Characterization of Charged Polymers using Asymmetrical Flow Field-Flow Fractionation with Smart Stream Splitting Option

Dr. Wenyi Yee, Dr. Richard Riehle
Solenis, LLC

General Information ID0069

Application	Polymer
Technology	AF4-MALS-RI, S3
Info	Postnova AF2000, PN3621 MALS, PN3150 RI, PN1650 Smart Stream Splitting
Keywords	Asymmetrical Flow Field-Flow Fractionation (AF4), Multi Angle Light Scattering (MALS), Charged Polymer, Dry Strength, Wet Strength, Anionic Polyacrylamide, Paper, Slot Outlet

Introduction

Dry strength (e.g., dry tensile) is a fundamental property of most materials. In paper and paperboard products, dry strength is dependent on the strength of the pulp fibers and the bonded area between the fibers. Although dry strength can be increased mechanically by refining, to increase bonding, refining has limitations. Fortunately, these limitations can be overcome by using dry strength additives that increase fiber bonding and therefore the dry strength of the paper [1, 2].

To achieve production, cost, and quality goals, pulp and paper mills and others in the paper industry use a wide range of dry strength additives. The most commonly used cationic dry strength additives are cationic starch, polyvinylamine (PVAm), glyoxalated cationic polyacrylamide (GPAM) and polyaminopolyamide-epichlorohydrin (PAE). PAE additives also provide permanent wet strength to the paper product. During paper manufacturing, the amount of a cationic strength additive that can be used is often limited by the cationic demand of the pulp furnish. To achieve good paper machine runnability and good quality paper, the charge of the pulp furnish should not become cationic. Anionic dry strength additives are used to maintain a neutral charge balance in the wet end during the manufacturing process and to provide additional dry strength to the finished paper [3, 4].

Solenis, LLC has developed a high molar mass aqueous anionic polyacrylamide dry strength product that has a much higher molar mass than traditional aqueous anionic polyacrylamide products. This product has a minimum average molar mass (MM) [a.k.a., weight average molecular weight (Mw)] of 550,000 daltons by size exclusion chromatography (SEC) using Solenis' best practice SEC method. Because of its high MM, this product was designed to have a Brookfield viscosity that allows easy pumping from shipping and storage containers. Since this product has both high MM and high charge density (-3.5 meq/dry g), Solenis intends to further characterize the molar mass properties using techniques beyond SEC that especially focus on the high molar mass portion of the molar mass distribution.

Charged polymers, such as anionic polyacrylamide, are challenging to characterize using traditional SEC technology because of strong column interactions, such as electrostatic interaction and hydrogen bonding formation, with the SEC column stationary phase. By replacing traditional SEC columns with an Asymmetrical Flow Field-Flow Fractionation (AF4) channel, this investigation demonstrated that AF4 coupled with Multi Angle Light Scattering (MALS) is a promising technology that can be applied to the characterization of charged polymers.

A potential limitation of using AF4 for the analysis of dry strength products lies in the dilution effect in the AF4 channel that further leads to another challenge for the characterization of water soluble polymers with low dn/dc (specific refractive index increment), low concentration or ultra-high molar mass. To solve this problem, Smart Stream Splitting (S3) was applied in this investigation, and the results demonstrated that the S3 option is an efficient tool for improving the sensitivity of the AF4-MALS analysis of dry strength products.

Working Principle of Smart Stream Splitting (S3)

In AF4, the separation mechanism results in the sample being located in the lower part of the fractionation channel. This means that at the detector outlet the sample is diluted by the upper, sample-free, part of the flow. Using S3 removes the upper, sample-free part of the channel flow and allows only the lower, sample-rich part of the channel flow to go to the detectors (Sample Out in Figure 1). The result is that increased analyte concentration passes through the detectors and therefore generates higher detector signal (see Figure 1).

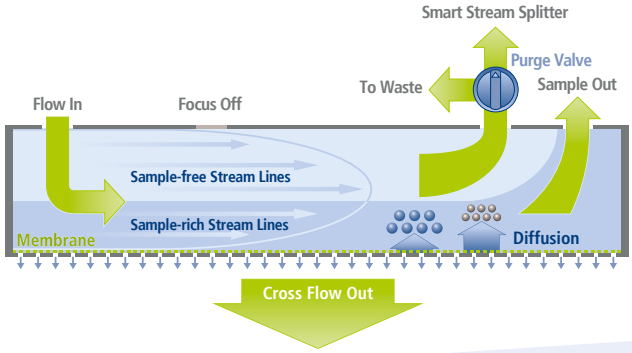

Figure 1: Principle of smart stream splitting using the S3 option.

Experiment

A 10 kDa polyethersulfone membrane was used throughout these experiments. The channel flow was set at 0.5 mL/min for both the non-S3 option and for the 1:1 split ratio (2x nominal enrichment of sample). The channel flow was set at 0.6 mL/min for the 2:1 split ratio (3x nominal enrichment). The eluent was 0.05 M $NaNO_3$+0.07 M Na_2HPO_4 (pH = 9). The dry strength product sample was prepared as a 5 mg/mL solution using the eluent and was analyzed without filtration with an injection volume of 50 µL.

Results and Discussion

The S3 option is used in this example to demonstrate the flexibility of this technology and the successful improvement of the sensitivity of the analysis by simply changing the split ratio. The overlay of the 90° LS fractograms of the same sample with and without using the S3 option and using a split ratio of 1:1 and 2:1 is demonstrated in Figure 2, and the sensitivity improvement in the peak height is summarized in Table 1.

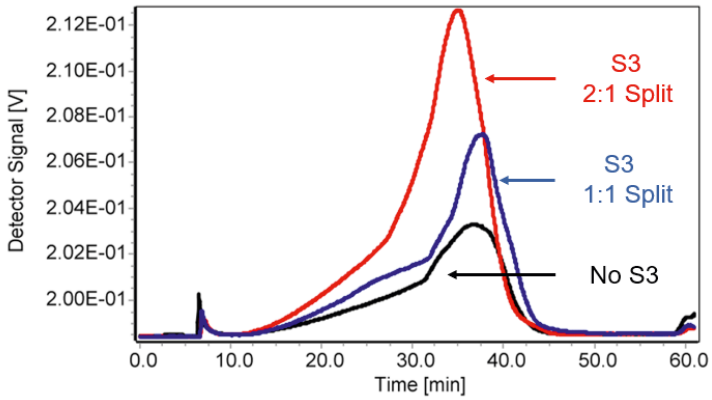

Figure 2: Improvement in sensitivity of 90° LS fractograms without S3 and using S3 at a split ratio of 1:1 and 2:1.

Condition	Sensitivity Improvement
No S3	NA
1:1 Split	2
2:1 Split	3.5

Table 1: Sensitivity improvement vs split ratio with and without using the S3 option.

The molar mass versus the retention time (RT) plot and the light scattering (LS) fractogram of the dry strength product are overlaid in Figure 3. The molar mass versus the RT plot clearly indicates a good size-based normal mode separation was achieved using the AF4 technology where smaller molecules elute first and larger ones later.

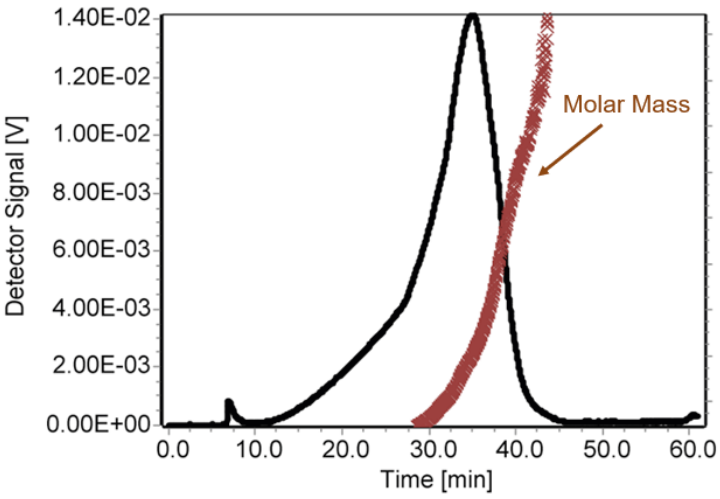

Figure 3: Molar mass profile overlay with 90° LS fractogram indicating size-based separation. Actual molar mass values withheld for confidentiality reasons.

Conclusion

Combining AF4 with MALS has been demonstrated to be an effective tool for the characterization of charged polymers that are challenging to characterize using traditional size exclusion chromatography technology. The S3 option improves the sensitivity of the AF4-MALS analysis, thereby providing flexibility in the application of the AF4 technology to different types of polymer products.

References

[1] J.S. Jenkins, in Application of Wet End Chemistry (I. Thorn and C.O. Au, Eds.) 2nd edn., Springer, Dordrecht, 2009, Chap. 7.
[2] S.J. Broschart, in Advances in Papermaking Wet End Chemistry Applications Technology (M. A. Hubbe and S. Rosencrance, Eds.), Tappi Press, Peachtree Corners, 2018, Chap. 11.
[3] M.T. Crisp and R.J. Riehle, in Application of Wet End Chemistry (I. Thorn and C.O. Au, Eds.) 2nd edn., Springer, Dordrecht, 2009, Chap. 8, pp. 158-160.
[4] H.H. Espy, in Wet-Strength Resins and Their Applications (L.L. Chan, Ed.), TAPPI Press, Atlanta, 1994, Chap. 2, pp. 33-34.

POSTNOVA

info@postnova.com
www.postnova.com

Postnova Analytics GmbH
86899 Landsberg, GERMANY
T: +49 8191 985 688 0

Postnova Analytics UK Ltd.
Worcestershire, WR14 3SZ, UK
T: +44 1684 585167

Postnova Analytics Inc.
Salt Lake City, UT 84102, USA
T: +1 801 521 2004

Postnova Northern Europe
00380 Helsinki, FINLAND
T: +358 9 8545 510