Analysis of elastomers by GPC/SEC

Application compendium

Authors

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Agilent Technologies, Inc.

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Contents Page

Polymer Laboratories was formed in 1976 to offer high quality columns, standards, instruments, and software for GPC/SEC. For over 30 years the company developed many market-leading products, including PLgel, PL aquagel-OH, PlusPore, PLgel Olexis, PolarGel columns, and EasiVial standards. Built on advanced in-house manufacturing technology, PL's products have the highest reputation for quality and performance, backed up by world-class technical and applications support.

With the acquisition of PL, Agilent offers an even wider range of GPC/SEC solutions for all types of polymer characterization of synthetic and bio-molecular polymers, with options for conventional GPC all the way up to complex determinations using multi-column and multi-detection methods.

Introduction

Elastomer is a general term used to describe rubbers – polymers that exhibit elasticity. Elasticity is the ability to deform under external stress but return to the original form after removal of the stress. Elastomers may be thermosets that require curing, or thermoplastics that contain both plastic and elastomeric species, and may be natural or synthetic in origin. Thermosetting elastomers are composed of polymeric chains joined by crosslinks, formed by curing reactions such as the vulcanization of natural rubber, creating a loose lattice structure. This allows chains to move relative to one another during deformation but return to their original positions when relaxed, allowing the material to reversibly extend. Without the crosslinkages the applied stress results in a permanent deformation. Thermoplastic elastomers contain plastic and elastomeric regions within the structure, with weaker non-covalent interactions between chains providing the anchor points, allowing the material to return to its original form after removal of the external force.

Gel permeation chromatography (GPC, also known as size exclusion chromatography, SEC) is a well-known technique for assessing the molecular weight distribution of polymers such as rubber, a property that influences many of their physical characteristics as shown in Table 1. In general, increasing molecular weight leads to higher performance, while an increase in the width of the distribution (the polydispersity) leads to a loss of performance but an increase in the ease of processing.

This application compendium describes the analysis of pre-cure thermosetting and thermoplastic elastomers by GPC.

Agilent Technologies, Inc. produces the most extensive range of GPC columns, standards and instruments that are ideally suited to the analysis of synthetic and natural rubber.

Agilent's columns are rugged and reliable, making them ideal for applications that rely on extremely reproducible analysis, such as in quality control environments. With extensive options in particle and pore size, you can select the column to match the molecular weight of the material under investigation, thereby ensuring you get the best quality data from your analysis. To complement our columns we also manufacture narrow polydispersity standards with very highly characterized molecular weights that are used as calibrants in the GPC analysis of rubber polymers.

The quality of our columns and standards is matched by an array of Agilent GPC instruments that cover the widest possible temperature range, from ambient to 220 °C.

These instruments perform all types of GPC/SEC experiments and can be used to analyze the complete range of polymer materials. Multiple detection options may be included in the instruments, such as light scattering and viscometry, or supplied in stand-alone formats, such as the Agilent evaporative light scattering range. Dedicated analysis software allows the biodegradation properties of the materials to be monitored.

The Agilent PL-GPC 50 Integrated GPC/SEC System

GPC/SEC analysis of natural rubbers

The first commercial elastomeric material was natural rubber, derived from the sap of the rubber tree **Hevea brasiliensis**. This substance is composed of a polymer of isoprene, most often cis-1,4-polyisoprene, although some natural rubber sources are composed of trans-1,4-polyisoprene. In the natural unrefined form, isoprene materials are accompanied by small amounts of proteins, fatty acids, resins and inorganic materials. Natural rubber is an elastomer and a thermoplastic. However, reacting the material with sulfur crosslinks the isoprene chains (a process known as vulcanizing), turns the polymer into a thermosetting material. Analysis of a natural rubber by GPC is always of the non-crosslinked, thermoplastic material.

Table 1. Effects of molecular weight distribution on the properties of elastomers

	Strength	Toughness	Brittleness	Melt Viscosity	Chemical Resistance	Solubility
Increasing Mw	+	+	+	+	+	-
Decreasing distribution	+	+	-	+	+	+

High sensitivity analysis of natural rubber with evaporative light scattering detection

Solutions of natural rubber are generally very difficult to prepare for GPC due to the fact that the polymer contains relatively high levels of 'gel' that are partially crosslinked. Normally, an aliquot of the eluent is added to the weighed sample. This is allowed to swell and dissolve overnight, and then the gel material is filtered out (0.5 µm) prior to GPC analysis.

In this case, the actual polymer concentration can be significantly lower than the original concentration prepared, depending on the gel content of the sample, and therefore detector response, usually RI, tends to be quite poor. The Agilent 380-ELSD evaporative light scattering detector exhibits significantly increased sensitivity compared to an RI and gives much greater response for this application. In addition, RI baseline drift, which commonly occurs, is very much emphasized when the actual peak response is so small. The 380-ELSD always gives a flat baseline which, together with the improved response, makes baseline and peak setting much more reliable for GPC calculations.

RI is also sensitive to system peaks around total permeation that usually occur even when samples are prepared in an aliquot of the eluent. These system peaks can interfere with low molecular weight components that are commonly found in natural rubber samples. With the 380-ELSD, system peaks are eliminated due to evaporation, leaving unadulterated sample peaks in the additives region.

The Agilent PLgel 10 µm MIXED-B columns, with their high efficiency (>35,000 plates/meter) and broad resolving molecular weight range (up to 10,000,000 daltons relative to polystyrene), are the columns of choice for high molecular weight polymers and demanding eluents. Separation of natural rubber reveals that the combination of PLgel MIXED-B columns with the 380-ELSD comprises a highly sensitive system for the discrimination of additives (Figure 1).

Columns: 3 x PLgel 10 µm MIXED-B, 300 x 7.5 mm
Eluent: Toluene
Flow Rate: 1.0 mL/min
Detection: 380-ELSD

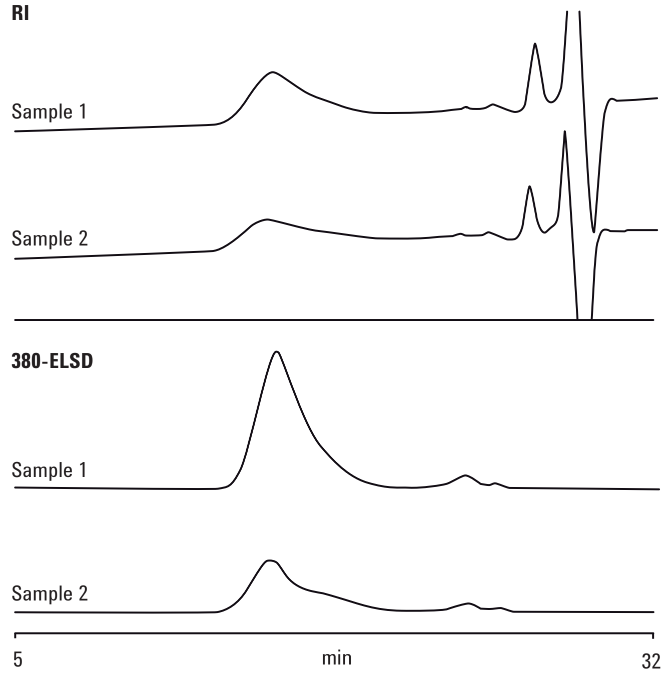


Figure 1. *Stable baseline and no interference from system peaks using the 380-ELSD evaporative light scattering detector (below) compared to RI detection (above) illustrating the advantages of ELSD in this application*

Figure 2 is a magnified view of the additive area revealing the unadulterated peaks in this region of interest.

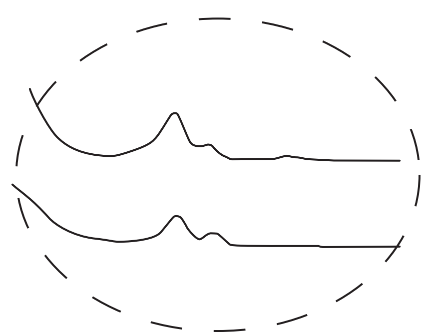


Figure 2. *Magnified view of the 380-ELSD plots showing the additive region - this region is masked with DRI detection, and so ELSD is a better detector for this application*

Analysis of natural rubber with triple detection

Triple detection GPC employs a concentration detector, a viscometer and a light scattering detector to assess the molecular weight distribution and molecular structure of polymers without having to rely on column calibrations. This can be important when analyzing complex materials for which no structurally similar standards are available.

Two samples of natural rubber were analyzed by GPC with triple detection. The objective was to determine why one of the materials had failed in end use. An integrated GPC system was used for the analysis.

The samples were analyzed using an Agilent PL-GPC 50 Integrated GPC/SEC System with differential refractive index detector, an Agilent PL-BV 400RT Online Integrated Viscometer, an Agilent PL-RTLS 15/90 Light Scattering Detector, and Agilent PLgel 10 µm MIXED-B columns. These columns provide high resolution of polymers that have high molecular weights, even in demanding eluents.

Figure 3 is a chromatogram of a natural rubber sample showing responses from the different detectors.

Samples:	2 x Natural rubber
Columns:	3 x PLgel 10 µm MIXED-B, 300 x 7.5 mm
Eluent:	Toluene
Injection Volume:	200 µL
Flow Rate:	1.0 mL/min
Temperature:	50 °C
Detection:	PL-GPC 50 with PL-BV 400RT Viscometer and PL-RTLS 15/90 light scattering detector

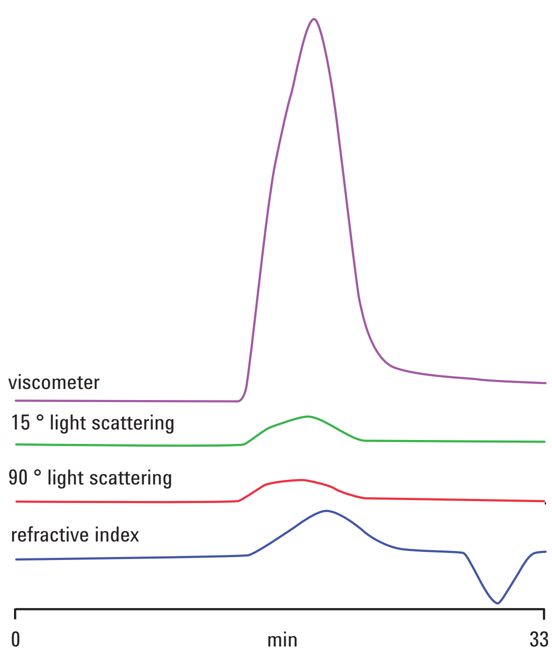


Figure 3. *Raw triple detection data for a natural rubber showing typical peak shapes observed for these materials*

Figure 4 indicates that one of the samples is considerably higher in molecular weight than the other, although the Mark-Houwink plots show that the two materials are structurally similar (Figure 5).

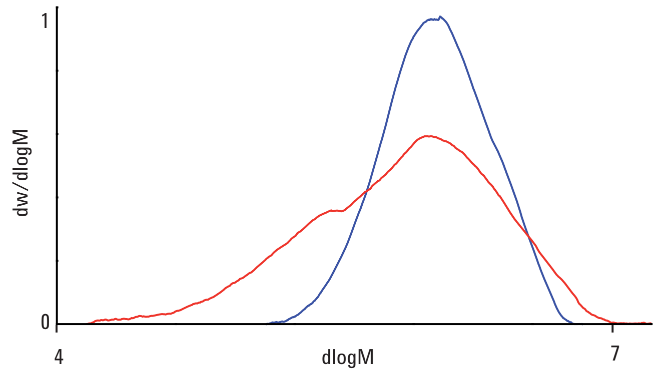


Figure 4. *Overlaid triple detection molecular weight distributions of two natural rubbers with very different distributions and therefore very different final properties*

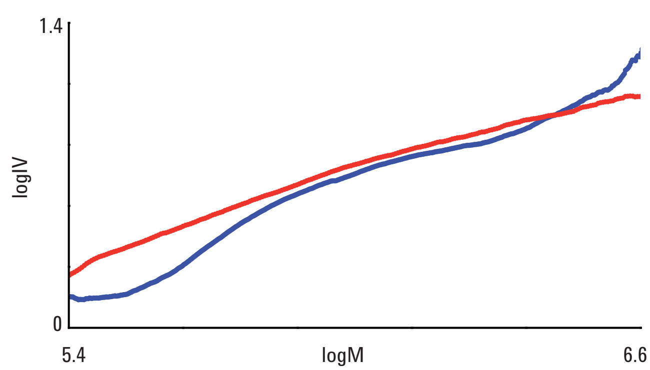


Figure 5. *Overlaid Mark-Houwink plots for two natural rubbers showing the similarity in structure of the materials, with deviation only at low molecular weight*

GPC/SEC analysis of synthetic rubbers

Analysis of synthetic polybutadiene with triple detection

Polybutadiene was one of the first types of synthetic elastomer to be invented and has largely replaced natural rubber in a wide variety of industrial applications.

Two Agilent PLgel 5 µm MIXED-C columns were used for this analysis with the results shown in Figures 6 and 7. The polybutadiene sample was prepared accurately at a nominal concentration of 2 mg/mL in tetrahydrofuran and injected into the system without further treatment. For the purpose of light scattering calculations, an average dn/dc was used for the sample.

Mark-Houwink (log intrinsic viscosity versus log M) plots (Figure 8) were generated from the viscometry and light scattering data. The curvature in the Mark-Houwink plot may be a result of structural changes in the polymer as a function of molecular weight.

Sample:	Polybutadiene
Columns:	2 x PLgel 5 µm MIXED-C, 300 x 7.5 mm
Eluent:	THF
Injection Volume:	100 µL
Flow Rate:	1.0 mL/min
Detection:	PL-GPC 50 with PL-BV 400RT and PL-RTLS 15/90

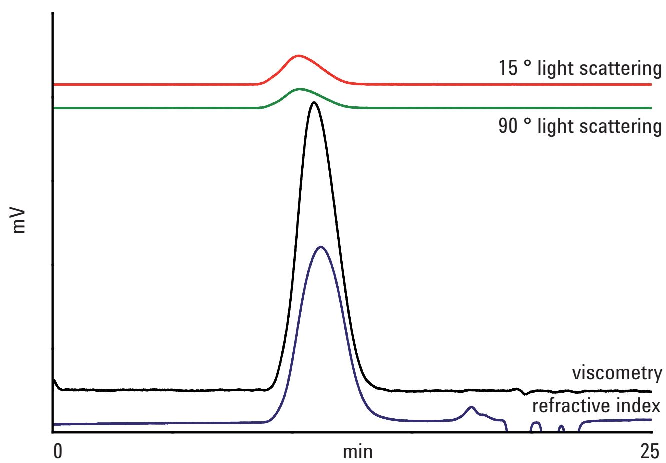


Figure 6. *Triple detection of a polybutadiene showing typical data for this type of sample*

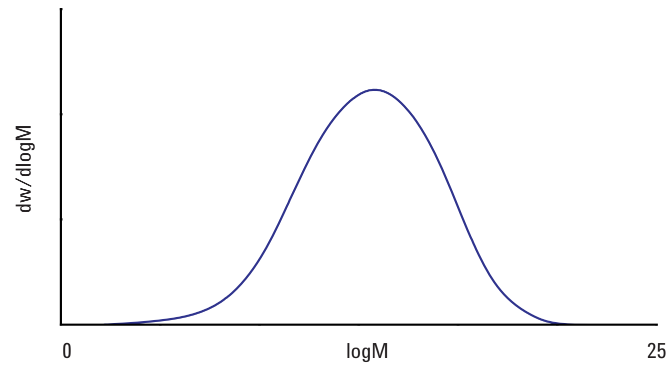


Figure 7. *Molecular weight distribution of a polybutadiene with a broad gaussian peak shape*

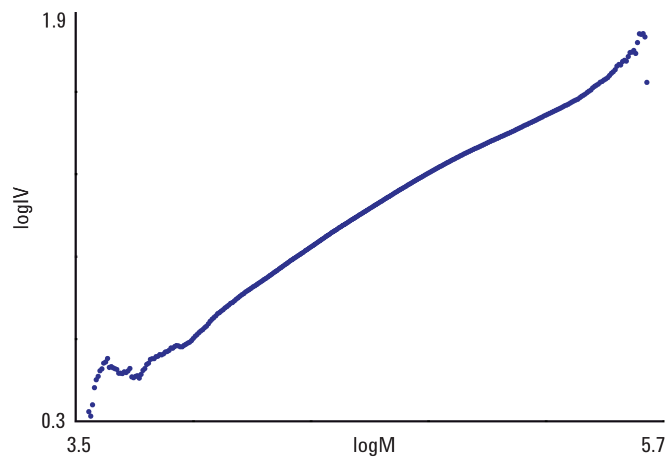


Figure 8. *Mark-Houwink plot of a polybutadiene with curvature that may be attributed to structural changes as a function of molecular weight*

General synthetic elastomer analysis

Polyisoprene can be produced synthetically. Together with polybutadiene and styrene butadiene, it is a common elastomeric material. Polybutadiene is a synthetic rubber manufactured from the monomer 1,3-butadiene. With high wear resistance, it is commonly used in tire manufacture, and to coat electronic assemblies due to its extremely high electrical resistivity. Polybutadiene exhibits 80% recovery after stress, one of the highest stress-recovery values of a synthetic material.

Styrene butadiene rubber (SBR) is a synthetic rubber copolymer of styrene and butadiene. With good abrasion resistance it is widely used in car tires, after blending with natural rubber.

The extended operating range of the PLgel 10 µm MIXED-B column (up to 10,000,000 MW) makes it ideally suited to the analysis of a wide range of high molecular weight elastomers (Figure 9). Sample solutions are routinely filtered prior to injection to remove insoluble "gel fractions", common to most elastomers.

Columns:	3 x PLgel 10 µm MIXED-B, 300 x 7.5 mm
Eluent:	THF
Flow Rate:	1.0 mL/min
Loading:	0.2% w/v, 100 µL
Temperature:	40 °C
Injection Volume:	200 µL
Detection:	Agilent PL-GPC 220

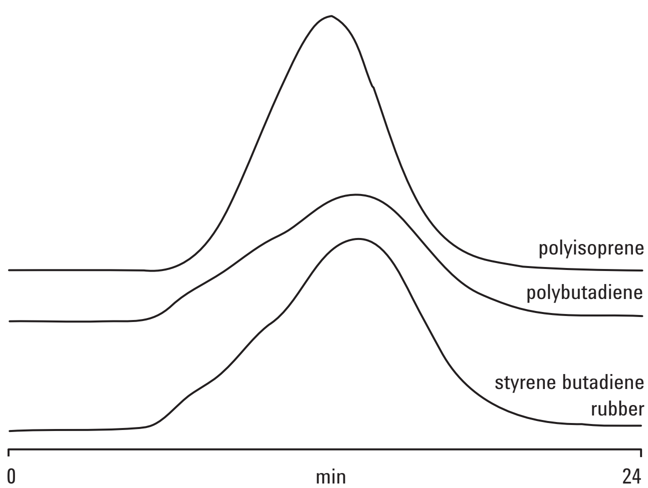


Figure 9. *Chromatograms of three types of synthetic rubber with multimodal peak shapes*

Hexane is a good solvent for butyl rubber although it can be chromatographed using other solvents, such as THF. The polarity of hexane is very low compared with more traditional solvents for GPC such as THF. However, it can be used successfully with PLgel columns (Figure 10).

Columns:	3 x PLgel 10 µm MIXED-B, 300 x 7.5 mm
Eluent:	Hexane
Flow Rate:	1.0 mL/min
Detection:	PL-GPC 50

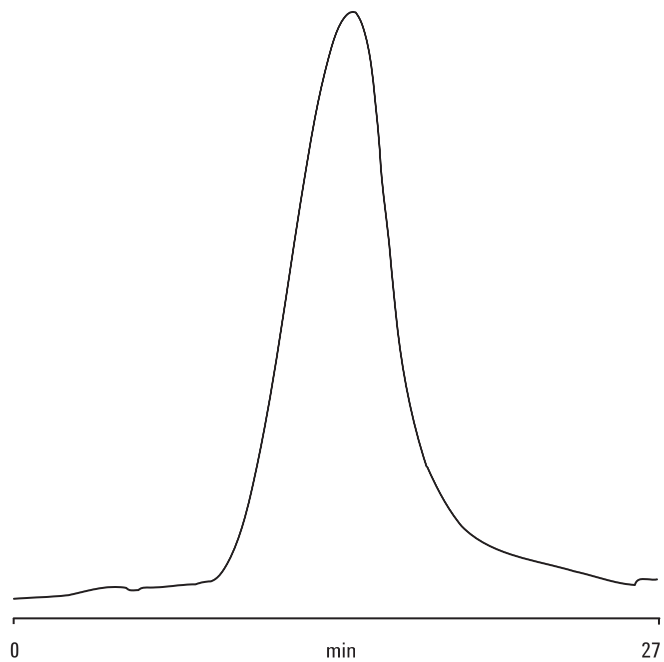


Figure 10. *Butyl rubber chromatogram in hexane showing that a good peak shape can be obtained*

Commercial grades of styrene butadiene rubber can contain very high molecular weight fractions and so, for successful GPC separations, the sample concentration must be minimized in order to avoid viscous streaming effects. Some grades of SBR can also contain low molecular weight mineral oil as a modifier (known as oil-extended grades) that can be resolved from the polymer peak, thus permitting quantification using Agilent ELSD (Figure 11).

Columns:	2 x PLgel 20 µm MiniMIX-A, 250 x 4.6 mm
Eluent:	THF
Flow Rate:	0.3 mL/min
Loading:	1 mg/mL, 100 µL
Detection:	380-ELSD (neb=45 °C, evap=90 °C, gas=0.7 SLM)

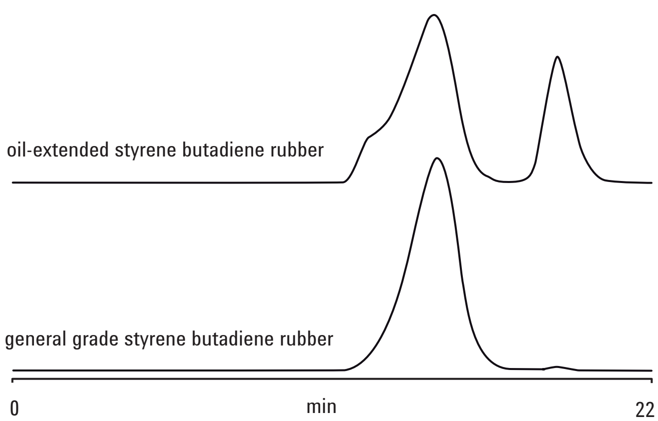


Figure 11. *Chromatograms of two styrene butadiene rubbers, one oil-extended, showing the presence of the low molecular weight additive*

The sample of oil-containing SBR, shown in Figure 12, was analyzed using refractive index detection. To ensure dissolution, the sample was warmed to 50 °C and gently stirred for three hours. Filtering using 0.5 µm filters is recommended to remove any gel fractions. The PLgel MIXED-B packing permits resolution of both polymer and oil peaks.

Columns:	2 x PLgel 10 µm MIXED-B, 300 x 7.5 mm
Eluent:	THF
Flow Rate:	1.0 mL/min
Injection Volume:	100 µL
Detection:	PL-GPC 50

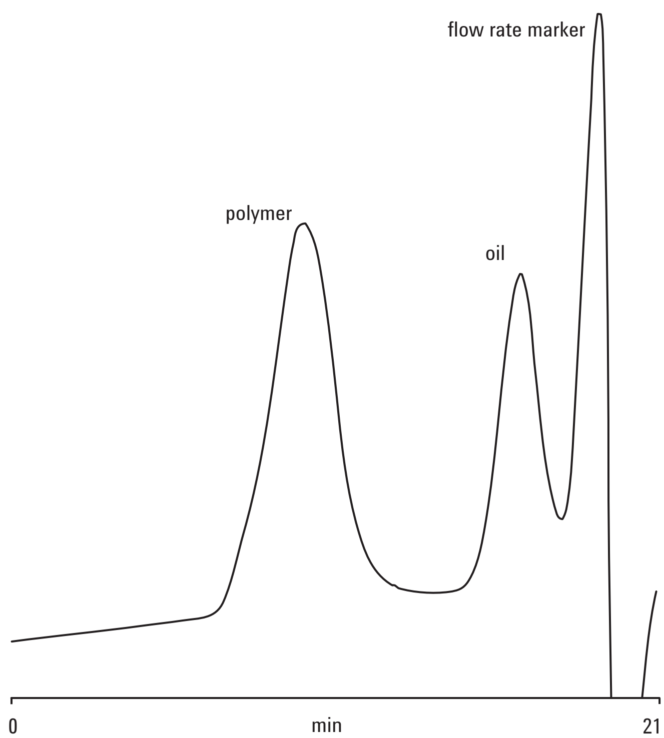


Figure 12. *Chromatogram of an oil-extended styrene butadiene rubber showing the presence of a low molecular weight oil additive*

Polydimethyl siloxane analysis using GPC/viscometry

Polydimethyl siloxane (PDMS) is a non-toxic, non-flammable silicon-based polymeric material noted for its unusual rheological behavior. Composed of polymer chains of formula $(CH_3)_3SiO[SiO(CH_3)_2]_nSi(CH_3)_3$, PDMS is a viscoelastic material which, with long flow times or at high temperatures behaves like a liquid, and with short flow times or at low temperatures behaves like a rubber. PDMS is produced in a range of grades from liquids through to rubbery semi-solids depending on the molecular weight of the constituent chains. It is a widely used material and can be found in applications such as silicone caulks, lubricants, damping fluids and heat transfer fluids, as well as in breast and knuckle implants. It is also a food additive (E900), used as an anti-foaming and anti-caking agent.

PDMS was analyzed by GPC using the PL-GPC 50 Integrated GPC/SEC System. Due to the importance of the viscometric properties of the material in many final applications, a PL-BV 400RT viscometer was included in the PL-GPC 50 as well as the standard refractive index detector. Results are shown in Figures 13 and 14. This combination of detectors also allows analysis of the material by the Universal Calibration method, giving accurate molecular weights that are not reliant on the chemistry of the standards used for calibration (in this case, polystyrene standards). Although PDMS is soluble in tetrahydrofuran, it is also isorefractive with this solvent and, therefore, THF is not suitable for the analysis and toluene is a more suitable solvent.

Columns:	2 x Agilent PolyPore, 300 x 7.5 mm
Eluent:	Toluene
Flow Rate:	1.0 mL/min
Injection Volume:	100 µL
Detection:	PL-GPC 50, PL-BV 400RT

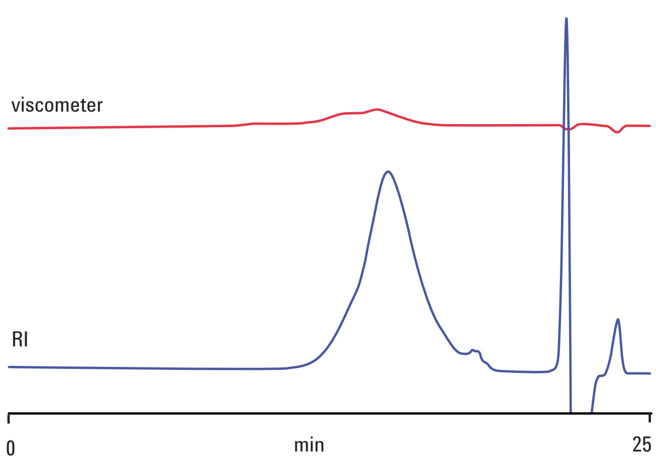


Figure 13. *Example overlaid refractive index and viscometer chromatograms for a sample of polydimethyl siloxane showing typical peak shapes*

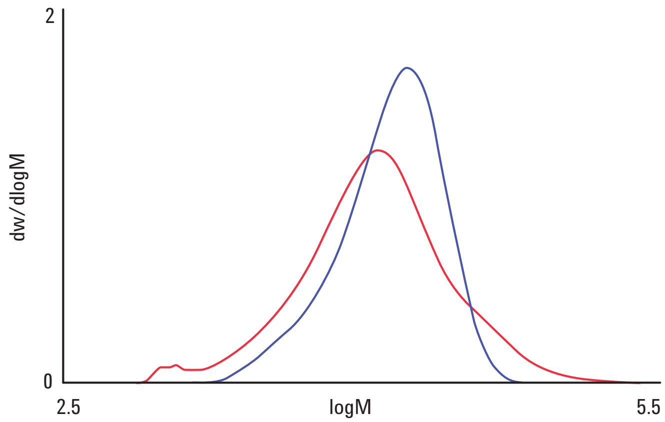


Figure 14. *Overlaid molecular weight distributions for two different grades of polydimethyl siloxane with different performance characteristics*

Although quite different in molecular weight, the Mark-Houwink plot (Figure 15) shows that the two materials are structurally very similar, indicating that their viscoelastic behavior as a function of molecular weight would be comparable.

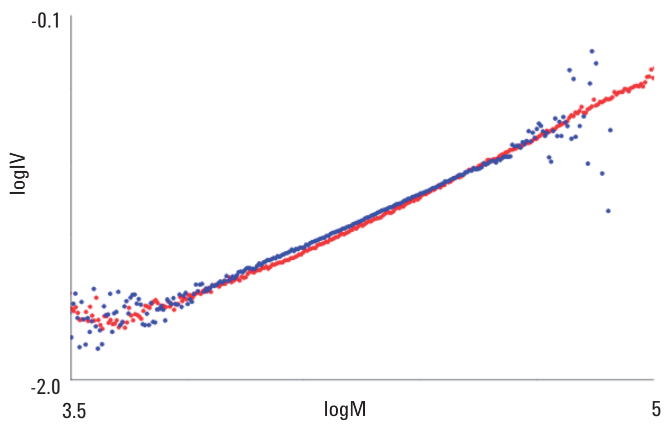


Figure 15. *Mark-Houwink plots calculated for two samples of polydimethyl siloxane show that the materials are structurally very similar*

Analysis of poly(styrene/butadiene) copolymers by conventional GPC

A poly(styrene/butadiene) block copolymer mimics many of the properties of natural rubber and has applications in a wide variety of industrial areas. Its characteristics are provided by the hard polystyrene chains being surrounded by a network of rubbery polybutadiene, which provides strength and flexibility over a large temperature range. The copolymer is a thermoplastic elastomer and therefore can be easily used in manufacturing by injection molding, or blended into an existing product to increase elasticity or impart toughness. The molecular weight distribution is critical, as any homopolymer will significantly affect the resultant end properties.

In the analysis described here distinct differences were observed arising from the presence of homopolymers along with the intended copolymer (Figures 16 and 17).

Columns:	2 x PLgel 5 µm MIXED-C, 300 x 7.5 mm
Calibration Standards:	Polystyrene EasiVial
Eluent:	THF (250 ppm BHT)
Temperature:	40 °C
Injection Volume:	100 µL
Detection:	PL-GPC 50

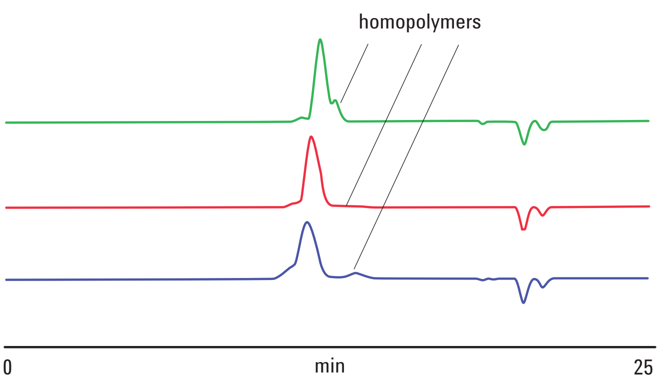


Figure 16. *Chromatograms for styrene butadiene rubbers showing the presence of homo- and copolymers*

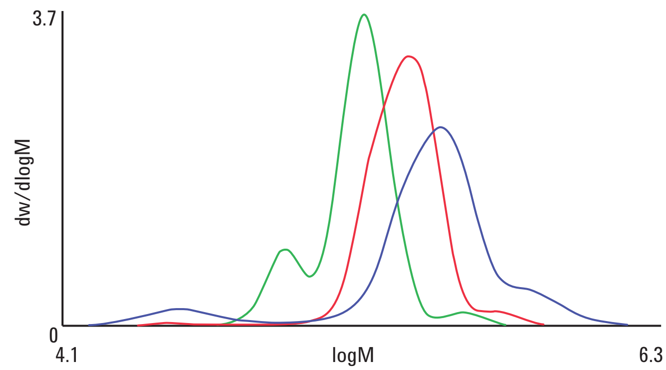


Figure 17. *Overlaid molecular weight distributions for the styrene butadiene rubber samples showing a clear change in molecular weight distribution between samples*

More Agilent solutions for the analysis of rubber

Although well-suited to the analysis of natural and synthetic rubber, GPC is not the only analytical technique available for the examination of these important materials. Agilent offers a range of instruments and consumables that can be used to test elastomers in environmental protection, recycling schemes, confirmation of equivalents, deformulation, quality control and failure analysis. Agilent instruments are particularly valuable for the detection of additives or modifiers, ubiquitous components found in most commercially useful rubbers.

NMR

Rubber NMR is a well-established subfield of Solids NMR. MAS (magic angle spinning) is used to improve shimming, and rubber spectra could be run in either a Solids MAS probe or a Nanoprobe. More advanced experiments that measure relaxation properties are employed to analyze dynamics and morphology, such as domain sizes, and the results have been used to explain the dielectric and mechanical properties of rubber. Agilent's 400, 500 or 600 MHz NMR systems are ideal for such tasks when equipped with accessories for solid state NMR.

Spectroscopy

Both the AA and ICP-OES techniques are suitable for determining the "filler" and trace levels of metals in compounded rubber products. For toys made from rubber materials, there are worldwide standards applicable that require the determination of a range of toxic elements.

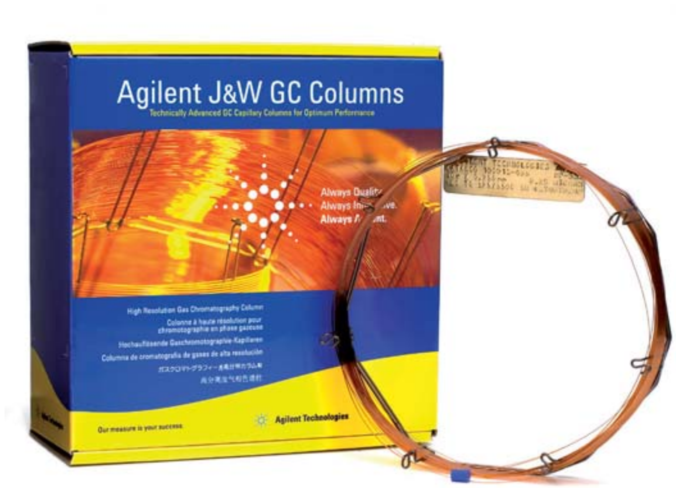
For example, the US Consumer Product Safety Improvement Act of 2008 (CPSIA), EN 71 Part 3 and AS/NZS ISO 8124.3:2003 standards define requirements for testing the migration of inorganic elements from toys and children's products. Agilent AA and ICP-OES instruments meet and exceed these testing requirements. Analysts may also use AA and ICP-OES for monitoring and evaluating the environmental impact of waste rubber products (especially used tires) in land fill sites, artificial reefs, or assessing trace element levels in fly ash from tire-derived fuel.

The Agilent 400-MR Magnetic Resonance Spectrometer is the system of choice for laboratories requiring a compact and easy-to-use instrument that delivers fast and reliable results day in and day out

GC

Toxic gases that are emitted during the processing and curing of rubber goods can be monitored using Agilent gas chromatography. The same technique helps ensure product safety when determining levels of plasticizers or nitrosamines in food rubbers, such as dummies for babies or teats for baby bottles. For the two ASTM rubber methods, we recommend Agilent J&W CP-PoraBOND Q GC columns to detect acrylonitrile in nitrile rubber.

The Agilent 7890A GC with 7693A Series Automatic Liquid Sampler



Agilent J&W offers the largest selection of the highest quality GC columns available today

FTIR

FTIR spectroscopy has a powerful ability to provide both chemical and structural information of a sample. Rapid, non-destructive, chemical identification is possible with easy-to-use Attenuated Total Reflectance (ATR) accessories. Agilent also provides thermally controlled accessories that enable users to investigate their elastomer sample under their desired environmental conditions. Or, if combined with thermogravimetric analysis (TGA), Agilent's hyphenated TGA/FTIR analyzer delivers real-time monitoring of gases evolved from rubber samples, and enables complex chemistries to be unravelled and understood. Our TGA/FTIR systems consist of an FTIR spectrometer and TGA/IR interface accessory with data interpretation performed using powerful Resolutions Pro software.

The Agilent 600 Series FTIR provides the highest level of sensitivity combined with detailed structural and compositional information for information-rich detection

Ordering information

Agilent offers robust instrumentation, application-based consumables, and customer-focused services, backed by our global team of product and applications experts, ready to help you solve your analytical challenges. Whether you're monitoring impurities in drinking water, designing new therapeutic drugs or developing cleaner fuels, our solutions deliver the sensitivity, flexibility and productivity your laboratory requires.

Columns

Description	Part No.
Agilent PLgel 5 µm MIXED-C, 300 x 7.5mm	PL1110-6500
Agilent PLgel 10 µm MIXED-B, 300 x 7.5 mm	PL1110-6100
Agilent PLgel 20 µm MiniMIX-A, 250 x 4.6 mm	PL1510-5300
Agilent PolyPore, 300 x 7.5 mm	PL1113-6500
Agilent EasiVial PS-H (2 mL)	PL2010-0201
Agilent EasiVial PS-H (4 mL)	PL2010-0200
Agilent EasiVial PS-L (2 mL)	PL2010-0401
Agilent EasiVial PS-L (4 mL)	PL2010-0400
Agilent EasiVial PS-M (2 mL)	PL2010-0301
Agilent EasiVial PS-M (4 mL	PL2010-0300
Agilent PS-H 2 mL Tri-Pack (90 Vials)	PL2010-0202
Agilent PS-H 4 mL Tri-Pack (90 Vials)	PL2010-0203
Agilent PS-L 2 mL Tri-Pack (90 Vials)	PL2010-0402
Agilent PS-L 4 mL Tri-Pack (90 Vials)	PL2010-0403
Agilent PS-M 2 mL Tri-Pack (90 Vials)	PL2010-0302
Agilent PS-M 2 mL Tri-Pack (90 Vials)	PL2010-0303

Standards

Description	Part No.
Agilent EasiVial PS-H (2 mL)	PL2010-0201
Agilent EasiVial PS-H (4 mL)	PL2010-0200
Agilent EasiVial PS-L (2 mL)	PL2010-0401
Agilent EasiVial PS-L (4 mL)	PL2010-0400
Agilent EasiVial PS-M (2 mL)	PL2010-0301
Agilent EasiVial PS-M (4 mL	PL2010-0300
Agilent PS-H 2 mL Tri-Pack (90 Vials)	PL2010-0202
Agilent PS-H 4 mL Tri-Pack (90 Vials)	PL2010-0203
Agilent PS-L 2 mL Tri-Pack (90 Vials)	PL2010-0402
Agilent PS-L 4 mL Tri-Pack (90 Vials)	PL2010-0403
Agilent PS-M 2 mL Tri-Pack (90 Vials)	PL2010-0302
Agilent PS-M 2 mL Tri-Pack (90 Vials)	PL2010-0303

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Instruments

Description	Part No.
Agilent PL-GPC 220 Integrated GPC/SEC System	PL0820-0000
Agilent PL-GPC 50 Integrated GPC/SEC System	PL0870-8500
Agilent PL-BV 400HT Online Integrated Viscometer	PL0810-3050
Agilent PL-BV 400RT Online Integrated Viscometer	PL0810-3060
Agilent PL-HTLS 15/90 Light Scattering Detector for PL-GPC 220	PL0640-1200
Agilent PL-RTLS 15/90 Light Scattering Detector for PL-GPC 50	PL0640-1210
Agilent 380-LC Evaporative Light Scattering Detector (110 V)	PL0890-0110
Agilent 380-LC Evaporative Light Scattering Detector (240 V)	PL0890-0240

Suggestions for further reading

Agilent has published application compendia on biodegradable polymers, engineering polymers, polyolefin analysis, and low molecular weight resins. In addition, we also offer a comprehensive and informative range of literature for all aspects of GPC/SEC, including application notes, datasheets and technical overviews.

Publication	Publication number
Introduction to GPC/SEC	5990-6969EN
GPC/SEC column selection guide	5990-6868EN
Biodegradable polymers	5990-6920EN
Engineering polymers	5990-6970EN
Polyolefin analysis	5990-6971EN
Low molecular weight resins	5990-6845EN

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