WOOD EXTRACTIVES OF RUBBERWOOD *(HEVEA BRASILIENSIS)* AND THEIR INFLUENCES ON THE SETTING OF THE INORGANIC BINDER IN GYPSUM-BONDED PARTICLEBOARDS

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Received July 1992

SIMATUPANG, M. H., SCHMITT, U. & ANWAR KASIM. 1994. **Wood extractives of rubberwood (*Hevea brasiliensis*) and their influences on the setting of the inorganic binder in gypsum-bonded particleboards.** The wood extractives of rubberwood were investigated. The amount of acetone extract was 1.95 % (based on oven-dry wood). It contained 0.89 % free fatty acids, 0.10% phenolic compounds, and 0.29% esters. The main fatty acids were palmitic and oleic acids. β-sitosterol and campesterol were detected in the unsaponified fraction of the neutral part. The water extract amounted to 4.58 % based on oven-dry wood. Gypsum setting retarding compounds were found mainly in this extract. Using TLC and gel filtration the active principles were isolated and identified as a mixture of amino acids. They consisted of glutamine, arginine, alanine, and asparagine. Their concentration was about 1% (oven-dry wood). Rubberwood was suitable for the manufacture of gypsum particleboards. However, the density of the boards should be about 1,250 $kg\ m^{-3}$ to compensate for the higher specific weight of the wood. The addition of the required additive has to be adjusted to the retarding properties of the wood extractives. Hydrolyzable tannin was less suitable as additive. The co-occurrence of rather high amounts of free carbohydrates and amino acids is probably the cause of the high susceptibility of freshly cut wood to blue stain.

Key words: Rubberwood - extractives - gypsum setting - retarding - additives - gypsum particleboards

SIMATUPANG, M. H., SCHMITT, U. & ANWAR KASIM. 1994. Bahan ekstratif kayu getah (*Hevea brasiliensis*) dan pengaruhnya terhadap proses pemejalan perekat inorganic dalam papan serpai gipsum. Bahan ekstratif kayu getah telah dikaji. Ia mengandungi 1.95% ekstrak aseton (berdasarkan kayu keringan ketuhar), 0.89% asid lemak bebas, 0.10 % sebatian fenolik dan 0.29% ester. Asid lemak bebas yang utama

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ialah asid palmitic dan asid olik. β - sitosterol dan kompesterol telah dikesan didalam pecahan yang yang tidak di sapon pada bahagian neutral. Jumlah ekstrak air ialah 4.58% berdasarkan kayu keringan ketuhar. Sebatian perencat pemejalan gipsum didapati terutamanya didalam ekstrak ini. Bahan aktif utama telah diasingkan dan dikenalpasti sebagai campuran asid amino dengan kaedah TLC dan penurasan gel. Campuran asid amino ini terdiri daripada glutamin, arginin, alanin dan asparagin. Kepekatan campuran ini ialah 1% (berdasarkan kayu keringan ketuhar). Kayu getah sesuai dalam pembuatan papan serpai gipsum. Walau bagaimanapun, ketumpatan papan serpai gipsum ini mestilah lebih kurang 1,250 *kg m* $^{-3}$ untuk mengimbangi berak spesifik kayu getah. Pencampuran bahan tambah yang diperlukan hendaklah disesuaikan kepada sifat-sifat rencatan bahan ekstraktif kayu getah. Tannin yang boleh dihidrolisis didapati kurang sesuai sebagai bahan tambah. Kehadiran bersama jumlah karbohidrat bebas dan asid amino yang agak tinggi mungkin menyebabkan kayu yang dipotong rentat terhadap pewarna biru.

Introduction

Rubberwood is presently an important commercial wood species, especially in Malaysia, Indonesia and Thailand (Ser 1990). These three countries produce about 80% of the world production of rubberwood. The total production of this wood amounts to 20,665 *t* annually. The wood is easy to work, has a nice light colour and a density of between 400 and 600 *kg m* $^{-3}$. It is presently used as a substitute for ramin (*Gonystylus bancanus*) in the manufacture of furniture and in light construction. Wood particleboard, medium density fiberboard and plywood are also made from rubberwood. Bark free wood is suitable for the manufacture of pulp (Killmannn 1987, Anonymous 1991). The utilization of rubberwood is presently intensively promoted. It is widely accepted, because the wood comes from plantations.

Freshly cut rubberwood is very susceptible to blue stain. For prevention the freshly cut logs are treated with fungicides or kiln dried within a short period after cutting. The high susceptibility to blue stain is due to its high content of free sugars.

In contrast to abundant data on the chemical properties of the latex of rubberwood, only little information is available on the extractives of this species. Patrick (1956) reports the occurrence of D-apiose in rubberwood. Mesoinosite, inosite, glucose, fructose, saccharose, and cyclite were detected in the root, bark and wood (D'Auzac & Pujarniscle 1967). The main constituent of the hemicelluloses of the wood is a xylan which on hydrolysis yields xylose and 4-0- methyl-D-glucuronic acid (Guha & Lee 1972). The wood consists of 77.8% holocellulose, 39.7% α - cellulose, and 17.8% Klason lignin. The content of wood extractive was reported as 3.4% (Chinchole & Apte 1969). According to Sandermann *et. al* (1965) no caoutchouc could be detected by chemical analysis in the wood. According to Lim (1985), however, a compound was detected by scanning electron microscopy in the vessels of rubberwood, which was supposed to be caoutchouc. Starch and calcium containing crystals were also present in the vessels.

Gnananharan and Dhamodaran (1985) found rubberwood to be less suitable than some other Indian wood species for wood wool cement board due to the high content of cold water solubles (3.35%). Azizol and Rahim (1989) determined the content of free sugars in freshly cut as well as in seasoned rubberwood logs. Freshly cut logs contained 1.05 to 2.29% of free sugars and 7.53 to 10.17% of starch. After 20 weeks of seasoning in the open the sugar content and the starch content decreased to 0.23 and 1.08% respectively. The freshly cut logs were unsuitable for the manufacture of cement particleboards, but seasoning gave particleboards with good properties. According to Schwarz (1989) the seasoning time of 20 weeks can be reduced to 24 *h* if wood chips are stored in piles. Within the piles free sugars and starch are rapidly degraded to compounds which do not inhibit the setting of cement.

According to Simatupang and Lu (1985), rubberwood retards the setting of gypsum, and the fabricated gypsum particleboards show poor properties. The active compounds responsible for this retardation are not known. It was, therefore, the purpose of this investigation to characterize the gypsum setting retarders in rubberwood and also determine the effects of the extractives on the manufacture and the properties of gypsum particleboard.

Materials and methods

The wood for the examination, obtained from the Forest Research Institute Malaysia, Kepong, was of clone TJ6, cut in August 1986 in Bukit Kiara, Kuala Lumpur. The wood was chipped and dried within 24 *h* after cutting. It was then shipped to Hamburg by air freight. The wood did not show any signs of blue stain. Part of the chips were milled to obtain wood meal and sieved. The fraction < 0.5 *mm* and > 0.3 *mm* was used for the extractions. The rest of the wood chips were then milled in a ring flaker of an industrial laboratory in order to obtain wood particles suitable for particleboard. Wood particles passing a screen of 2 *mm* were used for the outer layers of the gypsum particleboard. The middle layer was formed of wood particles which passed a screen of 6 *mm* and were retained on one of 2 *mm*.

Wood extractives

Acetone extract

The acetone extract was obtained by extraction of 20 *g* of rubberwood meal with a Soxhlet apparatus. The solvent was then evaporated and the residue successively treated with 100 *ml* portions of petroleum ether, diethyl ether, and ethyl acetate. The combined solutions were then heated separately under reduced pressure to distil the solvents. Part of the residues was used to determine the compatibility with β - gypsum hemihydrate using a semi-micro method by measuring the electrical conductivity of plaster paste. According to this method only 1 *g* of β - gypsum-hemihydrate and 0.5 *ml* of water which might contain wood extractives were required for each determination (Simatupang *et al.* 1988). Small amounts of compounds isolated by thin layer chromatography (TLC) or by gel filtration (GF) were examined using a second method which required only 100 *mg* of β-

gypsum-hemihydrate and 50 *μl* of the solution (Simatupang *et al.* 1992). The respective compounds were dissolved in distilled water and mixed with ß-gypsum -hemihydrate. The concentration of compounds in the gauge water was adjusted such that it was the same as in the original extract of 10 *g* of oven- dry wood - in 150 *ml* of solvent. If the compound was sparingly soluble in water, a suspension of it was used as make-up water.

A portion of the petroleum ether extract was dissolved in diethyl ether and then separated into free acids, phenolic compounds, and neutral parts by treating it successively with a solution of sodium carbonate (2 *N*) and potassium hydroxide (2 *N*). The sodium carbonate solution was acidified and the free acids were extracted with diethyl ether. This solution was washed with distilled water, and then treated with anhydrous sodium sulphate to remove moisture. After distilling the diethyl ether, the residue was esterified with methanol and sulphuric acid to obtain the methyl esters. The compounds soluble in potassium hydroxide solution - phenolic compounds - were isolated after acidification with sulphuric acid using diethyl ether for extraction, and the solvent was distilled. This fraction was not examined in detail.

The diethyl ether solution containing the neutral part was concentrated to dryness, and then saponified with an ethanolic potassium hydroxide solution (0.5 *N*). After removing most of the ethanol, distilled water was added. The unsaponified part was then extracted with diethyl ether, and after neutral washing with water and treating with anhydrous sodium sulphate, concentrated to dryness. The potassium hydroxide solution, which contained the acids, was then acidified, and the acids extracted with diethyl ether. These acids were also transformed into the methyl esters. All esters and the unsaponified parts were then analyzed by gas chromatography (GC) using a Perkin Elmer Type Sigma 2 B apparatus, equipped with a flame ionization detector. The peaks were integrated with a Shimadzu Recording Data Processor (Type Chromatopac, C RIB). Two kinds of capillary columns, each made of quartz 30 *m* long, were applied. They were lined with chemically bonded methyl - (5% phenyl) - polysiloxane and with carbowax respectively. The carrier gas was hydrogen with a flow rate of 2 *ml* min^{-1} and a split of 1:40. The temperature varied from 200 to 260°C. The separated compounds were identified by comparison with authentic samples.

Water extracts

Rubberwood meal (100 *g*) was treated for 30 *min* with one litre of distilled water. The solution was filtered off on a Buchner funne and the residual wood meal washed with warm water until the total filtrate had a volume of 1.5 *l*. The filtrate was then concentrated to dryness by lyophilization and the residue weighed. It was subsequently extracted with a mixture of water and acetone (1:1).

Determination of hydration time

Untreated or extracted wood meal (10 *g*, oven dried basis) was mixed with 200*g* of ß-gypsum-hemihydrate and 100*ml* of distilled water - taking into acccount the moisture content of the wood - in a plastic beaker. The beaker was placed in a Dewar vessel and provided with a cover. A thermocouple connected to a recorder traced the hydration temperature (Sandermann & Kohler 1964). Due to variation of the commercially available gypsum hemihydrate, results were presented with respect to the employed ß-gypsum-hemihydrate, and designated as relative hydration time. To determine the influence of small amounts of wood extractives in the hydration of gypsum, the extractives were isolated by TLC or gel chromatography as described earlier.

Thin layer chromatography (TLC) and column chromatography

Preparative TLC was carried out with glass plates precoated with cellulose (0.5 *mm* thick). Six percent acetic acid was used as mobile phase. The separated compounds were visualized with ammonia vapours, and the cellulose layers containing the detected compounds were then scraped off, extracted with water and filtered. The solution was concentrated to dryness in a rotary evaporator and the gypsum retarding effect of the residue was examined.

The isolated fraction with a R-value of 0.87 was further separated by TLC with n- butanol/acetic acid/water (4:1:5). A small strip of the TLC sheets was sprayed with an ethanolic solution of vanillin hydrochloric acid to localize the separated compounds.

Free carbohydrates were separated on TLC glass plates precoated with silica gel according to De Stefanis (1968). Diphenylamine aniline phosphoric acid was used to detect the sugars. The reaction according to Zand and Sandler (1957) was applied to distinguish between pentose and hexose. A solution of the compound was mixed with an ethanolic solution of β-naphthol, and underlaid with concentrated sulphuric acid. On the border between the sulphuric acid and the ethanolic solution, hexoses and pentoses will give a red and a blue ring respectively. Further analysis of the carbohydrates was accomplished by anion-exchange chromatography according to Sinner *et al*. (1975) and Sinner and Puls (1978).

Amino acids were analyzed by TLC and high performance liquid chromatography (HPLC). TLC separations were achieved according to Arx and Neher (1963), applying a two dimensional technique on silica gel precoated plates. For the first plate the mobile phase was a mixture of n-butanol/acetone/diethylamine/water (10:10:2:5) followed by isopropanol/formic acid/water (40:2:10). For the second plate the solvent was n-butanol/acetone/diethylamine/water (10:10:2:5) followed by phenol/water (75:25). The separated compounds were detected by spraying with ninhydrin solution.

For the HPLC analysis the o-phthalic aldehyde derivative of compound I was separated using a special reverse phase column based on a C_{18}* material. The mobile phase was buffer A (100%) to buffer B (100%) by a linear gradient within 43 *min*. Buffer A (basic buffer) was a solution of 1:60 *g* of phosphate buffer of pH 4.5 plus 2.10 *g* of phosphate buffer of pH 9.0 in 1000 *ml* of water plus 5 *ml* of tet

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* The analysis were carried by M. Grom, D-7033 Herrenberg.

rahydrofuran. Buffer B consisted of 35% methanol, 15% acetonitrile and 50% buffer A. The separated compounds were detected with a fluorometric detector.

Gel filtration (GF)

The separation was accomplished with Sephadex LH-20 and a mixture of acetone/water (1:1). The column was 1.25 × 70 *cm* and the flow of the mobile phase was 0.22 *ml* min^{-1}. The eluate was continuously monitored at 251 *nm* and collected in fractions of 3.3 *ml*. A total of 82 separations were performed.

Spectroscopic examinations

The UV spectra were recorded with a Shimadzu Spectrophotometer Type UV 200. IR-spectrum was recorded with a Perkin Elmer 299 IR- spectrophotometer (KBr- Disc), and for the determination of the ^{1}H-NMR-Spectra, an apparatus made by Bruker (Type WP80) was used. The chemical shifts quoted δ are relative to tetramethylsilane. Carbon and hydrogen were determined with a Heraeus CHN-O-Rapid apparatus.

Determination of the shear strength between veneer and gypsum

The specimens were manufactured and tested according to Seddig and Simatupang (1988). Two kinds of modified starch, AMIJEL 156, a corn starch and EMJEL E 30, a potato starch, were added to the β - gypsum hemihydrate to improve the bond between wood and gypsum. The concentration was 0.25% based on gypsum hemihydrate.

Manufacture, testing and scanning electron microscopy (SEM) of gypsum particleboards

The experimental gypsum particleboards were manufactured according to Simatupang and Lu (1985). The following recipe was used to produce a three layer particleboard of 40 × 40 × 1.2 *cm* with a target density of 1,200 *kg* m^{-3}. The total weight of the board was 40 × 40 × 1.2 × 1.2 *g* = 2,304 *g*. The weight ratios of the surface layer and the middle layer were 0.4 and 0.6 respectively, of the board weight. The weight of the hardened surface layer was 921.6 *g*, and the ratio of gypsum hemihydrate to wood (O. D.) and to bound water was 1: 0. 25: 0.17. The furnish for the surface layer contained 1/(1 + 0.25 + 0.17) × 921.6 *g* = 649 *g* of β-gypsum-hemihydrate and 0.25/1.42 × 921.6 g = 162.3 *g* (O.D.) of wood flakes. The effective water gypsum ratio was 0.35, and the required make-up water was 0.35 × 649 *g* + (0.3 - 0.1) × 162.3 *g* = 355.1 *g*, calculated according to Simatupang (1979). The moisture content (M.C.) of the wood flakes for the surface layer was 10%. The ratio of gypsum hemihydrate to wood (O.D.) and bound water in the middle layer was 1: 0.33 : 0.17. The required gypsum hemihydrate, wood flakes and water were calculated using the same formula for the surface layer. The furnishes for both layers were separately mixed using a pug mixer. The gauge water, which may contain a retarder, was dosed to the wood flakes. After blending the required β-gypsum hemihydrate was added. The blending was continued until a homogeneous mass was obtained. The furnish for the surface layer was divided into two equal parts and manually felted into a wooden form. On top of this first layer the furnish for the middle layer was manually felted. Finally, the surface layer was spread, and the formed board prepressed before inserting into the hydraulic press. The board was pressed between two stainless steel sheets. An iron-constantan thermocouple was inserted into the board to trace the temperature. Two stainless steel electrodes, insulated from the stainless steel cauls by thin teflon sheets, were put at the bottom and the top of the furnish respectively. The electrodes were connected to an electrical conductivity apparatus (Philips, Type 9505). The temperature and the electrical conductivity were simultaneously recorded (Simatupang 1988). Variable factors in the production of the gypsum particleboards were: presence of retarder, pressing temperature (20°C and 40°C), and pressing time (60, 150 or 450 *min*). The retarder was a hydrolyzable tannin from chestnut-tree wood.

The pressed gypsum particleboards were dried overnight at 40°C in an oven with forced air circulation. After one week storing in a room 20°C and 65 % RH, the boards were cut into samples of 23 × 5 *cm*. The bending strengths were determined according to German Industrial Standards (DIN 52 362).

Scanning electron microscopy was carried out with a Hitachi S 520 using surface and middle layer of the gypsum particleboards (Table 9).

Results and discussion

Detection of gypsum setting retarders and chemical composition of the acetone extract

Rubberwood exerted a very strong retarding effect towards gypsum. The extraction with acetone removed only a small part - about 5% of the retarder from the wood. By successive treatment with acetone and water nearly all retarding compounds could be extracted (Table 1).

The lipophilic fraction in the acetone soluble part contained traces of the gypsum retarding agent. These were found in the free acid and neutral fractions (Table 2). The free and esterified fatty acids in rubberwood were mainly palmitic, oleic and linoleic acids (Table 3). The percentage of saturated fatty acids in the free acid part was higher than in the neutral part. Two minor unidentified fatty acids (numbers 2 and 6) occurred in the chromatogram obtained with the carbowax column. These two compounds were not unsaturated C15 or C17 acids, because unsaturated fatty acids should have longer retention times than the saturated ones. The GC analysis of the unsaponified compounds on a polysiloxane column showed the occurrence of β - sitosterol and campesterol.

Table 1. Retarding effect on gypsum setting of wood and extractives of *Hevea brasiliensis*

Wood/extract	Yield of extract +) %	Relative hydration time %
Neat plaster		100
Plaster + untreated wood		245
Plaster + acetone extracted wood		220
Acetone extract	1.95	
Plaster + acetone extract		117
Plaster + acetone and water extracted wood		110
Water extract	4.58	
Plaster + water extract		205

+) Based on oven-dry wood.

Table 2. Fractionation of acetone extract and gypsum setting retarding effect

Fraction	Yield of extractives +) %	Relative hydration time %
Neat plaster		100
Petroleum ether extract		
Free fatty acids	0.89	104
Phenolic compounds	0.10	102
Neutral parts	0.29	109
Diethyl ether extract	0.03	100
Ethyl acetate extract	0.07	102
Water extract	0.57	117

+) Based on over-dry wood.

Table 3. Chemical composition and relative retention time of fatty acids methyl esters from *Hevea brasiliensis*

No	Methylester of	Fatty acid from* free acid %	Fatty acid from* neutral part %	Relative retention time column DB - 5	Relative retention time column DB - WAX
01	Myristic acid	3.12	4.46	0.45	0.34
02	?	-	1.74	0.56	0.44
03	Pentadecanoic acid	2.09	2.03	0.58	0.46
04	Palmitolecic acid	-	3.29	0.68	0.60
05	Palmitic acid	32.36	21.97	0.72	0.58
06	?	2.59	3.83	0.83	0.79
07	Margaric acid	1.59	-	0.86	0.88
08	Linoleic acid	7.14	11.99	0.96	1.15
09	Oleic acid	30.22	32.62	0.97	1.04
	Linolenic acid			**	1.32
10	Stearic acid	7.32	2.97	1	1

- Trace
* Calculated from the peak areas
** No separation with DB - 5 - column.

Fractionation of the water extract

Extraction with water removed about 85% of the gypsum setting retarders from rubberwood. The main retarder was isolated by preparative TLC and its Rf-value was > 0.87 (Table 4). By further preparative TLC , applying n-butanol/ acetic acid/water, this fraction was separated into two active components with Rf- values of 0.17 and 0.27 (Table 5). In order to obtain more of these active components gel filtration on Sephadex LH-20 proved to be suitable (Table 6). The 95 fractions were divided into five groups. A and B showed the strongest gypsum retarding effect. Based on a weight percent effect, B - tube numbers 30 to 33 - was the most active fraction. However, in order to obtain this active compound in the purest form only tubes 31 and 32 were used for further investigations. In the course of the further examinations the residues of both tubes were designated as compound I. Since the gel filtration gave no clear cut separation, some of the gypsum retarding compounds occurred also in fractions 28, 29, 34 and 35. To obtain enough material for the structure elucidation, 82 gel filtration separations were carried out. The gypsum retarding effect of compound I at various concentrations is presented in Table 7.

Table 4. R_f- value, colour, and yield of fractions separated by thin layer chromatography [1] of the acetone-water extract and gypsum setting retarding effect

Fraction	R_f - Value	Colour + NH_3 [2]	Yield %	Concentration % [3]	Relative hydration time %
1	Start	white	4.03	0.204	103
2	0.03	white	4.52	0.228	105
3	0.65	red green	2.85	0.144	140
4	0.74	white	5.93	0.300	97
5	0.87	orange	22.29	1.128	181
6	> 0.87	-	60.39	3.056	265

[1] Precoated with cellulose, and mobile phase 6% acetic acid; [2] viewed under UV light; [3] based on plaster .

Table 5. R_f - values, colour and yield of compounds after re-chromatography and gypsum setting retarding effect [1]

Fraction	R_f -value	Colour + VH*	Yield %	Concentration %**	Relative hydration time %
1	Start	white	11.30	0.30	116
2	0.17	green	30.49	0.80	199
3	0.27	green	19.44	0.52	183
4	0.40 + 0.43	greenish lilac	12.84	0.34	169
5	0.46 + 0.49 + 0.51	yellow blue red	10.54	0.26	115
6	0.54 0.61	red blue	7.58	0.20	123
7	> 0.61	-	7.83	0.20	113

[1] Cellulose precoated TLC plates and mobile phase mixture of n-butanol/acetic acid/water (4:1:5);
* Detection with 5 % vanillin-hydrochloric acid in ethanol; **based on plaster.

Table 6. Yield and gypsum setting retarding effect of compounds separated by gel filtration from the acetone/water soluble part of the water extract

Group	Fraction	Retention volume *ml*	Yield %	Concentration* %	Relative hydration time %
A	01-29	0-95.5	25.7	0.44	200
B	30-33	99-108.9	21.0	0.36	170
C	34-36	112.2-118.8	24.8	0.42	145
D	37-46	122.1-151.8	25.3	0.44	150
E	47-95	155.1-313.5	3.2	0.06	100

* Concentration in mixing water.

Table 7. Gypsum setting retarding effect of compound I at various concentrations

Concentration * %	Relative hydration time %
Plaster	100
0.05	140
0.10	162
0.25	185
0.50	240

*Based on plaster.

Characterization of compound I

Compounds I was a colourless and amorphous powder. All efforts to crystallize it failed. Compound I decomposed at 210°C. The powder was easily soluble in water, sparingly in methanol, and insoluble in diethylether. A 1% solution had a pH of 5.15, and a specific electrical conductivity of 610 $\mu s\ cm^{-1}$. The carbon content and hydrogen content were 40.60 and 6.54% respectively. It had a high oxygen content, resembling those of carbohydrates. Although the TLC revealed only one spot, compound I could not be regarded as a pure compound. The further analytical gel filtration separations showed that compound I was a mixture of two groups of compounds having molecular weights between 200 to 300 respectively. The IR-spectrum showed a strong and broad band between 2500 and 3200 cm^{-1}, typically for a carboxyl group. An absorption band between 1560 and 1650 cm^{-1} may be assigned to an amino group. According to both the IR-spectrum and the UV-spectrum, compound I did not contain an aromatic group. The ^1H NMR - spectrum showed a mayor peak at $\delta = 5.43$ *ppm*, assigned to a proton in a carboxyl group. Typical fragments in the MS - spectrum were found at 44, which can be assigned to CO_2, split from a COOH-group, and at m/e 58 and 72, indicating the occurrence of nitrogen in the molecule. Fragments at m/e 45 and 61 may indicate sulphur in compound I. According to the ion-exchange chromatography, a reducing carbohydrate occurs also in compound I. The retention time of this carbohydrate resembled that of arabinose. However, the colour reaction according to Zand and Sandler(1957) indicated the carbohydrate to be a hexose and not a pentose.

Compound I gave a strong reaction with ninhydrin, indicating the presence of an amine containing group. At least four amino acids were detected by further TLC. The HPLC confirmed that compound I contained : 1% asparagine, 1.6 % serine, 15.8% glutamine, 10.2 % alanine and 18.1 % arginine. Accordingly, the total amount of amino acids in compound I was 46.7%. The yield of compound I, based on oven dried wood, was 1.02%; hence the total amino acid content was 0.48%. However, the gypsum setting retarding compound occurred also in other fractions. The total amounts in the other fractions are estimated to be about the same as in compound I. Therefore the total amino acid content of the wood of *Hevea brasiliensis* is estimated to be about 1%.

Protein hydrolysates are widely used as gypsum setting retarders (Wirsching 1976). However, little information is available on the influence of the molecular weight of such hydrolysates on gypsum setting retarding properties. Table 8 lists the gypsum retarding effect of some pure amino acids. A comparison of the retarding properties of compound I at various concentrations (Table 7) with those of arginine, glutamine, alanine, serine, and asparagine shows that the retarding properties at equal concentrations are in the same range. It is concluded that the gypsum setting retarding compounds in the wood of *Hevea brasiliensis* are free amino acids.

Table 8. Gypsum retarding effect of some amino acids+)

No	Amino acid	Relative hydration time %
	Plaster	100
01	L-Serine	140
02	L-Histidine	164
03	DL -Trypthophan++)	128
04	L-Cysteine	184
05	DL - α - Phenylamino-acetic acid	124
06	Glycine	184
07	Glumatic acid	212
08	Alanine	120
09	DL-Amino-butyric-acid	116
10	L-Asparagine	116
11	L-Cystine	124
12	L-Glutamine	116
13	L-Phenylalanine	104
14	L-Arginine	136
15	L-Leucine	108
16	L-Proline	92
17	L-Histidine	104
18	L-Tyrosine	88

+) Concentration 0.125 % based on plaster;
++) Slightly soluble.

Suitability of rubberwood for the manufacture of gypsum - bonded particleboards

The shear strength between gypsum and rubberwood was only 0.25 *MPa* which was very low compared to that of spruce (about 1 *MPa*). The additions of potato starch and corn starch to the gypsum hemihydrate increased the shear strength to 0.48 *MPa* and 1.49 *MPa* respectively (Kasim 1990). The wood extractives had a high gypsum setting retarding effect, and the compression strength of a mixture of rubberwood and gypsum was low (Kasim & Simatupang 1989). Experimental gypsum-bonded particle boards made according to the method of Simatupang and Lu (1985) had poor bending strength (2.19 *MPa*) and low internal bond (0.02 *MPa*) properties.

Influence of added tannin as retarder

In the manufacture of gypsum-bonded wood composite a retarder is required to prolong the initial setting time of the binder in order to have ample time for blending and forming. If the retarding effect is not sufficient the gypsum hemihydrate may preset. Furnish containing preset gypsum cannot be used any more to make a gypsum particleboard. Tannin is currently not used as a gypsum retarding compound in the industrial manufacture of gypsum-bonded boards, althought its use is mentioned in a patent (Knauf 1966). Tannin is available in many tropical countries. Therefore the feasibility to use it as a retarder in the manufacture of gypsum-bonded particleboards was examined. The influence of tannin as a retarder in the manufacture of laboratory gypsum-bonded particleboards on the bending strength at various manufacturing conditions is shown in Table 9. The addition of tannin in combination with a press temperature of 40°C and a press time of 150 *min* (boards designated with A) gave boards with poor properties. Boards pressed according to the same conditions, but without tannin as retarder, showed good properties. If the pressing time was prolonged to 450 *min*, the addition of tannin did not show detrimental effects. In industrial practice the press time is two and half hour. Using tannin as retarder a longer time is required. The absence of tannin also allowed the press time to be reduced to 60 and 150 *min*.

The influence of press temperature on the properties of the gypsum particleboards is significant. According to Rößler and Odler (1989) an increase of the hydration temperature causes a displacement of the distribution towards larger pores and an increase of the size of the gypsum dihydrate crystals. In their investigations the temperatures were varied between 0 and 75°C. We used only 20 and 40°C, and an influence of temperature was already observed. Reducing the temperature from 40 to 20°C enabled the shortening of the press time from 450 to 150 *min* if no tannin was used. The temperature of gypsum during setting may be as high as 45°C, so a shorter press time due to a lower press temperature is not feasible.

In industrial manufacture of gypsum particleboards the addition of a retarder is necessary (Sattler & Lempfer 1989). Should rubberwood be used to manufacture such boards, an appropriate retarder has to be added.

Currently no industrial standard is available for gypsum particleboards. In Malaysia the standard for cement-bonded particleboards is used to evaluate the bending strength of experimental gypsum particleboards made from oil palm trunk (Khozirah *et al.* 1991). Table 9 shows that gypsum particleboards with bending strengths of about 8 *MPa* - comparable with commercially available gypsum particleboards - can be fabricated from rubberwood if the density is around 1, 250 *kg m*$^{-3}$.

Table 9. Properties of gypsum particleboards fabricated at various conditions

Type	Additive tannin %	Press temperature °C	Press time *min*	Bending strength *MPa*	Density *kg m*$^{-3}$
A	0.1	40	150	2.7	1,232
B	0.1	40	450	7.9	1,225
C	0.1	20	150	7.9	1,225
D	-	40	150	8.0	1,233
E	-	20	60	8.1	1,270
F	-	40	60	8.6	1,270

Influence of wood extractives on rubberwood properties

The extractives of rubberwood are mainly hydrophilic compounds. Higher amounts of free sugar and starch were observed in this wood. The examinations showed also the presence of about 1 % of free amino acids. The total amount of free sugar, starch, and amino acids in freshly cut wood can be estimated to be about 5 to 10%. It is possible that the combination of all three compounds make rubberwood so susceptible to blue stain. Kasim and Simatupang (1989) reported the occurrence of free amino acids and free carbohydrates in some woods known to be very susceptible to blue stain.

Micro structure of the particleboards

Examinations by scanning electron microscopy (SEM) revealed a close correlation of structure of gypsum matrices with bending strength properties of the manufactured boards. Low bending strength properties, as shown by boards containing tannin and pressed at 40°C during 150 *min* (Type A), were accompanied by a gypsum matrix consisting mainly of irregularly formed crystals at the gypsum/wood particle interface (Figure 1). Only few needle-like crystals were located in the texture. The irregular structure of the individual crystals resulted in a loose arrangement with large intercrystalline spaces (Figure 2); hence, the contact between crystals was reduced to a minimum as compared to the total surface of an individual crystal. Consequently, those crystals remaining on the surface of particles were not strongly attached after fracturing. Differences in the gypsum/wood particle texture between the surface layer and fracture planes at various levels were not observed.

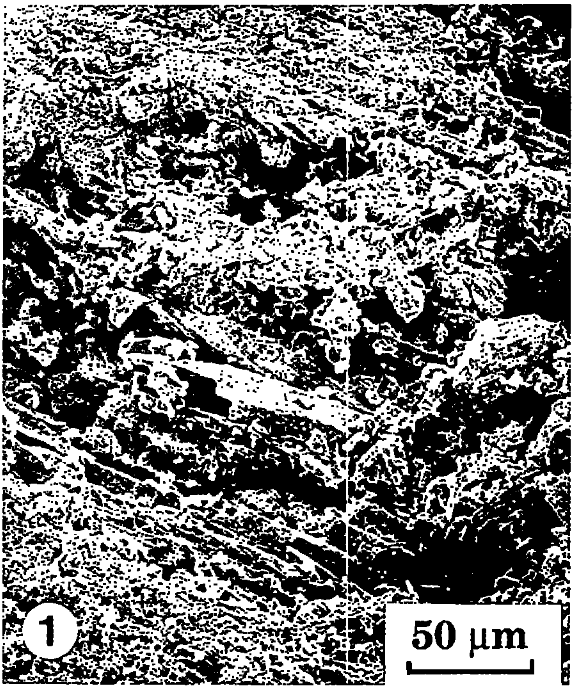

Figure 1. Surface layer of a type A-Board. Gypsum matrix consisting of irregularly formed crystals

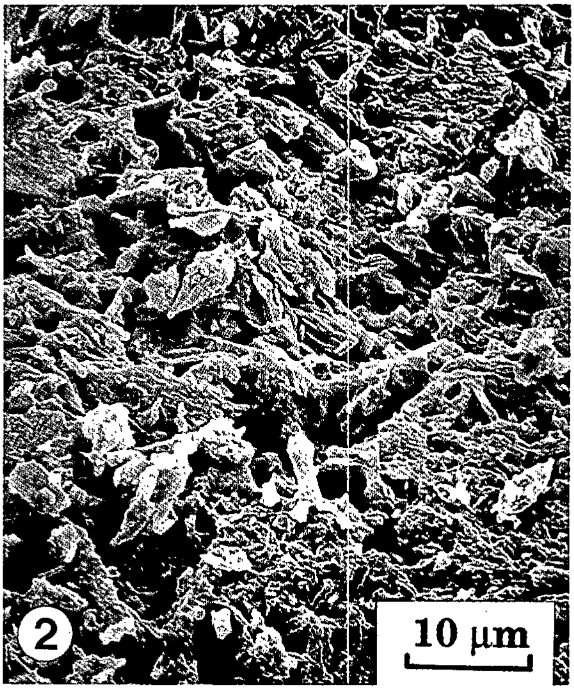

Figure 2. Type A-Board. Detail of irregularly formed matrix crystals

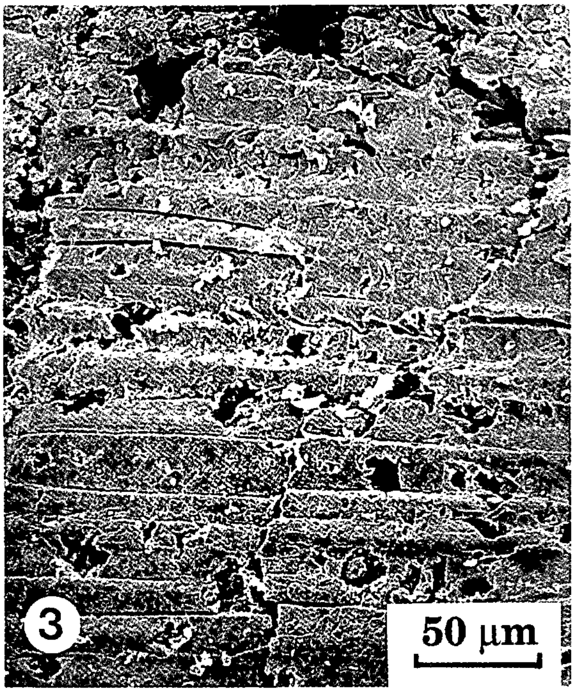

Figure 3. Fracture plane of a type F-Board. Gypsum/wood particle interface mainly composed of cubic/polyedric crystals

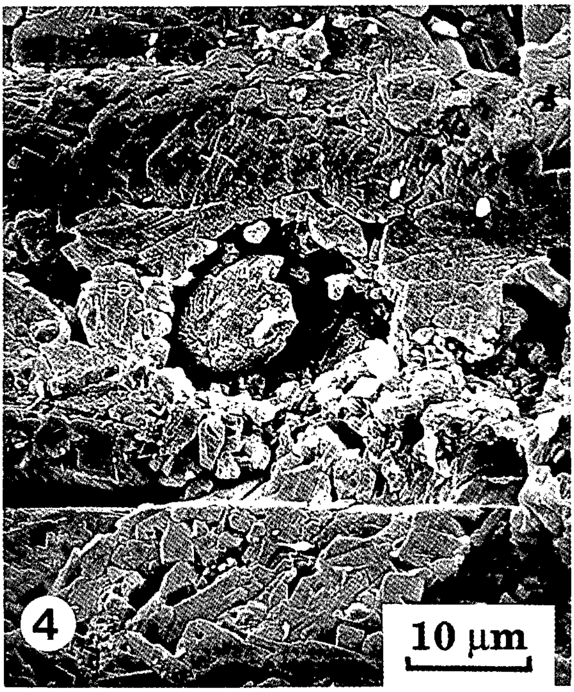

Figure 4. Type F-board. Detail of Figure 3 showing tightly packed crystals at the gypsum wood particle interface

In contrast to the aforementioned structural pattern all experimental boards manufactured according to optimized conditions fabricated with or without tannins (Type B-F) showed the same ultrastructure. The main criterion for the characterization of the gypsum matrices is their composition of cubic/polyedric crystals, which often form a matrix with almost no interspaces. Therefore the contact areas between crystals are larger. The fracture planes regularly show impressions of the particle surfaces independent of depth within the board (Figures 3 and 4). This clearly indicates the homogeneous structure of the gypsum matrix including the boundary to the particle surface.

Conclusion

The gypsum setting retarding compounds of rubberwood (*Hevea brasiliensis*) are water soluble. They are a mixture of amino aids, namely, glutamine, arginine, alanine and asparagine. The concentration of the free amino acids in wood was estimated to be about 1% (O.D. wood). Rubberwood is suitable for the manufacture of gypsum particleboards. However, the density of the composite should be about 1,250 $kg\ m^{-3}$, in order to compensate for the higher specific gravity of the wood. The occurrence of retarding compounds in the wood has to be taken into account when retarders are added to regulate the setting and hardening of the inorganic binder in order to gain ample time for blending, forming and prepressing the furnish. The use of hydrolyzable tannins as retarder is not advantageous. A close correlation was established between the micro structure of the set gypsum and the bending strength of the gypsum particleboards.

References

ANONYMOUS. 1991. *Wood Based Panels. Thin MDF.* Asia Pacific Industries, October 1991: 166 -172.

ARX, E. & NEHER, R. 1963. Eine multidimensionale Technik zur chromatographischen Identifizierung von Aminosäuren. *Journal of Chromatograply* 12 : 329 - 341.

AZIZOL ABDUL KADIR & RAHIM SUDIN. 1989. Carbohydrates in rubberwood. *Holzforschung* 43(3): 173-178.

CHINCHOLE, P. R. & APTE, K. P. 1969. Anatomical and chemical characteristics of Indian hardwoods with special references to their suitability for pulp. Part III. *Indian Pulp and Paper* 3: 512 - 527.

D'AUZAC, J. & PUJARNISCLE, S. 1967. Carbohydrates of *Hevea brasiliensis* and their variation. Pp. 154 -164 in *Proceedings of Natural Rubber Conference.* Kuala Lumpur 1960.

DE STEPHANIS, V. A. 1968. Separation of sugars by thin layer chromatography. *Journal of Chromatography* 34: 116 -120.

GNANAHARAN, R & DHAMODHARAN T.K. 1985. Suitability of some tropical hardwoods for cement-bonded wood wall board manufacture. *Holzforschung* 36(6): 336 - 340.

GUHA, S. R. D. & LEE, T.W. 1972. Structure of hemicelluloses isolated from rubberwood. *Journal of the Indian Academy of Wood Science* 3(2) : 49 - 52.

KASIM, A. 1990. Untersuchung über die Eignung einiger Tropenholzarten, insbesondere aus Indonesien, zur Herstellung gipsgebundener Spanplatten. Dissertation Universität Hamburg.

KASIM, A. & SIMATUPANG M. H. 1989. Influence of some tropical wood species on the setting and compression strength of wood and gypsum mixtures. *Holz Roh - Werkstoff* 47: 391- 396.

KHOZIRAH SHAARI, RAHIM SUDIN & KILLMANN, W. 1991. The feasibility of oil palm trunk as reinforcing fibres for gypsum-bonded particleboards. Pp. 169 -176 in Khoo, K. C. *et al.*

(Eds.)Seminar Proceedings on Oil Palm Trunk and other Palmwood Utilization. March 4 - 5, 1991. Kuala Lumpur. Ministry Primary Industries, Malaysia.

KILLMANN, W. 1987 : Eigenschaften und Nutzung des Heveaholzes. *Holz-Zentralblat* 3/4: 50-51.

KNAUF, N.K. 1966: *Verfahren und Vorrichtung zur Herstellung von Baukörpern.* DBP 1 104419. C 04b. 05.1966.

LIM, S. C. 1985. *Observations on the Anatomical Structure of Some Malaysian Woods by Means of SEM/EDXA.* Forest Research Institute Malaysia Report 42 : 12 - 18.

PATRICK, A. D. 1956: Nature 178:216 cited in W. Karrer : *Konstitution und Vorkommen der organischen Pflanzenstoffen (exclusiv Alkaloid).* Chemische Reihe Band 12, Birkhäuser Verlag, Basel, Stuttgart: 256.

RÖβLER, M. & ODLER. O. 1989. Relationship between pore structure and strength of set gypsum pastes. *Zement-Kalk-Gips* 42(2): 96 -100.

SANDERMANN, W., DIETRICHS, H. H., SIMATUPANG, M. H., PUTH, M. & SCHMITZ, G. 1965. Caoutchouc in wood. *Bulletin of the Nature Institute of India* 37: 175 - 177.

SANDERMANN, W. & KOHLER, R. 1964. Über eine kurze Eignungsprüfung von Hölzern für zementgebundene Holzwerkstoffe, VI. Mitteilung. *Hozlforschung* 18: 53 - 59.

SATTLER, H. & LEMPFER, K. 1989. Gypsum-bonded particleboards and fiberboards. In Moslemi, A. A. (Ed.) *Fiber and Particleboards Bonded with Inorganic Binders.* Forest Products Research Society, Madison, Wisconsin.

SCHWARZ, H. G. 1989: Cement-bonded board in Malaysia. Pp. 91- 93 in Moslemi, A. A. (Ed.) *Fiber and Particleboards Bonded with Inorganic Binders.* Forest Products Research Society, Madison, Wisconsin.

SEDDIG, N. & SIMATUPANG, M.H. 1988. Scherfestigkeitstest zur Eignungsprüfung verschiedener Holzarten für gipsgebundene Holzwerkstoffe und REM-Betrachtung der Scherflächen. *Holz Roh-Werkstoff* 46: 9 -13.

SER, CHENG SAM 1990. Rubberwood resource in Asean and the potential for its wider utilisation. Pp. 27 - 40 in Hong, L.T. *et al.* (Eds.) *Proceedings of the International Rubberwood Seminar*. May 21 - 22, 1990. Kuala Lumpur, Malaysia.

SIMATUPANG, M. H. 1979. Water requirement in manufacturing of cement-bonded particleboards. *Holz Roh - Werkstoff* 37: 379 - 382.

SIMATUPANG, M. H. 1988. Suitablility of some magnesia for the manufacture of particleboards. *Holz Roh - Werkstoff* 46: 223 - 229.

SIMATUPANG, M. H., KASIM, .A. & SEDDIG, N. 1988. Influence of wood extractives on the setting of gypsum. Mitteilung der Bundesforschungsanstalt für Forst- und Holzwirtschaft, Hamburg, Nr. 160: *Forschung für die Forst - und Holzwirtschaft; 7. Hamburger Forst - und Holztagung* 1988: 311- 319.

SIMATUPANG, M. H., LANGE., H. & KASIM, A. 1992. Semimicro electrical conductivity method to trace the hydration of β - gypsum hemihydrate in the presence of wood extractives of some tropical wood species. *Holzforschung* 46: 357 - 359.

SIMATUPANG, M. H. & LU, XU XIAN 1985. Influence of wood extractives on the hardening of β-gypsum-hemihydrate in the manufacture of gypsum-bonded particleboards. *Holz Roh-Werkstoff* 43: 325 - 331.

SINNER, M. & PULS, J. 1978. Non-corrosive dye reagent for detection of reducing sugar in borate complex ion-exchange chromatography. *Journal of Chromatography* 155: 197 - 204.

SINNER, M., SIMATUPANG, M. H. & DIETRICHS, H. H. 1975. Automated quatitative analysis of wood carbohydrates by borate complexion chromatography. *Wood Science and Technology* 9: 307 - 322.

WIRSCHING, F.W. 1976. Gips. Pp. 289-313 in *Ullmanns Encyclopädie der technischen Chemie.* 4 Auflage. Band 12. Verlag Chemie, Weinheim.

ZAND, H. & SANDLER, S. 1957. Chemist-analyst 46:36. Pp. 422 - 423 in Bauer, H. & Moll, H. *Die Organische Analyse.* 4 Auflage. Leipzig 1960. Akademische Verlagsgesellschaft Geest & Portig K. G.