GPC Analysis of Thermoplastic Engineering Polymers (PBT, PET)

Application Note

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Introduction

Engineering polymers are particularly difficult to analyze – they are generally tough and difficult to dissolve, often requiring aggressive solvents and elevated temperatures. They have only limited solubility in a small number of solvents. This is because high strength and toughness are usually a result of high molecular weight and/or high crystallinity.

Increasing molecular weight requires untangling the molecular chains to dissolve the material, whereas increased crystallinity requires break-up of any inter-chain bonds that may be present. If high temperatures are required to achieve this, a high performance integrated GPC system, such as the PL-GPC 220 High Temperature GPC/SEC System, is a necessity.

Polybutylene terephthalate (PBT) in HFIP – machined parts, bottles

Polybutylene terephthalate (PBT) resins are used in a wide variety of applications in which toughness and resistance to damage are highly advantageous. However, mechanical and thermal stress during the production of molded parts can cause degradation, giving a reduction in desirable physical properties.

The molecular weight distribution of the resin is a key measure of the onset of degradation and therefore of estimating the mechanical strength of the final product. PBT is soluble in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), a polar organic solvent, which is excellent for dissolving polar polymers such as polyamides and polyesters. The analysis was carried out in HFIP modified by the addition of 20 mM sodium trifluoroacetate to prevent aggregation.

Two Agilent PL HFIPgel columns, designed specifically for HFIP applications, were employed for the analysis at a temperature of 40 °C. The PL-GPC 220 High Temperature GPC/SEC System was used with differential refractive index and viscometry detection. GPC coupled with a molecular weight sensitive viscometer allowed calculation of molecular weights based on hydrodynamic volume using the Universal Calibration approach, leading to molecular weights independent of the standards used to generate the column calibration. Agilent polymethylmethacrylate (PMMA) standards were employed to generate the Universal Calibration.

Table 3 shows the molecular weight averages and intrinsic viscosity for the sample before and after molding, as determined by GPC/viscometry. Clearly, the molecular weight distribution indicates that after molding, the material has suffered from degradation and is less robust than the virgin material.

Conditions

Samples: PBT resin
Columns: 2 x PL HFIPgel, 7.5 x 300 mm (p/n PL1114-6900HFIP)
Eluent: HFIP + 20 mM NaTFA
Flow Rate: 1.0 mL/min
Inj vol: 200 µL
Temp: 40 °C
Instrument: PL-GPC 220 High Temperature GPC/SEC System, viscometer

***Table 1.** Molecular weight averages and intrinsic viscosity for the PBT resin sample*

	Mn/g mol^{-1}	Mw/g mol^{-1}	Intrinsic viscosity/g^{-1}
Virgin resin	24,400	48,600	0.535
Molded part	11,200	24,000	0.306

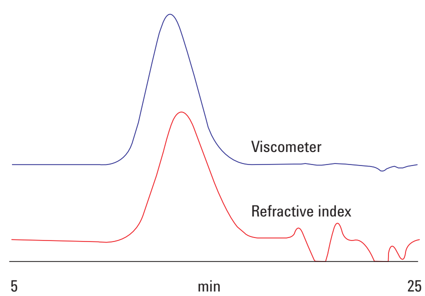

***Figure 1.** Example overlay of a dual-detector chromatogram of the virgin PBT resin before molding*

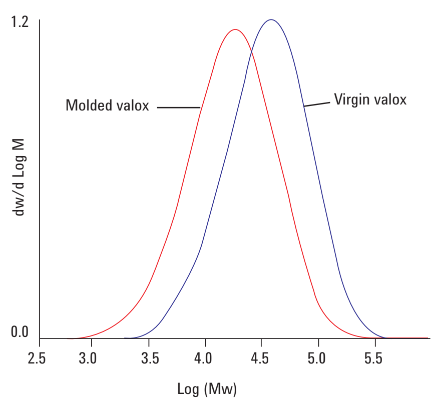

***Figure 2.** Molecular weight distributions of the two samples*

Polyethylene terephthalate in o-chlorophenol as an alternative solvent

As an alternative to the use of HFIP, PET can be analyzed in o-chlorophenol. This viscous solvent requires elevated temperatures and is a hazardous substance. The samples were dissolved by heating to 110 °C for 30 minutes. The polymer remains in solution at room temperature but the high viscosity of the eluent means that high temperature GPC is necessary. Three grades of PET, with different intrinsic viscosities, were analyzed and compared, showing minor differences between the materials.

Conditions

Samples: PET resin
Columns: 2 x PLgel 10 µm MIXED-B, 7.5 x 300 mm (p/n PL1110-6100)
Eluent: o-Chlorophenol
Flow Rate: 1.0 mL/min
Temp: 100 °C
Instrument: PL-GPC 220 High Temperature GPC/SEC System

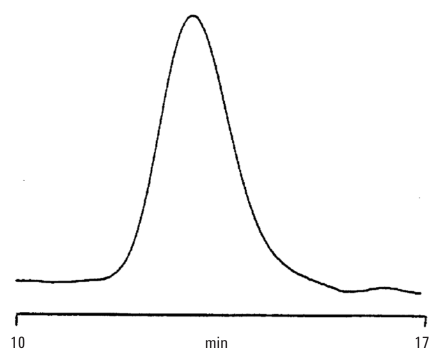

***Figure 3.** Chromatogram of a PET sample*

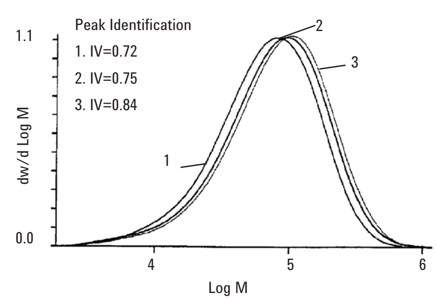

***Figure 4.** Molecular weight distributions of the PET samples*

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