Technological and Product Innovation in the Manufacturing Process of Ecologically Acceptable Lignocellulosic Materials

Eva Ruzinska 1, Lukas Polanecky 1, Daniel Kucerka 1

1 Institute of Technology and Business in České Budějovice, Faculty of Corporate Strategy, Okružní 571/10, 370 01 České Budějovice, Czech Republic
eva.ruzinska11@gmail.com

Abstract. Innovative products from the assortment of wood based panels – fibreboard composites are characterized by considerable diversification potential, which also gives them adequate development opportunities and predetermines their perspective. Besides the possibility of variable application and modification of disintegrated wood with chemical auxiliaries, the development potential is determined, in particular by using their dimensional diversity of wood particles - the degree of wood disintegration, which at the same time determines the level of transformation of the natural properties of wood into a large-scale wood product. By optimizing the manufacturing process of the preparation of fibrous wood composites by chemical modification with apply of waste lignocellulose preparations, as a new innovative product – fibrous based environmentally acceptable wood composites with the higher qualitative and hygienic characteristics can be prepared to expand the assortment of required products currently required by the woodworking industry. An important aspect of the sustainable ecologically acceptable production of wood fibrous composites is to reduce the formaldehyde emission content of used adhesives by adding lignocellulose additives.

The aim of our research was the proposal, experimental preparation and evaluation of the selected properties of fibrous wood composites with the addition of substances based on modified lignocellulose waste (from pulp and paper industry). The result of the research is the proposals for innovation of existing technologies in the production of environmentally acceptable innovative products, thus expanding the range of wood products demanded from furniture industry and customers.

1. Introduction

The production of wood based composites has developed into a sector that is an important part of the wood-processing industry. The consumer offers a semi-product and a high-performance product without which it could not be developed, for example, the furniture industry to its present form. In addition, it significantly contributes to a higher appreciation of wood raw material, in particular by the ability to process less valuable wood assortments as well as industrial waste [1, 2].

Wood based composites are characterized by considerable diversification potential, which also gives them adequate development opportunities and predetermines their perspective. Besides the possibility of variable application and modification of disintegrated wood with chemical auxiliaries, the development potential is determined, in particular by using their dimensional diversity of wood particles - the degree of wood disintegration, which at the same time determines the level of transformation of the natural properties of wood into a large-scale wood product [2].
In the manufacture of wood based composite materials in the woodworking industry, urea-formaldehyde adhesives (UF) are the most commonly used. In spite of their advantages (they are priced and raw material available, the technology of their production is fairly simple, they have a white colour and after curing they provide a transparent glued joint), they contain a part of the unreacted formaldehyde, which releases from the adhesives themselves as well as from the final products greatly degrades the environment with its toxic effects on humans [3, 5].

Minimizing release of formaldehyde emissions has become a strictly controlled parameter in the manufacture of wood based composites over the last decade and a strong condition for their commercial application. As a result of efforts to improve the environment, global developments in the field of adhesives lead to the development of new or effective modification of existing technologies with a focus on reducing formaldehyde emissions [4 - 7].

Formaldehyde (methylene oxide) belongs to a group of volatile organic compounds. Formaldehyde is an allergic, mutagenic, carcinogenic compound which causes irritation to the respiratory and nervous system. Formaldehyde is a real threat to the health of people exposed to its operations [3, 10]. Therefore, in many countries, standards limit the maximum allowable value of the formaldehyde emissions from wood-based panels for furniture industry or for construction applications [8, 9]. In Europe, according to EN 717-1, valid class with the lowest acceptable level of free formaldehyde emissions from wood based materials is the class E1, with a value of less than 0.124 mg/m² (by chamber method). Since modifications of amino-resins occurred to be not enough, new challenges for manufacturers arose. Meeting the limits allowed for Super E-Zero class imposes wide research on formaldehyde release from wood as well as novel approach for manufacturing.

Wood as a natural material contains some amount of formaldehyde [5, 6], which can be released e.g. during thermal treatment. However, emission levels depend on numerous factors – like species, moisture content, outside temperature or storing time [6, 9]. In order to develop E 0.5-class (4 mg/100 g) products, it seems essential to recognize emission levels at the consecutive processing steps – including wood in the store-house as well as cut or ground raw materials. According to the EN 717-2 gas analysis test method, the requirements for the released formaldehyde content of finished wood products (wood based composites) are within the range ≤ 3.5 mg/m²h or ≤ 5 mg/m²h within 3 days after production.

Based on strict ecological requirements, it is clear that the woodworking industry is currently looking for ways of sustainable ecologically acceptable production of a wide range of wood products, also using modification modifications of lignocellulose materials, resp. waste from the processing of biomass while maintaining the required qualitative characteristics of the products [1, 4, 14]. In our research, we focused on the proposal and experimental preparation and following evaluation of selected qualitative and hygienic characteristics of new types of fibrous wood composites that can be considered as environmentally acceptable innovative wood products, based on our own previous research work [1 – 4].

2. Experimental part

The basis of fibrous wood composites are wood fibres, which are joined by adhesive binding by means of adhesive properties of polymers or added adhesive agent (poly-condensation urea-formaldehyde resin: UF). Boards have homogeneous structure of pressed fibres in the whole cross-section. Smooth, stable surface and homogeneity in the cross-section create precondition for three-dimensional, i.e. relief working. Fine structure of fibres gives board high dimensional stability and high mechanical strength [1, 12, 14].

2.1. Proposal and preparation of fibrous wood composites

Experimental preparation of new innovative fibrous wood composites consisted of the same technological operations as the production of commercially manufacturing fibreboards (FB) by the dry method.
In the framework of technological and product innovation, we have proposed the following phases of fibre composites preparation to take account of environmental and quality requirements based on our own previous research work [1]:

- Preparation of raw materials: coniferous wood (is preferred due to bigger length of fibres) is stored, cleaned and debarking;
- Production of wood chips by disintegrating process: cutting, sorting and storage;
- Washing of wood chips: removal of mineral oil and metal dirt;
- Pulping of wood chips: defibration wood chips on wood fibres;
- Application of adhesive and other additives: adhesive (UF) is applied by spraying at 3 % wt., hydrophobic agent is applied at 1 % wt. and addition of modified lignocellulosic waste (5, 8, 10, 12, 15 % wt.);
- Formation of fibre materials humidity of dried and applied fibre is 5 %;
- Pressing and hardening of fibreboard: pressing temperature 180°C, total pressing time: 420 s;
- Unit pressure (MPa) / Pressing time (s): 8.5/60; 2.0/180; 8.5/180;
- Formatting and conditioning of fibreboards.

In order to obtain the assumed density of fibreboards of 1200 kg/m³ with a relatively low assumed thickness (3 mm), prepared materials were pressed in the electrically heated laboratory one-shelf press. Manufactured boards (wood based fibrous composites) were conditioned under laboratory conditions for 7 days (relative humidity: φ ~ 65%, temperature: t ~ 20 °C).

For the produced materials hygiene tests were performed in terms of formaldehyde emissions, which were based on the assumptions of EN 717-2. Test specimens were prepared in accordance with the provisions present in the standard.

2.2. Modification treatment of lignocellulose waste materials
The lignocellulosic material that we used as an additive (to UF adhesive) in the experimental preparation of fibrous wood composites was obtained from waste products of the pulp and paper industry in the sulphate pulp preparation process [2]. Sulphate waste (kraft black) liquor is characterized by relatively low reactivity of formaldehyde which does not required to be incorporated into a polymeric matrix of polycondensate adhesive (UF)[10, 11, 13]. It is therefore necessary to modify the reactivity of the original kraft sulphate liquors modification reactions, e.g. methylation, acidification or other reactions (hydroxymetylation, demethylation) [3, 10, 11, 13].

**Methylation** modification treatment of sulphate waste liquor [3, 10] has been carried out experimentally. The basis of methylated treatment was the reaction of formaldehyde with waste sulphate liquor at room temperature for 72 hours. The prepared methylated sulphate waste liquor was used as an additive in UF adhesive and applied to wood fibres in the form of aqueous solution having concentration of 10 %.

The second variant of the modification treatment was in the previous post-treatment procedure prepared methylated kraft liquor by **acidification** [3, 10] followed by a strong mineral acid with intensive stirring to value pH = 5. Also, this variant of modified sulphate waste liquors was used in the form of an aqueous solution.

For comparison we have also set up a reference fibrous board using the standard procedure where no additives (R – reference sample). Specification of composition of prepared modified and used lignocellulose additives are shown in Table 1.
| Variant | Content of Ingredients | Release emission of formaldehyde (mg/m²h) |
|---------|------------------------|------------------------------------------|
| M1      | 100/5                  | 0.84                                     |
| M2      | 100/8                  | 0.81                                     |
| M3      | 100/10                 | 0.72                                     |
| M4      | 100/12                 | 0.71                                     |
| M5      | 100/15                 | 0.70                                     |
| A1      | 100/5                  | 0.66                                     |
| A2      | 100/8                  | 0.49                                     |
| A3      | 100/10                 | 0.42                                     |
| A4      | 100/12                 | 0.41                                     |
| A5      | 100/15                 | 0.40                                     |
| R       | 100/0                  | 2.15                                     |

M1 – M5 methylated and A1-A5 acidified modified lignocellulose additives, R – reference sample

Table 1. Composition of modified lignocellulose additives and results of emission formaldehyde from laboratory prepared wood composites

All prepared fibrous wood composites are listed and specified in Table 1. Five species of fibreboards with successive methylated liquors as an experimental additive were prepared: 5, 8, 10, 12, 15% wt. (M1, M2, M3, M4, M5). Further, fibreboards were prepared with the application of an acidified modified lignocellulose additive to fibrous boards the same composition (A1, A2, A3, A4, A5). Traditionally prepared fibreboard (R) as a reference sample.

2.3 Evaluation of hygienic properties of prepared fibrous wood composites

The standard specifies determination of formaldehyde release by the gas analysis method (EN 717-2: Wood based panels - Determination of formaldehyde release. Part 2: Formaldehyde release by the gas analysis method). In that method the sample of determined dimensions in putted to closed chamber, in which parameters are defined.

Emitted formaldehyde from the sample is mixed with air in chamber. The air goes constantly into bottle with water. After 4 hours testing, concentration of formaldehyde in water is determined photometrically by Spectrophotometer Spectro UV-VIS, equipped with specific cuvettes with a path length of 50 mm. According to the EN 717-2 gas analysis test method, the requirements for the released formaldehyde content of finished wood products (wood based composites) are within the range ≤ 3.5 mg/m²h or ≤ 5 mg/m²h within 3 days after production.

The results of release formaldehyde emission from experimentally preparation fibrous wood based composites by gas analysis method are shown in the Table 1.

2.4 Evaluation of selected qualitative characteristics of prepared fibrous wood composites

Within the qualitative characteristics of the prepared fibrous wood composites, the most important - mechanical properties were evaluated. Modulus of rupture (MOR) and modulus of elasticity at the static bending strength (MOE) were determined according to EN 310(Wood-based panels: Determination of modulus elasticity in bending and bending strength). The tensile strength perpendicular to the surface of fiberboard (IB) was determined according to EN 319 (Particleboard and fibreboards. Determination of tensile strength perpendicular to the place of the board).
All measurements of mechanical parameters were performed on a universal testing machine INSTRON 3369. For each variant 30 repetitions were performed. Evaluated results of mechanical properties of prepared fibrous wood composites were shown in the Table 2.

Table 2. Mechanical characteristics of prepared fibrous wood composites

| VARIANT | MOR (N/mm²) | MOE (N/mm²) | IB (N/mm²) | S* |
|---------|-------------|-------------|------------|-----|
| M1      | 70.4        | 6169        | 0.51       | 0.08|
| M2      | 71.8        | 6244        | 0.49       | 0.06|
| M3      | 68.6        | 6383        | 0.48       | 0.10|
| M4      | 66.1        | 6512        | 0.46       | 0.09|
| M5      | 65.5        | 6647        | 0.44       | 0.11|
| A1      | 73.4        | 6341        | 0.56       | 0.08|
| A2      | 71.8        | 6455        | 0.53       | 0.05|
| A3      | 70.6        | 6634        | 0.54       | 0.06|
| A4      | 69.1        | 6708        | 0.49       | 0.12|
| A5      | 67.5        | 6847        | 0.48       | 0.09|
| R       | 64.7        | 6007        | 0.42       | 0.12|

S* – standard deviation, MOR – modulus of rupture, MOE – modulus of elasticity, IB – tensile strength perpendicular to the surface of fibreboard, R – reference sample

3. Results and discussions

From the evaluated results of free formaldehyde emissions from finished fibrous wood composites, it can be stated that both modified additives (methylated and acidified) have a positive effect on the reduction of the amount of this pollutant. With gradual increasing (5, 8, 10, 12, 15% wt.) of the methylated and acidified additives applied to wood fibers, we have seen a reduction in formaldehyde emissions from finished fibreboards. A more radical reduction in formaldehyde emissions was indicated with the use of a modified acidified sulphate waste liquor additive at 15% (by weight). Compared to the standard fibre board, the reference variant R represents a reduction in formaldehyde emissions from 2.15 to 0.40mg/m²h to 5.38-times the reduction.

When applying methylated sulphate liquor as a modified lignocellulose additive to wood fibers made of fibrous wood composites, were cored the most significant decrease in formaldehyde emissions by addition of 15% (by weight), up to 0.70 mg/m²h, representing a 3.07-times decrease compared to the reference sample.

With regard to all modified additive variants we can say that even in one variant of tested wood composites the limit value (according to EN 717-2) was not exceeded ≤ 3.5 mg/m²h, even the reference sample R reached 2.15 mg/m²h.

After measuring the formaldehyde emissions, we evaluated the most important qualitative - mechanical characteristics of the prepared fibrous wood composites. The mechanical characteristics are the most important parameters in the application of wood composites in the woodworking industry, in the furniture sector, as well as in the production of floor wood coverings. We have evaluated the strength characteristics of static bending strength (MOR), the static bending strength (MOE) and the tensile strength perpendicular to the surface (IB), which are shown in Table 2.

From the results of modulus of rupture(MOR), modulus of elasticity (MOE) and tensile strength perpendicular to the surface of fibreboard(IB), it is clear that all variants of prepared fibrous wood composites with modified and additive materials have achieved comparable (even better) values as the reference sample (R) – fibrous wood composites without additives. The best mechanical characteristics were recorded in the variant with the application of the acidified additives(variant C), which showed qualitatively higher values for MOE, MOR and IB in the full range addition of additives to compared to the reference sample - standard fiberboard.
4. Conclusions
At present, it is an important aspect of a sustainable environmentally acceptable production of fibrous wood composites to reduce the formaldehyde content of the adhesives used by adding lignocellulose additives (as waste from pulp and paper industry and modified adjustment). In our research, we focused on the proposal, experimental preparation and evaluation of the most important qualitative and hygienic characteristics of new types of wood fibre biocomposites that can be considered environmentally friendly innovative wood products. For comparison, commercial fibre boards were prepared - as a reference sample that did not contain any lignocellulose additives.

In the overall comparison of the variants of the modified additives applied in the preparation of fibrous wood composites, it has been shown that modification of additive obtained from industrial lignocellulosic waste can achieve a reduction in emissions of hazardous pollutant formaldehyde. Additives, especially acidified, have also shown significant reductions in formaldehyde emissions to be considered environmentally acceptable and to denote their fibrous wood bio composites.

We assume [1, 12, 14] that there as on for reducing formaldehyde emissions in fibrous wood composites could be the use of their activity of the functional groups of the alkali lignins of the polydisperse macromolecular chemical structure and their incorporation into the mixed poly condensation additive in combination with the present UF resin applied to the surface of the wood fibers in the fibrous fibre board curing (hardening) technology to incorporate formaldehyde in to the mixed adhesive matrix.

From the overall evaluation of the mechanical characteristics of the prepared fibrous wood composites, it is clear that both variants using modified additives (methylated, acidified) have comparable mechanical properties, which predestines them for the preparation of innovative wood bio-composites. The best mechanical characteristics were recorded in the variant with the application of the acidified additives (variant C), which showed qualitatively higher values for MOE, MOR and IB in the full range addition of additives to compared to the reference sample - standard fibreboard.

Our proposed innovation in manufacturing technology have contributed to the preparation of innovative product, which accepts the requirements for incorporating variants (with methylated and acidified modified lignocellulose waste from pulp and paper industry) as an environmentally acceptable wood fibrous bio-composites.

Acknowledgment
The article was created for financial support and as a result of the solution of the internal grant project No. 8110IGS201818 "Creating professional studies as a tool for innovation and development of pedagogical activities“ at the The Institute of Technology and Business in České Budějovice, Czech Republic.

References
[1] E. Ružinská et al., “Product and technological innovation - new fibrous wood biocomposites”. 31st IBIMA Conference, ISI Proceedings, Milan, Italy, 5 p. ISBN 978-0-9998551-0-2, 2018.
[2] P. Boruszewski, M. Maminski, and E. Ružinská (eds), "Raw materials and particleboards – a current status and perspectives”. SGGW Press, Publish.Warsaw University of Life Science, 111 p., ISBN 978-83-7583-389-8, 2012.
[3] E. Ružinská et al., “Risk substances in woodworking industry”. Monograph. Warsaw University of Life Sciences Press. 114 p. ISBN 978-83-7583-591-5, 2014.
[4] E. Ružinská et al., “The New Progressive Polymeric Materials for the Reduction of VOC in woodworking industry. Applied Mechanics and Materials, Vol. 711, pp. 214-217. doi:10.4028/www.scientific.net/AMM.711.214, 2015.
[5] E. Roffael,"Volatile organic compounds and formaldehyde in nature, wood and wood based panels”, Holz Roh Werkst., Vol. 64, pp. 144-149, 2006.
[6] E. Roffael et al., “On the formaldehyde release of wood particles”. European Journal of Wood and Wood Products, Vol. 70, No. 6, 2012, pp. 911-912, 2012.
[7] B. Meyer, C. Boehme, “Formaldehyde emission from solid wood”. *For. Product J.*, Vol. 47, No. 5 pp. 45-48, 1997.
[8] A. Duong, “Reproductive and Developmental Toxicity of Formaldehyde”. *Mutat. Res.*, Vol. 728, No.3, pp. 118-138, 2011.
[9] Z. Que, T. Furuno, “Formaldehyde emission from wood products. *Wood Sci Technol.*, Vol.41, pp. 267-279, 2007.
[10] A.J. Dolenko, M.R. Clarke, “Resin binders from kraft lignin”. *Forest Prod. Journ.*, 38, 8, pp. 41-46, 1978.
[11] H. Hatakeyama et al. “Lignin structure, properties and applications”. *Adv. Polym. Sci.*, 232, 1, pp. 223-269, 2010
[12] M. Sain et al., “Fiberboard from wood-fiber bonded with renewable wood resin. *J. of Reinfor. Plastics and Composit.*, Vol., 25, No. 16, pp. 22-39, 2006.
[13] M. Olivares et al., “Kraft lignin utilization in adhesives: *Wood Sci. Techn.*, Vol. 23, No. 2, pp. 157-165, 1988.
[14] M. Madhoushi et al., “Mechanical and Physical Properties of Green Biocomposite Based on MDF. *J. of Polym. and Environ.*, Vol. 25, No. 2, pp. 221-228, 2017.