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Properties of phenolic-tannin adhesives from pinus pinaster bark extracts as related to bond quality in eucalyptus plywoods*

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Resins were prepared from resoles and *Pinus pinaster* bark tannins by copolymerization at room temperature. Reducing the moisture content of the tannins to below 60% increased their stability, so allowing preparation of the resin before its application. Various formulations were tested, all of them substituting 50% of phenols by tannins. The resins obtained were used to manufacture 5-ply eucalyptus boards which met BS 1455 : 1963 WBP quality standards.

Eigenschaften von Phenol-Tannin-Harzen aus Rindenextrakten von Pinus pinaster als Kleber für Eucalyptus-Sperrholz

Durch Copolymerisation von Resolen und Rinden-Tannin aus *Pinus pinaster* wurden verschiedene Harze hergestellt. Erniedrigung des Wassergehaltes auf unter 60% erhöht ihre Stabilität, so daß die Harze schon einige Zeit vor der Anwendung hergestellt werden konnten. Verschiedene Zusammensetzungen, wobei jeweils 50% des Phenols durch Tannin ersetzt war, wurden getestet. Mit den so erhaltenen Harzen wurden fünfschichtige Sperrholzplatten aus Eucalyptus verleimt. Die Platten genügten den Anforderungen des Standards BS 1455 : 1963 WBP

1 Introduction

Bark extracts are complex mixtures of organic compounds including tannins, lignin, cellulose, and other minor natural substances, together with chemicals used in the extraction process. Their condensed tannins whose chemical structure is that of polyflavonoids (Pizzi 1983) provide the possibility of using them for replacing certain components of synthetic adhesives with the aim of both reducing manufacturing costs and possibly improving the final product.

The potential of bark as a raw material depends largely on the species of origin. Wattle tannins have been used commercially in South Africa since the 1970s, and extracts of Pinus radiata have been applied in New Zealand and Chile (von Leyser, Pizzi 1990). However, over the last decade most research work in this area has been directed rather towards understanding the structure and chemistry of bark extract components than towards the development of new products and applications (Harlan 1980; Hemingway 1981).

In spite of the appearance of numerous research reports, pine bark tannins have not been used comercially in Europe. The main reasons are threefold. Firstly, because of the greater reactivity of ring A of their flavonoid monomers, pine tannins are considerably reacting stronger with formaldehyde than are wattle or quebracho tannins, which means that adhesives prepared from them deteriorate rapidly. Secondly, pine bark extracts obtained in laboratory experiments have had active phenolic contents of only 50–60% as against 70–80% for wattle and quebracho; the large inactive fraction (comprising mainly sugars and high molecular weight gums) reduces adhesive strength and resistance to water (Pizzi 1983). Thirdly, formaldehyde forms methylene bonds with the tannin ring A, but because of the size and configuration of tannin molecules not all reactive centres can participate in such methylene bridges, i.e. crosslinking remains incomplete, and more incomplete for pine tannins than for wattle and *quebracho* tannins, having a smaller molecular weight (von Leyser, Pizzi 1990).

Because pine tannins are highly reacting with formaldehyde, it is preferable for extracts to be reacted with a resol of low molecular weight and high methylol content, in which case the crosslinking molecules are larger and bonding stronger. Mihai et al.'s (1985) proposal of copolymerization of phenol and tannins with formaldehyde has the disadvantage of requiring close control of the reaction (Vázquez et al. 1989).

For large-scale industrial use, the physical and chemical properties of adhesives have to be suitably reproducible, which in the present context depends largely on the bark applied as well as on extraction and concentration processes. Though the composition of bark depends not only on the species of origin but also on the site of origin, the age of the stand, the time of year and other variables, the results of extraction experiments have in fact proved to be satisfactorily reproducible, allowing determination of optimal operating conditions (Vázquez et al. 1987). We have also reported elsewhere the influence of the concentration stage (Vázquez et al. 1989). In the present article we report the results of experiments in which adhesives for WBP grade plywood were prepared using *Pinus pinaster* bark extracts in order to partially replace phenol. Resins were obtained by copolymerization of bark extracts at room temperature with a high-methylol resol, and the quality of plywood boards manufactured using these resins was determined.

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2 Material and methods

Pine bark was collected, pre-treated and extracted as described elsewhere (Vázquez et al. 1989). Tannins were concentrated by precipitation at pH 2: the difficulty in separating the gelatinous precipitate (Suomi-Lindberg 1984) was best overcome by centrifugal filtration. The precipitate was then dried so as to eventually achieve resins with the solids content of over 40% that is necessary for adequate board quality (Vázquez et al. 1990) and to ensure high substitution of phenols by tannins. The Stiasny number of the extracts was determined as per Voulgaridis et al. (1985).

Resoles were prepared in experimental apparatus allowing suitable reaction control and described elsewhere (Vázquez et al. 1990). The reactor was loaded with appropriate quantities of soda (S), phenol (P) and formaldehyde (F) (F/P ratios of 1.8, 2.0 and 2.5 were used, with an S/P ratio of 0.4 in all cases), and temperature was raised to 80 °C at rate of about 2 °C/min. The reaction was monitored by measurement of temperature, pH and viscosity (this last, using a ball viscosimeter, which requires smaller samples than other methods).

Resins were prepared at room temperature by mixing the resol with tannins redissolved in soda solution (so that the S/P ratio rose from 0.4 in the resoles to 0.5 or 0.6 in the resins). In all cases, 50% of phenol was replaced by tannins. As the result of the reaction between tannins and resol, viscosity rapidly increased during the first few minutes after mixing.

Differential thermal analysis (DTA) was performed in a Stanton 674 DTA apparatus. Samples weighing 150 mg were heated at a rate of 6 °C/min in an atmosphere of air.

The resins were used to prepare 5-ply eucalyptus boards measuring 250 × 250 × 1.5 mm. Adhesive consumption was 350–400 g/m^2 in a double glueline. Boards were pressed under a specific pressure of 1.2 MPa for 8 min at 130 °C (or, in subsequent productivity maximization experiments, for 3.5 min at 160 °C, 3 min at 180 °C or 2.5 min at 185 °C). Finished boards were subjected for 12 to in water vapour at a pressure of 0.2 MPa prior to knife testing as specified by BS 1455: 1963 for WBP grade boards.

All reagents were industrial grade except those used for analysis. Formaldehyde solutions were stabilized with methanol.

3 Results and discussion

The conditions used for the extraction of polyphenols from *Pinus pinaster* bark were the same that in previous work (Vázquez et al. 1986, 1987) have been found to maximize yield while minimizing impurities: 15 min in 1% (w/w) NaOH solution at 95 °C with a solid/liquid ratio of 1/10. These conditions allow the extraction of 90% of polyphenols and only 5% of carbohydrates; though higher alkali concentrations give higher polyphenols yield, they also increase the impurity content and lower stability, thus making the total extract less suitable for adhesive manufacture (Vázquez et al. 1989). The concentration of reactive products in the extracts was 75% rather than the 50–60% quoted for pine bark by Pizzi (1983), the improvement doubtless being due to the short extraction time thus reducing extraction of impurities.

Tannins were concentrated by precipitation at pH 2 (Hemingway, McGraw 1977). Though some 30% of the polyphenols are lost, this procedure nevertheless gives the best overall results because there are no problems with redissolution later on (Vázquez et al. 1989).

Separation of the precipitate by filtration was hampered by the gelatinous nature of the solid, as was previously found by Suomi-Lindberg (1984) for pressure filtration of fir bark extracts. To reduce this problem, we preferred to use centrifugal filtration, which afforded a better solids concentration (18%) and a better Stiasny number (92) than those reported by Suomi-Lindberg. In spite of the improvement, however, a solids concentration of merely 18% means that only low levels of phenol replacement can be used if the solids concentration in the resins is to exceed 40% (as it is necessary for good board quality). The filtered precipitate was therefore dried to a moisture content of less than 60%, which increased the Stiasny number to 100 (doubtless due to loss of soluble impurities).

Initially, resoles were prepared as described above with two degrees of condensation (reflected by viscosities

Table 1. Resoles prepared

Resol	F/P	μ (25 °C) mPa · s	pH	% solids
P1	2.5	100	11.40	44.9
P2	2.5	80.5	11.35	45.1
P3	2.0	98	11.74	50.3
P4	2.0	72	11.73	48.7
P5	1.8	78	11.42	51.8
P6	1.8	98	11.40	52.0

Table 3. Resin properties

Resin	pH	Solids (%)	Free Phenol (%)
R3	10.79	41.76	3.75
R3+	11.10	41.84	3.82
R4	10.88	41.56	4.29
R4+	11.14	41.75	4.94
R5	11.71	41.91	5.39
R5+	12.13	41.83	5.54
R6	11.50	41.72	3.50
R6+	11.78	41.78	3.98

Table 2. Resol properties 3 month after preparation

Resol	μ (25 °C) mPa · s	ρ (25 °C) g/cm^3	pH	t_{gel} (min)	Free Formol, %	Free Phenol, %	Solids %
P1	242	1.180	11.2	10.1	3.68	2.58	46.1
P2	152	1.180	11.1	11.0	3.36	2.97	46.4
P3	152	1.191	11.1	21.0	0.80	<6	46.7
P4	108	1.188	11.3	23.7	0.68	<6	50.6

Table 4. Delamination test

Plywood	AP 302	Press T (°C)	Press t (min)	Mean values
T3	Standard	130	8	4.8–6.0
T3+	Standard	130	8	5.0–5.5
T3+	Standard	160	3.5	5.0–4.3
T4	Standard	130	8	6.8–6.0
T4	Without paraf.	130	8	4.0–4.5
T4+	Without paraf.	130	8	5.3–4.3
T4+	1/2 paraf.	130	8	5.5–4.8
T5	Standard	130	8	6.5
T5	1/2 paraf.	130	8	5.8–6.8
T5*	Standard	130	8	4.5–3.5
T5+	Standard	130	8	5.5–4.0
T6	Standard	130	8	7.0–7.0
T6	Without paraf.	130	8	6.8–7.0
T6	Without paraf.	180	3	6.0–6.3
T6	Without paraf.	185	2.5	5.5–5.5.
T6+	Standard	130	8	5.8–6.5

* Plywoods with 15% moisture were used.
AP 302 is a filler with paraformaldehyde catalyst supplied by FORESA.

of approximately 75 and 100 mPa · s) and F/P ratios of 2.0 and 2.5 (P1–P4 in Table 1). After 3 months at 4 °C they were re-analysed (Table 2). Those with the higher F/P ratio were the less stable, releasing more free formaldehyde and so gelling faster, which meant that the reaction-induced increase in viscosity upon mixture with tannin solution was too fast for practical use as adhesive. In view of these results, resoles were then prepared with an F/P ratio of 1.8 (P5 and P6 in Table 1).

Resins were prepared from resoles P3–P6 with S/P ratios of 0.5 (for resins labelled Rn in Table 3, $3 \leq n \leq 6$) and 0.6 (resins labelled Rn+ in Table 3). The difference in soda content with respect to the resoles was due to the NaOH used for redissolution of the tannins. Condensation, and consequent progressive increase in viscosity, occurred at room temperature upon addition of the resol to the tannin solution. For homogeneous resins, the tannins must be well dissolved, making intense stirring necessary during both tannin redissolution and the mixture of tannin and resol. The resins with the lowest free phenol contents were those prepared from resoles P3 and P6, these being the most highly polymerized resoles used. All the resins had solids contents of over 41%, and no free formaldehyde was detected in any of them, which is of considerable relevance for industrial usage in view of the limits on formaldehyde content and emission imposed by most European countries (Marutzky, Dix 1984).

DTA of the resins showed three endothermic peaks. The most intense corresponded to the evaporation of water at 100 °C. More interesting here is the peak located between 130° and 140 °C, whose exact position and intensity depended on the S/P ratio and the degree of condensation respectively, the lower S/P ratio giving a cooler peak and greater polymerization reducing peak amplitude. The temperature of this peak is the temperature that must be reached for the resin to be cured completely. The third endothermic peak, located between 60° and 70 °C (the temperature increasing with F/P ratio), is related to the cold-curing properties of the resin.

For the manufacture of plywood boards, the viscosity of the resins was controlled by mixing them with filler (AP 302, from FORESA). In general, a filler/resin ratio of 15 : 100 (w/w) was appropriate. In some formulations the catalyst normally present in the filler, paraformaldehyde, was reduced or totally omitted.

The board quality results, obtained as per BS 1455 : 1963, are listed in Table 4. Most boards passed the test, and if the variability of ply quality and the degree of subjectivity of the standard are taken into account, there was good agreement between the two sample values. For a given F/P ratio, the better S/P ratio for the resin was 0.5. The best F/P ratio was 1.8, which is especially pleasing because the relatively low free formaldehyde content of the starting resol, making it less reactive with the extracts, means that the resin is correspondingly more stable; this finding is corroborated by the fact that resin R6 gave better results than the less polymerized resin R5.

To maximize productivity by minimizing press time, boards should be pressed at the highest temperature possible. When synthetic phenolic resins are used, a temperature of 130 °C is generally applied, allowing a press time of 8 min. In this work, boards pressed for shorter times at higher temperatures were found to be quite satisfactory, doubtless because tannin-based adhesives harden that fast (Hse, Kwo 1988). It is likewise this fast hardening rate that allows the use of filler with no paraformaldehyde hardener.

Though of poorer quality than those made from plys with moisture content below 8%, two boards were made from plys having a moisture content of 15%, which can not be prepared using commercial phenolic resins. The fact that it was possible to do this is in keeping Pizzi's (1983) information concerning the preparation of particleboards using wattle tannin resins.

4 Conclusions

Eucalyptus globulus plywood boards were manufactured using resins obtained by copolymerization, at room temperature, of resoles and tannins extracted from *Pinus pinaster* bark. Even boards prepared under the least favourable conditions used were superior to those prepared from this kind of wood using commercial phenolic resins, and met BS 1455 : 1963 WBP quality standards. The tannin-based resins also exhibited several operational advantages over commercial phenolic resins, including ease of application, high spreading, absence of detectable free formaldehyde, absence of bleeding at temperatures up to 185 °C, and absence of blowouts in the glueline when ply moisture content is above 8%. In future work we aim to optimize the formulation used and to investigate technological variables using press diagrams.

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Holz als Roh- und Werkstoff

Die Struktur von mit aerophyten Algen infiziertem Holz

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Subject: The effect of aerophytic algae on structure of Scots pine and beech wood

Material und Methode: Holz von Kiefer (Pinus silvestris L.) und Buche (Fagus silvatica L.), das 12 Wochen lang „in vitro" der Einwirkung der Algen Chlorhormidium flaccidum (Kützing) Fot. und Chlorococum lobatum (Kortschikoff) Fritsch et John ausgesetzt war, wurde mit Hilfe eines Auflicht- und Rasterelektronenmikroskops untersucht.

Resultate: **1.** Die Oberfläche des Holzes wurde mit einer intensiven Algenvegetation in grüner Farbe überzogen. **2.** Ch. flaccidum (Fadenalge) bildete einen einheitlichen netzförmigen Thallus, Ch. lobatum (Kugelalge) dagegen entwickelte sich in Form von geschlossenen Ansammlungen. **3.** Beide Algenarten wuchsen 1,5–2,5 mm in das Holzgewebe hinein, wobei sie natürliche Öffnungen ausnutzten. Sie siedelten sich in der Frühholzzone an und bildeten kugelförmige Anhäufungen von Fäden bzw. Kugeln (Kokken) innerhalb von Tracheiden und Markstrahlen bei Kiefer und nur in den Gefäßen bei Buche. **4.** Sowohl die mit den Zellwänden in Berührung kommenden Fäden als auch die Kugeln (Kokken) verbanden sich mit ihnen und schufen Erweiterungen in Form von Appresorien und Haustorien (Bilder 1 und 2). **5.** Die gelegentlich unter ihnen in den Zellwänden entstehenden kraterförmigen Vertiefungen lassen auf eine abbauende Wirkung der Algen auf das Holzgewebe (Bild 3) schließen, deren Mechanismus in weiteren Untersuchungen Aufklärung verlangt.

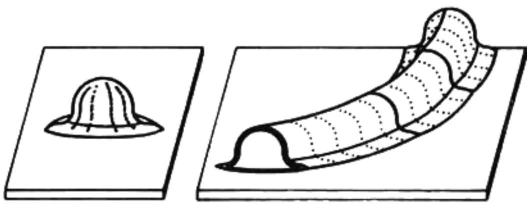

Bild 1 und 2. Appresorien und Haustorien an den Berührungspunkten zwischen Algen und Zellwand

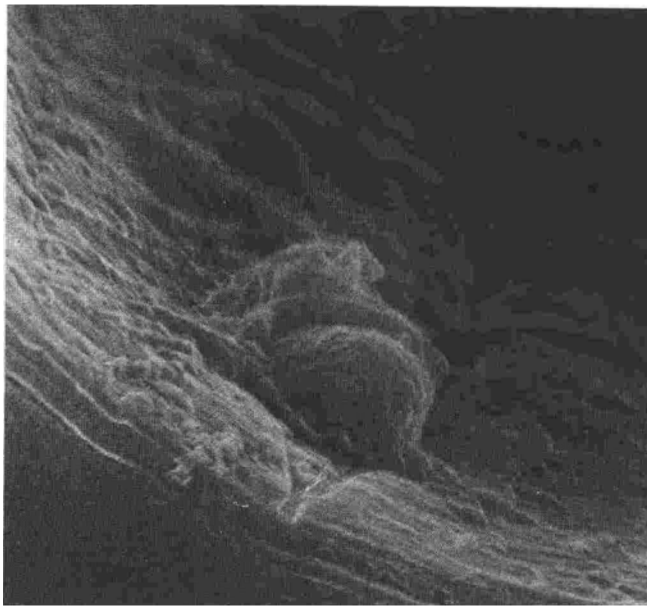

Bild 3. Abbau des Holzgewebes durch aerophyte Algen (REM-Aufnahme)