MATERIALS ANALYSIS

ADVANCED GPC ANALYSIS OF FLUOROELASTOMERS USING AN AGILENT 1260 MDS WITH RI AND VISCOMETRY DETECTION

Solutions for Your Analytical Business
Markets and Applications Programs

Authors
Ansuman Mahato & Dr. Samir Vyas
Agilent Technologies India
Alan Brookes
Agilent Technologies LDA UK Ltd

ABSTRACT

Fluoroelastomers are used in a wide variety of high-performance applications. Fluorinated synthetic rubbers show extraordinary levels of resistance to chemicals, oil and heat, while providing useful service life above 200°C. A wide range of molecular weights coupled with a high ratio of fluorine to hydrogen and the strength of the carbon-fluorine bond, provides premium, long-term reliability even in harsh environments.

INTRODUCTION

Fluoroelastomers are synthetic rubbers which have exceptional resistance to a broad spectrum of oils, gases, fluids, chemicals and elevated temperatures. Fluoroelastomers are synthesized through the polymerization of three monomers, Vinylidene fluoride, Hexafluoropropylene and Tetrafluoroethylene.

Here we show the use of advanced detection GPC to measure the accurate molecular weight of several polymers using the Universal Calibration method. Viscometry detection can also reveal many interesting properties such as branching, size and the shape of the polymer in solution.

Typically these polymers are used in the automobile and aerospace industry, for making safety seals, engine gaskets, cylinder liners, o-rings, valves, and tubing. However a more topical application sees a Fluoroelastomer adopted as the material of choice for the band of the Apple Watch Sport.

Why Advanced Detection is beneficial for the analysis of these fluoroelastomers

Conventional GPC with RI is a good tool for comparing the molecular weights of similar batches of the same material. However, when investigating materials that appear alike but behave differently, the use of advanced detectors such as a viscometer or a light scattering detector can be beneficial. In this example we show how the use of a viscometer can highlight high molecular weight differences between 2 samples. In a third sample it is possible to identify differences which are due to the presence of copolymer.

Agilent Technologies

Experimental	
Instrumentation	
Agilent 1260 Infinity Quaternary Pump	(G1311B)
Agilent 1260 Infinity High Performance Autosampler	(G1367E)
Agilent 1260 Infinity Thermostatted Column Compartment	(G1316A)
Agilent 1260 Infinity GPC/SEC Multi-Detector Suite	(G7800A)
MDS Viscometer Detector	(Option 032)
MDS Light Scattering Detector	(Option 033)
MDS Refractive Index Detector	(Option 031)

RT	PS Mw
11	6870000
11.60	3039000
13.10	508000
13.70	215000
13.77	184900
15.33	24600
16.03	10110
17.20	2590

Method for Analysis	
Detectors used	MDS VS, DRI
Mobile phase	THF
Columns	2x PLgel 10µm Mixed-B 7.5 x 300mm (PL1110-6100)
Standards	PS-H EasiVials (4ml) + PS-M EasiVials (4ml)
Temperature	40 ˚C (column and detector)
Injection volume	100 µL
Flow Rate	1.0 ml/min
Software	Agilent GPC/SEC software

Instrument/Detector/Column Calibration

The Instrument and Universal calibrations were generated with polystyrene standards. Points used are shown in the table opposite. Both calibrations exhibited a linear fit across the molecular weight range.

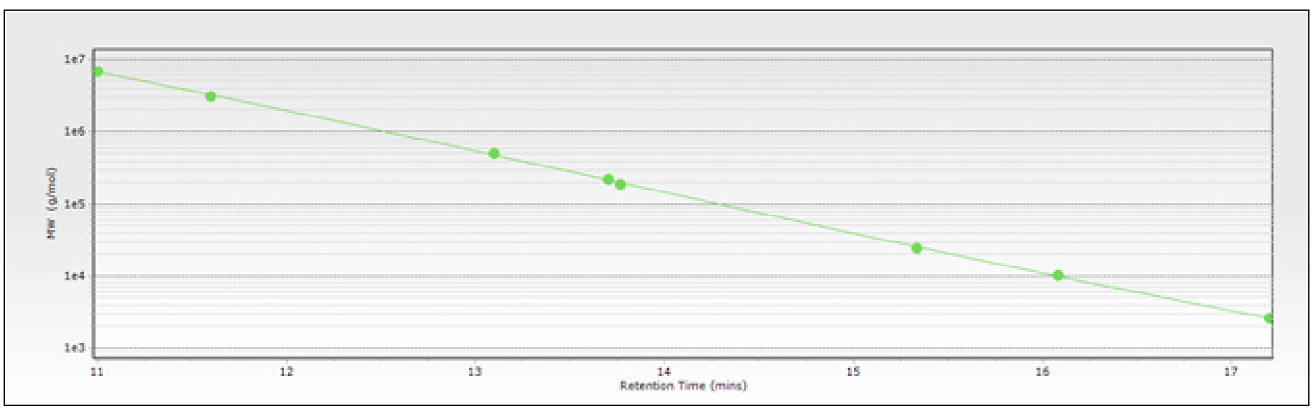

Figure 1: Conventional Calibration with Polystyrene

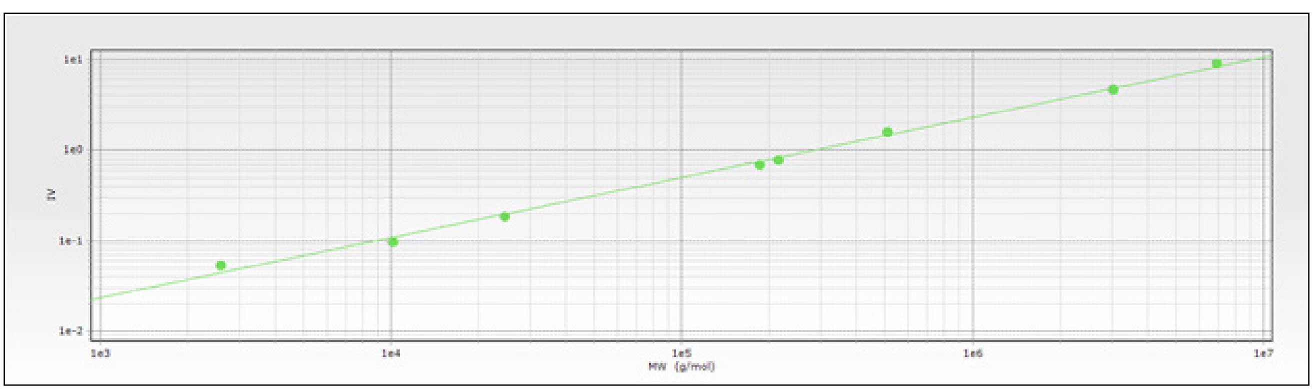

Figure 2: Universal Calibration with Polystyrene

SAMPLE ANALYSIS

Two different Fluoroelastomer polymers were analyzed which possess dissimilar properties when used in industrial applications. By conventional GPC (RI Detection) slight differences were observed in the molecular weight profile. The raw data chromatograms and overlaid molecular weight distributions of Samples A and B are shown below.

By viscometry detection the enhanced sensitivity to higher molecular weights show a considerable advantage. In Figure 4 using the same two samples overlaid, the differences between their higher molecular weight profiles becomes clear.

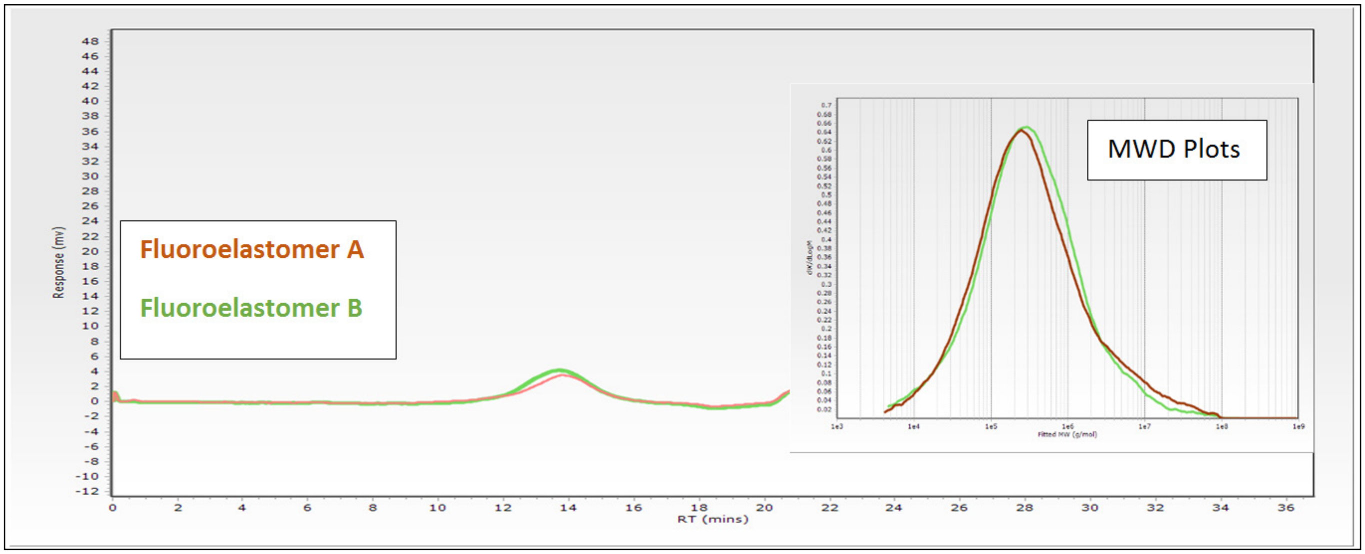

Figure 3: RI detector chromatograms of two fluoroelastomers, samples A and B

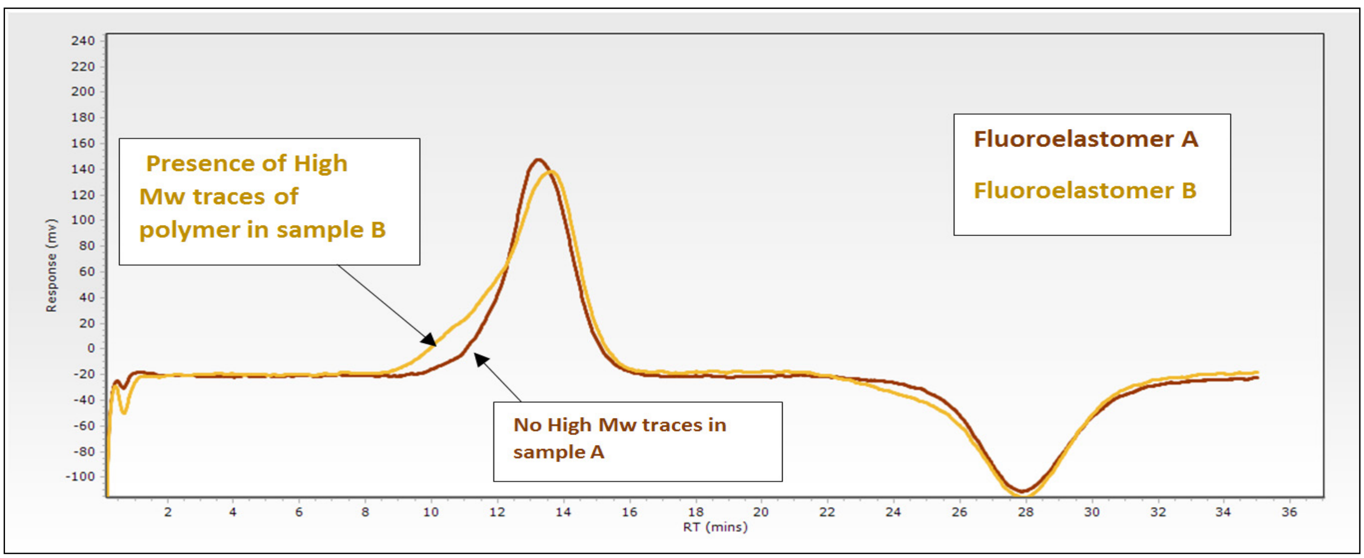

Figure 4: Viscometer Chromatograms of two fluoroelastomers, samples A and B

In a second experiment another type of Fluoroelastomer is analyzed which is produced with a lower molecular weight copolymer. Figures 5-6 shows the Fluoroelastomer Sample C chromatogram and this sample overlaid with Samples A and B. The lower molecular weight copolymer present in Sample C is clearly illustrated.

In Figures 7-8 we show the Mark Houwink(MH) plots for sample A and sample C individually. These plots can give us information about the polymer structure by investigating the position and slope. The presence of two different polymers in the copolymer sample C can be seen in the MH Plot as 2 different slopes.

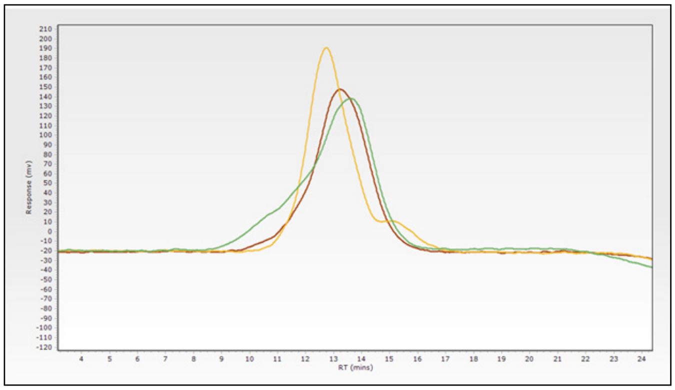

Figure 5: Viscometer overlay for three Fluoroelastomers

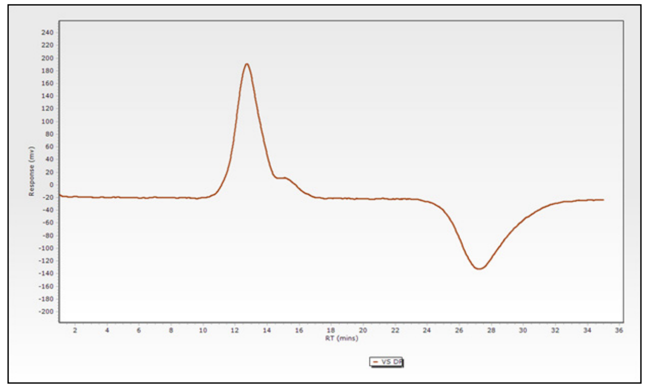

Figure 6: Viscometer signal for Sample C

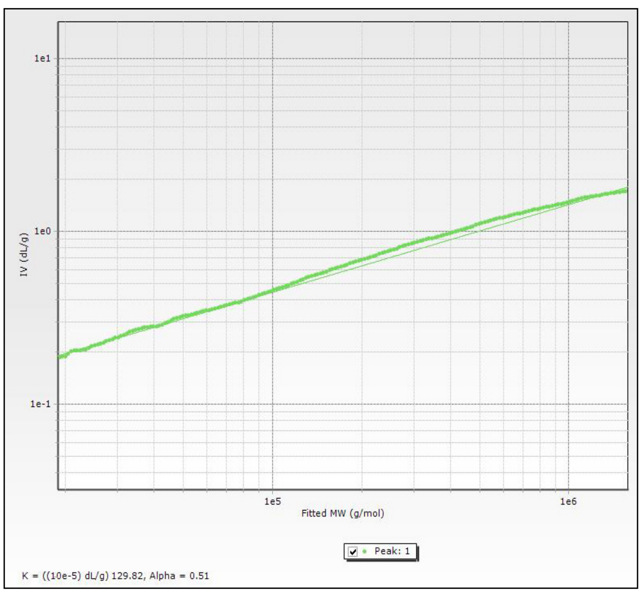

Figure 7: MH plot for Fluoroelastomer Sample A.

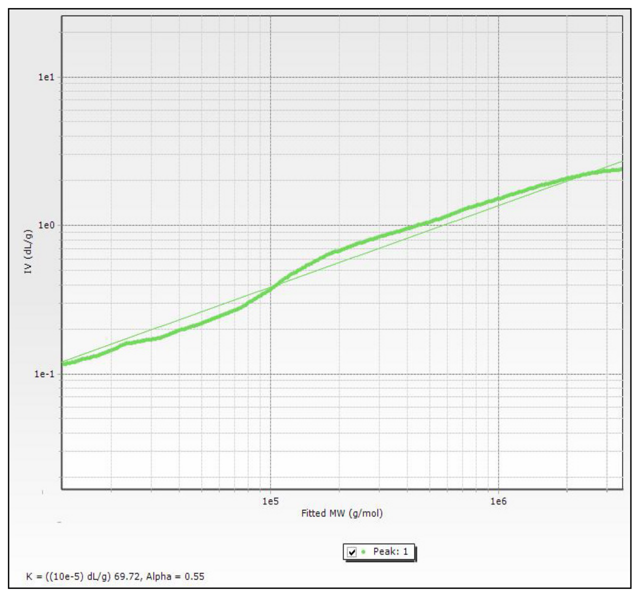

Figure 8: MH plot for Fluoroelastomer Sample C

Molecular weight averages for all Fluoroelastomer samples

Sample Name	Mp	Mn	Mw	PD
Fluoroelastomers A	294422	100439	1260094	12.55
Fluoroelastomers B	246526	100200	1649562	16.46
Fluoroelastomers C	38940	39818	822816	20.66

CONCLUSIONS

Using advanced detectors allows the improved characterization of polymers by GPC. In particular, the sensitivity of the viscometer to higher molecular weight material shows differences more effectively than RI alone, and also reveals structural information of the polymers and co-polymers. In addition, the Universal calibration generated by using a viscometer and RI provides accurate molecular weight information independent of the type of standards used.

Solutions for your analytical business
Markets & Applications Programs
www.solutions-to-win.com

Printed in EU, 2016-01-01
5991-6624EN

Agilent Technologies