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The possible reduction of phenol-formaldehyde resin spread rate by its nanocellulose-reinforcement in plywood manufacturing process

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Abstract: *The possible reduction of phenol-formaldehyde resin spread rate by its nanocellulose-reinforcement in plywood manufacturing process.* The aim of the study was to investigate the possibility of phenol-formaldehyde (PF) resin consumption in plywood by its reinforcement with cellulosic nanoparticles (NCC). In order to determine the possible reduction of resin spread rate bonding quality was assessed both after boiling in water for 24h and after ageing test including i.e. boiling in water. Studies have shown that the addition of nanocellulose made it possible to significantly reduce the amount of the applied adhesive. Reference samples were characterized by similar shear strength values to experimental plywood manufactured with the adhesive application of 140 g/m^2. NCC-reinforcement resulted also in the increase of mechanical properties such as modulus of elasticity and bending strength. The analysis of the data confirmed the tendency observed during bonding quality evaluation and it was concluded that resin modification allowed to reduce its spread rate by 30 g/m^2.

Keywords: nanocellulose, phenol-formaldehyde adhesive, filler, plywood

INTRODUCTION

Global wood-based materials production reached 416 million m^3 in 2016. There was a 4% and 24% increase in comparison with 2015 and 2012, respectively (FAO 2017). Particleboards, OSB boards, MDF boards and plywood stand out as currently the most popular on the market and plywood production dominates other wood-based materials in the Asia-Pacific region (mainly in China). Its widespread use is due to the unique properties resulting from the layered construction (Kawalerczyk et al. 2019a). Thanks to its great mechanical properties and increased water resistance plywood finds the application e.g. in furniture, buildings, automotive industry etc. (Poljansek et al. 2005). There are two main factors determining the properties of manufactured plywood such as the quality of veneers and the type of adhesive used in the production process (Kawalerczyk 2019b). Urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-urea-formaldehyde resins (MUF) are the most commonly used in the industry (Ong et al. 2018). PF adhesive due to its water resistance and chemical stability finds the application for gluing materials intended for the use in variable weather conditions.

For plywood production, adhesive formulation consists of resin and filler. The purposes of introducing various kinds of fillers are to regulate viscosity, support bonding between components, and reduce penetration of resin into porous surface of veneer (Reh et al. 2019). In recent years, an interesting concept of using cellulosic particles as filler for wood adhesives became popular. Among others bio-based polymers, it is the most abundant renewable biomaterial (Klemm et al. 2005; Vineeth et al. 2019). Cellulose is a linear condensation polymer which forms the basic materials of all plants fibers. Individual cellulose nanocrystals (NCC) are obtained by breaking down cellulosic chains and isolating the crystalline regions. The crystalline parts have estimated strength of around 10 GPa and modulus of elasticity in the range of 138 GPa (Zimmerman et al. 2004, Veigel et al. 2011). Many studies have been carried out in order to investigate the potential application of NCC as a reinforcing agent for various wood adhesives. According to Veigel et al. (2012) the addition of cellulosic nanoparticles can affect properties of both liquid and cured adhesives. The introduction of NCC led to elongation of gel time and an increase in the viscosity of UF resin. Similar observations regarding viscosity were noted by Atta-Obeng et al. (2013) in case of PF resin reinforcement, moreover, the modification led to the reduction of the cure temperature by 4°C. Zhang et al. (2011) investigated the possibility of using modified nanocrystalline cellulose in order to improve properties of manufactured plywood glued with UF resin. Studies have shown a significant improvement in bonding quality and free formaldehyde content. Furthermore, Veigel et al. (2011) conducted research about the effect of cellulose nanofibrils on the specific fracture energy of wood-adhesive bonds. Based on the increase of toughening effect up to 45% it was found that NCC is suitable as a reinforcing agent for UF resin.

Considering many successful research on the nanocellulose applications in adhesives and constant striving for the reduction of resin spread rate in wood-based materials production, the aim of the study was to investigate the possibility of lowering the amount of applied PF resin in plywood by its nanocellulose-reinforcement.

MATERIALS AND METHODS

The resin used for the research purposes was PF resin with following characteristic: no. 4 For Cup viscosity of 153 s, solid content of 48%, gel time at 130°C 190 s, pH 12.5, density of 1.22 g/cm^3. Nanocrystalline cellulose (NCC) was purchased from Nanografi Nanotechnology Co. Ltd. (Ankara, Turkey) and characterized by following particle sizes declared by the producer: 300–900 nm in length and 10–20 nm in width. In order to make viscosity of resin mixtures suitable for plywood production, a tannic filler (UT-10) containing chalk and mimosa tannins was added. Formulations of reference and experimental variants are presented in Table 1.

Table 1. Compositions of adhesive mixtures

Variant	Quantity (g / 100 g of PF resin dry matter)	
	UT-10	NCC
Reference	20	0
Experimental	17	3

After the addition of fillers, mixtures were homogenized at 1000 rpm for 3 minutes with the use of CAT-500 homogenizer. Three-layered plywood was manufactured from birch veneers with average thickness of 1.5 mm and moisture content of 6±1%. Reference plywood according to industrial formulations were manufactured with the adhesive application in the amount of 170 g/m^2 and was labeled as 170 REF. Experimental panels were produced with various resin spread rate: 170, 160, 150, 140, 130, 120 (g/m^2). The plywood was hot-pressed under the following conditions: unit pressure 1.4 MPa, temperature 140°C, pressing time 4 min.

The evaluation of possible reduction of resin spread rate during plywood production was made based on i.e. bonding quality which is a common indicator for adhesives behavior according to EN 314-1 (2004). Tests were performed on samples after pretreatment process in accordance with EN 314-1 (2004) including soaking in water for 24 h and after ageing test involving boiling in water for 4 h followed by drying in laboratory oven for 18 h at 60°C, second boiling in water for 4 h and cooling in water at 20°C for 1 h. Moreover, to fully investigate mechanical properties of plywood bending strength (MOR) and modulus of elasticity (MOE) test was carried out according to EN 310 (1993) parallel and perpendicular to the grains of face layer. Obtained values were subjected to statistical analysis using Tukey test on the significance level $\alpha = 0.05$.

RESULTS AND DISCUSSION

The obtained results of shear strength tests conducted both after soaking and after boiling are summarized in Figure 1. An analysis of presented data confirmed that the introduction of cellulosic particles had a significantly beneficial effect on the bonding quality of plywood. Shear strength increased through the adhesive modification by 17% and 14% after soaking and boiling, respectively. Singha et al. (2008) reported that the reinforcement effect is due to chemical bonding between the methylol groups of PF resin and the hydroxyl groups of cellulose.

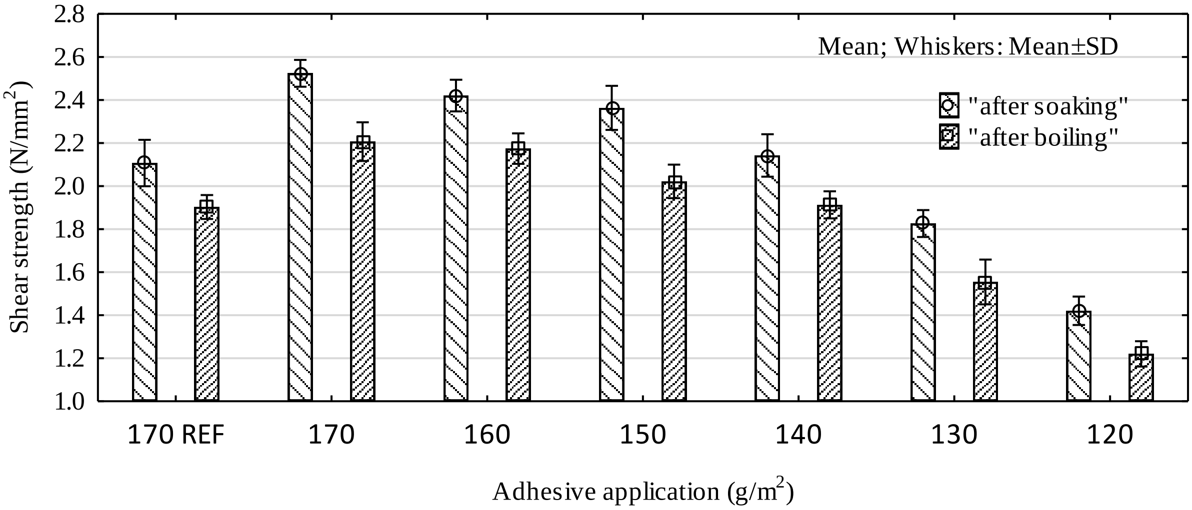
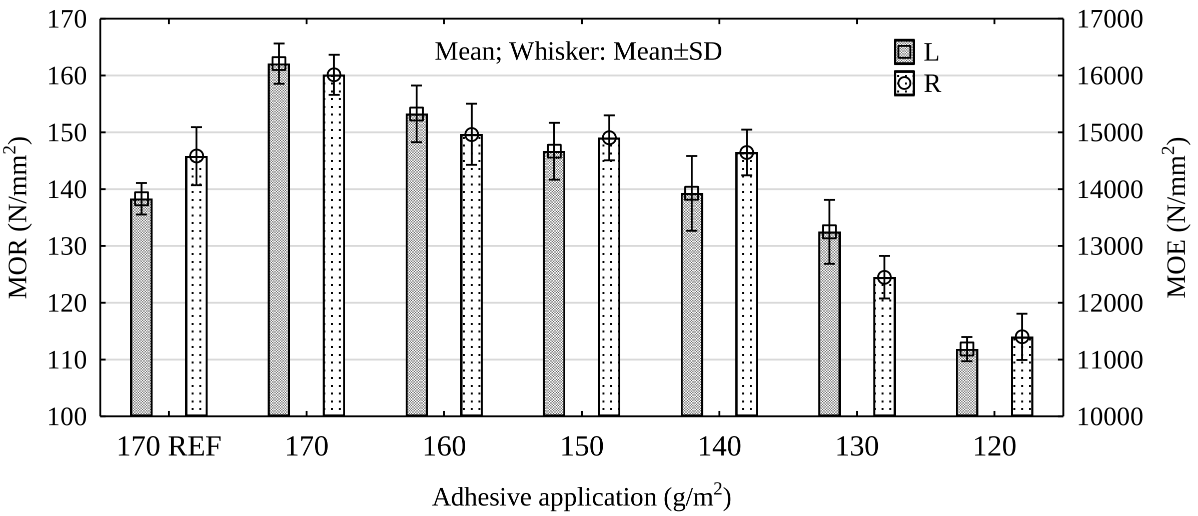


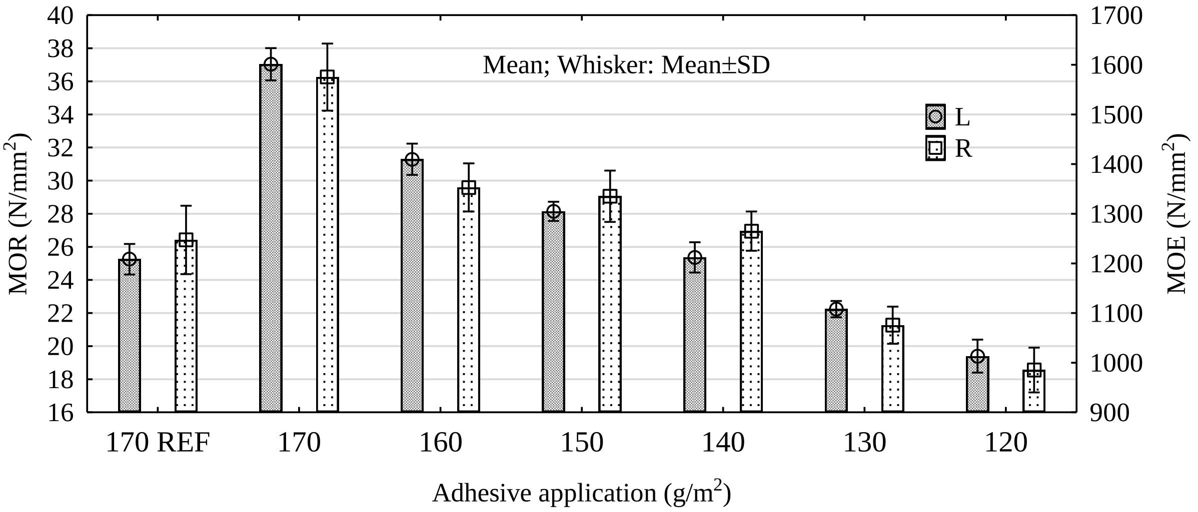
Figure 1. Shear strength of plywood

A reduction in resin spread rate led to a considerable deterioration of bonding quality. As can be seen in the graph, there is a clear tendency that as the amount of modified adhesive decrease, the shear strength values also decreased. Bekhta et al. (2007) reported that bonding quality of plywood deteriorates with lowering adhesive application because the amount of glue is insufficient to fully cover the veneer surface and to create cured glue line of a necessary thickness. The addition of NCC to PF resin allowed to reduce its spread rate. Reference plywood manufactured with glue consumption of 170 g/m^2 had as good glue joint properties as plywood glued with modified resin applied in the amount of 140 g/m^2. The quantity of 30 g of glue per square meter of veneer is a major reduction which can reduce production costs. The effect of NCC addition was similar to the results obtained by Dukarska and Czarnecki (2016) because of MUPF adhesive modification with fumed silica. Each of manufactured plywood achieved values exceeding 1 N/mm^2 required by EN 314-2 (1993).

Figure 2 presents the effect of PF resin modification on a possible decrease of adhesive spread rate. Both bending strength (MOR) and modulus of elasticity (MOE) results confirmed the tendency obtained in bonding quality investigations.



(a)



(b)

Figure 2. Bending strength (MOR) and modulus of elasticity (MOE) tested: (a) parallel and (b) perpendicular to the grains of face layer

The determined mechanical properties of plywood glued with reference resin mixture in the amount of 170 g/m^2 had similar properties as the samples manufactured with the use of NCC-reinforced glue in the amount of 140 g/m^2. Liu et al. (2014) reported that even non-modified PF resin can improve the modulus and hardness of wood cell walls by migration into the cell lumens. Moreover, it was concluded that modification of PF adhesive with cellulosic nanoparticles led to an extension of the migration far from the glue line and significant improvement of mechanical properties of glue joints. Thus, the significant increase of cured adhesives strength allowed the reduction of applied resin amount by 30 g/m^2 without the deterioration of plywood properties.

CONCLUSIONS

1. The modification of PF resin with nanocellulose led to a significant improvement in mechanical properties of cured adhesives.
2. Shear strength of the experimental plywood glued with the resin whose spread rate was 140 g/m^2 was as good as the reference plywood manufactured with an adhesive with consumption in the amount of 170 g/m^2.

3. Reinforcement of PF adhesive with cellulosic nanoparticles made it possible to manufacture plywood with equally good bending strength and modulus of elasticity values while reducing resin spread rate by about 30 g/m^2.

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Streszczenie: *Możliwość obniżenia ilości nanoszonej żywicy PF w produkcji sklejki poprzez jej modyfikację z wykorzystaniem nanocelulozy*. Celem badań było określenie możliwości obniżenia ilości nanoszonej na forniry żywicy fenolowo-formaldehydowej (PF) poprzez jej modyfikację z wykorzystaniem nanocelulozy. Zbadana została jakość sklejenia sklejki zarówno po moczeniu w wodzie przez 24 h, jak i po gotowaniu. Na podstawie otrzymanych wyników stwierdzono, iż nanomodyfikacja żywicy pozwoliła na zmniejszenie ilości mieszaniny klejowej nanoszonej w procesie produkcyjnym sklejki. Próbki referencyjne charakteryzujące się naniesieniem w ilości 170 g/m^2 osiągnęły wartości na poziomie próbek wytworzonych z naniesieniem modyfikowanej żywicy w ilości 140 g/m^2. Dodatek nanocelulozy spowodował również poprawę właściwości mechanicznych sklejki takich jak moduł sprężystości czy wytrzymałość na zginanie. Na podstawie uzyskanych wyników stwierdzono, iż wprowadzenie nanocząstek do żywicy PF pozwoliło na obniżenie ilości nanoszonej żywicy o 30 g/m^2.

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