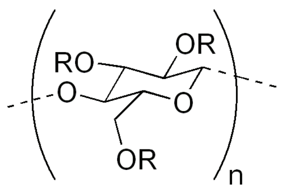
Application Note

ANALYSIS OF HYDROXYETHYLCELLULOSE IN PERSONAL CARE PRODUCTS

INTRODUCTION

Hydroxyethylcellulose (HEC), Figure 1, is a water soluble polymer derived from alkali cellulose and ethylene oxide or ethylene chlorohydrin by etherification. HEC is the most hydrophilic and widely used cellulose ether. This non-ionic soluble cellulose ether is useful for thickening, suspending, dispersing, emulsifying, film-forming and water-protecting as well as providing other protective colloidal properties. HEC is widely used for applications such as oil exploitation, coatings, building, medicine, food, textile, and papermaking. In the personal care chemical industry HEC is found in products such as toothpaste, soap, lotions, and cosmetics, as HEC acts as a thickener, dispersing agent, binder and stabilizer to increase the density, lubrication or mercerized appearances of products. For example, in personal care products such as shampoos, body washes, shower gels, and eye drops HEC has the ability to thicken solutions and reduce the amount of suds or foam they form, thus increasing the cleaning effect.[1]

STRUCTURE OF HYDROXYETHYLCELLULOSE



R = H or CH_2CH_2OH

Figure 1

The ability to characterize a polymer in its end use environment is essential as the molar mass and size of a polymer can change depending on experimental conditions such as mobile phase. One powerful tool for the characterization of the molar mass of cellulose derived molecules is size exclusion chromatography (SEC).[1,2] Unlike cellulose itself, which is insoluble in water, HEC is water soluble thus can be characterized in an environment similar to that used in most personal care products. In general, the characterization of cellulose derived polymers by SEC can provide information regarding the molar mass distributions, and when coupled to various physical detection methods, can provide information regarding polymeric size and architecture. Here we report the use of the EcoSEC® GPC System with an internal dual flow RI detector and semi-micro SEC columns for the molar mass determination of pure HEC and HEC within two personal care products using conventional or peak-position calibration.

EXPERIMENTAL

Sample analysis was performed on a system consisting of an EcoSEC GPC System equipped with a RI detector. Separation of unfiltered 25 μL injections occurred over a column bank consisting of three 4.6 mm ID × 15 cm, 8 μm TSKgel® SuperMultiporePW-H columns (P/N 0022791 exclusion limit 1 × 10^7 g/mol) preceded by the appropriate guard column. The mobile phase and solvent was water with 0.1 mol/L $NaNO_3$ and 0.02% NaN_3 at a flow rate of 0.50 mL/min. Detector, pump, and column oven were maintained at 35 °C. Three samples were analyzed: hydroxyethylcellulose (HEC) and two personal care products with hydroxyethylcellylose.

For all chromatographic determinations, results are averages of three injections. The molar mass and molar mass distribution of the HEC samples was determined based on a polyethylene oxide and polyethylene glycol calibration curve. The calibration curve was created for the RI at 35 °C using polyethylene oxide and polyethylene glycol standards ranging in molar mass from 615 to 1.4 × 10^5 g/mol. All standards were prepared at a concentration of ~1 g/L. Calibration curve data for 0.50 mL/min was fitted with a cubic function and error values were less than 5%.

RESULTS AND DISCUSSION

Hydroxyethylcellulose is a cellulose derivative commonly used in personal care products such as toothpaste, shampoos, and eye drops that can be characterized based on molar mass by size exclusion chromatography. The chromatograms of the pure HEC and the HEC found within two personal care products, as monitored by the dual flow RI detector in the EcoSEC GPC System, are shown in Figure 2. The elution profile of the pure HEC displays the presence of one species while the two personal care products display two very different elution profiles. Personal care product 1 displays a distinctive bimodal distribution in the location of the pure HEC as well as two additional components in the low molar mass region of the chromatogram. Personal care product 2 displays a single peak spanning a very similar elution window as does pure HEC as well as one of the two additional components observed in personal care product 1. The bimodal distribution in the HEC region of the chromatogram for personal care product 1 could be a result of either two completely different polymer species in the product or the presence of two distinctive size (molar mass) distributions of HEC in the product with the lower molar mass portion of the HEC being present at a higher concentration than the high molar mass portion. The two later eluting species in the chromatogram for personal care product 1 and the one late eluting species in the chromatogram for personal care product 2 appear to be additional components that are significantly smaller in size than the main polymeric components of the personal care product,.

The polyethylene oxide and polyethylene glycol RI relative number-, weight-, and z-average molar mass values of

SEC ELUTION PROFILE OF PURE HYDROXYETHYLCELLULOSE AND HYDROXYETHYLCELLULOSE IN TWO PERSONAL CARE PRODUCTS

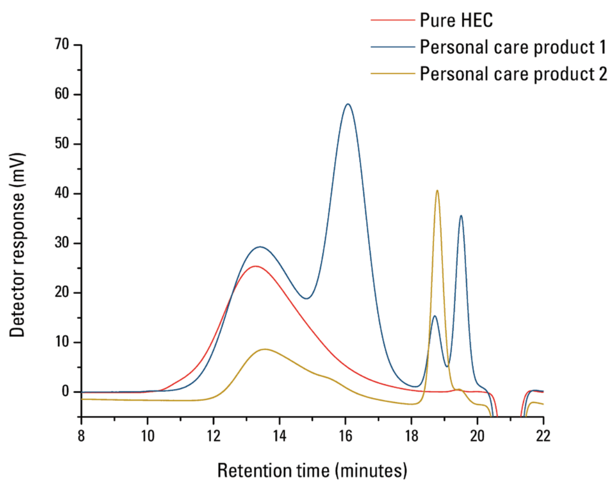


Figure 2

MOLAR MASS AVERAGES AND POLYDISPERSITY INDEX OF PURE HYDROXYETHYLCELLULOSE AND HYDROXYETHYLCELLULOSE IN TWO PERSONAL CARE PRODUCTS

Sample	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
Pure HEC	1.50×10^5 $\pm 0.04^b \times 10^5$	1.47×10^6 $\pm 0.01 \times 10^6$	5.93×10^6 $\pm 0.01 \times 10^6$	9.82 ±0.20
HEC in personal care product 1 (collectively)	4.67×10^4 $\pm 0.01 \times 10^4$	5.89×10^5 $\pm 0.02 \times 10^5$	2.78×10^6 $\pm 0.06 \times 10^6$	12.61 ±0.03
HEC in personal care product 1 (separately)	5.21×10^5 $\pm 0.06 \times 10^5$	1.12×10^6 $\pm 0.04 \times 10^6$	2.47×10^5 $\pm 0.16 \times 10^5$	2.29 ±0.01
	2.69×10^4 $\pm 0.07 \times 10^4$	4.32×10^4 $\pm 0.09 \times 10^4$	6.38×10^4 $\pm 0.01 \times 10^4$	1.61 ±0.23
HEC in personal care product 2	3.13×10^5 $\pm 0.01 \times 10^5$	1.69×10^6 $\pm 0.05 \times 10^6$	4.95×10^6 $\pm 0.01 \times 10^6$	5.43 ±0.23

[a] *PDI = M_w/M_n* [b] *Standard deviations from three injections*

Table 1

the pure HEC and the HEC within a personal care product are given in Table 1. The molar mass averages for the HEC within the personal care product 1 were shown to vary from that of the pure HEC when the molar mass averages of both components in the HEC region of the chromatogram for the personal care product were detemined collectively and separately. The molar mass averages for the pure HEC are approximately 30-50% greater than that of the HEC found in the personal care product 1. The weight- and z-average molar mass values for personal care product 2 are relatively close to that of the pure HEC while the number-average molar mass was twice as large. The differences between the molar mass averages, not to mention SEC elution profile, between the two personal care products is an indication that the two personal care products will perform differently in their end use application.

The molar mass distribution of the pure HEC and the HEC region of the personal care products indicate a polydisperse polymer. For the pure HEC the polydispersity index value, PDI, is 9.82 and for personal care product 1 the PDI=12.64 (collectively) or PDI=2.27 and 1.59 (separately) and for personal care product 2 the PDI=5.43. Personal care product 1 has a slightly larger polydispersity than the pure HEC while personal care product 2 has a significantly smaller polydispersity than that of the pure HEC. From the SEC elution profile and molar mass averages and distributions of both products it appears that personal care product 2 is more similar to that of pure HEC than personal care product 1, but both products contain species with elution profiles and molar masses similar to HEC.

CONCLUSIONS

The EcoSEC GPC System with a dual flow RI detector was used to compare and contrast two personal care products containing hydroxyethylcellulose, a water soluble derivative of cellulose, based on SEC elution profile and polyethylene oxide and polyethylene glycol relative molar mass averages. The two personal care products have distinctive differences form one another and pure HEC. Personal care product 1 was bimodal with molar mass averages significantly less and a polydispersity slightly higher than that of pure HEC. Personal care product 2 had the same single SEC peak as that of HEC and weight- and z-molar mass averages relatively close to that of the pure HEC but a significantly higher number-average molar mass thus a much lower polydispersity index value.

The use of SEC/RI allowed for the characterization of a cellulose derived polymer, HEC, in an environment similar to its end use based on molar mass averages and distributions. The single detector SEC set-up used here could be coupled to various physical detection methods such as multi-angle or dynamic light scattering and differential viscometry to provide additional information regarding polymer size or architecture of the pure HEC and the HEC in personal care products.

REFERENCES

1. Liu, X.M.; Gao, W.; Maziarz, E.P., Salamore, J.C.; Duex, J.; Xia, E. J. Chromatogr A., 2006,, 1104, 145-153.
2. Li, y.; Meunier, D.M.; Partain, E.M. J. Chromatogr A., 2014, 1359, 182-188.