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PROPERTIES OF THE WATER-RESISTANT PLYWOOD GLUED WITH PF RESIN WITH THE ADDITION OF TANNIN FILLER AND NANOCLAY

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ABSTRACT

The conducted study was aimed at finding the phenol-formaldehyde adhesive formulation containing both the nanoclay and the tannin filler which allows to manufacture water-resistant plywood characterized by the improved properties. The research assumed the application of six experimental variants having a different proportions of the mentioned components which were compared with the mixture prepared according to the industrial recipe. Properties of liquid mixtures such as their gelation time and viscosity were investigated. Moreover, the differential scanning calorimetry (DSC) was performed. The manufactured plywood panels were tested in terms of bonding quality, bending strength and modulus of elasticity. Studies have shown that after the adjustment in components proportions it is possible to achieve the proper viscosity level of adhesive mixtures. The results also indicated that the suitable amount of nanoclay can contribute to the acceleration of resin gel time, however, the DSC analysis showed no effect on its reactivity. The nanoclay concentrations ranging from 2 to 4 pbw (parts by weight) per 100 g of adhesive positively influenced the bonding quality of plywood. Furthermore, there was no clear tendency in case of the effect of applied formulation on the modulus of elasticity and bending strength of plywood. The mixture containing 3 pbw of nanoclay and 5.3 pbw of tannin filler was distinguished as the most beneficial taking into account the improvement in the properties of manufactured plywood.

KEYWORDS: Nanoclay, plywood, phenol-formaldehyde adhesive, filler.

INTRODUCTION

Nanoclays are the fine-grinded mineral silicates with layered structural units forming the complex clay crystallites by stacking these adjacent layers to each other with a van der Waals forces (Guo et al. 2018). The individual layers are composed of sheets whose arrangement plays a crucial role in distinguishing and defining these clay materials (Nazir et al. 2016). Despite the constantly emerging reports on the morphology and properties of nanoclays, they have been known to the humankind since prehistoric times. Their advantages listed by Guo et al. (2018) include among others the availability, the relatively low cost and environmental impact. As a result, the number of publications on nanoclays increases every year which indicates the constantly growing interests in this kind of materials. Moreover, due to the outstanding properties, the clay nanocomposites have shown a great potential in wide range of applications (Lei et al. 2010) such as for example: polymer composites (Bandyopadhyay and Ray 2019), biomedical treatments (Gaharwar et al. 2019), coatings (Aloui and Khwaldia 2017), packing materials (Rahman et al. 2018) etc.

The emerging nanotechnology has revealed the unique physicochemical properties of nanoparticles in general, such as: their biodegradability, bioavailability, stability, chemical compatibility etc. (Kiio and Park 2021, Rafiee and Shahzadi 2019). Consequently, as a result of many advantageous features they have also penetrated into the field wood-based materials manufacturing. The nanomaterials of both the natural origin (e.g. nanocellulose) and the synthetic origin (e.g. nanosilica) were found to be effective as a reinforcing additives for the formaldehyde-containing adhesives. It was reported that the introduction of mentioned nanoparticles resulted in manufacturing wood-based panels, such as plywood or particleboard, characterized by the improved physicomechanical properties (Dukarska and Czarnecki 2016, Kawalerczyk et al. 2021).

The clay nanoparticles were also studied in order to determine the possibility of their applications in the adhesives formulations. The addition of the small amounts of Na -montmorillonite (NaMMT) caused the improvement in the thermosetting performance of UF (urea-formaldehyde) resins and led to manufacturing of plywood having the increased water resistance (Lei et al. 2008). NaMMT was also studied as a secondary filler for amino resins (UF and MUF). The outcomes have shown that the formulation consisting of wheat flour and 5% nanoclay allowed to produce the three-layered plywood with the improved physical properties (Doosthoseini and Zarea-Hosseinabadi 2010). Moreover, the introduction of nanoclay to the flour-containing UF adhesive mixture was studied also in case of plywood made of veneers obtained from tropical fast growth plantations. The research have shown that the addition of nanofiller in the amount of 0.75% had the most visible reinforcing effect and it increased both the physical and mechanical properties of the panels (Muñoz et al. 2018). Besides the amino resins, the phenol-formaldehyde adhesives have been used in wood gluing for over 100 years. The water, heat and wear resistance made them a popular binding agent especially for the exterior and structural applications (Kawalerczyk et al. 2020). The organo-modified NaMMT was introduced to phenolic resin and the studies have shown a good dispersion within the polymer matrix. Furthermore, the applied nanoclay had a particularly positive effect on the bonding strength especially after the accelerated durability test. Due to the beneficial strain transfer across the glue lines, the added nanoparticles have contributed to the improvement in the plywood strength (Wang et al. 2017). Moreover, studies performed by Ku et al. (2012) confirmed that the PF composites with 5% of nanoclay were characterized by the improved tensile strength and Young's modulus while maintaining the reasonable fluidity for the casting. However, the thermal analysis of PF-NaMMT adhesive showed no effect of nanoclay on the mixture thermosetting performance. Additionally, the differential scanning calorimetry (DSC) results indicated that there is no accelerating effect related to the nanomodification, contrary to the UF resin (Lei et al. 2010).

In summary, there were many studies aimed to explain the effect of nanoclay introduction on the performance of various adhesives. However, as concluded by Doosthoseini and Zarea-Hosseinabadi (2010), the interaction between the clay nanoparticles and the resins is still not fully understood. Moreover, despite that plywood manufacturing process requires the significant adjustment in adhesive viscosity most of the previously conducted studies assumed the addition of only clay nanoparticles. In this case it would be difficult to attain the proper viscosity level and that considerable amount of nanofiller can be a limiting factor from the financial perspective. Thus, the aim of presented study was to find a beneficial PF resin formulation containing both the commercially applied tannin filler and the small amounts of nanoclay.

MATERIALS AND METHODS

Materials

The commercially available PF resin was purchased from the market and used to perform the experiments. It was characterized by the following properties: viscosity of 933 mPa·s, density of 1.213 g·cm^{-3}, solids content of 51%, pH 12.5 and gel time at 130°C of 193 s. The selected formulations assumed the addition of two types of fillers in different proportions. The first one was the commercially applied tannin filler for phenolic resin labeled as UT-10, containing mimosa tannins and chalk. The second one was the synthetic nanoclay powder GARAMITE-1958 (Byk-Chemie GmbH) having the properties summarized in Tab. 1. The plywood panels were produced using the rotary cut birch veneer sheets with the dimensions of 250 × 250 mm, thickness of 1.4 ± 0.1 mm and moisture content (MC) of 4%.

Tab. 1: Characteristics of nanoclay.

Feature	Value
Form	White powder
Moisture content	< 6%
Volumetric density	130 g·l^{-1}
Specific gravity	1.5 – 1.7 kg·l^{-1}

Preparation of adhesive mixtures

The primary criterion in determining the amount of each fillers introduced to the adhesive mixtures was their viscosity. Since it is an essential parameter in plywood manufacturing process, the experimental design assumed that the nanoclay-containing variants should reach a similar values of viscosity as the reference variant prepared according to industrial formulation (REF). The compositions of the investigated mixtures are presented in Tab. 2. The adhesives filled with a proper amounts of additives were mixed with the CAT-500 homogenizer for 60 s at 1000 rpm until the expected homogenization level was achieved.

Tab. 2: Compositions of the adhesive mixtures.

Variant label	**Quantity (pbw per 100 g of PF resin)**	
	UT-10	**Nanoclay**
REF	14.0	-
NC 1	7.3	1
NC 2	5.3	2
NC 3	5.3	3
NC 4	3.0	4
NC 5	1.7	5
NC 6	-	7

Note: pbw - parts by weight.

Properties of adhesive mixtures

The viscosities of prepared mixtures were determined with the use of Brookfield DV-II + Pro viscometer (Middleboro) at 50 rpm, 23°C using a spindle number 5. Moreover, the measurements of gel time at 130°C were carried out in accordance to the relevant Polish standard PN-C-98352-3 (1996).

Differential scanning calorimetry (DSC) analysis

In order to confirm the results of gelation time measurements of the tested adhesive mixtures, the DSC analysis was performed for the selected variants (REF, NC 3, NC 6). DSC analysis was carried out on DSC1 apparatus (Mettler Toledo) in closed aluminium crucibles, in nitrogen atmosphere with the flow of 20 $ml \cdot min^{-1}$. The temperature range was 20-250ºC at the heating rate of 10 ºC/min. STAR Software (Mettler Toledo) was used to analyse the results. The values of the glass transition temperature (T_g), the beginning (T_{onset}) and the end ($T_{endpoint}$), the total reaction heat (ΔH) and the maximum heat value corresponding to T_g were determined. Additionally, the glass transition width (ΔT_g), which is defined as the temperature range from onset to endpoint of glass transition, was estimated from the obtained data. The ΔT_g value was calculated using the following equation (Šahinović and Mušič 2020):

$$\Delta T_g = T_{endpoint} - T_{onset} \quad (1)$$

Plywood manufacturing and testing

The adhesives were applied on the surfaces of outer veneers in the amount of 160 $g \cdot m^{-2}$. The pressing process was conducted at 135°C for 4 min with the unit pressure of 1.6 $N \cdot mm^{-2}$. Then, the manufactured three-layered plywood were conditioned for 7 days at 65% relative humidity and 22 ± 1°C. After conditioning, the obtained panels having a moisture content of 7.5% were tested in terms of bonding quality and mechanical properties such as: bending strength (MOR) and modulus of elasticity (MOE). Bonding quality was determined according to EN 314-1 (2004) both after soaking in water at 20°C for 24 h and after pre-treatment consisting of: boiling in water for 4 h, followed by drying in laboratory oven at 60°C for 18 h, re-boiling in water for 4h and cooling in water at 20°C for 1 h. The mechanical properties were examined according to EN 310 (1993) perpendicularly to the direction of fibers in the outer layers of plywood.

In order to analyse the results, the multivariate statistical analysis ANOVA was performed. Furthermore, in order to distinguish the homogeneous groups, the Tukey test on the significance level of $\alpha = 0.05$ was carried out with the use of Statistica 13.0 software.

RESULTS AND DISCUSSION

According to Hong and Park (2017) factors affecting the bond line strength can be divided into three groups: wood-related, process-related and resin-related. In case of plywood panels manufacturing, the viscosity is an essential parameter strongly influencing all of their properties (Mirski et al. 2020a). The results of viscosity measurements are presented in Fig. 1.

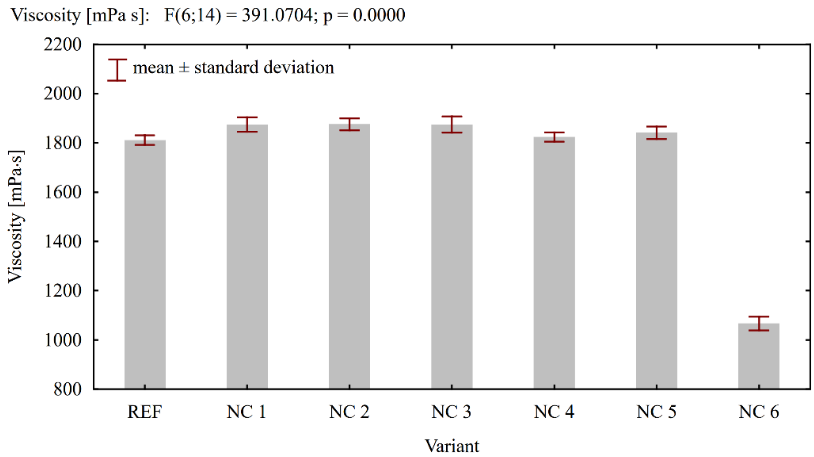

Fig. 1: Viscosity of adhesive mixtures depending on the variant.

The results show that the mixtures containing nanoclay in the amount ranging from 1 to 5 pbw per 100 g of PF resin reached the similar values as the reference formulation. The average values in case of these variants ranged from 1811 mPa·s (REF) to 1875 mPa·s (NC 1 and NC 2). However, the addition of only nanoclay without the additional filler resulted in the decrease of viscosity level by approx. 40% in comparison with the other variants which can be a limiting factor for the potential use. It is particularly important since too low viscosity can cause a difficulties during the application consisting in the flow of resin into the cavities of wavy veneer (Mirski et al. 2020b). Moreover, as reported by Hong and Park (2017) the unsuitable rheological properties of adhesive strongly affect the strength properties of plywood cured bond lines. The reason for this is the possible excessive penetration into the veneer surface and consequently the insufficient amount of remaining adhesive to ensure a good bonding quality (Hogger et al. 2020).

Gel time is one of the important parameter, commonly used for the resins characterization in order to determine their performance in wood bonding (Gonçalves et al. 2018). According to Mirski et al. (2011) gel time should be as short as possible to ensure a high efficiency of the pressing process. Hence, Fig. 2 presents the results of gel time measurements depending on the applied adhesive formulation.

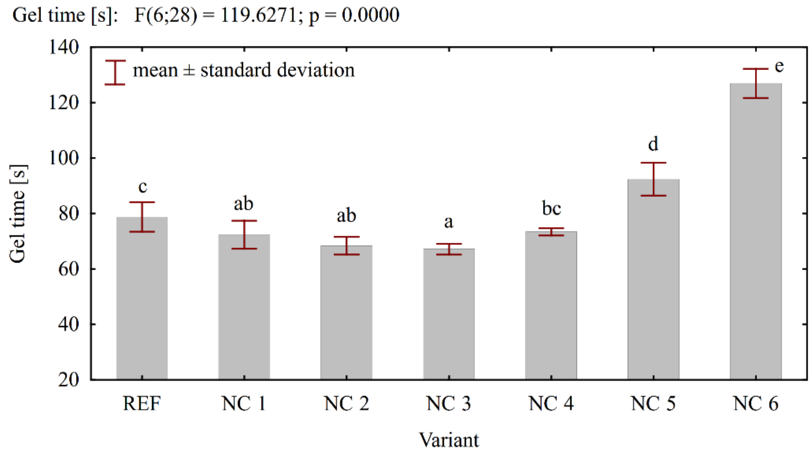

Fig. 2: Gel time depending on the variant (a, b, c, d letters mark the homogeneous groups in the HSD Tukey test).

The results show that the introduction of small amounts of the nanoclay (1 – 3 pbw per 100 g of PF resin) caused a statistically significant changes in the adhesive gel time. The observed acceleration in resin gel time is in a good agreement with the results of studies previously carried out by Nabil et al. (2015) and Jianmin et al. (2009). As reported by Authors, the curing time of phenolic resin is accelerated due to the reduced pH of the mixture while maintaining the alkaline state. In case of phenolic resins characterized by the high pH values (above 10) a slight decrease in their pH can contribute to the shortening of curing time (Pizzi 2000, Pizzi and Ibeh 2014). The formulation containing 4 pbw of nanoclay was characterized by similar gel time as the reference mixture. However, further increase in the amount of added nanofiller led to statistically significant extend in resin curing time. The results of measurements in case of nanoclay-filled variant without the addition of tannin filler (NC 6) were increased by 70% when compared with the reference one. The possible explanation is the adverse effect of large amount of introduced nanoclay particles having a high thermal capacity. Moreover, nanoparticles in general have a strong tendency to form agglomerates which can also affect the crosslinking of the resin. In conclusion, it can be stated that the introduction of appropriate amounts of tannin filler and nanoclay (NC 3) to the adhesive allows for statistically significant shortening of the resin gel time, thus it may favourably influence its reactivity.

In order to confirm this observation, the additional DSC analysis was performed, comparing the course of thermograms and selected parameters of the NC 3 mixture in relation to the mixture containing only tannin filler or only nanoclay. According to the literature, DSC analysis of the adhesive resins provides information about the physical and chemical changes that involve endothermic and exothermic processes. Moreover, the observed changes in thermal capacity allow to explain the curing behaviour of these resins and thereby determine their reactivity (Ab. Wahab et al. 2014, Vázquez et al. 2002). This type of study is also useful to assess the reactivity of adhesive resins doped with different types and amounts of fillers for plywood manufacturing (Dukarska and Bartkowiak 2016, Lei et al. 2010, Marbun et al. 2020, Zhang et al. 2018). However, the performed analysis did not allow any clear conclusions to be drawn regarding the reactivity of the investigated mixtures. The recorded DSC thermograms are presented in Fig. 3.

Moreover, the selected kinetic parameters of the tested mixtures are summarized and shown in Tab. 3.

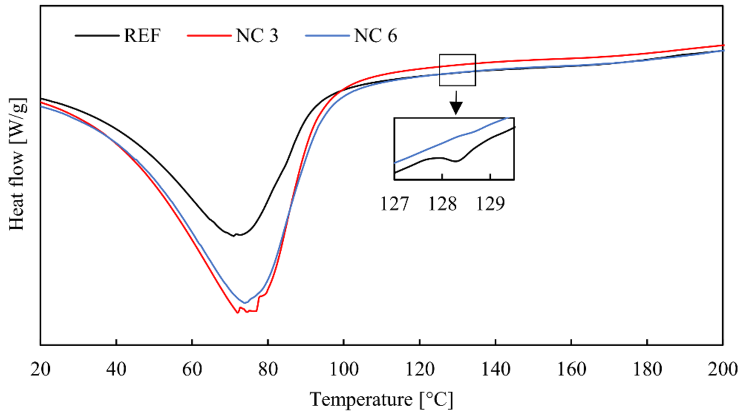

Fig. 3: DSC analysis of selected variants of adhesive mixtures based on PF resin with and without nanoclay.

Tab. 3: Kinetic parameters of selected adhesive mixtures consisting of PF resin with and without nanoclay.

Variant	T_{onset} (°C)	$T_{endpoint}$ (°C)	T_g (°C)	ΔT_g (°C)	ΔH ($J \cdot g^{-1}$)	Max. heat value ($W \cdot g^{-1}$)
REF	34.67	71.16	70.85	36.49	-591.2	2.51
NC 3	36.33	109.05	71.94	72.72	-888.0	3.83
NC 6	37.52	95.21	73.79	57.69	-812.5	3.56

As can be observed, all analysed variants show a wide endothermic peak at glass transition temperature (T_g), which is attributed to water evaporation. The T_g values of the mixtures are at similar levels although it can be noted that the complete replacement of the tannin filler by nanoclay causes a slight shift of T_g towards higher values (from 70.9°C to 73.8°C). Above T_g, long-range translational motion of the polymer chain segments becomes active (Šahinović and Mušič 2020). For this reason, for PF resins in the temperature range from 105°C to even 150°C (or higher depending on the resin properties) a second peak of exothermic character is generally observed due to the condensation either between methylol groups and phenol reactive sites to form methylene bridges or between two methylol groups to form dimethylene ether bridges (Lei et al. 2010). In the case of the tested mixtures, no such type of peak was observed. Only the thermogram of the reference mixture showed a small exothermic peak with a maximum at 128.5°C, i.e. the temperature at which the crosslinking reaction of the pure resin usually takes place. Similar observations were made by Ab. Wahab et al. (2014), who also did not record a peak associated with the curing of the PF resin in the case of a high molecular weight resin. This is probably due to the fact that the curing process of nanoparticles-filled adhesive mixtures is more complex than that of a mixture with tannin filler alone. This may be evidenced by the thermograms of these mixtures as well as the estimated T_g values. It can be observed that while T_{onest} and T_g for particular variants are similar and range from 34-37°C and 70-73°C, respectively, the temperature of endpoint of glass transition ($T_{endpoint}$) in case of NC 3 and NC 6 mixtures is shifted up to 109.1°C and 95.2°C, respectively. For the reference mixture, the $T_{endpoint}$ is as low as 71.2°C, which suggests that the recorded peak in this case is directly related to the water evaporation (Ab. Wahab et al. 2014). Consequently, a significant variation in the T_g value, the enthalpy ΔH and maximum heat values were recorded. Such a significant increase in $T_{endpoint}$, significant differences in the width of the glass transition and the enthalpy in case of mixtures containing nanoclay compared to the reference mixture, may indicate that in this temperature range, in addition to water evaporation, other more complex processes take place, including those related to resin curing. They are undoubtedly influenced by the particle size of the fillers used in the study, their amount and degree of dispersion, and thermal capacity. Nevertheless, as shown in studies by other authors, the addition of nanoclay to pure phenolic or amino resin does not significantly affect its reactivity (Lei et al. 2010, Xian et al. 2013).

The bonding quality test is considered to be crucial in terms of plywood quality control and the classification of manufactured panels as the suitable or unsuitable for specific usage areas (Demirkir et al. 2013). It is also a fundamental indicator of the adhesive behavior in the plywood glue lines (Bekhta et al. 2016). The results of the shear strength test performed after soaking the samples in water and after pre-treatment consisting of boiling in water twice are presented in Figs. 4 and 5, respectively. The outcomes confirmed that the key for achieving an optimum reinforcement effect is the right amount of introduced clay nanoparticles.

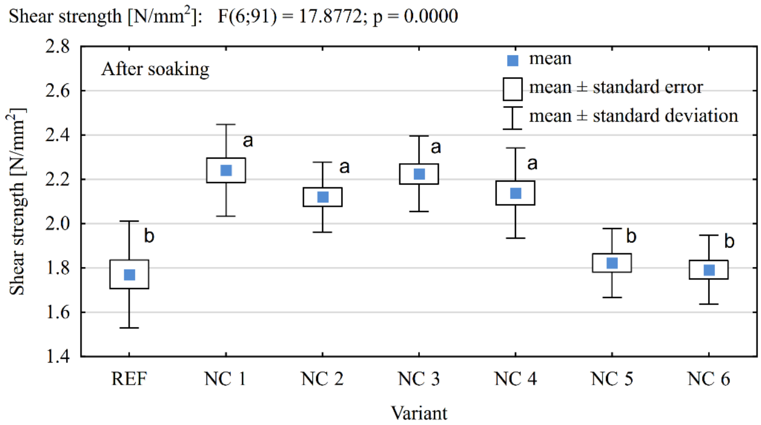

Fig. 4: Bonding quality results of plywood after soaking in water for 24 hours (a, b letters mark the homogeneous groups in the HSD Tukey test).

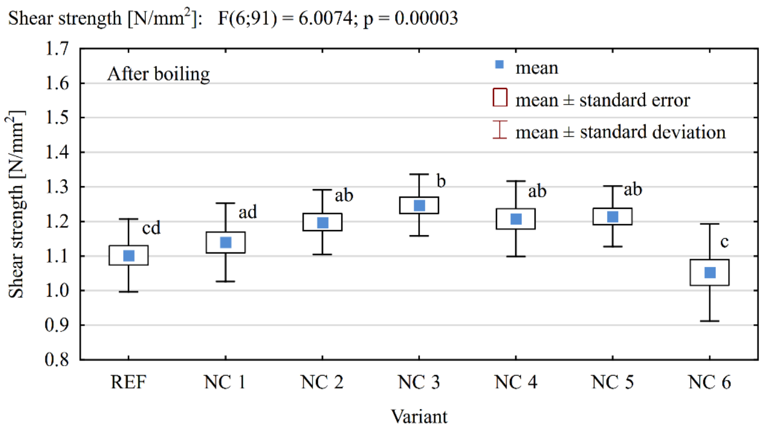

Fig. 5: Bonding quality results of plywood after pre-treatment by boiling test (a, b, c, d letters mark the homogeneous groups in the HSD Tukey test).

In case of samples soaked in water the reinforcing effect was observed in variant assuming the addition of nanoclay in the amount from 1 to 4 pbw per 100 g of resin (NC 1 – NC 4). The best result was achieved by adding 1 pbw of nanoclay mixed with 7.3 pbw of tannin filler. In this case bonding quality was improved by 26% in comparison with the reference variant. However, further increase in the amount of introduced nanofiller to more than 4 pbw did not caused any statistically significant differences. The analysis of the results obtained after boiling the samples in water showed that variants containing clay nanoparticles in the amount ranging from 2 to 5 pbw (NC 2 – NC 5) were characterized by the statistically significant improvement. The most notable increase in bonding quality was observed in the variant NC 3 and it was 11% when compared to the reference formulation. Similarly as in case of soaked samples, the addition of only nanoclay without the supplementary tannin filler resulted in the lack of reinforcing effect. Nevertheless, each of manufactured plywood variants reached values exceeding 1 $N \cdot mm^{-2}$ at which, according to EN 314-2 (1992), there is no necessity to specify the percentage of wood failure. The reason for the increase in investigated bonding quality was probably the optimized number of available reinforcing elements for carrying the load and reduction in the presence of cracks (Kaboorani et al. 2013). It was confirmed by Kawalerczyk et al. (2021) that limiting the occurrence of microcracks in the plywood bond lines is one of the crucial factors influencing their strength. Moreover, the coupling between the polymer matrix and the tremendous surface area of clay nanoparticles assist the stress transfer to the reinforcement phase (Kaboorani et al. 2013). However, as the concentration of nanofiller increased to 7 pbw, the reinforcing effect was no longer visible and it was probably due to the formation of agglomerates. Nanoparticles have a tendency to assemble around each other and form the agglomerations as a result of van der Waals forces (Hamed et al. 2019). Their formation negatively affect the performance of polymer matrix because of the concentration of stress at a certain points of the glue line (Mirski et al. 2020a). Study conducted by Lei et al. (2010) did not show the positive effect of inorganic monmorillonite on the plywood bonding quality. Thus, it can be assumed that the addition of only nanoclay does not cause the improvement in the strength of the glue lines, however, finding the right proportion between the dedicated filler and the nanoparticles allows to obtain the reinforcing effect.

Mechanical properties of manufactured plywood such as bending strength and modulus of elasticity are shown in Fig. 6. On the basis of presented results it can be summarized that the applied adhesive formulations did not influenced the bending strength of plywood in a statistically significant way. The addition of nanoclay in the concentration ranging from 3 to 5 pbw (NC 3, NC 4 and NC 5) showed the improvement in modulus of elasticity. The best outcome was obtained in case of NC 3 variant. However, it is hard to clearly determine the relation between the amount of introduced nanofiller and the results of MOE. The observed differences between the variants may also result from the properties of the birch veneers themselves, rather that from the composition of the adhesive mixtures used to manufacture these plywood panels.

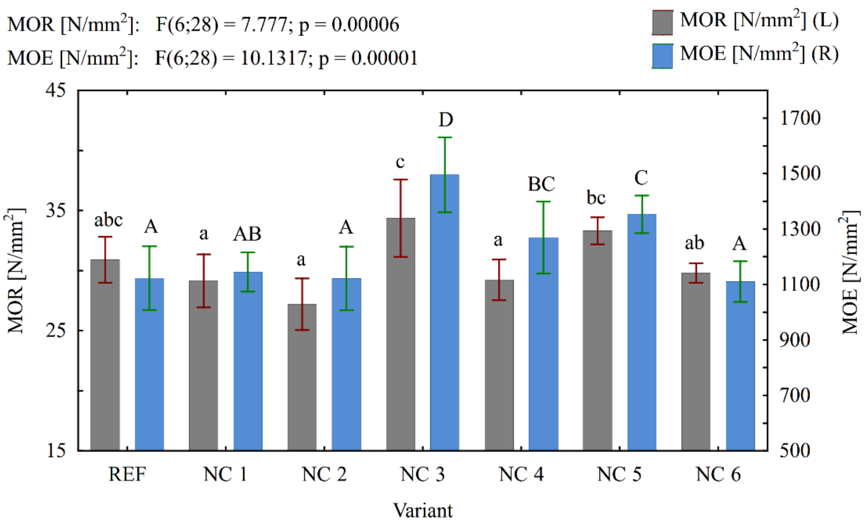

Fig. 6: Modulus of elasticity (MOE) and bending strength (MOR) of plywood tested perpendicularly to the direction of fibers in the outer veneers (a, b, c, d, A, B, C, D letters mark the homogeneous groups in the HSD Tukey test).

CONCLUSIONS

Based on the performed experiments it can be concluded that the different proportions of nanoclay and tannin filler do not affect the viscosity of adhesive mixtures. However, the addition of clay nanoparticles without the supplementary tannin filler leads to the apparent decrease in the viscosity level, not suitable for plywood manufacturing. Moreover, the small amounts of nanoclay can contribute to acceleration of resin gel time. The results of DSC analysis do not show any notable changes in the reactivity of investigated mixtures. Bonding quality results indicate that the proper amount of nanoclay is a key to obtain the reinforcing effect. It is particularly favourable in case of the concentrations ranging from 2 to 4 pbw per 100 g of resin. The outcomes of mechanical properties such as modulus of elasticity and bending strength do not allow to clearly conclude the effect of used adhesive formulation. The presented research shows that application nanoclay-reinforced phenolic resin, after the adjustment in the amount of particular components, leads to obtaining plywood characterized by the improved properties. In general, the formulation containing 3 pbw of nanoclay and 5.3 pbw of tannin filler per 100 g of PF resin can be distinguished as the most beneficial for plywood production.

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