Effects of Using Bark Particles with Various Dimensions as a Filler for Urea-formaldehyde Resin in Plywood

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The possibility of replacing the rye flour commonly used as a filler for urea-formaldehyde resins was investigated for plywood production with birch bark characterized by various particle dimensions. The effects on the curing and rheological properties of the adhesives were investigated. Moreover, the plywood was tested to evaluate the formaldehyde emissions, bonding quality, modulus of elasticity, and bending strength. The results showed that the size of the bark particles had a significant effect on the viscosity of the adhesives but did not affect other properties of the resin. Replacing the flour with the bark significantly decreased the formaldehyde release, but there was no clear correlation with the dimensional fraction of the bark powder. The particle size had notable effects on bonding quality and mechanical properties. The best results were obtained for a sieve with square holes whose inside lengths were 0.315; however, all plywood samples achieved shear strength values exceeding the requirements of EN 314-2 (1993).

Keywords: Bark; Filler; Urea-formaldehyde; Plywood

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INTRODUCTION

Worldwide, the woodworking industry generates much waste, including shreds, sawdust, and bark (Cichy 2012). Still, the most common use of bark is as a fuel, incinerated in boilers (Pedieu *et al*. 2008). Due to its low heat production in comparison with solid wood and its high ash content, bark is not the most suitable material for energy production. Nevertheless, the chemical composition and abundance of unused bark create opportunities in many industries. Gupta (2009) reported that North American forest industries produce at least 50 million tons of bark annually. In addition to its availability, its advantages include a high amount of phenolic components and its fibrous nature (Aydin *et al*. 2017). It has not yet found wider industrial use possibly due to its complexity and the variability of its chemical components.

There is active research on substituting wood in particleboard's production (Dukarska *et al*. 2015; Mirski *et al*. 2018), and bark has great potential in the wood-based materials industry. Blanchet *et al*. (2008) showed that it is possible to manufacture particleboard with the incorporation of black spruce bark with a short curing time in a pressing schedule. Furthermore, Sahin and Arslan (2011) demonstrated that red pine bark is also a suitable material for particleboard production. They also pointed out that continuing research on using forest residues in wood-based materials production could lead to practices that mitigate raw wood shortages. According to the results obtained by Medved *et al*. (2019), substitution of wood particles with bark can decrease the formaldehyde release, which is a very desirable effect. In addition to its application in particleboard manufacturing, bark can also be used in the production of adhesives. For years, the bark has been intended to extraction process to obtain tannins, which are commonly used compounds in wood adhesives. However, Nakamoto *et al*. (2011) developed a method of producing bark powder with high tannin content excluding the expensive extraction process. Since then, technology assuming the use of bark particles in the wood adhesives industry is still developing (Matsumae *et al*. 2019).

An interesting concept for bark application is to introduce it as a filler to amino resins. Urea-formaldehyde (UF) adhesives have many advantages, and they remain one of the most popular binding agents (*e.g*., in plywood production) (Dziurka and Mirski 2010; Dziurka and Mirski 2014; Kawalerczyk *et al*. 2019a). Fillers are usually lignocellulosic or inorganic particles that are non-volatile, non-gluing, and insoluble in the adhesives. They are mixed with resins to adjust their viscosity, improve the strength properties of glue joints, and reduce the absorption of the adhesive mixture into the porous surface of the veneer. Ružiak *et al*. (2017) investigated the effect of beech bark addition to UF resin on the properties of plywood. Their results showed that the replacement of flour with bark led to a significant decrease of formaldehyde emissions, increased mechanical properties, and decreased water absorption. Moreover, Aydin *et al*. (2017) investigated the possibility of using bark obtained from walnut, chestnut, fir, and spruce instead of wheat flour in plywood production. It was found that the replacement yielded satisfying results, especially with the chestnut and fir barks, which worked efficiently as formaldehyde scavengers. Réh *et al*. (2019) revealed that introducing beech bark to the adhesive mixture slightly decreased heat transfer during the pressing cycle. Furthermore, using bark particles as filler for UF resin did not affect the modulus of elasticity and bonding quality. In all the aforementioned studies, the authors investigated the effects of the wood species from which the bark was obtained and the amount of added filler. However, in each work, the bark particles introduced into the resin had different dimensions, which might affect the properties of the manufactured material. Thus, the aim of this study was to find the dimensional fraction of added particles to achieve the optimal reinforcement effect.

EXPERIMENTAL

An industrial UF resin (Pfleiderer Silekol, Kędzierzyn-Koźle, Poland) was used, and the applied adhesive had the following properties: a solid resin content of 69%, a viscosity of 610 mPa·s, a gel time at 100 °C of 69 s, a pH of 8.09, and a density of 1.282 g/cm^3. Reference samples were glued with an adhesive mixture filled with rye flour in accordance with industrial formulations, with 20 g of flour per 100 g of dry matter of resin. The birch bark used in this study was purchased from a local sawmill processing birch timber. The obtained bark was washed in water to eliminate mineral particles and then dried in a laboratory oven to a moisture content of 6% ± 2%. After drying, the bark was disintegrated into particles using a grinder. The obtained bark powder was subjected to a sieve analysis using a mechanical sieve shaker to investigate the average size of the particles (Fig. 1).

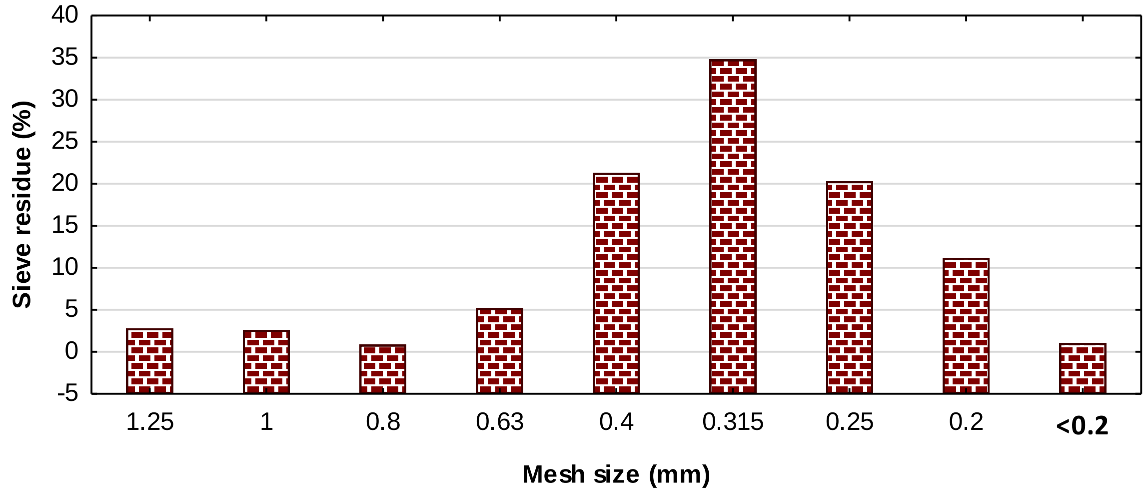

Fig. 1. Fractional composition of ground birch bark

The most abundant fractions were bark particles retained on the screens with mesh sizes of 0.315, 0.4, 0.25, and 0.2 mm× mm; they were used in the further stages of the experiment to manufacture plywood labeled with the corresponding dimensions. After the sieve analysis, bark powders with previously known particle dimensions were added to the adhesive mixture at 20 wt% per 100 g of dry matter of resin. The amount of introduced filler was adjusted based on the authors' previous research (Mirski *et al*. 2019). Resin filled with bark was mixed with NH_4NO_3 (20 wt%), used as a hardener at a ratio of 2 g per 100 g of adhesive dry matter, using a magnetic stirrer (600 rpm, 5 min) to obtain a homogeneous mixture.

To investigate the effects of the addition of the birch bark characterized by various dimensions on the properties of the UF resin mixture, the following parameters were measured: viscosity and its changes at 20 °C for 6 h (Brookfield DV-II+Pro viscometer, Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA), gel time at 100 °C (according to Polish standard PN-C-89352-3 1996), pH (according to EN 1245 2011), and solid content (according to EN 827 2005).

The experimental plywood was produced from three layers of rotary-cut veneer sheets of birch with dimensions of 320 mm × 320 mm and an average thickness of 1.5 mm. After conditioning to a moisture content of 7%, the adhesive mixture was applied in the amount of 170 g/m^2 on the surfaces of the prepared veneers. The veneers were hot pressed using a unit pressure of 1.4 MPa for 4 min at 120 °C in a laboratory press. Next, the manufactured plywood was tested to evaluate the following properties: formaldehyde emission, using the flask method according to EN 717-3 (1996); bonding quality, according to EN 314-1 (2004) in the shear test performed on both dry samples and samples previously soaked in water for 24 h as required by EN 314-2 (1993); and bending strength (MOR) and modulus of elasticity (MOE), according to EN 310 (1993), parallel and perpendicular to the grains of the face layers.

To fully evaluate the effects of using birch bark as a filler for UF resin and, moreover, to identify the dimensional fraction for optimal properties, the results were statistically analyzed using the Tukey test with a significance level of $\alpha = 0.05$.

RESULTS AND DISCUSSION

Figure 2 presents the changes of viscosity during 6 h of testing. In both the reference and bark-filled adhesive mixtures, regardless of particle size, the changes could be considered linear, so the resins were acting as Newtonian fluids. In addition to the filler's hydrophilic properties, the increase in viscosity over time was also caused by the progressing polycondensation of the UF resin (Réh *et al*. 2019). Resin filled with bark powders from the dimensional fractions 0.4 and 0.315 achieved viscosity values less than those of the reference mixture. The viscosity of the mixture containing fraction 0.315 was acceptable, and it was possible to evenly spread it on the surface of the veneer. However, adhesives filled with bark characterized by greater dimensions did not achieve the required viscosity and would be difficult to use in practice without adjusting the amount of introduced filler. When the viscosity of an adhesive is too low, it can sink into the veneer during application and pressing; consequently, the layer remaining on the surface is insufficient to ensure good glue joint properties (Kawalerczyk *et al*. 2019b). Urea-formaldehyde resins with added bark particles with sizes of 0.2 and 0.25 achieved greater viscosities than the control mixture, and it was difficult to evenly apply the adhesives on the veneer surfaces. The increase in viscosity was probably due to the high density of bark powder containing particles with small sizes and the formation of agglomerates.

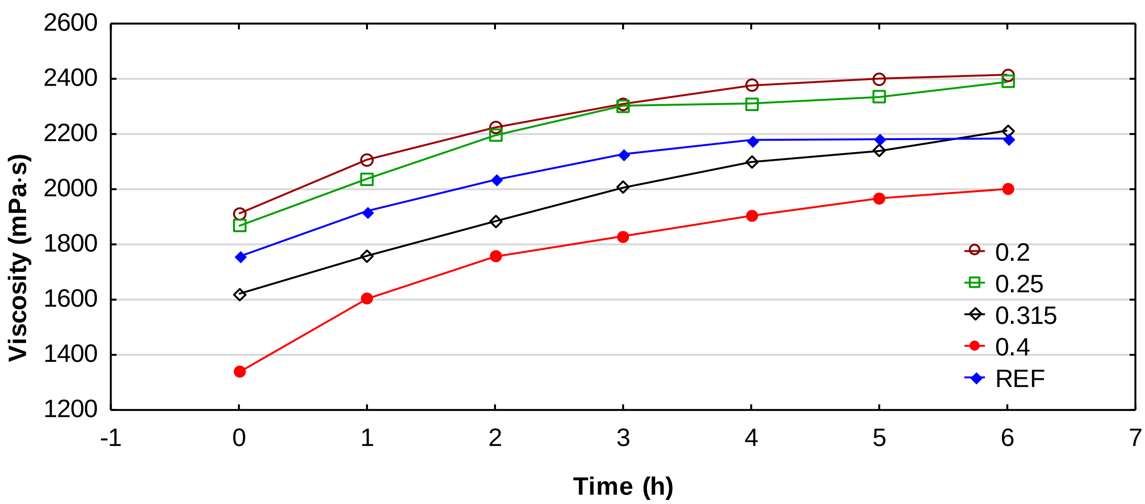

Fig. 2. Viscosities of adhesive mixtures and changes over 6 h

Properties of the adhesive mixtures filled with both rye flour and bark powder are summarized in Table 1. Based on this data, the replacement of flour with bark did not affect the solid content of the resin. However, the introduction of bark instead of flour slightly decreased the pH and decreased the gel time. The decreased pH may contribute to accelerating the gel time because the condensation of UF resin occurs under acidic conditions (Kawalerczyk *et al*. 2019c). This effect may be beneficial if it decreases the pressing time, which should be minimized to maximize production efficiency (Mahrdt *et al*. 2016). However, it appeared that the size of the particles introduced into the resin did not affect the aforementioned properties.

Table 1. Properties of Adhesive Mixtures

Variant Label	pH	Solid Content (%)	Gel Time (s)
REF	7.9	67.58	82
0.2	6.1	66.91	74
0.25	6.7	67.11	77
0.315	6.3	67.05	76
0.4	6.1	68.23	73

To investigate the effects of substituting rye flour with bark powder on the formaldehyde emissions in the manufactured plywood, proper tests using the flask method were performed. Due to potential carcinogenicity, formaldehyde is categorized more restrictively than most other pollutants (Salem *et al*. 2013; Demir *et al*. 2018). As shown in Fig. 3, the addition of bark powder decreased the formaldehyde release, which indicates bark as a bio-based scavenger, as expected from previous studies (Hoong *et al*. 2010; Gangi *et al*. 2013). The decrease in formaldehyde emissions was due to the high amount of tannins in the bark. Condensed polyflavonoid tannins of the bark, because of their phenolic nature, can easily undergo reactions with formaldehyde under both acidic and alkaline conditions (Jahanshaei *et al*. 2012). Furthermore, formaldehyde reacts with tannins to produce polymerization through methylene bridge linkages to reactive positions of the flavonoids molecules (Pizzi 1979). However, there was no clear, linear tendency in the effect of particles size on the formaldehyde emissions. The greatest decrease (approximately 17%) was observed in the glue joint made of adhesive mixed with bark of the 0.25 dimensional fraction. With further decrease of the particle sizes, there was a slight increase in the amount of emitted formaldehyde. As reported by Ayrilmis *et al*. (2016), this can be caused by aggregation of the particles.

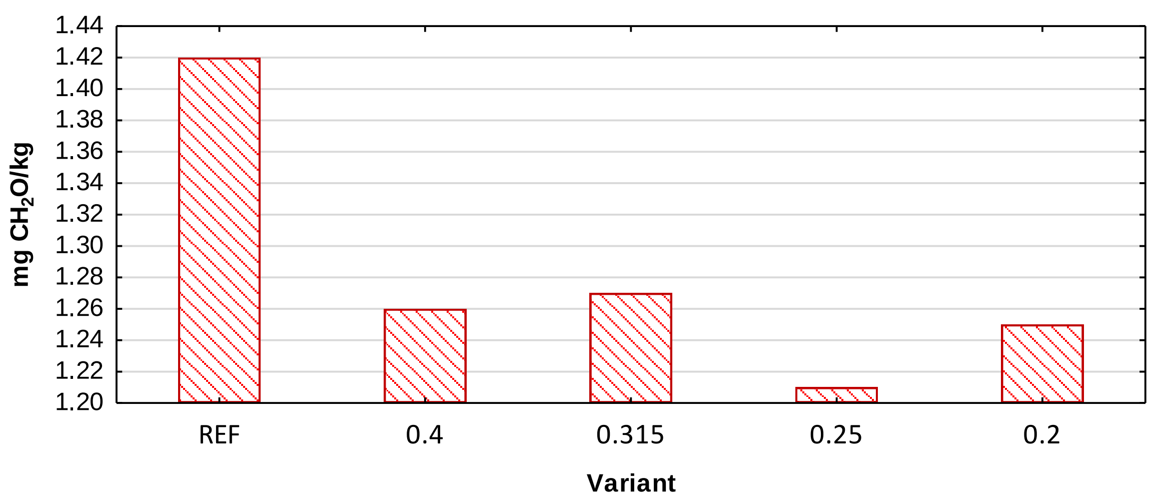

Fig. 3. The amount of formaldehyde emitted from the plywood

Figure 4 shows the results of the shear strength test, which is a fundamental indicator of the resin behavior in plywood (Bekhta *et al*. 2016). Compared to the reference plywood, the plywood glued with bark-filled adhesive mixtures showed a slight decrease in bonding quality, contrary to the study of Réh *et al*. (2019) on beech bark.

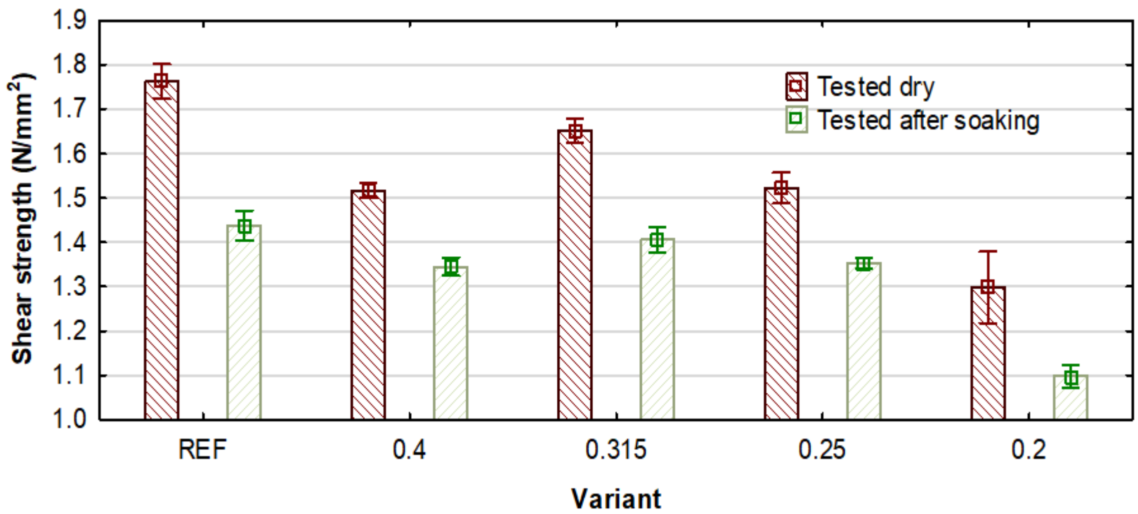

Fig. 4. Shear strength of plywood

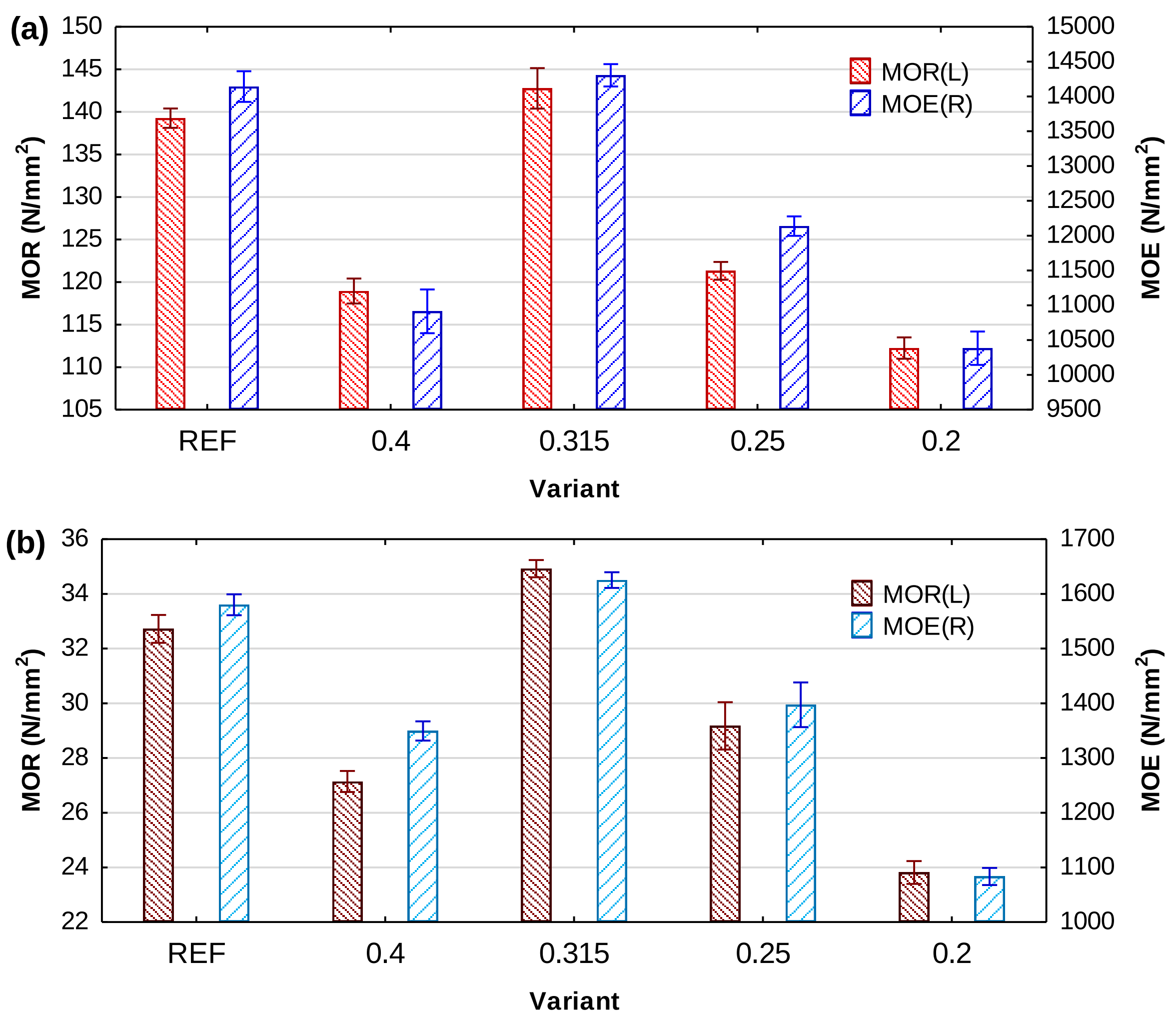

Fig. 5. MOR and MOE results: (a) parallel and (b) perpendicular to the grains of the face layer

However, after further analysis, it was concluded that for the 0.315 size fraction, the changes were not statistically significant (the p-values were 0.4194 and 0.8914 for the samples tested dry and after soaking, respectively). The greatest decreases were observed with the 0.2 dimensional fraction (26.3% and 23.6% for the samples tested dry and after soaking, respectively). The decreases in shear strength were probably due to the viscosity being too great, which caused some difficulties when applying the adhesives on the veneer surfaces. Moreover, excessively high viscosity can indicate a lack of water in the mixture, and water reacts with hydroxymethyl and isocyanate groups in UF resin during crosslinking and enhances joint strength. Regardless of the dimensional fraction of the bark powder, all plywood samples achieved good shear strength values exceeding 1.0 N/mm^2, as required by EN 314-2 (1993).

As shown in Fig. 5, bark powder of dimensional fraction 0.315 could be used instead of rye flour to manufacture plywood with equally good mechanical properties. In this case, the results were slightly better in comparison to the control samples. However, the values achieved for every other variant were significantly lower than those of the reference samples. This result was probably due to the viscosities and homogenization levels of the adhesive mixtures. Viscosity being too low or too great made it impossible to evenly distribute the resin on the veneer surfaces and consequently decreased the mechanical properties. The adhesive mixture filled with bark of the 0.315 dimensional fraction had a similar viscosity to the reference mixture. In this case, good rheological properties allowed for even application and resulted in joints with the greatest strength values.

CONCLUSIONS

1. The bark particle size significantly affected the viscosity of the adhesives. The best results were obtained for dimensional fraction 0.315, and they were very similar to the reference samples prepared in accordance with industrial formulations.
2. Using different dimensional fractions of bark powder as fillers for UF resin did not affect the pH level, solid content, and gel time.
3. Birch bark may be used as a formaldehyde scavenger for UF resins in plywood production; however, the size of the particles had no effect on the amount of emitted formaldehyde.
4. Bonding quality, MOR, and MOE depended on the dimensional fraction of the filler. The best results, very similar to those of the control samples, were obtained for fraction 0.315. All plywood samples achieved shear strength values exceeding the requirements of EN 314-2 (1993).

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