AMMRC TR 79-59

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HPLC AND GPC ANALYSIS OF EPON 828 EPOXY RESINS

LEVEL II

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POLYMER RESEARCH DIVISION

November 1979

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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ABSTRACT

EPON 828 samples manufactured in Australia, Canada, the United Kingdom, and the United States are analyzed using gel permeation chromatography (GPC) and reverse bonded-phase high performance liquid chromatography (HPLC). Variations in resin composition are monitored and quantitatively analyzed. Molecular weights calculated from GPC data are in close agreement with values determined by vapor phase osmometry. Differences in chemical composition are much more apparent when the resins are monitored using the HPLC method than by GPC. The results of the analyses and limitations of the methods are discussed.

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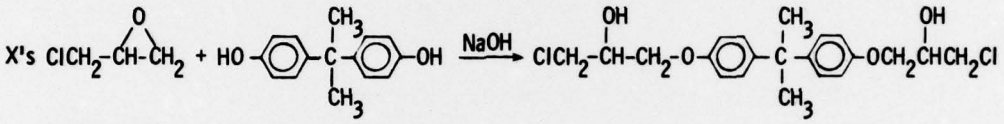
INTRODUCTION

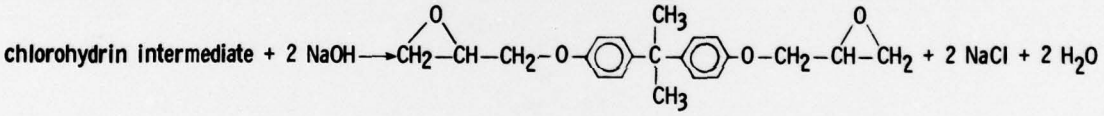
There is concern that resins with the same name but produced commercially in different locations may vary in chemical composition and that such variations may affect the properties of materials manufactured from such resins. Shell Chemical's epoxy resin EPON 828 is typical in that it is produced in different parts of the world and is widely used, for example, in the manufacture of composites for critical structural applications. Conceivably, the chemical composition of EPON 828 could vary as a result of differences in raw materials used in its manufacture as well as of differences in manufacturing technology and handling procedures.

EPON 828 is obtained by reacting an excess amount of epichlorohydrin with bisphenol A in the presence of a caustic such as sodium hydroxide.[1,2] The caustic catalyzes an initial reaction to form the chlorohydrin intermediate.



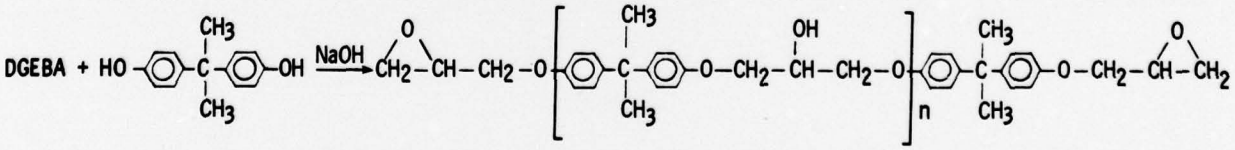
epichlorohydrin bisphenol A chlorohydrin intermediate

The caustic then acts as a dehydrohalogenating agent to form the epoxide rings (DGEBA-diglycidyl ether of bisphenol A) and neutralize HCl resulting from the reaction.



DGEBA

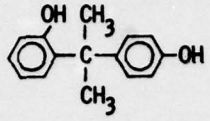
And, in the presence of excess caustic, higher molecular weight DGEBA oligomers are formed by the reaction of DGEBA with bisphenol A.



Process conditions are controlled such that the product, designated EPON 828, has an average repeat unit n = 0.2 with an epoxy equivalent weight 185 to 192 g/eq and a viscosity of 100 to 160 poise at 25 C.[1]

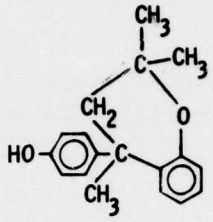
Depending upon source and grade, commercial bisphenol A varies in purity from 92% to 99+% of the para-para isomer 4,4'-isopropylidenediphenol.[3] Major organic impurities include the ortho-para isomer

1. LEE, H. and NEVILLE, K. *Handbook of Epoxy Resins.* McGraw-Hill Book Company, New York, 1967.
2. *Epoxy Resins* in Encyclopedia of Polymer Science and Technology, v. 6, N. M. Bikales, ed., John Wiley & Sons, Inc., 1967, p. 213-216.
3. SZAP, P., KESSE, I., and KLAPP, J. *The Analysis of Bisphenol A by High Performance Liquid Chromatography.* Journal of Liquid Chromatography, v. 1, 1978, p. 89-96.



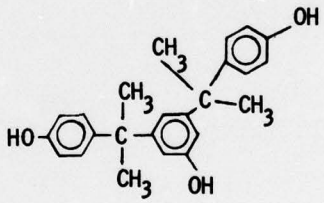
2,4'-isopropylidenediphenol,

Dianin's compound



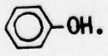
4,4'-hydroxyphenyl-2,2,4-trimethylchroman,

the triphenol BPX



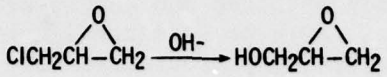
2,4-bis(α,α-dimethyl-4-hydroxybenzyl)phenol (BPX),

and phenol

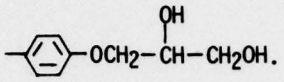


The most critical impurity with respect to EPON 828 production is probably BPX since its trifunctionality gives rise to cross-polymerization and leads therefore to higher viscosities. The BPX impurity in bisphenol A may be as much as 1.5 wt%. Being monofunctional, Dianin's compound and phenol are chain terminators and would tend to lower viscosities. However, the level of Dianin's compound and phenol is generally too low (<0.1 wt%) to have much of an effect. The ortho-para isomer of bisphenol A may be present in concentrations as high as 5 wt% but is considered of minor importance because of its similarity to the para-para isomer.[3]

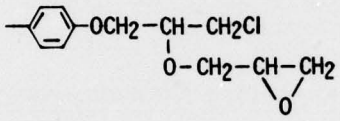
Under the basic reaction conditions, some epichlorohydrin may undergo hydrolysis



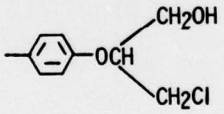
which upon reaction with bisphenol A gives rise to species with the group



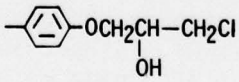
Also, epichlorohydrin may oligomerize to produce species of the type



which contain chlorine that is not readily saponifiable. Although the bisphenol A anion generally adds to the least substituted epoxide carbon atom of epichlorohydrin, it is possible that some reaction may occur at the most substituted carbon atom to produce 1,3-chlorohydrins



which are not subject to ring closure. Even with excess epichlorohydrin a small amount of bisphenol A may not react and thereby give rise to species with the group  in EPON 828. And incomplete dehydrochlorination in reaction (2) may lead to impurities of the type



with saponifiable chlorides.

Other components, such as monofunctional phenols or polypropylene glycol, may be added during synthesis to reduce viscosity, or higher molecular weight epoxy resins may be mixed with the DGEBA products to increase viscosity. Water, organic solvents, and inorganic salts not completely removed after synthesis may also be present as impurities in EPON 828.

The object of this report is to analyze EPON 828 samples obtained from different countries to determine how extensively the samples may differ from one another in chemical composition. Samples for this study were furnished by

representatives from member countries of the Technical Cooperation Program Sub Group P, Technical Panel 3 (TTCP-3) for Organic Materials and include EPON 828 samples manufactured in Australia, Canada, the United Kingdom, and the United States. Elemental analyses were obtained and number-average molecular weights were evaluated for each sample. High performance liquid chromatography (HPLC) and gel permeation chromatography (GPC) procedures were developed to fingerprint the chemical compositions and to quantitatively analyze major components of the EPON 828 samples. The results of the analyses and limitations of the methods are discussed.

EXPERIMENTAL

The EPON 828 samples are identified by the country in which they were manufactured. Batch or lot numbers are given in Table 1. The purified resin, denoted as DGEBA, is the p-p' diglycidyl ether isomer of bisphenol A with n = 0. The p-p' DGEBA is a white, crystalline solid with a melting point of 44 to 45 C.

Table 1. RESIN IDENTIFICATION, ELEMENTAL ANALYSIS AND $\bar{M}_n$ VALUES

Sample	Batch or Lot No.	%C	%H	%Cl	$\bar{M}_n$ (g/mol)
AUST	17191	74.13	7.04	0.20	395
CAN	781-435 Lot #1	74.16	7.16	0.041	384
UK	1U3819	74.17	7.03	0.29	374
USA	Lot 11THJ19	74.25	7.19	0.32	381
DGEBA*	--	74.16	7.20	0.051	339

*Purified by crystallization from a concentrated solution of Dow DER332 in methyl ethyl ketone at -10 C.

Carbon, hydrogen, and chlorine analyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee. A Hitachi-Perkin Elmer model 115 vapor phase osmometer was used to determine the number-average molecular weights $\bar{M}_n$ with ethyl acetate as the solvent at 35 C.

A Waters ALC/GPC-244 instrument, with 6000A solvent delivery system, 660 solvent programmer, WISP auto-injection system or U6K injector, and 440 UV absorbance detector was used for the HPLC and GPC analyses. A Spectra Physics SP4000 data system with SP4020 data interface and SP4050 printer/plotter was used for peak integration and data formatting.

Freshly distilled solvents were used. Tetrahydrofuran (THF) was dried over molecular sieves and distilled from calcium hydride. ASTM-type reagent grade water was prepared from distilled water using a Millipore Milli-Q2 water purification system. Solutions were prepared by weighing 0.5-g samples in 50-ml volumetric flasks and diluting to the mark with THF. All solvents and solutions were filtered through 0.22 μ Millipore filters.

For gel permeation chromatography (GPC), four μStyragel columns (120 cm × 7.8 mm ID) having porosities of 1000, 500, 100, 100 A were used with THF as the mobile phase. The flow rate was 2.0 ml/min and standard injection volume was

10 μℓ. Effluents were monitored using a 254-nm UV detector and a recorder chart speed of 0.5 cm/min. Samples were manually injected using the U6K injector.

Reverse bonded-phase HPLC was performed with gradient elution using a Bondapak C18 column (30 cm × 3.9 mm ID). The mobile phase was programmed with a linear gradient (Gradient 6) from (40/60) THF/H_2O to 100% THF over a period of 30 minutes at a flow rate of 2.0 ml/min. The standard injection volume was 10 μℓ and the effluents were monitored using a 280-nm UV detector and a recorder chart speed of 1.0 cm/min. Samples were automatically injected using the WISP autoinjection system.

A 0 to 10-volt input range card on the Spectra Physics SP4020 data interface was used to interface the SP4050 printer/plotter to the Waters model 440 UV absorbance detector output (0 to 2 volts). An attenuation setting of 10 was used for plotting all chromatograms. Data system parameters were adjusted to optimize integration for quantitative analysis. Peak retention times are printed on the chromatograms in "seconds" (sec) immediately following each peak.

RESULTS AND DISCUSSION

The elemental analyses and $\bar{M}_n$ values for the resin samples are shown in Table 1. Assuming n = 0.2, the theoretical elemental analysis of EPON 828 is C, 74.40%; H, 7.06%; O, 18.55%; Cl, 0%. Calculated from its epoxy equivalent weight, assuming 2 equivalents per mole, the molecular weight of EPON 828 should be in the range 370 to 384 g/mol. It is noted that the percent carbon tends to be slightly less than the theoretical values and that the samples contain chlorine with the possible exception of the sample manufactured in Canada. Except for the Australian sample, the $\bar{M}_n$ values are in the range expected for EPON 828. The elemental analysis and $\bar{M}_n$ of the standard DGEBA are in quite good agreement with its theoretical values: C, 74.12%; H, 7.06%; O, 18.82%, and $\bar{M}_n$ = 340 g/mol.

GPC and reverse bonded-phase HPLC fingerprints for the EPON 828 samples are compared in Figures 1 and 2. Variations in resin composition are apparent in both sets of chromatograms. As shown in Figure 2, not only do the relative amounts of resin components differ, as indicated by the peak heights, but also components, indicated by peak retention times, appear in some samples but are not evident in others. The dominant peak in the GPC and HPLC chromatograms is due to the p,p' DGEBA isomer. Peaks in the GPC chromatogram were correlated with those in the HPLC by collecting the effluent producing each peak in the GPC analysis and analyzing the GPC effluents by HPLC. If peaks in the GPC chromatogram are assigned numbers 1, 2, 3, 4, and 5, their counterparts will occur at the retention times designated in Figure 3. The effluent from the GPC peak 5 does not produce a peak upon HPLC analysis since the molar absorptivity of the component is apparently too low to produce a peak with 280-nm UV detection. The GPC peak at 1301 to 1305 sec is due to a solvent impurity.

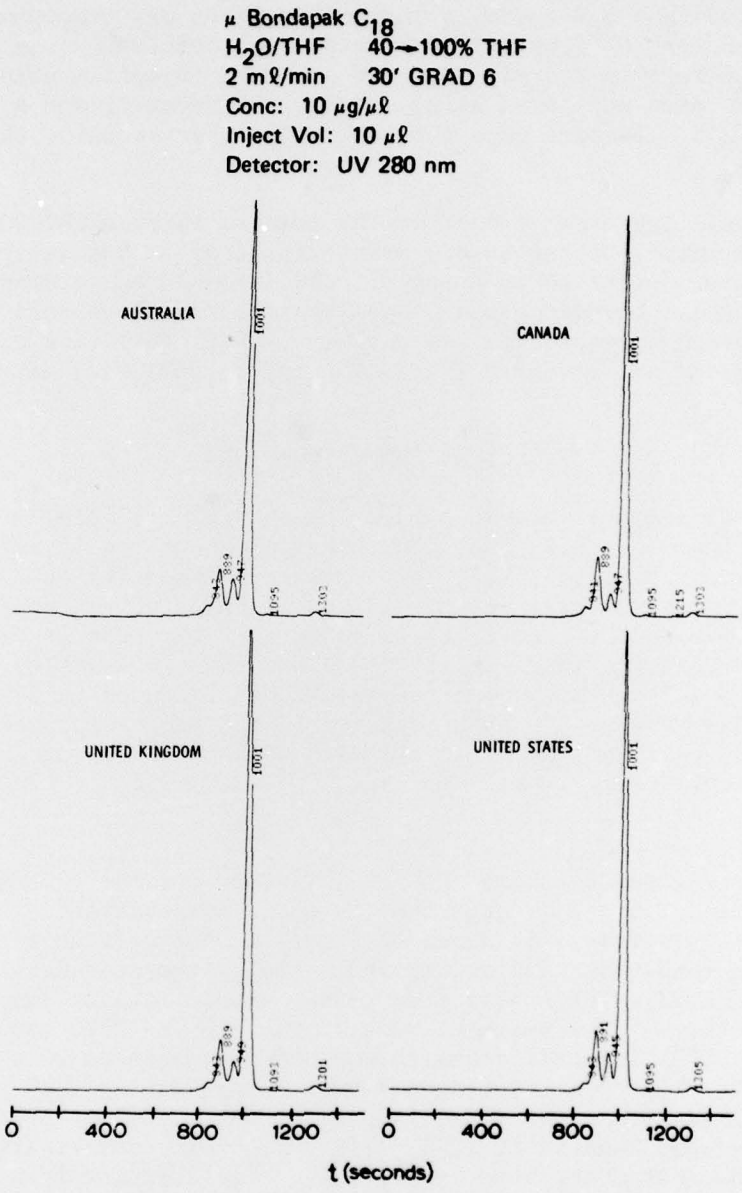


Figure 1. GPC analysis of EPON 828.

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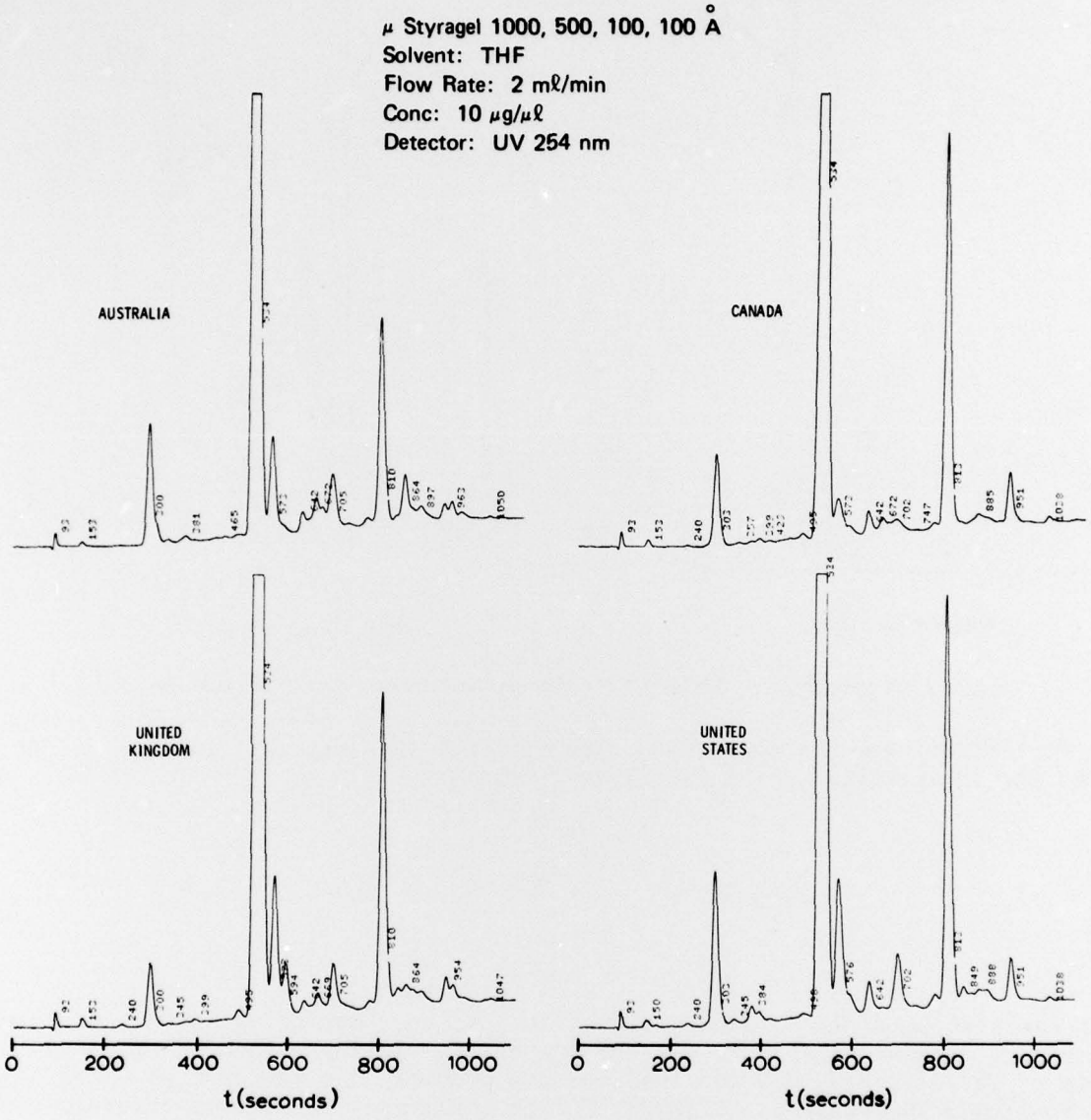


Figure 2. HPLC analysis of EPON 828.

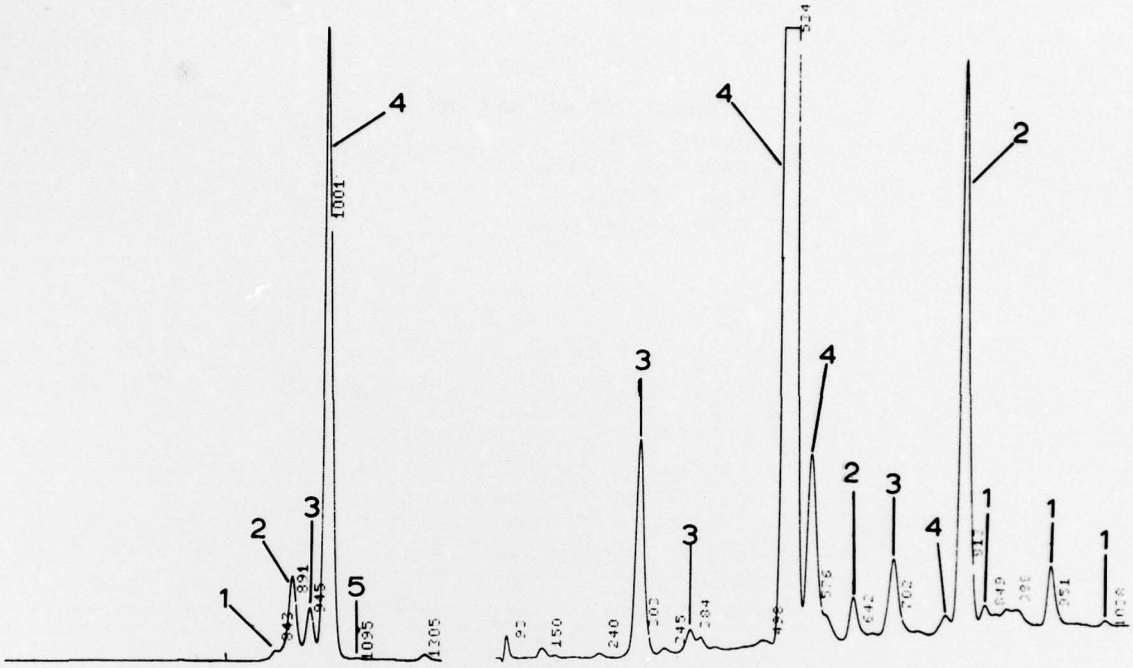
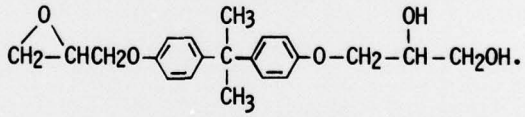


Figure 3. A comparison of GPC and HPLC effluent peaks obtained in EPON 828 analysis.

Preliminary spectroscopic data suggests that the component eluting at 300 to 303 sec in the HPLC is the dihydroxy species



The p,p' DGEBA (n=0) isomer elutes at 534 sec. According to GPC and HPLC separation mechanisms (Figure 3), the components eluting with HPLC retention times of ca. 575, 810, 950 and 1040 sec are probably due to the o,p' DGEBA monomer (n-0) and the DGEBA dimer (n=1), trimer (n=2) and tetramer (n=3), respectively.

A quantitative estimate of how the resins differ in composition may be obtained by comparing the area percentages of the GPC peaks (Table 2). Using the standard DGEBA, the weight percentage of DGEBA (n=0) may be determined from peak area and peak height measurements. The calibration constants obtained from peak area and height measurements of the DGEBA standard are K_a = 0.200 g/mV-sec and K_h = 0.592 g/mm, respectively. The weight percentage DGEBA (n=0) may be calculated as follows

$$\text{WT\% DGEBA (n=0)} = \frac{K_a \cdot A}{V \cdot C} \cdot 100\% \quad (1)$$

or

$$\text{WT\% DGEBA (n=0)} = \frac{K_h \cdot H}{V \cdot C} \cdot 100\% \quad (2)$$

where C is the sample concentration in $\mu g/\mu \ell$, V is the injection volume in $\mu \ell$, and A or H is the DGEBA (n=0) peak area (mV-s, millivolt-second) or height (mm, millimeter). The difference in weight percent DGEBA (n=0) determined by the peak area and height methods (Table 3) is mainly due to the presence of components other than the one used for calibration eluting under the GPC peak 4. Also, the weight percent method of determining differences in DGEBA (n=0) concentration tends to be less precise than the area-percent method because the calculation depends on the amount of resin injected. The average error in the injection volume for the manual injection is about 2%. The tendency for slightly smaller percent DGEBA (n=0) values using the area-percent method may be a consequence of differences in the molar absorptivities of the various resin components as well as to peak shape differences which enter into the area-percent calculation.

The weight-percent DGEBA (n=0) values obtained from the GPC analysis of the EPON 828 samples agree within experimental error. However, the area-percent values for each component peaks in Table 2 show differences which are analytically significant. By GPC analysis it is possible to discriminate between the EPON 828

Table 2. GPC ANALYSIS OF EPON 828

	Area-Percent						
GPC Peak #	1	2	3	4	5		
Main Component	DGEBA (n>1)	DGEBA (n=1)	Dihydroxy DGEBA	DGEBA (n=0)	Unknown	M_n (g/mol)	M_w (g/mol)
AUST	2.83	12.04	7.80	77.08	0.25	368	391
CAN	2.28	13.67	4.60	79.09	0.28	370	391
UK	1.29	10.83	5.44	82.33	0.12	362	379
USA	0.97	12.32	6.68	79.50	0.10	364	381

*The M_n and M_w values are calculated from the area-percent and molecular weights of the known main components.

Table 3. GPC ANALYSIS OF DGEBA (n=0)

	Weight-Percent	
Sample	Peak Area	Peak Height
AUST	80.8	81.1
CAN	81.1	84.7
UK	82.6	81.6
USA	81.7	82.5

samples. It is also noted that the molecular weights calculated from the data in Table 2 are in quite close agreement with the experimentally determined values in Table 1. The number-average molecular weight M_n and the weight-average molecular weight M_w are calculated according to the equations

$$M_n = A_i / \sum_{i=1}^{4} (A_i/M_i) \tag{3}$$

or

$$M_w = (A_i M_i) / \sum_{i=1}^{4} A_i \tag{4}$$

where A_i is the area-percent of peak $\underline{i}$ and assuming $M_1 = 906$, $M_2 = 624$, $M_3 = 358$, and $M_4 = 340$ g/mol.

Quantitative analysis of component peaks in the reverse bonded-phase HPLC chromatograms also indicate differences in resin composition (Table 4). The p,p' DGEBA (n=0) isomer is quantitatively analyzed using Equation 1 with K_a = 0.0567 μg/mV-s. The percent p,p' DGEBA (n=0) determined by the area-percent method is less than the weight-percent value probably because the molar absorptivities of other components tend to be somewhat larger at 280 nm than that of p,p' DGEBA (n=0). The weight-percent p,p' DGEBA (n=0) is determined with greater precision by HPLC than by GPC analysis since automatic injection reduces the error in the injection volume to less than 1% and because p,p' DGEBA (n=0) is fully resolved from other components by HPLC.

Table 4. HPLC ANALYSIS OF EPON 828

	Area-Percent			
Retention Time (seconds)	300	534*	575	810
Component	Dihydroxy DGEBA	p,p' DGEBA (n=0)	o,p' DGEBA (n=0)	DGEBA (n=1)
AUST	4.22	63.78 (69.8)	4.64	9.54
CAN	2.94	67.22 (76.0)	1.60	13.97
UK	1.84	67.38 (71.6)	3.79	10.93
USA	4.24	71.19 (72.1)	4.89	11.86

*Weight-percent values are in parentheses.

Significant quantitative differences are evident in all four components listed in Table 4. The relatively small amount of o,p' DGEBA (n=0) in the Canadian sample suggests that a higher quality bisphenol A may have been used in the manufacture of the Canadian EPON 828. It is also noted that the DGEBA (n=1) dimer is more abundant in the Canadian sample. If a component such as dihydroxy DGEBA

has an effect on epoxy reactivity, differences in its relative concentration may be of considerable importance when considering the aging and curing behavior of the EPON 828 samples. Furthermore, unidentified components which appear as minor peaks in the HPLC chromatograms and which may be present in some samples but not in others may have profound effects on resin stability and on the durability of items manufactured from the resin. Due to the number of separated components as suggested by the variety of peaks and because of the differences in peak areas, it is quite easy to discriminate between the EPON 828 samples using the HPLC method.

CONCLUSION

EPON 828 resins manufactured in different countries have variations in their chemical compositions that can be monitored and quantitatively analyzed using GPC and reverse bonded-phase HPLC. Differences are discerned in DGEBA isomer and oligomer concentrations. Molecular weights calculated from GPC data are in close agreement with values determined by vapor phase osmometry. Better resolution of components is obtained using the HPLC method than by GPC. If pure standards are available for calibration, the HPLC method is more accurate for quantitative analysis than GPC. Differences in chemical composition are much more apparent using the HPLC method.

A limitation of HPLC and the ultimate problem in quality control is that all the components in EPON 828 have not been identified and it is uncertain which components need to be monitored. Indeed, components may be present which are important to monitor but which are either not resolved from other components by the HPLC method or are not detectable by the 280 nm UV monitor. For example, elemental analysis shows that some of the EPON 828 samples contain as much as 0.3% chlorine, but no peaks in the chromatograms are identified as being produced by chlorine-containing compounds. As described in the Introduction, a variety of chlorine-containing compounds may be present in EPON 828; and some of these compounds may have profound effects on resin stability as well as on the durability of items manufactured from the resin. To help solve this dilemma in quality control, it is necessary to identify as many of the components in EPON 828 as possible and to determine which components are most important to control. The HPLC method must then be modified, if necessary, to optimize the separation and detection of such components. For example, a photoconductivity detector such as the model 965 manufactured by Tracor Instruments, Austin, Texas, is a selective detector for certain types of halogenated organic compounds and could be used with HPLC or GPC to monitor EPON 828 for certain chlorine-containing compounds.

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