ADHESIVES AND WOOD-BASED PANELS WITH MATERIALS FROM SUNFLOWERS

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BIOREF Project

Full title: Development of a biorefinery for the valorisation of biodiesel production residues to produce biodegradable polymers and high added-value products.

Project duration: 2011-2014

Financial support: Greek General Secretariat for Research and Technology, European Union

Partners:

- ARGO SA, Athens Greece – Packaging industry
- Pettas SA, Patra, Greece – Industrial plant for biodiesel production
- CHIMAR HELLAS S.A., Thessaloniki Greece – SME – K-H developer for the wood industry

Sub contractors:

- Agricultural University of Athens, Greece
- Institute of Chemical Engineering Sciences in Patra, Greece

BIOREF Project

The **main objective** of Bioref project is the development of novel biorefineries that convert residual biomass through integrated physical, (thermo)chemical and biological processes into bio-products suitable for various applications.

The project **focuses** on the exploitation of the residual streams resulted during the production of biodiesel from sunflower seeds.

The by-products produced are crude glycerol and sunflower cake (the protein-rich residue that remains after the extraction of oil from the sunflower seeds).
Crude glycerol is converted through microbial fermentations into **poly-hydroxy-alkanoates** (PHAs), **hydrogen** and **microbial lipids** (Single Cell Oils, SCOs), while sunflower cake is used for the production of **protein**. The Bioref bio-materials find application in food packaging, food additives and adhesives for the wood-industry.

The role of CHIMAR in Bioref

- Use of protein in the synthesis of phenol-formaldehyde (PF) polymers suitable for the production of plywood panels
- Use of sunflower cake as wood substitute in the production of particleboards

Sunflower meal
(seeds after oil extraction)

Protein – wood adhesive

Husks – wood substitute

Use of protein in PF polymers as additive

Initially, crude protein (produced by 2 different eluents) was used as additive in PF resins at the levels of 2.5 and 5%.

Results of plywood panels (3 layers)

Formula	1	2	3	4	5
Resin	**PFstd**	**PFstd**	**PFstd**	**PFstd**	**PFstd**
Sample No	**-**	**1**	**1**	**2**	**2**
Protein level, % s/s	**-**	**2.5**	**5.0**	**2.5**	**5.0**
EN314.1					
Pre-treatment 5.1.1	*Immersion in water of 20°C for 24h*				
Shear strength, N/mm²	1.04	1.04	1.18	1.09	1.21
Wood failure, %	83	**93**	84	**89**	73
Pre-treatment 5.1.3:	*4h in boiling water-16h drying at 60°C-4h in boiling water-1h in cool water*				
Shear strength, N/mm²	0.88	0.94	0.95	0.91	0.93
Wood failure, %	91	**96**	92	85	87
Desiccator, mg/L	0.070	0.059	0.064	0.068	0.075

Sample 1: Eluent = sodium hydroxide NaOH
Sample 2: Eluent = sodium sulfite - Na_2SO_3

Results:

- *Sample 1 was the best performed*
- *2.5 % addition level was enough for performance improvement*

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Comparison of crude and hydrolysed proteins

- Crude and hydrolysed proteins (appx. 35%) were evaluated as additives in PF resins at the levels of 2.5%.

Results of plywood panels (3 layers)

Formula	1	2	3	4
Resin	**PFstd**	**PFstd**	**PFstd**	**PFstd**
Protein sample No	**-**	**1 (C)**	**2 (C)**	**3 (H)**
Protein level, % s/s	**-**	**2.5**	**2.5**	**2.5**
EN314.1				
Pre-treatment 5.1.1:	*Immersion in water of 20°C for 24h*			
Shear strength, N/mm^2	0.74	1.00	0.75	**1.64**
Wood failure, %	95	85	90	90
Pre-treatment 5.1.3:	*4h in boiling water-16h drying at 60°C-4h in boiling water-1h in cool water*			
Shear strength, N/mm^2	0.73	0.91	0.70	**1.21**
Wood failure, %	90	85	90	75
Desiccator, mg/L	0.033	0.050	0.034	0.096

Sample 1: Eluent = sodium hydroxide NaOH
Sample 2: Eluent = sodium sulfite -Na2SO3
Sample 3: Hydrolysed protein

Results:

- *All protein samples have comparable if not advantageous performance to the control resin.*
- *Hydrolysed protein has better performance than the crude proteins*

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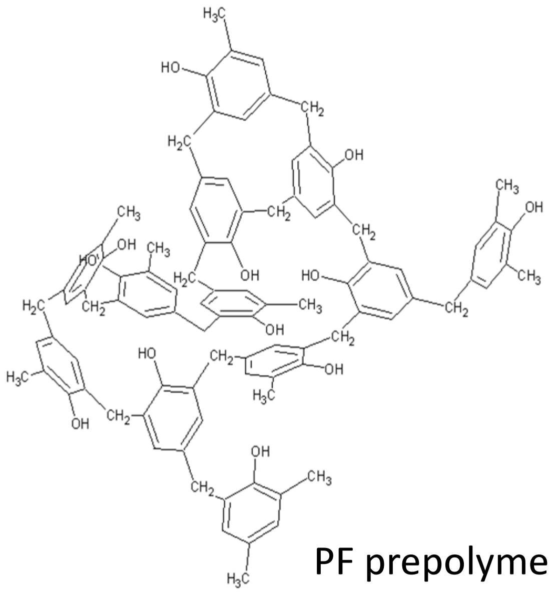
Evaluation of hydrolysed proteins

Proteins were hydrolysed at the levels of 30 and 40% and were tested both as additives and as phenol substitute during the synthesis of the resin at the level of 5%.



PF prepolymer

Results of plywood panels - 1

Results of Plywood panels’ evaluation produced with resins where hydrolysed proteins were used **as additive** at the level of 5%

PW structure	O/P/O	O/P/O	O/P/O	O/P/O	O/P/O
Resin - 5% addition	PF std	**P30 in resin**	**P40 in resin**	P30 in GM	P40 in GM
EN314.1	Dry				
Shear strength, N/mm^2	1,95	2,31	**2,29**	1.97	1.97
Wood failure, %	85	58	**77**	65	59
Pre-treatment 5.1.1:	Immersion in water of 20°C for 24h				
Shear strength, N/mm^2	1,36	**1,50**	1,61	1.07	0.98
Wood failure, %	54	**58**	49	77	51
Pre-treatment 5.1.3:	4h in boiling water-16h drying at 60°C-4h in boiling water-1h in cool water				
Shear strength, N/mm^2	1,24	**1,43**	1,31	1.27	1.24
Wood failure, %	47	**61**	31	59	48
Desiccator, mg/L	0,205	0,236	0,160	0.214	0.211

O/P/O = Okume/Poplar/Olume
GM = Glue mixture (resin, water, flour)

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

Shear strength testing

Wood failure evaluation

Results:

- *The samples performed better when used as additives in the resin.*
- *The **30% hydrolysed protein** performed better than the one with 40% hydrolysis*

Results of plywood panels - 2

Results of Plywood panels' evaluation produced with resins where proteins were hydrolysed at the levels of 10 and 30% and were used **as phenol substitute** at the level of 5%. A resin with crude protein and a conventional PF resin were also included in the test for comparison reasons.

Resin	**PF std**	**PF-5P non hydrolysed**	**PF-5P10**	**PF-5P30**
		Dry		
Shear strength, N/mm^2	2.25	1.86	1.80	**2.00**
Wood failure, %	40	70	90	40
EN314.1				
Pre-treatment 5.1.1:	Immersion in water of 20°C for 24h (24h test)			
Shear strength, N/mm^2	1.52	1.46	1.67	**1.63**
Wood failure, %	72	59	49	**60**
Pre-treatment 5.1.3:	4h in boiling water-16h drying at 60°C-4h in boiling water-1h in cool water (cyclic test)			
Shear strength, N/mm^2	1.26	**1.30**	1.27	**1.35**
Wood failure, %	85	**86**	78	**79**
ISO 12460				
Desiccator, mg/L	0.280	0.159	0.201	**0.149**

Results:

- *In all cases the panels with experimental resins have reduced free formaldehyde emissions.*
- *The 30% hydrolysed protein performed overall slightly better than the other samples.*

Results of plywood panels - 3

Results of Plywood panels' evaluation produced with resins where proteins were hydrolysed at the levels of 30 and 40% and were used **as phenol substitute** at the level of 5%.

PW structure	**S**	**S**	**S**
Resin	PF std	PF-5P30	PF-5P40
5% addition	-	P30 in resin	P40 in resin
EN314.1	Dry		
Shear strength, N/mm^2	1.52	**2.07**	1.76
Wood failure, %	66	**40**	39
Pre-treatment 5.1.1:	Immersion in water of 20°C for 24h		
Shear strength, N/mm^2	1.00	1.11	**1.16**
Wood failure, %	61	24	**36**
Pre-treatment 5.1.3:	4h in boiling water-16h drying at 60°C-4h in boiling water-1h in cool water		
Shear strength, N/mm^2	1.06	1.11	**1.15**
Wood failure, %	66	28	**33**
Desiccator, mg/L	0.245	0.475	0.267

S= spruce

Results:

- *The 40% hydrolysed protein performs better than the 30% hydrolysed protein.*

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Future work

Resins with higher substitution levels of phenol.

S= spruce

Particleboards with sunflower cake

Sunflower cake (after the oil was removed) was used as wood substitute at the level of 20% for the production of particleboards.

Formula No		**1**	**2**
Resin:		PF std	PF std
Wood sub.		**-**	**20%**
Internal Bond, ave (EN 319)	N/mm^2	**0.22**	**0.33**
STD		*0.13*	*0.10*
Thickness Swelling 24h, 20°C, ave (EN 317)	%	**19.89**	**19.75**
STD		*0.66*	*0.84*
Modulus of rupture, ave. (EN 310)	N/mm^2	**18.38**	**13.61**
Modulus of rupture-A, ave	N/mm^2	**9.51**	**7.83**
Perforator value (EN 120)	mg/100g	4.54	3.52
Formaldehyde content at 6.5% MC	mg/100g	**3.94**	**3.16**

Result: Improved internal bond – all other properties practically the same

CHIMAR Activities in Brief

- ✓ Developer and supplier of industrial technology and services in the field of adhesive systems for wood based panels.

- ✓ Focus on safe, environmentally friendly products and technologies. Technology for bio-based adhesive systems.

- ✓ Pioneer in the reduction of formaldehyde emission from wood panels (technology for emission at the level of natural wood).

Acting globally and helping locally

- ✓ Engineering & equipment procurement services for formaldehyde/UFC/resin/chemical additives plants

- ✓ Versatility of services: R&D for third parties, Testing and evaluation, Technical support for field industries (remotely and on-site), Consulting and Training, Chemicals production on demand, Accredited formaldehyde testing (EN ISO/IEC 17025), Patent services, Industrial Equipment Representation.

Indicative references

- Hadjilucas
- Sapemus
- Kronospan Bulgaria
- Flakeboard
- Duraplay
- Alto Parana
- GPC Química
- Wood Chemicals
- P.G. Bison
- Karpatsmoly
- Borg Group
- Finsa
- Tableros de Aglomerado
- UPM
- Forestal
- Borisov

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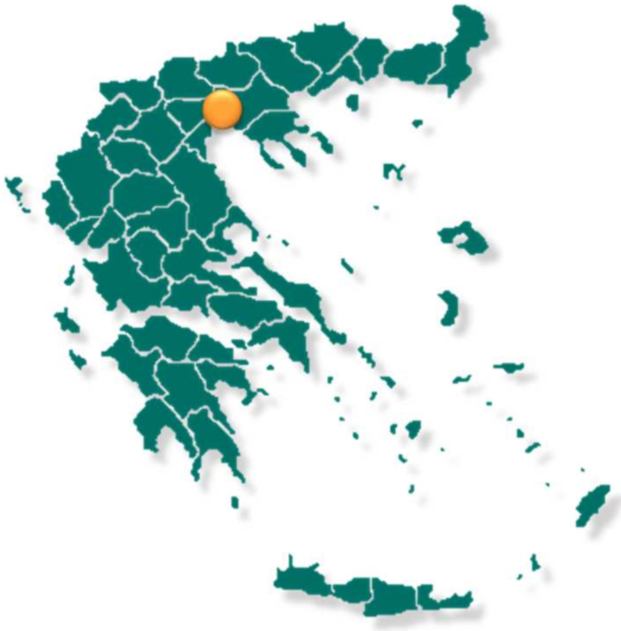

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