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THE EFFECT OF pH AND *P*-FORMALDEHYDE CONCENTRATION ON TANNIN - FORMALDEHYDE REACTION

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Tannins are composed of a mixture of different polyphenols. They have been used as partial substituent of phenol in preparation of phenolformaldehyde resin. Their reaction with formaldehyde is acid as well as base catalysed. In present study tannins from *Pinus roxburghii* were used to study the effect of pH and *p*-formaldehyde concentration on their potential to react with formaldehyde. The shear strenght of adhesive prepared at different pH has also been measured. Maximum shear strength was obtained at pH 9.0. It is concluded from this study that the reaction in basic medium (pH>8) is more effective than that in acid condition and the concentration of the *p*-formaldehyde should be kept between 5-10% w/w.

Key words: Tannin-formaldehyde, Gelation time, Shear strength.

Introduction

Several researchers investigated the effect of pH and formaldehyde concentration on tannin-formaldehyde reaction using different species. A.E. Manas reported [1] that different species as well as pH could change the gelation rates and spreading characteristics of an adhesive. Adhesive prepared from Bakauan bark tannin at pH 5 could easily spread while at the same pH adhesive prepared from Ipil Ipil bark [2] extract is rough in texture. Accoridng to W.E. Hillis and G. Urbach [3] the uptake of formaldehyde by catechin is greater at high pH (10) than that at lower (pH1) and is minimum at 4.5 pH at 20°. W.J. Herzberg studied [4] the effect of *p*-formaldehyde concentration on shear strength of *Pinus radiata* tannin-formaldehyde adhesive. He found that the shear strength increased (893-1015 Ib failing load) when the concentration of *p*-formaldehyde was increased from 4-10%. Further increase in concentration decreased the bond quality. F.W. Herrick and R.J. Conca [5] used bark extract in cold-setting water proof adhesive and concluded that the shear strength of adhesive increased from 53-210 psi with the increase of pH from 7.6-9.1.

In our previous paper we reported [6] the results of qualitative and quantitative studies on tannins from *Pinus roxburghii* bark. We also investigated the sugars in the bark. In the present work the reactivity of tannins with formaldehyde have been studied at different formaldehyde concentrations and at various pH values.

Experimental

Effect of pH on gelation time. Tannin solution (40%) was prepared with aqueous ethanol (50%). The pH of the solution was measured on precision pH meter (OP-205/1) and it was adjusted to various values by adding sulfuric acid (10%) or sodium hydroxide (5 N). The tannin solution (7 ml) was taken in a test tube and placed in water bath registering 72°*p*-formaldehyde (0.15 g) was added when the temperature of the solution reached 70°. It was stirred thoroughly throughout the reaction. The time taken to change the liquid into gel (gelation time) was taken as the period elasping until the sample applied on a glass rod supported a weight of 1.0 g for 2 mins. A plot of pH versus gelation time (in minutes) was constructed to illustrate the effect of pH on gelation process.

Effect of p-formaldehyde concentration on gelation time. The effect of *p*-formaldehyde concentration on gelation time was studied at 60° and at pH 4.7. To 5.0 g of the solution, a known amount of *p*-formaldehyde (ranging 0.15 - 0.5 g) was added and the solution was stirred thoroughly. The gelation time was determined by the method described above. The result is illustrated in Fig.2b.

Moisture content measurement of wooden blocks. The moisture content of the wooden blocks were determined by drying them in an oven at 105°. It was observed that the wooden blocks changed their surface level on heating for a longer period so they were allowed to dry for only 2 hrs.

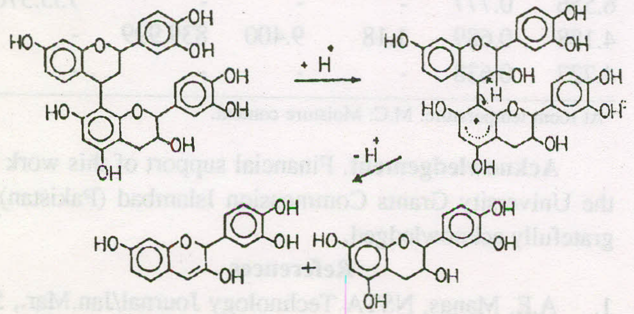
Influence of pH on shear strength. Ten grams of tannin solution (40%) was taken in a beaker (250 ml) and a known amount of sodium hydroxide (5 N) solution was added to it. The pH of the system was measured. *p*-Formaldehyde (0.15 g) and wood flour (0.4 g) were added to it and stirred thoroughly. When the solution attained gelly like appearance it was uniformly spread on the surface of 2 wooden blocks whose densities and moisture content were already measured. The blocks were allowed to dry for 5 min then they were pressed for 24 hrs. At the end of 7 days the assembled blocks were used to measure the shear strength of adhesive on universal testing machine (UHP 20 Losenhausenwerk). The results obtained at various pH are illustrated in Fig. 3.

Results Discussion

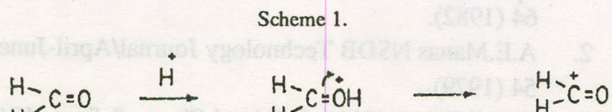
It has been reported [8,9] that the rate of reaction between tannin and formaldehyde is pH dependent. The reaction rate of wattle tannin with formaldehyde is lowest in the pH range 4.0 - 4.5 and for pinus species between 4-5. The same trend is followed in the present study i.e. the gelation time was maximum at natural pH (4.0 - 5.9) of the tannin extract (Fig. 1b). This may be due to the fact that at natural pH, 2 to 11 flavonoid units of tannin are attached to each other and their reactive sites are restricted to a fixed position and the formaldehyde molecules have less chances to reach these sites [10]. In acidic condition, the gelation time is very low and this may be due to two seasons (1) degradation (Schme 1) (2) activation of formaldehyde molecule (Scheme 2). In degradation process high molecular weight polymers are converted to low molecular weight units. In this way the reactive sites are comparatively more exposed to the activated formaldehyde molecules. But in strong acidic condition (pH<2) the reaction is very fast and the condensate solidifies in few seconds. This result is consistant with the finding of Hillis and Urbach [3], i.e. self polymerization of tannin molecule occurs at very low pH (pH=1) Scheme 3. In alkaline medium, hydroxyl ions react with polyphenolic rings of tannins to produce nucleophiles as shown in scheme 4. Comparing the maximum gelation time with other reported [11] species (Fig. 1a) at the same pH, it appears that *p roxburghii* tannin (Fig. 1b) is comparatively more reactive.

It has been observed [11] that gelation time changes rapidly around 5-10% *p*-formaldehyde concentration, and it is this range where good adhesive strenght is obtained. Similar observation has been made in this tudy. However gelation time is comparatively very low (Fig. 2b) which confirms the high reactivity of the *pinus roxburghii* tannins.

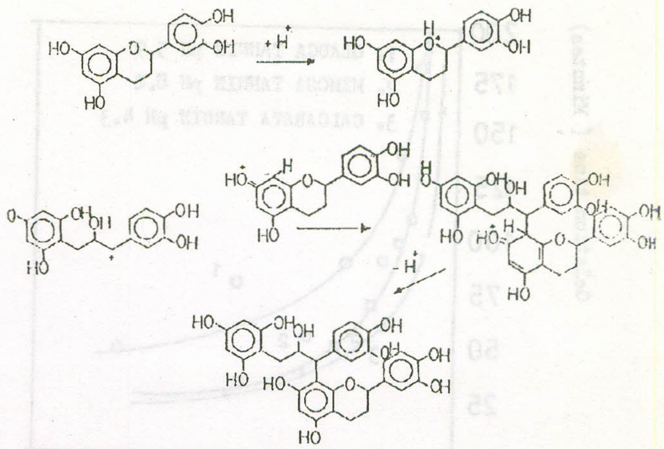
It has been reported [9] that the shear strength of glue increased with the increase of sodium hydroxide concentra-



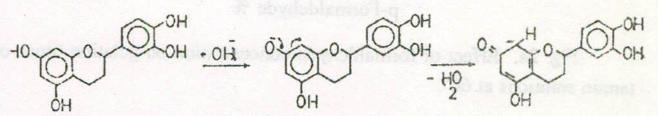
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

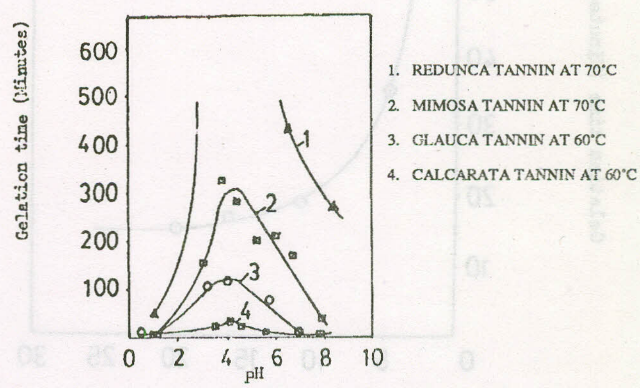


Fig. 1a.Gelation of tannin solutions with 8% formeldehyde.

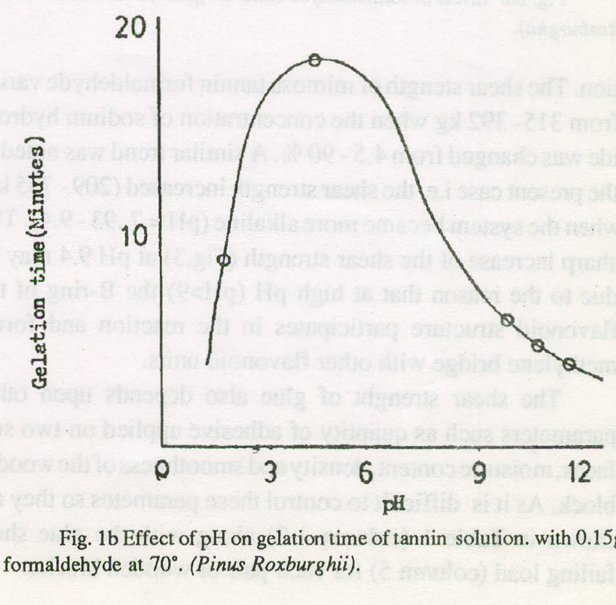


Fig. 1b Effect of pH on gelation time of tannin solution. with 0.15g *P*-formaldehyde at 70°. *(Pinus Roxburghii).*

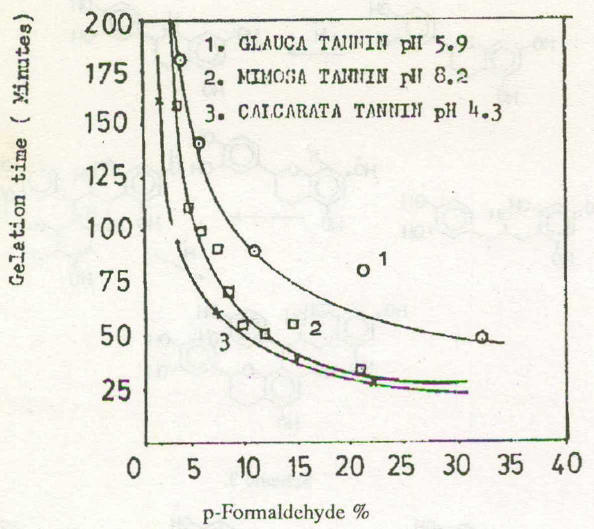


Fig. 2a. Effect of formaldehyde concentration on gelation times of tannin solutions at 60°.

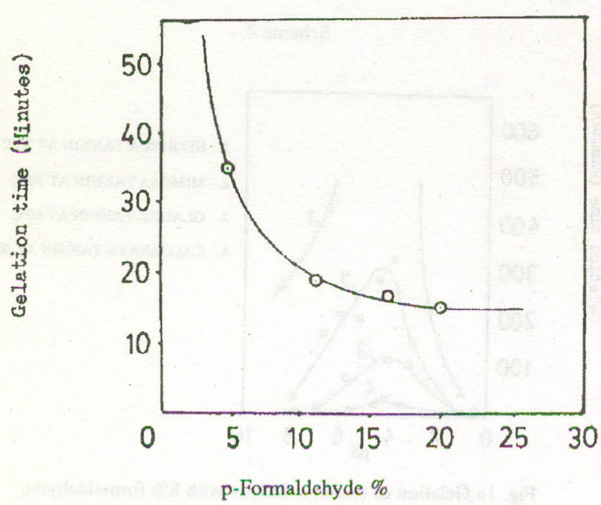


Fig. 2b. Effect of formaldehyde conc. on gelation time at 60° *(Pinus Roxburghii)*.

tion. The shear stength of mimosa tannin formaldehyde varied from 315- 392 kg when the concentration of sodium hydroxide was changed from 4.5 - 90 %. A similar trend was noted in the present case i.e. the shear strength increased (209 - 735 kg) when the system became more alkaline (pH = 7..93 - 9.4). The sharp increase of the shear strength (Fig.3) at pH 9.4 may be due to the reason that at high pH (pH>9) the B-ring of the flavonoid structure participates in the reaction and forms methylene bridge with other flavonoid units.

The shear strenght of glue also depends upon other parameters such as quantity of adhesive applied on two surfaces, moisture content, density and smoothness of the wooden block. As it is difficult to control these parameters so they are shown in Table 1 (column 1-3) along with the glue shear failing load (column 5) for each pair of wooden blocks.

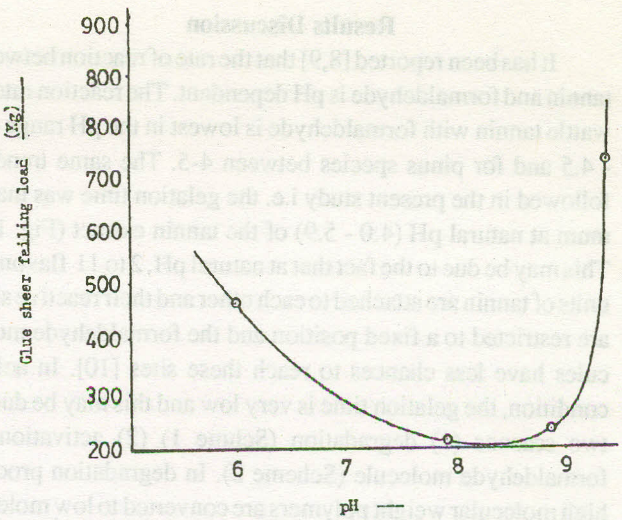


Fig. 3. Influence of pH on shear strength of Cold-Press adhesive.

TABLE. 1. INFLUENCE OF pH ON SHEAR STRENGTH OF COLD-PRESS ADHESIVE.

M.C.of wooden blocks (%)	Density of wooden blocks (g/cm³)	Wt. of adhesive applied (g)	pH* of adhesive	Glue shear failing load (Kg)	Average glue shear failing load (Kg)
6.532	0.750	1.20	6.035	539.665	-
4.198	0.799	-	-	-	474.830
6.379	0.586	1.71	6.035	409.995	-
4.626	0.692	-	-	-	-
6.705	0.605	1.52	7.930	231.788	
6.400	0.640	-	-	-	209.113
6.220	0.673	1.15	7.930	186.438	-
6.379	0.580	-	-	-	-
5.797	0.712	1.13	8.850	224.999	-
4.726	0.600	-		-	22.7.499
6.307	0.705	1.21	8.850	229.999	-
5.082	0..667	-		-	-
5.796	0.722	1.09	9.400	630.741	-
6.556	0.777	-	-	-	735.370
4.188	0.689	1.18	9.400	839.999	-
4.727	0.638	-	-	-	-

*At room temperature. M.C: Moisture content.

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