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Wood adhesives based on tannin extracts from barks of some pine and spruce species

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Barks available in commercial quantities in Australia and overseas have been examined for their efficacy as raw materials for conversion to high quality adhesives for reconstituted wood products. Previously bark from mature *Pinus radiata* was found to be suitable. This paper examines the suitability of barks from four mature pine species (*Pinus caribaea, Pinus elliottii, Pinus pinaster* and *Pinus sylvestris*), one young pine species (*Pinus radiata*) and one spruce species (*Picea abies*). Only the bark extracts of *Pinus caribaea* and *Pinus pinaster* gave high quality (Type A bond, WBP) wood adhesives. The gluing properties of the adhesives derived from the extracts appeared to be dependent on their contents of formaldehyde-reactive polyflavanoids as indicated by their Stiasny values, with a value of 65 % being the minimum for producing a high quality adhesive by the methods used.

Holzkleber auf der Grundlage von Tanninextrakten aus Rinden einiger Kiefern- und Fichtenarten

Rinden, die in Australien und Übersee im Handel sind, wurden überprüft hinsichtlich ihrer Eignung zur Umwandlung in hochwertige Leime für Holzwerkstoffe. Vor allem die Rinde von *Pinus radiata* erwies sich in früheren Untersuchungen als geeignet. In dieser Arbeit werden auch Untersuchungen an Rinden anderer Baumarten vorgestellt, und zwar: *Pinus caribaea, Pinus elliottii, Pinus pinaster, Pinus sylvestris,* junge *Pinus radiata* und *Picea abies* species. Nur aus Rinden von *Pinus caribaea* und *Pinus pinaster* konnten hochwertige Kleber hergestellt werden (Typ A-Bindung, WBP). Die Kleber-Eigenschaften scheinen vom jeweiligen Gehalt an Polyflavanoiden abzuhängen, die mit Formaldehyd reagieren können, wie die Stiasny-Zahlen anzeigen. Ein Wert von 65 % war für die hier angewandten Methoden das Minimum zur Herstellung eines hochwertigen Klebers.

1 Introduction

Tannin extracts from barks of various commercially important softwood trees contain polyflavanoids which react with formaldehyde to form condensation products. The polyflavanoids-formaldehyde condensates have been widely studied particularly with a view to producing suitable adhesives for reconstituted wood products such as plywood, particleboard and laminated timber.

Such softwood species studied relating to wood adhesives for these applications include *Pinus radiata* (Dalton 1953; Booth et al. 1958; Herzberg 1960; Plomley 1966; Jenkin 1982; Pizzi 1982; Weißmann and Ayla 1982; Woo 1982; Dix and Marutzky 1984; Crammond and Wilcox 1992; Sealy-Fisher and Pizzi 1992), *Pinus brutia* (Ayla and Weißmann 1982), *Pinus pinaster* (Vázquez et al. 1989, 1992), *Pinus taeda* (Kreibich and Hemingway 1985, 1987), *Picea abies* (Liiri et al. 1982; Suomi-Lindberg 1984), *Larix* spp. from Siberia (Takano and Karasawa 1981) and *Larix leptolepis* (Komazawa et al. 1985).

However, difficulties have been encountered in the utilisation of the tannin extracts from these softwood barks primarily due to low extract yields, low Stiasny values, excessive viscosity and variable quality of extracts. These problems have been found to be related to methods of extraction and subsequent processing of the extracts.

The previous papers (Yazaki and Collins 1994a, 1994b) reported that high bond quality (Type A bond, WBP, fully weather and boil proof) plywood could be produced using adhesives based on appropriately treated high yield extracts from the bark of *Pinus radiata* obtained by a four-stage squeeze extraction. In order to know how widely this technology can be applied, samples of bark from various commercially important species of pine and spruce have been examined.

2 Experimental

2.1 Bark samples

The bark samples used in this study were commercially available ones which consisted of outer bark, inner bark and woody material and were taken directly from debarkers of saw mills, particleboard mills or a paper mill. The details of bark samples are given in Table 1. The air-dried bark samples were conditioned to 12% moisture content and then ground to pass a 12.5 mm screen in a Wiley mill.

2.2 Bark extraction

The details of the extraction procedures have been described previously (Yazaki and Collins 1994a). The ground bark sample (1.12 kg) was mixed with water(2.38 kg) and steam injected directly into the slurry for 15 minutes so that the final weight of solvent was 3 kg. The hot water-bark mixture was poured into a pre-heated (100°C) die, pressed and held for a total of 2 minutes. The squeezed extracts were freeze-dried. A four-stage extraction was carried out in the same manner with the following sequence; 2 × hot water + 1 × hot water at pH 8.3 + 1 × hot water washing.

2.3 Separation of insolubles from the extracts at pH 6

One part of proportionally recombined extracts was dissolved in nine parts of water and the pH of the solution was adjusted to pH 6.0 with 99.7% acetic acid. The soluble and insoluble portions

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Table 1. Details of bark samples

Species	Common name	Age (year old)	Place
Pinus radiata	Radiata pine	12	Oberon, NSW Australia
Pinus pinaster	Maritime pine	30–35	Mt Gambier, SA Australia
Pinus caribaea	Caribbean pine	25–35	Tuan Forest, Qld Australia
Pinus elliottii	Slash pine	30	Stoney Creek, Qld Australia
Pinus sylvestris	Scots pine	60*	Finland
Picea abies	Norway spruce	70*	Finland

* Average age

were separated by centrifuging at 1000 × g for 30 minutes and then freeze-dried.

2.4 Sulphitation

Either the insolubles (25 parts by mass) from the recombined extracts solution at pH 6 or the proportionally recombined pH 8.3 and hot water washing extracts (25 parts) were mixed with sodium metabisulphite (1.25 parts) and water (75 parts), heated under reflux for 2 hours and then freeze-dried.

2.5 Adhesive formulation

All the adhesive formulations consisted of the freeze-dried and recombined extracts (40 parts), paraformaldehyde(4 parts), macadamia nut shell flour (10 parts)and water (60 parts) unless otherwise mentioned.

2.6 Gluing conditions and gluebond assessment

Plywood samples of 3-ply construction were prepared by bonding veneers (300 × 300 × 2.5 mm) of coachwood (*Ceratopetalum apetalum*). The gluing conditions are summarised in Tables 5 and 6 and the gluebond assessments were made according to the Australian Standards AS 2098.2-1977, AS 2271-1979 and AS 2754.1-1985. The details on gluing conditions and gluebond assessment have been described (Yazaki and Collins 1994a).

2.7 General methods

The details of other methods used have been described (Yazaki and Hillis 1980; Yazaki 1987).

3 Results and discussion

3.1 Extractives yield and Stiansy value

The previous paper (Yazaki and Collins 1994a) reported that the extraction of radiata pine bark using a four-stage squeeze extraction provided a high extractives yield (approximately 30%), despite the fact that the particle size of the major bark fraction (63%) varied between 1.4 and 12.5 mm and a ratio of 1 bark to 3 solvent (by mass) was used. Furthermore, this mild extraction, which consisted of two successive hot water extractions followed by hot water extraction at pH 8.3 and washing, provided the highest quality extracts suitable for producing Type A bond (WBP, fully weather and boil proof) wood adhesives. Here, the bark samples from the five pine and one spruce species have been extracted in the same manner.

Table 2. Extractives yields from barks of pines and spruce

	Extractives yields (%)				
	Hot water 1	Hot water 2	pH 8.3	Washing	Total
Pinus radiata	13.4	5.7	9.8	4.0	32.9
Pinus pinaster	9.9	4.2	8.2	2.6	24.9
Pinus caribaea	7.5	3.4	7.3	2.9	21.1
Pinus elliottii	4.5	2.0	5.8	1.9	14.2
Pinus sylvestris	2.0	1.1	5.3	2.1	10.5
Picea abies	4.3	2.0	5.3	2.2	13.8

Considerable differences in extractives yields were observed between these species(Table 2). Low yields were obtained from *Pinus silvestris, Picea abies* and *Pinus elliottii*, particularly in the hot water extracts 1 and 2 from *Pinus sylvestris.* On the other hand, the bark sample of young (12-year old) *Pinus radiata* logs provided the highest yield (32.9%) followed by *Pinus pinaster* (24.9%) and *Pinus caribaea* (21.1%). It appears that higher extractives yields are partly due to higher yields from hot water extracts 1 and 2. For example, the yield of hot water extracts 1 and 2 from *Pinus radiata* bark was 58% of the total extracts while that from *Pinus sylvestris* was only 29.5%.

Approximate amounts of polyflavanoids reactive to formaldehyde in the extracts can be determined by the Stiasny method (Yazaki and Hillis 1980) and expressed as the Stiasny value (Table 3). The highest Stiasny value (80.1%) was obtained from the recombined extracts of *Pinus caribaea* which was equivalent to that (82.0%) of 30-year old *Pinus radiata*, while the lowest value (43.8%) was obtained from the recombined extracts of *Pinus sylvestris* bark. The Stiasny value (59.4%) of the recombined extracts from *Picea abies* was very similar to those reported by Prasetya and Roffael (1991).

Although 12-year old *Pinus radiata* bark provided the highest extractives yield (32.9%), which was slightly higher than that (29.4%) from 30-year old *Pinus radiata* bark, the Stiasny value (56.2%) of the recombined extracts from young *Pinus radiata* bark was considerably less than that (82.0%) from old *Pinus radiata.* This may be due to the bark samples from young *Pinus radiata* logs containing a much greater proportion of inner bark and woody material so that the extracts contain more carbohydrates.

3.2 Methods to reduce the viscosity of tannin extracts

All the recombined extracts had viscosities greater than 8,000 mPa.s at 40% solids content and 25°C. The results of a study on the solubility of extracts from *Pinus radiata* bark (Yazaki, 1987) revealed that the insoluble components of the extracts at pH 6 are basically higher polymerized procyanidins which are equivalent to the high viscosity producing components obtained by the

Table 3. Stiasny values of extracts from bark samples

	Stiasny value (%)				
	Hot water 1	Hot water 2	pH 8.3	Washing	Recombined
Pinus radiata	55.1	60.5	53.6	59.0	56.2
Pinus pinaster	60.0	73.4	75.2	73.3	68.7
Pinus caribaea	84.1	79.6	77.1	79.5	80.1
Pinus elliottii	45.2	38.5	60.7	55.0	51.4
Pinus sylvestris	22.5	26.5	52.9	47.7	43.8
Picea abies	61.3	62.0	59.2	59.6	59.4

Table 4. Fractionation of the recombined extracts at pH 6.0

	Portion of extracts (%)	
	Insolubles	Solubles
Pinus radiata	31.2	68.6
Pinus pinaster	25.1	74.9
Pinus caribaea	24.3	75.7
Pinus elliottii	35.4	64.6
Pinus sylvestris	24.5	75.5
Picea abies	35.3	64,7

ultrafiltration. In order to decrease the viscosity of those extracts, the extracts were seperated into solubles and insolubles at pH 6 by centrifuging (Table 4) and the insolubles were sulphited and recombined with solubles. This process provided low viscosity extracts for adhesive formulations.

Although the separation of insolubles from the aqueous extracts solution at pH 6 was carried out effectively by centrifuging, the centrifugation process between the extraction and the sulphitation of the insolubles would be an expensive practice in industry. However, when the combined pH 8.3 and hot water washing extracts were sulphited and recombined with hot water extracts 1 and 2, the viscosity of the recombined extracts was suitable for the formulation of adhesives which provided high quality gluebonds (Yazaki and Collins 1994b). Therefore, the sulphitation of the combined pH 8.3 and hot water washing extracts was carried out in this study.

3.3 Gluing properties

Gluing conditions and gluebond quality from adhesives based on the extracts from barks of five pine and one spruce species are summarized in Tables 5 and 6. When all the extracts were recombined and the pH was adjusted to 6.0, approximately 25% of the recombined extracts from *Pinus pinaster* and *Pinus caribaea* barks were insolubles (Table 4). These insolubles were sulphited, recombined again with the solubles and the mix formulated as adhesives. The adhesives thus prepared provided plywood samples of good gluebond quality. However, adhesives based on the extracts, which were treated in the same manner, from barks of young *Pinus radiata* and *Pinus elliottii* provided some bonding but failed to pass the Australian Standards, whilst the extracts from barks of *Pinus sylvestris* and *Picea abies* resulted in little or no bonding (Table 5).

Similar results were also obtained when the combined pH 8.3 and hot water washing extracts were sulphited and recombined with the hot water extracts 1 and 2 (Table 6). Adhesives based on the extracts from barks of *Pinus pinaster* and *Pinus caribaea* produced plywood samples of high gluebond quality, while those from young *Pinus radiata* and *Pinus elliottii* barks could not produce plywood samples which passed the Australian Standards. Because of insufficient amounts of extracts, the gluing tests on extracts from *Pinus sylvestris* and *Picea abies* were not attempted.

The previous papers (Yazaki and Collins 1994a, b) reported that the extracts from 30-year old *Pinus radiata* bark provided plywood samples of excellent quality bonding. However, this study revealed that the extracts from 12-year old *Pinus radiata* bark could not produce plywood samples of good quality bonding. This difference appears to correspond to the difference in Stiasny values with the value for the recombined extracts from bark of 30-year old *Pinus radiata* logs being 82.0% while that of 12-year old *Pinus radiata* logs from thinnings was only 56.6%.

Furthermore, comparing the results from gluing tests with the

Table 5. Gluing conditions and gluebond quality from adhesives based on the extracts in which insolubles were seperated at pH 6.0, sulphited and recombined with solubles

Bark extracts from	Veneer moisture content (%)	Total assembly time (min)	Glueline* moisture content (%)	Gluebond quality**	
				Dry	Wet after 72 h boiling
Pinus radiata	5	25	24.0	1.0	–
Pinus radiata	12	55	22.0	2.5	–
Pinus pinaster	5	45	20.5	6.0	6.0
Pinus pinaster	12	85	22.0	6.0	5.0
Pinus caribaea	5	40	22.0	6.0	6.5
Pinua caribaea	12	55	23.0	6.5	7.0
Pinus elliottii	5	45	21.0	1.0	–
Pinus elliottii	12	90	21.0	2.0	–
Pinus sylvestris	5	40	22.0	0.0	–
Pinus sylvestris	12	55	23.0	0.0	–
Picea abies	5	40	22.0	0.0	–
Picea abies	12	55	23.0	0.0	–

* These numbers are readings directly obtained by Delmhorst resistance moisture meter model J-I

** Bond quality assessment(AS 2754.1-1985) of the two gluelines of each test panel, O, no wood failure to 10, 100% wood failure

Stiasny values, the extracts from *Pinus caribaea* and *Pinus pinaster* barks produced plywood samples of high quality bonding and the Stiasny values of the recombined extracts from these pine species were 80.1% and 68.7% respectively. On the other hand, the extracts from bark of *Pinus sylvestris* resulted in little or no bonding in the plywood sample and the Stiasny value was only 43.8%. Since the extracts from *Picea abies* failed to produce any well bonded plywoods and the Stiasny value was 59.4%, a critical Stiasny value for wood adesives of good quality may be 65%. However, although the Stiasny values for the young *Pinus radiata* bark were lower than those for *Picea abies*, the extracts provided some bonding in the plywood samples. This indicates that some other factors such as structure, compositions and degree of polymerization of reactive polyflavanoids and carbohydrates also affect the bonding quality. For example, when the insolubles at pH 6 of the extracts from *Picea abies* was sulphited, recombined and then formulated, the viscosity of the adhesives was much higher than those from *Pinus radiata, Pinus pinaster* and *Pinus caribaea*. This viscosity affects the flow of adhesives at the glueline so that different gluebond quality might be obtained.

Table 6. Conditions and gluebond quality from adhesives based on the extracts in which extracts from pH 8.3 extraction and hot water washing were sulphited and combined with hot water extracts 1 and 2

Bark extracts from	Veneer moisture content (%)	Total assembly time (min)	Glueline* moisture content (%)	Gluebond quality**	
				Dry	Wet after 72h boiling
Pinus radiata	5	20	22.0	1.0	–
Pinus radiata	12	65	22.5	3.0	–
Pinus pinaster	5	30	21.0	6.0	6.0
Pinus pinaster	12	65	18.0	6.5	7.0
Pinus caribaea	5	30	20.0	6.0	7.0
Pinus caribea	12	75	23.0	8.5	7.0
Pinus elliottii	5	35	18.5	0.0	–
Pinus elliottii	12	75	20.0	0.0	–

* These numbers are reading directly obtained by Delmhorst resistance moisture meter model J-I

** Bond quality assessment (AS 2754. 1–1985) of the gluelines of each test panel, O, no wood failure to 10, 100% wood failure

Consequently, the technology described in the previous papers (Yazaki.and Collins 1994a, b), which involves high yield extractives obtained from a four-stage squeeze extraction, sulphitation of high molecular weight procyanidin polymer extracts and recombination with the rest of the extracts, may be applicable only for bark extracts which give Stiasny values of higher than 65%.

Work has already commenced to develop new technology to convert lower quality extracts such as those from barks of young *Pinus radiata*, *Pinus elliottii*, *Pinus sylvestris* and *Picea abies* into wood adhesives of high quality.

4
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