

# The Effect of Nanocellulose Addition to Phenol-formaldehyde Adhesive in Water-resistant Plywood Manufacturing

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This study examined the effect of applying cellulose nanoparticles as a filling material for phenol-formaldehyde (PF) resin in the process of manufacturing water-resistant plywood. Based on investigations that concerned the rheological behavior of resin mixture containing various amounts of nanofiller, the modification of resin resulted in a major increase of viscosity. Although Fourier transform infrared spectroscopy did not fully explain the effect of modification on the chemical structure of the adhesive, there was a noticeable improvement in the morphology of cured nanocellulose-reinforced resin. Based on the bonding quality results, the optimum amount of nanocellulose was 3 PBW (parts by weight) per 100 PBW of resin and it allowed the achievement of a notable increase in shear strength values. Moreover, introduction of cellulosic nanoparticles had a positive effect on mechanical properties such as bending strength and modulus of elasticity. In summary, the research showed that it is possible to apply nanocellulose as a modifier for the adhesives in the process of manufacturing water-resistant plywood.

*Keywords:* Phenol-formaldehyde adhesive; Nanocellulose; NCC; Plywood; Filler; Resin

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## INTRODUCTION

In the last 20 years, global production of wood-based materials has significantly increased due to the growing demand for both finishing and construction materials. This tendency results from the continual growth of other industries such as eco-friendly buildings and furniture (Pawlak and Boruszewski 2018; Kawalerczyk *et al.* 2019a). The potential application of wood-based materials depends on their properties, and the selection of resin has a major effect on materials performance. Adhesives, depending on the type, have specific properties such as wettability (Stöckel *et al.* 2010), chemical properties (Dunky and Niemz 2013), distribution (Loxton *et al.* 2007; Pakdel *et al.* 2008), and penetration (Liu *et al.* 2014).

Phenol-formaldehyde (PF) adhesive has been used in the wood-based materials industry for over 100 years. Because of its water, heat, wear resistance, strength, and chemical stability, it is a popular binding agent for gluing wood. Studies have demonstrated that PF resins can infiltrate the cell walls of wood (Liang *et al.* 2011; Atta-Obeng *et al.* 2013). The phenolic resins, because of the cell walls and lumens penetration, create the bonds characterized by a great resistant to hydrolysis, mechanical stability, and durability

(Hunt *et al.* 2010). Moreover, PF adhesive can improve the hardness of cell walls (Liu *et al.* 2014). Despite its many undeniable advantages, studies to improve certain properties of PF are still ongoing. One of the methods of resin modification that leads to improvement of the wood-based materials' properties is modification of their chemistry (Dziurka and Mirski 2010, 2014; Mirski *et al.* 2011). An alternative way to produce materials with better properties is the introduction of fillers to the adhesives. There are many purposes of the addition of filling substances, such as to adjust the resins viscosity, to improve the bond strength, to reduce the adhesive absorption into a porous veneer surface, to limit the formaldehyde emissions, and to decrease the raw material costs (Sellers *et al.* 2005; Kawalerczyk *et al.* 2020b). The filling materials can be added in various forms such as powders (aluminium dioxide, silica), fibers (mica, glass fibers), *etc.*, but they have some properties in common, *i.e.*, fillers are non-volatile, non-gluing, and insoluble in the adhesives (Mahrtdt *et al.* 2016). However, the above-mentioned fillers are characterized by relatively large particle sizes, which makes it difficult to obtain a high level of homogenization of the adhesive mixture. Consequently, it is hard to evenly spread the modified resin on the surface of the veneer or lignocellulosic particles.

The solution may use smaller-sized particles within the dimensional range of nanotechnology (Dukarska and Bartkowiak 2016). Gao and Du (2013) investigated the effect of nano-cupric oxide and surfactants on the curing kinetics of PF resin and properties of plywood. The results showed that the addition of nano-CuO with alkaline surfactant improved the condensation of the PF adhesive. Moreover, the shear strength of plywood manufactured with modified resin has met the requirements of EN 314-2 (1993). Dukarska and Czarnecki (2016) reported an interesting study concerning the introduction of fumed nanosilica as a filler for MUPF resin. Results revealed that the addition of nano-SiO<sub>2</sub> expands the durability and increases reactivity of the resin. The modification also led to a significant decrease of formaldehyde (HCHO) release and allowed the reduction of adhesive consumption in the production process. Furthermore, the introduction of nanosilica to urea-formaldehyde resin made it possible to produce other wood-based materials, such as particleboards and rape straw boards, which were characterized by improved mechanical properties, water resistance, and mycological resistance (Dukarska 2013; Dukarska and Derkowski 2014; Dukarska *et al.* 2017). In recent studies, Özçifçi *et al.* (2018) concluded that the bonding strength of wood-based materials manufactured with TiO<sub>2</sub> and SiO<sub>2</sub>-reinforced PF resin was significantly improved. Furthermore, Zhang *et al.* (2009) revealed that the addition of nano-BaCO<sub>3</sub> can effectively delay pyrolysis of PF resin.

One of the new types of nano-sized fillers is cellulose, a polysaccharide with linear, stereo-regular structure (Hubbe *et al.* 2008; Ioelovich 2008). The availability of this environmentally friendly polymer is estimated at  $1.5 \times 10^{12}$  tons per year (Klemm *et al.* 2005). Moreover, cellulosic nanoparticles are characterized by the great mechanical properties, such as modulus of elasticity in the range of 138 GPa and strength around 10 GPa (Zimmermann *et al.* 2004). Both its high energy conversion capacity and chemical compatibility with other substances make it suitable for the use as a modifier of resins (Sokołowska *et al.* 2008; Abitbol *et al.* 2016). Using the cellulosic nanoparticles also presents some environmental benefits such as biocompatibility and biodegradability (Lu *et al.* 2013).

While a considerable amount of research regarding the reinforcement of UF resins with microfibrillated cellulose (MFC) and nanocrystalline cellulose (NCC) can be found, the number of publications on the PF resin modification with natural fibers is scarce

(Veigel *et al.* 2011, 2012; Zhang *et al.* 2011; Ayrilmis *et al.* 2016b; Mahrtdt *et al.* 2016). Consequently, the aim of this study was to investigate the influence of NCC addition to PF adhesive on the properties of manufactured water-resistant plywood.

## EXPERIMENTAL

The commercially available phenol-formaldehyde (PF) resin was purchased from Silekol Pfleiderer (Kędzierzyn-Koźle, Poland) and it was characterized by the following properties summarized in Table 1.

**Table 1.** Properties of PF Resin

Properties of Resin	Value	Standard
Density (g/cm <sup>3</sup> )	1.21	ISO 8962 (1996)
No. 4 Ford Cup viscosity (s)	153	EN 12092 (2002)
Solid content (%)	47	EN 827 (2005)
pH	12.52	EN 1245 (2011)
Gel time at 130°C (s)	192	PN-C-89352-3 (1996)

The nanocellulose powder (Nanografi Nanotechnology Co., Ltd., Ankara, Turkey) had an average particle sizes declared by the producer to be 10 to 20 nm wide and 300 to 900 nm length, and it was used as a modifier for the research purposes. To adjust and regulate the viscosity of the adhesive mixture, the industrially available and common in water-resistant plywood production tannic filler (UT-10) containing mimosa tannins and chalk was added. The reference resin mixture including only mimosa filler was prepared in accordance with technological formulations. Due to the low content of resin dry matter, there was no need to introduce cellulosic nanoparticles in the form of an aqueous suspension. Both fillers in the form of powders were added directly to the adhesive in the amount depending on the variant (Table 2).

**Table 2.** Compositions of Adhesive Mixtures Depending on the Variant

Variant Label	Quantity (g / 100 g d.m. <sup>1</sup> of Resin)	
	UT-10	NCC
0	20	0
N3	15	3
N5	15	5
N7	15	7

<sup>1</sup> Note: d.m. stands for dry matter

After the addition of the fillers, the mixtures were subjected to a homogenization process with the use of a CAT-500 homogenizer (Ingenieurburo CAT, M. Zipperer GmbH, Ballrechten-Dottingen, Germany) at 1000 rpm for 3 min to achieve a high level of dispersion of cellulosic nanoparticles. In order to investigate whether there was any major effect of the filler introduction on the chemical structure of cured PF resin, infrared (IR) spectroscopy was performed. Both the control adhesive mixture and experimental mixture labeled as N3 (which was characterized by the best reinforcement effect in later sections of the study) were condensed at 140 °C, disintegrated in the grinder, and sieved to attain the dimensional fraction retained on the screen with a mesh size of 0.125 mm. The obtained

powders were mixed with KBr at a 1/200 mg ratio. Spectra were registered using a Nicolet iS5 spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) with Fourier transform within a range of 500 to 4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , registering 16 scans. To assess the rheological behavior of prepared adhesive mixtures, the viscosity test and its changes for 8 h were characterized using a Brookfield DV-II + Pro viscometer (Middleboro, MA, USA). The morphology of the cured PF resin was evaluated using a scanning electron microscope. The samples were mounted on an aluminum stub with the help of double adhesive carbon tape and coated with a layer of gold (Sputter Coater S150B; Edwards, West Sussex, UK). The structures of cured adhesive mixture (N3) and reference adhesive mixture samples were investigated using a Zeiss Evo 40 analytical scanning electron microscope (Zeiss, White Plains, NY, USA) at an accelerating voltage of 20 kV with the magnification of 500 $\times$ .

The plywood panels were manufactured in the three-layer system from birch veneers with an average thickness of 1.5 mm and moisture content of  $6 \pm 1\%$ . The adhesives mixtures were spread on the surface of veneer sheets in the amount of 160  $\text{g}/\text{m}^2$ . The pressing process was conducted at 140  $^{\circ}\text{C}$  for 4 min, with a unit pressure of 1.4 MPa. The average moisture contents of plywood samples were calculated in accordance with EN 322 (1999) and found to be  $5 \pm 1\%$ . The manufactured panels were subjected to evaluation of bonding quality according to EN 314-1 (2004) by shear test both after soaking in water at a temperature of 20  $^{\circ}\text{C}$  for 24 h, and after an aging test. This test involved first boiling the panels in water for 4 h followed by drying in a laboratory oven at 60  $^{\circ}\text{C}$  for 18 h, and then boiling them in water for 4 h, and finally cooling them in water at 20  $^{\circ}\text{C}$  for 1 h. In order to determine the mechanical properties, such as modulus of elasticity (MOE) and bending strength (MOR), tests were conducted in accordance with EN 310 (1993) perpendicular and parallel to the grain of the face veneer layer. The results were subjected to statistical analysis using Tukey test on the significance level of  $\alpha = 0.05$  with the use of Statistica 13.0 software (StatSoft Inc., Tulsa, OK, USA).

## RESULTS AND DISCUSSION

The viscosity of an adhesive mixture is a key property that determines the suitability of a substance for the use as a filler or modifier in plywood production. As expected, based on previous research, the viscosity of the NCC-modified mixtures increased dramatically compared to the mixtures containing only mimosa filler (Veigel *et al.* 2012).

The continual increase observed in the viscosity values results with the passage of time most likely resulted from progressive polycondensation reactions of PF resin. Although the particles were not introduced in the form of an aqueous suspension, no dispersion of fillers was observed during the viscosity measurements. For 7 g of NCC addition to 100 g d. m. of solid resin, the viscosity increased 12% immediately after preparation, and 13% after 8 h in comparison to the reference mixtures. The highly hydrophilic cellulosic nanoparticles were absorbing the aqueous medium contained in adhesive mixture. Moreover, the effect may also be explained by a noticeable density of nanocellulose powder and the number of hydroxyl groups located on the surface of the fibrils, which can lead to the formation of temporary bonds between the fibrils (Iotti *et al.* 2011). This is highly possible, considering the increased chemical activity of nanoparticles in general (Shahbazi *et al.* 2013). However, the viscosity of the mixtures remained at a proper level that allowed even distribution of the adhesives on the surface and did not cause

any difficulties during the application on a wavy veneer. Exceedingly low viscosity of the adhesive mixture can lead to difficulties during both the application and pressing processes. It can also result in excessive penetration into the veneer surface and, as a result, the layer remaining on the surface is not able to ensure good properties of the glue joint. The research conducted by Hong and Park (2017) confirms that adjusting the viscosity level can significantly affect the strength properties of the bond.

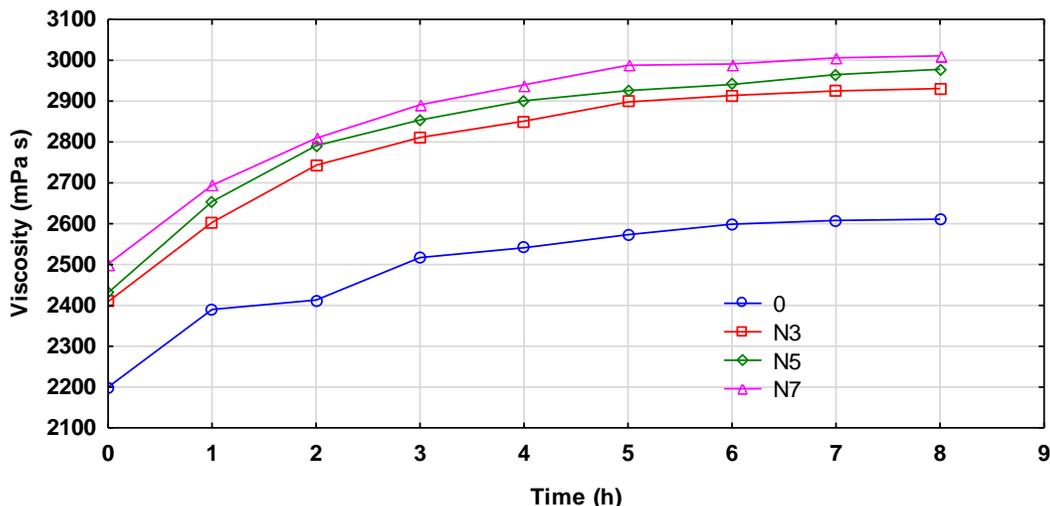


Fig. 1. Viscosity of adhesive mixtures and its changes for 8 h

The surfaces of cellulose nanoparticles are full of hydroxyl groups (Fig. 2). Their location on the equatorial positions of glucopyranose rings makes them highly hydrophilic (Yamane *et al.* 2006).

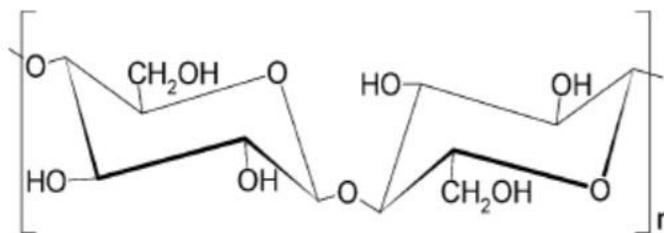
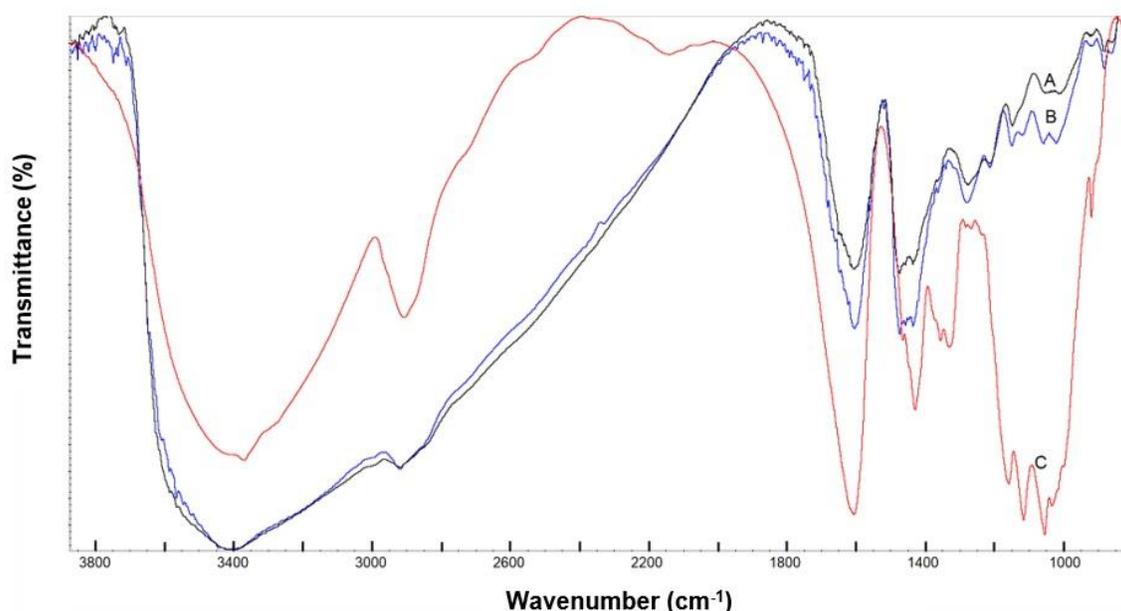


Fig. 2. The chemical structure of cellulose (Atta-Obeng 2011)

According to literature, interfacial bonding of nanocellulose with phenolic resin can be attributed to the reaction between hydroxyl groups of cellulose and the methylol groups of resin (Singha and Thakur 2008). Because the reinforcing effect of NCC is associated with chemical bonding, the Fourier transform infrared was used to investigate the possible interactions between the phenol-formaldehyde adhesive and the cellulosic nanoparticles.

The transmittance spectra of cured, modified, and unmodified PF resins are presented in Fig. 3. Overall, the course of spectra of the conventional and NCC-reinforced adhesives looked similar. Moreover, the spectra of all modified resins were identical, regardless of the variant. Based on a literature review, characteristic peaks were assigned as follows (Holopainen *et al.* 1998). The broad band at  $3400\text{ cm}^{-1}$  was observed and assigned to the O-H stretching of hydroxyl groups in each sample. The C-H stretching of

methylene groups was recorded at  $2920\text{ cm}^{-1}$  (Luo *et al.* 2015). At a range of  $1640$  to  $1600\text{ cm}^{-1}$ , a clear peak occurred. This peak corresponded to the C=C aromatic ring of phenol presented in sample A and B. Moreover, this peak was observed for the nanocellulose sample and was assigned to the C=O stretch and overlapped with OH scissors of water (Poljansek and Krajnc 2005). In the frame of samples A and B, the peaks corresponding to the aromatic ring were presented at  $1480\text{ cm}^{-1}$  and  $1430\text{ cm}^{-1}$ . The peak at  $1060\text{ cm}^{-1}$  corresponded to vibration from the pyranose ring (spectra of NCC) (Wulandari *et al.* 2016). Chen *et al.* (2016) reported that two peaks at  $1115\text{ cm}^{-1}$  and  $915\text{ cm}^{-1}$  corresponded to the C—O—C pyranose ring skeletal vibration and  $\beta$ -linkages, respectively.



**Fig. 3.** IR spectra of: (A) – unmodified PF resin; (B) – NCC + PF resin; (C) – NCC

The FTIR spectroscopy did not explain the chemical interaction between the modifier and PF resin and the effect on its chemical structure, like the case of UF resin modification (Kawalerczyk *et al.* 2020a). Future studies could investigate that using other spectroscopic methods.

The shear strength test is a commonly used indicator of adhesive behavior in plywood (Bekhta *et al.* 2016; Mirski *et al.* 2020). Figure 4 presents the results of shear strength investigations conducted both after soaking in water for 24 h and after the previously described aging test.

The analysis of the data included in Fig. 4 confirmed that the key for achieving the optimum reinforcement effect is the amount of added filler (Veigel *et al.* 2012). The best results were obtained for the variant with the addition of 3 g NCC / 100 g d.m. of resin. In this case, the shear strength values increased approximately 19% and 16% in comparison with reference samples tested after soaking and after boiling, respectively. The addition of 5 g NCC / 100 g d.m. of resin also led to slightly higher bonding quality compared to the control plywood. However, further addition of cellulosic particles in amount of 7 g / 100 g d.m. of resin caused a major deterioration of bonding quality. A similar tendency was observed by Zhang *et al.* (2011) in studies on the UF resin reinforcement. The shear

strength of all plywood samples regardless of the variant retained values exceeded 1 N/mm<sup>2</sup> and met the requirements of EN 314-2 (1993).

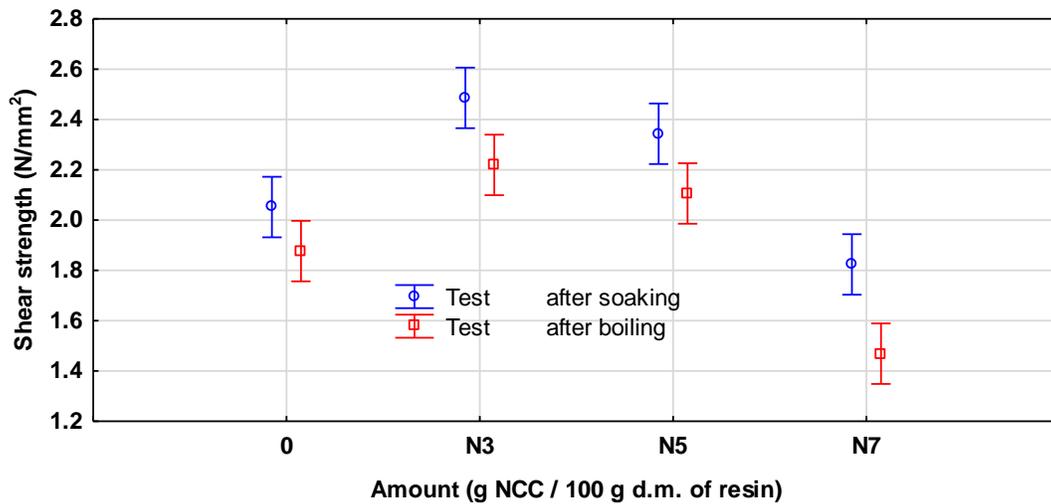


Fig. 4. Shear strength of plywood

The reinforcing effect of nanocellulose addition can be explained by the enhancement in fracture mechanical properties of the glue joint. Studies performed by Vegiel *et al.* (2011) have shown that the introduction of cellulosic particles can lead to significant improvement in fracture toughness and fracture energy. Moreover, Ayrilmis *et al.* (2016a) confirmed that the addition of nanocellulose can cause an improvement in plasticity of the wood-adhesive bond. The modification of PF resin with the NCC also caused significant changes in the morphology of cured adhesive cross sections. Based on the SEM images presented in Fig. 5, the nanocellulose-reinforced resin was characterized by a more solid, compact, less porous structure, as noted in the findings of Gao *et al.* (2012).

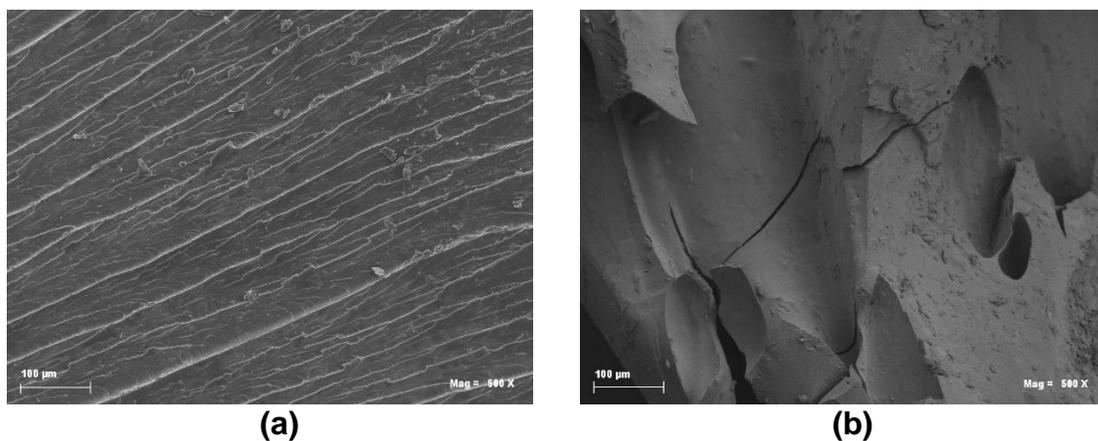
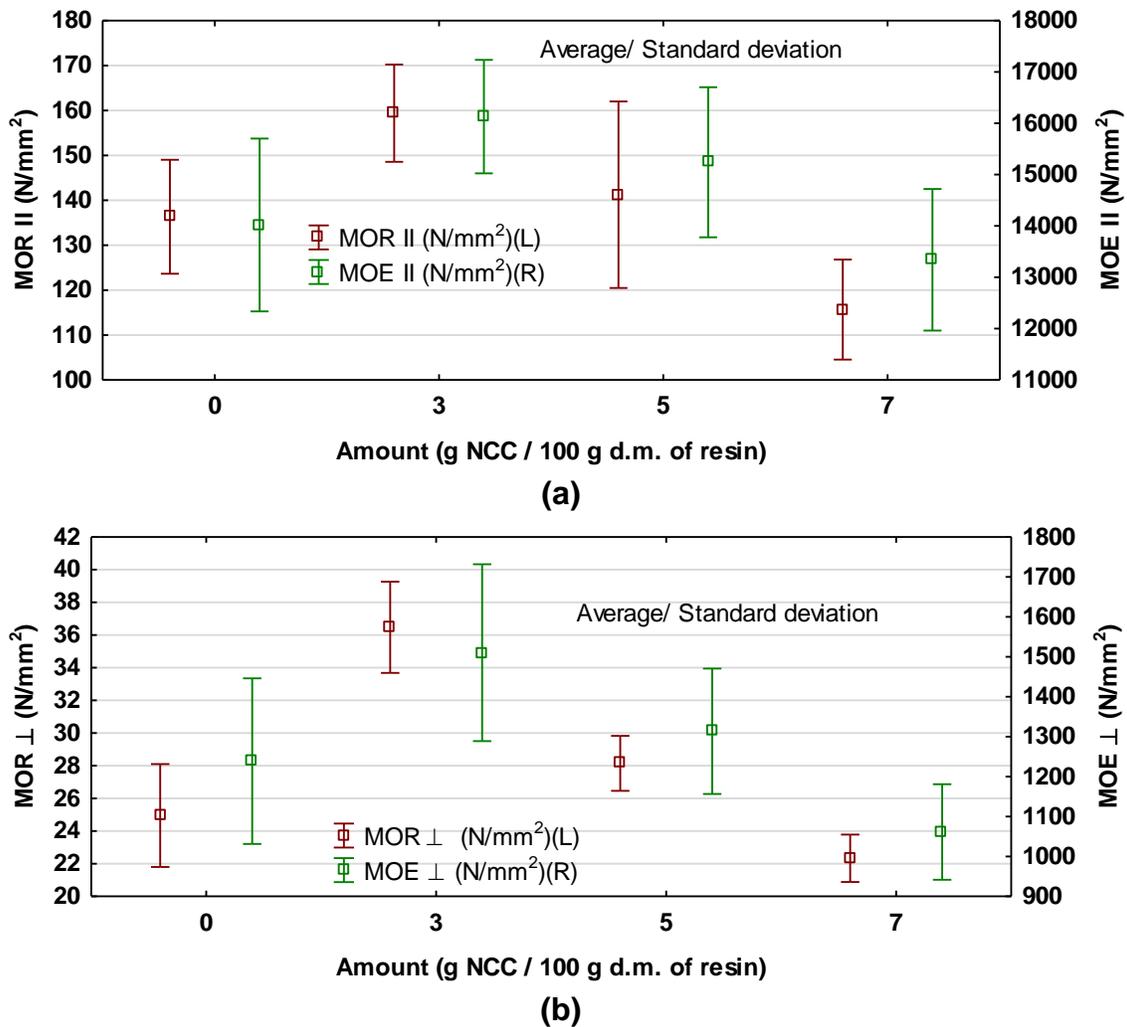


Fig. 5. SEM images taken with 500x magnification of: (a) NCC-reinforced resin labeled as N3 and (b) reference resin

Limiting the occurrence of microcracks in the bond lines contributes to the improvement in the glue joint strength (Kawalerczyk *et al.* 2019b). All of the modified variants presented similar differences in adhesive morphology in comparison with

reference sample. The deterioration observed in the variant containing the highest content of nanoparticles likely resulted from the agglomeration. Nanocellulose act like carriers of load and stress along the polymer matrix. The formation of agglomerates led to the accumulation of stress at a certain point of the bond and consequently decreased its shear strength values (Singha and Thakur 2008).

To fully evaluate the effect of nanocellulose addition to the adhesive mixture on the properties of plywood, the results of bending strength (MOR) and MOE are summarized in Fig. 6.



**Fig. 6.** Bending strength (MOR) and MOE of plywood tested: (a) parallel and (b) perpendicular to the grains of face veneer layer

The results included in Fig. 5 provide further evidence that adjusting the amount of filler had a dramatic impact on the properties of manufactured plywood. As in the case of the shear strength results, the best values were obtained for the variant assuming the introduction of a small amount, *i.e.*, 3 g of NCC to 100 g d.m. of resin. Plywood glued with the adhesive mixture containing 5 g of NCC achieved slightly better mechanical properties compared to reference panels. Major deterioration of plywood mechanical properties was noted when 7 g of cellulosic particles were added to PF resin. The results corresponded

with the shear strength values described earlier. The addition of small amounts of nanocellulose can effectively transfer stress along the bond line (Chirayil *et al.* 2014). Moreover, during the polycondensation process of wood-adhesive bond, the PF resin penetrated to the surface of the veneer and filled the cell lumens. Liu *et al.* (2014) reported that the introduction of cellulosic particles can extend the migration of phenolic glue line and consequently leads to significant improvement in the mechanical properties of wood-adhesive bonds.

## CONCLUSIONS

1. Based on time-viscosity dependence, introducing nanocellulose into phenol-formaldehyde (PF) resin increased its viscosity, which was technologically beneficial.
2. The infrared (IR) spectra of modified and non-modified resin mixtures showed no significant interaction between the cured PF adhesive and the filler.
3. Introduction of cellulosic nanoparticles in the amount of 3 PBW per 100 PBW of the resin guaranteed an optimum reinforcement effect and made it possible to manufacture plywood with a significantly improved bonding quality.
4. Mechanical properties, such as bending strength and modulus of elasticity, of plywood produced with an optimum amount of nanocrystalline cellulose (NCC) was greatly increased in comparison to the control samples.
5. The partial replacement of tannic filler with cellulosic nanoparticles dramatically improved the morphology of the cured adhesive and made the glue joint more durable by eliminating the occurrence of microcracks.

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