

Molecular weight distribution of phenol–formaldehyde resols by high performance gel permeation chromatography

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Resol resins are particularly difficult to characterize with respect to molecular weight because of the large amounts of caustic soda (10–20% w/w) which they contain. A method is described for solubilizing these materials using trichloroacetic acid, such that molecular weight distribution can be measured using a normal gel permeation chromatography system with μ -Styragel columns and tetrahydrofuran as solvent.

Keywords Phenol–formaldehyde; resols; molecular weight distribution; gel permeation chromatography

INTRODUCTION

Resol resins are produced by the reaction of phenol and formaldehyde in alkali solution. The molecules contain reactive methylol groups which condense on heating without additives, unlike the related novolac resins which require the addition of a hardening agent.

The formation of resins from the reaction of phenols with aldehydes has been known since 1872 when the reaction was first studied by Baeyer¹, and these compounds have been produced commercially since 1910². Despite their long commercial history, the chemistry of phenol–formaldehyde resins is far from understood—mainly because of the complex mixture of products which are formed in the strongly alkaline medium, and efforts continue to elucidate the mechanism of reactions using the most modern techniques available^{2,3}. The high alkalinity of the final resin is a serious impediment to many types of study, e.g. fractionation, and the resins are unstable in neutral or acid solution.

Phenol–formaldehyde resols are extensively used as adhesives in the timber industry, e.g. in the manufacture of plywood. One of the factors which influences the strength of the bond formed, particularly in porous species of timber is the degree of diffusion of the resin away from the glue line⁴. Molecular weight distribution plays an important role in determining the degree of penetration. High performance gel permeation chromatography is a well known method of measuring molecular weight distribution, and this technique has been extensively used to measure *MWD* of novolacs (acid catalysed resins) or first stage resol resins which are prepared at pH 8, both of which are soluble in tetrahydrofuran^{5–7}. In this paper a method is described for the measurement of *MWD* of the high alkaline resols.

EXPERIMENTAL

Phenol–formaldehyde (PF) resins were presented as 40%

aqueous solutions at pH 14 or powders containing 10–25% sodium hydroxide. The problems in obtaining molecular weight distribution data is one of rendering the material soluble in a suitable solvent for gel permeation chromatography, preferably tetrahydrofuran so that the sample can be run routinely on conventional g.p.c. systems.

A method using acetic acid to neutralize and solubilize the resin in THF was found to give incomplete dissolution of our samples and even the soluble resin was unstable and liable to precipitate from solution. Matsuzaki *et al.* have commented on the insolubility of PF resins in THF in their work with DMF as solvent⁸.

Pizzi and Scharfetter described the use of trichloroacetic acid to neutralize tannin–formaldehyde resins for thin layer chromatography⁹. This technique was applied to phenol–formaldehyde resins and the use of a 10% solution of trichloroacetic acid was found to effectively solubilize phenol–formaldehyde resins prepared in the Laboratory and a number of commercial resins. The following procedures were therefore adopted.

Dissolution of the resins

(a) 1st stage resin—low caustic content—directly soluble in tetrahydrofuran apart from the final part of this stage which required a drop or two of 10% trichloroacetic acid in THF.

(b) 2nd stage (final) product—high caustic. Sufficient resin was weighed out to give 25 ml of a 0.25% w/v solution. A solution of 10% trichloroacetic acid was added dropwise, with stirring, until the pH was between 6 and 7 (Merck pH strips). This produced complete dissolution of the samples even when the solution was made up to 25 ml with THF.

All samples were run as soon as possible after preparation. Although the solutions of phenol–formaldehyde in trichloroacetic acid are relatively stable a curing reaction eventually does take place and the samples precipitated. If

this were to occur inside the g.p.c. column it would be very expensive. No problems have been encountered so far.

Chromatography

Samples were run on a modular high performance g.p.c. system consisting of a Waters M6000 pump, Waters U6K injector and a Cecil UV Spectrophotometer operating at 283 nm. A low molecular weight μ -Styragel column set (100, 500, 1000) was used. The addition of a second 100 Å column gave no significant increase in resolution of the low molecular weight components. To maximize resolution it is desirable to work with as few columns as possible, as long as the porosity is sufficient to span the entire MWD of the sample. Solvent was HPLC grade tetrahydrofuran (Fisons or Rathburn Chemicals' which is free of u.v. absorbing materials).

After more than two years intermittent usage the μ -Styragel columns are showing only a slight decrease in resolution. There is no sign of material eluting from the columns after the total permeation volume, which would be an indication of adsorption of material onto the column packing. Certain polymers, however, produce peculiar chromatograms when run immediately after phenol-formaldehyde resins. It is therefore advisable to keep a set of columns solely devoted to PF resin work.

Calibration

Since the objective was to compare samples from different synthetic routes or manufacture it was deemed unnecessary to search for phenol related calibrating systems. All molecular weight data have been calculated relative to polystyrene (or polypropylene glycol) calibrants. In many cases visual comparison of the chromatograms was satisfactory. Reproducibility of calibration was a good indication that the resins were not adversely affecting the columns.

RESULTS

Figure 1 shows chromatograms of three commercial resins used in plywood manufacture. Although the molecular weight range of the three samples is the same, sample 3 contains much more low molecular weight material (AB region) than samples 1 and 2. Sample 3 was found to be inferior in adhesion properties to 1 and 2.

The phenol-formaldehyde ratio can be adjusted to minimise the amount of low molecular weight material in the sample and therefore produce a satisfactory plywood adhesive.

CONCLUSIONS

The use of trichloroacetic acid in tetrahydrofuran to neutralize and solubilize highly alkaline resol resins has been shown to give a consistently soluble material which can be characterized with respect to molecular weight distribution by high performance gel permeation chro-

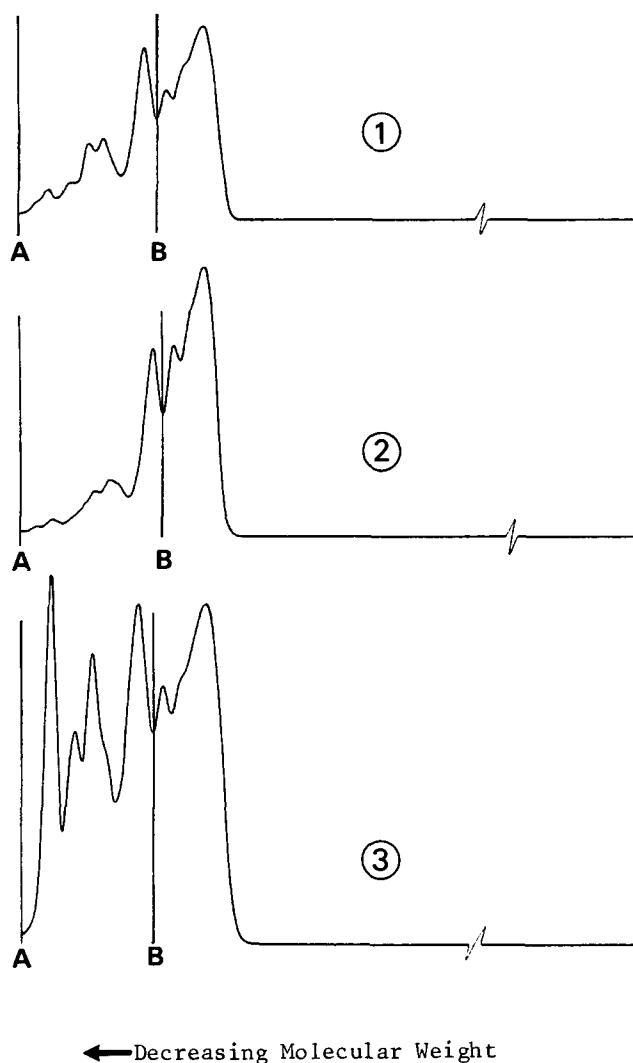


Figure 1 Comparison of the molecular weight distribution of phenol-formaldehyde resols by high performance gel permeation chromatography

matography in THF. The method can therefore be used for the routine characterization of phenol-formaldehyde resins, e.g. to compare materials from different suppliers or to optimize manufacture.

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