EWLP 2014
13TH EUROPEAN WORKSHOP ON LIGNOCELLULOSICS AND PULP

PROCEEDINGS

24-27 June 2014
Seville, Spain

© Institute of Natural Resources and Agrobiology of Seville (IRNAS-CSIC), 2014
Editors: J.C. del Río, A. Gutiérrez, J. Rencoret and Á.T. Martínez
Printed in Spain, 2014
Cover design: E.D. Babot

ISBN: 978-84-616-9842-4

EVALUATION OF GREY ALDER BARK TANNIN AS PHENOL SUBSTITUTE IN THE SYNTHESIS OF PHENOL-FORMALDEHYDE RESINS SUITABLE FOR PLYWOOD

Sarmite Janceva[1], Electra Papadopoulou[2], Laimonis Kulinsh[3], Maris Lauberts[1], Tatiana Dizhbite[1], Galina Telysheva[1]*

[1]*Latvian State Institute of Wood Chemistry, 27 Dzerbenes st., LV-1006 Riga, Latvia;* [2]*Chimar Hellas S.A.,* 88 Them. Sofouli, 55131 *Thessaloniki, Greece;* [3]*Latvia University of Agriculture, 41 Dobeles st., LV-3001 Jelgava, Latvia; (*ligno@edi.lv)*

ABSTRACT

With the aim to develop green adhesives for wood, an adhesive system formed by condensed tannins (CT), isolated from grey alder bark, polyethyleneimine (PEI) and phenol-formaldehyde resins (PF) including this one containing micro/nanoparticles of extracted bark as a filler, and a PF resin, where CT were used as phenol substitute on the synthesis stage were studied for plywood manufacture. The results of the gluing quality tests have shown that the modulus of elasticity of plywood glued using the (CT-PEI):PF based adhesives with 40-60% substitution of PF was very close to that for plywood obtained with the traditional 100% PF glue and meet the European norms EN 312 (2004) in terms of share strength for plywood used both in indoor or outdoor conditions. Introduction of extracted bark residue micro/nanoparticles into composition of adhesives investigated led to increasing of physical-mechanical properties and strength of gluing. The experimental PF resin was prepared by substitution of 20% phenol following processes proprietary of CHIMAR. The produced resin had properties close to that of a typical PF resin. Plywood panels produced with this CT:PF resin (PFT) may be used for exterior application. The resins obtained using both (CT:PEI) gel and CT extract are suitable for the fabrication of plywood panels for interior application because their formaldehyde emission is very low.

I. INTRODUCTION

Phenol-formaldehyde (PF) based wood adhesives still today dominate in markets. However, toxic formaldehyde emission [1] and necessity to diminish petrochemicals consumption stimulate the search of alternative environmentally safe adhesives. Tannins, natural polyphenolic compounds, are present in large concentrations in wood barks. They are natural hydrophilic complexing agents. Wood adhesives from condensed tannins have been developed, especially on the basis of acacia (Mimosa – *Acacia mearnsii* De Wild) and quebracho (*Schinopsis lorentzii*) tannins [2]. It has been established earlier [3] that the bark of grey alder (*Alnus incana*), the tree widely spread in the European countries including Latvia, contains condensed tannins (CT) in rather large quantity (about 12% on o.d. bark) Using ^{13}C NMR spectroscopy, it has been shown that the grey alder CT contain mostly epicatechin units connected by C4-C8 and C4-C6 interflavonoid bonds to B-type procyanidins double bond flavanyl units in the molecule (2C-O-7C), which is typical for A-type procyanidins. The TOF-MS analysis has shown that oligomeric CT of grey alder bark ranged from the dimer to the heptamer (Figure 1). The preliminary experiments have shown suitability of alder bark tannins for obtaining of eco-friendly wood adhesives [3,4].

The present study continues our works aimed on the developing of green adhesives and is focused on investigation of the alder bark oligomeric tannins as substitutes of petrol-based adhesives used in plywood panels manufacturing. With this aim, a polymeric gel obtained on the basis of CT by its modification with polyethylenimine (PEI) was tested as an additive in a typical PF resin for plywood manufacturing. Besides, the grey alder CT were tested as a phenol substitute during the synthesis of PF wood adhesive (PFT).

II. EXPERIMENTAL

Formulation of CT-based polymeric gel and (CT-PEI):PF adhesives

Grey alder bark (*Alnus incana*) was collected from the forest in East-South part of Latvia. Tannin fraction of bark extractives was sequentially extracted as described in [3] using solvents with increasing polarity: hexane, ethyl acetate and finally aqueous ethanol (1:1, v/v). The ethanol was removed under vacuum and the remaining aqueous solution was frozen and freeze-dried. CT content in the tannin extract was measured by buthanol–HCl method [5] using procyanidin dimer B2 from Extrasynthese as a reference compound.

Copia gratuita. Personal free copy http://libros.csic.es

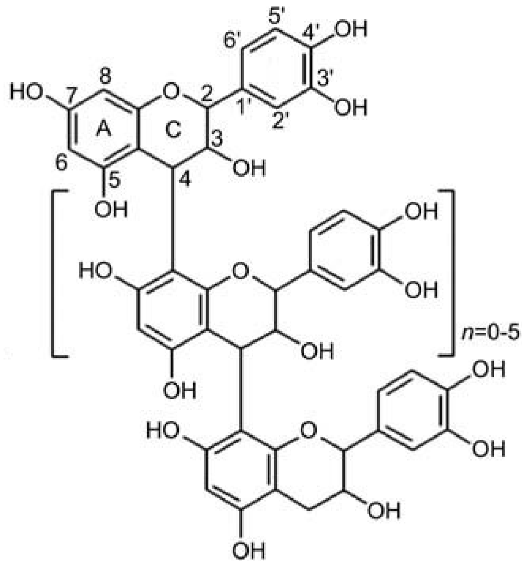

Figure 1. B-type oligomeric structure of grey alder condensed tannins.

The CT–based gel was obtained by mixing of aqueous tannins solution (pH 7) with 50% (w/v) aqueous polyethylenimine (PEI) solution (mass ratio 2:1,w/w) was purchased from Sigma-Aldrich. The tannin adhesive were characterized by differential scanning calorimetry (DSC) on a Metter Toledo DSC 828. and the results obtained from the DSC scans show a large heat absorption peak at about 120°C, which indicated that the reaction CT with PEI proceeds in the temperature range 100-140°C.

Adhesives for plywood manufacture were made by mixing of (CT-PEI) gels with PF resin at the mass ratios (CT-PEI):PF = 20:80, 40:60, 50:50, 60:40, 80:20. The resulting adhesives were tested for obtaining of plywood panels.

Synthesis of a PFT resin with phenol substitution by CT

For the synthesis of the phenolic resins, phenol 90% and formaldehyde water solution 37.4% were used. A PFT resin with 20% phenol replacement by CT was produced smoothly following the CHIMAR proprietary process for the synthesis of a PFT type resin.

Plywood panels production and characteristics

The (CT-PEI) based adhesives were applied for obtaining of birch plywood panels. The plywood panel samples were made using tree layers of birch (thickness of 2 mm each), and 170 g/m2 of adhesive. The panels were pressed for 10 minutes at 140°C and pressure of 2 MPa. The samples obtained were conditioned in a climate room (25˚C and 65% humidity) for 24 h. Then the quality of plywood panel gluing was evaluated by the statistic bending (modulus of elasticity) and bonding shear tests, carried out according to EN 314 -1 [6].

The bonding ability of PFT resin with 20% phenol substitution by CT under study was tested in the production of laboratory plywood panels of 3 layers: the face veneers were from okoume and the core veneer was from poplar. The plywood panels were produced with a process simulating industrial practices, while panel testing and evaluation was conducted according to the European standards EN 314.1 and EN 314.2. Formaldehyde emissions were determined according to the Desiccator (JIS A 1460) method.

III. RESULTS AND DISCUSSION

(CT-PEI)-based PF adhesive

It was found that the major components (0.36 g/g of extract or 12 % on bark dry mass) of the tannins extract isolated from grey alder bark are condensed tannins (proanthocyanidins). The new (CT-PEI):PF adhesive compositions were prepared on the basis of this extract.

The results of the gluing quality tests of the birch plywood panels glued using the all (CT-PEI):PF based adhesives showed (Table 1) that the values of elasticity modulus for plywood panels obtained with PF substitution by 20-60% were close to those for control panels glued by the typical PF only.

 © CSIC © del autor o autores / Todos los derechos reservados

It was found that the values of share strength for these panels after treatment by immersion in water at 20°C for 24 h (bonding class for dry interior) and cyclic treatment in boiling water (bonding classes for exterior application) passes the threshold values requested by the EN standard 314.2 (Table 1). However, the adequacy of the plywood panels to the standard requirements has to be confirmed further by evaluation of the gluing quality using the apparent cohesive wood failure criteria.

Table 1. Influence of composition of adhesives prepared on (CT-PEI) basis on the modulus of elasticity of plywood panels glued

Adhesive composition	Plywood panel elasticity modulus, N/mm^2		Shear strength, N/mm^2	
	Transverse modulus	Longitudinal modulus	After immersion in water at 20°C	After cyclic treatment in boiling water
Control: traditional PF	1190±160	16270±1800	2.28±0.38	1.68±0.30
(CT-PEI):PF = 20:80	1000±150	14610±660	1.79±0.38	1.56±0.28
(CT-PEI):PF = 40:60	1070±140	14480±880	1.84±0.34	1.36±0.27
(CT-PEI):PF = 50:50	1030±110	14085±1300	2.04±0.29	1.30±0.32
(CT-PEI):PF = 60:40	1030±120	13980±1730	1.45±0.30	1.3±0.29
(CT-PEI):PF = 80:20	1060±200	11720±1380	0	0

Introduction of extracted bark residue micro/nanoparticles into composition of (CT-PEI):PF adhesives led to increasing of physical-mechanical properties and strength of gluing.

Phenol substitution by CT during PF synthesis

An experimental resin was prepared by substitution of 20% phenol during the synthesis of the PFT resin following processes proprietary of CHIMAR. The produced PFT resin had properties close to that of a typical phenol-formaldehyde PF resin.

The results of evaluation of quality of gluing for plywood panels produced with a process simulating industrial practices, have shown (Figure 2, Table 2) that the experimental PFT resin passes the threshold values requested by the EN standard 314.2, for all classes: for Class 1 - dry interior and Class 3 – non covered exterior (the conditions of corresponding tests are shown in the Table 2).

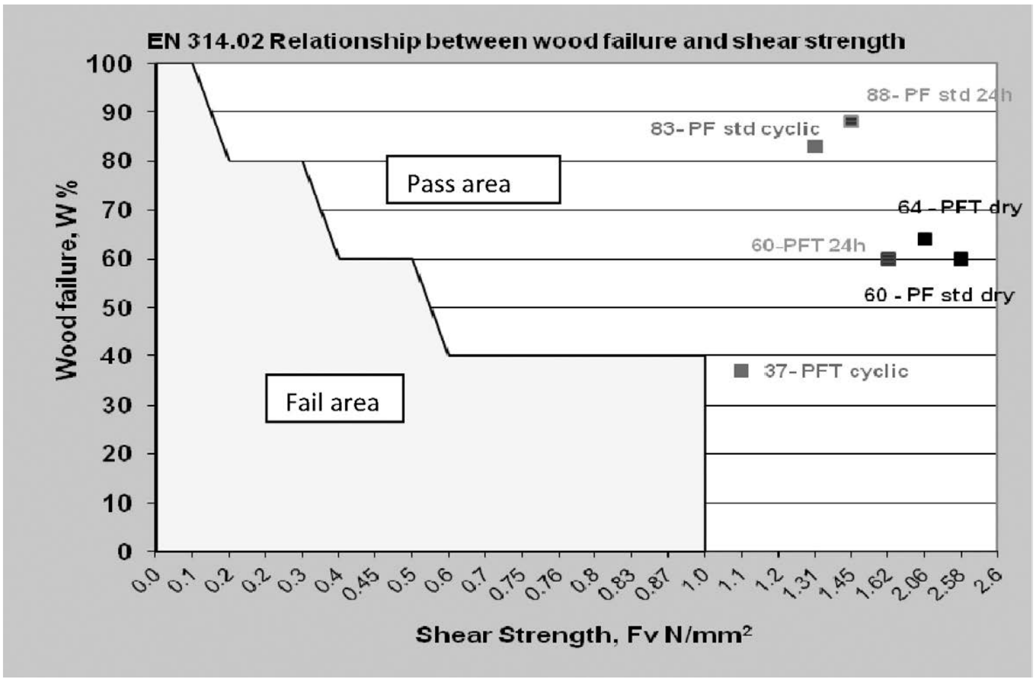

Figure 2. The relationship between wood failure and share strength of plywood panels and the experimental results. std dry – panels without pretreatment; std 24 h – panels after pretreatment required by Class 1; std cyclic – panels after pretreatment required by Class 3.

Copia gratuita. Personal free copy http://libros.csic.es

For all three bonding classes (EN 314. 2), each glue line has to satisfy two criteria, namely, the mean share strength and the mean apparent cohesive wood failure as combined in the Figure 2.

Table 2. The results of evaluation of plywood panels produced with PFT

Index	Resin	
	Standard PF	PF with 20% phenol substitution by CT
No treatment		
Shear strength, N/mm^2	2.58±0.23	2.06±0.31
Wood failure, %	60±2	64±1
Pretreatment required by Class 1: immersion in water of 20°C for 24 h		
Shear strength, N/mm^2	1.45±0.22	1.62±0.35
Wood failure, %	88±2	60±1
Pretreatment required by Class 3: 4 h in boiling water–16 h drying at 60°C–4 h in boiling water–1 h in cool water		
Shear strength, N/mm^2	1.31±0.19	1,14±0.11
Wood failure, %	83±2	37±1
Formaldehyde emission: desiccator values, mg/L	0.090±0.008	0.047±0.009

Comparison of the desiccator values showed (Table 2) that the plywood panels fabricated with the experimental PFT resin (20% substitution of phenol by CT) showed much lower formaldehyde emission than that released by the panel produced using a typical PF resin. The reducing formaldehyde emission provide the advantage of the CT-based adhesive interior application in comparison with typical PF resins.

IV. CONCLUSIONS

The synthesised wood adhesives containing oligomeric tannins that are available in large quantities from grey alder bark, could be used for production of plywood for exterior applications, although the further investigations needed for improvement their wood failure performance.

Due to very low level of formaldehyde emission, the synthesised CT-containing adhesives are suitable for the fabrication of plywood panels for interior needs.

V. ACKNOWLEDGEMENT

Financial support from Collaborative European project BIOCORE, Contract FP7-241566, LSC Research Grant 564/2012 and Latvian Government Research Program 2010.10-4/VPP-5 is gratefully acknowledged.

VI. REFERENCES

[1] International Agency for Research on Cancer (IARC) and World Health Organisation (WHO), June 14, **2004**.
[2] Bertaud, F.; Tapin-Lingua, S.; Pizzi, A.; Navarrete, P.; Petit-Conil, M. Development of green adhesives for fibreboard manufacturing, using tannins and lignins. *Cellulose Chem. Technol*., **2012**, *46*, 449-455.
[3] Telysheva, G.; Dizhbite, T.; Bikovens, O.; Ponomarenko, J.; Janceva, S., Krasilnikova, J. Structure and antioxidant activity of diarylheptanoids extracted from bark of grey alder (*Alnus incana*) and potential of biorefinery-based bark processing of European trees. *Holzforschung,* **2011**, *65*, 623 – 629.
[4] Janceva, S.; Dizhbite, T.; Telysheva, G.; Arshanitsa, A.; Spulle, U.; Kulinsh, L.; Dzenis, M. Isolation and testing of condensed tannins from alder bark for obtained environment friendly adhesives and biofuel granules. Proceedings of NWBC 2011, Stockholm, March 22-24, **2011**, 351 – 352.
[5] Waterman, P.G.; Mole, S. Analysis of phenolic plant metabolites.Blackwell Scientific Publications, Oxford, 1994.
[6] Zanuttini, R.; Cremonini, C. Optimization of the test method for determining the bonding quality of core plywood (blackboard). Mater. Struct., **2002,** *35*, 126-132.

© CSIC © del autor o autores / Todos los derechos reservados