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The influence of laccase modifications of lignin on the properties of biocomposites from natural-fiber material with lignins as binder

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Abstract. A biocomposite made of natural fibers compounded with laccase-modified or non-modified lignins was manufactured in an injection molding process. Physical and mechanical properties of the material were examined and compared to typical high density hardboard. It was shown that the enzymatic modification only slightly affected mechanical performance of biocomposites, while their hydrophilicity strongly increased.

Keywords: lignin, laccase, fiberboard, injection molding process

1. Introduction

Lignin, apart from cellulose and hemicelluloses, is one of the main constituents of wood. Lignin content ranges from 15 to 35% [1]. According to Klason and Freudenberg lignin is an aromatic polymer bearing phenylpropane backbone. Softwood lignin is mainly composed of guaiacyl building blocks while hardwood lignin is made of guaiacyl and syringyl moieties in 2:1 ratio. Therefore, methoxyl groups (-OCH3) abundance and methoxyls / hydroxyls ratio are higher in softwood lignin [2]. Due to glass transition temperature at ca. 90^{o}C and melting point at ca. 170^{o}C [3], lignin should be considered as thermoplastic material. It is generated as a by-product from paper production in amounts reaching 80 million tones.

As a natural biopolymer lignin seems to be a convenient raw material for polymer- and natural fiber-based composites [4, 5, 6, 7, 8, 9, 10]. As Widsten and Kandelbauer [11] report enzymatic treatment of lignin improves its applicability in manufacturing of eco-friendly composites. The reported results prove that performance of this type of biocomposites is comparable to that of glass fiber-based composites [12]. Biocomposites find their applications in furniture industry or automotive (i.e. car door interior panels). Due to their high density (1200-1400 kg/m^3) they can be used as substitutes for thin traditional wood-based composites bonded with synthetic binders – e.g. HDF. Moreover, they are prone to easy 3D forming (injection molding) which is their undoubted advantage.

2. Materials and methods

Three types of panels were prepared and tested:

- (1) 4-mm thick non-modified lignin-bonded injection molded fiberboard of density 1250 kg/m^3,
- (2) 4-mm thick laccase-modified lignin-bonded injection molded fiberboard of density 1250 kg/m^3,
- (3) reference 4-mm thick hardboard of density 1250 kg/m^3 made with traditional wet method.

Boards of series (1) and (2) were manufactured at the Faculty of Mechanical Engineering, Chemnitz University of Technology, boards (3) were manufactured at the Faculty of Wood Technology, Warsaw University of Life Sciences – SGGW.

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Series (1) and (2) of dimensions 300 x 300 x 4 mm^3 were compounded of 45% hemp fibers (STW 150) and 55% Kraft pine lignin (Indulin AT). Prior to injection molding raw materials were dried at 60ºC to 2% moisture content. Mat forming pre-pressing ~10 N/mm^2, hot pressing ~1 N/mm^2, post-pressing ~5 N/mm^2. Injection temperature 162ºC. The hardboards of dimensions 300 x 150 x 4 mm^3 were made of the pulp of freeness 45 DS, PF glue load was 2% (based on dry fibers). After draining, the boards were pressed at 200ºC and pressing regimé as follows: 19 N/mm^2 – 4 min → 3 N/mm^2 – 4 min → 19 N/mm^2 – 5 min. Draining nets were used on both sides of the mat. The boards were conditioned for 7 days.

The following parameters of the prepared boards were analyzed:

- density profile on a laboratory density profile measuring system GreCon DA-X. Measurement resolution 0.02 mm at rate 0,05 mm/s.
- MOR and MOE (according to EN 310:1994), hardness (according to EN 1534:2000)
- swelling and water absorption after 2 and 24 h soaking (according EN 317:1999)
- surface water wetting on a contact angle analyzer Phoenix 300 (Surface Electro Optics, Korea). Contact angle was measured after 60 s since droplet deposition.

Ten specimens were tested in each batch. Statistical significance of differences was tested by Student t-test at 95% confidence interval.

3. Results and discussion

The tested boards exhibited comparable densities (Table 1). In Fig. 1 variations of cross-sectional density profile were presented. One can see that the density profiles for lignin-bonded series were more uniform than that for the reference hardboards. Maximum density of the biocomposite boards (~ 1335 kg/m^3) was developed in the core zone, while maximum density of the hardboards (~ 1326 kg/m^3) was achieved in sub-surface zone.

Those differences may be explained by the manner of board forming. Injection imposes that thermoplastic material is plasticized prior to molding, while in case of hardboards, the material is plasticized at the moment of pressing - after temperature and pressure were applied. In consequence, more intense densification occurs in sub-surface zones.

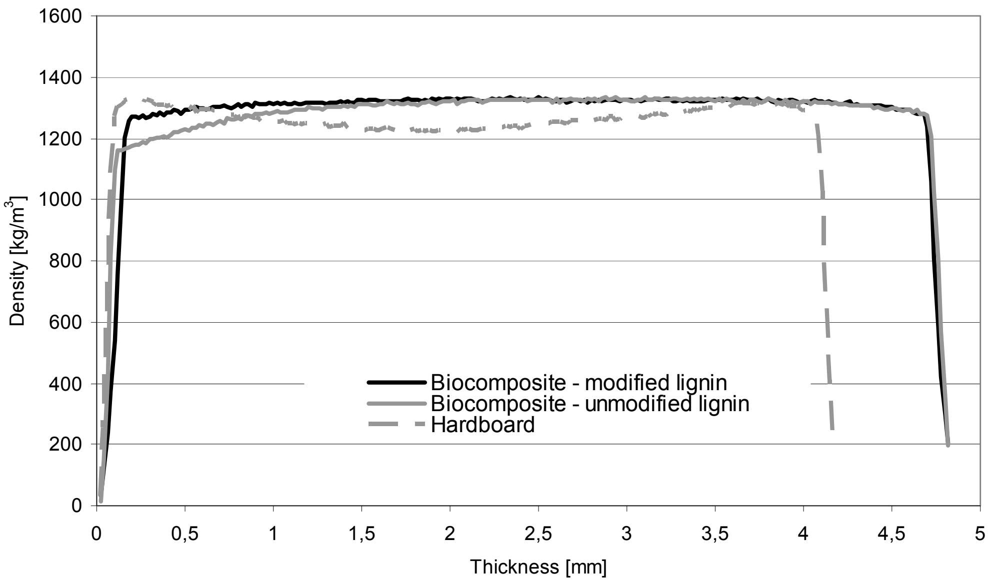

Fig. 1: Density profiles of the studied boards.

Table 1. Properties of the studied boards

Series	Density	MOR		MOE		Brinell hardness	
	[kg/m^3]	[N/mm^2]	x	[N/mm^2]	x	[N/mm^2]	x
Biocomposite – unmodified lignin	1299	22.2	11	4501	9	232.89	19
Biocomposite – modified lignin	1287	23.3	16	4667	15	265.40	14
Hardboard	1201	82.1	14	5507	16	137.43	18

x – variation coefficient

The presented results indicate that lignin modification had little influence on the mechanical performance of the tested boards. MOR and MOE of the modified-lignin series increased by 4.7% and 3.5%, respectively, when compared to non-modfied series (Table 1), however the differences are not statistically significant. On the other hand, the reference hardboards exhibited MOR and MOE values higher by 73% and 18%, respectively, than those of the modified series. Lignin-bonded series exhibited 2-fold higher hardness than the reference hardboards. Moreover, lignin-bonded boards had higher brittleness which was revealed upon MOR tests.

Fracture loci of the boards after MOR tests were shown in Fig. 2. Hardboard fracture locus Fig. 2C was rugged, while those of lignin-bonded boards (Figs. 2A and 2B) were smoother. Increased hardness and brittleness of lignin-bonded series come from higher content of lignin which, in a native form, works as a binder in cell wall. Also, hardness of the laccase-modified lignin-bonded boards was 12% higher than that of the non-modified lignin-bonded ones.

A B C

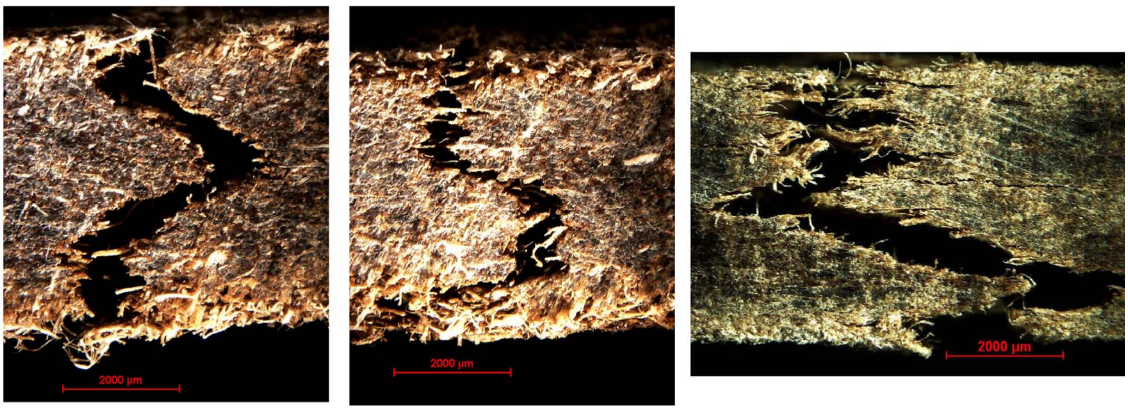

Fig. 2: Fracture loci after MOR tests: A – non-modified lignin-bonded board, B – laccase-modified lignin-bonded board, C – hardboard.

In Table 2 swelling and water absorption results were shown. It is apparent that the values obtained for the lignin-bonded series were comparable to those of the reference hardboards. The differences were not statistically significant.

Table 2. Swelling, water absorption and surface water wetting

Series	Density [kg/m^3]	Swelling [%]				Absorption [%]				Contact
		2 h	x	24 h	x	2 h	x	24 h	x	angle θ [º]
Biocomposite – unmodified lignin	1299	25.0	23	46.8	8	27.2	18	49.1	8	42.5 ± 5.4
Biocomposite – modified lignin	1287	25.9	14	53.1	14	25.1	4	50.9	10	52.0 ± 5.0
Hardboard	1201	24.3	15	41.2	10	27.7	16	44.6	8	37.8 ± 3.4

x – variation coefficient [%]

Water contact angle (θ) is an estimator of material interactions with water – the lower contact angle, the better wetting. As data shown in Table 2 indicate, the contact angles determined for biocomposites were higher than those for hardboard. The observed wetting was easiest for the laccase-modified series, middling wetting for the non-modified series and the poorest for the hardboards. The wetting phenomena are in accordance with the observations from swelling and water absorption which confirms that the hydrophlicity of injection-molded lignin-bonded boards was higher than that of reference hardboard.

4. Conclusions

The obtained results allow to conclude that enzymatically modified lignin when used as binder for wood fibers influenced mechanical performance of boards manufactured by injection molding. MOR and MOE were sligtly affected, however the highest increase was observed for hardness of the material (12%) and in water wetting (18%). Reference hardboards exhibited higher mechanical parameters, lower hardness and lower hydrophilicity.

5. Acknowledgements

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