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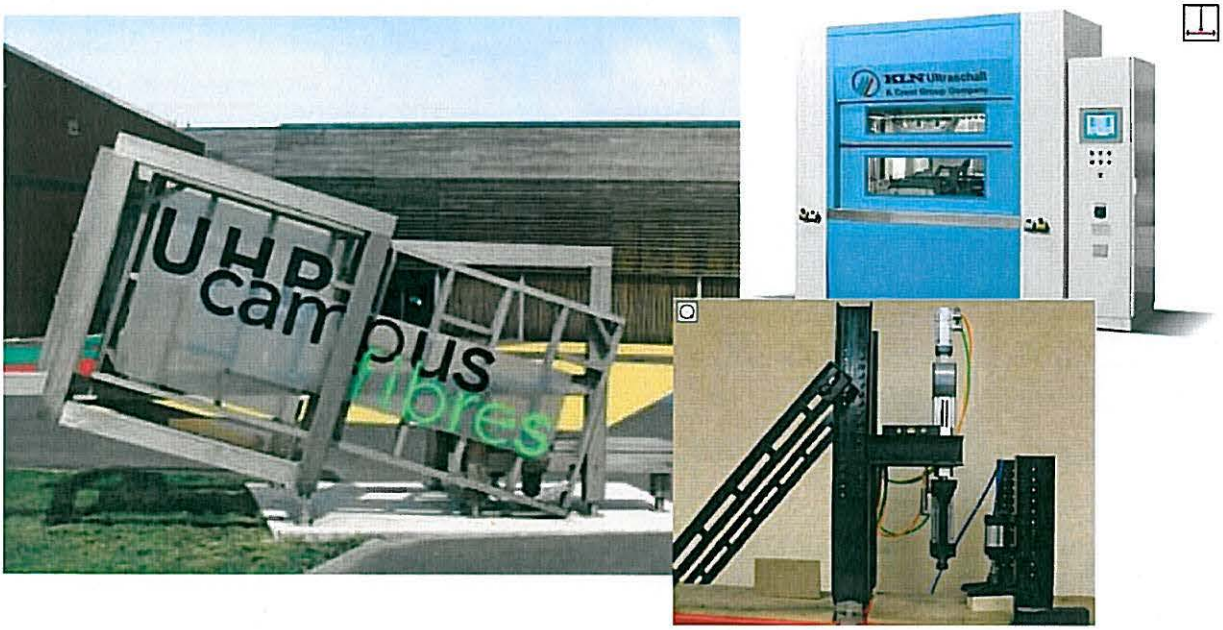

Optimisation du soudage du bois avec des additives naturel non toxique respectueux de l'environnement

Optimization of Wood Welding with Some Natural, Non-toxic, Environmental-friendly Additives

Jinbo HU

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Tuteur universitaire : Monsieur le Professeur Antonio PIZZI

Accueil : **Laboratoire d'Étude et de Recherche sur le MAtériau Bois à l'ENSTIB**

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1 Presentation of the research institute

This professional training was carried out at the LERMaB(Le Laboratoire d'Etudes et de Recherches sur le Matériau Bois) - ENSTIB(École Nationale Supérieure des Technologies et Industries du Bois). The research unit is the unit of physical chemistry of polymers.
The ENSTIB, the only national and university engineering school specialized in wood in France, is the heart and the origin of Lorraine university « Fibers Campus » is a thematic campus that federates training, research and process and materials evaluation on the same site. Its field of activity, both multi- and cross-disciplinary, is that of fibers, including natural, wood, paper, textile, synthetic, carbon fibers, fiberglass and many others. Last, they solve technical problems together with the technology transfer centers by meeting the industrial request received. The laboratories at the ENSTIB: LERMaB, and CRAN(Centre de Recherche en Automatique de Nancy). The academic research laboratories work also in close collaboration with several technology transfer centers: CRITT Bois(Centre de Ressources pour les Industries du Bois), CETELOR(Centre d'Essais Textile Lorrain), CTP(Centre Technique du Papier) and Pôle de Compétitivité Fibres.
Research sector of LERMaB at ENSTIB: wood composites, panel products drying, wood energy, adhesives, gluing and surface treatments, wood preservatives and microbiology.
Research teams present at the ENSTIB: wood anatomy and physics, physical chemistry of polymers, energy and processes, mechanics, civil engineering and manufacturing, byproducts and recycling.
The physical chemistry of polymers has two main missions who are dominated by Prof. Antonio Pizzi. The principal programme of the unit is currently focused on studies of the product of tannins, so as to develop new more environment-friendly materials. This programme involves the promotion of alternative tannin and the optimisation of the implementation of alternative methods. These goals require fundamental research to be achieved. The joint of wood welding is another main research axis in this unit. This work is carried out in order to obtain environment -friendly bonding some pieces of wood without any adhesive.

2 Introduction and aims of this report

Wood welding is a novel joining procedure with challenging perspectives for producing new environmentally-friendly wooden products. In the actual wood welding study, it was indicated that what was obtained were only interior-grade bonded wood joints (Omrani et al. 2007, Omrani et al. 2008). There had been interest in overcoming this limitation by improving welding process without the use of synthetic waterproofing chemicals which don't have totally environment-friendly characteristics (Vaziri, 2011). Other studies show that some additives that could be beneficial to improve this drawback should also be sought to expand the area of applicability of the wood-welding process (Wieland et al. 2005, Properzi et al. 2006).
In LERMaB-ENSTIB, the preliminary results of a former series of experiments showed that some bio-materials (acetylated lignin, a mix of a number of sesquiterpenoid acids, rosin) were the most efficient in order to enhance the water resistance of wood welding joints. Tannin is inexpensive and easily commercially available extracts from some plants, is natural and non-toxic hence maintaining environment-friendly characteristics of the joint, and it is acetylated or improved, does it protect the weldline ? About a natural rosin being

capable of waterproofing, Is it effective when welding process is changed?
My work consisted in acetylating tannin, analyzing the effects of the acetylated tannin, obtaining the solution of tannin by simulating the padauk wood, welding wood pieces and seeking the optimal process with the respective additive. The work carried out in the last six months will be partly published in scientific journals. As there are still data sets under analysis in the laboratory, I tried to focus on the main aspects and to select the most relevant parameters/variables to be analyzed firstly. This report aims at giving an overview of the whole project.
The main aspects of this report focus on:

I. Acetylation of tannin and analysis of acetylated tannin

This first part aims at obtaining and analyzing some acetylated tannins by some appropriate methods.

II. Welding some wood pieces with additives

Two welding styles of rotation and vibration were carried out. The first one aimed at seeking the best protection for dowel rotation welding with acetylated tannin or rosin. The second one aimed at studying the optimal process for linear vibration welding with solution of tannin or rosin.

Ⅲ. Making some products by wood welding

This body of work develops further to get some wood welding products on a different scale.

3 Literature review

3.1 Introduction

Wood welding, this process offers advantages over gluing and mechanical fasteners, such as short curing times of less than one minute, low cost, environmental
-friendliness. The two types of wood welding without adhesives in operation, namely linear vibration welding(LVW) and high-speed rotation welding(RDW) (see Figure 1), will both be presented with the structural assemblies already achieved. These structures contain

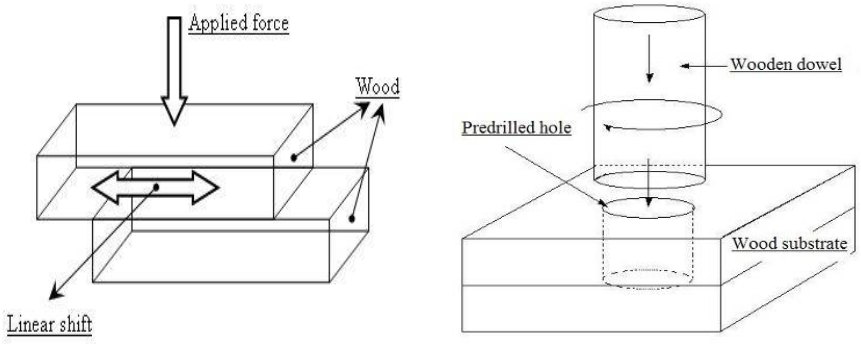


Figure 1 Schematic representation of the vibrational movements of two solid wood surfaces (Left), Schematic representation of the insertion of a cylindrical dowel in a predrilled hole of wood substrate (Right) (Gfeller et al. 2004, Pizzi et al. 2004)

100% wood, thus they are totally natural. LVW is used to weld two flat wood surfaces to each other by rubbing in parallel with the surface of the joint. RDW is used to assemble wooden parts by wooden dowel rotating. It differs considerably from linear vibration welding as the friction generated is obtained by a continuous unidirectional movement rather than an alternating one. Both mechanisms of wood-to-wood welding are that

temperature-induced by friction is melting and flowing wood components of the amorphous and forming at the interface between the two wood surfaces to be joined a composite of entangled wood fibres drowned into a matrix of molten wood intercellular material, mainly lignin, but also hemicelluloses(Gfeller et al. 2004, Pizzi et al. 2004, Gfeller et al. 2003, Pizzi et al. 2006, Stamm et al. 2006, Rodriguez et al. 2010).

The application of the process without any additives to wood was not shown until 1996, when Suthoff et al patented work carried out in Germany(Suthoff et al. 1996). This patent and a subsequent patent (Suthoff et al. 1997) firstly demonstrated that wood could be welded by means of either an oscillating or linear frictional action, then suggested the possibility of joining pieces of timber with a dowel. Since 2003, a joint Swiss-French team led by Antonio Pizzi from France and Balz Gfeller from Switzerland have studied and analyzed this technology with different types of welding machine and have improved the technology significantly.

3.2 Some developments of LVW

LVW is one of many techniques in which heat is generated by the mechanical movement of parts to be welded. The first hypothesis is that the quality of a linear friction welded joint correlates with certain welding parameters. Therefore, strength and water resistance of the welded joints are measured and examined as a function of these parameters (Stamm et al. 2005, Properzi et al. 2010, Omrani et al. 2010). These parameters (Table 1) are divided into the machine setting and the material properties.

The design of wood welding machines is based on the welding machines for thermoplastic which generally have different working frequencies of 100-300Hz and 1.8-4.0mm. The vibration machine is basically formed by a frame in which a mobile table is suspended on springs. The mobile part is put into vibrations with the response of tension of springs to an electromagnetic principle (Figure 2). The machine set-ups are the welding time, the pressure, the amplitude and the hold time.

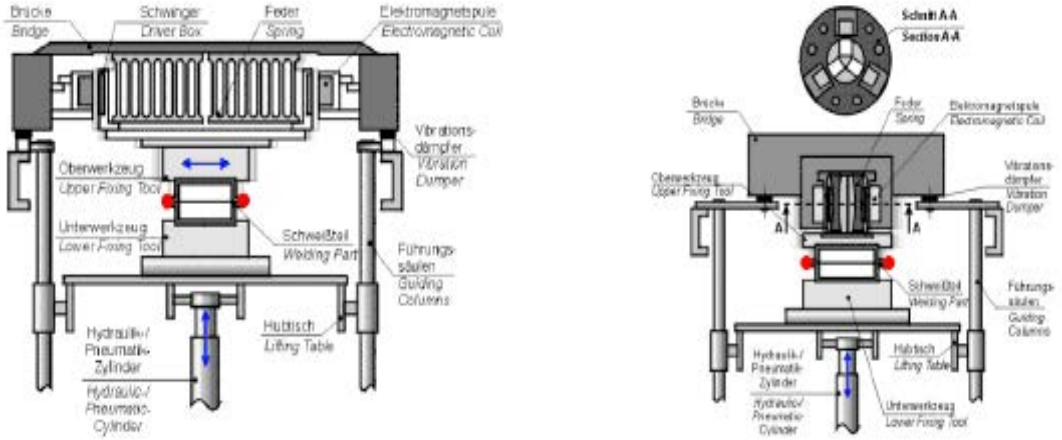


Figure 2 description and diagrams of vibration welding technologies (Gerber et al. 2000)

3.3 Some developments of RDW

Wood species, relative diameter differences between the dowel and the receiving hole, and pressing time were shown to be parameters yielding significant strength differences (Pizzi et al. 2004). If the dowel or the substrate is too soft and prone to cellular collapse, as spruce is, the pressure exerted on the two moving surfaces is lower. Thus, either a lower

Table 1 some main parameters of LVW

	Parameter of LVW	Unit	Descriptions
Machine setting	Welding pressure, WP	KN	The Pressure is exerted on the specimen during frictional movement.
	Welding frequency, WF	Hz	The rate at which an electrical current alternates, expressed as the number of cycles per unit of time.
	Holding pressure, HP	KN	The clamping pressure exerted on the welded specimen after termination of the frictional movement.
	Holding time, HT	s	Duration of holding the specimen under clamping pressure after termination of the frictional movement.
	Welding time, WT	s	Duration of the welding process until the frictional movement is stopped.
	Length of displacement	mm	Amplitude of frictional movement.
Material property	Wood species		Hardwood, softwood, heartwood, or sapwood.
	Wood grain		The alternating regions of relatively darker and lighter wood resulting from the differing growth parameters occurring in different seasons.
	Equilibrium moisture content of wood, EMC	%	The moisture content at which the wood is neither gaining nor losing moisture.
	Dimensions of the specimen	mm	The size of the specimen.

temperature is reached, or the temperature of softening is reached at a slower rate, or both, and the result is a lower welding strength(Bogner et al. 2008). As regards the diameter of the substrate hole, the real variable is the dowel/substrate hole diameter ratio. Within the ranges of hole and dowel diameters used this appears as a reasonable deduction(Bogner et al. 2008). Oven-dry dowels, insertion of hot dowels, cross-cut dowels, substrate holes of step decreasing diameter as a function of depth, use of ethylene glycol or other compounds able to decrease the glass transition temperature of wood components have all been shown to contribute to improving weld joint strengths in a variety of less drastic conditions than the 10 mm/8 mm dowel/substrate hole diameter difference(Kanazawa et al. 2005).

At present, the rotational friction to weld the dowels is applied by some machine in the research. Syderic SH 32 of Syderic-Vernier-Cato and Mecasonic MCRI 72 of Annemasse are made in France (Pizzi et al. 2004,). But the cordless screwdrivers (Bosch GSR 18 VE-2LI, PROTOOL DRC 18-4 TEC LI) is used with 1800-1850 rpm in manual mode in Austria (Trainotti et al. 2010).

The developping wood welding can be applied to weld two flat pieces of timber, originating from the same or different tree species, and can be used in the manufacture of furniture and wood joinery(The only limitation is that the joint is not exterior-grade, but only suitable for interior joints)(Gfeller et al. 2004, Wieland et al. 2005, Boonstra et al. 2006, Mansouri et al. 2008, Omrani et al. 2008, Ganne-Chedeville 2008, Mansouri et al. 2011). The application

of this welding technique to interior furniture manufacture, a great variety of joint types are used for furniture(Segovia-Brandt 2010). The minimalist chair designed by the Dutch architect Gerrit T. Rietveld (1888–1964) is made by rotation dowel welding(Figure 15) (Renaud 2009). The suspended floor, of 4 x 4 meters and 216mm thickness, was built of spruce wood slats of 4000 x 90x24 mm dimensions(Bocquet et al. 2007). Multi-layered wooden beams with welded wood dowels is an interesting alternative to traditional poly(vinyl acetate) (PVAc)-glued dowels and nailing systems(O'Loinsigh et al. 2011).Furthermore the technique at this stage is only usable for solid wood joints and perhaps joints among premanufactured panels presenting the same type of characteristics as solid wood, such as panel products(particleboard, OSB, plywood and MDF) (Ganne-Chedeville et al. 2007).

3.4 Needs to be resolved for the new wood welding technique nowadays

Now there are two limitations of wood welding of wood-wood: the improving strength of bonding and the resistance of welding joint after a time treatment of humidity.

4 Material & Methods

4.1 Materials

4.1.1 Tannin

Mimosa (*Acaciamearnsii*, formerly *mollissima*, *de Willd*) bark from Italy was obtained. The bark was dried and ground to coarse chips followed by further drying until a constant weight was obtained. The extraction of tannin from the black wattle bark was carried out in an industrial reactor of the company Silvachimica Srl (Cuneo, Italy) by total immersion under continuous stirring of the ground bark in a water solution containing 2% sodium bisulphite and 0.5% sodium bicarbonate. The extract so obtained, after spray-drying was used.

4.1.2 Rosin and solution of rosin

Rosin is a solid form of resin obtained from pines, produced by heating fresh liquid resin to vaporize the volatile liquid terpene components. It is semi-transparent and yellow crystalline chunks and powder. At room temperature rosin is brittle, but it melts at stove-top temperatures. It is soluble in alcohol, ether, benzene and chloroform. The practical melting point varies at 80°C to 120°C. It is supplied by Acros Organics BVBA in Belgium. Some rosin who was milled was placed in 1:3 by weight of absolute ethyl alcohol, and they were stirred in a beaker until all rosins were dissolved.

4.1.3 Wood species

In the investigation, all specimens and dowels are commercial beech(*Fagus sylvatica*) wood. They are dried to 12% moisture content conserved in an environmental chamber (20°C and 65% RH).

4.2 Methods of acetylating tannin and analysis of acetylation

4.2.1 Acetylation of tannin

Tannins were acetylated by three processes (Table 2). Some tannins were placed in a proportion mixture by weight of pyridine and acetic anhydride. The mixture was refluxed at a temperature for some time and then cooled. The acetylated tannins were then precipitated with ice water, the mixture was centrifuged and the acetylated tannins solid were separated from the supernatant residual solution. The acetylated tannins were then washed with cold water 5 times and separated by centrifugation at every wash. The acetylated tannins were

then allowed to air dry at ambient temperature.

Table 2 process of the acetylated tannin

No.	Tannin (g)	Acetic anhydride (g)	Pyridine (g)	Temperature (°C)	Time (h)
1	20	50	Without	80	2
2	20	100	10	80	2
3	20	100	100	50	8

4.2.2 CP-MAS ^{13}C NMR of acetylated tannin

The acetylated organosolv tannin resins were dried before being ground finely for NMR analysis. The hardened tannin resins were analysed by solid state CP MAS ^{13}C NMR. Spectra were obtained on a Bruker AVANCE II 400 MHz spectrometer at a frequency of 100.6 MHz and at sample spin of 12 kHz, using a recycling delay of 1s, and contact time of 1 ms. Number of transients was about 15000, and the decoupling field was 78 kHz. Chemical shifts were determined relative to tetramethyl silane (TMS) used as control. The spectra were accurate to 1 ppm. The spectra were run with suppression of spinning side bands so that each peak observed corresponded to a chemical group and no reflected multiple peaks corresponded to any one single group. Only the spectra of the unreacted tannin and of the tannin dried directly at 103°C for two hours are reported, as the spectrum of the latter was the same as that of the glyoxalated tannin precipitated in any other manner.

4.2.3 MALDI-TOF of acetylated tanin

The tannin samples were dissolved in acetone (4 mg/ml, 50/50% by volume). The sample solutions were mixed with an acetone solution (10 mg/ml in acetone) of the matrix. As the matrix 2, 5-dihydroxy benzoic acid was used. For the enhancement of ion formation NaCl was added to the matrix (10mg/ml in water). The solutions of the sample and the matrix were mixed in the proportions 3 parts matrix solution + 3 parts polymer solution + 1 part NaCl solution and 0.5 to 1 µL of the resulting solution mix were placed on the MALDI target. After evaporation of the solvent the MALDI target was introduced into the spectrometer. To each peak value in the resulting positive mode spectrum the 23 Da of the Na+ of the matrix must be subtracted to obtain the molecular weight of the chemical species.

The spectra were recorded on a KRATOS Kompact MALDI AXIMA TOF 2 instrument. The irradiation source was a pulsed nitrogen laser with a wavelength of 337 nm. Each laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight path-linear, mass-high (20 KV acceleration voltage), and 100-150 pulses per spectrum. The delayed extraction technique was used by applying delay times of 200-800 ns.

4.2.4 Thermal gravimetric analysis of tannins and acetylated tannins

TGA was applied in the preliminary experiments to investigate the decomposition of tannins and acetylated tannins. TGA can characterize catalysts by evaluating their activity in terms of the shift of degradation temperature. The instrument used was Pyris 6 TGA from the Perkin Elmer company. The initial mass of the samples was 7 mg. The experiments were carried out at ramp 10°C/min from room temperature to 600°C under nitrogen atmosphere with a flow rate of 20 ml/min and a purge time of 10 min.

4.3 Preparing solution of tannin and adding the solution into the samples of LVW

No. 1 method: Measure and mix 150g deionized or distilled water and 150g ethanol in a glass beaker. Gradually add 100 g tannin to the water/ethanol solution, stirring constantly. To accelerate the process, gently heat the solution at 30/40°C on a hot plate. When the tannin has dissolved, store the tannn solution in a labelled, sealed container preferably in a refrigerator. On the side, prepare a 10%-15% dilute phosphoric(H_3PO_4) acid solution by pouring deionized or distilled water into a glass container and adding concentrated phosphoric acid, usually sold in an 85% concentration. Before welding, one face of sample(200×20×20mm) was soaked in the solution of tannin for one hour. When the surface of dipped sample was dry, the dilute phosphoric acid was brushed on the immersed and dry sample. Constantly brushing as the acid dried in order to distribute the solution evenly and to introduce oxygen. Two pieces wood were welded as some samples dried.
No 2. method: Measure and mix 150g deionized or distilled water and 150g ethanol in a glass beaker. Gradually add 100 g tannin to the water/ethanol solution, stirring constantly. When the tannin had dissolved, 600g 10%-15% dilute phosphoric acid solution was added. To accelerate the process, gently heat the solution at 30/40°C on a hot plate. The obtained solution was filtered, and the precipitation was washed and dried in the air. Then some power of treated tannin was dissolved in some acetone. Before welding, one face of sample(200×20×20mm) was soaked in the solution of tannin for one hour. When the surface of dipped sample was dry, two pieces wood were welded.

4.4 Equipments and preparation of specimens for RDW

The rotational wood dowel welding conditions used were as follows: commercial beech (*Fagus sylvatica*) wood fluted dowels, 8 mm in diameter and 10 cm in length, were jointed using a high rotation rate fixed-base, digital- controlled friction welding equipment (Design by ENSTIB – LERMAB -CRITTBOIS) two pieces (70×50×20mm) of beech wood at 12% moisture content with 8mm diameter pre-drilled holes. The assembly configurations studied are shown in figure 3.
Before welding, there were some dowels without anything, and some dowels were laid by PVAc, and some tannins or acetylated tannins were laid on the dowel (figure 4a), and other dowels(figure 4b) which were immersed in the solution of rosin and 100% ethanol for 2 minutes were conditioned for one day in an environmental chamber (20°C and 65% RH). The dowel was welded to the surfaces of the hole in the substrate to form a bonded joint by a fast rotational movement at increasing rotation rates of respectively 1500 revolutions per minute (rpm). The pressure exercised during insertion was maintained constant at 4.5 bar. The insertion time was 2 seconds according to the rotation rate used.

4.5 Equipments and preparation of specimens for LVW

The linear vibration welding conditions used were as follows: Beech (*Fagus sylvatica*), a hardwood, was used. The equilibrium moisture content of the samples was 12%. Specimens composed of two pieces of beech wood, each of 200×20×20mm, were welded together to form a bonded joint of 200×20×40mm by a vibrational movement of one wood surface against another at a frequency of 150 Hz (The mechanical welding machine used was a KLN linear welding machine with CPC (Complete Process Control) - vibration technique, type 2261, 150 Hz, normally used to vibrationally weld plastic.). When the fusion and bonding were achieved, the vibration process was stopped. The clamping pressure was then briefly maintained until the solidification of the bond. The welded

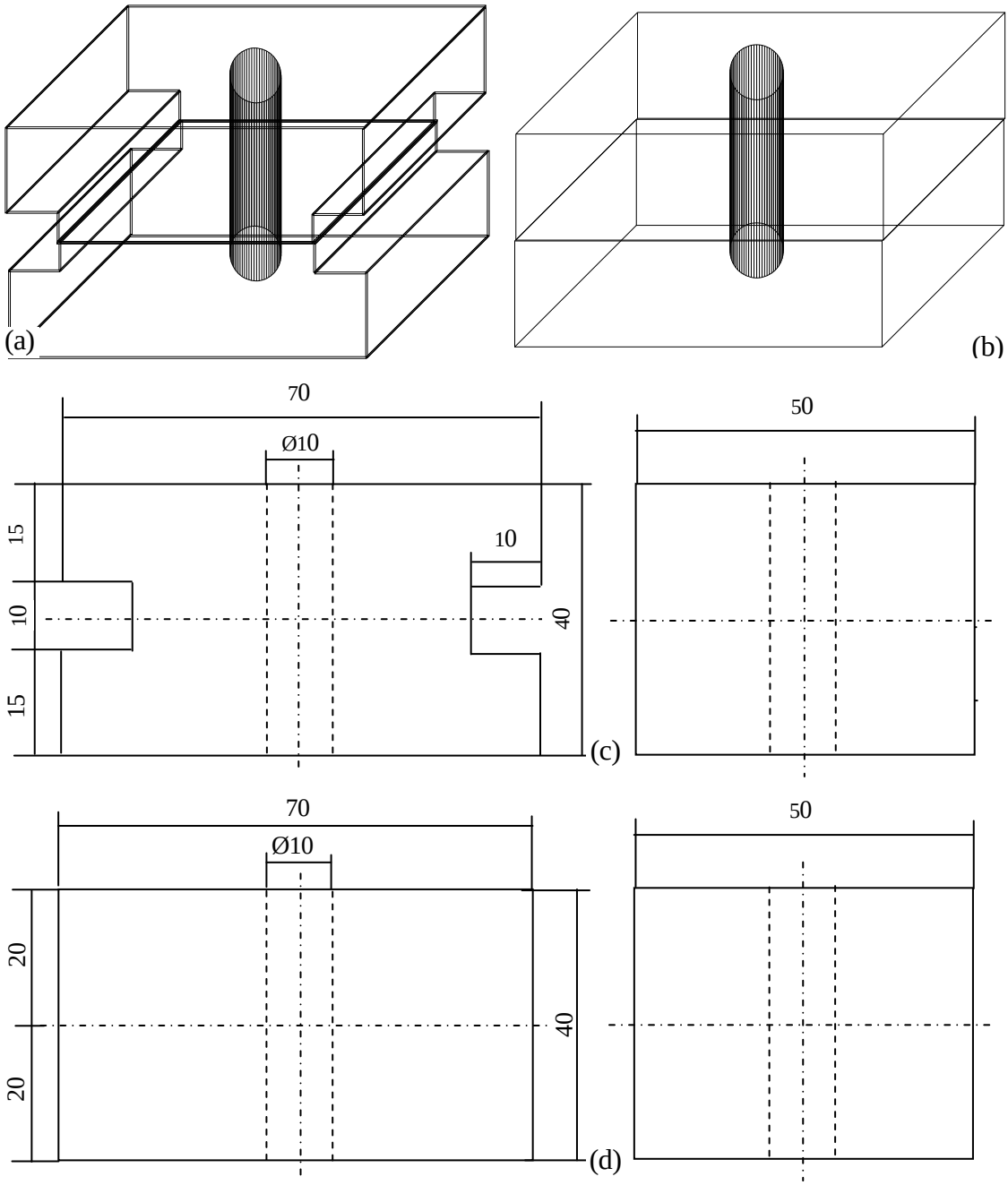


Figure 3 assemblage and size of samples for RDW (a) is a joint for testing the tensile strength, (b) is a joint for the shear strength, (c) presents the dimension of the tensile strength, and (d) presents the dimension of the shear strength

samples were conditioned for one week in an environmental chamber (20°C and 65% RH) before testing. The parameters which were varied in the various experiments were: the welding time, maintained after the welding vibration had stopped, the welding pressure exerted on the surfaces, the holding pressure exerted on the surfaces after the welding vibration had stopped, and the amplitude of the shift imparted to one surface relative to the other during vibrational welding. The different welding parameters studied are shown in table 3. For every variation, at least five tests were carried out.

For LVW, other specimens(70×50×20mm) are made by a finger-joint. The surfaces to be joined were grooved prior to welding with a milling cutter. Different types of grooves

running parallel to the direction of welding displacement were used. The small grooves (ENT 01) were 2.5 mm high and their top vertexes were separated by 4.5 mm. The big grooves (ENT 02) were 4.3 mm high and their top vertexes were separated by 8 mm. All is shown in figure 5.

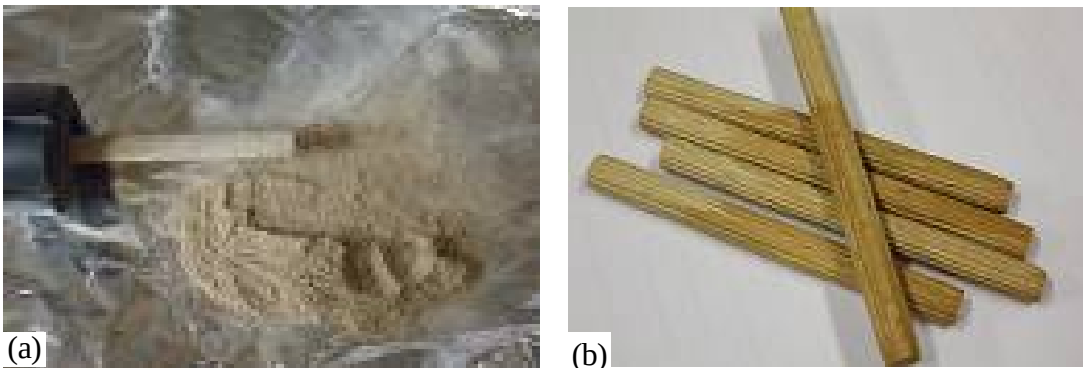


Figure 4 dowels laid on some additives (a) additives are tannins or acetylated tannins, and (b) additive are the solution of gum rosin.

Table 3 different process with welding parameters

No. process	WP(KN)	HP(KN)	WT(S)	HT(S)	Amplitude(mm)
1	1/1/3	8	1/1/3	5	1/1.5/1.5/0
2	1/1/3	8	1/1/3	5	1/2/2/0
3	1/1/3	8	1/1/2	5	1/1.5/1.5/0
4	1/1/2	6	1/1/3	5	1/2/2/0
5	1/5/7	8	1/1/1.5	5	1/1/2/0
6	1/1/3	8	1/1/2	5	1/2/2/0
7	1/1/3	8	1/1/2	5	1/2/1/0
8	2/3/3	9	1/2/1	9	1/1.5/2/0
9	1/5/8	9	1/1/5	8	1/2/2/0
10	1/4/9	12	1/1/1.5	5	1/1/2/0
11	1.5/2/3	15	1/3/2	60	1/1.5/2/0
12	1.5/3/3	15	1/4/1	60	1/2/2/0
13	2/3/3	15	1/2/2	60	2/1.5/1/0
14	2/3/3	15	1/2/2	60	1/2/2/0
15	2/5/4	15	1/3/2	20	1/2/2/0
16	2/5	15	1/5	30	1/2/0
17	5	15	4	30	2/0
18	2/5	15	1/5	30	1/2/0
19	2/5/4	15	1/3/2	20	1/2/2/0
20	2/3/5	9	1/2/1	9	1/2/2/0

4.6 Scanning electron microscopy of joints obtained by RDW

Scanning electron microscopy (SEM) micrographs of (1) the surfaces of the joints opened by mechanical testing, and (2) the sides of still closed joints obtained after metallizing with gold–palladium. The SEM equipment used was a TM3000 microscope employed at different magnifications.

4.7 Methods of some mechanical tests

4.7.1 Tensile strength and shear strength for RDW

The samples jointed by RDW were tested in tension and compress (figure 6) with an Instron universal testing machine at a displacement rate of 2 mm/min. The samples were tested dry, after 24-hours cold water immersion and after air redrying after the specimens were taken out of the water. Every test value reported was the average of 10 test specimens testing.

Figure 5 three types of grooved wood specimens prior to welding. From left to right: small grooves (ENT 01) and big groove (ENT 02).

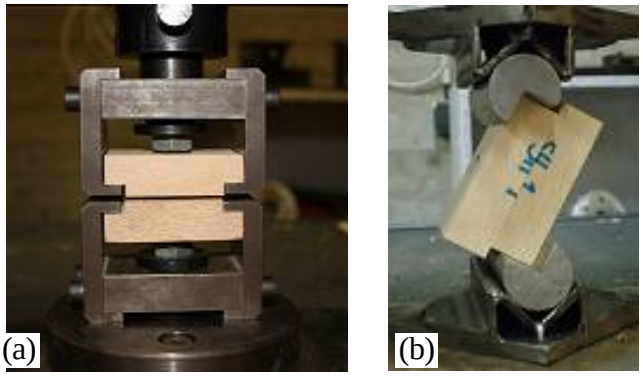


Figure 6 mechanical tests of joints obtained by RSD, (a) shows a test of tensile strength, and (b) shows a test of shear strength

4.7.2 Tensile strength for LVW

The specimens of finger-joint were cut every 5mm width(figure 7). The specimens were also cut according to the method described in European standard EN 205 by LVW (figure 8). In the middle of the specimens two cuts perpendicular to the weldline were made. The distance between the two cuts was 10 mm. The samples were formed so that they were appropriate for the test equipment. Detailed information about the form and dimensions of the test specimens suitable for the test equipment is given in Figure . The welded samples were conditioned for one week in an environmental chamber (20°C and 65% relative humidity) before testing. The shear strength of the joints was measured with an Instron universal testing machine at a rate of 2 mm/min according to the standard.

4.7.3 Calculation of mechanical strength

The strength (P) was calculated from the applied force and exposed welded surface area and was indicated in MPa as:

$$P=\frac{F\max}{S}=\frac{F\max}{l\times w}$$

where

P = strength (MPa)

Fmax = maximum force (N)

S = surface area (mm^2)

l = length of the surface area (mm)

W = width of the surface area (mm)

4.8 Experimental design

In figure 9, it presents the experimental design.

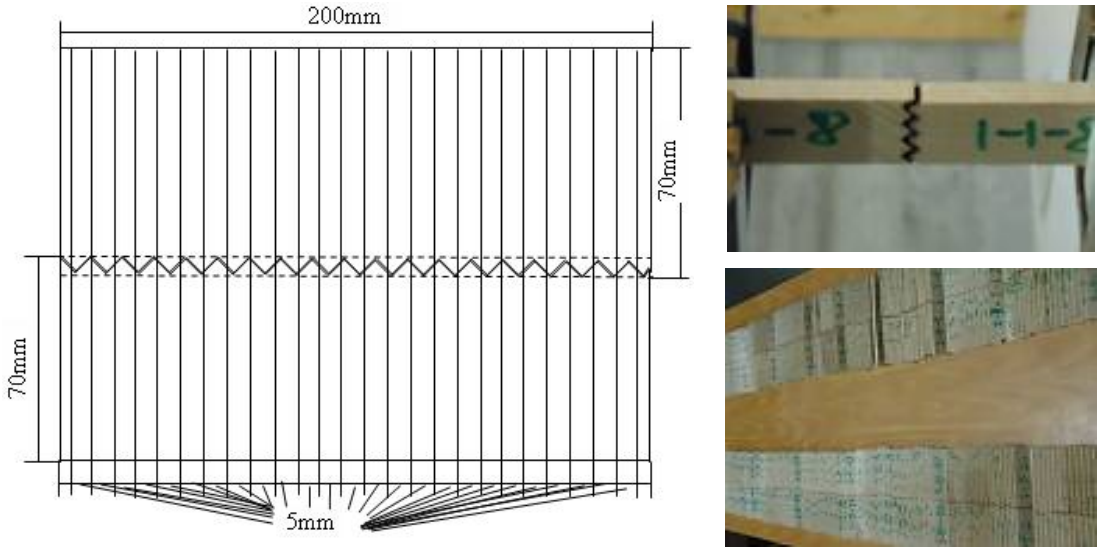


Figure 7 sawing the jointed pieces of grooved surface for the mechanical tests

Figure 8 tensile-shear strength of the welded connections

4.9 Statistical analysis

All data were handled initially using Microsoft Excel 2003. Descriptive statistics were used to create graphs and statistical analysis was performed using Origin7.5 software. To simplify data visualization, values were expressed as percentages.

5 Results

5.1 Acetylation of tannins

The ^{13}C NMR spectra in figure show some samples of three different acetylated tannin (figure). The ^{13}C NMR chemical shift assignments for the tannins are indicated on the spectra themselves corresponding to the relevant notations on the flavonoid. Flavonoid units in such tannin present phloroglucinol o resorcinol A–rings and catechol or pyrogallol B-rings is presented in the figure 10(Navarretea et al. 2010, Pizzi et al. 1997). The structure unit of acetylated tannin is in the figure12. In this way, from the figure 13, the rearranged tannin samples show: for No. 3 acetylated tannin, on C5 and C7 (153.5383ppm), C3' and C4' (143.0799ppm) much acetylation occurs progressively because the signal of free hydroxyl group decreased rapidly, and the signal of C1' (136.1292ppm) decreased C-ring and affected C2', C5' and C6' (118-131ppm), and some interflavonoid condensations increased slightly, and on some sugars (79.0365ppm) and C3 (70.5017ppm) all hydroxyl

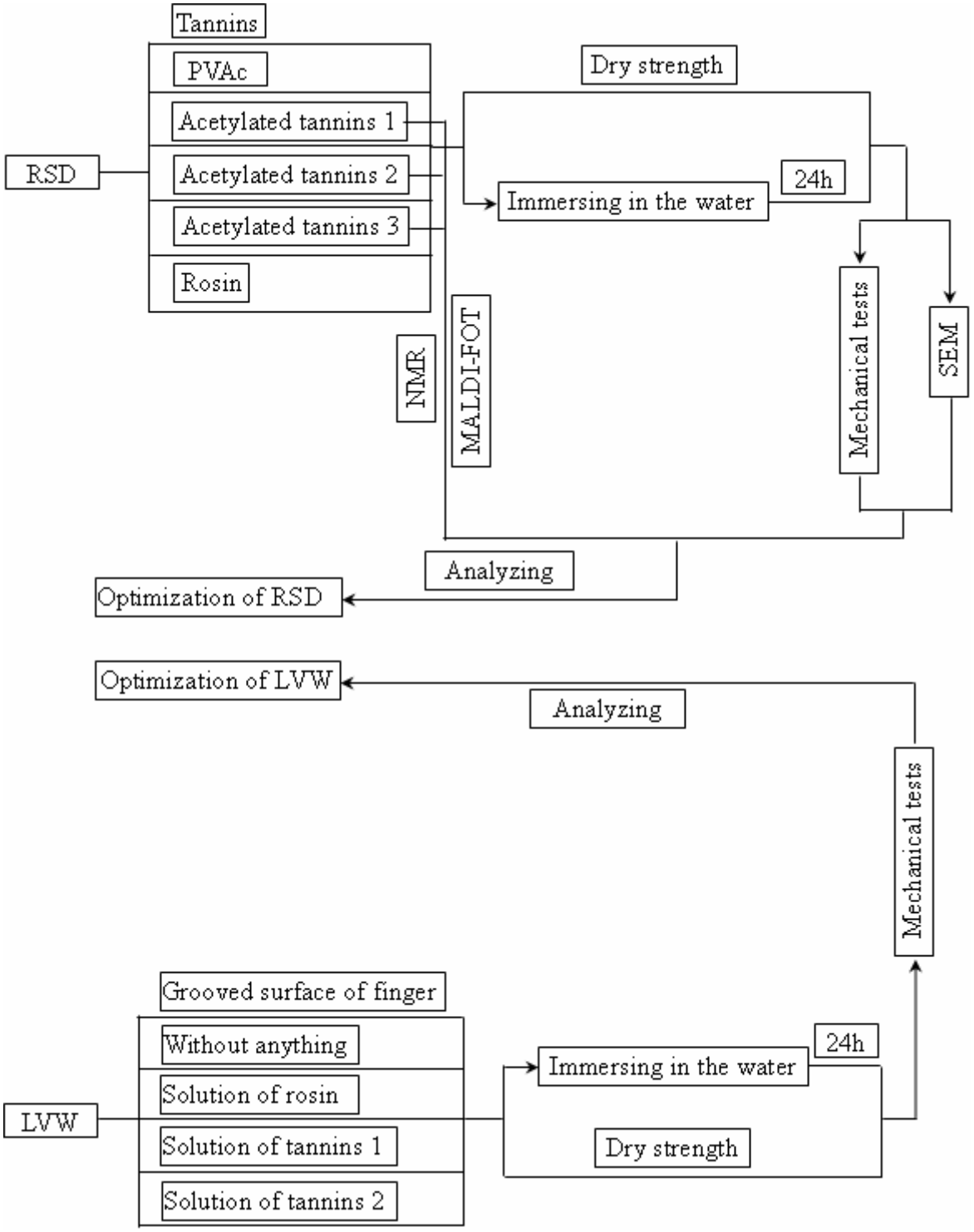


Figure 9 flow diagram showing the experiment

groups had been acetylated and replaced by some acetates; for No. 1 acetylated tannin and No. 2 acetylated tannin, acetylation happened like No. 3 acetylated tannin, but those peaks of sugars and C3 were relatively small. Thus the No. 3 acetylated tannin is more acetylated than others.

To determine what was obtained by No. 3 acetylated tannin, the acetylated tannins were analyzed by Matrix Assisted Laser Desorption Ionisation-Time of Flight (MALDI-TOF) mass spectrometry. The flavonoid repeating units present in mimosa tannin are of type A, B

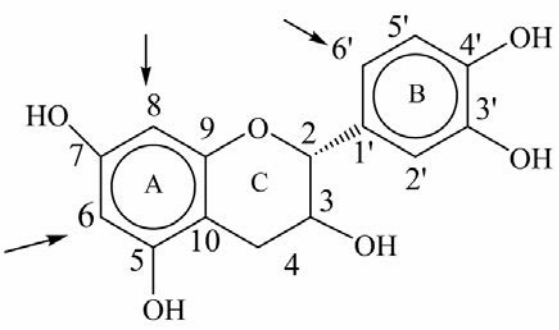


Figure 10. flavonoid structure

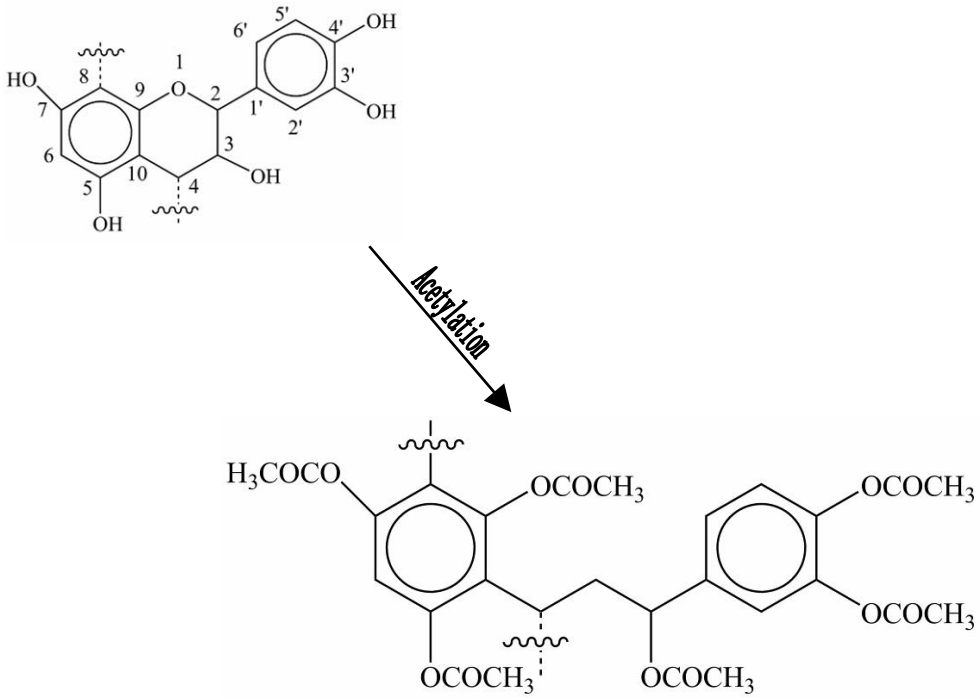
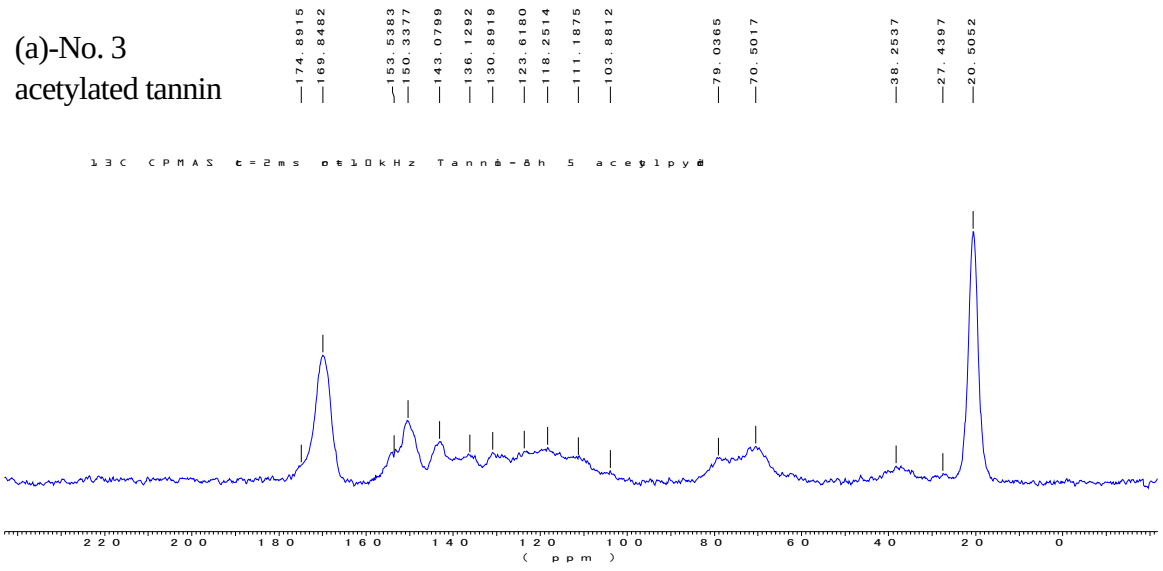


Figure 12 acetylation of tannin

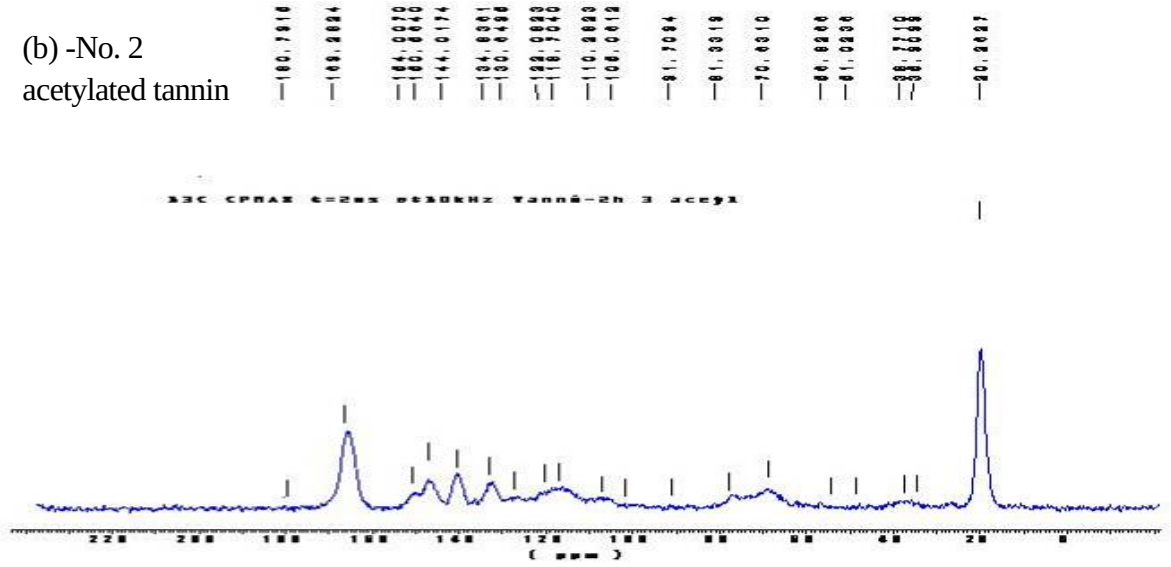
and C (figure 14)(Pizzi et al. 1997), and the mass of three units is 274, 290 and 306. The results obtained for three types of tannins so tested are reported in Tables 4, and Figures 15. The MALDI mass spectrum of No. 3 acetylated tannin confirms that extensive acetylation has occurred. From the values in Figs 15 of the experimental peaks 23 Da due to the Na+ residual of the matrix must be subtracted to obtain the molecular weight of the oligomer observed. The equation to calculate the different possibilities is namely $M + Na^{+}=23(Na) + 274A + 290B + 306C + 43(CH_3CO-) – 1H$.

According to acetylated tannin peaks of MALDI mass spectrum, there are three repeating units at high molecular weights, one very present, namely (290+4xCH3CO-) of value 458 Da, a second one also present but less, namely (306+5xCH3CO-) of value 516 Da, and a rare one of (306+6xCH3CO-) of value 558 Da. Thus many peaks are composed a acetylated flavonoid B-unit where 4 hydroxyls have been replaced by the acetate, 1352Da, 1378Da, 1394Da, and so on; and the peaks at 1866 Da, 1950Da, 2406Da 2903Da and 3359 Da are composed of a same acetylated flavonoid C-unit where all 5 hydroxyls have been replaced by the acetate; and only two peaks at 2761 Da and 3856 Da are composed of a same acetylated flavonoid C-unit where all 6 hydroxyls have been replaced by the acetate. The indications are that the depolymerized tannins are depolymerized naturally of low

(a)-No. 3
acetylated tannin



(b) -No. 2
acetylated tannin



(c) -No. 1
acetylated tannin

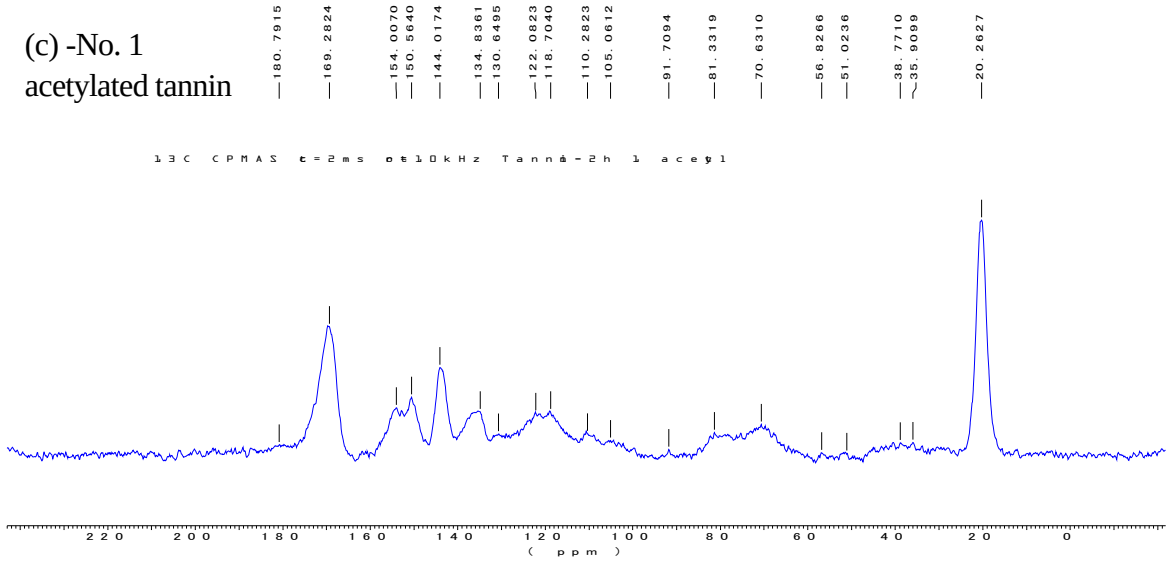


Figure 13 CP MAS ^{13}C NMR solid state spectra of (a) No. 3 acetylated tannin, (b) No. 2 acetylated tannin, (c) No. 1 acetylated tannin

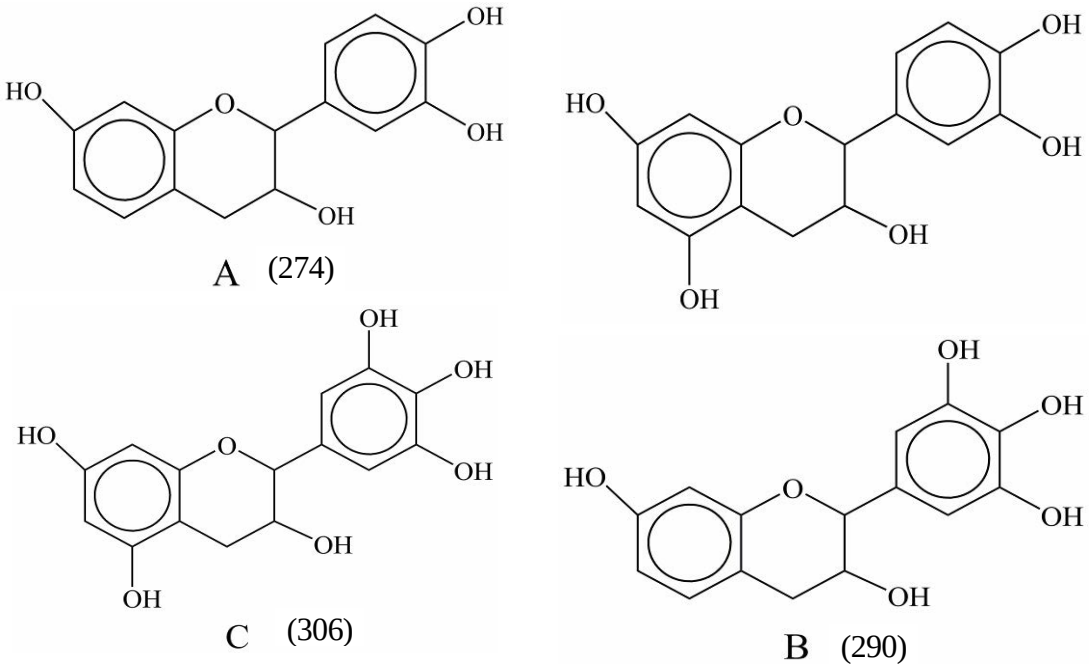


Figure 14 structure of different flavonoid units

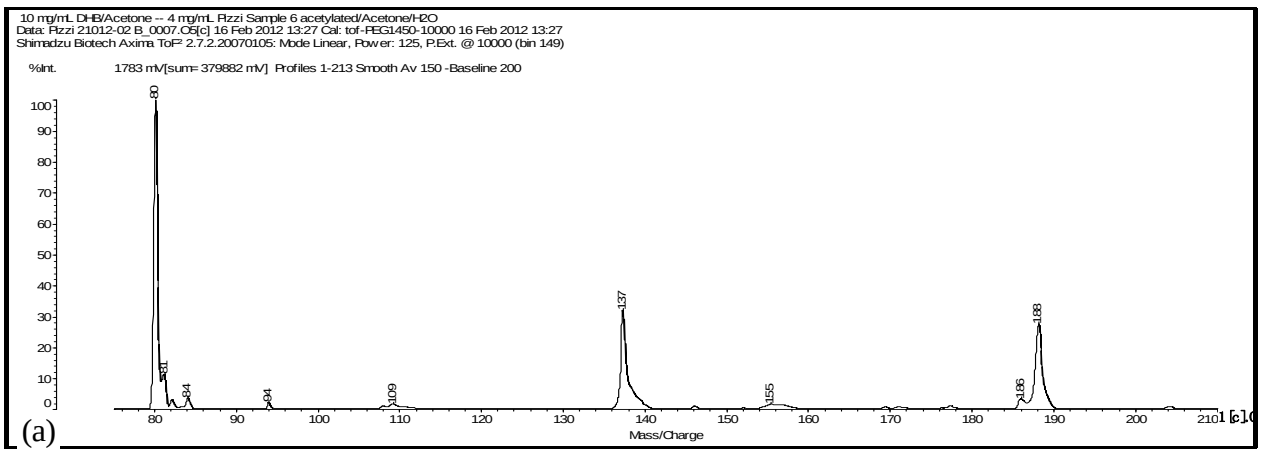
molecular weight. Thus, in Tables 4 a 274 + 5x43 Da occurs self-condensation such a fragment belongs is an acetylated oligomer. and wherever a 290 + 5x43 Da, 306 + 43 Da or a 306 + 2x43 Da fragment is indicated the oligomer such a fragment belongs is an acetylated oligomer. Equally acetylation are the oligomers where the fragment (acetylated flavonoid A, B or C unit) appears, hence the peaks at 686, 702, 718, 896, 922, 938, 964, 980 and 987 (or 993) Da. Thus the acetylated oligomers are in majority in the reaction mix obtained (Table 4), and multiacetylated oligomers such as the 517 Da ones also occur in little quantities (Table 4, Figure 15).

Table 4 fragmentation peaks for acetylated tannin by MALDI-TOF

M + Na Experimental	M + Na Calculated	Rel. proportions (%)	Flavonoid unit types			Acetyls repeating unit	Notes
			A	B	C		
274	274	26	1				
368	371	9			1	2	
410	413	80			1	2	
517	507	10	1			5	
525	523	1		1		5	
686(685)	685	3	1		1	2	
702	701	70		1	1	2	
718	717	10			2	2	
896	899	3	2	1		1	
922	957	2	1	2		2	
938(936)	931	13		3		1	
964	957	4	2		1	2	
980	979	23		2		9	
987 or	989		1		2	2	

(Following the above table 4)

M + Na Experimental	M + Na Calculated	Rel. proportions (%)	Flavonoid unit types			Acetyls repeating unit	Notes
			A	B	C		
993	989	21		2	1	2	
1294	1281	7	4			4	
1352	1355	37	2	2		5	(290+4xCH_3CO-)
1378	1381	30	3	1		6	(290+4xCH_3CO-)
1394	1413	79	1	3		6	(290+4xCH_3CO-)
1420	1413	35	2	1	1	6	(290+4xCH_3CO-)
1436	1435	100		3		13	(290+4xCH_3CO-)
1468	1491	20	1012+	1		4	(290+4xCH_3CO-)
1478	1435	65		3		13	(290+4xCH_3CO-)
1494	1517	76	1038+	1		4	(290+4xCH_3CO-)
1536	1558	35	1079+	1		4	(290+4xCH_3CO-)
1750	1737	7	4	1		8	(290+4xCH_3CO-)
1808	1811	20	2	3		9	(290+4xCH_3CO-)
1866	1869	28	2	2	1	10	(304+5xCH_3CO-)
1892	1891	46		4		17	(290+4xCH_3CO-)
1950	1949	42		3	1	18	(304+5xCH_3CO-)
1992	2014	30	1079+	2		8	(290+4xCH_3CO-)
2206	2193	5	4	2		12	(290+4xCH_3CO-)
2263	2309	12	2	4		14	(290+4xCH_3CO-)
2348	2347	26		5		21	(290+4xCH_3CO-)
2406	2405	27		4	1	22	(304+5xCH_3CO-)
2761	2749	8	4	2	1	18	(304+6xCH_3CO-)
2846	2803	12		6		25	(290+4xCH_3CO-)
2903 or	2861	12		5	1	26	(304+5xCH_3CO-)
	2903			5	1	27	
3301	3259	5		7		29	(290+4xCH_3CO-)
3359	3359	5		6	1	31	(304+5xCH_3CO-)
3798	3715	3		8		33	(290+4xCH_3CO-)
3856	3815	3		7	1	35	(304+6xCH_3CO-)



(a)

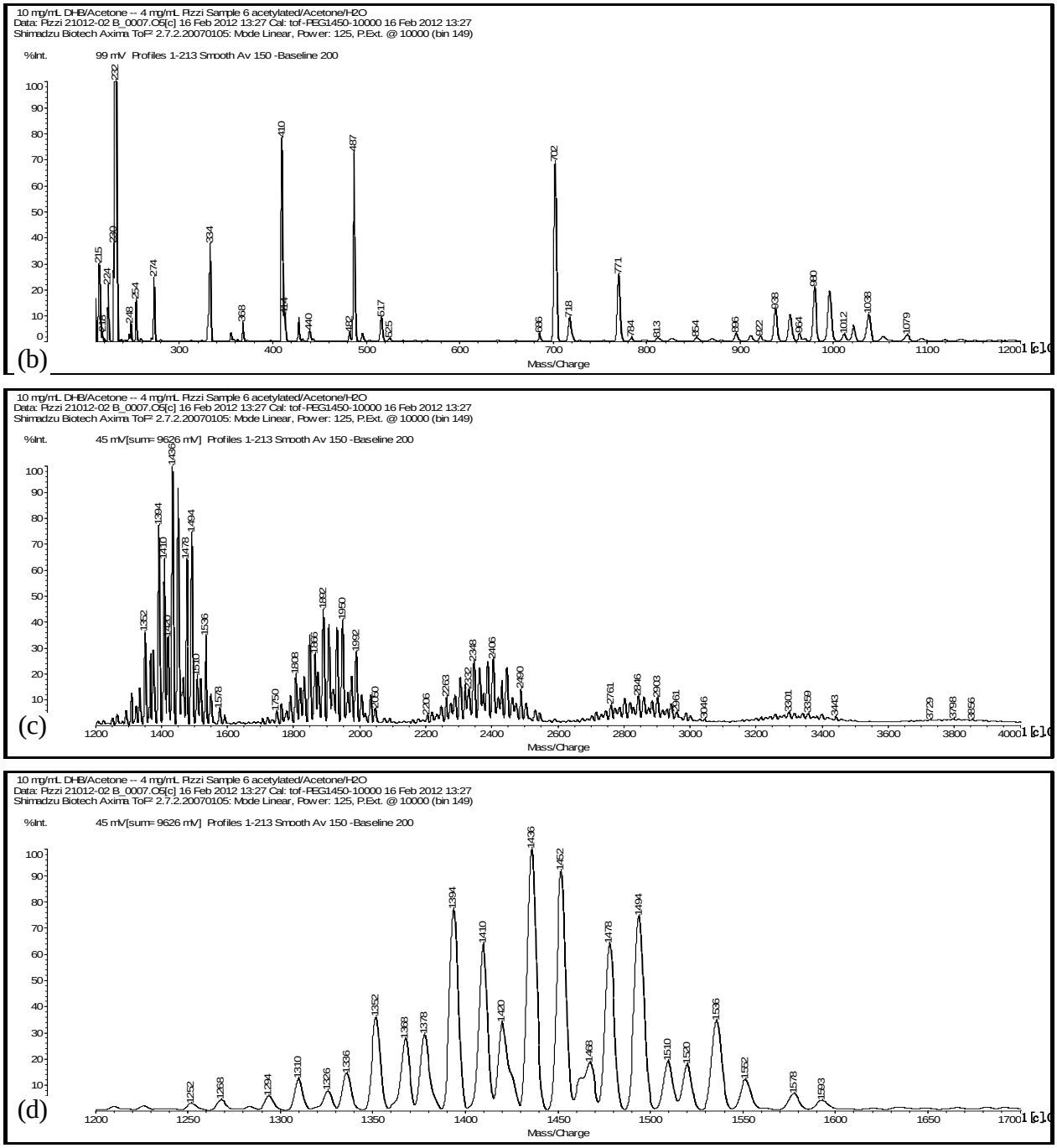


Figure 15 (a) MALDI-TOF of tannin 8h-acetylated with pyridine in the 75-210 Da range, (b) MALDI-TOF of tannin 8h-acetylated with pyridine in the 210-1200 Da range, (c) MALDI -TOF of tannin 8h-acetylated with pyridine in the 1200-4000 Da range and (d) MALDI -TOF of tannin 8h-acetylated with pyridine in the 1200-1700 Da range

5.2 TGA of tannin and acetylated tannin

As experimental method of TGA, the thermogravimetric behaviour of the various forms of tannin was analyzed, and it indicates in the figure 16. it can be seen that tannin had lost up to 10% of its weight by the time it reached 200°C; and the decomposition of the acetylated tannin at around 300°C occurred, because the TGA automatically detected the weight losses of the tannin and acetylated tannin and the polymer by automatically holding the rubber under isothermal conditions while the oil is evaporated and the polymer thermally degraded.

The evaporation of the tannin at about 100°C got off.

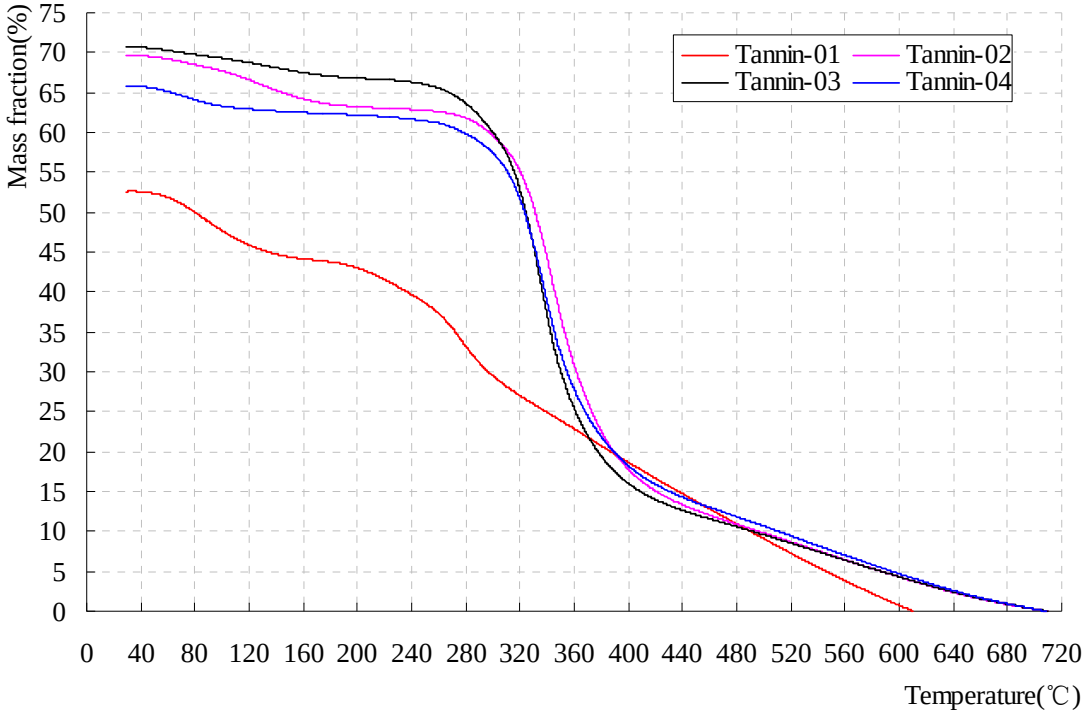


Figure 16 TG curves of tannin and three acetylated tannin in nitrogen (N_2) atmospheres

5.3 Mechanical strength of RDW

In the table 5, the mechanical result is the average of 10 samples for tensile strength and shear strength of welded dowel joints. It presents that the tensile strength of dry joints with no-treating tannin is the strongest, and the tensile strength of humid joints with rosin is the strongest, and the shear strength of dry joints with No. 3 acetylated tannin is the strongest, and the shear strength of humid joints with No. 3 acetylated tannin is the strongest. About the resistance of water for tannin and three acetylated tannin, No. 3 acetylated tannin is the best. But it is noticeable that the tensile strength of joints with rosin changes a little after immersing in the water for 24h.

From figurre 17, the welded joint with or without additives breaks at the point of the maximum dry tensile-strength, the displacement stops, but when the value of humid tensile-strength arrives at the maximum point, the displacement continues and decreases. About all graphs of shear-strength, it is found that dowel occurs to slide except the humid shear-strength of joint with rosin when joints are broken.

5.4 Mechanical strength of LVW

Some finger joints obtained by LVW are cut and tested according to the experimental part. From table 6, the tensile strength of ENT01 and ENT02 finger joints is respectively got by process No. 2 and No. 3. Furthermore, the tensile strength distributed in every part is relatively well-proportioned by their optimal process(Figure 18 and 19). About some following test, hence, process 2 is choose for ENT01 finger joint, and process 3 is choose for ENT02 finger joint.

From the table 7, it is clear that LVW is a complex system because the results of mechanical test is greatly different according to the surface of specimen, with or without additives, the

Table 5 tensile strength and shear strength for welded dowel joints with and without addition

Additives	Tensile strength						Shear strength					
	No-immersing			24-h immersing			No-immersing			24-h immersing		
	Mean(MPa)	Max(MPa)	SD	Mean(MPa)	Max(MPa)	SD	Mean(MPa)	Max(MPa)	SD	Mean(MPa)	Max(MPa)	SD
Without any additives	1.064	1.268	0.28	0.36	0.60	0.25	1.61	2.13	0.90	1.53	1.84	0.49
PVAc	0.428	0.796	0.62	0.32	0.69	0.36	1.79	2.33	1.01	1.58	2.30	1.33
No-treating tannins	1.2	1.34	0.30	0.37	0.48	0.16	1.76	2.23	0.82	1.70	2.36	1.12
No. 1 acetylated tannins	0.772	0.992	0.42	0.32	0.50	0.19	1.85	2.38	0.78	1.74	2.19	0.64
No. 2 acetylated tannins	0.668	0.956	0.35	0.30	0.40	0.16	1.73	2.12	0.61	1.73	2.12	0.55
No. 3 acetylated tannins	0.644	0.928	0.34	0.38	0.51	0.17	1.95	2.38	0.95	1.78	2.59	1.35
Rosin	0.592	0.776	0.28	0.52	0.66	0.27	1.69	1.85	0.54	1.59	1.87	0.74

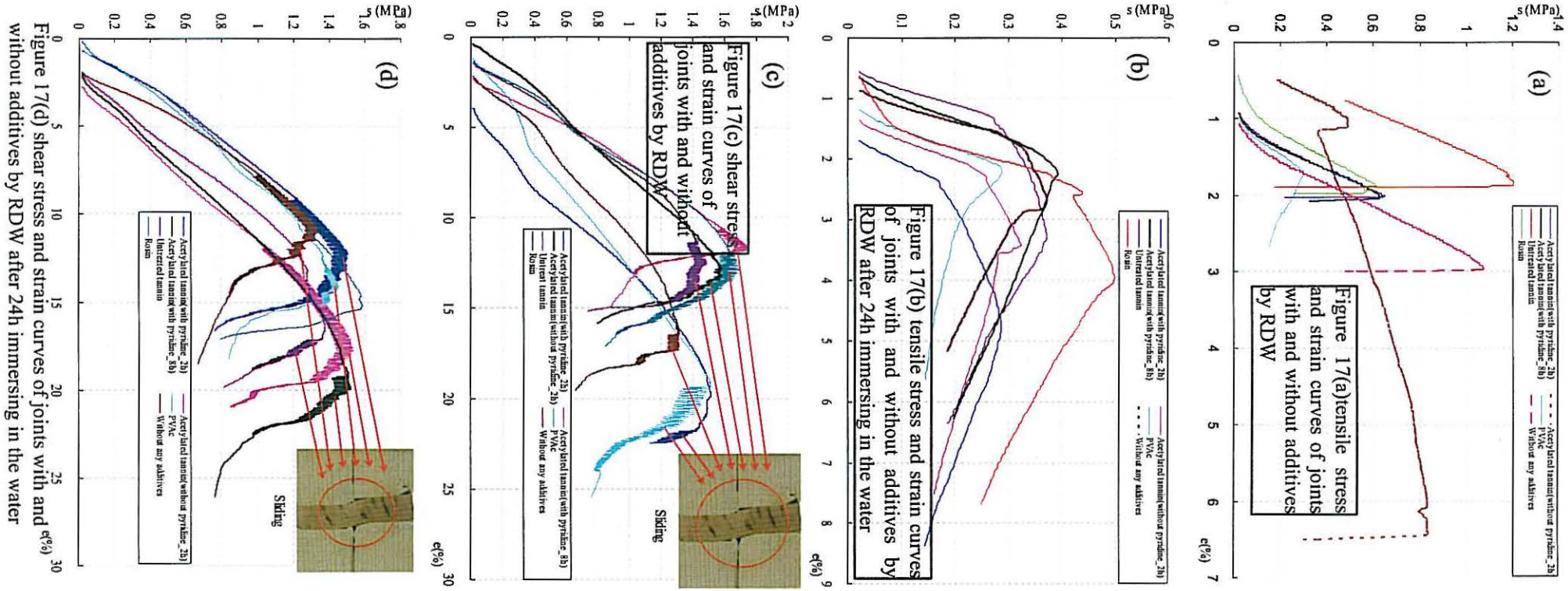


Figure 17(a)tensile stress and strain curves of joints with and without additives by RDW

Figure 17(b) tensile stress and strain curves of joints with and without additives by RDW after 24h immersing in the water

Figure 17(c) shear stress and strain curves of joints with and without additives by RDW

Figure 17(d) shear stress and strain curves of joints with and without additives by RDW after 24h immersing in the water

Table 6 tensile strength of wood joints of grooved surfaces by LVW

Type of finger joint	No. process	Mean(MPa)	Max(Mpa)	SD
ENT 01	1	1.26	1.30	0.05
	2	1.43	1.77	0.24
	3	1.29	1.60	0.22
	4	0.96	1.14	0.18
ENT 02	1	1.42	1.68	0.18
	2	1.54	1.70	0.11
	3	1.58	1.73	0.10
	4	1.28	1.58	0.23

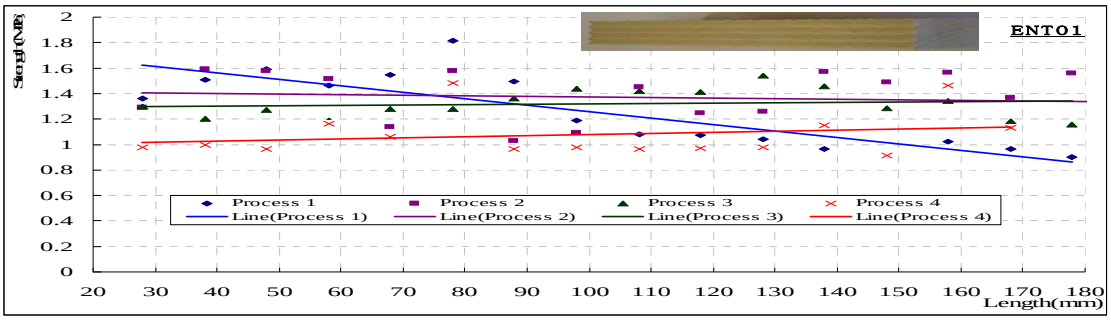


Figure18 tensile strength of every 5mm piece for wood welded joints of grooved surfaces(ENT01)

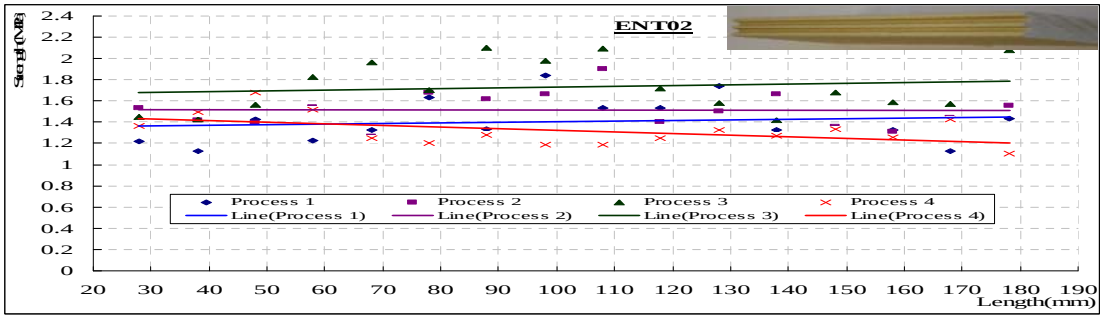


Figure19 tensile strength of every 5mm piece for wood welded joints of grooved surfaces(ENT02)

type of additive, the process and so on. The most appropriate process obtained by some previous tests for the wood piece of grooved surface of finger-joint is welded some samples with rosin, and the strength of joint of grooved surface with rosin is worse than the strength of joint of the same pieces without rosin by the identical process, and the strength of surface of ENT02 is more than the strength of surface of ENT01 by adding the rosin. This is influenced by smoother surface of sample because of adding the rosin, and so the same process is not viable. Table 7 also indicates the tensile strength of bonding flat pieces with or without rosin and tannin which are soaked in the cold water. The results in Table 7 show any improvements on the control when the grooves of the two surfaces fit tightly onto each other whether tannin or soaking. Although welding bonding with No. 1 tannin solution has a tolerable dry-strength and a awful wet-strength, it is pity that the dry or humid strength of welding bonding with 2 tannin solution couldn't get (see some photos in the figure 20), and the reasons are probably a high concentration of phosphoric acid which cuts the cellulose molecule chain and a weak formation of entangled wood fibres into the bonding of tannin and fused wood intercellular materials.

Table 7 tensile strength of wood welded joints by LVW of different process with or wothout additives

No. process	Mean(MPa)	Max(Mpa)	SD	Additives	Note
2	0.94	1.26	0.35		Grooved face of ENT 01
2	0.80	0.86	0.08	Rosin	Grooved face of ENT 01
3	2.76	3.25	0.83		Grooved face of ENT 02
3	1.13	1.29	0.14	Rosin	Grooved face of ENT 02
3	1.12	1.20	0.07	Rosin	Grooved face of ENT 02, Wet strength
5	7.11	11.13	3.13		
6	7.61	9.11	1.09		
7	3.69	4.48	0.54		
8	7.55	8.11	0.39		
8	5.38	6.01	0.77	Rosin	One face with rosin
8	6.68	7.32	0.89	Rosin	Two face with rosin
8	5.41	6.10	0.75	Rosin	One face with rosin in the water
8	6.62	6.71	0.08	Rosin	Two face with rosin in the water
9	6.30	7.89	1.30		
10	5.61	6.87	1.02		
11	8.54	10.80	1.88	Rosin	
11	8.39	9.13	0.65	Rosin	Two face with rosin in the water
12	5.90	8.25	2.04	Rosin	Two face with rosin in the water
13	7.26	7.75	0.80	Rosin	
14	8.37	10.16	1.83	Rosin	
15	6.56	7.89	1.50	Rosin	
16	7.40	8.76	1.41	Rosin	
17	11.22	12.52	1.36	Rosin	
17	6.96	7.60	0.90	Rosin	Two face with rosin in the wate
18	10.32	11.28	0.83	Rosin	
18	7.27	7.62	0.37	Rosin	Two face with rosin in the wate
19	12.26	14.63	2.23	Rosin	
19	8.24	9.09	0.59	Rosin	Two face with rosin in the wate
20	5.26	6.26	0.95	Tannin	Brushing some phosphoric acid before welding wood

5.5 Ultramicrographic Character of joints obtained by mechanically induced wood fusion welding

The entangled net of cellulose fibres immersed in wood fusion band is observed by

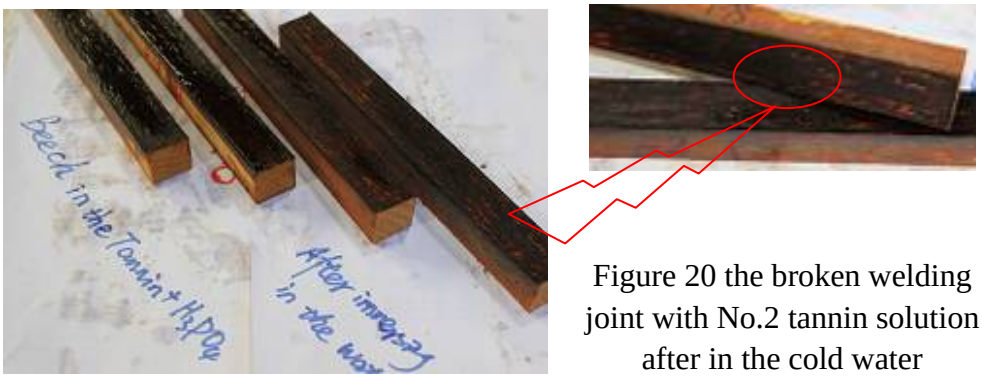
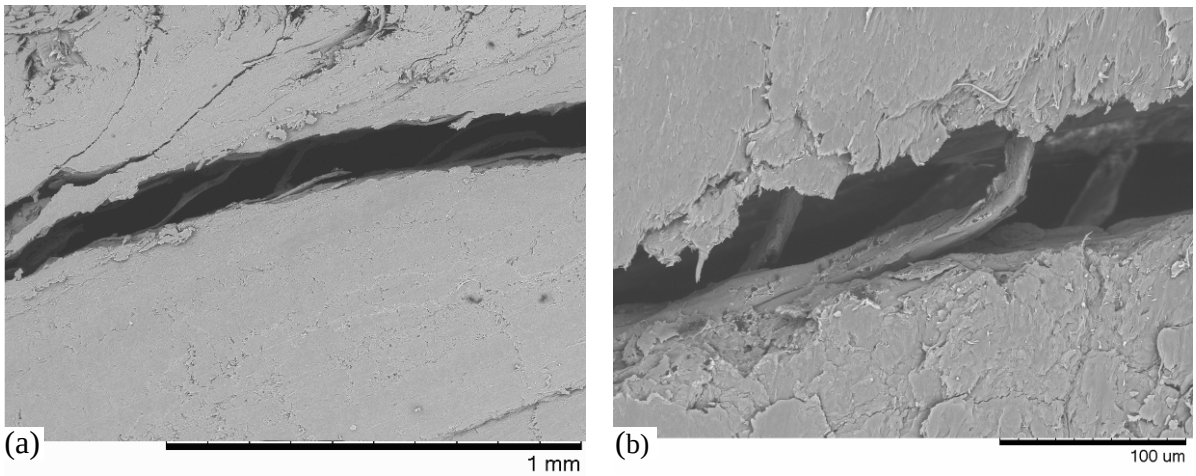
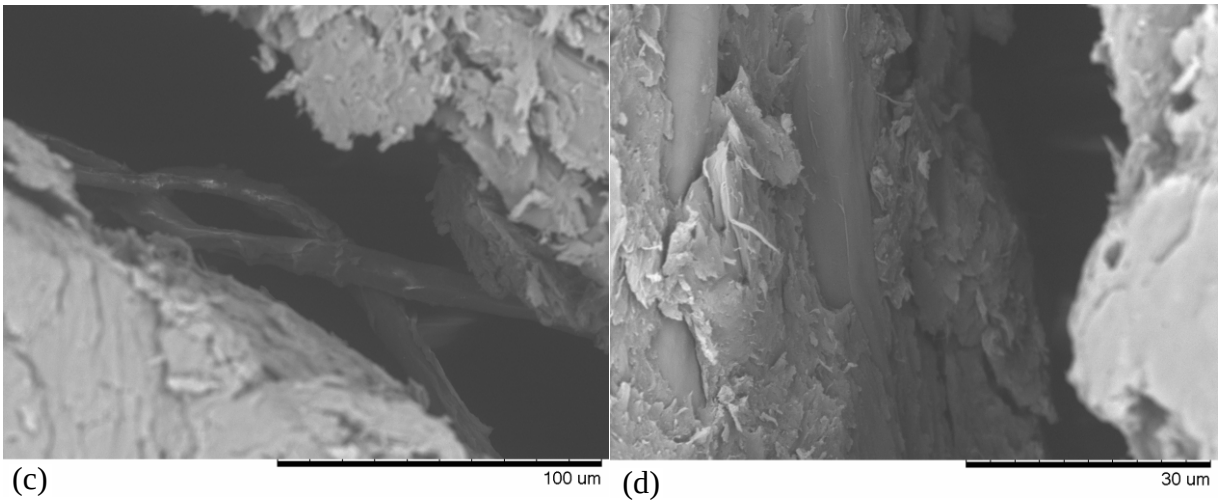


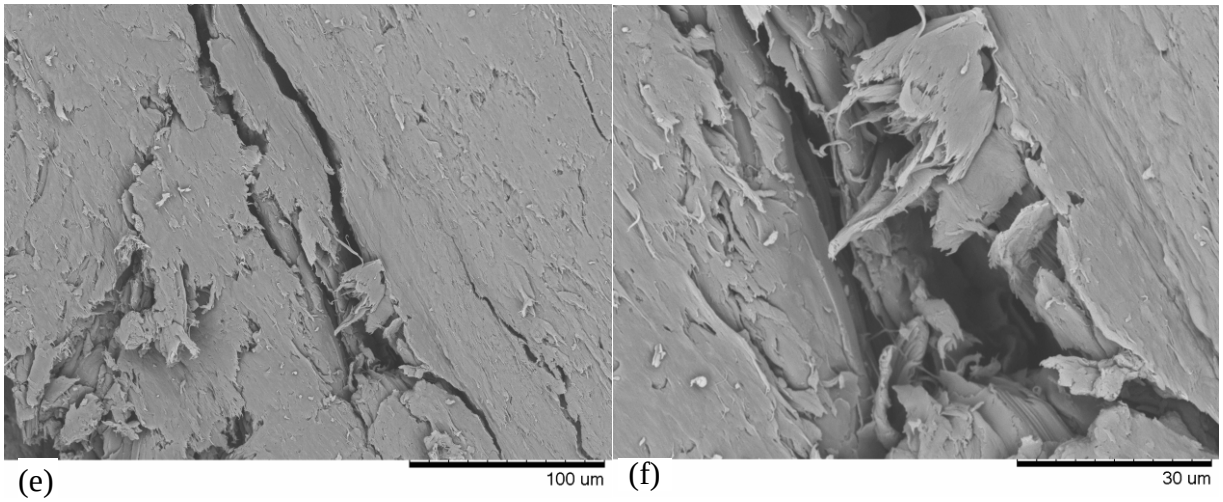
Figure 20 the broken welding joint with No.2 tannin solution after in the cold water

SEM. In Figure 21a and b is shown one of the characteristic bands of rotational wood-dowel welding between dowel and substrate, and the orientation of welded bands is identical with the orientation of rotational dowel during welding. Especially, Figure21 b of the same type of band confirms the presence of a mass of entangled wood fibres of dowel and substrate each other immersed in a matrix of amorphous, fused intercellular material, almost certainly composed of lignin, possibly including some hemicelluloses(Gfeller et al. 2003, Stamm et al. 2006), and every fibre is enwrapped by some abundant fusion. But it is indicated that some adhesive fusions of on the surface of some fibres in the bondline and the wall of dowel and substrate are peeled off after 24-h immersing in the cold water by RDW without anything (Figure 21 c and d). The joint obtained by RDW with some tannins is possibly worse than bonding by RDW without anything, it is confirmed by SEM. In figure21 e and f, some fibres are not completely wrapped by some fusion. Are some acetylated tannins useful for enhancing the water resistance of RSD joints? From figure 21 g, h, i, j, k, l, m, n, o, p, q, r, s, t, u and v, some acetylated tannins are melted by the temperature during dowel rotating and don't protect the bondline to resist the water. There are some acetylated tannins on the surface of dowel and substrate of broken welded joint (Figure 21 u and v). This result is confirmed by the measurement of tannin and acetylated tannin TGA, because the about 200°C temperature reached during welding could be not enough to melt the acetylated tannin(Kanazawa et al. 2005). It is seen that some adhesions of some rosins and intercellular connecting tissue or middle lamella among wood cells exist greatly in the weldline regardless without soaking or soaking in the cold water(Figure 21 w, x, y and z).

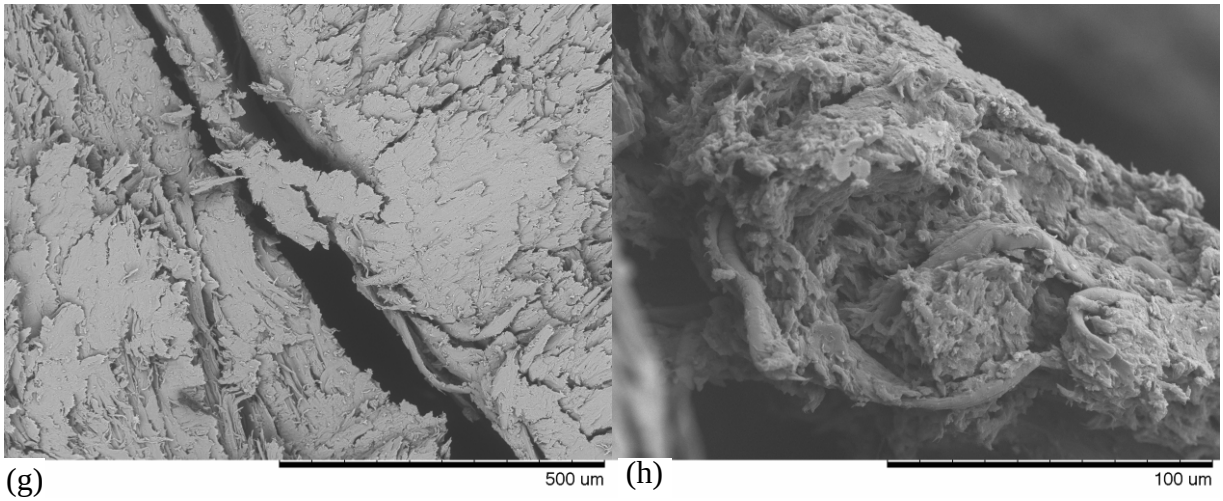




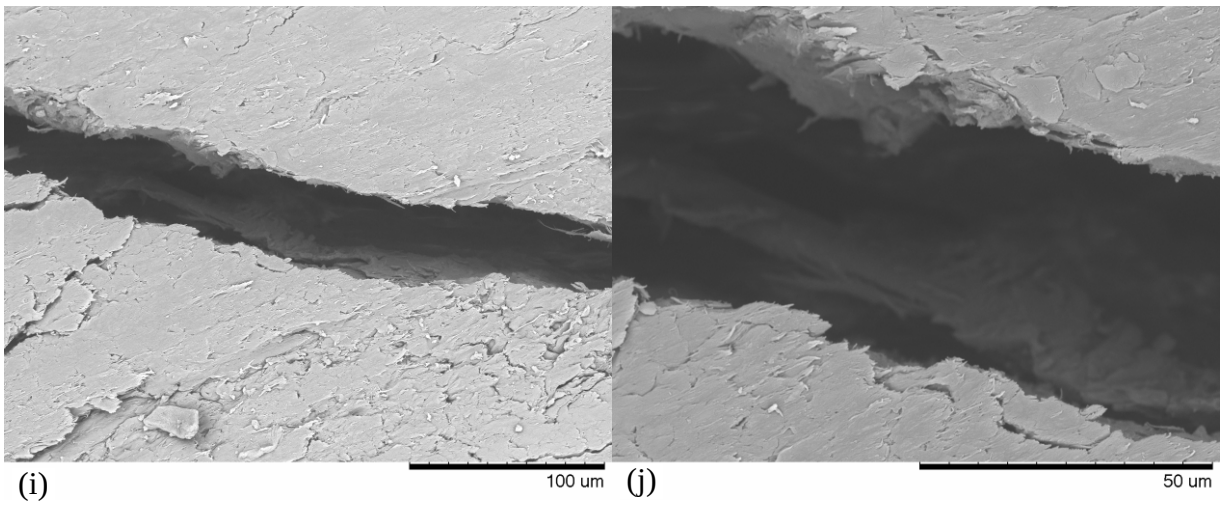
(c) (d)



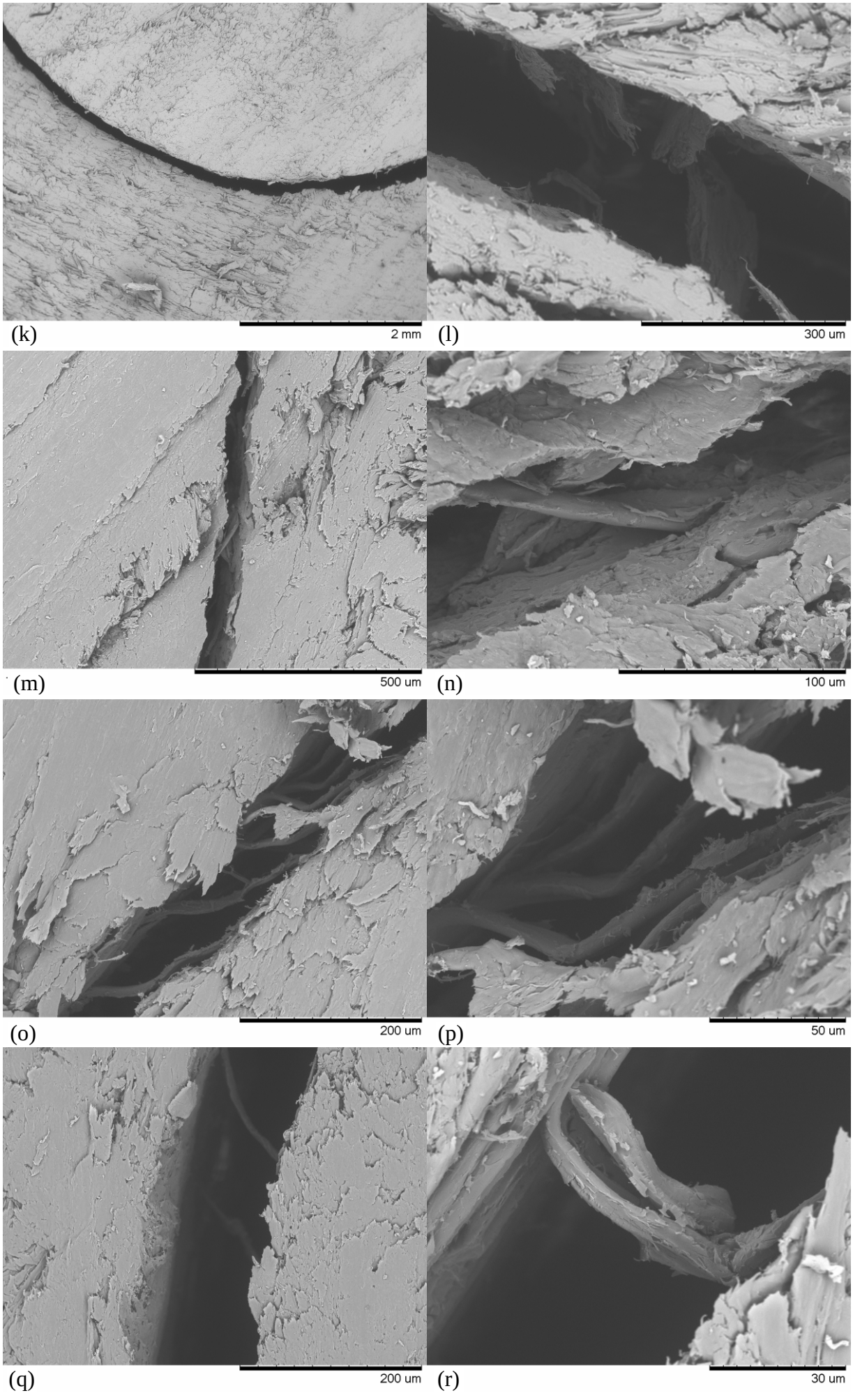
(e) (f)



(g) (h)



(i) (j)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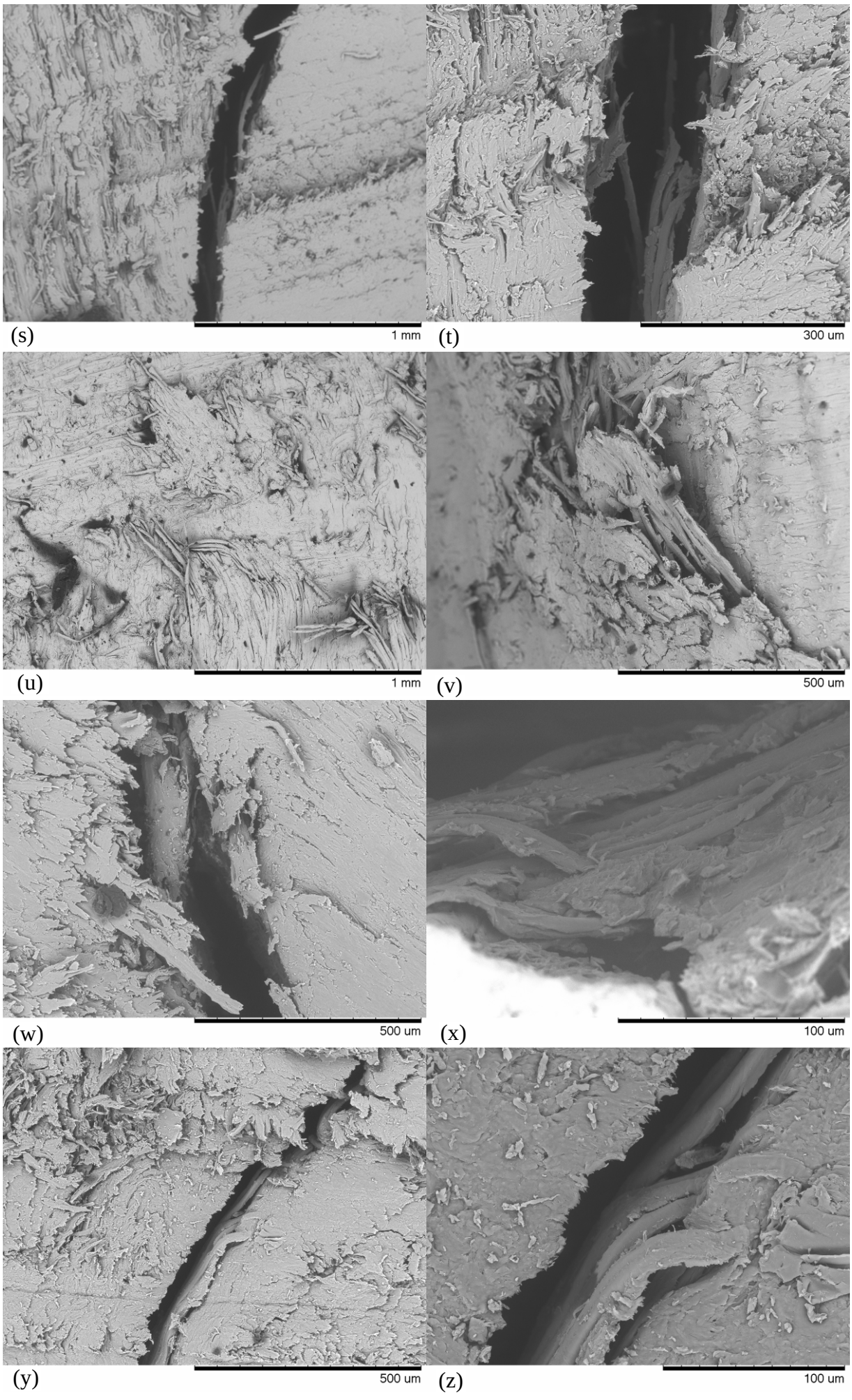
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100 um

Figure 21 scanning electron microscopy images of bondline and dowels of broken joints by RDW (a) magnification=100× showing weldline of RDW without anything, (b) with same (a) at 600× magnification, (c) magnification=1000× showing weldline of RDW without anything after soaking in the water, (d) with same (c) at 2500× magnification, (e) magnification=600× showing weldline of RDW with tannin, (f) with same (e) at 2000× magnification, (g) magnification=200× showing weldline of RDW with tannin after soaking in the water, (h) with same (g) at 1000× magnification, (i) magnification=600× showing weldline of RDW with No. 2 acetylated tannin, (j) with same (i) at 1800× magnification, (k) magnification=40× showing weldline of RDW with No. 2 acetylated tannin after soaking in the water, (l) with same (k) at 300× magnification, (m) magnification=200× showing weldline of RDW with No. 1 acetylated tannin, (n) with same (m) at 1000× magnification, (o) magnification=400× showing weldline of RDW with No. 1 acetylated tannin after soaking in the water, (p) with same (o) at 1200× magnification, (q) magnification= 400× showing weldline of RDW with No. 3 acetylated tannin, (r) with same (q) at 2000× magnification, (s) magnification=100× showing weldline of RDW with No. 3 acetylated tannin after soaking in the water, (t) with same (s) at 300× magnification, (u) magnification=100× showing a dowel after joints breaking, (v) magnification =200× showing another dowel after joints breaking, (w) magnification= 200× showing weldline of RDW with rosin, (x) with same (w) at 1000× magnification, (y) magnification=200× showing weldline of RDW with rosin after soaking in the water, and (z) with same (y) at 800× magnification

5.6 Summary of the results

It is ensured the strength of wood welding joint exceeds the strength of PVAc bonding (see table 5). The enhancement in the water resistance of the weldline should be obtained both for linear friction welding as well as for dowel rotational welding. The impact of rosin protecting wood welding band system in the cold water is further confirmed a few effective, but the modified tannin doesn't exert its effect of enhancing water resistance (figure 20, figure 21g, h, k, l, o, p, s, t, u and v). This research will contribute to improve these bio-additives during welding wood pieces and more open the door to the utilization of wood welded joints for exterior applications. The parameters of process, whether having additives and wood properties are critical for the strength of welding joint, once one of influencing factors will be changed and the process should have to be amended in succession.

6 Some products by LVW

The LVW-series with CPC-Vibration technique have been well applied in the auto-mobile industry, the household appliances industry and the general technical articles. Wood welding technique have researched for more than a decade, and this technology has its own characteristics in the field of industrial wood, such as wood is a particular material, and it is important that some technical parameters of wood welding should be decided according to the species, the grain, with or without additives, the applied area, and so on. The technique of RSD has had some attempts in the furniture, the floor, and the construction (Segovia et al. 2011, Bocquet et al. 2007, O'Loinsigh et al. 2011). Recently we also have some examples by LVW (figure 22, 23, and 24).

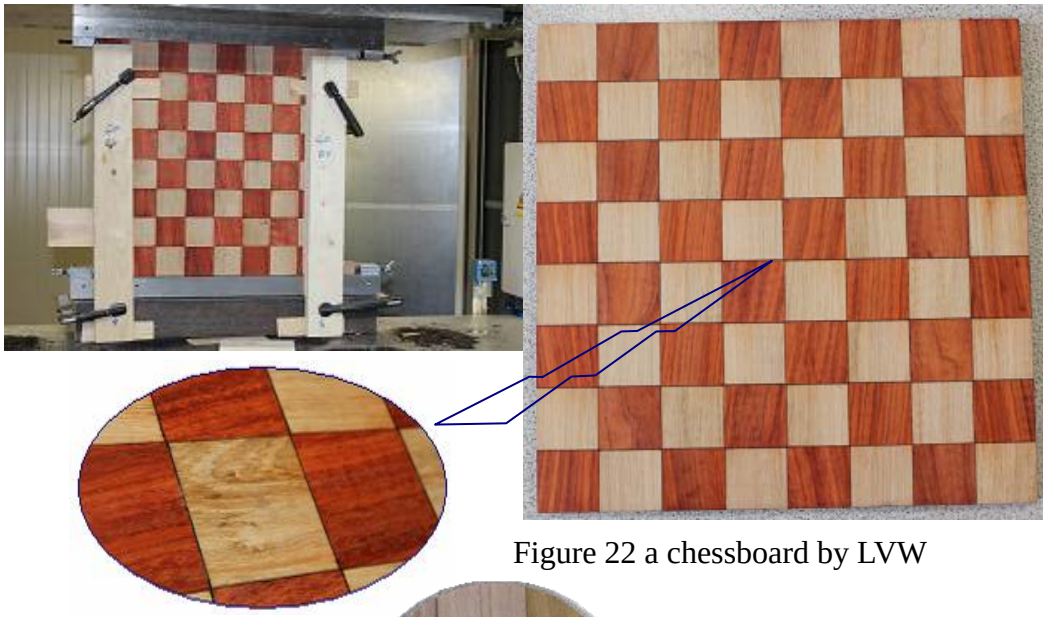

Figure 22 a chessboard by LVW

Figure 23 a bottom of barrel by LVW

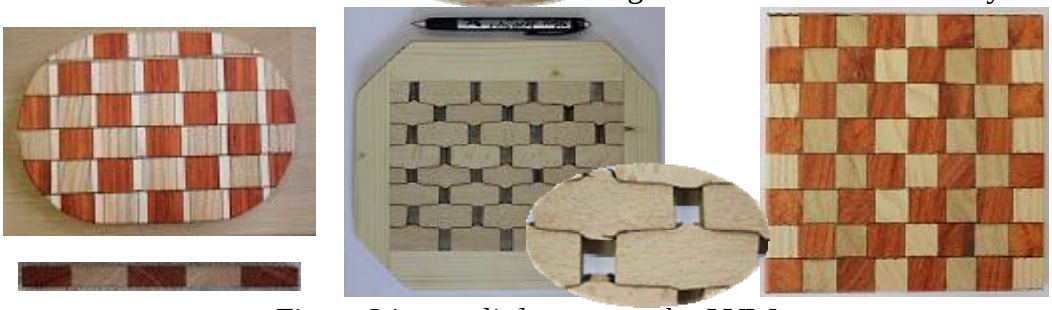

Figure 24 some little artwares by LVW

7 Discussion

Tannin is a compound that is naturally-derived, non toxic and that can melt and solidify. Acetylation of tannin greatly effects by three different processes. It is certain that tannin is capable of being acetylated, but in this report the melting point of acetylated tannin increases more than the original tannin. However, the temperature RSD brings about when the dowel rotates by high-speed welding is not enough to melt acetylated tannin. In order to easily melt, it is a hypothesis that something will be added when tannin is acetylated, or some friendly-environmental additives are mixed with tannin when welding is proceeding.

In order to simulate a species of padauk which is fabricated a welded joint of excellent wet-strength, some samples of beech wood are treated by a solution of tannin and

phosphoric acid. But some researches show the effects of these variables on wood that has been treated with phosphoric acid. MOE, MOR, and WML all decrease with increasing temperature and time. Significant losses in glucose, xylose, galactose, arabinose, and mannose also occur as the time and temperature increase(M. Rowell 2005). Hence, the amount of phosphoric acid and its concentration are very important to welding and dry(/wet)-strength.

The research of enhancing water resistance of wood welding banding focused on the protection of weldline, but it is concerned that the humidity of wet wood welding joint changes. Because a dry-stress is considerable when a lot of wood species are dried, and that it is possible that the dry-stress breaks a welding bonding. In this research, it is visible some wet welding pieces possess a great strength, but after some days the bondings break itself.

Providing that some fixtures of welding machine are suit for those various components, it is undoubted that the technique of LVW greatly applies in many wood products. The force is very strong when the sample is welded, and fixing the sample is very important.

8 Conclusion & Outlook

(1) The acetylation occurs by different process acetylating tannin, and the result of No.3 acetylated tannin is best.

(2) Until now, adding small amounts of rosin to the weldline is perfect for improving the water resistance of wood welding joint.

(3) For the technique of RDW, the wet strength of joint with acetylated tannin can't be ameliorated. For the of LVW, the wet strength is improved if the process is amended according to the solution of tannin and rosin.

(4) The technique of wood welding applying in the manufacture, especially the LVW, should be equipped by some appropriate parts.

9 Reference

Bocquet J.F., Pizzi A., Resch L. Full-scale industrialwood floor assembly and structures by welded-through dowels. *Holz Roh Werkst*, 2007, vol. 65, p.149–155.

Bogner M., Zupcic G. H. Welding of solid wood. *Drvna Industrija*, 2008, vol. 59, n° 3, p. 113-119.

Boonstra M, Pizzi A, Ganne-Chedeville C, Properzi M, Leban J-M, Pichelin, F. Vibration welding of heat-treated wood. *Journal of Adhesion Science and Technology*, 2006, vol. 20, p.259-269.

Fengel D., Wegener G. Wood: Chemistry, Ultrastructure. Reactions. Walther de Ciruyter, Berlin, Germany, 1989.

Ganne-Chedeville C. *Soudage linéaire du bois: étude et compréhension des modifications physicochimiques et développement d'une technologie d'assemblage innovante*, Th. Science. 2008. UHP NANCY 1, EPINAL.

Ganne-Chedeville C., Properzi M., Pizzi A., Leban J.M., Pichelin F. Edge and face linear vibration welding ofwood panels. *Holz Roh Werkst*, 2007, vol. 65 p.83–85

Gerber, C., Gfeller, B. Joint connection with welded thermoplastic dowels and Wood Welding Technologies. *Proceedings of the World Conference on Timber Engineering*, 2000, British Columbia, Canada

Gfeller B., Lehmann M., Properzi M., Pichelin F., Zanetti M., Pizzi A., Delmotte L. Interior wood joints by mechanical fusion welding of wood surfaces, *Forest Prod. J*, 2004, vol. 54, p.72-79.
Gfeller B., Pizzi A., Zanetti M., Properzi M., Pichelin F., Lehmann M., Delmotte L. Solid wood joints by in situ welding of structural wood constituents. *Holzforschung*, 2004, vol. 58, n° 1, p. 145-52.
Gfeller B., Properzi M., Zanetti M., Pizzi A., Pichelin F., Lehmann M., Delmotte L. Wood Bonding by Mechanically-Induced in Situ Welding of Polymeric Structural Wood Constituents. *Journal of Applied Polymer Science*, 2004, vol. 92, p.243-251.
Gfeller B., Zanetti M., Properzi M., Pizzi A., Pichelin F., Lehmann M., Delmotte L. Wood bonding by vibrational welding. *Journal of Adhesion Science and Technology*, 2003, vol. 17, n° 11, p.1573-1589.
Kanazawa F., Pizzi A., Properzi M., Delmotte L., Pichelin F. Parameters influencing wood-dowel welding by high-speed rotation. *Journal of Adhesion Science and Technology*, 2005, vol. 19, vol. 12, p.1025-1038.
Leban J.M., Mansouri H.R., Omrani P., Pizzi A. Dependence of dowel welding on rotation rate. *Holz Roh Werkst*, 2008, vol. 66, p.241–242
Lopretti M., Cabella D., Morais J., Rodrigues A. Demethoxylation of lignin-model compounds with enzyme extracts from Gloeophilum trabeum. *Process Biochemistry*, 1998, vol. 33, p.657-661.
M. Rowell R. Handbook of Wood Chemistry and Wood Composites, CRC, Florida, 2005, p.330-335
Mansouri H.R., Omrani P., Pizzi A. Improving the Water Resistance of Linear Vibration-Welded Wood Joints. *Journal of Adhesion Science and Technology*, 2009, vol. 23, n° 1, p.63-70.
Mansouri H.R., Pizzi A., Leban J.M., Delmotte L., Lindgren O., Vaziri M. Causes for the improved water resistance in pine wood linear welded joints. *Journal of Adhesion Science and Technology*, 2011, vol. 25, p.1987-1995.
Navarretea P., Pizzi A., PaschH., Rodec K., Delmotted L. MALDI-TOF and ^{13}C NMR characterization of maritime pine industrial tannin extract. *Industrial Crops and Products*, 2010, vol. 32, p.105-110.
O'Loinsigh C., Oudjene M., Shotton E., Pizzi A., Fanning, P. Mechanical behaviour and 3D stress analysis of multi-layered wooden beams made with welded-through wood dowels. 2011, *Compos Struct*, doi: 10.1016/ j.compstruct. 2011.08.029
Omrani P., Bocquet J.F., Pizzi A., Leban J.M., Mansouri H.R. Zig-zag rotational dowel welding for exterior wood joints. *J. Adhesion Sci. Technol*. vol.21, No. 10, p. 923-933, 2007.
Omrani P., Mansouri H. R., Pizzi A., Masson E. Influence of grain direction and pre-heating on linear wood welding. *European Journal of Wood and Wood Products*. 2010, vol. 68, p.113-114.
Omrani P., Mansouri H.R., Pizzi A. Weather exposure durability of welded dowel joints, *Holz. Roh. Werkstoff*, 2008, vol. 66, p.161-162.
Pizzi A., Despres A., Mansouri H., Leban J.M., Rigolet S. Wood joints by through-dowel rotation welding: Microstructure, 13C-NMR and water resistance.

Journal of Adhesion Science and Technology, 2006, vol. 20, n° 5, p.427-436.
Pizzi A., Leban J.-M., Kanazawa F., Properzi M., Pichelin F. Wood dowel bonding by high-speed rotation welding. *Journal of Adhesion Science and Technology*, 2004, vol. 18, n° 11, p.1263-1278.
Pizzi A., Mittal K. L. Handbook of Adhesive Technology, Dekker, New York, 2003, p.155-160.
Properzi M., Ganne-Chédeville C., Tondi G., Pichelin F., Pizzi A., Wood bonding by melting of non-toxic fillers using linear friction welding. *2nd International Conference on Environmentally-Compatible Forest Products*, p.507-512 Oporto, Portugal, 2006.
Properzi M., Leban J. M., Pizzi A., Wieland S., Pichelin F., Lehmann M. Influence of grain direction in vibrational wood welding. *Holzforschung*, 2005, vol. 59, p.23-27.
Renaud A. Minimalist Z chair assembly by rotational dowelwelding. *Eur. J. Wood Prod*, 2009, vol. 67, p.111–112
Resch, L. *Développement d'éléments de construction en bois de pays lamellés assemblés par tourillons thermo-soudés*, Th. Science. 2010. UHP NANCY 1, EPINAL.
Rodriguez G. , Diouf P., Blanchet P., Stevanovic T. Wood-dowel bonding by high-speed rotation welding - Application to two Canadian hardwood species. *Journal of Adhesion Science and Technology*, 2010, vol. 24, n° 8, p.1423-1436.
Segovia C., Renaud A., Pizzi A. Performance of Dowel-Welded L-joints for Wood Furniture. *Journal of Adhesion Science and Technology*, 2011, vol. 25, n° 15, p. 1829-1837.
Segovia-Brandt C. *Performances des assemblages par tourillons soudés*, Th. Science. 2010. UHP NANCY 1, EPINAL.
Stamm B. Development of friction welding of wood-physical, mechanical and chemical studies, Th. Science. 2006. EPFL, LAUSANNE.
Stamm B., Natterer J., Navi P. Joining wood by friction welding. *Holz als Roh- und Werkstoff*, 2005, vol. 63, p.313–320.
Stamm B., Weinand Y. Joining Wood by Friction Welding-Fabrication of Multi-layered Components. *World Conference in Timber Engineering*, Portland, USA, 2006.
Stamm B., Windeisen E., Natterer J., Wegener G. Chemical investigations on the thermal behaviour of wood during friction welding. *Wood Science and Technology*, 2006, vol. 40, n° 7, p.615-627
Stamm B., Windeisen E., Natterer J., Wegener G. Thermal behaviour of polysaccharides in wood during friction welding, *Holzforschung*, 2005, vol. 63, p.388-389
Sutthoff B., Franz U., Hentschel H., Schaaf A. Verfahren zum reibschweissartigen Fügen und Verbinden von Holz. Germany, Patent DE 19620273 C2. 96.05.20
Sutthoff B., Kutzer H.J. Verfahren zum reibschweißartigen Fügen von Holz. Germany, Patent DE 19746782 A1. 97.10.23
Tondi G., Andrews S., Pizzi A., Leban J. M. Comparative potential of alternative wood welding systems, ultrasonic and microfriction stir welding. *Journal of Adhesion Science and Technology*, 2007, vol. 21, n° 16, p.1633-1643.

Trainotti A., Wieland S., Tondi G. Determination of some influencing parameters in the rotational wood dowel friction welding process for the use in handcrafted solid wood furniture production. *Processing Technologies for the Forest and Biobased Products Industries*, 2010, Kuchl, Austria.
Vaziri M. Water resistance of Scots Pine joints produced by linear friction welding. Th. Sciences. 2011. Lulea University of Technology
Wieland S., Shi B.Z., Pizzi A., Properzi M., Stampanoni M., Abela R., Lu X.N., Pichelin F. Vibration welding of wood: X-ray tomography, additives, radical concentration. *Forest Products Journal*, 2005, vol. 55, p.84-87.

Abstract:
Mechanically-induced wood welding, the linear vibration welding and the rotational dowel welding, is shown here to enhance the water resistance of wood joints with some natural, non-toxic, environmental -friendly additives for outdoor structural application. The motive of wood welding with some additives is shown to be due mostly to form a protection by the melting additives and some amorphous, cells-interconnecting polymer material in the structure of wood. One of additives namely tannin is acetylated by three different processes. The acetylation is identified by CP-MAS 13C-NMR and MALDI-TOF, however the melting point of acetylated increase. The temperature-induced of high-speed rotation is shown here to not be capable of softening acetylated tannins, furthermore Microscopy of SEM confirms that some acetylated tannin can’t be melted. Small amounts of rosin are perfect for improving the water resistance of wood welding joint. Some relative parameters of wood welding, which is important for dry/wet-strength of joint, should be emended according to sample. The products of LVW are obtained with some fixtures.

Keywords:
Optimization; wood welding; tannin and rosin; product

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Jinbo HU