The Challenge of Bio-Adhesives for the Wood Composite Industries

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Introduction

The last decades environmentally friendly materials are becoming more widely used as our society becomes aware of the consequences associated with the use of petrochemical derived products. By using 'green' materials, we moderate the intense exploitation of fossil resources, reduce the amount of carbon dioxide that enters the atmosphere and take upon the responsibility of using earth's resources in a sustainable manner, thus improving resource management, indoor air quality (IAQ), and generally the overall performance and efficiency of human kind on earth.

In order to serve and expedite the replacement of fossil products by others of natural origin, the governments instituted a more environmentally friendly legislation and released directives relative to products and processes that the industry has to comply with, within certain dates. In particular, the United States of America (USA) resolved that by 2012 quite 8 billions tons of fuel should be derived from biomass while the cost of bio-ethanol should be reduced to 1.07$/kg. Likewise, the European Union, through the "Biomass Action Plan" [1] communicated its decision to increase biomass use to around 150 million ton by 2010, while the Kyoto protocol on global climate change [2], signed by the majority of the countries on earth, includes a shift of feedstock for energy and chemical industries from petrochemical to renewable resources.

Wood, as biomass, is a sustainable and dependable resource with many applications. It can be used in constructions as such or as a wood-based panel resulting in a more profitable exploitation, while it can also be used as raw material for the production of paper and chemicals.

One of the major challenges associated with the wood-based panels, in order to be eligible for qualification as totally natural products, is the replacement of the formaldehyde-based resins used for their production, by others of natural origin. Common formaldehyde-based resins are urea-formaldehyde, melamine-formaldehyde and phenol-formaldehyde while other phenolic compounds (e.g. resorcinol) can also react with formaldehyde to provide polymers of the same type with differences in adhesive cost and reactivity. Wood-based panels, like particleboards (PB), fibreboards (e.g. medium density fibreboard-MDF), oriented stand boards (OSB), plywood (PW) etc are produced by adhering together parts of wood in various sizes with these resins under heat and pressure.

Among the resins used for the production of these boards, the phenolic resins (PF) are the preferred adhesives for producing panels of exterior grade. This kind of resin represents the second important type of wood adhesives following amino resins in terms of consumption volume. Nevertheless, the cost of phenol-formaldehyde resins is high and follows the fluctuations of petroleum prices while the components of the resin are considered as a major indoor pollutant and harmful for the human health. Thus, it is not coincidental that the attempts for replacing the petrochemical raw materials of the resins for the wood-based panels by other of renewable or recyclable resources started from this type of resins.

The idea of using natural-derived materials as adhesives is not new. The first natural raw materials used in this purpose were blood from animals, casein and soy protein. Adhesives derived from animal and vegetable resources dominated the market till 1940 but their usage was gradually reduced after 1970 when the petrochemical materials entered the market enabling the synthesis of

adhesives with specific properties, constant quality and lower cost. Currently, the most exciting new trend in natural products research is the development of new synthetic materials using the natural sources as starting point.

In the industrial field of the wood-based panels many literature references may be found for the synthesis of thermosetting resins from renewable raw materials although in most of the cases the natural material is used for partial replacement of phenol in phenol-formaldehyde resins.

In particular:

The thermochemical liquefaction technology, which was developed in the 1970s in Japan, applied successfully to the liquefaction of wood in the presence of phenols or alcohols with or without acidic catalysts, including sulfuric acid, phosphoric acid and so forth. The resulted liquid wood, commonly known as "liquefied or phenolated wood", has been proved effective raw material in the synthesis of phenol-formaldehyde resins [3, 4, 5, 6, 7]. Over the years two general methods have been developed for the preparation of phenolated wood, the acid-catalysed liquefaction at moderate temperatures (120-160ºC) and the non-catalysed liquefaction at elevated temperatures (200-250ºC). It has been found that the properties of the phenolated wood prepared under these two sets of conditions are quite different and the mechanisms of lignin reactions forming such products are not clarified yet. Despite the promising results of this technique, it didn't find broad application since the use of phenol as a liquefying reagent is associated with a number of drawbacks, including the difficulty of recovering the phenol from the liquefied materials and the problem of toxicity. Moreover, the complicated molecular structures of phenolated wood as well as the higher molecular weight and melting temperature of the resulted resin make their utilisation difficult as compared to the conventional phenolic resins.

Lignin is the dominant phenolic substance in biomass. It is obtained as a residue from the pulp and paper industry and from wood acid hydrolysis. The polyphenolic structure of lignin combined with its abundant availability and low cost offer a potential for phenol replacement in resin synthesis while its low cost contributes to its utilisation as adhesive component. Lignin is not available in constant quality and chemical structure as it depends on the raw material species and the chemical method followed for its recovery. Thus not all of the lignin kinds have the same reactivity. Lignin-based wood adhesives have been prepared with formaldehyde [8] or with other aldehydes like glyoxal [9] and furfural as well as with polyaminoamide-epichlorohydrin [10]. Such adhesives showed sufficient reactivity to yield panels with properties comparable to those of conventional formaldehyde-based resins. Lignin has also been evaluated as a component of phenolic resin systems. High phenol replacement levels (~50%) have been reported by applying several modification steps while such resins have been used for the production of wood panels such as plywood and Oriented Strand Board [11, 12, 13, 14, 15, 16].

References for the use of tannin as adhesive in wood industry are dated back to 1958. There are two types of tannin (the hydrolysable and the condensed tannins) both of which are amply available in nature. Especially the condensed tannins may be found in high concentrations in the wood and bark of various trees like acacia (wattle and mimosa), hemlock, quebracho, pine etc. Tannins, being phenolic in nature, undergo the same reaction of phenol with formaldehyde and since the early 1970's they have been successfully used in the production of exterior grade particleboard, plywood and laminating wood products [14]. However, tannin use has been limited due to its high reactivity which leads to quick viscosity development and thus short pot life to the resin, while the lack of intermolecular crosslinking causes weak adhesive bonds. Some solutions proposed for these problems refer to pH adjustments and use of other hardeners [17, 18].

Proteins of various resources have also been used as starting material in the production of adhesives since old times. Resins from casein, blood and soy reached their apex in 1960, while they shaded off till 1970 [19]. Current literature references [20, 21] report adhesive systems combining soy with phenol-formaldehyde and urea formaldehyde resins. Nevertheless, their industrial application is still limited.

More recently, bio-oil derived from the pyrolysis of biomass, or its phenolic fraction, has also been used with success as phenol substitute in phenol-formaldehyde resins [22]. Substitution levels of up to 50% have been reported, however, in order to increase the amount of phenolic compounds present in

the oil, specific pyrolysis conditions or post-pyrolysis fractionation steps are needed, which raise the final product cost.

In this framework, the Chimar Hellas research group has investigated the use of various natural derived materials like tannin, lignin, cellullose, crude pyrolysis oil of wood and various chemicals derived from it, proteins (soy), starch and bio-liquids derived from various agri-wastes (olive stone, cashew nut shell, sugar beet). These materials have been used alone or in combination with other petrochemical products in resins for the production of wood-based panels [23, 24, 25] with the aims to:

- reduce the demand on fossil fuels and promote sustainable development by using alternative resin feedstocks derived from renewable resources
- obtain resins with the same or enhanced quality than the ones conventionally synthesized.
- identify resin raw materials that in conjunction with natural fibres they are inherently non-toxic, environmentally friendly and emission-free.

These adhesives are able to induce a high quality of adhesion, while the formaldehyde emissions from the wood-based panels produced with them are similar to that of the commercial resins or even lower. These results are presented below, while CHIMAR Hellas keeps working on their further investigation.

Experimental part

1. Raw materials
Chimar Hellas has developed technology for the use of natural materials either as phenol substitutes in the synthesis of PF resol resins or as additives in the synthesis of UF resin for the improvement of their performance, or as the major ingredient (up to 92%) in totally natural adhesive systems. In particular, the raw materials used for the synthesis of the resins are:

Natural products
- **Liquefiat**: a liquid derived from olive stone residue via liquefaction process - EC project **BIOLIVE (QLK5-CT-2000-00766)**
- **Bio-oil**: Wood pyrolysis oil derived from hardwood and additionally subjected to fractionation and evaporation of water and other volatiles
- **Tannin:** Condensed tannin extracted from the bark of Black Wattle tree, a species of acacia native that was additionally modified to be used as adhesive. The tannin was provided by Bondtite Pty Ltd Company, South Africa.
- **Soy**: soy was used either in form of flour or as isolated protein. Soy protein was provided by "Du Pont" company, Belgium, while the soybean flour was provided by "Soon-Soon Oil Mills SDN BHD Company, Malaysia.
- **Lignin:** It was obtained from French wheat straw by a new acid fractionation process developed in the framework of the Biosynergy program by ARD company, Pomacle - **EC project Biosynergy [038994 – (SES6)]**

Petrochemical products
- Phenol as 91% water-based solution
- Formaldehyde as 37% water-based solution
- Sodium hydroxide as 30% water-based solution

2. Resins
The various natural resins along with the type of wood-based panel produced at the various production scales are presented below:

2.1 Phenol-Formaldehyde resins with partial phenol substitution by a natural product
The highest phenol substitution levels performed successfully are:

Industrial scale
Liquefiat: 50% phenol replacement – Plywood
Wood Pyrolysis oil: 40% phenol replacement – Oriented Strand Board (OSB)
                          20% phenol replacement – Plywood
Tannin: 20% phenol replacement – Plywood

Pilot scale
Wood Pyrolysis oil: 50% phenol replacement - Oriented Strand Board (OSB)

Lab scale
Liquefiat: 75% phenol replacement – Plywood
Tannin: 30% phenol replacement – Plywood
Soy: 25% phenol replacement – Plywood
Lignin: 50% phenol replacement – Particleboard

2.2 Urea - Formaldehyde resins with natural products as additives
Standard Urea-Formaldehyde resins produced according to CHIMAR Hellas technology and soy protein was added at level **1%** s/l at various stages of the synthesis process (S_1). Soy protein was in the form of flour (SF) or isolated soy protein (SPI). The best of the resins were used for **particleboard production at lab scale.** The addition of soy did not affect the specifications of the resin.

2.3 Totally natural resins
A totally natural binding system was used as alternative to urea-formaldehyde resins. The said binding system was based on condensed tannin while a hardener was used at level 8-10% to expedite the curing of the resin. This resin was used for **particleboard production at lab scale** according to CHIMAR know-how.

3. Production and evaluation of wood-based panels

3.1 Phenol-Formaldehyde resins with partial phenol substitution by a natural product
In the case of the Phenol-Formaldehyde resins with partial phenol substitution by a natural product, various types of wood-based panels were produced at different production scales. The ones with the highest phenol substitution level at the highest production scale are presented below:

3.1.1 Industrial scale
Liquefiat – plywood
In this industrial trial a PF resin with **50% substituted phenol** by liquefiat was tested and compared to one commercial PF resin. Thus, 7-layer boards 2500 x1250mm with 15mm thickness were produced using for core/inner layers spruce and for face/back ocume veneers. The panels were hot pressed at 115°C for 13min.
The GPC analysis of the resins illustrated a molecular weight distribution (MWD) as presented in the following table 1:

Table 1: MWD of control and liquefiat modified PF resin

Sample	Control	Modified
Mn	265	264
Mw	637	679
Mz	1353	1662
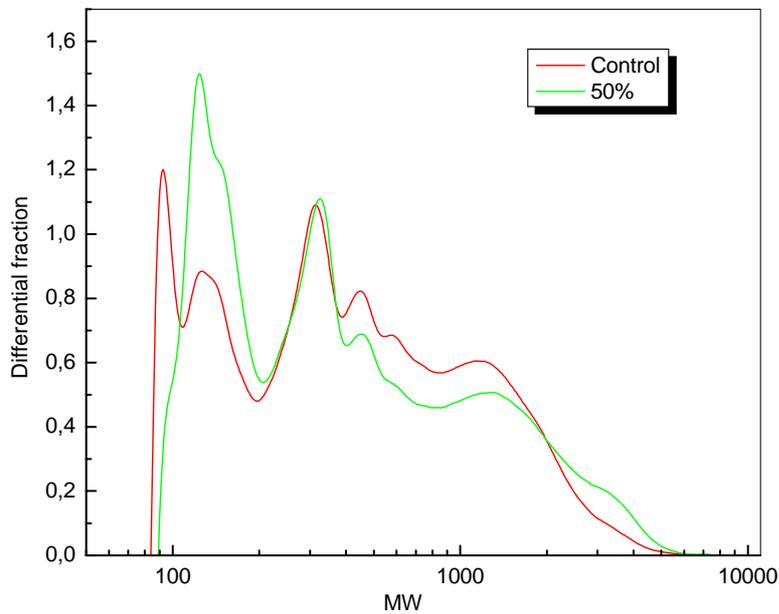
Graph 1: MWD of control and liquefiat modified PF resin

The WBP (whether and boil proof) test was performed according to BS 6566 (knife test) and the results are summarised on the next table 2.

Table 2: Evaluation results of plywood according to BS 6566

Sample	Bond quality	Average
Control	8-9-8-9-7-7	8.0 (8.0)
Test 1	10-9-8-9-9-8	9.0 (8.9)
Test 2	7-10-8-10-8-9	9.0 (8.7)

Pyrolysis oil - OSB

Industrial trial for the production of OSB panels was performed testing a PF modified resin with **40% substituted phenol** by bio-oil. The modified resin was applied on surface layer, while PMDI was used for the core. Aspen strands were used to manufacture 7/16" boards at identical parameters to the conventional production. The testing of boards was performed in accordance with CSA O437-1 93 standard.

The GPC analysis of the resins illustrated a molecular weight distribution (MWD) as presented in the following table 3, while their Differential Scanning Calorimetry (DSC) analysis signified the critical temperatures of their curing that are presented in the following table 4 and the relative graph 2.

Table 3: MWD of control and liquefiat modified PF resin

Sample	Control resin	Modified resin
<200	24.7	33.5
200-1000	42.6	44.4
>1000	32.7	22.1

Table 4: Critical temperatures according to DSC study

Sample	Control	Modified
Onset, ^{o}C	85	79
Maximum, ^{o}C	146	147
Endset, ^{o}C	195	206
Specific heat, J/g	95.2	110.0
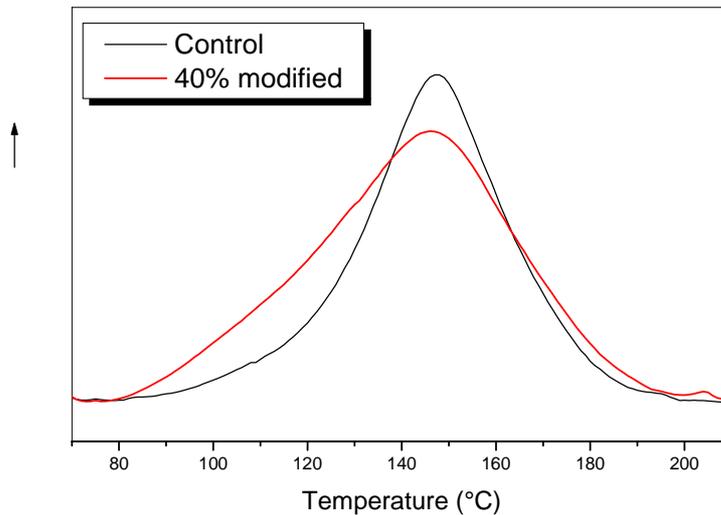
Graph 2: DSC analysis results of pyrolysis oil modified resin

The evaluation results of OSB panels produced with wood pyrolysis oil modified PF resin towards the requested values by the CSA O437.1 93 standard are presented in the following table 5.

Table 5: Evaluation results of OSB produced with pyrolysis oil modified PF resin

Test methods	Units	CSA O437.1 93 standard requirements	Modified resin results
MOR parallel	psi	4200	4939
MOR perpendicular	psi	1800	2253
MOE parallel	psiX1000	800	895
MOE perpendicular	psiX1000	225	286
Internal bond	psi	50	59
Density parallel	lbs/ft^3	-	37.6
Density perpendicular	lbs/ft^3	-	38.2
24h Swells	%	15	13.04
24h Absorption	%	N/A	32.22

* parallel and perpendicular – indicates direction on face alignment

Pyrolysis oil-plywood
PF resin with 20% substituted phenol by pyrolysis was tested in the production of 9-layer boards with 18 to 20mm thickness using for core/inner layers either poplar or poplar and ocume veneers, and for face/back always ocume. The veneer moisture content for all veneers was bellow 5%. The hot press had 120°C temperature and the press cycle was adjusted according to the thickness. The WBP (whether and boil proof) test was performed according to BS 6566 and the results are summarised on the next table 6

Table 6: Evaluation results of plywood produced with pyrolysis oil modified PF resin

Sample	Face	Core	Inner	Bond quality
Test 1	ocume	ocume	poplar	9.0
Test 2	ocume	poplar	poplar	9.0
Control	ocume	poplar	poplar	8.0

Tannin – plywood
For this trial a PF resin with 20% substituted phenol by tannin was synthesised. 7-layer panels were produced using for the core/inner layers either spruce or spruce and poplar and for the face/back

always ocume veneers. The hot press had 115°C and the press cycle was 13.5min. The properties of the boards obtained were determined according to the BS 6566 standard and are presented in the following table 7.
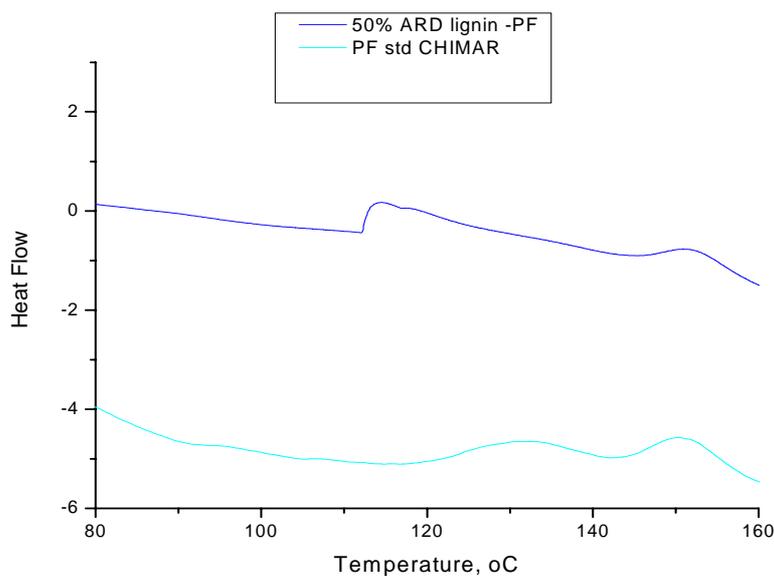
Table 7: Evaluation results of plywood produced with tannin modified PF resin

Sample	Face	Core	Inner	Thickness	Density	Bond quality	Average
Test 1	ocume	spruce	spruce	15.0	448	10-8-8-8-8-10 10-8-8-8-8-10 6-10-8-10-8-8	**9.0** (8.5)
Test 2	ocume	spruce	poplar	15.1	462	10-8-6-10-10-10 10-8-6-8-6-10 10-8-8-10-8-8	**9.0** (8.6)
Control	ocume	spruce	spruce	14.8	487	6-10-10-10-9-10 8-10-10-9-10-10 10-10-8-10-10-10	**9.0** (9.4)

3.1.2 Lab scale

Lignin-particleboard
The process applied for the production of this lignin type may be classified under the organosolve technology. According to the producer, the smooth hydrolysis conditions applied allow the provision of lignin in the form of linear oligomers with a low degree of polymerisation. The PFL experimental resin, synthesised with 50% phenol replacement by this lignin, subjected in DSC analysis. The DSC thermograph (graph 3) proved that both the control and the experimental resin have similar curing temperature, close to 150°C. This PFL resin used for particleboard production at lab scale, following the steps of the industrial procedure. The prepared particleboards had dimensions 44x44x1.8cm and density 680 Kg/m^3. The level of the resin sprayed on the wood particles was 12% w/w based on the weight of the particles, while two different pressing cycles were employed for the preparation of the boards. The performance of the lignin-modified (PFL) resin evaluated towards a standard PF resol resin. The results are reported in the following table 8.

Graph 3: DSC analysis results of PFL & PF resins

Table 8: Evaluation results of particleboards produced with PFL resin

Type of resin:	PF std	PFL 50% Ph. sub.
	Long press time	
IB, N/mm^2	0.99	0.82
Swells 24h, *at 25°C*, %	14.72	16.13
MOR, N/mm^2	24.14	21.34
2h boiling MOR, N/mm^2	11.93	9.13
	Short press time	
IB, N/mm^2	1.02	0.83
Swells 24h at 25°C, %	14.32	16.14
MOR, N/mm^2	21.97	20.69
2h boiling - MOR, N/mm^2	10.23	8.86
Moisture content, %	18.32	17.94
Perforator, *at 6.5% moisture*, mg/100g dry	0.57	0.29

Soy-plywood

PF resol resin with 25% phenol replacement was prepared and evaluated in the production of 3-layer plywood at lab scale. The veneers used were from spruce and had dimensions 50x50. The panels prepared according to the standard industrial process and pressed at 115°C while the press cycle was adjusted to the thickness of the panel. The panels were subjected to whether and boil proof test (WBP), for the evaluation of bond quality, according to the British Standard BS 6566 (knife test) while the formaldehyde emissions were determined according to the Japanese Industrial Standard JIS 1460:2001 (desiccator method). The results are summarised in the next table 9.

Table 9: Evaluation results of plywood produced with soy-modified PF resin

	Bond quality	Free Formaldehyde, mg/l
Control	9.5	0.52
Experimental – SPI modified	8.3	0.56
Experimental – Soy Flour modified	7.6	0.65

3.2 Urea - Formaldehyde resins with natural products as additives

Urea-Formaldehyde resins with final mole ratio F:U 1.07 were prepared according to CHIMAR technology and 1% s/l of soy was added at a certain point of the synthesis procedure. Particleboards with dimensions 44x44x1.8 cm prepared at lab scale according to the standard industrial process and pressed at 210°C in two different pressing cycles. The results are cited in the following table 10. Similar results are received by using either isolated soy protein (SPI) or soy flour.

Table 10: Evaluation results of particleboards with soy-UF resin.

Type of resin	Control (UF)	UF-SPI (1%)
	Long press time	
Density, kg/m^3	695	688
IB, N/mm^2	0.51	0.57
Swells 24h at 25°C, %	28.14	24.44
MOR, N/mm^2	14.79	16.49
	Short press time	
Density, kg/m^3	693	677
IB, N/mm^2	0.34	0.47
Swells 24h at 25°C, %	27.21	22.98
MOR, N/mm^2	15.31	16.54
Moisture content, %	7.68	7.59
Perforator, *at 6.5% moisture*, mg/100g dry	6.34	6.25

3.3 Totally natural resins

A totally natural binding system was used as alternative to urea-formaldehyde resins. The said binding system is based on condensed tannin while a chemical agent is used as hardener at level no higher than 8-10% s/s. This resin used for particleboard production at lab scale. The boards prepared according to the standard process and had dimensions 44x44x1.8cm and density app. 700 kg/m^3. The pressing temperature was 200°C. The results are reported in the following table 11.

Table 11: Evaluation results of particleboards prepared with a totally natural binding system

Type of resin	Control (UF)	Tannin binder
Density, kg/m^3	695	691
IB, N/mm^2	0.50	0.59
Swells 24h at 25^oC, %	33.41	29.36
MOR, N/mm^2	15.09	13.57
Moisture content, %	6.98	8.94
Perforator, mg/100g dry at 6.5% moisture	7.03	1.5

4. Conclusion

All the above resins modified with raw materials from natural origin proved efficient for successful production of wood-based panels at various production scales. In particular, plywood boards produced industrially with liquefied olive stone, wood pyrolysis oil and tannin may be considered effective phenol substitutes in PF resins. Moreover, soy addition up to 1% in standard urea-formaldehyde resin proved effective enough for improvement in the internal bond and dimensional stability performance of particleboards produced with this resin. Last but not least, the application of a natural binder based on tannin and with no other petrochemical component than the hardener at levels lower than 10 % proved robust enough to yield particleboards with wet and dry properties relative to that of a standard urea-formaldehyde resin but with formaldehyde emissions relative to that of natural wood.

CHIMAR HELLAS continues the research on "green" adhesives focusing either on the replacement of even more petrochemical raw materials (eg formaldehyde) by other of natural origin or the development of totally natural binder systems from even more natural products as to provide feasible and cost effective resin solutions based on regional plant species in each continent.

This research paves the way for the development and commercial adoption of natural resins for wood products, offering significant competitive advantage to the resin and panel industries and helping to increase the positive environmental impact.

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