NovaSheet

Technology: TF3-MALS/ELSD

Application: Gel Content of Poly(Butadiene-Acrylonitrile Methacrylic Acid)

Analysis Conditions / System Set-up

- Solvent	: THF	- Channel Thickness	: 127 µm
- Injection Volume	: 20 µL	- Channel Flow	: 0.2 mL/min
- Sample Concentr.	: 0.04 mg/mL	- Stop Flow	: 0
- Initial deltaT	: 15° C	- T1/ Ta	: 2 min.s/-4 min.s
- Initial Cold Wall T	: 31° C	- ELSD Detector	: div.
- FFF System	: postnova T100 Series Thermal FFF	- MALS Detector	: postnova PN3000MALS

Poly(Butadiene-Acrylonitrile Methacrylic Acid) rubbers (PBAMA) are gaining increased interest in the technical applications of high-tech polymer materials and not only in the tire and sealing industry. In the following, an example for the fast and complete characterization of this polymer using Thermal Field-Flow Fractionation is given. Not only the molar mass and its distribution, but also gel-like particles which may be present in the rubbers are of extreme significance as they strongly affect the macroscopic properties of these compounds.

For the analysis of this group of rubbers, chromatographic methods have been used in the past. But these methods, e.g. GPC, can only resolve the polymeric fraction of the rubber compound. The gel particles are simply filtered off by the column. Also a significant amount of shear force is acting onto the polymers when separated via a GPC column. By using Thermal FFF, which separates the polymers in an open rectangular channel without stationary phase, these problems and limitations of GPC can be overcome.

The following figure shows the characterization of Poly(Butadiene-Acrylonitrile Methacrylic Acid) rubber using TF3, Laser Light Scattering (MALS) and ELSD detection:

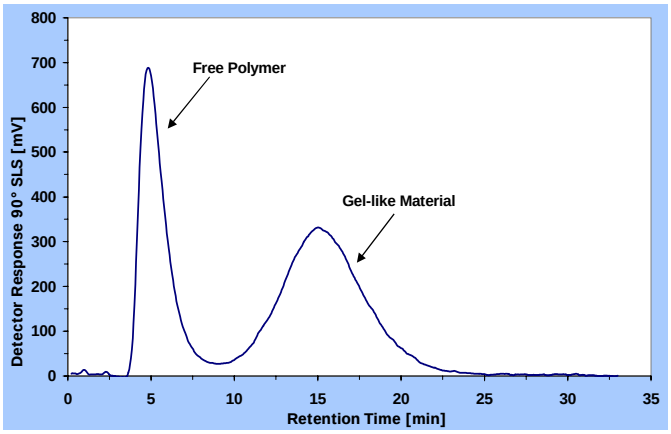

Fig. 1: Fractogram of a PBAMA sample using TF3 and Evaporative Light Scattering detection (ELSD).

Figure 1 shows the results of the analysis using TF3 and ELSD detection. Other detectors as MALS have been used as well, but are not shown in the figure. The measurements show clearly that the gel-like material can be separated from the free polymer quickly and easily. The gel content was quantified and determined as 66%. In the literature many more rubber applications have been described already using postnova´s FFF systems:

[1] Lewandowski, L., M. S. Sibbald, E. Johnson and M. P. Mallamaci (2000). "New emulsion SBR technology: Part I. Raw polymer study." Rubber Chem. Technol. **73**(4): 731-742. A novel emulsion-prepd. SBR (ESBR) has been developed using postnova Thermal FFF. ThFFF was found to be superior to size exclusion chromatography for fully characterizing the mol. wt. and mol. wt. distribution of the polymers.

[2] Sibbald, M., L. Lewandowski, M. Mallamaci and E. Johnson (2000). "Multidisciplinary characterization of novel emulsion polymers." Macromol. Symp. **155**(Emulsion Polymers): 213-228. A series of novel emulsion styrene-butadiene copolymer blends were characterized. TF3 was unique in its ability to detect ultra-high mol. wt. (> 107 Da) fractions showing that traditional SEC under-estimates polymer MW.

[3] Fulton, W. S. and S. A. Groves (1997). "Determination of the molecular architecture of synthetic and natural rubber by the use of thermal field-flow fractionation and multi-angle laser light scattering." J. Nat. Rubber Res. **12**(3): 154-165. Combination of TF3 and MALLS has allowed absolute molar mass/size distribution to be obtained without the need for calibration, standards or assumptions. Complex mixtures of polymer, micro-gel and macro-gel have been studied in a single run without the need for filtration. With TF3 a more comprehensive MW distribution, including branching, could be determined than by GPC.

[4] Lee, S., C. H. Eum and A. R. Plepys (2000). "Capability of thermal field-flow fractionation for analysis of processed natural rubber." Bull. Korean Chem. Soc. **21**(1): 69-74. Applicability of TF3 was investigated for the anal. of masticated natural rubber (NR) adhesives produced by a hot-melt mastication process.

[5] Lee, S. and A. Molnar (1995). Determination of Molecular Weight and Gel Content of Natural Rubber Using Thermal Field-Flow Fractionation." Macromolecules **28**(18): 6354-6. Thermal field-flow fractionation (ThFFF) was used to det. the mol. wt. (MW) and mol. wt. distribution (MWD) of natural rubber.

[6] Shiundu, P. M., E. E. Remsen and J. C. Giddings (1996). "Isolation and characterization of polymeric and particulate components of acrylonitrile-butadiene-styrene (ABS) plastics by thermal field-flow fractionation." J. Appl. Polym. Sci. **60**(10): 1695-1707. TF3 was used to isolate the polymeric and rubber particulate components of acrylonitrile-butadiene-styrene (ABS) plastic. The particle-size distribution of the rubber particles and the MW distribution of the polymer components were obtained. The results agreed favorably with values determined by dynamic light scattering and by size-exclusion chromatography.

[7] Williams, S. K. R. and M. A. Benincasa (2000). "Field Flow Fractionation in Analysis of Polymers and Rubbers." Encyl. of Anal. Chem.: 7582 - 7608. In this article, the fundamental mechanism of FFF is shown at play in the separation and characterization of polymers and rubbers by the two techniques par excellence in this field: flow FFF and thermal FFF.

Why use TF3 for Rubber Characterization?

- ► High resolution separation of polymers and gels.
- ► Fast, gentle and nearly interaction free separation without stationary phase and shear forces.
- ► Complete view on the original rubber sample without prior sample preparation / filtering steps.
- ► Collect fractions and direct coupling with further analytical techniques as MS, FT-IR, Rheometry etc.