Flour Fillers with Urea-Formaldehyde Resin in Plywood

Jakub Kawalerczyk,* Dorota Dziurka, Radosław Mirski, and Adrian Trociński

Various flours were added as fillers for urea-formaldehyde (UF) resin, and effects on the rheological behavior and the curing properties of the resin were evaluated. The plywood properties such as bonding quality, bending strength, modulus of elasticity, and formaldehyde-release were tested. Five types of flours were used, *i.e.*, rye flour, hemp flour, coconut flour, rice flour, and pumpkin flour. The type of flour had a major influence on the properties of resin mixture such as gel time, solid content, and viscosity. The use of rye and pumpkin flour resulted in a longer gelling time, and the adhesive mixture filled with rice flour did not attain the desired viscosity value needed for the production of plywood. The best mechanical properties and bonding quality were achieved by addition of pumpkin flour. However, the bonding quality of plywood glued with an adhesive filled with every other flour retained good values exceeding 1 N/mm^2 as required by the standard EN 314-2 (1993). The use of hemp flour as a filler for UF resin led to a substantial decrease of free formaldehyde content.

Keywords: Plywood; Urea-formaldehyde; Filler; Flour; Viscosity; Mechanical Properties

Contact information: Department of Wood-based Materials, Faculty of Wood Technology, Poznań University of Life Sciences, 28 Wojska Polskiego Str., 60-637 Poznań, Poland;
** Corresponding author: jakub.kawalerczyk@up.poznan.pl*

INTRODUCTION

Plywood is a widely used material that finds many applications in construction, furniture, and as a decorative material. Continuous demand has driven ongoing research related to plywood; in the last six years, the production of plywood increased worldwide by 40% (Xiaona *et al.* 2015; Bekhta *et al.* 2016; Dziurka *et al.* 2017; Kawalerczyk *et al.* 2019). The properties of wood-based materials are mainly determined by two factors, *i.e.*, the quality of wood used in the production process and the nature of the adhesive. Various types of resins are used in plywood production: urea-formaldehyde (UF), melamine-urea-formaldehyde (MUF), and phenol-formaldehyde (PF). The widespread use of UF resins is due to their high reactivity, low cost, ease of use, and a lack of color (Zhang *et al.* 2011; Dukarska 2013). Despite many advantages, they also have disadvantages such as formaldehyde emission and low water resistance. The decreased mechanical properties in conditions of increased humidity has restricted the usage of this resin mostly for the production of wood-based panels intended for interior use. Moreover, formaldehyde has carcinogenic effects on human health (Luo *et al.* 2015; Demir *et al.* 2018). There are many reports in the literature regarding the effect of adhesive modifications on the properties of wood-based materials. One method for improving parameters of UF resin is the addition of various fillers (Pawlak and Boruszewski 2018). Introducing an ideal filler leads to improvement in rheological properties and regulates the viscosity of the adhesive mixture. Furthermore, the addition of a suitable filler may improve the mechanical properties of wood-based materials, *e.g.* by limiting the occurrence of microcracks in the joints. The properties of resins are especially important in plywood production. Adhesives with low viscosity sink into the surface of veneer during the application and the pressing. Moreover, it is difficult to evenly distribute the adhesive with low viscosity on the surface of the veneer.

According to Ružiak *et al.* (2017), the replacement of flour with beech bark decreased the amount of formaldehyde emitted from plywood and increases its mechanical properties such as bending strength and modulus of elasticity. Zhang *et al.* (2011) investigated the possibility of using nanocrystalline cellulose as a filler for UF resin in plywood; the addition of nanocellulose resulted in a considerable improvement in bonding strength and decreased formaldehyde emissions. Furthermore, the addition of nanosilica to MUPF resin increased its reactivity and reduced the spread rate of applied resin mixture. The use of nanosilica as a filler can decrease the amount of formaldehyde emitting from plywood (Dukarska and Czarnecki 2016). The above-mentioned studies are only a few examples of an ongoing search for new fillers for resins in the production of wood-based materials. In addition to rye flour, which is widely used in the plywood industry, there are various other types of flour that haven't previously been tested for suitability as a filler for adhesives. In recent years, the "alternative flours" have gained popularity especially in the food industry (Pourafshar *et al.* 2015). Increasing popularity is associated with growing commercial availability and falling prices which were the leading motivations to start the research. Thus, this study investigated the possibility of substituting rye flour, which is popular filler in the plywood industry, with various kinds of commercially available flours.

EXPERIMENTAL

Due to the fact that various types of flours are made from different raw materials, they were characterized by the different composition. The list of chemical components was provided by the suppliers and it is shown in Table 1. The composition of flours can determine among others their hydrophilic properties and reactivity.

Table 1. Composition of Various Kinds of Flours

Component	Type of flour				
	Rye	Hemp	Coconut	Rice	Pumpkin
	(g / 100 g of flour)				
Fat	2.8	10	10	1.8	14
Carbohydrates	51.2	42	18	77	4.2
Proteins	5.9	37	17	7.3	28
Dietary fibres	11.4	25	40	2	31

Besides of the chemical composition, the size of the flour particles is also very important. The right particle size allows a high level of homogenization of resin with added fillers and an even distribution of adhesive mixture on the surface of the veneer, which may determine the strength properties of plywood joints. In order to investigate the size of particles, flours were subjected to a sieve analysis (Table 2). The greatest percentage share of particles retained on the screen was with a mesh size of 0.63×0.63 mm^2. The second most abundant fraction was the one retained on 0.4×0.4 mm^2 screen. The fractions left on these screens constituted 66.5, 54.0, 67.2, 61.5, and 71.1% weight share for rye, hemp, coconut, rice, and pumpkin flours, respectively.

Table 2. Fractional Composition of the Investigated Flours

Mesh size (mm)	Type of flour				
	Rye	Hemp	Coconut	Rice	Pumpkin
	Sieve residue (%)				
1.25	1.71	1.29	1.95	0.74	1.39
1.00	6.98	10.44	5.22	2.51	3.31
0.80	14.22	18.61	15.85	13.74	12.61
0.63	41.78	30.86	47.47	44.38	42.28
0.40	24.69	23.08	19.76	17.11	28.81
0.25	8.36	12.29	8.56	14.78	9.89
< 0.25	2.26	3.44	1.19	6.75	1.71

The urea-formaldehyde resin purchased from Silekol (Kędzierzyn-Koźle, Poland) had the following characteristics: solid resin content of 68%, viscosity of 615 mPa.s, gel time of 65 s at 100 °C, pH 8.1, and density 1.28 g/cm^3. Rye flour was used as a reference filler because it is widely used in the plywood industry. Resin mixtures containing various kinds of flours were prepared as presented in Table 3. Ammonium nitrate (20 wt%) was added as a hardener.

Table 3. Variants and Composition of Adhesive Mixture

Variant Label	Type of Flour	Flour (g/100 g d. m. of resin)	H_2O (g/100 g d. m. of resin)	Hardener (g/100g d. m. of resin)
Ry	Rye flour	15	15	1
He	Hemp flour	15	15	1
Co	Coconut flour	15	15	1
Ri	Rice flour	15	15	1
Pu	Pumpkin flour	15	15	1

Note: “d. m.” stands for “dry matter”.

After the addition of fillers, the adhesive mixtures were subjected to a mechanical mixing process to achieve high level of homogenization. To determine the effect of flour-addition on the properties of adhesive the following tests were carried out: changes in viscosity for 6 h using a Brookfield DV-II + Pro viscometer (Middleboro, MA, USA), gel time at 100 °C in accordance with PN-C-89352-3 (1996), pH, and solid content according to EN 1245 (2011) and EN 827 (2005) methods. A three-layered experimental birch plywood sample was prepared from veneers with an average thickness of 1.5 mm and moisture content of 8%. The adhesive mixtures were applied at 170 g/m^2 on the surface of the veneers. After the opening time elapsed, the veneers were pressed at 120 °C and 1.4 MPa for 4 min. The following properties of plywood samples were determined:

- Shear strength (f_v) was tested both in dry and after soaking in water for 24 h according to EN 314-1 (2004),
- Bending strength (MOR) and modulus of elasticity (MOE) according to EN 310 (1993),

- Free formaldehyde content using a flask method according to EN 717-3 (1996).

The obtained results were subjected to the statistical analysis using the Tukey test with a significance level of $\alpha = 0.05$.

RESULTS AND DISCUSSION

The results presented in Table 4 show that the addition of various flours had an effect on the curing properties of the resin mixture. Using hemp, coconut, and rice flours caused considerable shortening of adhesive gel time, which can be beneficial, considering that pressing time can be important from the technological point of view (Mirski *et al.* 2011). The longer gel time in the case of rye and pumpkin flours addition was attributed to the proportional reduction of UF adhesive solids content. The reason for the differences in curing properties between adhesive mixtures with different types of flour was probably the chemical composition of flours, which determines their reactivity, and it will be investigated as a future work. The flour fillers did not greatly affect the pH of the mixtures. In the resin mixed with pumpkin flour, the pH was slightly lower.

Table 4. Properties of Adhesives Depending on the Variant

Variant	Gel time (s)	pH	Solid content (%)
Ry	81	7.86	60.09
He	68	7.73	65.13
Co	65	7.62	64.07
Ri	65	7.91	63.61
Pu	74	6.91	61.54

Figure 1 shows that regardless of the type of flour used as a filler, the viscosity of adhesive mixtures increased during the testing time. Major increases in viscosity occurred within the first two hours of measurements, and then the dynamics of growth systematically decreased.

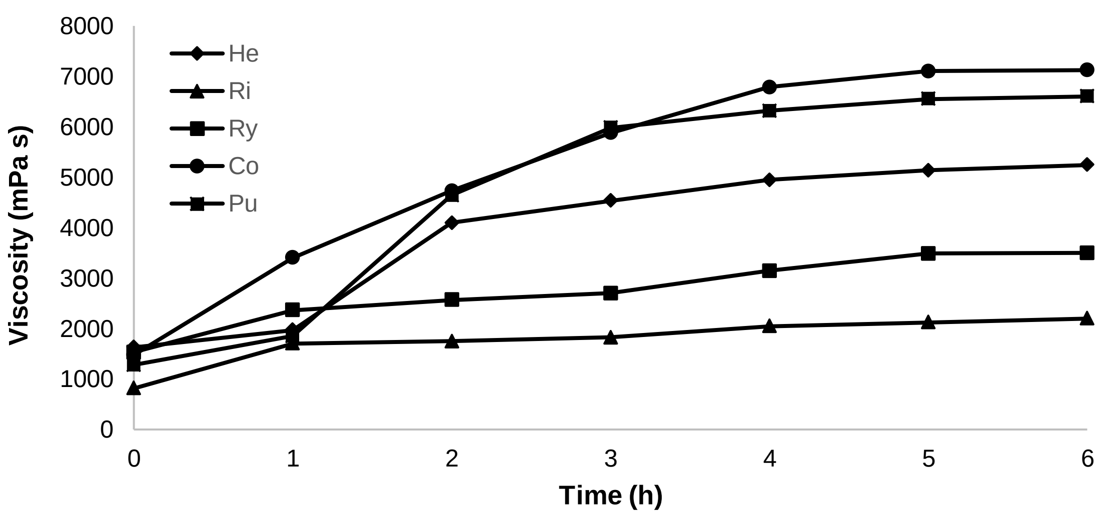


Fig. 1. Viscosity and its changes depending on the variant

Adhesive mixtures filled with coconut and pumpkin flours exhibited the highest viscosity. The high viscosity results from the strong hydrophilic properties of the filler. Both coconut and pumpkin flour were characterized by a very high content of dietary fiber, which is a highly hydrophilic component. It would be necessary to adjust their amount added to the resin for future work. The viscosity of the UF-rice flour mixture did not attain density values comparable to the control adhesive prepared by industrial methods. Similarly, as in case of the mixtures with the highest viscosity, the reason was the hydrophilicity of the filler. Contrary to coconut and pumpkin flour, rice flour contains very small amounts of water-absorbing dietary fiber. Low viscosity results in sinking of the adhesive into the surface of the veneer, and consequently, the amount of adhesive remaining on the veneer surface became insufficient to ensure high bonding quality. Moreover, due to the low level of viscosity the resin mixture cannot be evenly spread on the surface because it flows down into the cavities of the wavy veneer (Sellers 1989).

Figure 2 presents the bonding quality test data conducted with dry samples and with samples after soaking in water for 24 h according to EN 314-1 (2004). The type of flour added as a filler for UF resin had an effect on the shear strength of manufactured plywood. The best results were obtained for the variant with pumpkin and rye flours, and they remained at a very similar level. Major deterioration of bonding quality was noted for plywood glued with the mixture filled with coconut flour. The shear strength decreased by 19% and 16%, respectively, for samples tested dry and after soaking. However, the bonding quality of all plywood regardless of the type of filler used achieved good values exceeding 1.0 N/mm^2 and consequently met the requirements of EN 314-2 (1993).

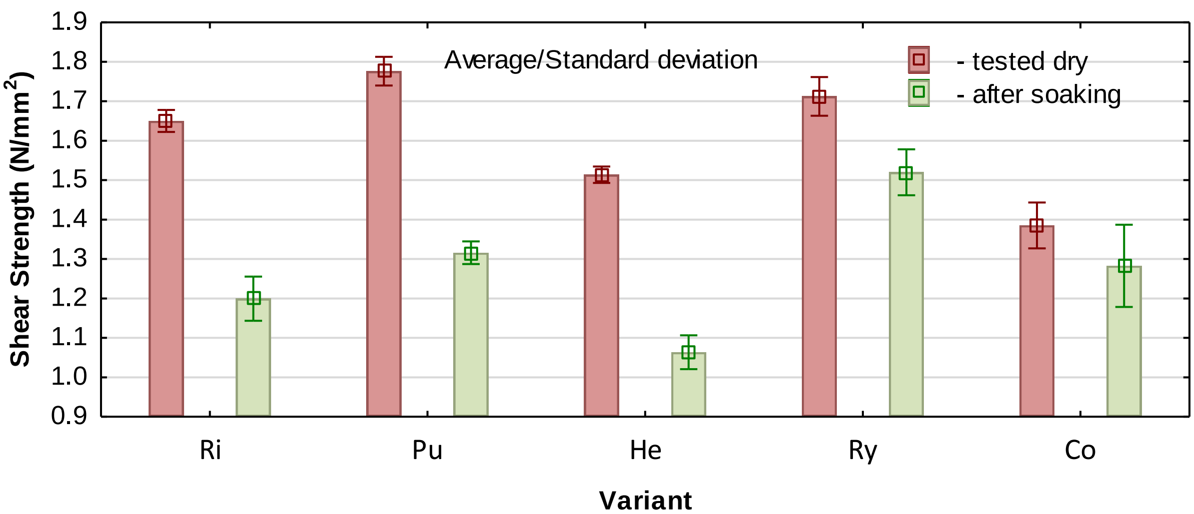
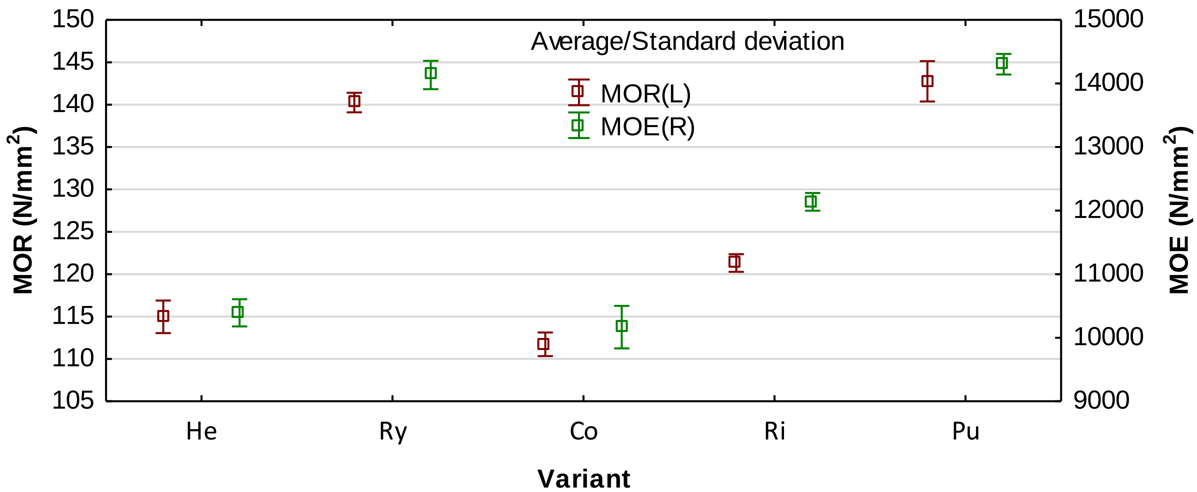
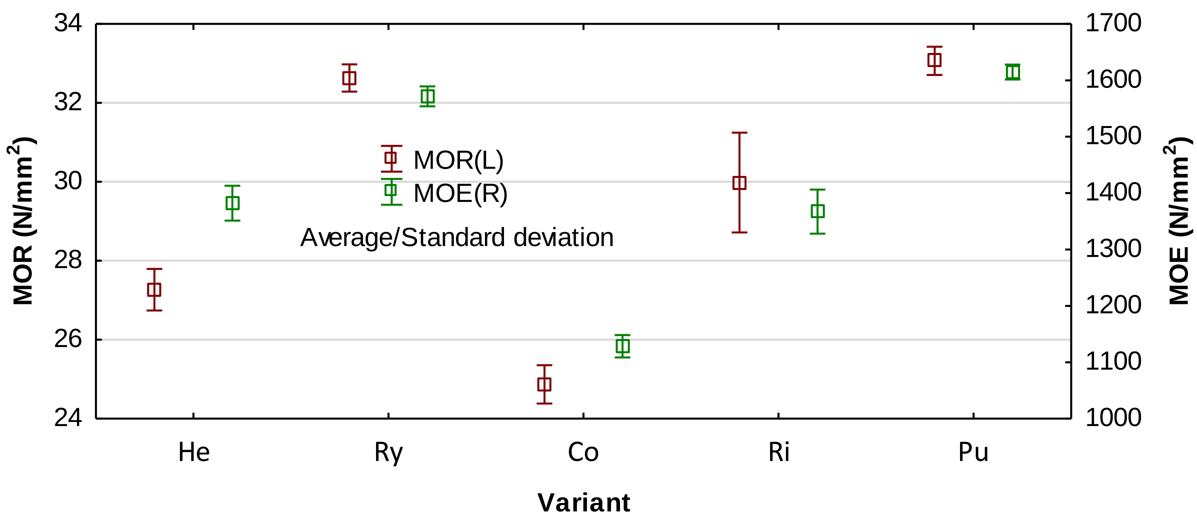


Fig. 2. Shear strengths of plywood samples depending on the variant

The mechanical properties such as bending quality (MOR) and modulus of elasticity (MOE) are shown in Fig. 3. The type of filler had a statistically significant effect on the mechanical behavior of plywood. Thus, these results were very similar to the bonding quality results. The best mechanical properties were obtained for plywood glued with pumpkin and rye flours (rye flour was used as a reference adhesive filler). The addition of coconut flour negatively affected and caused a major decrease of bending strength and MOE values obtained from both parallel and perpendicular to the grain of face layer. The addition of strongly hydrophilic coconut flour caused an increase of viscosity, and consequently the adhesive mixture was not evenly distributed on the surface of the veneer. Intensively swelling flour particles prevented the preparation of a homogeneous resin mixture and led to deterioration of bonding quality and modulus of elasticity. Moreover, the use of such a highly hydrophilic filler prevents water from evaporating and may hinder polycondensation of the adhesive (Mahrdt *et al.* 2016).



(a)



(b)

Fig. 3. Bending strength (MOR) and MOE values: (a) parallel and (b) perpendicular to the grains of face layer

Table 5. Formaldehyde Release from Plywood Depending on the Variant

Variant	Formaldehyde content (mg CH_2O/kg)
Ry	2.31
He	0.61
Co	2.65
Ri	2.47
Pu	2.17

Table 5 presents the results of the investigation on the effect of various kinds of flours addition as a fillers for UF resin on the formaldehyde emission from plywood. In all of the kinds of flours studied, the type of flour did not significantly affect the amount of formaldehyde emitted. However, introducing the hemp flour into the UF resin reduced the formaldehyde release by 26% in comparison to plywood glued with the control adhesive mixture filled with the rye flour. The reason for such a major reduction in the amount of emitting formaldehyde was most likely the composition of hemp flour. It contains very large amounts of proteins, and formaldehyde can combine with different kinds of functional groups found in proteins. It can react with such groups even at room temperature, forming a methylene bridge between them, which probably led to the observed reduction of the free formaldehyde content (French and Edsall 1945; Lukin and Bitiutskikh 2017).

CONCLUSIONS

1. The replacement of rye flour as a filler for UF resin with a various kinds of other flours had a significant effect on curing properties and rheological behavior of the adhesive. Using flour other than rye or pumpkin shortened the gel time of adhesive mixture. The addition of rice flour in the same amount as other flour did not provide the viscosity required for the production of plywood.
2. The type of flour used as filler had a significant effect on the mechanical properties such as bending strength, modulus of elasticity, and bonding quality of plywood. The best results were obtained for plywood glued with adhesive filled with pumpkin and rye flour. The addition of coconut flour led to major decreases in mechanical properties; however, all plywood samples met the requirements of EN 314-2 (1993).
3. Formaldehyde emission was significantly lowered by the addition of hemp flour as a filler for the adhesive.

ACKNOWLEDGEMENTS

This study was partially funded within the framework of Ministry of Science and Higher Education programme, ‘Regional Initiative of Excellence’ in years 2019-2022, Project No. 005/RID/2018/19.

REFERENCES CITED

Bekhta, P., Bryn, O., Sedliačik, J., and Novák, I. (2016). “Effect of different fire retardants on birch plywood properties,” *Acta Facultatis Xylologiae Zvolen* 58(1), 59-66.

Demir, A., Aydin, I., and Ozturk, H. (2018). “Formaldehyde release from plywood manufactured with two types of urea formaldehyde resins after fire retardant treatment of veneers,” *Drvna Industrija* 69(2), 193-199. DOI: 10.5552/drind.2018/1734

Dukarska, D. (2013). “The effect of an addition of nano-SiO_2 to urea resin on the properties of board manufactured from rape straw," *Annals of WULS-SGGW Forestry and Wood Technology* 82, 242-245.

Dukarska, D., and Czarnecki, R. (2016). "Fumed silica as a filler for MUPF resin in the process of manufacturing water-resistant plywood," *European Journal of Wood and Wood Products* 74(1), 5-14. DOI: 10.1007/s00107-015-0955-4

Dziurka, D., Brachaczek, N., Jastrząb, M., and Kalinowski, T. (2017). "Effects of a method of introducing a fire retardant on bond quality of experimental plywood," *Annals of WULS-SGGW Forestry and Wood Technology* 99, 32-36.

EN 1245 (2011). "Adhesives – determination of pH," European Committee for Standardization, Brussels, Belgium

EN 310 (1993). "Wood-based panels - Determination of modulus of elasticity in bending and of bending strength," European Committee for Standardization, Brussels, Belgium

EN 314-1 (2004). "Plywood - Bonding quality Test methods," European Committee for Standardization, Brussels, Belgium

EN 314-2 (1993). "Plywood - Bonding quality Requirements," European Committee for Standardization, Brussels, Belgium

EN 717-3 (1996). "Wood-based panels - determination of formaldehyde release - part 3: formaldehyde release by the flask method," European Committee for Standardization, Brussels, Belgium

EN 827 (2005). "Adhesives – determination of conventional solid content and constant mass solids content," European Committee for Standardization, Brussels, Belgium

French, D., and Edsall, J. T. (1945). "The Reactions of formaldehyde with amino acids and proteins," *Advances in Protein Chemistry* 2, 277-335. DOI:10/1016/S0065-32339(08)60627-0.

Lukin, A., and Bitiutskikh, L. (2017). "On potential use of hemp flour in bread production," *Bulletin of the Transylvania University of Brasov Series II: Forestry, Wood Industry, Agricultural Food Engineering* 10(59), 114-118.

Luo, J., Luo, J., Gao, Q., and Li, J. (2015). "Effects of heat treatment on wet shear strength of plywood bonded with soybean meal-base adhesive," *Industrial Crops and Products* 63, 281-286.

Kawalerczyk, J., Dziurka, D., Mirski, R., and Grześkowiak, W. (2019). "The effect of veneer impregnation with a mixture of potassium carbonate and urea on the properties of plywood," *Drewno* 62(203), 107-116. DOI: 10.12841/wood.1644-3985.281.12

Mahrdt, E., Pinkl, S., Schmidberger, C., Van Herwijnen, H. W. G., Veigel, S., and Gindl-Altmutter, W. (2016). "Effect of addition of microfibrillated cellulose to urea-formaldehyde on selected adhesive characteristics and distribution in particle board," *Cellulose* 23(1), 571-580. DOI: 10.1007/s10570-015-0818-5

Mirski, R., Dziurka, D., and Łęcka, J. (2011). "Potential of shortening pressing time or reducing pressing temperature for plywood resinated with PF resin modified using alcohols and esters," *European Journal of Wood and Wood Products* 69, 317-323. DOI: 10/1007/s00107-010-0436-8

Pawlak, D., and Boruszewski, P. (2018). "Influence of addition of microfibrillated cellulose (MFC) on selected properties of low-density particleboard," *Annals of WULS-SGGW Forestry and Wood Technology* 102, 139-148. DOI:

PN-C-89352-3 (1996). "Wood adhesives test methods – Determination of gelation time," Polish Committee for Standardization (in Polish).

Pourafshar, S., Rosentrater, K.A., and Krishnam P.G. (2015). "Using alternative flours as partial replacement of baribari bread formulation (traditional Iranian bread)," *Journal of Food Science and Technology* 52(9), 5691-5699.DOI: 10.1007/s13197-014-1640-z

Ružiak, I., Igaz, R., Krišťák, L., Réh, R., Mitterpach, J., Očkajová, A., and Kučerka, M. (2017). "Influence of urea-formaldehyde adhesive modification with beech bark on chosen properties of plywood," *BioResources* 12(2), 3250-3264. DOI: 10.15376/biores.12.2.3250-3264

Sellers, T. (1989). "Diiscyanate/furfural adhesives for bonding plywood," *Forest Product Journal* 39, 53-56.

Xiaona, L., Jingjing, L., Jianzhang, L., and Qiang, G. (2015). "Effect of sepiolite filler in melamine-urea-formaldehyde resin on the properties of three-ply plywood," *BioResources* 10(4), 6624-6634. DOI: 10.15376/biores.10.4.6624-6634

Zhang, H., Zhang, J., Song, S., Wu, G., and Pu, J. (2011). "Modified nanocrystalline cellulose from two kinds of modifiers used for improving formaldehyde emission and bonding strength of urea-formaldehyde resin adhesive," *BioResources* 6(4), 4430-4438. DOI: 10.15376/biores.6.4.4430-4438

Article submitted: April 25, 2019; Peer review completed: June 17, 2019; Revised version received and accepted: July 2, 2019; Published: July 3, 2019.
DOI: 10.15376/biores.14.3.6727-6735