Analysing crystalline polymers by gel permeation chromatography at high temperature

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Polymers used in engineering applications are particularly difficult to analyse - they are generally crystalline, tough, and often require elevated temperatures or exotic solvents for dissolution and to maintain solubility. For these applications a high performance, integrated GPC system is required that maintains the temperature of the sample throughout the analysis. Two classes of engineering polymers were investigated by GPC to illustrate the conditions and equipment required for their analysis at high temperature.

Introduction

Plastics are increasingly utilized to perform structural and mechanical roles in the construction and engineering industries. Favorable properties such as mechanical strength, durability, and resistance to chemical and physical degradation, coupled with their relative cheapness, mean that polymers outperform many traditional materials, such as wood and metals, in key applications. With the creation of new polymeric materials, this shift towards plastics is becoming even more pronounced as products with new properties are designed and developed. An understanding of the behavior of polymers is key to designing new materials with appropriate performance characteristics for specific applications. Analysis of these materials is therefore a critical component of the development and manufacture of engineering polymers.

Gel permeation chromatography (GPC, also known as size exclusion chromatography, SEC) is a well-known technique of column-based liquid chromatography used for assessing the molecular weight distribution of polymers, a parameter that influences many of their physical properties. In GPC the separation occurs by a size exclusion mechanism involving partitioning of polymer molecules between a flowing mobile phase and a stationary phase of stagnant liquid trapped in the pores of a porous media. Movement between the mobile and stationary phases occurs through diffusion of molecules into and out of the pores, with a resulting size separation due to the restricted access of larger molecules to the total pore structure.

The result of the GPC experiment is a molecular weight distribution, an assessment of the spread of chains lengths in the sample. This is of interest as, in general, increasing molecular weight leads to higher performance characteristics, while an increase in the width of the distribution (the polydispersity) leads to a loss of performance but an increase in the ease of processing.

The following applications illustrate the GPC conditions and equipment needed for two classes of polymers that require high temperature to maintain sample solubility in exotic solvents.

Experimental

The analyses were performed on a PL-GPC 220 integrated high temperature GPC system fitted with a differential refractive index detector. This system was designed to run almost all polymer, solvent and temperature combinations, from 30-220 °C. Multiple detection options can be included in the instrument, such as light scattering and viscometry, but were not employed in this study.

This paper discusses the analysis of samples of polyolefin and polyphenylene sulphide. The columns and injection conditions employed for the samples are detailed in the results below.

Results

Polyolefin analysis

Polyolefins range from low molecular weight hydrocarbon waxes to ultra high molecular weight rigid plastics. The molecular weight distribution of polyolefins is directly related to physical properties such as toughness, melt viscosity and crystallinity. Unfortunately, high crystallinity results in only limited solubility and then only at high temperatures, as considerable energy is required to break down the ordered crystalline structure. On cooling, the material will re-crystallize and precipitate from solution. For these applications, high temperature

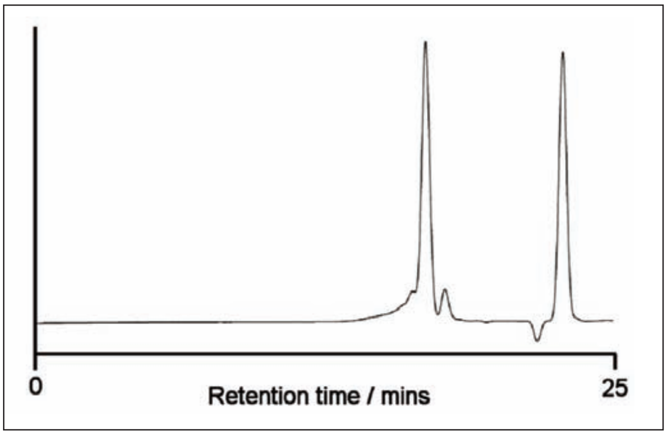


Figure 1. Analysis of a hydrocarbon wax. Columns: 2 x PLgel 5 µm MIXED-D (300 x 7.5 mm), eluent: trichlorobenzene + 0.0125% BHT, flow rate: 1.0 mL/min, injection volume: 100 µL, analysis temperature: 160 °C, instrument: PL-GPC 220 fitted with a differential refractive index detector.

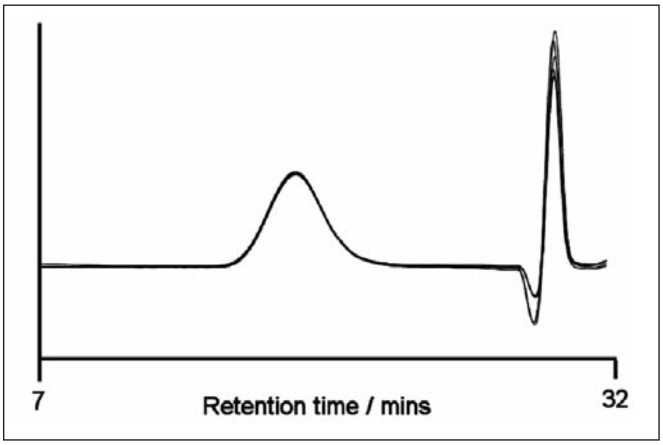


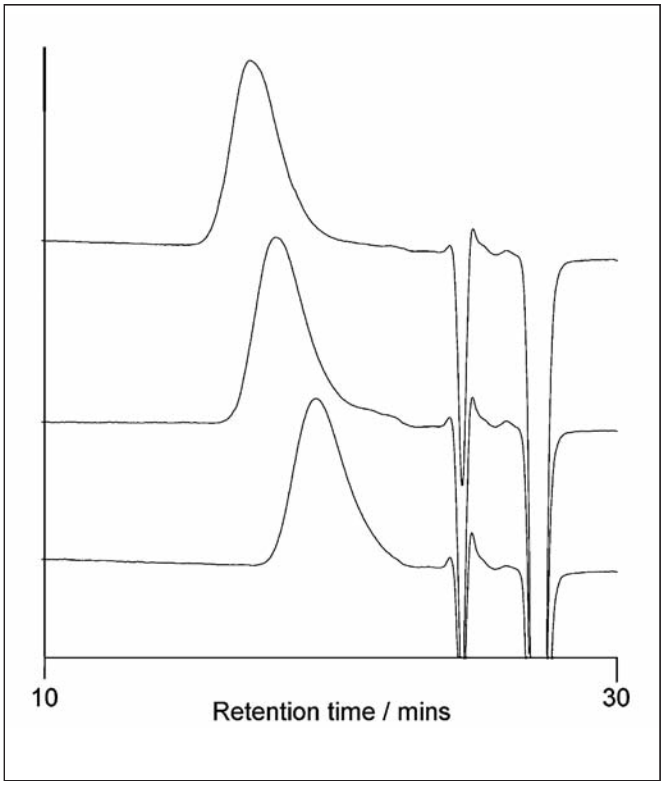
Figure 2. Analysis of several repeat injections of polypropylene. Columns: 3 x PLgel Olexis (300 x 7.5 mm), eluent: trichlorobenzene + 0.0125% BHT, flow rate: 1.0 mL/min, injection volume: 200 µL, analysis temperature: 160 °C, instrument: PL-GPC 220 fitted with a differential refractive index detector.

is required throughout the entire analysis to ensure that the samples remain in solution throughout the experiment. A temperature of 160 °C is required for the analysis of polyolefins.

The selection of GPC columns for the analysis of a polyolefin is dependent on the molecular weight range of the sample. Low molecular weight samples can be analysed using high efficiency, relatively low-pore-size columns. Higher molecular weight materials require media with large particle sizes to minimize shear effects, with a wide pore size distribution. Figure 1 illustrates the analysis of a polyolefin wax by GPC.

High molecular weight materials require analysis on high-pore-size GPC columns that minimize shear degradation. Figure 2 shows the analysis of several injections of a sample of high-density polypropylene by GPC.

These applications illustrate the diversity of polyolefin samples and indicate the flexibility of the PLgel series of columns in addressing the analysis of such samples.



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Polyphenylene sulfide analysis

Polyphenylene sulfide (PPS) is an engineering polymer with a rigid backbone of alternating aromatic rings linked by sulfur atoms. It is useful as a structural material due to its high resistance to both chemical and thermal attack and the material is very stiff, even at high temperatures. PPS is used in a number of applications, including as a filter fabric for coal boilers, in felts used in paper making, in electrical insulation applications and in the manufacture of specialty membranes. PPS is naturally insulating, although the addition of a dopant can be used to make the material semi-conducting.

PPS is particularly difficult to analyse by GPC. The high chemical and thermal resistance of the material means that it is only soluble in specialist solvents such as ortho-chloronaphthalene at elevated temperatures around 200 °C, as shown in Figure 3.

Conclusions

Although the analysis of highly crystalline engineering polymers at high temperature presents particular challenges, it is evident from these examples that with careful choice of GPC instrument and columns it is possible to get good quality results from such materials.

References

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