Changes in Molecular Weight and Molecular Size with Reaction Time of a Phenol–Formaldehyde Resol

INTRODUCTION

Phenol–formaldehyde (PF) thermoset polymers are used to bond wood together to make panels. The relatively low molecular weight resin used for this process is called a resol when base-catalyzed. The molecular weight and size of a resol or any thermoset polymer is expected to increase in a predetermined manner during resin synthesis. However, aggregation and solvation effects may obscure the true nature of the polymerization. In the highly competitive wood products industry where resin performance is continually under scrutiny, precise information on average molecular size is required in order to establish correlations with the mechanical properties of wood composites made from such resins. Results are presented of measurements by size-exclusion chromatography on resols made with two different procedures.

EXPERIMENTAL

The resols examined in this study were prepared according to the procedure of Chiu.[1] A low molecular weight and a high molecular weight resin were prepared separately. In the first synthesis, the temperature of the reaction mixture was maintained at 65°C for 65 min; then the phenol–formaldehyde/water mixture was returned to room temperature. Samples were withdrawn at regular intervals as shown in Table I. In the second synthesis, a more complex temperature programming was followed as shown in Figure 1. In this case, the letters correspond to the chromatograms of Figure 2. Samples were withdrawn at regular intervals as shown in Table II.

Table I Resol Molecular Weight, Relative to Poly(ethylene Oxide), Evolution During a Low Molecular Weight Cook, with Tetrahydrofuran/ 0.4% Trichloroacetic Acid as Solvent at 25°C

Time (min)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
10	210	235	260	1.10
30	200	225	240	1.10
55	220	245	270	1.10
Final LMW resin	230	260	290	1.15

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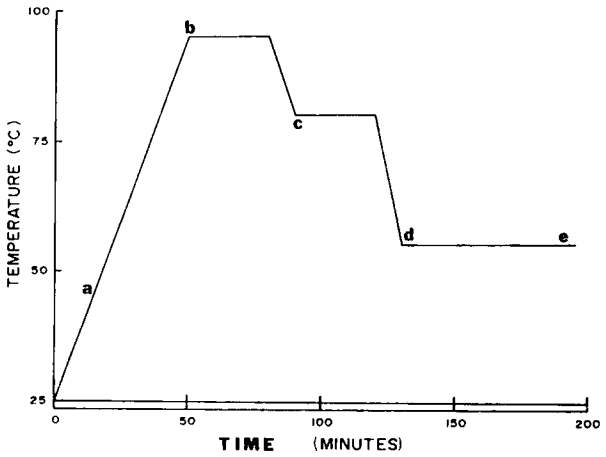

Figure 1 Time–temperature programming employed in preparing the resins. The letters correspond to molecular weight and size distributions given in Figure 2.

The molecular weight and molecular size distributions were determined as in previous publications.[2,3] Briefly, size exclusion chromatography was performed on the phenol–formaldehyde resols. Ultrastyragel (Waters) 100 and 500 Å columns connected in series at 25°C with tetrahydrofuran with 0.4% trichloroacetic acid as solvent[4] were calibrated with poly(ethylene oxide) (PEO). The experimental setup consisted of a Waters WISP 710B injection system, an M45B pump, an R401 differential refractometer, and a programmable system controller with data module.

RESULTS AND DISCUSSION

The change in the number and weight average molecular weights for a low molecular weight resol and a high molecular weight resol is given in Tables I and II, respectively. The change of the molecular weight with cook time (synthesis time) of the a-type resol follows normal stepwise polymerization kinetics, i.e., the average molecular weight increases more or less linearly with time. The temperature programming of the cook of the resol is such that it ap-

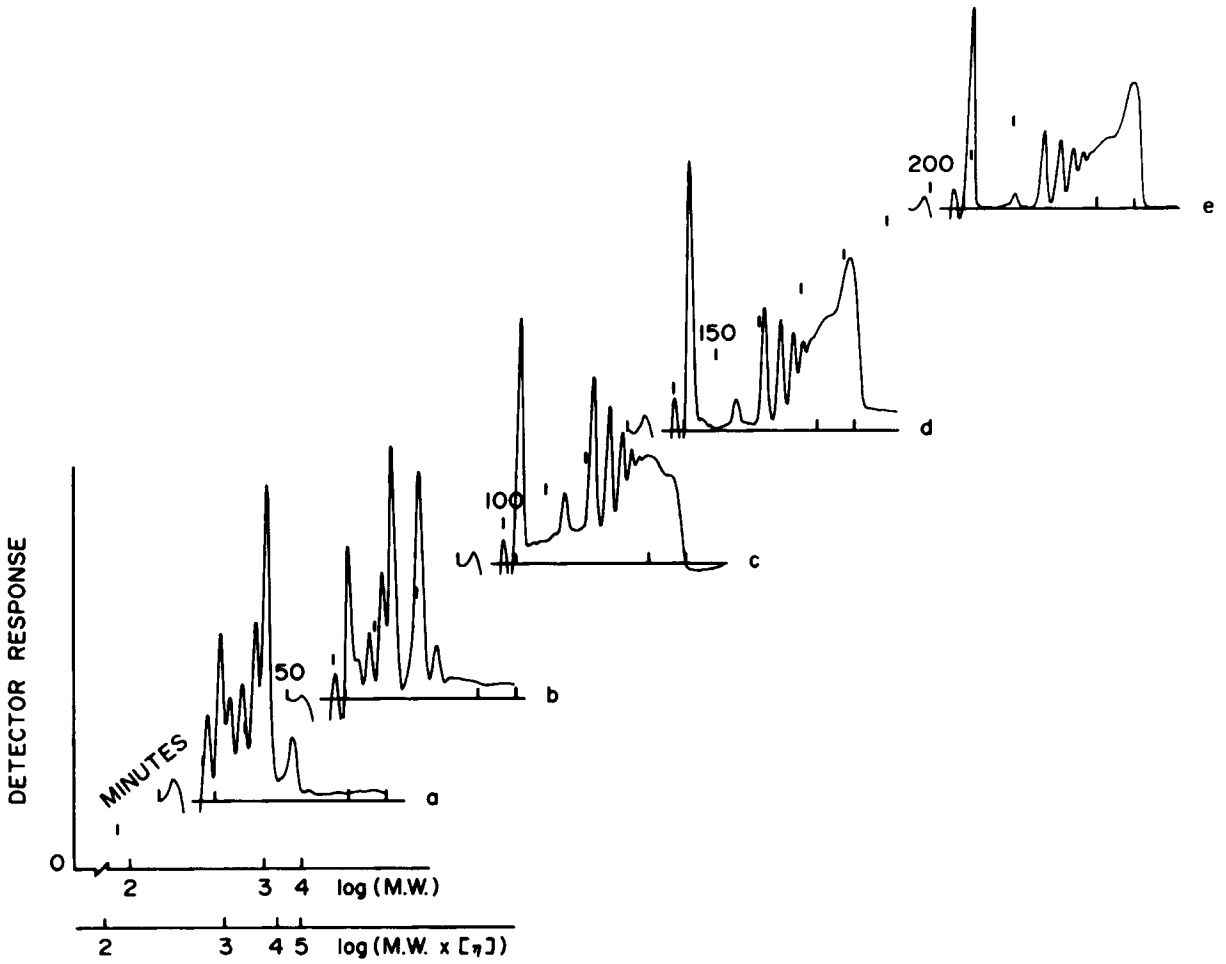

Figure 2 Molecular weight and molecular size distributions for a high molecular weight resol, as a function of cook (polymerization) time, on the Z-axis. The letters correspond to the time of withdrawal of samples from the resin reactor (Fig. 1).

Table II Resol Molecular Weight, Relative to Poly(ethylene Oxide), Change During a High Molecular Weight Cook, with Tetrahydrofuran/0.4% Trichloroacetic Acid as Solvent at 25°C[a]

Time (min)	Sample No. Figs. 1 and 2	Viscosity (P)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
			($\times 10^{-2}$)			
20	a	—	2.00	2.25	2.45	1.1
50	b	0.4	2.15	2.45	2.70	1.15
80	—	1	3.50	9.00	24.0	2.60
90	c	1.5	3.50	9.25	27.0	2.65
120	—	2.9	3.70	14.5	45.0	3.95
130	d	3.7	4.30	24.0	68.0	5.55
195	e	5	4.45	27.0	70.0	6.05
Final HMW resin		6	5.40	53.0	180	9.85

[a] For the molecular weight averages, the precision is ±5 on the last significant digit.

proximates, in a reverse manner, the exponential rise in viscosity of the polymer, thus achieving a fairly constant increase in molecular weight with time. The polydispersities, $\bar{M}_w/\bar{M}_n$, as given in Table II, increase regularly. Measurements of average molecular weights of mixtures of resols of different molecular weight averages confirm that aggregation is minimal in tetrahydrofuran with 0.4% trichloroacetic acid as solvent.[3]

Figure 2 gives the change of the molecular weight of samples withdrawn from the resin reactor at different times, for the high molecular weight cook only. The detector response is shown as a function of the cook time (Z-axis), with the X-axis being the logarithm of the weight average molecular weight; the lower X-axis in Figure 2 is a molecular size scale, independent of solvation of the calibration polymer[3] and is given in terms of the logarithm of intrinsic viscosity, η, $\times$ molecular weight, where η is in $cm^3\ g^{-1}$. This last scale is given only for illustration purposes. A complete discussion on molecular size determination was presented in a previous report.[3]

The first chromatogram for a sample withdrawn at 20 min contains oligomers corresponding to a molecular weight of approximately 500 PEO. High molecular weights (greater than an MW of 1000 of PEO) species appeared between 50 and 90 min, and increased in proportion with time. Intermediate peaks corresponding to oligomers of degree of polymerization (DP) between 2 and 4 were observed to disappear. The large peak (low molecular weights) for samples c, d, and f was identified as methylolated phenol. Thus the final high molecular weight resin is a mixture of methylolated phenols and oligomers of phenol-formaldehyde with DPs greater than 4.

With this procedure and type of solvent, it is thus possible to characterize the molecular weight and size of any soluble sample of PF and establish correlation with the strengths of panels produced and other variables such as the effect of extenders.

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