ADHESIVES FROM RENEWABLE RESOURCES FOR BINDING WOOD-BASED PANELS

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ABSTRACT

Nowadays, there is an increasing requirement by the industry of composite wood panel (particleboard, fiberboard, plywood etc) for replacement of the petrochemical raw materials used in the synthesis of wood adhesives, by others from renewable resources, so that the wood panels can be characterized as totally bio-products. CHIMAR Hellas, a private research institute with activities in the development of adhesives and additives for the wood-based panels industry, foresaw this need and has already developed thermosetting phenol-formaldehyde resins where a substantial part of the contained phenol has been replaced by natural raw materials from renewable resources. These bio-based resins have a performance comparable to the relative adhesives from petrochemical raw materials and may be well introduced for the production of wood-based panels even at industrial scale.

Key words: thermosetting resins, natural raw materials, bio-based resins, wood-based panels, formaldehyde based resins

AIMS

Wood is a substantial renewable resource while wood-based panel products contribute to our comfort and well-being. Nowadays, a healthy indoor environment is a matter of public interest highlighted by the recent publication of a number of regulations and guidelines. At present, thermosetting resins, which are used for the production of wood-based panels, are synthesized from raw materials derived from petrochemicals. The development of “green” resins via bio-based polymers would promote the use of raw materials from natural resources and the eco-efficiency of the wood-based products.

BACKGROUND

Today, the need for immediate response to the environmental pollution of our planet and the finite of the fossil resources have led the scientific community, the policy makers and the business sector to seek for products and processes that are sustainable and environmental friendly. Among the various natural resources, biomass is considered to be the most prosperous one because its exploitation provides not only an alternative renewable solution toward fossil fuels and energy but it can also be converted effectively to various chemicals and bio-based products. The biorefinery concept posits that some of these products, while possibly small in volume, could be high in value. The United States of America resolved that by 2012 quite 8 billions of fuels should be derived from biomass while the cost of bio-ethanol should be reduced to 1.07$/g. Likewise, the European Union, through the “Biomass Action Plan” [COM (2005)628] communicated its decision to increase biomass use to around 150 million toe by 2010. Moreover, transition to a more sustainable bio-based economy, as a political consequence of the Kyoto protocol on global climate change (UN fcc 1997), includes a shift of feedstock for energy and chemical industries from petrochemical to renewable resources.

Wood as biomass resource has many advantages. It is a renewable resource, offering a sustainable and dependable supply. Moreover wood consists of 45% cellulose, 20% hemicellulose and 25% lignin and thus may be considered as an excellent reservoir of raw materials for the production of chemicals and bio-based products.

Traditionally, the wood-based panels, like particleboard (PB), medium density fibreboard (MDF), plywood (PW), oriented strand board (OSB) etc, are produced from byproducts of the wood processing, like chips, fibres and veneers, adhered together with a thermosetting resin. Such resins are mostly formaldehyde based. The most common types are urea-formaldehyde, phenol-formaldehyde and melamine-formaldehyde resins. These types are usually synthesized by petrochemical raw materials.

The idea of replacing the petrochemical raw materials with other of natural origin is not new. Adhesives derived from animal and vegetable resources dominated the market till 1940. Nevertheless, their use was gradually declined after 1970 when the petrochemical materials entered the market enabling the synthesis of adhesives with specific properties, constant quality and of 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 points.

There are abundant literature references for the use of various materials from renewable resources in the synthesis of adhesives. In most of the cases the natural material is used for partial replacement of phenol in phenol-formaldehyde resins.

Namely:

- The polyphenolic structure of lignin in combination with its abundant availability, offers a promising raw material for the synthesis of resins. Nevertheless, the functional groups attached to the lignin phenolic rings differ depending on the raw material species and are said to influence the reactivity of lignin. High phenol replacement levels (~50%) in PF resins have been reported for the production of PW and OSB(1,2,3).
- Phenolated wood from thermochemical liquefaction of wood and wood residues in the presence of phenol has been successfully tested as phenol substitute in the production of PF resin(4). The complicated molecular structures of phenolated wood, their higher molecular weights and melting temperatures as compared to conventional phenolic resins were considered to be the main hindrances for their practical utilization.
- Tannin, that is considered as the best substitute of phenol for the production of resin(5), has been used with success in many countries in the south hemisphere since seventies (1970). These resins found application in the production of PB, PW, and coated wood panels for indoor applications(1). Nevertheless, for the time being the use of tannin is restricted due to the high reactivity and the viscosity that lead to short pot life, while due to the development of weak intermolecular bonds, tannin is not able to create strong adhesion properties(1). Pizzi and Stefanou(6) suggest pH adjustments to control the reactivity of tannin in the production of PB, while Kim et al(7), justified that the performance of resins based on tannin is attributed mainly to the hardener used.
- 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(8). 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.

- Proteins of various resources have been used as adhesives since old times. Resins from casein, blood and soy reached their apex in 1960, while they shaded off till 1970[9]. Current literature references [10, 11] report adhesive systems combining soy with phenol-formaldehyde and urea formaldehyde resins. Nevertheless, their industrial application is still restricted.

Chimar Hellas carries out research in the field of bio-resins from renewable resources and has developed phenol-formaldehyde resins where a substantial part of phenol has been replaced with raw material from natural resources[12,13,14]. These adhesives are able to induce a high quality of adhesion, while the formaldehyde emissions from the wood-based panels produced with them are significantly low (formaldehyde emissions of natural wood <2mg/100g).
Chimar Hellas, has started the research on bio-based polymers by replacing phenol in PF resins because it is toxic and one of the most expensive raw materials used for the production of thermosetting resins. So, the higher cost of the natural alternative would be compensated while the modified resin would be less toxic and environmental friendly product. In parallel, Chimar carries out research for the replacement of other petrochemical raw materials too, like formaldehyde, in all types of resins in its portfolio.

EXPERIMENTAL

1. Resin Synthesis

1.1 Phenol-Formaldehyde resins

Modified phenol formaldehyde resins were produced having various phenol substitution levels by raw materials of natural resources. The petrochemical raw materials used were in form of water-based solutions. In particular they were: Phenol 91%, formalin 37% and sodium hydroxide 30%. The raw materials from natural resources used were liquefied olive stone, bio-oil from wood pyrolysis, tannin, soy, lignin.
These resins used for the preparation of wood-based panels at various production scales; namely: industrial, pilot, lab.
The following comprehensive table 1 presents the natural raw materials used for phenol replacement at the upper substitution level achieved together with the successful production of wood-based panels at any production scale.

Table 1: PF resins modified with natural raw materials and wood-based boards produced with them at various production scales.

		Production scale			
		Industrial	**Pilot**	**Lab**	Type of wood panel
	Natural raw materials	*Pheno substitution level, %*			
1	**Liquefied Olive stone**	50		75	Plywood (PW)
2	**Wood pyrolysis liquid**	40			Plywood (PW)
			50		Oriented strand board (OSB)
3	**Tannin**	30			Plywood (PW)
4	**Soy**			25	Plywood (PW)
5	**Lignin**			20	Plywood (PW)

* EC project QLK5-CT-2000-00766 (BIOLIVE)

The resins prepared with different specifications according to the needs of the type of boards they were applied to. In particular, two main synthesis routes of CHIMAR technology were followed: T1 and T2. In particular, the resins intended for plywood application produced according to T1 technology while the resins used for OSB production were synthesized according to T2 technology.
Some of the differences between these two technologies are the polymerization stages and the addition order of the raw materials. The specifications of the resins produced with each technology are reported in the following table 2.

Πίνακας 2: Specifications of the resins produced according to T1 & T2 CHIMAR technology.

	T1	**T2**
solids, %	42±1	50±1
viscosity, cp	400-500	100-130
NaOH, % (alkalinity)	6.0	2-3

The viscosity carried out with a Brookfield viscometer, at 25°C.
The solid content of the resins was determined by weighing a certain amount of resin before and after drying in an oven of 120°C for 2 hours.
The alkalinity was determined by titration with HCl.

1.2 Urea Formaldehyde resins
Urea-Formaldehyde resins produced according to CHIMAR 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 or isolated soy protein (SPI). The best of the resins were used for particleboard production at lab scale. The properties of the boards evaluated following the relative European standards procedures and compared to the performance of particleboards prepared with a conventional urea formaldehyde resin (Control). The specifications of the resins are reported in the following table 3.

Table 3: Specifications of control and modified urea-formaldehyde resins

Resin	Control	S_1
pH, 25°C	7,66	7,81
viscosity, cP	255	225
Water tolerance, 25°C ml/ml	1/4	>1/10
Solids, %	66,5	61,2
Gel time, s	56	60
Buffer Capacity, ml	11,15	10,7

2. Production and evaluation of wood-based panels

2.1 Plywood boards

The plywood boards were prepared with the same specifications regardless of the production scale. The veneers were from poplar, okume and spruce while their moisture content was varying between 5-6%. The glue mix was prepared with a certain quantity of the resin, hardeners and fillers according to the common practice and was spread on the veneers. After the assembling of boards was finished they were pressed at 120°C for a time proportional to their thickness. Depending on the production scale, panels of nine, seven and three layers were prepared.

The plywood boards tests followed two methods:

a) The British standard 6566, where the bond quality of resins was determined after 72 hours of boiling and using a special knife.
b) The European standards EN 314.01 and EN314.02 in which both the bond quality and shear strength of boards were determined.

The threshold values set by the European standards are presented in the following table 4.

Table 4: EN 314-2 requirements.

Mean shear strength fv, N/mm^2	Mean apparent cohesive wood failure w, %
0.2 ≤ fv < 0.4	≥ 80
0.4 ≤ fv < 0.6	≥ 60
0.6 ≤ fv < 1.0	≥ 40
1.0 ≤ fv	No requirement

The formaldehyde emissions from plywood boards were determined according to the desiccator method (Japanese standard JIS A1460).

2.2 Oriented Stand Boards (OSB)

For OSB pilot scale production, standard aspen strands (populus tremuloides) with a nominal thickness of 0.7mm and a length of 142mm containing 4-5% moisture were used. Panel target density and thickness were 640kg/m^3 and 11 or 12.5mm respectively. For the core, MDI binder was used at 3% level and for the face 5% of PF resin where 50% of phenol had been replaced by bio-oil. Panel dimensions were 76 x 76cm with face to core ratio 55/45 and random orientation. Platen temperature was 210°C whereas press cycle was 220s. The experimental boards were evaluated towards relative boards produced with a conventional PF resin.

2.3 Particleboards

For the glue mix preparation a certain quantity of the resin was admixed with hardener and was applied on the chips whose moisture content was up to 4%. Particleboards of one layer were produced with density 680kg/m^3 and dimensions 44x44x1.8cm. The boards were pressed at 200°C for two different pressing cycles.

Both OSB and PB panels were evaluated according to the European standards cited in the following table 5.

Table 5: Standards for the evaluation of OSB and PB panels

Property	Standard
Internal bond (IB)	EN319
Modulus of rapture (MOR)	EN310
Swelling (24h, 20°C)	EN317
Moisture content	EN322
Free Formaldehyde content (Perforator test)	EN120

RESULTS AND DISCUSSION

Table 6: Evaluation results of OSB panels with PF modified resin - Pilot scale production

Properties	**Control**	**PF with 40% phenol substitution**	**PF with 50% phenol substitution**
Density, kg/m^3	647	650	652
IB, N/mm^2	0.57	0.74	0.66
MOR, N/mm^2	33.79	34.61	35.13
24h swelling, %	13.9	12.9	12.6
48h swelling, %	19.3	15.7	16.1
Water absorption, 24h, %	22.8	24.6	25.3
Water absorption, 48h, %	32.3	34.5	34.8

Table 7: Evaluation results of plywood boards with PF modified resin-Industrial and lab scale production

Production scale			**Industrial**	**Lab**			
	Phenol sub. level, %	Specimen	Knife test	Knife test	EN 314.02		FF/Desiccator
			face/core %,x10	**%,x10**	**Fv, N/mm^2**	**W, %**	**mg/l**
Liquefied olive stone		Control	80/90	-	-	-	-
	50	1st	80/80	-	-	-	-
		2nd	90/90	-	-	-	-
		Control	-	80	1.04	56	-
	75	1st	-	60	1.05	36	-
Wood pyrolysis liquid		Control	80/90	-	-	-	-
	40	1st	80/85	-	-	-	
		2nd	85/90	-	-	-	-
Tannin		Control	80/90	-	-	-	-
	30	1st	90/90	-	-	-	-
		2nd	85/90	-	-	-	
Soy		Control	-	95	1.04	74	0.52
	20	S_1-Flour	-	30	0.69	12	-
	25	S_1-flour	-	76	0.89	70	0.65
		S_1-SPI	-	83	1.42	74	0.56
Lignin		Control	-	80	1.04	56	-
	20	1st	-	75	1.09	42	-

Table 8: Evaluation results of particleboards with UF/SPI resin – Lab scale production

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^{o}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^{o}C*, %	27.21	22.98
MOR, N/mm^2	15.31	16.54
Moisture content, %	7.68	7.59
Perforator, mg/100g dry at 6.5% moisture	6.34	6.25

CONCLUSION

All the above resins modified with raw materials from natural origin proved efficient for successful wood-based panel production at various production scales. CHIMAR Hellas promotes these resins to the market while continues the research on the replacement of petrochemical raw materials by others of renewable resources in order to improve the performance of the already available products and develop a totally natural binding system with performance comparable to the one of the synthetic binders but with no formaldehyde emissions.

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TABLES