BIO-BASED RESINS FOR WOOD COMPOSITES

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SUMMARY

The adhesive resins used for producing wood-based panels are synthesized from petroleum and natural gas derived chemicals. The increased concern with the environmental sustainability and the long-term security of supply of petrochemicals has raised considerable interest in resins obtained from renewable resources. The promising candidates should match the reactivity, applicability, bonding performance and cost requirements of the synthetic resins and outperform them in environmental acceptability and safety of use.

CHIMAR HELLAS has extensively worked on developing resins from renewable resources for application in wood-based panels production, aiming at:

- Environmentally friendly adhesives for the wood panel sector ("natural binders")
- Adhesive resins that contribute to the reduction of panel formaldehyde emission
- High performance, low cost resin products for the wood panel manufacturers and the panel end users: the society as a whole.

The **know-how and experience gained** focuses on resins derived from natural products or by-products. An extensive but not exhaustive list includes: tannin, lignin from paper production, pulping spent liquor, pyrolysis oil (bio-oil), extraction or liquefaction products of agricultural and forestry residues (cashew nut shell liquid (CNSL), liquefied wood, liquefied olive stones), soy. The above resins developed by CHIMAR have been tested in the production of panels at the lab scale, pilot scale and the most successful ones at the industrial scale, in direct comparison with commercial resins that are commonly applied.

INTRODUCTION

Synthetic resins like urea-formaldehyde (UF), phenol-formaldehyde (PF), and melamine-formaldehyde (MF) are commonly applied in the production of wood-based panels, to bind the wood elements together and form the final panel products. These resins are synthesised from petroleum and natural gas derived chemicals and therefore their prices are directly dependent on the fluctuation of the oil prices. Moreover, given the finite nature of the oil deposits, the long-term availability of petroleum-derived products is not guaranteed.

The use of wood panel products contributes to more efficient forest utilization and provides thus a cost effective solution to related environmental problems. To utilize large quantities of forest residues for conversion into low cost panel products, it is necessary to develop less expensive adhesives with secured availability, in order to derive meaningful advantage. Adhesives from renewable (non-petroleum) raw materials have a noteworthy role to play in this direction.

Large quantities of renewable biomass materials and natural derivatives are available which can be converted into adhesives for panel products. The use of biomass as a source of chemicals and energy enables closed cycle materials fluxes and contributes to the efforts to reduce the atmospheric CO_2 emissions worldwide (Danner and Braun, 1999). PF resins are the preferred adhesives for producing exterior grade panels and their cost is very high as compared to the cost of UF resins. Several attempts have been made to replace or partially substitute phenol with naturally occurring phenolic materials in the preparation of PF adhesives.

Lignin, a natural binder in all plants, has been evaluated as a component of phenolic resin systems dedicated to the production of wood panels such as plywood and OSB (oriented strand board), (Forss and Fuhrmann, 1979, Doering and Harbor, 1993, Chen, 1995 & 1996, Senyo *et al.* 1996, Singh, 2000). The polyphenolic structure of lignin combined with its abundant availability offer a potential for resin synthesis. One major source of lignin is the spent pulping liquor obtained as a by-product in paper manufacture. Its low cost contributed to the attractiveness of lignin incorporation in wood adhesives. 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%) have been reported by applying several modification steps, which complicate the resin synthesis.

Polyphenolic compounds and other reactive components of various agricultural and forest biomass residues were converted into aqueous solution and/or suspension by alkaline extraction and/or digestion (Chen, 1993 & 1996). The biomass residues included among others peanut hulls, pecan nut pith and shell flour, southern pine bark and foliage and the respective alkaline-digested aqueous products were used to replace up to 80% of the phenol used in phenol-formaldehyde resins. The extraction process involved several stages and was time-consuming.

Thermochemical liquefaction of wood or wood wastes in the presence of phenol has been proposed as a way to produce a reactive material called phenolated wood, which was used in the preparation of phenolic resins (Lin *et al.* 2001). Over the years two methods have been developed for the preparation of phenolated wood, the acid-catalysed liquefaction at moderate temperatures (120-160°C) and the non-catalysed liquefaction at elevated temperatures (200-250°C). 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. By application of phenolic resins prepared from liquefied wood in the production of wood panels, inferior panel properties are obtained as compared to conventional phenolics (Shiraishi and Hse, 2000). 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.

Among suitable raw materials, tannins are said to represent the best substitute for phenol in resin preparation (Santana *et al.* 1995). Wattle tannin adhesives have been commercially and successfully used in several southern hemisphere countries since the early 1970's for exterior grade particleboard, plywood and laminating wood products (Chen, 1996). Quebracho and pine tannins are also available commercially (Pizzi and Scharfetter, 1981, Pizzi *et al.* 1993). Tannin use, however, has been limited by its high reactivity and viscosity, which cause short pot life, and by its lack of intermolecular crosslinking, which causes weak adhesive bonds. Chemical modification or fortification has been proposed as a means to overcome these problems. Simple pH adjustment of the glue mix was also found suitable for the control of reactivity of tannin extracts in particleboard production (Pizzi and Stefanou, 1994, Pizzi *et al.* 1994). The tannin-based adhesive performance depends on the combination of tannin and hardener types used (Kim *et al.* 2003).

More recently, the oil obtained by the pyrolysis of biomass or its phenolic fraction has been successfully used to substitute phenol in phenol-formaldehyde resins (Chum *et al.* 1989, Chum and Black, 1990, Chum *et al.* 1991, Himmelblau *et al.* 2000, Chan *et al.* 2000). Substitution levels of up to 50% have been reported, however 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, CHIMAR HELLAS has extensively worked on developing resins from renewable resources for application in wood-based panels production, aiming at:

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The objective of the present paper is to summarize the industrial scale tests performed in plywood production using PF resins modified with tannin material. A brief discussion on previous important findings regarding bio-based resins is included.

MATERIALS AND METHODS

Phenol-formaldehyde resole resin batch was successfully produced by substituting 20% of the phenol needed in the formulation with tannin and modifying the CHIMAR proprietary Know How for PF synthesis. The resin was intended for application in the production of industrial plywood (PW) panels.

Materials

A commercial phenol sample was purchased and diluted to 91% w/w concentration. Formaldehyde solution 37% w/w was employed. The tannin material was a commercial product from S. Africa namely Bondtite 345.

PF Resin Synthesis & Testing

The PF resole resin was synthesised using various polycondensation stages and addition of sodium hydroxide solution to catalyse the condensation. The incorporation of tannin in the resin molecule was effected by appropriate modifications, e.g. increase of the level of sodium hydroxide used. The polycondensation reaction was controlled via continuous measurement of viscosity and temperature. The final resin specifications are given in Table 1 and are almost the same with the plant control resin used for comparison.

Table 1: Specifications of PTF resin synthesized.

Property	PTF
Resin solids, %	44.4
Viscosity at 25°C, cp	230
pH	12.5

Viscosity measurements were performed using a Brookfield viscometer, at 25°C using a small sample adaptor. The amount of solids content was determined by weighing resin sample before and after drying in an oven at 120°C and for 2 hours.

Plywood Preparation & Testing

Two different types of wood veneers were employed for the industrial scale plywood production: spruce (softwood) and ocume (tropical hardwood) veneers with 5-6% moisture. Glue mixture with hardener and filler was spread on the veneers at a quantity of 125g/m^2. 7-layer panels with dimensions 2500 x 1250 x 15mm were formed. After 40 min assembling time, the panels were subjected to cold pre-pressing for 15min. The hot pressing step followed after 1h and it was run at 115°C for 12min.

Samples were taken from each of the plywood boards (control PF- and PTF-bonded) following two days from their production and they were subjected to WBP (Weather and Boil Proof) test: 24hours boiling in an autoclave at approximately 119°C followed by the determination of percentage of wood failure via knife test. The shear strength and the percentage of apparent cohesive wood failure (EN 314-1&2), the MOR (modulus of rupture) and MOE (modulus of elasticity) were measured too.

RESULTS AND DISCUSSION

During the production of industrial plywood panels using the PTF resin neither dry out nor tack problems were noted. The knife test results are shown in Table 2.

Table 2: Knife test results.

Resin	Face	Core	Inner	Thickness mm	Density kg/m^3	Wood failure, %
PF-control	ocume	spruce	spruce	15.0	448	90
PTF	ocume	spruce	spruce	14.8	487	100

In Table 3 the shear strength, the percentage of apparent cohesive wood failure, MOR and MOE figures are presented.

Table 3: Shear strength, percentage of apparent cohesive wood failure, MOR and MOE results.

Resin	Density kg/m^3	Shear strength N/mm^2	Apparent cohesive wood failure, %	MOR N/mm^2	MOE N/mm^2
PF-control	464.76	1.26	87	40.14	5101
PTF	478.68	1.20	91	41.64	5708

Finally, the requirements for mean shear strength fv and mean apparent cohesive wood failure w according to EN 314-2 are depicted in Table 4.

It is seen that the PTF-bonded plywood well conforms to the EN 314-2 standard requirements.

Table 4: EN 314-2 requirements.

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

IMPORTANT ACHIEVEMENTS ON BIO-BASED RESINS

Previous R&D efforts of CHIMAR had focused on the potential use of pyrolysis oils (bio-oils), a portion of which comprises of phenolic compounds, for replacing part of the phenol needed in the formulation of a phenol-formaldehyde resin (Nakos, 1998, Markessini and Tsiantzi, 1999, Tsiantzi and Athanassiadou, 2000, Nakos *et al.* 2001, Athanassiadou *et al.* 2002, Lappas *et al.* 2005). Phenol-formaldehyde resins were produced by substituting **up to 50%** of the phenol needed in the formulation with bio-oils and by modifying the synthesis procedure. Glue mixes containing these resins together with/without using proprietary CHIMAR activator technologies also based on renewable resources, were successfully applied in large-scale production of OSB and plywood. Adaptation of the resin production sequence was made to accommodate for this difference in the field of application. The use of bio-oil resin systems has provided in both products reactivity and performance equal to the non-modified PF resin systems. Such systems are currently being used commercially in North America.

Furthermore, tannin adhesives for particleboard were developed and applied commercially. A system of tannin and urea-formaldehyde pre-condensate (UFC, the amount of which is approx. 12% w/w on tannin) is applied in the core phase of three-layer particleboard at levels 11-13% w/w on wood chips. Thus the tannin represents almost **90%** of the adhesive used in the core phase. Tannin is also added sometimes in the surface layers of the particleboards together with melamine-urea-phenol-formaldehyde resin. The particleboards obtained exhibit on average internal bond strength of 0.8 N/mm^2 and 2h thickness swell of 1.4% (19mm boards).

CONCLUSIONS

It was proven that PTF resole resins prepared by substituting 20% of the phenol with tannin provide plywood panels with acceptable performance at industrial scale. The tannin material offers cost savings to the resin and panel manufacturers and to the panel consumers. It also promotes the sustainability of the same industries and respective products. Most importantly, it is in line with the efforts to prepare natural resins and environmentally friendly products. Further increase in the substitution level is envisaged, with the aim to achieve a higher reduction of the resin cost and increase the positive environmental impact.

The previously developed bio-based adhesive systems of CHIMAR highly contribute to the above positive effects and pave the way for the development and commercial adoption of natural resins for wood products.

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