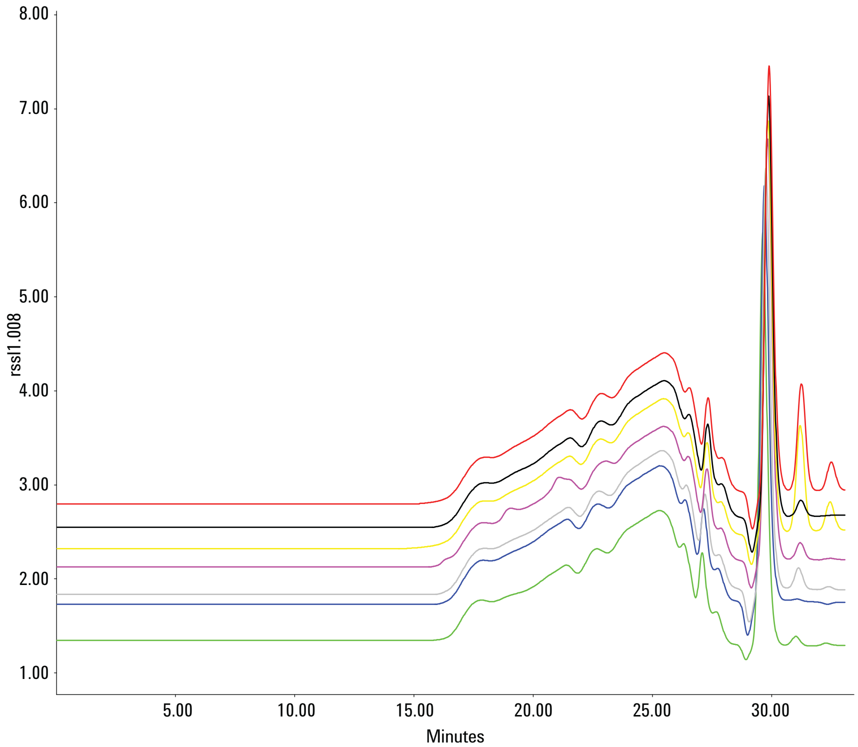

Figure 3. Raw data chromatogram of repeat injections of a colophonic resin on a 3 column set of Agilent PLgel MIXED-B 10-µm columns.

The molecular weight data for 7 injections are shown in Figure 3 and in tabular form in Table 2, and good run-to-run reproducibility was observed. From the experimental evidence, it could be seen that the MIXED-B column set provided excellent run-to-run reproducibility for the sample and good resolution of the marker peak.

Table 2. Molecular weight characteristics from 7 injections of rosin.

Sample	Mp	Mn	Mw	Mz	Mz+1	Mv	Dispersity
1	1477	1656	109480	809462	1292797	64171	66.104
2	1604	1736	110996	787832	1248795	66012	63.926
3	1499	1704	117614	852021	1384709	69528	68.983
4	1528	1725	123933	957860	1615801	72580	71.828
5	1528	1701	118522	896714	1476650	69480	69.675
6	1545	1724	114346	849285	1363886	67244	66.299
7	1518	1706	115178	868146	1419423	67692	67.489

Bitumen

In this example, we investigate differences between 3 batches of asphalt from different sources, one of which behaved unusually when melted, with poor flow.

Materials and methods

The bitumen samples were prepared as nominally 0.2% (w/v) solutions. They were filtered through a 0.45 µm membrane prior to injection. The system was calibrated with Agilent EasiCal PS-1 narrow polystyrene standards and, therefore, polystyrene-equivalent molecular weight data are quoted.

Conditions

Column(s):	2 x Agilent PLgel MIXED-D, 7.5 × 300 mm, 5 µm (p/n PL1110-6504)
Calibrants:	Agilent EasiCal PS-1 (polystyrene)
Eluent:	THF (stabilized)
Injection volume:	100 µL
Flow rate:	1.0 mL/min
Flow rate marker:	None
Temperature:	Ambient
Pressure:	6.4 MPa
Sample concentration:	0.2% (w/v)
Detector:	Refractive index

Results and discussion

The calibration data are shown in Figure 4.

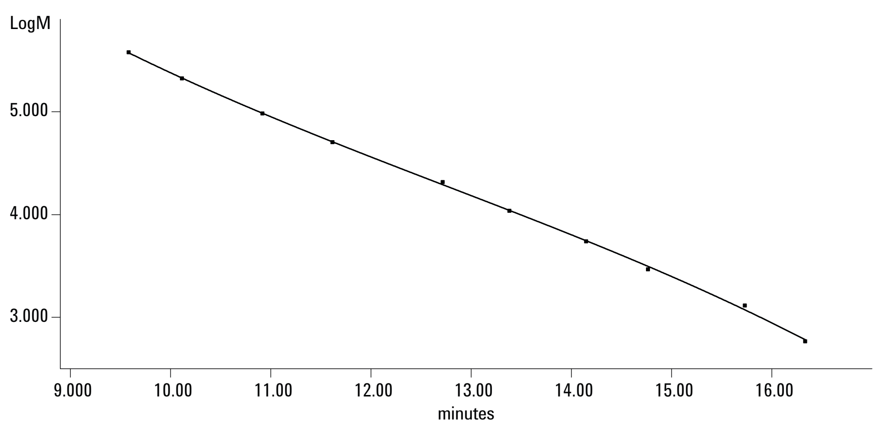

Figure 4. Calibrating an Agilent PLgel MIXED-D 5-µm column using Agilent EasiCal PS-1 standards.

Overlaid raw data chromatograms for the 3 samples are presented in Figure 5. Samples B and C contain one main peak with a high molecular weight shoulder. In addition, Sample A contains a high molecular weight polymer peak. The peaks eluting after 18 minutes are system peaks due to solvent imbalances.

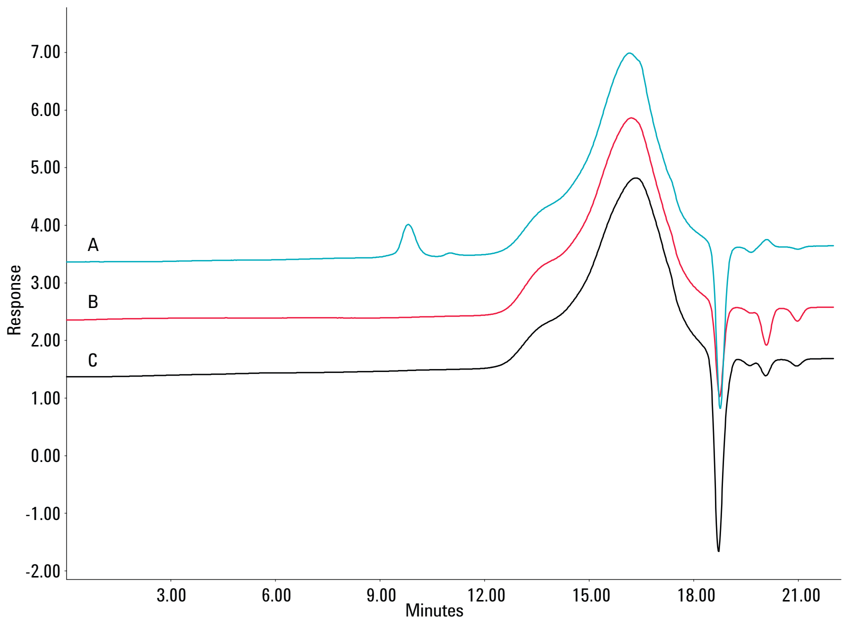

Figure 5. Raw data chromatogram of repeat injections of bitumen on a 2-column set of Agilent PLgel MIXED-D 5-µm columns.

As an example, molecular weight distributions and calculated molecular weight averages for Sample C are illustrated in Figure 6 and Table 3.

It is clear from the chromatograms that Sample A contained a small amount of very high molecular weight material, which will significantly alter the melt flow characteristics of the bitumen. This material is the source of the melt flow differences observed between the samples.

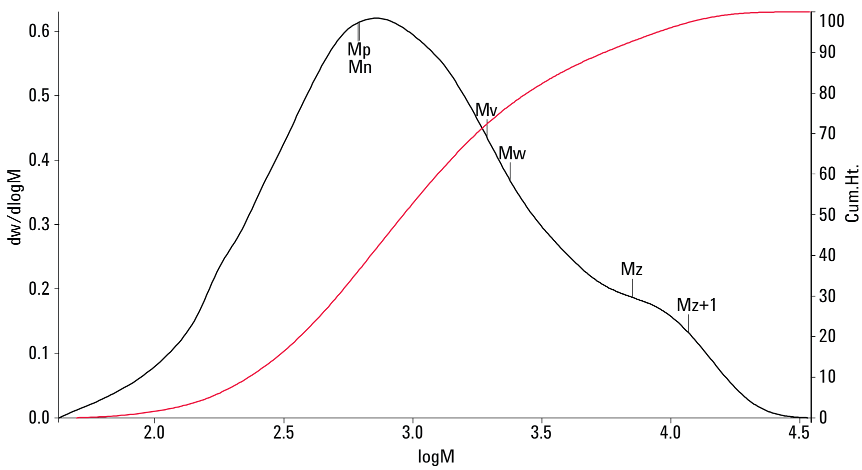

Figure 6. Molecular weight averages calculated for bitumen Sample C.

Table 3. Molecular weight characteristics of bitumen Sample C.

Mz+1	11,666
Mz	7,066
Mw	2,375
Mp	616
Mn	610
Polydispersity	3.893
Peak area	95,255

Conclusions

The chemical composition of rosin and bitumen is not completely understood. An illustration of their complex nature can be seen in this work, particularly in the rosin resin, where a multimodal distribution is observed by GPC as opposed to the Gaussian peak shapes seen for most synthetic materials. Both materials are analytically challenging as unwanted interactions between the components of the materials and the packing material cannot be ruled out, but in each case, gel permeation chromatography can be used to derive information regarding physical properties, such as melt flow and rigidity, that are important for their end-use application.

For More Information

These data represent typical results. For more information on our products and services, visit our Web site at www.agilent.com/chem.

Printed in the USA
April 30, 2015
5991-0518EN

Agilent Technologies