

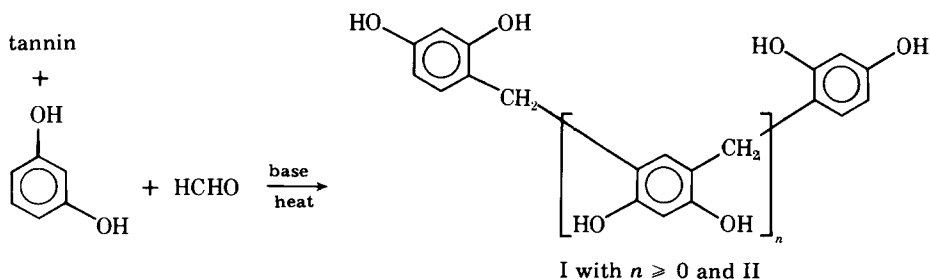
Tannin-Based Neutral and Alkaline Phenolic-Type Foams

INTRODUCTION

Tannin-based cold-setting foams obtained by the acid-catalyzed condensation of wattle tannins with furfuryl alcohol and formaldehyde have already been described as substitutes for synthetic phenolic ones, have good mechanical characteristics, and present far better fire resistance than the polyurethane foams they are aimed at substituting.⁸ However, the very acid pH needed to prepare these foams constitute a serious disadvantage when they are used as an insulating material between wood walling panels; they could lead to serious problems of corrosion and consequent weakening of the wood panels with which they come into contact. Neutral and alkaline pH values cannot be used with these formulations as the needed exothermic polymerization of furfuryl alcohol with polyflavonoid tannins does not take place under such conditions.

This paper describes a resin system for the production of tannin-based neutral and alkaline phenolic-type foams. The tannins of the bark of the black wattle tree (*Acacia Mearnsii*), commercially available, were used for this study. The structures of the main polymeric constituents of wattle tannins, their advantages, disadvantages, and physical and chemical characteristics as regards the use of their condensates with formaldehyde for adhesives have already been described.⁷ The approach adopted was to use a series of materials that could polymerize exothermically with wattle tannins at neutral and alkaline pH values. Because the peak of temperature reached during the formation of a phenolic foam should be reached at the nearest possible time before foam setting, or better afterward,⁸ in order to obtain higher amounts of closed cell structures (the mechanical properties of which are preferable to those of an open cell structure), a mixture of two resins, a tannin/resorcinol-based one and a tannin *m*-hydroxylaniline-based one, was used. Each of these two resins can produce foams in its own right, but the temperature peak is always reached before foam setting. The mixture of the two resins instead produces foams in which the temperature peak is reached after foam setting and which have better overall mechanical properties. The resins used were the following:

1. Simultaneous synthesis of resorcinol/formaldehyde and polyflavonoid/formaldehyde condensates. The reactions involved are:



II = $-\text{CH}_2$ -flavonoid polymer- CH_2 - and uncombined resorcinol and uncombined flavonoid polymers

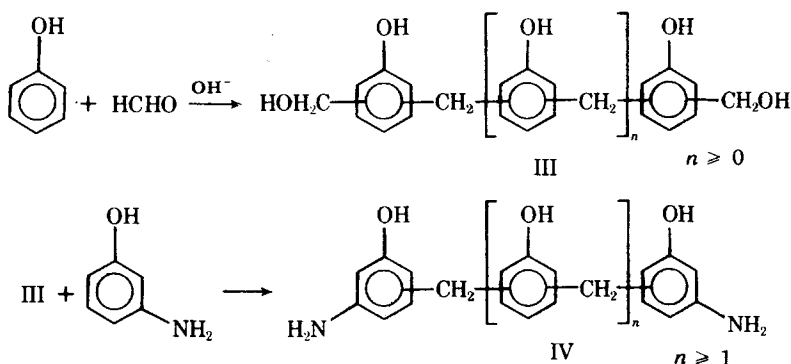
Mixture II can be cured at ambient temperature by addition of formaldehyde. All the other tannin-based resorcinol-fortified cold-setting resins already reported^{1,5,6,10} can also be used with generally comparable results.

2. Synthesis of stable phenol/*m*-hydroxylaniline/formaldehyde resins and subsequent addition

TABLE I
Glue Mixes Used to Prepare Foams A and B

Component No.	Component	A (0.12 g/cm ³)	B (0.25 g/cm ³)
1	Wattle extract powder	60	60
2	Resin 1	100	100
3	Resin 2	40	40
4	Water	25	25
5	NaOH 45% solution	25	25
6*	Arcton 113 (boiling point 45°C)	10	6
7*	Arcton 11 (boiling point 30°C)	5	3
8	Paraformaldehyde	20	20
*	Blowing agents (commercial; chlorinated hydrocarbons)		

to flavonoid polymers. The reactions involved are:



The mixture of resin IV and flavonoid polymers (tannins) is a resin that can be cured at ambient temperature by addition of paraformaldehyde.

EXPERIMENTAL

Resins preparation

System 1. A mixture of 259 parts by weight of a 58% aqueous solution of commercial powder wattle extract (containing 6% moisture), 42 parts methanol, 0.8 part of a commercial defoamer, and 75 parts 99% resorcinol was prepared at ambient temperature. To this mixture 24.5 parts 38% formalin solution and 20 parts of a 45% aqueous sodium hydroxide solution were added still at ambient temperature. The mixture was brought to 70°C under stirring and held at this temperature for 1 hr, then cooled and stored.

System 2. A mixture of 12.8 parts 100% phenol, 3.2 parts methanol, and 3.9 parts water was prepared at ambient temperature and warmed, and 4.3 parts 96% paraformaldehyde and 2.5 parts of a 14% aqueous sodium hydroxide solution were added. The mixture was brought to reflux (90°C) in 30 min and held refluxing for 2½ hr; 8.2 parts *m*-hydroxyaniline is then added and the mixture is held refluxing for a further 2 hr and then cooled and stored.

Glue Mixes Preparation

The glue mixes used to prepare foams of 0.12 and 0.25 g/cm³ (in parts by weight) are shown in Table I.

Glue mixes components 1 to 5 are mixed together, then the mixture is cooled to ±25 mdegC, components 6 and 7 are mixed in, and paraformaldehyde is added. The foam's setting time, densities, and physical characteristics vary only slightly when the proportions of the sum of components (1 + 3) versus component 2 are changed from 1:1 to 1:2 or 2:1. The results are shown in Table II.

TABLE II
Physical Characteristics of Tannin-Based Phenolic-Type Foams Testing Results

Resin systems	Glue mix Type	Preparation of glue mix components (1 + 3):2, wt:wt ratio	Foam Density g/cm ³	Compression strength, psi		Stability test Pinking ratio	Foam setting time, min
				Direction of foam rise	Across direction of foam rise		
1 + 2	B	50:50	0.25	560	375	0.99	7
2	A	100:00	0.12	59	52	0.99	18
1 + 2	A	75:25	0.12	67	58	0.99	9½
1 + 2	A	67:33	0.12	71	60	0.98	7½
1 + 2	A	50:50	0.12	73	60	0.98	7
1 + 2	A	33:67	0.12	86	63	0.98	7½
1 + 2	A	25:75	0.12	102	77	0.97	8½
1	A	0:100	0.12	194	165	0.96	40
Commercial polyurethane foam			0.10	155	120	not flame resistant (burned completely)	—
Commercial phenolic foam			0.10	81	64	0.97	—

Testing Procedure

The foams prepared were tested for compression (crushing) strength and for fire resistance according to relevant South African Bureau of Standards provisional specification for synthetic resin foams.

Compression Strength Test

Eight days after the foam preparation, cubes 50 × 50 × 50 mm in dimension were cut from the different foams after having trimmed the foam of 5 cm in every direction to avoid "skin" effects that can affect the value of the results. Each cube (10 for each type of foam) was subjected to compressive strength in a universal testing machine at a rate of 2.5 mm/min up to crushing and the values recorded and averaged.

Flame Stability Test and Pinking Test

Eight days after foam preparation, cubes 50 × 50 × 50 mm in dimension were cut from all the foams. Every cube was positioned over a stainless steel plate having a square hole 40 × 40 mm in dimension. Beneath the plate a gas burner was left burning for 5 min. If the foam crumbles or burns during the 5 min of exposure to the flame, the foam has poor or no flame stability. If the foam cube is still in reasonable shape, the foam cube is weighed hot immediately after the 5 min of flame exposure and is then weighed again after 10 min of cooling has elapsed. The pinking ratio is the ratio given by the cube mass after 10 min of cooling divided by the cube mass immediately after the 5 min of flame exposure. Pinking ratios of 1 are good; those below 0.9 are useless and indicate afterburn.

DISCUSSION AND CONCLUSIONS

The results shown in Table II indicate that neutral and alkaline tannin-based phenolic-type foams can be produced. Higher or lower pH values can be obtained by simple variation of the amounts of caustic soda used, the foam setting time shortening with the increasing pH. A considerable deviation from the given proportion of components 1 + 3 and 2 is permissible [from a (1 + 3):2 ratio by weight of 1:2 to 2:1], allowing elasticity in the formulation costs. Temperature peaks are reached after foam setting (Table III), giving foams of reasonably good strength. The formulations given are not able to produce foams of density lower than 0.1 g/cm³. This limiting factor can be partially overcome by using as glue mix component 1 a sulfite or bisulfite wattle extract² or a wattle extract

the viscosity of which has been considerably decreased by simple chemical procedures already reported³ and decreasing the amount of water or other solvents in the formulations given.

The physical characteristics obtained indicate that such foams are suitable as insulating materials between double-skinned wood walling panels and as underroofing or ceiling panels. Tannin-based polyurethane adhesive formulations already reported⁴ or with increased tannin content have also been successfully used for preparation of foams. But while their strength is lower than that of the phenolic-type foams, though still acceptable (± 55 –60 psi), their fire resistance is much poorer.

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