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High Performance GPC Analysis of Epoxy Resins with the KF Series Columns

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Introduction

The analysis of epoxy resins by GPC is certainly nothing new, but the use of the KF Series columns to characterize epoxies provides the analyst with a powerful tool for both QC and research labs. The columns are packed in THF, and the 5 micron particle size and increased pore volume over conventional columns results in over 20,000 plates per column (4 sigma). When four columns are connected in series (such as for analysis of low molecular weight epoxy resins), the total column bank plate count may approach 100,000 plates.

Epoxy resins were first introduced commercially in 1946, with one of the major applications in the coatings industry. Today, epoxy resins are also used in preparing composites and laminates, which are of major use in the aerospace industry. Epoxy resins are synthesized by reacting epichlorohydrin (ECN) with a compound containing an active hydrogen group, followed by dehydrohalogenation. Another way to prepare them is by the epoxidation of olefins by peracids. One of the most important characteristics of epoxy synthesis is the formation of the diglycidyl ether of bisphenol A (DGEBA), which is the reaction product of BPA and excess epichlorohydrin. The ratio of epichlorohydrin and BPA determines the molecular weight; the higher the BPA fraction, the greater the molecular weight. Typical liquid epoxy resins will have molecular weights ranging from a few hundred to under 1,000. As the

ECN:BPA ratio approaches 1.0 (as for solid epoxy resins), the number average molecular weight may get as high as 4,000 - 5,000. This wide range of molecular weights will provide a variety of different physical properties. The chemist may target a specific molecular weight for a certain application, and GPC analysis will provide the molecular weight information needed to monitor the synthesis.

There are numerous types of epoxies, such as epoxy/novolac resins, made from phenol/formaldehyde condensates, glycidyl amines, such as tetraglycidylmethylenedianiline, glycidyl esters, ethers and epoxidized oils. The resins are characterized prior to curing, and the overall GPC profile provides a wealth of information as to how the material will perform both physically and chemically (e.g., for adhesion, chemical resistance, flexibility, mechanical and thermal properties and processability).

GPC Analysis

Before discussing determination of the molecular weight distribution by GPC, it should be noted that a great deal of information may also be obtained from reverse phase gradient HPLC analysis. A Nova-Pak C₁₈ (4 micron) column will separate the numerous components present in the formulation, such as the ortho and para isomers of the BPA and DGEBA. Also, the degrees of polymerization may be observed (such as the isomers of n=0, 1, 2, 3, etc.) for the resin. The HPLC analysis is also capable of detecting some of the impurities that may be

present (isomers of residual reactants such as for BPA, epichlorohydrin, etc.). A multi-wavelength UV detector such as the Waters™ 490 or 996 Photodiode Array is typically used for the reverse phase gradient separation. Wavelength ratioing (230 and 280 nm, for example) is employed to further garner information of the components contained therein. For many chemists, however, the detail provided by the HPLC analysis is excessive; the GPC analysis which provides for the various degrees of polymerization gives a "fingerprint" of the resin for comparison. For the GPC analysis, the Waters 410 differential refractive index detector was used; however, a UV detector could also have been employed.

(DUP?)

As is the case in any GPC analysis, the systems must first be calibrated with known narrow standards, such as polystyrene, if accurate molecular weight information is to be generated. The system used here consisted of a bank of four KF columns: 801, 802, 802.5, and 803. ($\sim 50\text{\AA} - 10^3\text{\AA}$). Tetrahydrofuran (degassed) was used as the eluent, at a 0.80 mL/minute flow rate. For the calibration procedure a series of styrene oligomers, $dP=2-8$, plus a 1250, 2980, 3250, 6200, 10,300 and 19,600 narrow polystyrene standard were used. The resulting third order curve is shown in Figure 1.

There is approximately 13 mL of useful pore volume in the calibration curve. Figure 2 shows the GPC chromatogram for a typical solid epoxy resin, with the peak of the high molecular weight shoulder eluting at a polystyrene equivalent MW of $\sim 3,000$.

The various oligomers elute after, with the final peak at just under 46 minutes, eluting at the same time as DGEBA monomer (see Figure 3).



Figure 1: Calibration Curve for the 4-Column Set, Using Polystyrene Narrow Standards

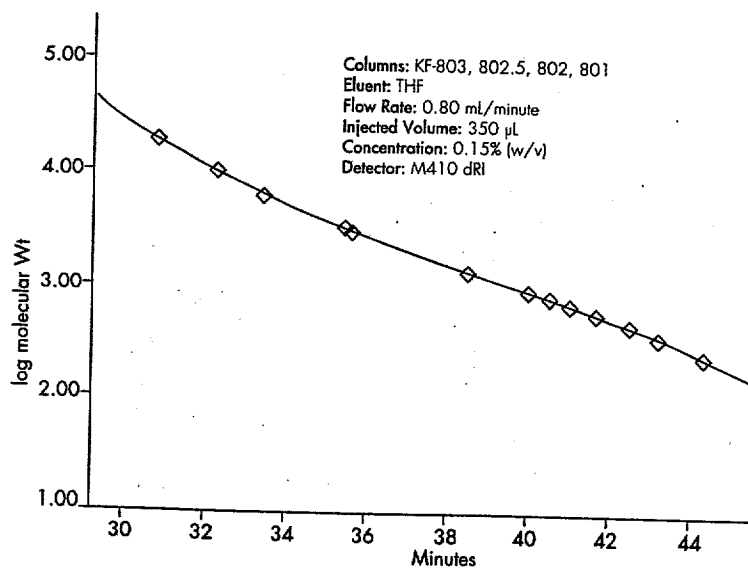


Figure 2: GPC Chromatogram for a Typical Solid Epoxy Resin

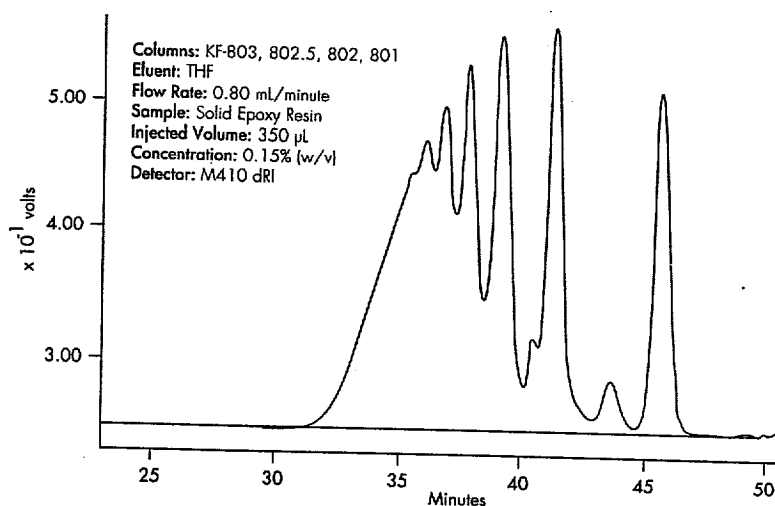


Figure 3: GPC Chromatogram for Pure DGEBA

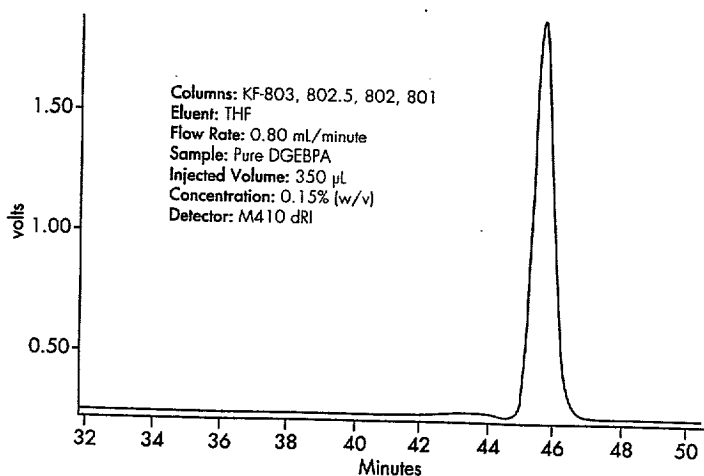


Figure 4 illustrates the chromatogram for an amine-based epoxy resin. The differences when compared to the DGEBA solid epoxy are quite easy to see.

Figure 5 shows a chromatogram for a liquid epoxy resin, with all of the components eluting >38 minutes (<1200 polystyrene equivalent molecular weight).

The last figure (Figure 6) is that of a high molecular weight epoxy novolac. Note that the material begins to elute at 27.5 minutes, which is very close to the void volume (determined to be 27.3 minutes with a 1,000,000 polystyrene standard). The lower molecular weight oligomers are separated very nicely between 40 and 47 minutes, which is what most analysts are concerned with, but we may be losing some information on the high molecular weight end. An addition of the KF-804 column would prevent this resin from eluting near the void volume.

Summary

The KF Series columns are excellent for the use of characterizing low molecular weight materials such as epoxy resins. The various degrees of epoxy polymerization are separated with high resolution. Subtle molecular weight differences between epoxy resins with only slightly varying reaction mechanisms may be observed due to the linear pore volume range (>3 mL/column) in the calibration. Working with a 4-column set at a THF flow rate of 0.80 mL/min provided us with a total system plate count of 87,600 plates (4 sigma).

For ordering information on KF Series Columns, see page 29. To have a GPC specialist contact you, please check box number 8 on the business reply card and return today.

Figure 4: GPC Chromatogram for an Amine-Based Epoxy Resin

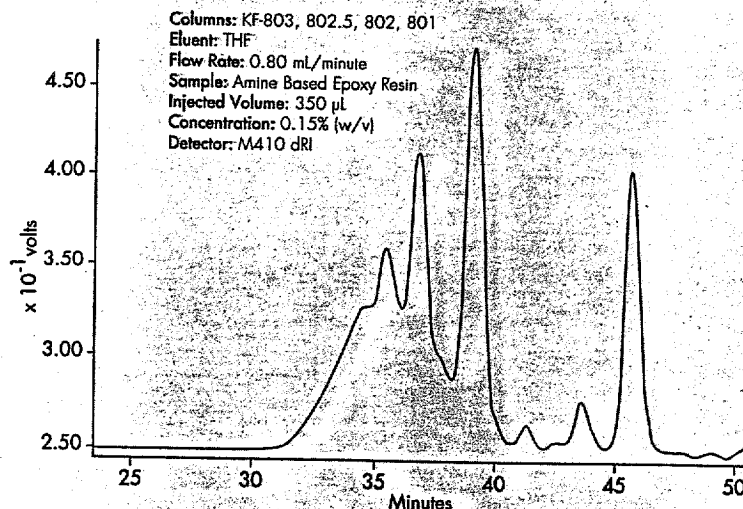


Figure 5: GPC Chromatogram for a Liquid Epoxy Resin

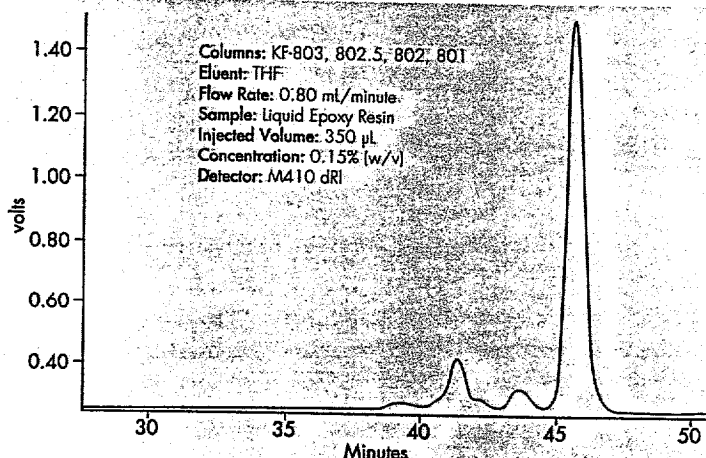
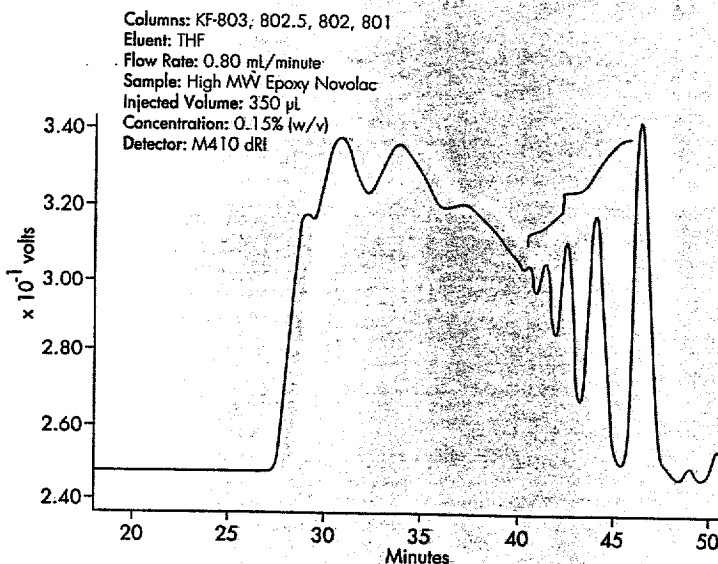


Figure 6: GPC Chromatogram of a High Molecular Weight Epoxy Novolac



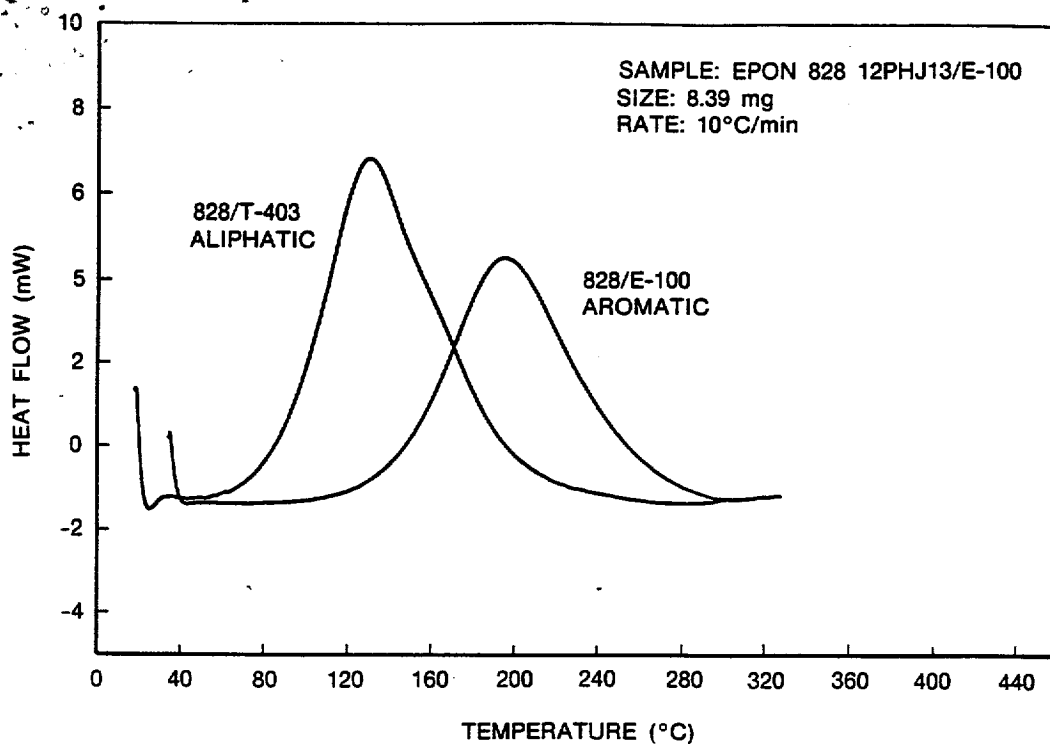


Figure 9. Dynamic DSC Scans of Amine-Cured EPON 828

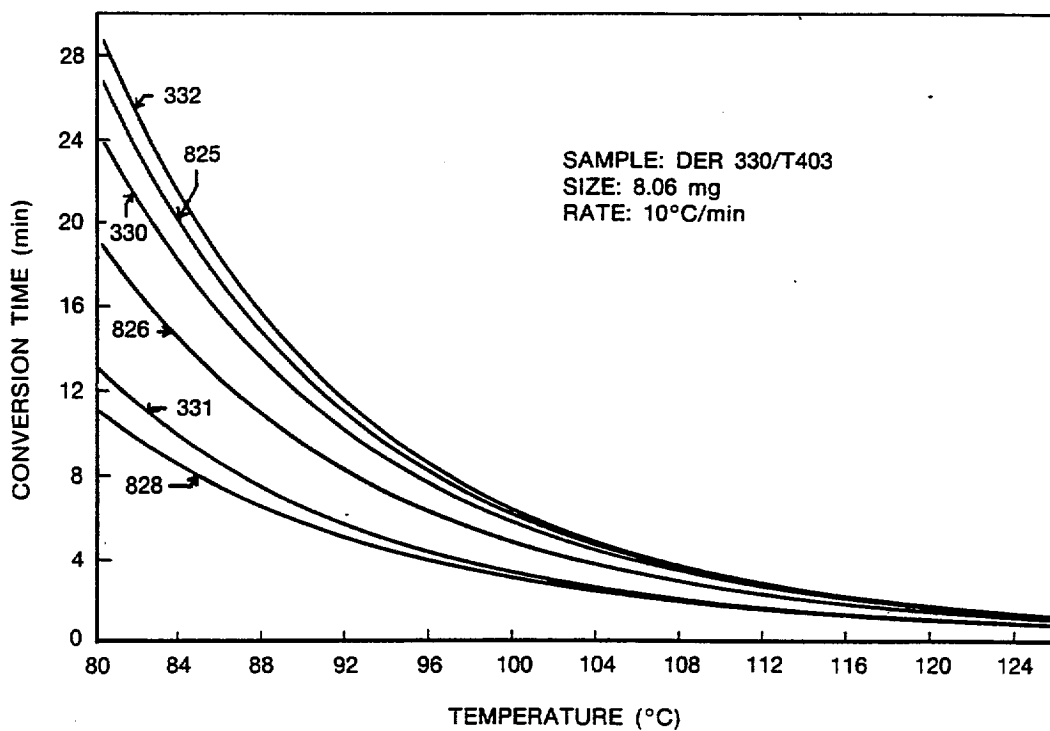


Figure 10. DSC of DER and EPON Series T-403, 20 Percent Isoconversion Plot

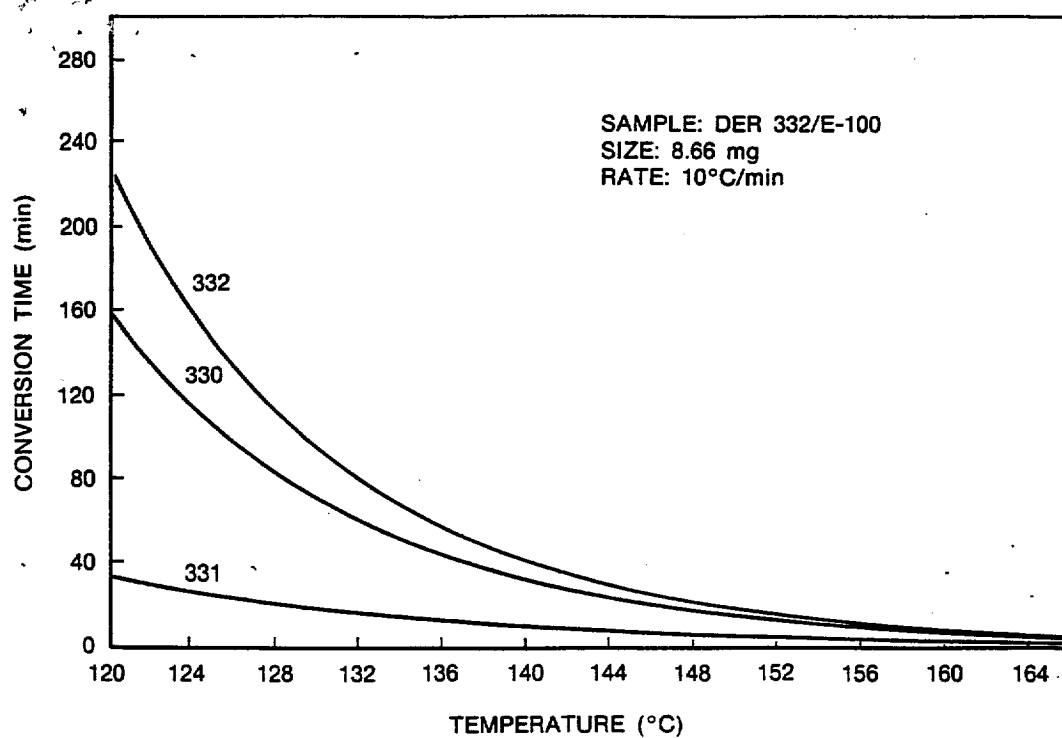


Figure 11. DSC of DER Series E-100, 20 Percent Isoconversion Plot

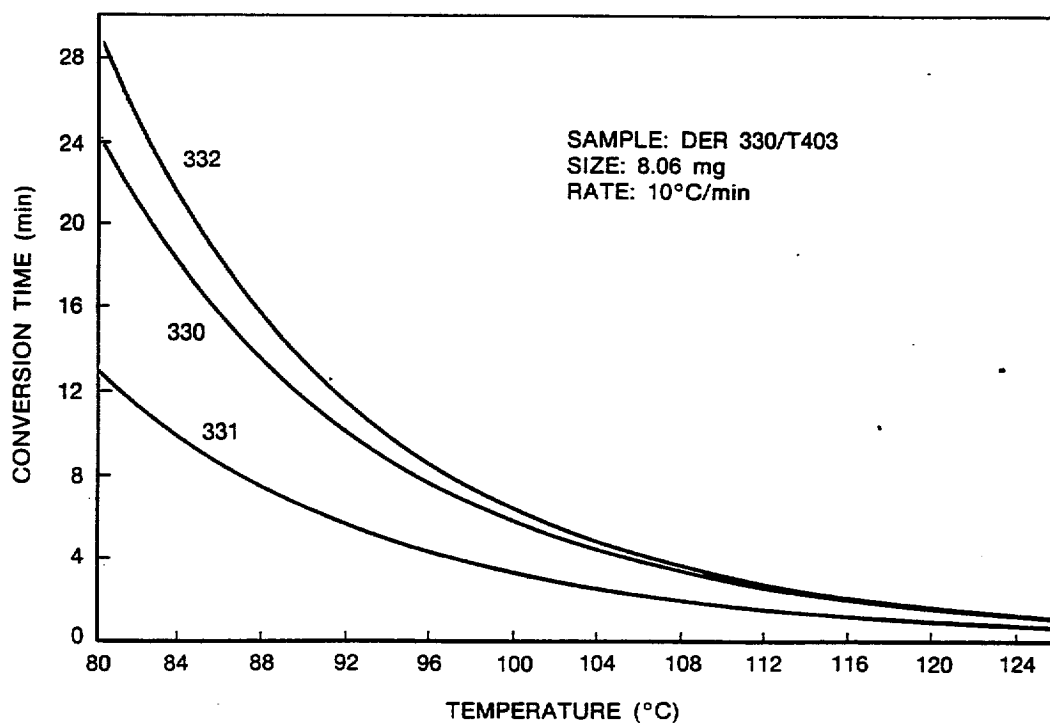


Figure 12. DSC of DER Series T-403, 20 Percent Isoconversion Plot