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MICROCELLULOSE AS A MODIFIER FOR UF AND PF RESINS ALLOWING THE REDUCTION OF ADHESIVE APPLICATION IN PLYWOOD MANUFACTURING

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ABSTRACT

The cellulosic derivatives has become widely investigated modifiers for urea-formaldehyde (UF) and phenol-formaldehyde (PF) adhesives in recent years. As microcellulose is more cost-effective and commercially available than nanocellulose, the aim of the presented study is to investigate the possibility of reducing the amount of applied UF and PF resins due to their microcellulose reinforcement. Plywood was manufactured with different amounts of modified resin and compared to the reference one containing rye flour or tannin based filler. The panels were tested in terms of shear strength and formaldehyde release (in the case of plywood glued with UF resin). The studies have shown that the addition of microcellulose (MFC) allowed reducing the amount of applied resin by 6% while maintaining the equally good bonding strength. Moreover, this reduction led to a decrease in the formaldehyde release by 9%.

Key words: microcellulose, UF and PF resins, reinforcement, plywood, shear strength, formaldehyde.

INTRODUCTION

Cellulose is an almost inexhaustible polymeric natural raw material with unique structure and properties, the highly functionalized, linear stiff-chain homopolymer formed by D-glucose building blocks (KLEMM *et al.* 2005). Significant amounts of cellulose are produced each year from various crop sources such as wood fibres, annual plants, flax, sisal, jute, hemp etc. (EICHHORN *et al.* 2001). Moreover, besides the plants it is also distributed through nature in algae, animals, minerals, fungi (HEINZE 2016). Nowadays, among the various cellulosic derivatives, microcellulose and nanocellulose (NCC) are mostly studied for possible ways of their application (HALDAR and PURKAIT 2020).

Microcrystalline cellulose (MCC) was discovered in 1955 by Battista and Smith (THOORENS *et al.* 2014). Usually it is obtained by a partial hydrolysis of amorphous regions in cellulosic chains, which leads to formation of particles characterized by a diameter of approx. 50 µm and length of 100-1000 µm (TRACHE *et al.* 2016). Microcellulosic particles have some desirable features such as non-toxicity, biodegradability, tremendous surface area, high chemical reactivity and biocompability that create the opportunities for applications in many industrial areas (AYRILMIS *et al.* 2016, VINEETH *el al.* 2019, PAŽITNÝ *et al.* 2019). The example of promising use for cellulosic derivatives is a wood-based materials industry.

Many studies concerning the introduction of cellulosic particles as a modifier for the adhesives have been already done. The modification significantly influence the properties of resins such as a viscosity and their curing behaviour (TSCHURTSCHENTHALER 2012, VEIGEL *et al.* 2012). Moreover, studies performed by VEIGEL *et al.* (2011) showed that the nanocellulose addition caused a toughening of urea-formaldehyde (UF) adhesive-wood bond. VEIGEL *et al.* (2012) also determined how the modification with NCC affects the properties of particleboards and oriented strand boards (OSB). Studies have shown that their mechanical performance was significantly enhanced. However, the investigations performed by PAWLAK and BORUSZEWSKI (2018) indicate that the addition of MFC to UF resin in 3-layer lightweight particleboards manufacturing had no significant effect on their mechanical properties i.e. modulus of rupture, modulus of elasticity and internal bond.

The example of widely used wood-based material having advantageous properties resulting from its layer structure is plywood (BEKHTA *et al.* 2016, KAWALERCZYK *et al.* 2019a). ZHANG *et al.* (2011) introduced silanized NCC to UF resin in plywood manufacturing process. The modification resulted in the improvement of bonding quality and formaldehyde emission from produced panels. Similar study conducted by KAWALERCZYK *et al.* (2020a) determined the effect of NCC and MFC addition to UF resin. Based on the results it was concluded that application of both modifying derivatives led to the improvement in plywood shear strength. However, the results varied depending on the type of used cellulosic derivative and the NCC was more effective. A similar dependence can be observed in studies concerning phenol-formaldehyde (PF) adhesive. Both MFC and NCC introduction to PF resin resulted in the improvement in plywood properties, however, the particles in the dimensional range of nanotechnology had a more advantageous effect (KAWALERCZYK *et al.* 2019b, KAWALERCZYK *et al.* 2020b).

The improvement in the strength properties of plywood can result in the opportunity to reduce the resin spread rate, which is the least amount of resin necessary to produce a quality material (BEKHTA and MARUTZKY 2008). An interesting concept of the veneer surface modifications and their effect on the reduction in adhesive consumption became recently investigated. Studies have shown that both DBD (dielectric barrier discharge) plasma treatment (CAO *et al.* 2018) and the veneer compression (BEKHTA and MARUTZKY 2008) can lead to reduction in UF resin spread rate. The enhancement in glue line strength due to the adhesives modification can also reduce their consumption in plywood manufacturing. The introduction of fumed nano-SiO_2 to MUPF (melamine-urea-phenol-formaldehyde) allowed decreasing the amount of applied resin by 30% (DUKARSKA and CZARNECKI 2016). Similar studies performed by KAWALERCZYK *et al.* (2020c, 2021) showed that the addition of NCC can reduce the UF and PF resins spread rate by 30% and by 20%, respectively.

This paper is a continuation of the studies on cellulosic particles incorporation to the plywood manufacturing process. The effect of NCC addition differs from the addition of MFC. Moreover, when compared to the NCC, the MFC can be used as more cost-effective and commercially available modifier for the widely used UF and PF resins. Thus, the aim of presented study was to investigate the effect of microcellulose application on the possible reduction of adhesive spread rate in plywood manufacturing process.

MATERIALS AND METHODS

The PF and UF resins were purchased from Silekol (Kędzierzyn-Koźle, Poland) with the following characteristics summarized in Table 1.

Tab. 1 Properties of applied resins.

Parameter	UF resin	PF resin
Viscosity (mPa·s)	650	471
Solid content (%)	69	48
Gel time at 100 °C (s)	69	–
Gel time at 130 °C (s)	–	190
pH	8.1	12.5

Ammonium nitrate (20 wt%) was included in the UF adhesive composition as a hardener. In order to adjust the viscosity, the rye flour and the tannin based filler (UT-10) containing chalk and mimosa tannins were added to UF and PF resins, respectively. Microfibrillated cellulose commercially named as ARBOCEL (Rettenmaier GmbH, Poland) with an average particle sizes of 6 - 12 µm was applied as a modifier. Plywood panels were manufactured using rotary cut birch (*Betula*) veneer sheets with an average density of 560 kg/m^3, a moisture content of 6 ± 1%, an average thickness of 1.5 mm and dimensions of 320 × 320 mm.

In the case of UF resin, the MFC was introduced in a state of 10% aqueous suspension prepared with the use of magnetic stirrer (700 rpm, 10 min). Due to the lower solid content, there was no necessity to apply cellulosic particles in wet state to the PF resin, and therefore they were added directly to this adhesive type. The amounts of MFC included in both compositions were selected based on the results of previously conducted research (Kawalerczyk *et al.* 2019b, Kawalerczyk *et al.* 2020a). Tables 2 and 3 present the compositions of prepared adhesive mixtures. The experimental and reference variants differed in the amount of water contained in the formulations due to the fact that the control variants were prepared according to industrial regulations.

Tab. 2 Composition of UF resin mixture.

Variant label	Quantity (g/100 g of solid resin)			
	MFC suspension	Rye flour	Water	Total solution weight of hardener
Reference	0	15	15	2
Experimental	10	4	0	2

Tab. 3 Composition of PF resin mixture.

Variant label	Quantity (g/100 g of solid resin)	
	MFC powder	UT-10
Reference	0	20
Experimental	5	17

After the addition of fillers the adhesives were mixed at 1000 rpm for 2 min with the use of CAT-500 homogenizer to attain proper level of homogenization. The reference mixtures were spread on the veneer in the amount of 170 g/m^2 and these variants were labelled as 170REF. The experimental adhesives containing MFC were applied on the surface of the veneers in the amount of 170, 160, 150, 140, 130 g/m^2 (the calculations were made in relation to the total adhesive mixture mass). The veneer sets for 3-layered plywood were hot pressed with the unit pressure of 1.4 MPa, temperature of 120 °C in case of UF resin and 140 °C in case of PF resin for 4 minutes.

The manufactured plywood panels were tested in terms of bonding quality according to EN 314-1 (2004). In case of UF resin the shear strength was determined in dry state and after soaking in water for 24 h. Plywood glued with PF resin were tested after soaking in water for 24 hours and after a pre-treatment consisting of boiling in water for 4 h followed by drying in laboratory oven for 16 h at 60 °C, another boiling in water for 4 h and cooling in water for 1 h at 20 °C. The assessments involved 11 samples of each variant. In addition to bonding quality, the formaldehyde emission of plywood bonded with UF resin was investigated with a flask method according to EN 717-3 (1996).

The results were analysed with the use of multivariate statistical analysis ANOVA. Tukey test was carried out in order to distinguish the homogeneous groups on a significance level of $\alpha = 0.05$ using Statistica 13.0 software.

RESULTS AND DISCUSSION

The results of shear strength test of plywood bonded with UF resin are presented in Fig. 1. The samples soaked in water were characterized by lower strength values due to the hydrolysis of the UF resin in the presence of water. As expected based on the previous results the addition of MFC resulted in the increase of bonding quality in comparison with the flour-filled adhesive applied in the same amount. The bonding quality was improved by 14% and by 8% in case of panels tested in dry conditions and after soaking in water, respectively. As the amount of applied adhesive decreased, the shear strength also decreased. The results of statistical analysis showed that the addition of MFC allowed to reduce the resin spread rate by 10 g/m^2 while maintaining as good bonding strength as the reference plywood. Further decrease in the amount of applied resin to 130 g/m^2 resulted in a deterioration of bonding quality by up to 24% in dry state and by 27% after soaking.

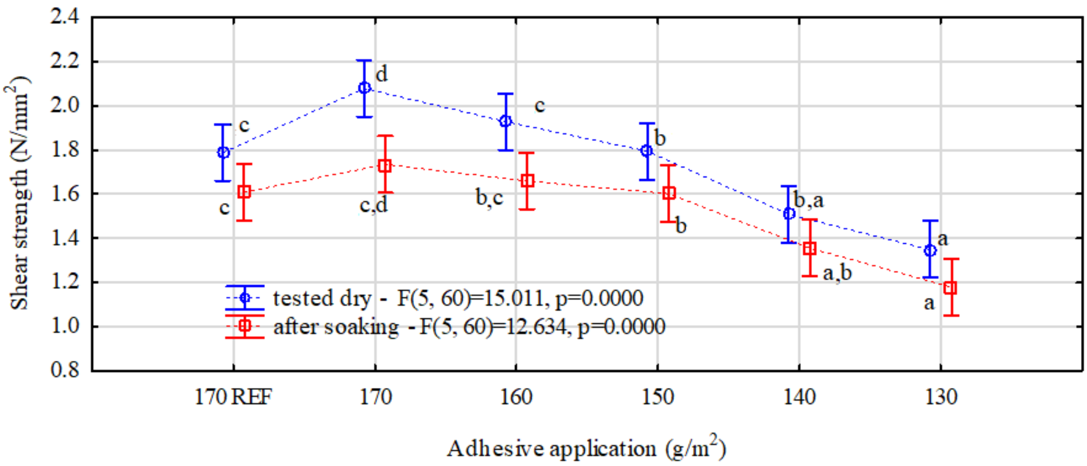

Fig. 1 Shear strength of plywood glued with UF resin (a, b, c, d letters mark homogenous groups in the HSD Tukey test; F[x,y] = z,p where, F is Roland Fisher's test method, x is number of degrees of freedom, y is number of tests, z is value of F test, p is probability level).

Fig. 2 presents the results of bonding quality investigated in plywood glued with PF resin. Similarly as in panels with UF resin the introduction of MFC led to the improvement in bonding strength. The shear strength was improved by 10% and 6% in the case of plywood tested after soaking and after boiling, respectively. The reinforcing effect of MFC allowed the reduction in adhesive application by 10 g/m^2 and manufacturing plywood with equally good bonding quality as the reference one. BEKHTA and MARUTZKY (2006) explained that the further reduction in shear strength might result from the insufficient glue quantity to cover the veneer surface and maintain the required glue line thickness.

The improvement in bonding quality can be associated with the chemical bonding between the hydroxyl groups of cellulosic derivatives and the functional groups of resin, which consequently allow obtaining a highly cross-linked structure. Moreover, studies have shown that the introduction of cellulosic particles can improve resin morphology. The structure of cellulose-reinforced adhesive was more solid, less porous and had significantly less microcracks (KAWALERCZYK *et al.* 2021). Since water participates in the crosslinking reactions during the resin condensation, the lowered amount of water in experimental variant could also have an influence on the results in case of the UF resin-bonded plywood. The addition of MFC instead of NCC resulted in less efficient reduction of adhesive spread rate. The reason could be an increased chemical reactivity of particles within the dimensional range of nanotechnology. Furthermore, the nanoparticles are characterized by a tremendous surface area which favours a chemical bonding process.

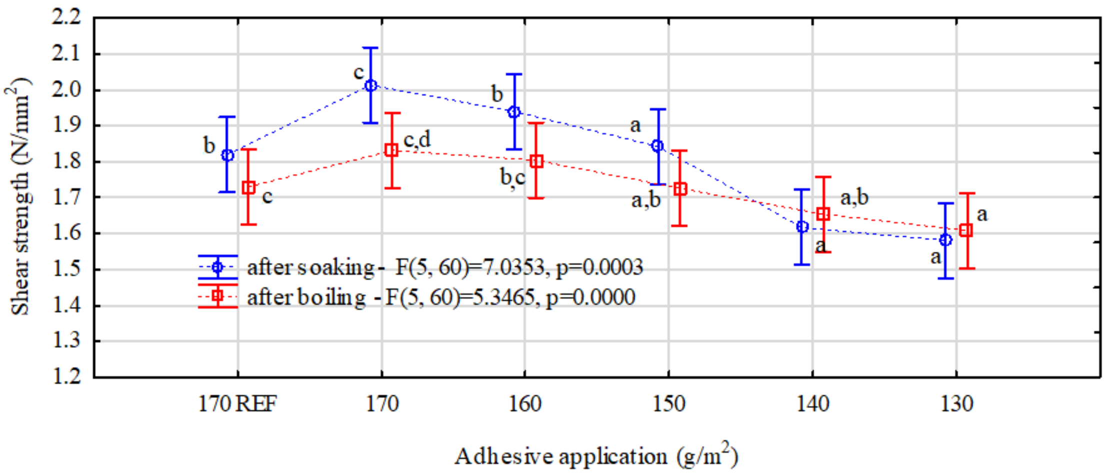

Fig. 2 Shear strength of plywood glued with PF resin (a, b, c, d letters mark homogenous groups in the HSD Tukey test; F[x,y] = z,p where, F is Roland Fisher's test method, x is number of degrees of freedom, y is number of tests, z is value of F test, p is probability level).

The application of MFC allowed reducing the amount of resin by 6% in the case of both UF and PF resin which is less effective also when compared with the addition of nano-SiO_2 (DUKARSKA and CZARNECKI 2016). The adhesives reinforcement with MFC seems to be also slightly less effective than the veneer surface modification with compression or DBD plasma (BEKHTA and MARUTZKY 2006, CAO *et al.* 2018). However, the reduction of adhesive consumption resulted in a decrease of formaldehyde release (Fig. 3).

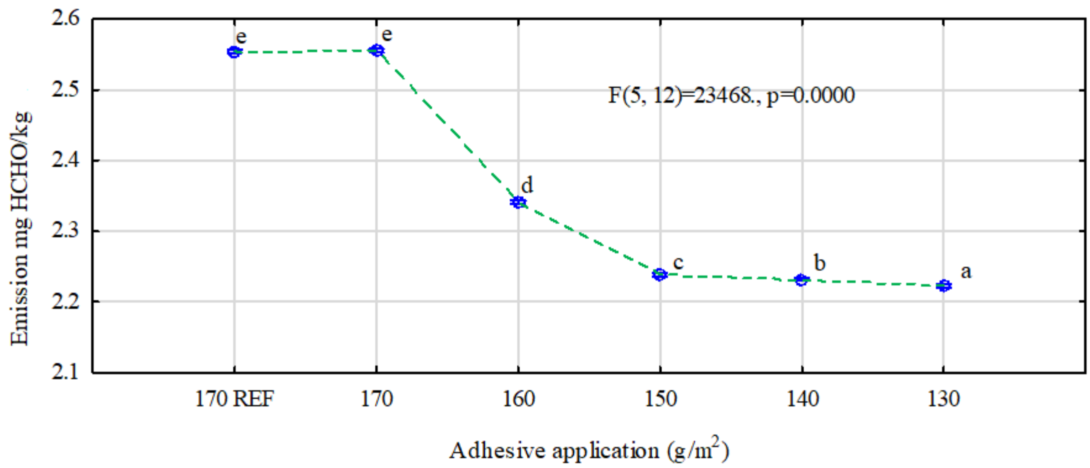

Fig. 3 Formaldehyde emission from plywood glued with UF resin (a, b, c, d, e letters mark homogenous groups in the HSD Tukey test; F[x,y] = z,p where, F is Roland Fisher's test method, x is number of degrees of freedom, y is number of tests, z is value of F test, p is probability level).

On the basis of the formaldehyde release results it can be concluded that the introduction of MFC itself has not caused a decrease in the amount of emitted formaldehyde which is similar to the effect observed by AYRILMIS *et al.* (2016) and KAWALERCZYK *et al.* (2020a). Studies performed by ZHANG *et al.* (2011) suggest that modification of cellulosic particles with 3-aminopropyltriethoxysilane (APTES) can contribute to the more effective scavenging abilities. The reduction of adhesive application by 6% (10 g/m^2) led to a decrease in formaldehyde release by 9%. As the resin spread rate decreased, the amount of emitted formaldehyde also decreased. The further reduction in the amount of applied resin to 130 g/m^2 resulted in lowering the investigated emissions by 13% which was expected since the adhesives are the main sources of emitting formaldehyde.

CONCLUSIONS

The introduction of MFC to UF and PF resins led to the statistically significant improvement in bonding quality. The MFC addition allowed to reduce the amount of applied resin by 6% while maintaining the equally good strength of the reference, rye flour-containing variant. The microcellulose-reinforcement itself did not cause the reduction in formaldehyde release. However, the reduction in adhesive application by 6% resulted in a decrease in HCHO emission by 9%. Further reduction in resin spread rate led to a significant deterioration in glue line strength.

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