Analysis of Renewable-Based Polymers using the EcoSEC® GPC System Coupled to Multi-Angle Light Scattering

EcoSEC GPC System
APPLICATION NOTE

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Introduction

Scientist are continuously working on reducing the nation's reliance on fossil fuels by developing environmentally friendly and cost effective plastics from natural, sustainable and renewable materials, such as vegetable oils, starches, and sugars. The overall goal is to reduce the reliance on petroleum-based plastics and help mitigate environmental damage by designing materials that are compostable and less harmful while in use. Manufacturers within the automotive, footwear, carpet, and furniture sectors are starting to demand renewable or bio-based polymers as they seek to sell more sustainable products. A renewable or bio-base polymer is a plastic material that addresses the needs of a consumer without damaging our environment, health and economy. The feedstock of renewable polymers is typically a plant and production of such polymers uses less net water and non-renewable energy, emits less greenhouse gases and has a smaller carbon footprint than their non-renewable counterparts, while still being economically viable.

One group of polymers gaining a great deal of interest is thermoplastic polyurethanes or TPUs. A TPU is an elastomer that resembles rubber in consistency and feel but, by nature has outstanding abrasion resistance, great low temperature flexibility, resistance to oil, and a high threshold for support weight, in addition to being very bondable, durable, paintable, and impact resistant. The physical and chemical properties of renewable polymers can be analyzed using the same methods used for the analysis of non-renewable polymers such as infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), and melt flow. Each of these techniques provides details about the macromolecular properties and thus provides information about the end-use properties of the renewable polymer.

The specific end-use properties of a batch of TPUs, such as tensile strength, elongation, conductivity, chemical resistance, and toughness, depends on macromolecular properties such as molar mass, branching, degree of crosslinking, and polymeric size. The molar mass and polymeric size of TPUs can be determined using GPC coupled to a series of detection methods. Here we have implemented the use of the EcoSEC GPC System encompassing a dual flow refractive index (RI) detector with a multi-angle light scattering detector (MALS) to determine the absolute molar mass, absolute molar mass distribution, and polymeric size of two different batches of TPUs.

Experimental

Dual detector GPC analysis was performed using the EcoSEC GPC System (HLC-8320) equipped with a refractive index detector (RI) (Tosoh Bioscience LLC) coupled in series to a DAWN® 8+ MALS photometer (Wyatt Technology Corporation). Separation of unfiltered 100 µL injections occurred over a column bank consisting of two 7.8 mm ID × 30 cm TSKgel® GMH_{HR}-H columns (separation range ~500 to 4 × 10^8 g/mol) (Tosoh Bioscience LLC) (PN 17360). The mobile phase and solvent were dimethylformamide (DMF) with 0.01% LiBr at a flow rate of 1.0 mL/min. Detector, pump oven, and column oven were maintained at 45 and 50 °C depending on the component. Data was processed using Wyatt's ASTRA® 6.1 software. Two TPU samples were prepared with a final concentration of 1.0 g/L. All chromatographic determinations are averages of three injections from one sample dissolution.

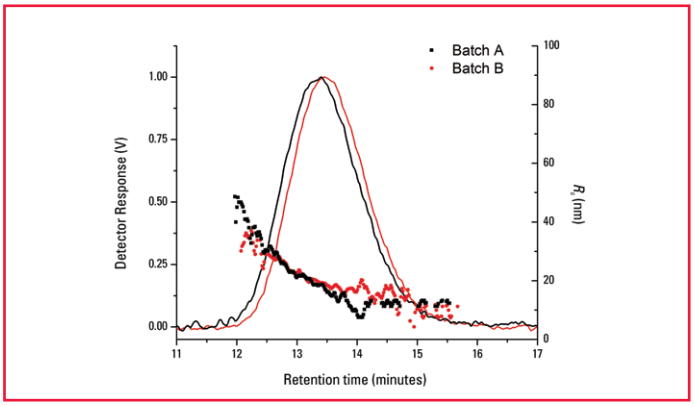
The DAWN 8+ detector was normalized in-house using a polystyrene standard, with a molar mass of 3.79 × 10^4 g/mol. Calculations for interdetector delays and interdetector band broadening corrections were performed using the same polystyrene standard used to normalize the detector. Calibration of the MALS unit was performed using toluene. All MALS data were fitted using a Zimm model. The $\partial n/\partial c$ values for each sample were determined using an online 100% mass recovery method using the RI detector housed within the EcoSEC GPC System.

Results and Discussion

Several macromolecular properties of renewable polymers can be characterized using GPC coupled to detection methods such as refractive index and multi-angle light scattering. The coupling of a size-based separation method such as GPC to an absolute detection method such as multi-angle light scattering allows for the determination of the absolute molar mass, absolute molar mass distribution and polymeric size of polymers such as TPUs. Two different batches of TPUs were analyzed in DMF. The GPC experiments provided several forms of comparison between the two different batches of TPUs: GPC chromatograms, absolute molar mass and molar distributions, and polymer size (radius of gyration) and polymer size distribution.

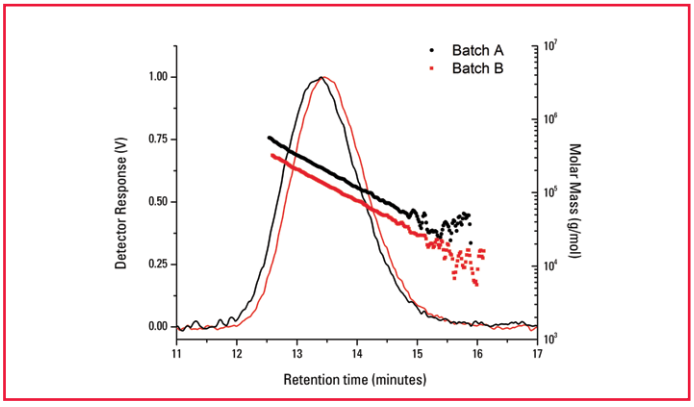
The GPC elution profiles of the two different batches of TPUs as monitored by the MALS detector is shown in *Figure 1*. TPU Batch B elutes after TPU Batch A. The longer retention time of TPU Batch B indicates that TPU Batch B is slightly smaller in polymeric size compared to the TPU Batch A: as elution order in GPC is that of an "inverse-sieving" technique, smaller analytes elute after the larger analytes.

Figure 1. GPC elution profile of two batches of TPUs as monitored by MALS and radius of gyration distribution across the elution profiles as determined by MALS



The polymeric size comparison can also be done quantitatively as the addition of a MALS detector to the EcoSEC GPC System permits for the determination of a polymeric sizing parameter, the root-mean-square radius or radius of gyration, R_G. The average radius of gyration for both TPUs, A and B, were identical, R_G = 20 nm, but TPU Batch A does contain some species larger in polymeric size than TPU Batch B. The radius of gyration distribution as plotted across the GPC elution profile, as monitored by the 90° light scattering signal as well as the radius of gyration polydispersity index values can be used to determine the size polydispersity of the sample, which may influence end-use properties of the TPUs. As seen in *Figure 1*, the size of both TPUs decreases as a function of increasing retention time, an indication that the samples are polydisperse with respect to size. The size *PDI* value for batch A is slightly greater than that of batch B, 1.3 and 1.1, respectively. *Figure 1* also provides evidence that the TPU samples are eluting from the GPC column by a true size exclusion mechanism as the polymeric size is decreasing as a function of increasing retention time.

Figure 2. GPC elution profile of two batches of TPUs as monitored by MALS and absolute molar mass distribution across the elution profiles as determined by MALS



The absolute molar mass averages and the molar mass distributions of the two different batches of TPUs were also determined. The molar mass distribution of the two batches of TPUs as plotted across the GPC elution profile, as monitored by the 90° light scattering signal, are shown in *Figure 2*. The absolute weight average molar mass, M_w, is slightly higher for A than B, 1.64 × 10^5 and 1.42 × 10^5 g/mol, respectively. Both batches of TPUs, A and B, show a polydispersity in molar mass as the molar mass decreases as a function of increasing retention time, *Figure 2*. Additionally, the molar mass polydispersity index, *PDI*, of the two batches indicate samples polydisperse in molar mass as *PDI* = 1.6 for both batches. TPU Batches A and B when analyzed by GPC coupled to RI and MALS produce GPC elution profiles, absolute molar mass averages and distributions as well as polymeric size measurements similar enough to one another to create products with the same end-use properties.

Conclusions

Two batches of thermoplastic polyurethanes, a renewable-based polymer, was characterized based on the GPC elution profile, absolute molar mass averages and absolute molar mass distribution, and polymeric size and polymer size distribution using the EcoSEC GPC System with a dual flow refractive index detector coupled to a multi-angle light scattering detector. The GPC elution profiles of the two batches of TPUs were found to vary slight as TPU Batch A elutes slightly later than TPU Batch B. The absolute molar mass averages and absolute molar mass distribution of the two TPU samples were found to be similar to one another, with TPU Batch A being slightly higher in molar mass than TPU Batch B and both batches having identical polydispersity index values. The polymeric size of the two the TPU Batches was also determined to be identical as the radius of gyration and radius of gyration distribution were almost identical to one another. The coupling of the EcoSEC GPC System encompassing a dual flow refractive index detector with multi-angle light scattering detector (MALS) allowed for the determination of several macromolecular properties, e.g. absolute molar mass, absolute molar mass distribution, and polymeric size, which influence the end-use properties of a polymer.

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