Performance PerSPECtives

Waters® Alliance® GPC/V 2000 System:
Monitoring Polymer Degradation

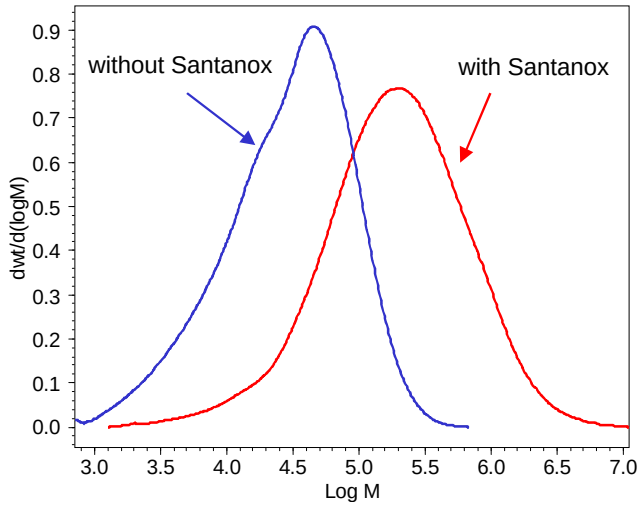
Introduction: One of the most important uses of gel permeation chromatography (GPC) is to check for polymer degradation. Polymers may undergo degradation at a variety of points, from the initial polymerization step to the final stage of finished product manufacture. Certain polymers have even been shown to degrade during the sample preparation process, particularly when performed at elevated temperatures. This Performance PerSPECtive demonstrates how two types of polymers (polypropylene and polyurethane) can undergo severe degradation during the sample preparation process as well as at the point of final product testing.

Polyolefins are typically dissolved at ~135° C to 170° C, depending upon their structure, prior to GPC analysis. Polyethylenes are less susceptible to oxidative degradation than polypropylene, which has the pendant methyl group that is subject to attack. Since degradation is accelerated by temperature, it is necessary to protect the sample with an antioxidant, such as a hindered phenol. Highly crystalline polypropylene needs to be dissolved at a temperature of 170° C for two hours. The sample may then be chromatographed at a lower temperature, typically 145° C. 1,2,4 trichlorobenzene, containing a few hundred parts per million antioxidant, is used for dissolution.

The chromatograms below illustrate what happens to polypropylene when it is run with and without antioxidant (Santanox R) protection. For this analysis, the polypropylene sample remained in the sample carousel for 12 hours prior to injection. Note the large shift in the molecular weight distribution to lower MW values when the antioxidant stabilizer was absent from the sample.

Effect of Dissolution Conditions on GPC Results

MWDs of a Crystalline Polypropylene Sample



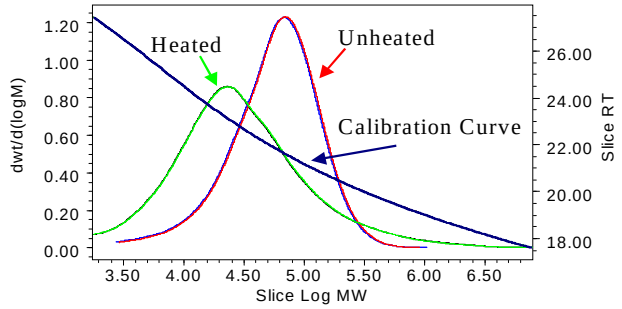
Sample Name	Conditions	Santanox	M_n	M_w	M_z	Intrinsic Viscosity
PP	170° / 2hrs	Yes	80,701	390,615	1,267,418	2.142
PP	170°/ 2hrs	No	13,529	48,229	100,083	0.308

Waters Corporation 34 Maple Street Milford, MA 01757 508 478 2000

Degradation of Polyurethane: When working with synthetic urethane, the chemist has a wide variety of available isocyanate, diol, and polyol chemistries to prepare the polyurethane for use in the final manufactured product (e.g., use as a flexible seal material or to function as part of a head to a hammer). When used as a flexible seal material, a chain extender may be added to the urethane to add flexibility and give it “rubber-like” properties similar to that of an elastomer. In order to analyze the polyurethane, the material can be dissolved at room temperature in tetrahydrofuran (THF), or more frequently, in n, n’ dimethylformamide (DMF) at elevated temperatures. When using DMF (a very polar solvent), electrolyte (0.05M lithium bromide or lithium chloride) is added to the solvent to minimize the polar interactions with the urethane. This minimizes association effects during the GPC separation that can result in the generation of artificially high molecular weight averages. Shown below are duplicate GPC analyses from elastomeric polyurethane seal samples that were tested before and after heat treatment in an environmentally controlled test protocol. (Note: In this application, the tested polyurethane seal material was used in an automotive application where temperatures frequently exceed 200° F. The manufacturer of the seal material reported difficulty getting the seal to pass physical property criteria after the heat treatment testing.) As shown by the GPC analyses, major compound degradation was evidenced by a dramatic change in molecular weight distribution before and after heat treatment confirming why the seals failed during product use. The GPC overlays were nearly perfect, owing to the remarkable reproducibility of the Waters Alliance GPCV 2000 System. The GPC calibration curve is shown overlaid with the four molecular weight distributions.

Overlay of MWDs for a Polyurethane Sample (2 Injections of Each)

Chromatographic Conditions: DMF, 80°C, 3 Styragel HT Columns



GPC Results

	SampleName	Vial	Injection	Mn	Mw	Mz	Mz+1	Polydisp.
1	NOHEAT	1	1	37864	78738	132887	206495	2.08
2	NOHEAT	1	2	36284	76873	131117	208569	2.12
3	HEAT	2	1	15921	84275	812344	2422765	5.29
4	HEAT	2	2	15759	84888	809180	2299026	5.39

Summary: 1) For analysis of polyolefins (and polypropylene in particular), an antioxidant such as a hindered phenol must be added to the solution to protect against polymer degradation.

2) GPC is an excellent technique for polymer degradation studies.