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APPLICATIONS OF GEL PERMEATION CHROMATOGRAPHY IN THE MANUFACTURE OF EPOXY-GLASS PRINTED CIRCUIT LAMINATES

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SUMMARY

An IBM 1440 data processing system has been adapted to perform on-line data collection and analysis and has been applied to the analysis of an epoxy resin system used in printed circuit lamination. A feature of the computer program allows performance of independent calculations on selected portions of the chromatogram.

In practice, gel permeation chromatography has been effectively applied to monitor epoxy resin molecular distributions through each step of a laminating process to final gel. It has been shown that molecular weight distribution is a more useful parameter than epoxy equivalent weight for describing resin reactivity variations. Gel permeation chromatography also provides a convenient means of following resin advancement through the prepreg state. Studies of the "B" stage resin relate gel-time sensitivity to small changes in molecular weight distribution.

INTRODUCTION

Applications of gel permeation chromatography (GPC) to the characterization of epoxy resins are well known and have been previously discussed in the literature[1-3]. This paper describes the application of GPC to the study of performance factors, as related to molecular distribution, at several stages of epoxy-glass printed circuit laminate manufacturing. The computerized data acquisition and analysis system used for this work is also described.

Fig. 1 is a flow diagram describing the steps required to manufacture a glass-

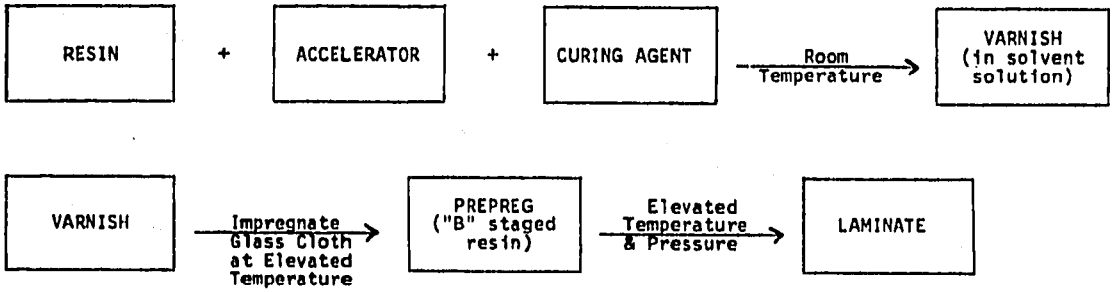

Fig. 1. Flow diagram for laminate manufacture.

filled epoxy laminate. The resin can be separated by gel chromatography at each step including prepreg manufacture. Prepreg is a dry, stable, and storable form of partially advanced or "B" staged resin on glass cloth. The resin in the cured or laminate form is too highly crosslinked for solvent solubilization. Discussion will center on (1) the relationship of molecular distribution to reproducible resin reactivity at constant epoxide equivalent weight (EEW) and (2) the effect of "B" stage advancement on the molecular distribution.

EXPERIMENTAL CONDITIONS

All samples were run on a Waters* Model 200 gel permeation chromatograph with automatic sample injection. The chromatograph is operated with tetrahydrofuran (THF) solvent at room temperature, a 1 ml/min flow rate, and a 2.5 ml syphon. Two mixed gel columns are included in an eight column configuration. Exclusion limits for the eight Styragel packed columns are 2000 to 700 Å (mixed), 700 to 50 Å (mixed), 500 Å, 350 Å, 250 Å, 250 Å, 100 Å, and 60 Å. Sample concentration is 0.25% by weight injected automatically from the 2 ml sample loop.

A calibration curve of effective chain length *versus* elution volume was prepared from three different types of molecules: *n*-alkanes, polypropylene glycols and polystyrenes. Four *n*-alkanes from Applied Science Laboratories, Inc.** were C_{12}, C_{20}, C_{25}, and C_{36}. Two polypropylene glycols of peak Å 56.9 and 84.4 (corrected for THF association) and four polystyrenes of peak Å 117, 244, 480, and 1,220 were obtained from Waters Associates'. The actual curve was constructed from two linear polynomial equation fits to the two most linear portions of the curve. Apparent molecular sizes for each 2.5 ml elution volume or single count were subsequently determined through substitution into the appropriate equation. Apparent molecular size was selected as the criteria for comparison. This method of calibration was considered adequate for the intended purpose of comparing similar polymers within the same laboratory.

The "gel time" is the time in seconds required for a solvent-containing varnish to reach a tack-free gel at 300° F. In practice there are many variations of this test but any reproducible test (± 3 sec) measuring the same approximate degree of crosslinking would suffice for the intended purpose of determining relative degree of reactivity.

Chromatographic characterization of resin

The starting brominated bisphenol A type resins used in this work were received in solvent solution and can be separated by gel chromatography without alteration. Fig. 2 is a typical chromatogram for this resin. Solvents are eluted beyond count 127 and do not interfere in the chromatogram analysis. The peak labeled $n = 0$ is the diglycidyl ether of bisphenol A (DGEBA) referred to as monomer. The probable sequence of steps in the synthesis of brominated bisphenol A type polymers requires an excess of DGEBA in the presence of brominated bisphenol A. This produces even numbered oligomers almost exclusively with alternating repeating units of brominated and nonbrominated bisphenol A units as shown in an idealized structure in Fig. 3. The small amount of $n = 1$ in Fig. 2 can be attributed to the nonbrominated starting

* Waters Associates, Inc., Framingham, Mass.
** Applied Science Laboratories, Inc., State College, Penn.

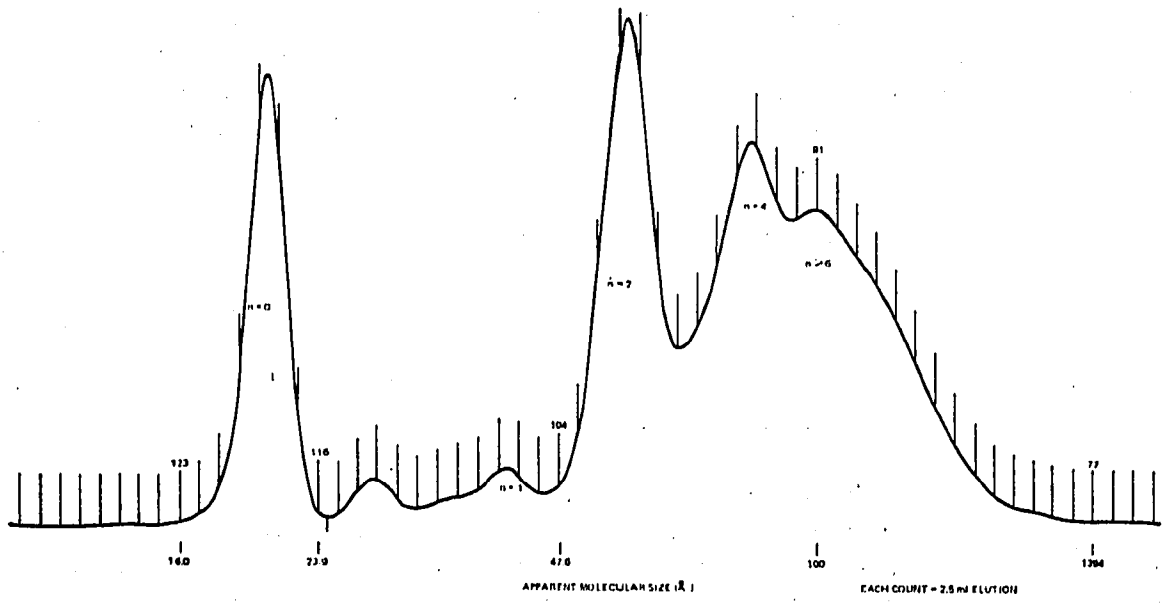

Fig. 2. Brominated bisphenol A resin.

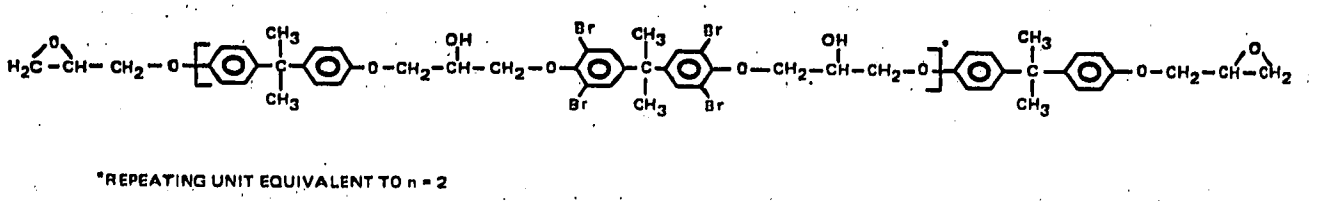

Fig. 3. Structure of brominated bisphenol A resin.

material which always contains a small quantity of all low-numbered oligomers. If $n = 0$ is considered monodisperse, then $n = 2$ closely approximates a monodispersed oligomer. Although not monodisperse, $n = 4$ and 6 are clearly defined oligomer peaks in the resin. Beyond this oligomers are not discernible but probably exist in small quantities as high as $n = 100$ or more.

DATA ACQUISITION SYSTEM

The data acquisition and reduction system consists of a modified IBM 1440 data processing system programmed for the specific application. The system program monitors the output from the GPC for a predetermined number of elutions, places the data in a table, and performs the following functions after the run is completed: (1) calculates linear base line drift and applies the correction to area accumulation and all molecular weight parameters; (2) calculates the molecular weight parameters of $\bar{A}_n$, $\bar{A}_w$, $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ for the overall chromatogram and, also for three independently designated portions or subareas of the same chromatogram; (3) performs area integration of the chromatogram based on a summation of concentration values

obtained from a signal reading every six seconds; and (4) records the run in histogram form giving chain lengths, accumulated areas, and accumulated weight percentages.

The semidedicated IBM 1440 data processing system was modified to accommodate the output of the Model 200 gel permeation chromatograph. Modifications include an altered serial I/O channel for attachment of nonstandard devices and the addition of a sense and operate matrix (SOM) with a single-level interrupt capability. These features enable the system program to control external equipment.

The IBM 1311 disc drive, indicated in Fig. 4, stores up to 12 previously entered calibration curves. Because the computer system is conveniently located with respect to the GPC, the IBM 1447 console is used as input for experiment initiation and exception message output. Elution and injection signals are cabled to the SOM and the analog signal from the differential refractometer is cabled to the SOM analog-to-digital converter. An IBM 1443 printer records all results in tabular and frequency polygram form. Figs. 5A and 5B are examples of a typical printout for an epoxy resin. The operator enters information for each sample as shown under "auto run". "Measurement range" designates the range for overall curve analysis. This feature allows overlap of samples for more efficient chromatographic usage. "Base range" designates the two counts from which linear baseline drift is calculated. "Skip areas" can include a maximum of three portions of the chromatogram that can be intentionally omitted from the analysis. These might be areas containing solvents or extraneous portions of polymers that interfere or do not contribute to the intended analysis. "Sub areas" can include three portions of the chromatogram for which independent calculations are made. The areas are designated by elution counts and may be wholly resolved peaks such as DGEBA in epoxy resins or portions of other broader distributions.

A preliminary chromatographic run of any unknown polymer is necessary to determine the run parameters for the program.

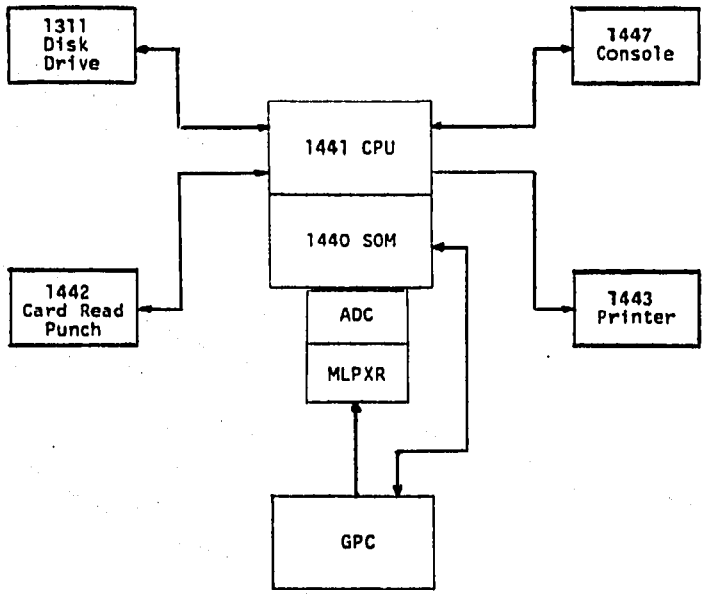

Fig. 4. 1440 System configuration.

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SAMPLE NUMBER 0004

FLOW RATE - 1.0 ML/MIN                CHART SPEED - 10 MIN/IN
SYPHON SIZE - 2.5 ML                  SENSITIVITY -  8 TIMES
SAMPLE LOOP SIZE - 2.0 ML             COLUMN SET B AUTO 2000 to   60

AUTO   RUN
CALIBRATION CURVE  1                  Q - 010
MEASUREMENT RANGE -077 123            BASE RANGE -076 149
SKIP AREAS -                          COLUMN TEMP -022 C
SUB AREAS - 077 091-010/091 104-010/116 123-010

 NAMS A N  -      52.7
 NAMW M N  -        52.7
 WAMS A W  -       87.4
 WAMW M W  -         87.4
 M W /M N  -  1.66

                    SUB AREA 1

 NAMS A N  -    138.9
 NAMW M N  -      138.9
 WAMS A W  -     171.6
 WAMW M W  -       171.6
 M W /M N  -  1.24

                    SUB AREA 2

 NAMS A N  -      70.4
 NAMW M N  -        70.4
 WAMS A W  -       73.6
 WAMW M W  -         73.6
 M W /M N  -  1.05

                    SUB AREA 3

 NAMS A N  -      20.5
 NAMW A N  -        20.5
 WAMS A W  -       20.5
 WAMW M W  -         20.5
 M W /M N  -  1.00
```

CHAIN XXXXXX.X	COUNT XXX	CONCENTRATION 0 0 0 0 0 1 1 1 1 1 2 2 2 2 2 3 3 3 3 3 4 4 4 4 5 / 0 2 4 6 8 0 2 4 6 8 0 2 4 6 8 0 2 4 6 8 0 2 4 6 8 0 / 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	AREA XXX.XX	ACCUM WT SUB-AREA XXX.XX		ACCUM WT TOTAL XXX.XX
15.56.0	INJ	*				
05.06.1	76	* BEGIN BASE DRIFT REF A * 054 *				
1394.0	77	* 000 *	0.00	100.00		100.00
1133.0	78	* 000 *	0.00	100.00		100.00
921.0	79	** 002 *	0.03	100.00		100.00
748.0	80	** 006 *	0.15	99.82		99.95
05.15.6	INJ	*				
608.0	81	** 009 *	0.34	99.26		99.81
494.0	82	* * 016 *	0.64	98.44		99.59
401.0	83	* * 030 *	1.16	96.96		99.21
326.0	84	* * 048 *	2.09	94.20		98.48
265.0	85	* * 071 *	3.54	89.79		97.33
215.0	86	* * 098 *	5.59	83.26		95.62
175.0	87	* * 121 *	8.26	74.24		93.26
142.0	88	* * 148 *	11.53	63.11		90.34
113.0	89	* * 164 *	15.15	49.49		86.78
106.0	90	* * 182 *	19.32	34.41		82.83
100.0	91	* * 192 *	23.87	17.66	100.00	78.44
94.8	92	* * 188 *	28.46	91.89		73.82
89.5	93	* * 198 *	33.04	83.94		69.29
84.5	94	* * 232 *	38.25	75.57		64.52
79.8	95	* * 212 *	43.74	65.77		58.94
75.4	96	* * 157 *	48.19	56.80		53.83
71.2	97	* * 121 *	51.50	50.17		50.05
67.2	98	* * 109 *	54.21	45.05		47.13
63.5	99	* * 160 *	57.26	40.45		44.51
59.9	100	* * 279 *	62.60	33.69		40.66
56.6	101	* * 287 *	69.53	21.89		33.94
53.4	102	* * 155 *	75.01	9.76		27.02
50.4	103	* * 055 *	77.42	3.21		23.29
47.6	104	* * 021 *	78.29	0.89		21.97
45.0	105	* * 021 *	78.77			21.46
42.5	106	* * 032 *	79.38			20.95
40.1	107	* * 033 *	80.20			20.18
37.9	108	* * 021 *	80.84			19.39
35.8	109	* * 016 *	81.28			18.88
33.8	110	* * 014 *	81.64			18.50
31.9	111	** 010 *	81.92			18.16
30.1	112	* * 016 *	82.20			17.92
28.4	113	* * 027 *	82.74			17.53
26.8	114	* * 021 *	83.37			16.88
25.1	115	** 006 *	83.68			16.38
23.9	116	** 007 *	83.81	100.00		16.23
22.6	117	* * 063 *	84.43	98.96		16.06
21.3	118	* * 224 *	87.79	89.61		14.55
20.2	119	* * 251 *	94.09	56.38		9.15
19.0	120	* * 097 *	98.32	19.14		3.11
18.0	121	* * 024 *	99.60	4.75		0.77
17.0	122	** 006 *	99.91	1.19		0.19
16.0	123	** 002 *	100.00	0.30		0.05
08.07.0	149	* END BASE DRIFT REF B * 045 *				

Fig. 5. A and B, computer printout.

TABLE I

GPC DATA FOR BROMINATED RESINS

Sub area 1 = count 77–91; sub area 2 = count 91–104; sub area 3 = count 116–123.

Batch No.	*Overall distribution*			*Sub area 1 High molecular weight*				*Sub area 2 Mid molecular weight*				*Sub area 3 DGEBA (n = 0)*				*Gel time (sec)*
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	*Weight (%)*	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	*Weight (%)*	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	*Weight (%)*	
15E	52.5	116.3	2.21	164	240	1.46	31.3	70.7	74.0	1.05	43.8	20.2	20.3	1.00	18.5	132
9F	52.3	91.6	1.75	143	191	1.34	23.5	69.8	73.4	1.05	53.5	20.5	20.6	1.00	15.8	148
85E	52.0	94.1	1.81	145	206	1.42	23.0	70.1	73.3	1.05	53.6	20.7	20.7	1.00	16.7	151
9E	50.8	85.2	1.68	139	180	1.30	21.0	69.6	73.0	1.05	54.6	20.4	20.5	1.00	16.5	157
8E	50.3	87.0	1.72	141	186	1.32	21.7	69.7	72.9	1.05	53.3	20.4	20.5	1.00	17.4	162
42E	50.0	85.7	1.72	140	188	1.35	20.2	69.5	72.7	1.05	55.3	20.5	20.5	1.00	17.8	165
95E	48.9	83.2	1.70	139	181	1.31	20.0	69.5	72.7	1.05	53.4	20.3	20.4	1.00	18.7	168
44E	49.2	77.0	1.57	132	160	1.21	17.7	69.3	72.4	1.05	57.5	20.5	20.5	1.00	17.7	175

RESULTS AND DISCUSSION

Molecular distribution areas of greatest interest in epoxy resin chromatograms are the monomer portion (sub area 1), middle molecular weight region from count 104 to 91 (sub area 2), and high-molecular-weight portion from count 91 to the interstitial volume at 77 (sub area 3) (see Fig. 2). Other chemical factors being equal, it is these areas that are the best indicators of the reproducible reactivity of an epoxy resin system. Table I gives the results for 8 different batches of the same brominated resin. All batches fall within a relatively narrow EEW range of 422 to 442. Data for all portions is shown although emphasis is on the columns of "overall distribution", "weight percent" of sub area 1, "weight percent" of sub area 2, and "weight percent" DGEBA. The data for batch 15E indicates it to be significantly different from the others. An 8 to 13 % increase in high-molecular-weight material, a like decrease in mid molecular weight, both reflected in the overall weight average, are the key indicators. Indeed, the chemical reactivity reflected in the gel time indicates it to be faster by 19 sec over its nearest neighbor. Although 15E best dramatizes the effect of increased quantities of high molecular weight material on gel time, the trend is apparent for the remaining batches. In general, as the weight average and/or weight percent of high molecular weight material increases, reactivity of the system increases resulting in lower gel times. Any variance in EEW within the range of 422 to 442 cannot account for the observed differences in reactivity. EEW is an average value only which cannot describe molecular distribution and is not a sufficient indicator of resin reactivity.

To demonstrate the effect on reactivity of a change in specific oligomeric content, DGEBA was sequentially added in known quantities to a base resin and the gel times obtained (Table II). As expected, increased quantities of low molecular weight epoxy material decreases the reactivity as indicated by longer gel times. It was necessary to demonstrate the molecular weight-reactivity relationship with low molecular weight materials because discrete oligomers of high molecular weight epoxies were not available.

In a varnish, see Fig. 6, the presence of the curing agent can be seen and quantified. The curing agent is dicyandiamide and is usually employed in quantities of 3 to 5 % by weight. Its appearance is at an approximate elution count of 124.5 and a simple calibration procedure corrects for its different refractive index response; therefore, it can be determined as a percentage of the varnish solids.

Resin from the glass impregnated prepreg in the advanced "B" stage state is soluble in THF and its molecular weight (size) distribution can be determined by

TABLE II

EFFECT OF INCREASED DGEBA CONTENT ON REACTIVITY

DGEBA content	*Gel time (sec)*
15.9 %	164
17.2 %	167
19.6 %	172
22.5 %	179

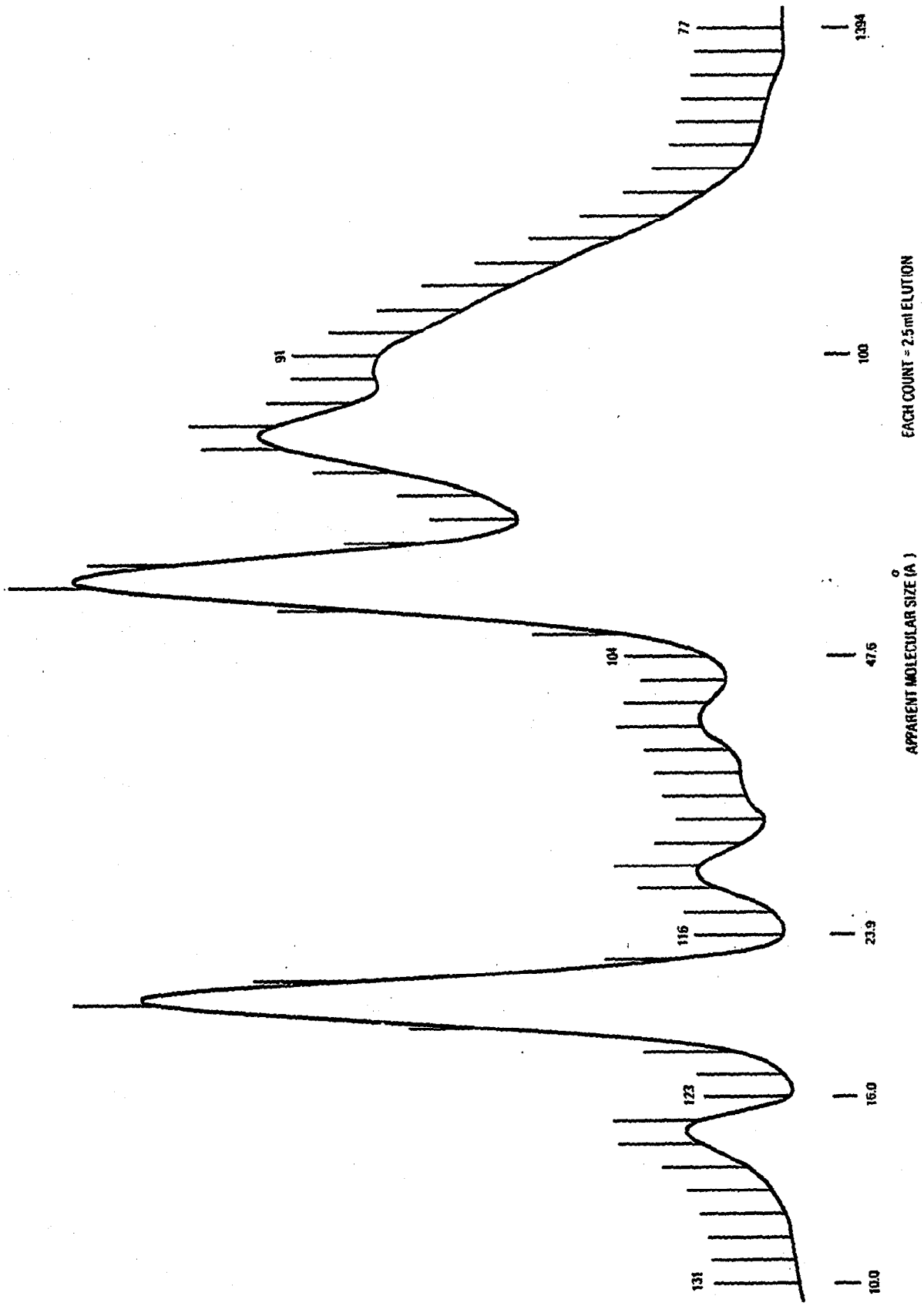

Fig. 6. Varnish.

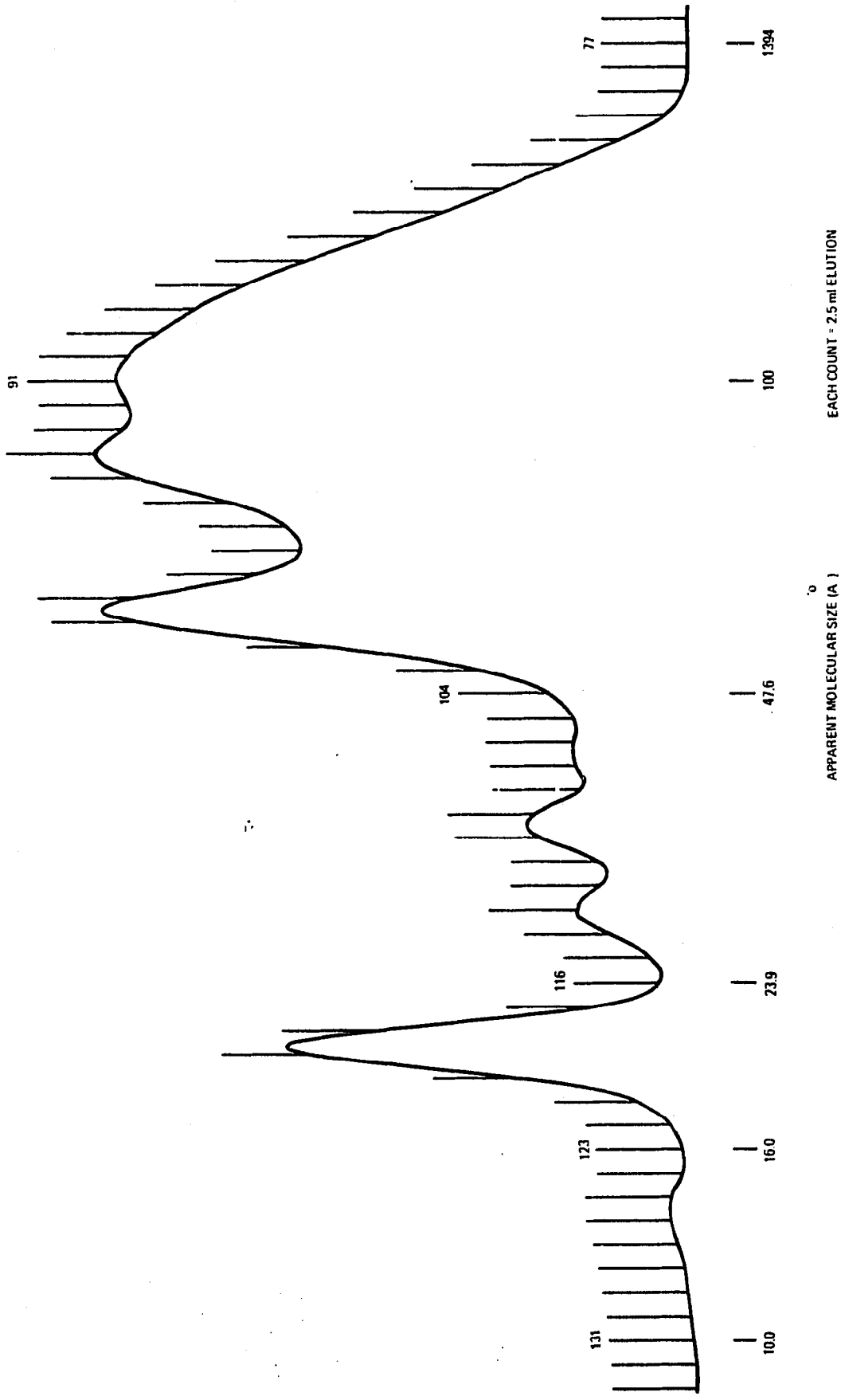

Fig. 7. Prepreg ("B" staged resin).

TABLE III

GPC DATA FOR PREPREG AND CORRESPONDING RESIN

Sub area 1 = count 77–91; sub area 2 = count 91–104; sub area 3 = count 116–123.

Sample	*Overall distribution*			*Sub area 1* *High molecular weight*				*Sub area 2* *Mid molecular weight*				*Sub area 3* *DGEBA (n = 0)*			
	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	*Weight* (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	*Weight* (%)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	*Weight* (%)
9E-Resin	50.8	85.2	1.68	139	180	1.30	21.0	69.6	73.0	1.05	54.6	20.4	20.5	1.00	16.5
9E-Prepreg	57.6	96.0	1.67	144	184	1.28	27.6	71.0	74.3	1.05	51.6	20.4	20.5	1.00	10.4
65E-Resin	50.0	81.7	1.64	172	172	1.27	19.6	69.7	72.9	1.05	54.7	20.4	20.6	1.00	17.2
65E-Prepreg	57.2	93.3	1.63	177	177	1.24	26.9	70.0	74.6	1.05	51.6	20.4	20.5	1.00	10.9

TABLE IV

GPC DATA FOR PREPREG

Sub area 1 = count 77–91; sub area 2 = count 91–104; sub area 3 = count 116–123.

Sample	*Overall distribution*			*Sub area 1* *High molecular weight*				*Sub area 2* *Mid molecular weight*				*Sub area 3* *DGEBA (n = 0)*				*Percent dicyandiamide of original concentration*
	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	*Weight* (%)	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	*Weight* (%)	$\bar{A}_n$	$\bar{A}_w$	$\bar{A}_w/\bar{A}_n$	*Weight* (%)	
150	51.9	83.3	1.61	136.5	164.5	1.21	22.26	70.5	73.7	1.05	53.27	20.2	20.3	1.00	13.94	57
200	54.9	88.1	1.60	139.0	170.4	1.23	24.39	70.7	74.0	1.05	52.91	20.4	20.5	1.00	11.99	35
250	56.3	92.0	1.63	141.5	177.3	1.25	25.87	70.8	74.1	1.05	52.18	20.4	20.5	1.00	11.08	29
300	56.7	96.6	1.70	145.2	188.0	1.29	27.26	71.0	74.4	1.05	50.41	20.3	20.4	1.00	10.63	26
350	58.0	96.0	1.66	144.3	180.9	1.25	28.06	71.1	74.5	1.05	50.52	20.3	20.4	1.00	10.05	20

GPC. The chromatogram in Fig. 7 indicates the nature of the distribution. At this point the free dicyandiamide content is less than one-third its original concentration in the varnish. Table III contains the data for two prepregs and their corresponding batches of raw resin. For each batch, the overall polydispersity remains constant but the weight and number averages are shifted to higher molecular weights. This is more clearly observed in the 6 to 7 % increase in high-molecular-weight material that indicates polymer advancement. A corresponding decrease in mid molecular weight and in DGEBA content occurs as expected.

It is possible to follow advancement of a resin through the prepreg state by means of GPC. Table IV provides data pertaining to distinct states of advancement. Relative stability of the overall weight-to-number average molecular weight material increases from 22 to 28 % while the amount of DGEBA decreases from 14 % to 10 %. These molecular distribution changes are comparable to those observed for raw resins that produced maximum gel time variations of 20 %. In the "B" stage, however, these molecular distribution changes produce considerably greater effects. Sample 350 required only one-half of the time to gel as sample 150. All of the advancement towards gel is apparently occurring through the reaction of the dicyandiamide curing agent that is being consumed at a similar rate. Whatever the mechanism, the conclusion reached is that the reactivity of "B" staged resin is particularly sensitive to small changes in molecular weight distribution.

ACKNOWLEDGEMENTS

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