

**EFFICIENCY OF BARK FOR REDUCTION OF
FORMALDEHYDE EMISSION FROM PARTICLEBOARDS**

SERGEJ MEDVED, URŠKA GAJŠEK
UNIVERSITY OF LJUBLJANA, BIOTECHNICAL FACULTY
DEPARTMENT OF WOOD SCIENCE AND TECHNOLOGY
LJUBLJANA, SLOVENIA

EUGENIA MARIANA TUDOR
TECHNICAL UNIVERSITY IN ZVOLEN
ZVOLEN, SLOVAK REPUBLIC
SALZBURG UNIVERSITY OF APPLIED SCIENCES
SALZBURG, AUSTRIA

MARIUS CATALIN BARBU
SALZBURG UNIVERSITY OF APPLIED SCIENCES
SALZBURG, AUSTRIA
TRANSYLVANIA UNIVERSITY OF BRASOV
FACULTY OF WOOD ENGINEERING
BRASOV, ROMANIA

ALAN ANTONOVIĆ
UNIVERSITY OF ZAGREB, FACULTY OF FORESTRY
ZAGREB, CROATIA

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ABSTRACT

Bark is much underutilized material. Most of the bark is used as fuel and for landscaping but there are still significant amounts of unused bark, hence creating a problem when disposed. Due to the aspects like colour, shape/size and ratio, and mechanical properties, bark is not a desired constituent for particleboard production. One of the possible uses of bark is related to its chemical compositions, specifically due to the phenolic-like components, bark can be used as formaldehyde scavenger. The aim of the paper is to present the usability of bark as particleboard formaldehyde scavenger. Single-layer particleboard made from wood particles spruce (*Picea abies*) and pine (*Pinus* sp.) bark mixture using urea-formaldehyde and melamine-urea formaldehyde as resin were tested for formaldehyde release. The formaldehyde release was determined by the Perforator method (EN 12460-5), gas analysis (EN 12460-3) and Flask method (EN 717-3). The experiment showed that the presence of bark lowers the formaldehyde release.

KEYWORDS: Particleboard, spruce (*Picea abies*) bark, pine (*Pinus* sp.) bark, formaldehyde.

INTRODUCTION

Formaldehyde is a chemical that severely influences indoor air quality. Due to its highly volatile nature, formaldehyde easily emits from material(s) into the surrounding air. One of the sources of formaldehyde in home(s) and office(s) are wood-based panels from which furniture is made (mostly particleboards), floors (mostly high-density fibreboards) or walls (mostly OSB) (Salthammer et al. 2010). Owing to the formaldehyde hazardous nature (IARC 2006, Athanassiadou and Ohlmeyer (2009), producers of formaldehyde-based adhesives and wood-based panels are constantly searching for the way to lower this emission. For this reason, several synthetic and/or natural based scavengers are used in production of wood-based panels. One of potential natural based scavengers mentioned in literature is also bark (Herrick and Bock 1958, Maclean and Gardner 1952, Roffael 1982, Cameron and Pizzi 1985, Prasetya and Roffael 1991, Lelis and Roffael 1995, Roffael et al. 2000, Nemli and Çolakoglu 2005, Takano et al. 2008). Bark constitutes between 10 to 20% of total tree weight and varies with regard to the wood species. Bark constitutes an outer part of tree occurring outside the vascular cambium and is divided into outer bark (deadly tissue) and inner part (living cells). Comparing the chemical composition of wood and bark, it can be concluded that the bark contains a higher content of ash, accessory materials (extractives) and lignin, and a lower content of polysaccharides cellulose and hemicelluloses (Antonović et al. 2010, Antonović et al. 2018). Bark is an underutilized lignin-cellulose based material with great usability potential. Most of the bark created during debarking is nowadays burned (energy utilization), while insignificant amount is used in horticulture (for landscaping), in pharmacy (Miranda et al. 2012), for leather tanning (Pizzi 2008), insulation purposes (Kain et al. 2016) and as coating layer for flooring (Tudor et al. 2018). Despite its previous mentioned usage, there is a substantial amount of bark that remains unused, which can sometimes create a disposal problem (Harkin and Rowe 1971). Burning of bark for energy production is not the best possible practice of bark utilization due to its caloric value (Gupta et al. 2011). The question of bark usability is especially important when a large quantity of bark is available due to natural disasters (wind, snow storm, ice storm, etc.) and to bark beetle attack (like recently in Slovenia).

As mentioned above, one possibility of utilizing bark is also to use it as a formaldehyde scavenger in the production of particleboards, which is also the aim of this paper.

MATERIALS AND METHODS

Two separate experiments, employing bark from softwoods (spruce and pine) were conducted to evaluate the efficiency of bark for reduction of formaldehyde release in particleboards.

Wood particles used in both experiments were produced in a laboratory chipper from wood chips, obtained from local industry. Wood particles were a mixture of surface and core layer particles (Tab. 1).

Tab. 1: Sieve analysis of wood particles.

Sieve opening (mm)	Share (%)
4.000	0.74
2.000	20.98
1.500	17.38
1.270	11.18
1.000	13.63
0.600	21.73
0.237	12.46
0 (bottom)	1.90

Experiment 1

Spruce bark (*Picea abies* L.) was crushed in a laboratory chipper (Condux LT 61). The size related composition of bark particles is shown in Tab. 2.

Tab. 2: Sieve analysis of spruce bark particles.

Sieve opening (mm)	Share (%)
6.140	2.59
4.000	8.56
2.000	21.23
1.500	11.88
1.270	6.98
1.000	8.32
0.600	15.59
0.237	17.71
0 (bottom)	7.14

Bark and wood particles were dried for 16 hours at 70°C, to achieve moisture content between 2 and 4%. Dried bark and wood particles were mixed together as shown in Tab. 3.

Tab. 3: Composition of boards made from bark particles.

Panel	Share of bark
	(%)
A	20
B	35
C	50
D	65
E	80

Appropriately mixed bark and wood particles were blended with 10% urea-formaldehyde resin (dry weight resin/dry weight particles ratio). As hardener, ammonium sulphate was used (3% dry weight hardener/dry weight resin ratio). Total time of blending was 6 minutes (3 minutes resin spraying and mixing and 3 minutes additional mixing). Resinated particles were subsequently hand formed into 500 × 500 mm large particle mat. Target thickness was 16 mm, while target density was 0.54 g·cm⁻³. Pressing temperature was 180°C, while pressure was set to 3 N·mm⁻². Total pressing time was 4 minutes.

Experiment 2

Since formaldehyde emission is also important for construction grade particleboards, the second experiment, where small bark particles and melamine-urea formaldehyde resin were used, was conducted. Bark chips (pine (*Pinus* sp.)) were crushed into small bark particles (fraction that passed through sieve with mesh size 0.237 mm) in a laboratory mill (Retsch SM2000). The main reason for different fraction used in experiment is related to the activation potential of smaller particles. Baldosano et al. (2015) determined that higher extraction yield is higher at smaller particles. The main reason for such behaviour is related to the specific surface area, which is higher at smaller particles. Since smaller bark particles have higher specific surface area, it was expected that they could be also more efficient as formaldehyde scavenger. The change in size of bark particles employed in the second experiment is also related to the mechanical properties of particleboard with bark particles. The increasing share of bark particles in particleboard causes a decrease in particleboard mechanical properties and an increase in thickness swelling (Lehmann and Geimer 1974, Muszynski and McNatt 1984, Blanchet et al. 2000, Nemli and Çolakoğlu 2005, Ngueho Yemele et al. 2008, Aydin et al. 2017). Quite the opposite was determined by Ruźiak et al. (2017) when using bark flour. When beech bark flour was employed as filler, plywood mechanical properties, thickness swelling, and formaldehyde emission were improved. A positive impact of small bark particles on internal bond was also determined by Ngueho Yemele et al. (2008) and Marashdeh et al. (2011). Additional reason for using small bark particles are also the findings by Gupta et al (2011). A particleboard made from small bark particles is more aesthetically appealing than board made with big bark particles. Since Ruźiak et al. (2017) mentioned that share of bark higher than 12.25% (in core layer of particleboard) causes a decrease in strength of particleboard; we decided to keep the amount of small bark particles below 10% (Tab. 4).

Tab. 4: Composition of boards made from small bark particles.

Panel	Share of bark
	(%)
G	0
H	0.5
I	1
J	5
K	10

Wood particles and small bark particles mixture was mixed with 11% melamine-urea formaldehyde resin (dry weight resin/dry weight particles ratio). The use of melamine-urea formaldehyde resin was related to a better bond quality as well as to a higher moisture resistance (possibility to its use in moist conditions). As hardener, ammonium sulphate was used (3% dry weight hardener/dry weight resin ratio). Total time of blending was 6 minutes (3 minutes resin spraying and mixing and 3 minutes additional mixing). Afterwards, resinated small bark particles/wood particle mixture, was hand formed into 500 × 500 mm large mat. Target thickness was 16 mm, while target density was 0.6 g·cm⁻³. The temperature of pressing was 200°C, while pressure was set to 3 N·mm⁻². Total pressing time was 4 minutes.

Formaldehyde determination

Formaldehyde release was determined using three different methods:

- Flask value (EN 717-3): experiment 1,
- Extraction method called perforator method (EN ISO 12460-5): experiment 2,
- Gas analysis method (EN ISO 12460-3): experiment 2.

The determination of formaldehyde release was conducted 72 h after the panel production. During this period, panels were placed into a controlled environment (temperature $21 \pm 1^\circ\text{C}$ and relative air humidity $65 \pm 3\%$). Moisture content was determined according to EN 322 and EN 323 respectively.

Bark efficiency (BEf) was calculated using Eq. 1.

$$BEf = \frac{(\chi_{bh} - \chi_{bl})}{(F_h - F_l)} \quad (1)$$

where: χ_{bh} - the highest bark share in % (80% - experiment 1; 10.0% - experiment 2),
 χ_{bl} - the lowest bark share in % (20% - experiment 1; 0.5% - experiment 2),
 F_h - formaldehyde release at the highest bark share (also the highest formaldehyde release detected),
 F_l - formaldehyde release at the lowest bark share (also the lowest formaldehyde release detected).

RESULTS AND DISCUSSION

Experiment 1

Results of the first experiment show similar effect as determined by Roffael (1982) Cameron and Pizzi (1985), Prasetya and Roffael (1991), Lelis and Roffael (1995), Nemli and Çolakoğlu (2005) and Takano et al. (2008) and Gajšek (2008). The increase in bark content results in lower formaldehyde release (Fig. 1). Formaldehyde release of reference particleboard (0% bark) was $13.76 \text{ mg}\cdot\text{kg}^{-1}$.

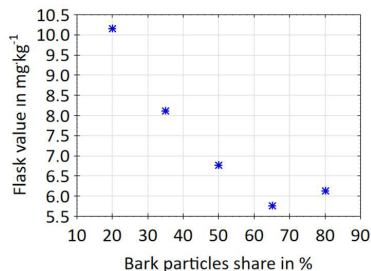


Fig. 1: Formaldehyde release - flask value related to the bark particles share.

Partial substitution of wood particles by bark particles (20% to 65%) resulted in a decrease of formaldehyde release (flask value) by 43%.

Chemical composition of bark, especially the content of polyphenolic components and tannins, are important for lowering the formaldehyde emission. As reported by Roffael (1982), Cameron and Pizzi (1985), Prasetya and Roffael (1991); if polyphenolic components and tannins react with formaldehyde, the formaldehyde emission from particleboards will decrease. Therefore bark is rich with polyphenols and tannins; it makes bark an important bio-based scavenger, which was also demonstrated in Fig. 1.

The efficiency of bark particles was 10.25. It means that in order to reduce formaldehyde determined by flask value for $1 \text{ mg}\cdot\text{kg}^{-1}$, 10.25% of wood particles need to be substituted by bark particles.

Experiment 2

Although the share of small bark particles was lower than in our first experiment, the impact on formaldehyde emission is evident (Fig. 2). Even small addition of small bark particles (0.5%) resulted in significantly lower formaldehyde emission.

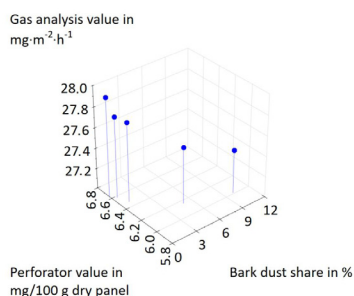


Fig. 2: Impact of small bark particles share on formaldehyde release (perforator value and gas analysis value).

In relation to formaldehyde release, the increase in small bark particles share results in decrease of formaldehyde release - perforator value (from $6.6 \text{ mg}/100 \text{ g dry panel}$ at 0.5% to $6.0 \text{ mg}/100 \text{ g dry panel}$ at 10%) and decrease in formaldehyde release - gas analysis value (from $27.8 \text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 0.5% to $27.4 \text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ at 10%). Small bark particles efficiency was 15.83 (perforator method) and 23.75 (gas analysis method). For reduction of formaldehyde determined by perforator method for $1 \text{ mg}/100 \text{ g dry panel}$, 15.83% of small bark particles need to be used, while for reduction of formaldehyde determined by gas analysis method for $1 \text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, 23.75% small bark particles are needed. Comparing the values obtained with modified flask method (test conditions: room temperature, 7-day exposure) the bark efficiency was 7.25 (from $14.59 \text{ mg}\cdot\text{kg}^{-1}$ at 0.5% to $13.28 \text{ mg}\cdot\text{kg}^{-1}$ dry panel at 10%) (Fig. 3).

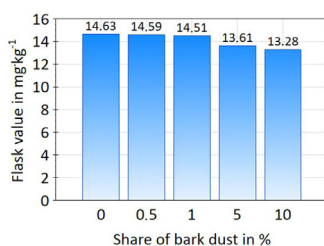


Fig. 3: Impact of bark share on formaldehyde release - flask method.

During the manufacture of particleboards or even other wood-based composites, bark acts as formaldehyde adsorbent. Since smaller bark particles have higher specific surface area, the degree of absorption is higher compared to bigger particles (lower specific surface). The formaldehyde absorption potential of bark was also reported by Takano et al. (2008). In addition to formaldehyde absorption of bark, Prasetya and Roffael (1991) also reported on the reaction

between polyphenolic components and tannins with formaldehyde. Formaldehyde fumes activated by high temperatures during particleboard production start to migrate together with moisture from the surface towards the core and subsequently towards the edge of the panel. On their path they are absorbed by bark particles. The absorbed formaldehyde starts reacting with polyphenolic components and tannins creating stable bond.

Since smaller bark particles have higher specific surface area, even small share becomes important formaldehyde adsorbent and scavenger.

Other properties

Regarding the results obtained in this experiment it was determined that significant reduction of formaldehyde release could be achieved with 5% bark share and higher, but other properties like internal bond and thickness swelling of finished boards need to be considered as well.

Properties of particleboards with bark depend on bark particle size and share. In particleboard with bark particles, the share of bark up to 50% results in higher internal bond (compared to reference particleboard). The internal bond increased from 0.23 N·mm⁻² (at reference) to the highest value of 0.33 N·mm⁻² (at 20% bark share). In particleboard with bark particles a positive effect of bark was detected at thickness swelling where lower swelling was determined (compared to reference particleboard). For example, the thickness swelling of reference panel was 56.59%, while the lowest was at 20% bark share (27.80%).

A quite different observation was noted in particleboard with small bark particles. The employment of small bark particles up to 1% resulted in higher internal bond (0.66 N·mm⁻²), while higher share resulted in significantly lower internal bond. Internal bond of reference panel was 0.56 N·mm⁻². Increase in small bark particles resulted in higher thickness swelling. Thickness swelling of reference panel was 11.53% and the highest determined was 15.62% (at 10% small bark particles share) (Medved et al. 2019).

CONCLUSIONS

In the presented experiment, various amounts of spruce bark particles and small bark particles (pine) were used to make single layer particleboards in order to determine the impact of bark on formaldehyde release. According to the obtained results, the following conclusions can be made:

- 1) Substitution of wood particles by bark particles lowers the formaldehyde release.
- 2) Formaldehyde release lowers with increasing bark share. To achieve the positive influence of bark on formaldehyde emission, the bark share needs to be higher than 5%.
- 3) Bark efficiency regarding formaldehyde emission depends on bark size and test method. Bark efficiency was 10.25 (spruce bark particles, urea-formaldehyde resin, flask method), 7.25 (pine bark – small particles, melamine-urea-formaldehyde resin, modified flask method), 15.83 (pine bark – small particles, melamine-urea-formaldehyde resin, perforator method) and 23.75 (pine bark – small particles, melamine-urea-formaldehyde resin gas analysis).

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REFERENCES

1. Antonović, A., Jambrečević, V., Franjić, J., Španić, N., Pervan, S., Ištvanić, J., Bubić, A., 2010: Influence of sampling location on content and chemical composition of the beech native lignin (*Fagus sylvatica* L.). *Periodicum Biologorum* 112(3): 327-332
2. Antonović, A., Barčić, D., Kljak, J., Ištvanić, J., Podvorec, T., Stanešić, J., 2018: The quality of fired Aleppo pine wood (*Pinus halepensis* Mill.). *Biomass for Biorefinery Products. Croatian Journal of Forest Engineering* 39(2): 313-324.
3. Aydin, I., Demirkir, C., Colak, S., Colakoglu, G., 2017: Utilization of bark flours as additive in plywood manufacturing. *European Journal of Wood and Wood Products* 75: 63-69
4. Athanassiadou, E., Ohlmeyer, M., 2009: Emission of formaldehyde and VOC from wood-based panels. In: *Performance in use and new products of wood-based composites* ed. Fan M, Ohlmeyer M, Irle, M). London, Brunel University Press: 219-240
5. Fan, M., Ohlmeyer, M., Irle, M., Haelvoet, W., Athanassiadou, E., Rochester, I., 2009: Performance in use and new products of wood based composites. London, Brunel University Press: 219 - 240 pp.
6. Baldosano, H.Y., Castillo, B.M., Elloran, C.D., Baca, F.T., 2015: Effect of particle size, solvent and extraction time on tannin extract from *Spondias purpurea* bark through Soxhlet extraction. *Proceedings of the DLSU Research Congress*, 3 Vol., 6 pp.
5. Blanchet, P., Cloutier, A., Riedl, B., 2000: Particleboard made from hammer milled Black spruce bark residues. *Wood Science and Technology*, 34: 11-19
6. Cameron, F.A., Pizzi, A., 1985: Tannin-induced formaldehyde release depression in urea formaldehyde particleboard. In: Meyer, B., Kottes-Andrews, B.A., Reinhardt, R.M. (ed.), *Formaldehyde Release from Wood Products. American Chemical Society Symposium Series*, No. 316, Washington, DC, Chapter 15, 205 pp.
7. Gajšek, U., 2008: Influence of bark particles in particleboard on emission of free formaldehyde. *Graduation thesis – University of Ljubljana, Biotechnical Faculty*: Pp 35.
8. Gupta, G., Yan, N., Feng, M.W., 2011: Effects of pressing temperature and particle size on bark board properties made from beetle-infested lodgepole pine (*Pinus contorta*) barks. *Forest Products Journal* 61(6): 478-488.
9. Harkin, J.M., Rowe, J.W., 1971: Bark and its possible uses. *USDA Forest Service Research Note*, FPL-091: 56 pp.
10. Herrick, F.W., Bock, L.H., 1958: Thermosetting, exterior-plywood type adhesives from bark extracts. *Forest Product Journal* 8(10): 269-274.
11. IARC (2006): Formaldehyde, 2-butoxyethanol and 1-tert-butoxypropan-2-ol. *IARC Monographs on Evaluation of Carcinogenic Risks to Humans* 88: 1-478.
12. Kain, G., Charwat-Pessler, J., Barbu, M.C., Plank, B., Richter, K., Petutschnigg, A., 2016: Analyzing wood bark insulation board structure using X-ray computed tomography and modelling its thermal conductivity by means of finite difference method. *Journal of Composite Materials* 50(6): 795-806

13. Lehmann, W.F., Geimer, R.L., 1974: Properties of structural particleboards from douglas-fir forest residues. *Forest Products Journal* 24(1): 17-25.
14. Maclean, H., Gardner, J.A.F., (1952): Bark extracts in adhesives. *Pulp and paper magazine of Canada* 8: 111-114.
15. Marashdeh, M.W., Hashim, R., Tajuddin, A.A, Bauk, S., Sulaiman, O., 2011: Effect of particle size on the characterization of binderless particleboard made from *Rhizophora* spp. mangrove wood for use as phantom material. *Bioresources* 6(4): 4028-4044
16. Medved, S., Tudor, E.M, Barbu, M.C., Jambreković, V, Španić, N., 2019: Effect of pine (*Pinus sylvestris*) bark dust on particleboard thickness swelling and internal bond. *Drvna industrija* (in press).
17. Miranda, I., Gominho, J.,Pereira, H., 2012: Incorporation of bark tops inEucalyptus globulus wood pulping. *BioResources* 7(3): 4350-4361.
18. Muszynski, Z., McNatt, J.D., 1984: Investigations on the use of spruce bark in the manufacture of particleboard in Poland. *Forest Products Journal* 34(1): 28-35.
19. Nemli, G.,Çolakoğlu, G., 2005: Effects of mimosa bark usage on some properties of particleboard. *Turkish Journal of agriculture and forestry* 29: 227-230.
20. NguemoYemele, M.C; Blanchet, P; Cloutier, A; Koubaa, A. 2008: Effects of bark content and particle geometry on the physical and mechanical properties of particleboard made from black spruce and trembling aspen bark. *Forest Products Journal*, 58(11): 48-56
21. Pizzi, A., 2008: Tannins: Major sources, properties and applications. In: *Monomers, Polymers and composites from renewable resources* (1st ed.), Gandini, A., Naceur Belgacem, M., Elsevier, Oxford, Pp 179-199.
22. Ružiak, I., Ignaz, R., Krišták, L., Réh, R., Mitterpach, J., Očkajová, A., Kučerka, M., 2017: Influence of urea-formaldehyde adhesive modification with beech bark on chosen properties of plywood. *BioResources* 12(2): 3250-3264.
23. Salthammer, T., Mentese, S.,Marutzky, R., 2010: Formaldehyde in the indoor environment. *Chemical Reviews* 110(4): 2536-2572.
24. Takano, T., Murakami, T., Kamitakahara, H.,Nakatsubo, F., 2008: Formaldehyde absorption by karamatsu (*Larixleptolepis*) bark. *Journal of Wood Science* 54: 332-336.
25. Tudor, E.M., Barbu, M.C., Petutschnigg, A., Réh, R., 2018: Added-value for wood bark as a coating layer for flooring tiles. *Journal of Cleaner Production* 170: 1354-1360.
26. EN 322 (1993): Wood-based panels. Determination of moisture content.
27. EN 323 (1993): Wood-based panels. Determination of density.
28. EN 717-3 (1996): Wood-based panels. Determination of formaldehyde release. Formaldehyde release by the flask method.
29. EN ISO 12460-3 (2015): Wood-based panels. Determination of formaldehyde release. Gas analysis method.
30. EN ISO 12460-5 (2015): Wood-based panels. Determination of formaldehyde release. Extraction method (called the perforator method).

SERGEJ MEDVED, URŠKA GAJŠEK
UNIVERSITY OF LJUBLJANA
BIOTECHNICAL FACULTY, DEPARTMENT
OF WOOD SCIENCE AND TECHNOLOGY
LJUBLJANA
SLOVENIA

EUGENIA MARIANA TUDOR
TECHNICAL UNIVERSITY IN ZVOLEN
ZVOLEN
SLOVAK REPUBLIC
SALZBURG UNIVERSITY OF APPLIED SCIENCES
SALZBURG
AUSTRIA

MARIUS CATALIN BARBU
SALZBURG UNIVERSITY OF APPLIED SCIENCES
SALZBURG
AUSTRIA
TRANSYLVANIA UNIVERSITY OF BRASOV
FACULTY OF WOOD ENGINEERING

BRASOV ROMAN, ALAN ANTONOVIĆ
UNIVERSITY OF ZAGREB
FACULTY OF FORESTRY
ZAGREB
CROATIA