

Applications of gel filtration chromatography for resole phenolic resins using aqueous sodium hydroxide as solvent

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(First received November 1st, 1989; revised manuscript received April 24th, 1990)

ABSTRACT

Suggested applications are demonstrated for a gel filtration technique previously described with a suitable gel packing material (Sephacryl) for the analysis of phenol-formaldehyde resins (resoles) and phenolic-like compounds. An alkaline solution was used as eluent which saved preparation time for the alkaline resole resins. Sodium polystyrene sulphonates were used as standards. Several chromatographic systems were used to study the phenolic resins which are typically used to bond wood composite panels including plywood, hardboard, oriented strandboard and waferboard. The studies focused on commercial and laboratory resins, formulation process variables, freeze-dried and liquid treatments of resins, varying gel packing materials, various end-use type resins, lignin-modified phenolic polymers, and lignin raw materials. The system is suitable for characterizing the molecular weight of resoles and as a quality control tool.

INTRODUCTION

Size-exclusion chromatography (SEC), such as gel filtration chromatography (GFC) and gel permeation chromatography (GPC), is a useful technique for the analysis of macromolecules. The technique is a type of chromatography that separates molecules according to molecular size. Gels of very narrow sieve fractions (approximately 5–40 μm) are used as stationary phase. The chromatograph of such a system reveals a fingerprint of the molecular weight distribution of a resin. In this article, GFC refers to aqueous SEC at less than 1 atm (1 kPa); whereas, systems using higher pressures in non-aqueous solvents are referred to as GPC.

In the U.S.A., where phenol-formaldehyde (PF) resins consume over 35% of the phenol produced, resole-type PF resins are the preferred binder for structural wood composites^{1,2}. While some chromatography data have been reported about molecular weights for resoles used by the wood industry^{3–7}, faster methods would be more practical for a quality control tool.

Efforts to develop more accurate and faster chromatographic techniques for

phenolic resins have been ongoing since the instrumentation has been developed. Many polymers such as resole phenolic resins are not totally soluble in common GPC solvents such as *N,N*-dimethylformamide (DMF) and tetrahydrofuran (THF), and altering the polymers' solubility changes their hydrodynamic volume and behaviors in GPC systems^{6,8}. Precipitating or drying the resoles causes the molecular weight to increase and solvation in such solvents as THF to decrease⁶. Acetylation of resole resins in THF did not eliminate all artifacts associated with dissolving the high-molecular-weight fractions in some studies⁶. However, artifacts of high-molecular-weight groups in phenolic resins on Merckogel Si were reported eliminated by acetylation of these groups or by the addition of lithium chloride to the mobile phase (DMF)⁹. But acetylation procedures for a phenolic resin sample take about 24 h and such time-consuming techniques do not facilitate speedy monitoring of resin production or quality control.

The development of suitable chromatography systems that use an alkaline solution as eluent, which is the medium of the alkaline resoles (*ca.* 10% caustic solids in phenol-formaldehyde wood binders), would provide a faster method for characterizing resins and serve as a quicker quality control tool when compared to current GPC methods. The time saved is related to the preparation time (5 min) and not the analytical separating flow-rate (30 to 60 min). This article summarizes some applications of just such a system.

EXPERIMENTAL

GFC system

The GFC system used in this study has been previously reported¹⁰ and may be summarized as follows: A peristaltic pump was connected to a Pharmacia preparative or an analytical chromatographic column with two adapters. The columns contained Sephadex G-100 or Sephacryl S-200 (HR). The eluent was 0.10 *M* sodium hydroxide. Blue dextran was used to determine the exclusion volume and phenol was used to determine the permeated volume. A standardization curve was produced by using sodium polystyrene sulphonate (SPS) standards (Polymers Labs.). Because of the low polydispersities, the standards M_p (peak molecular weights) were considered weight-average molecular weights (M_w) in the standardization calculations. The column was connected to an ultraviolet detector with a 280-nm filter and interfaced with a chromatographic data acquisition system. Resin samples (25 μ l) were injected onto the column using a low-pressure injector valve. The sample preparation consisted of 0.1 g of resin diluted to 10 ml with 0.1 *M* sodium hydroxide. Chromatographs were produced on a graphics plotter. Tabular molecular weight data were generated by the Nelson Chromatograph GPC software.

High-pressure GPC system

A high-pressure GPC system used for comparison is described as follows: Waters Assoc. Model 510 solvent delivery system, Model U6K injector, Model 481 Lambda-Max UV spectrophotometer, and calculations on Waters Assoc. software using commercial polystyrene molecular weight standards. The separation was performed on a Polymer Laboratory 60 cm \times 1 cm mixed gel of 10 μ m, a mobile phase of mainly DMF, a flow-rate of 1 ml/min, an injection volume of 25 μ l, a sample

preparation of 0.1 g of resin in 3 drops of water added to 5 ml of mobile phase and a run time of 31 min.

RESULTS AND DISCUSSION

Table I shows the molecular weight distribution of three commercial phenolic resins used to bond plywood, hardboard and oriented strandboard wood composites. The chromatographs for these resins are shown in Fig. 1. The plywood resin (A) has the highest \bar{M}_w average (11 237), followed by the dry-process hardboard resin (B) (3903 \bar{M}_w) and the oriented strandboard resin (C) (1574 \bar{M}_w). In terms of distribution, the plywood resin has over 40% above 10 000 \bar{M}_w and less than 5% below 2000 \bar{M}_w ; the hardboard resin has 11% above 10 000 \bar{M}_w and over 50% below 2000 \bar{M}_w ; and the OSB resin has less than 2% above 10 000 \bar{M}_w and over 70% below 2000 \bar{M}_w (with over 50% below 1000 \bar{M}_w).

As shown in Fig. 2, resoles used to make similar wood composite products are diverse in molecular weight. This diversity is dictated by the resin raw materials, composite process, wood species and the end use (exterior vs. interior) of the wood composite products. In this hardboard case, the wet process depends heavily on precipitating of the phenolic resin solids prior to final cure and the dry process depends on accelerated condensation at immediate high temperatures.

Most PF resin types have molecular weights below 18 000. However, column packing material should be able to accommodate the higher ranges (ca. 35 000 \bar{M}_w) of molecular weight distribution such as occurs in North American plywood PF resins.

TABLE I

COMPARISON OF GFC MOLECULAR WEIGHT DISTRIBUTION (AREA PERCENT) OF THREE LIQUID COMMERCIAL RESOLE RESINS USED TO BOND WOOD COMPOSITES

M_w = weight-average molecular weight; M_n = number-average molecular weight.

Molecular weight range	Area percent ^{a,b}		
	OSB (C)	Hardboard (B)	Plywood (A)
> 35 000	0.0(0.0)	0.3(0.3)	0.4(0.4)
35 000–18 000	0.3(0.3)	5.7(6.0)	25.9(26.3)
18 000–10 000	1.3(1.6)	5.1(11.1)	16.0(42.3)
10 000–5000	5.1(6.7)	6.5(17.6)	14.6(56.9)
5000–3000	8.0(14.7)	12.3(29.9)	23.6(80.5)
3000–2000	8.7(23.4)	13.8(43.7)	15.3(95.8)
2000–100	18.8(42.2)	19.8(63.5)	3.9(99.7)
1000–500	20.0(62.2)	17.4(80.9)	0.3(100.0)
500–100	37.8(100.0)	19.1(100.0)	0.0(100.0)
\bar{M}_w	1574	3904	11237
\bar{M}_n	343	769	5079
\bar{M}_w/\bar{M}_n	4.58	5.07	2.21

^a The results were obtained using Sephacryl S-200 HR and were based on sodium polystyrene sulphonate standards. The area percent values in this table correlate to the letters in Fig. 1 with (C) oriented strandboard (OSB), (B) dry-process hardboard and (A) plywood-type phenolics.

^b The numbers in parentheses represent accumulations.

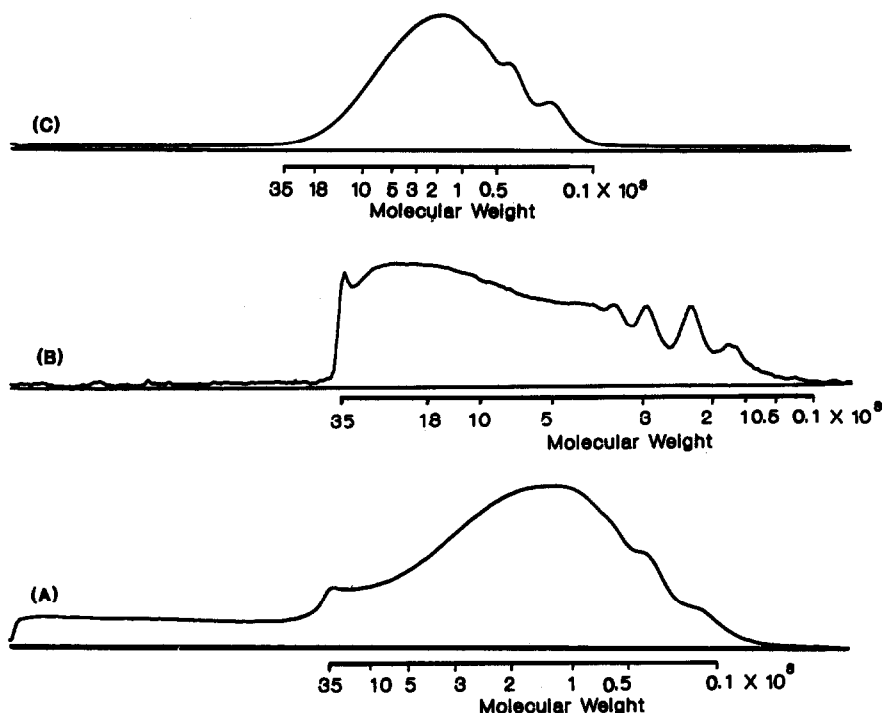


Fig. 1. Chromatographs of GFC molecular weight of three commercial phenolic resins used to bond wood composites. (A) Plywood; (B) dry-process hardboard; (C) Oriented strandboard. (See Table I).

Fig. 3 compares chromatographs using Sephadex G-100 and Sephacryl S-200 HR for a single commercial oriented strandboard PF resin (results exclude urea content). While providing a higher molecular weight range for delineation than Sephadex, Sephacryl also enhances the percent of the area within the 2000–5000 \bar{M}_w range. However, above Sephadex's upper limit, the reaction of higher molecular weight

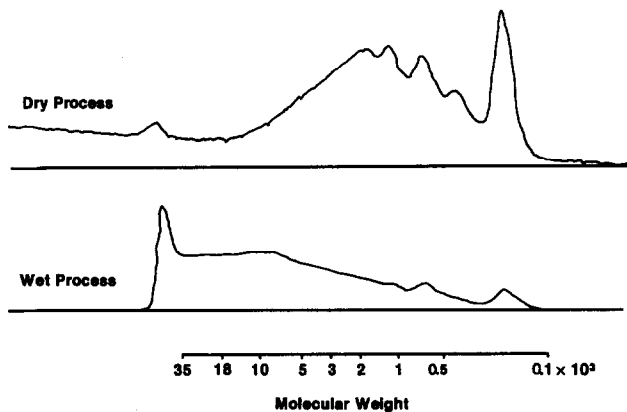


Fig. 2. Chromatographs of GFC molecular weight of two commercial resins used to bond hardboard manufactured by two different processes.

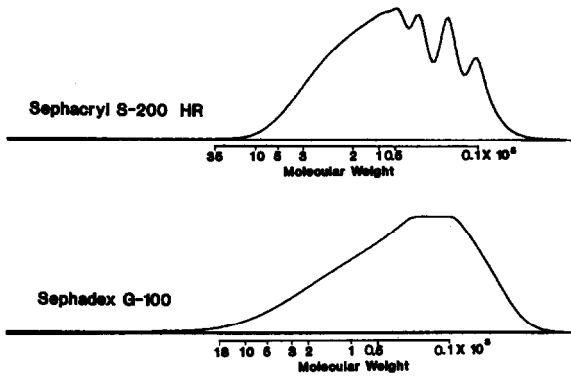


Fig. 3. Chromatographs of GFC molecular weight for an oriented strandboard phenolic resin using Sephadex G-100 and Sephacryl S-200 HR column packing materials (SPS standards).

materials in plywood resoles is unknown, although higher standards ($35\,000 \bar{M}_p$, SPS) are available for comparison (Table I). Therefore, Sephacryl S-200 HR is the gel of preference in this GFC system.

One use of GFC is to examine the progression of a phenolic resin synthesis during the cook compared to the final finished form (Table II). This application is particularly useful when formulation changes are made such as adding a two-charge sodium hydroxide catalyst instead of a single-charge caustic catalyst to plywood-type phenolic formulations^{11,12}.

Comparisons of typical high pressure GPC results to the GFC data obtained in

TABLE II

MOLECULAR WEIGHT DISTRIBUTION OF PLYWOOD-TYPE PHENOLIC RESIN SAMPLES TAKEN AT SEVEN POINTS DURING THE COOK AND AT THE END OF THE COOK

Molecular weight range	Area percent by sample number ^a							
	1	2	3	4	5	6	7	8 ^b
> 35 000	0.0	0.0	0.0	0.0	0.3	0.5	1.0	0.0
35 000–18 000	0.0	0.0	0.1	0.2	0.2	0.3	0.4	2.2
18 000–10 000	0.0	0.1	0.7	1.6	2.9	3.9	4.3	5.9
10 000–5000	0.0	0.8	2.6	5.0	6.0	6.7	7.6	8.7
5000–3000	0.0	6.4	11.2	13.6	14.9	16.2	16.5	16.6
3000–2000	1.2	13.9	16.4	17.3	17.2	17.0	16.5	16.2
2000–1000	7.0	20.6	20.1	19.3	18.4	17.7	16.8	16.1
1000–500	17.2	20.5	18.1	16.3	15.2	14.5	14.0	13.2
500–100	74.6	37.7	30.8	26.7	24.9	23.2	22.9	21.2
\bar{M}_w	406	1166	1722	1997	2640	3622	6610	7174
\bar{M}_n	225	417	492	555	589	620	625	675
\bar{M}_w/\bar{M}_n	1.80	2.79	3.50	3.59	4.48	5.84	10.57	10.62

^a The analyses are based on sodium polystyrene sulphonate standards and using Sephacryl S-200 HR.

^b Sample No. 8 is the finished resin.

this work are shown in Figs. 4 and 5. While both methods provide qualitative and semi-quantitative data relative to any series of tests, it is thought that greater association of organic solvents with phenolic methoxy groups yield higher molecular weight values in the GPC method compared to the GFC method.

Phenolics are "living polymers" that are constantly changing toward gelation and decreasing in stability with increasing time and temperature. In the U.S.A., a plywood phenolic resin may increase from 600 to 2000 mPa · s (cP) in two weeks at 25°C. Due to these changes, the essence of physical characteristics of these synthetic resins over time is difficult to capture, even with experimental precautions. GFC offers an opportunity to observe or monitor changes which occur with alterations in conditions. Freeze-drying may offer an opportunity to protect the integrity of the GFC data on sample retains of PF resins for periods of up to six months or more (Table III).

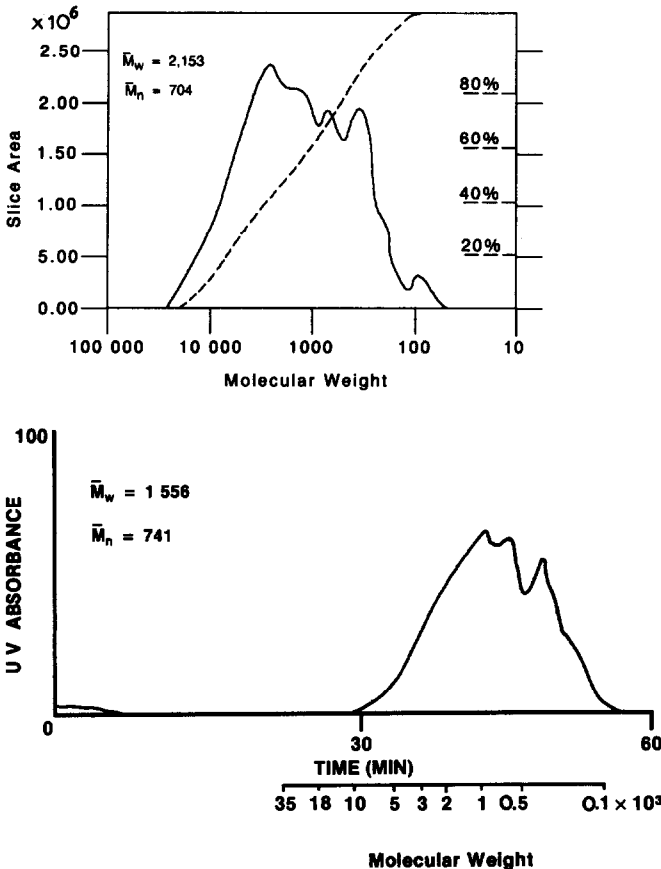


Fig. 4. Chromatograms of a flakeboard phenolic resin using high-pressure GPC (upper) and GFC (lower).

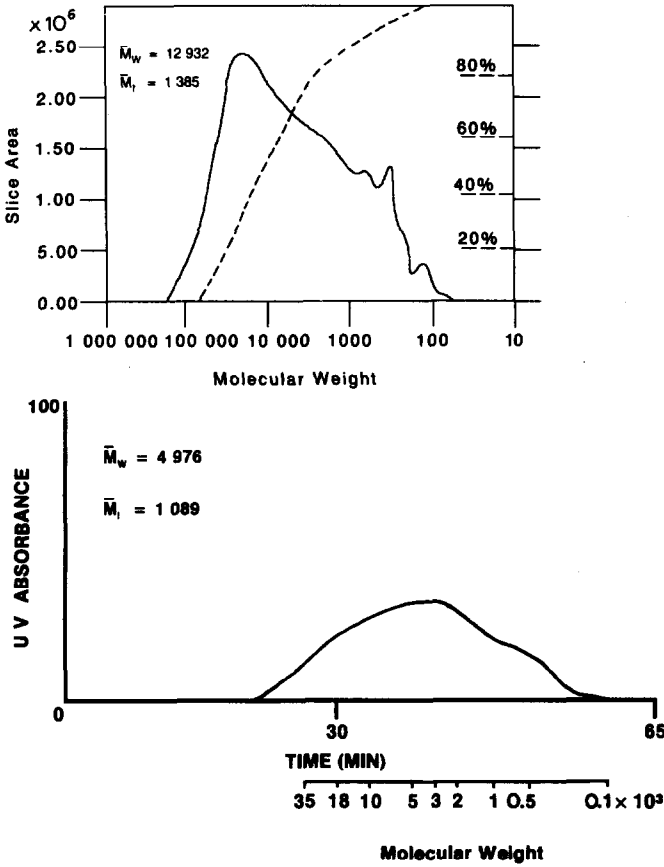


Fig. 5. Chromatographs of a plywood phenolic resin using high-pressure GPC (upper) and GFC (lower).

TABLE III

COMPARISON OF MOLECULAR WEIGHT DISTRIBUTION OF A PHENOLIC RESIN BEFORE AND AFTER FREEZE-DRYING USING SEPHACRYL S-200 HR COLUMN-PACKING MATERIAL

Molecular weight range	Area percent ^a	
	Before	After
> 35 000	0.3(0.3)	0.1(0.1)
35 000-18 000	5.9(6.2)	3.8(3.9)
18 000-10 000	6.0(12.2)	5.4(9.3)
10 000-5000	7.6(19.8)	7.8(17.1)
5000-3000	12.9(32.7)	12.9(30.0)
3000-2000	12.7(45.4)	12.8(42.8)
2000-1000	16.8(62.2)	17.0(59.8)
1000-500	14.6(76.8)	17.0(76.8)
500-100	23.2(100.0)	23.2(100.0)
\bar{M}_w	4075	3397
\bar{M}_n	670	716
\bar{M}_w/\bar{M}_n	6.08	4.74

^a The numbers in parentheses represent accumulations.

CONCLUSIONS

The GFC technique developed in this work showed usefulness in many applications analyzing the PF resins and phenolic-like compounds as manufactured with a minimal alteration of their molecular structures. The procedure uses aqueous sodium hydroxide as solvent reducing resin preparation time by not requiring acetylation or conversion to a non-aqueous solvent system. Having relative GFC data over time for various types of common phenolic-like polymers allowed comparative evaluation of similar resins and potential raw material extenders. The technique described in this study can be used to characterize resoles with a wide range of molecular weight (low and high) and to serve as a quality control tool. Eventually correlation of \bar{M}_w data of resins to end-use performance of bonded wood composites is a likely goal¹³⁻¹⁶.

ACKNOWLEDGEMENTS

Financial support from the U.S. Department of Agriculture Wood Utilization Research Grant Program and the Mississippi Forest Products Utilization Laboratory is gratefully acknowledged.

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