Fast Discrimination of Industrial Polyamide Gears with Varying Regrind Material Content Using Advanced Polymer Chromatography for SEC/GPC

Donald A. Trinite, Jennifer Gough

Waters Corporation

Abstract

This application note demonstrates the advantages of using the Waters ACQUITY Advanced Polymer Chromatography (APC)™ System for size exclusion chromatography (SEC)/gel permeation chromatography (GPC) analysis of polyamide blended with various percentages of regrind material with hexafluoro isopropanol (HFIP) as the solvent.

Benefits

- A 15-minute per sample analysis time compared to traditional GPC of 45-minute run time

- Polyamide GPC analysis option that uses less solvent and creates less hazardous waste

- APC Isocratic Solvent Manager (ISM) system with demonstrated performance for the analysis of polymeric samples using a variety of solvents including HFIP

Introduction

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GPC is an analytical technique used to characterize polymers that use the addition of recycled (regrind) material. The recycled polymers being used as a raw material are only acceptable when performing like the original non-recycled polymers. Therefore, polymer properties such as molar mass distributions, molar mass averages, and polydispersity must be sustained for the final product properties to be preserved. This is important as reprocessing of the polymer could potentially cause chain-length degradation and have properties different from the original starting material.

Due to the chemical resistance of polyamides, such as nylon 6,6, dissolving the polymer in an organic solvent for analysis using GPC is challenging.[1] Industrial manufacturers use high temperature (HT) GPC (>100 °C) to determine the molecular weight distribution of these nylon polymers, and the analysis often uses ortho dichlorobenzene (ODCB), trichlorobenzene (TCB), m-cresol or N-methyl pyrrolidone (NMP) as the mobile phase with traditional styrene divinylbenzene (SDVB) GPC columns. However, this technique consumes large amounts of solvent which creates large hazardous waste costs, and a lengthy 45-minute analysis time.[2-4]

In this study, an alternative approach to HT-GPC analysis for polyamides (such as nylon 6,6) is employed with HFIP mobile phase and an APC system.

Experimental

In this APC analysis, an HFIP mobile phase with salt additive was used to run a size-based separation of various polyamides (Table 1). Polyamide gear samples containing virgin and varying percentages of regrind material were obtained from Thyssenkrupp Presta AG, Liechtenstein. The samples were dissolved in HFIP at 1 mg/mL overnight in scintillation vials and transferred to instrument vials.

LC Experimental Conditions

System:	APC™ with ISM
Pump:	Isocratic
Mobile phase:	Hexafluoro-2-propanol w/0.1 % sodium

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	Trifluoroacetate (NaTFA)
Wash/purge:	Hexafluoro-2-propanol
Seal wash:	80/20 Water/Isopropanol
Seal wash rate:	2 min. intervals
Flow rate:	0.45 mL/min.
Run time:	15 min.
Sample temperature:	20 °C
Syringe draw rate:	Automatic
Sample conc:	1 mg/mL
Injection volume:	20 µL
Column temperature:	50 °C
Column set:	ACQUITY APC XT™:
	450 Å (2.5 µm, 4.6 x 75 mm), p/n 186007253
	125 Å (2.5 µm, 4.6 x 75 mm), p/n 186006998
	45 Å (1.7 µm, 4.6 x 75 mm), p/n 186006993
Detector:	RI (50 °C)

Data Management

Instrument control as well as data acquisition, processing, and reporting were done by Empower™ 3 Chromatography Data System.

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Results and Discussion

The polymethyl methacrylate (PMMA) calibration standards were first analyzed to establish a relative calibration curve prior to the analysis of gear samples (Figure 1).[7] The highest molecular weight points were on a bend in the calibration curve, and this is due to the lower resolution of a shorter separation path and shorter column, yet this does not affect the quality of the unknown polyamide sample analysis due to their eluting in the linear range of the curve. A 5th order curve was used to obtain an excellent R^2 value of 0.9996 (Figure 1).

Equation Log Mol Wt = 1.10e+02 - 7.68e+01 T^1 + 2.26e+01 T^2 - 3.33e+00 T^3 + 2.44e-01 T^4 - 7.11e-03 T^5   R^2 0.999626
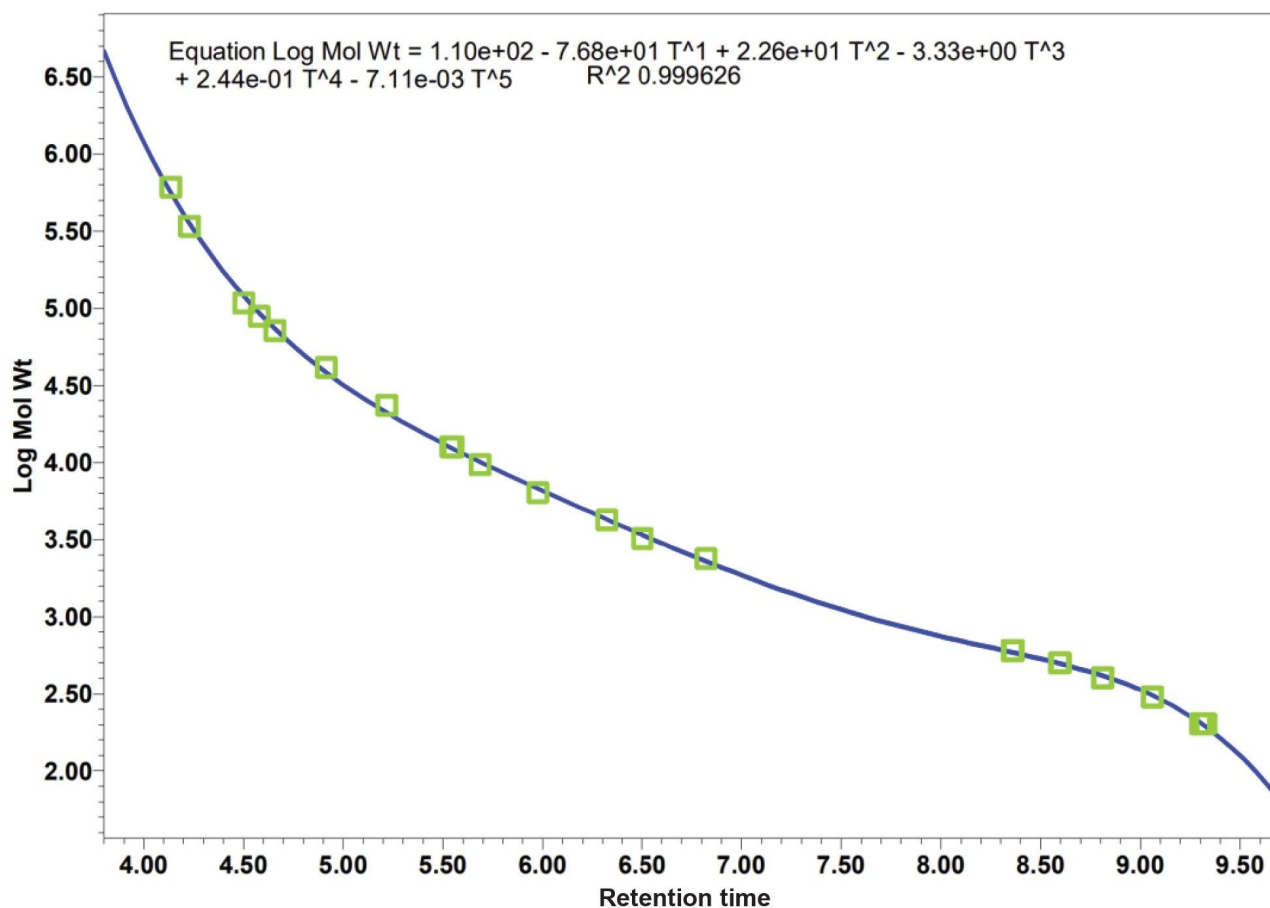
Figure 1. Empower calculated PMMA calibration curve.

The unknown polyamide gear samples were integrated and calculated using the relative calibration PMMA

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standard curve and overlayed to display the differences in peak shape and height (Figure 2). The samples were prepared and injected identically. Therefore, peak differences are based on the recycled material added to the ratio. As more recycled (regrind) material is added, the peaks have a higher retention time and slightly lower and broader shape. This change in shape change indicates a lower molecular weight and a broader molecular weight distribution. Changes in polymer molecular weight and distribution can be indicative of a lower heat and impact resistance, which is often confirmed through thermal analysis using a differential scanning calorimeter (DSC).[8]
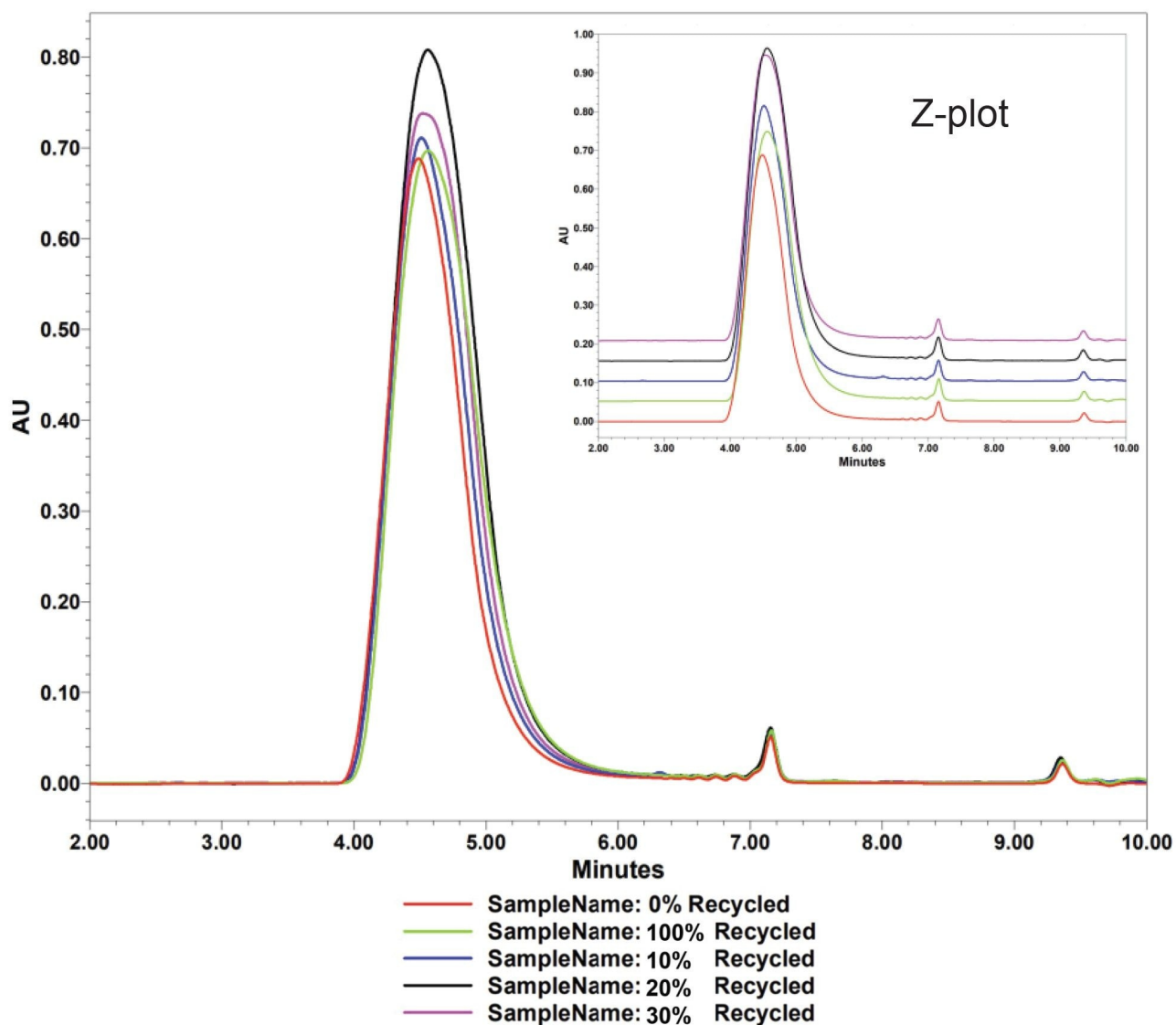
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Figure 2. Empower chromatographic overlay of five polyamide samples with zero to 100% recycled material added to virgin material and z-plot inlay.

Although the overlay of peaks does not appear to have large differences in peak shape, the calculated molecular weight is a 24% difference between the zero percent and the 100 percent peaks. The gear containing zero percent recycled nylon has a peak maximum (MP) molecular weight of 127 k Dalton (Da) compared to the 97 k Da gear with 100 percent recycled polymer. The difference in the peak values is also seen in the weight average (Mw), number average (Mn), z-average, and polydispersity index (PDI) in table 4. Each change in these various

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values can affect the properties of the polymer strength, melt flow, and flexibility.

Sample name	Retention time (min.)	Mn (g/mole)	Mw (g/mole)	MP (g/mole)	Mz (g/mole)	Polydispersity
0% Recycled	4.487	36342	148999	125645	332214	4.10
10% Recycled	4.511	33732	130976	115642	280346	3.88
20% Recycled	4.561	31911	119856	98296	271789	3.76
30% Recycled	4.519	33527	126655	112612	280864	3.78
100% Recycled	4.564	30971	111982	97290	239448	3.62

Table 1. GPC sample results of 0% to 100% recycled polyamide gear samples.

The APC system, with an ACQUITY APC XT™ Column bank operated at high pressures, enables the HFIP size separation of polyamides in 15-minutes as compared to the HT and HPLC systems. In addition to high pressure capability, the APC XT Columns are resistant to solvent swelling. The advantages of using the APC option over a HT GPC is a three-fold time savings and six times less solvent consumption. Less solvent consumption equals less hazardous waste which contributes to an improvement in sustainability (Table 3).[9]

System	Mobile phase	Run temp °C	Flow rate (mL/min.)	Analysis time (min.)	Solvent mL/ analysis	Column particle
HT	ODCB	145	1	45	45	SDVB
GPC	HFIP	50	0.5	45	22.5	SDVB
APC	HFIP	50	0.5	15	7.5	BEH

Table 2. Comparison of total analysis time and solvent use of HT GPC, traditional GPC, and APC.

Conclusion

The results from the experiments described demonstrate that the APC has the capability to differentiate polyamide gear samples containing varying percentages of regrind material (considered here as recycled) dissolved in HFIP with a calibration curve having and R^2 value of 0.9996.

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This analytical method delivers the results three times faster than traditional GPC with a 15-minute analysis per injection. The shorter run time uses less than 7 mL of HFIP solvent per injection, as compared to traditional GPC using greater than 22 mL per injection.

The analytical approach described has the potential to increase laboratories sample throughput offering a more sustainable, cost-effective separation option and a viable alternative to high temperature GPC.

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