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THE EFFECT OF VENEER IMPREGNATION WITH A MIXTURE OF POTASSIUM CARBONATE AND UREA ON THE PROPERTIES OF MANUFACTURED PLYWOOD

It was determined how the impregnation of birch veneers with a mixture of potassium carbonate and urea affected the fire protection properties, shear strength, modulus of elasticity and modulus of rigidity of plywood glued with PF and UF resin. Veneers were impregnated by soaking in aqueous fire retardant solutions with concentrations of 20% and 30%. Measurements of mass loss, burned area and time of ignition showed the fire protection provided to be very effective. Impregnation did not significantly affect the modulus of elasticity or modulus of rigidity of the plywood. Impregnation caused a decrease in bonding quality, especially in the case of plywood with UF resin soaked in water. For the samples with PF resin, both immersed and boiled in water, impregnation had less impact on the shear strength: its values exceeded 1 N/mm^2, thus meeting the requirements of EN 314-2.

Keywords: plywood, fire retardant, impregnation, flammability, veneer, mechanical properties

Introduction

Birch plywood is a valuable material used in many fields, including furniture production, building joinery and other applications in buildings, both as a finishing and a structural material. The wide range of applications results from the very good mechanical properties provided by its layered construction [Wang and Rao 1999; Bekhta et al. 2016]. Plywoods are characterized by a high susceptibility to inflammation because of their chemical structures – the main components of wood have a large number of oxygen atoms [Mahr et al. 2012; Grześkowiak et al. 2016]. To reduce flammability, fire retardants are commonly used, for example to extend the time of ignition and reduce mass loss and burned area [Grześkowiak et al. 2016]. There are a number of chemical substances used in industry that can improve the flammable properties of materials, but usually

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they consist of toxic chemicals. Fire retardants can also impair the mechanical properties of plywood, which may cause limitations on its use in many areas. There are many ways of decreasing the flammability of plywood, among them the impregnation of veneers before gluing [Borysiuk et al. 2011; Wang et al. 2014; Bekhta et al. 2016]. Studies show that impregnation of individual veneers improves the flammable properties of plywood; however, in many cases impregnation also leads to deterioration of mechanical properties. Besides the type of substance, an important factor is the species of wood from which veneers are made. As reported by Borysiuk et al. [2011], in the case of beech veneer impregnation caused a decrease in the shear strength of plywood by about 20%, while it did not affect the bonding quality of plywood made of pine veneers. It is also possible to modify the adhesives used in plywood manufacture by adding fire retardants [Grexa et al. 1999; Cheng and Wang 2011; Wang et al. 2012]. This is also an effective means of decreasing flammability, but as with the previous method, impregnation can lead to deterioration of mechanical properties. As reported by Cheng and Wang [2011], a change in the composition of adhesive caused a decrease in bending strength by 25% compared with non--protected plywood samples. However, there exists the possibility of modifying fire retardants used as additives to adhesives, for examples using zeolites, to reduce their negative impact [Wang et al. 2012]. Another way to protect the material is the impregnation of finished plywood. Kim et al. [1984] found that impregnation by soaking plywood in aqueous fire retardant solutions can improve their mechanical properties, such as modulus of elasticity. However, LeVan et al. [1996] reported that plywood protected in this way shows a higher tendency to degrade under conditions of cyclical temperature changes. Another example of an effective method is surface protection with fire retardants. These substances are transformed by high temperature into a solid, insulating mass or a swelling, dispersive coating [Chou et al. 2010; Chang et al. 2011; Yew et al. 2015]. Among the methods presented, the most effective is to soak the veneers in fire retardant solution, because this allows the material obtained to be protected along the whole of its cross-section [Bueno et al. 2014].

The aim of this study was to investigate the effect of veneer impregnation on the flammable properties, shear strength, modulus of elasticity and modulus of rigidity of plywood. The fire retardant used consists of potassium carbonate and urea, and it is known to be effective in the case of solid wood protection.

Materials and methods

Birch veneers of size 300 × 300 mm and 1.5 mm in thickness were used in the tests. For fire protection impregnation, an aqueous solution of a mixture of potassium carbonate and urea in a weight ratio of 1:1 was used. Veneers with a moisture content of 8% were impregnated for an hour by soaking in a container filled with fire retardant in two different concentrations: 20% and

30%. After the impregnation process the veneers were left under ambient conditions for 24 hours, and were then dried in a laboratory oven at (60 ±5)°C to 4% moisture content. For the veneers before impregnation and after drying, moisture content was calculated in accordance with EN-322. Phenol-formaldehyde (PF) and urea-formaldehyde (UF) resin with the characteristics listed in table 1 were used for plywood production.

Table 1. Characteristics of resins

Properties of resin	Standard	Values
		UF
Density, g/cm^3	PN-ISO 8962	1.282
No. 4 Ford Cup viscosity, s	EN 12092	89
Solids content, %	EN 827	65
pH	EN 1245	8.09
Gel time at 100°C, s	PN-C-89352-3	86
Gel time at 130°C, s	EN-ISO 9363	–

The veneers were glued with UF and PF resins applied to their surfaces at 180 g/m^2 and 160 g/m^2 respectively. The materials thus prepared were pressed using a laboratory press at 120°C (UF) or 140°C (PF) under a unit pressure of 1.5 MPa for 1 min per millimeter of plywood thickness after pressing (ca. 4 min). Reference plywood samples were pressed for the same time; these were manufactured in the same way except for the step of protection of the veneer with fire retardant. The variants of manufactured three-layer plywood are shown in table 2.

Table 2. Variants of plywood

Code	Type of resin	Protection
0PF	PF	non-protected
20PF	PF	20% aqueous solution
30PF	PF	30% aqueous solution
0UF	UF	non-protected
20UF	UF	20% aqueous solution
30UF	UF	30% aqueous solution

To determine the quantity of absorbed fire retardant, the absorption content per unit volume was calculated:

$$A = \frac{m_2 - m_1}{V} \cdot C$$

where: A is absorption, kg/m^3

m_1 is the mass of veneer before treatment, kg
m_2 is the mass of veneer after treatment, kg
V is the volume of veneer, m^3
C is the concentration of fire retardant solution as a decimal fraction (unitless).

Moreover, to evaluate the effectiveness of fire protection, a flammability test using a slightly modified version of the "French method" was applied [Lutomski 2002]. Similar methods are commonly used in scientific research and industry [Peterson 2006; Taghiyari 2012; Grześkowiak et al. 2016; Soltani et al. 2016]. Samples of plywood with a moisture content of 6% were placed on a tripod at 45°. A spirit burner filled with ethanol, with a cotton wick and flame about 3 cm high, was placed centrally under the sample. The flame temperature was 600°C. The time of the test was 2 minutes, during which the time of ignition of the plywood surface was recorded. Ignition time was measured from the moment the specimens were exposed to fire. The top of the flame was in direct contact with the surface of the plywood and burned during the whole test. To determine mass loss, samples were weighed again when they stopped glowing. Based on the difference in the weights before and after the test, weight loss (WL) was calculated:

$$WL = \frac{W_b - W_a}{W_b} \cdot 100\%$$

where: W_b is the mass before the test, g
W_a is the mass after the test, g

After cooling of the samples, the carbon layer was removed and the burned area was measured with a planimeter. The effectiveness of fire protection was determined by calculating the coefficient Z [Grześkowiak et. al. 2016]:

$$Z = \frac{P_z}{P_k} \cdot 100\%$$

where: P_k is the burned surface area of control samples, cm^2
P_z is the burned surface area of impregnated samples, cm^2

Assessment of protection quality was made based on values of the coefficient Z as follows: >75% – poor protection, 50-74% – average protection, <50% – good protection.

The modulus of rigidity (MOR) and modulus of elasticity (MOE) were tested according to the EN 310 standard along and across the direction of the wood fibers.

Bonding quality was assessed by means of a shear test (f_v) according to EN 314-1. UF resin plywood samples were tested both dry and following treatment in water at a temperature of 20°C for 24 h (according to section 5.1.1 of EN 314-1). PF resin samples were tested after water immersion at 20°C for 24 h (section 5.1.1 of EN 314-1) and boiling in water for 4 h, followed by drying in a laboratory oven at 60°C for 18 h, re-boiling in water for 4 h and cooling in water at 20°C for 1 h (according to section 5.1.3 of EN 314-2 for exterior plywood).

Results and discussion

The outcomes of absorption for treated plywood samples are shown in table 3. It was found that the concentration of the fire retardant solution has a significant effect on the absorption values. During soaking in 30% impregnation solution, the veneers absorb two times more fire retardant than in case of 20% solution.

Table 3. Absorption of fire retardant

Parameter	20PF	30PF	30UF
Absorption [kg/m^3]	18.71	36.33	38.38
	*1.84**	*3.02*	*2.53*

*Standard deviation.

Results of the investigation of the effect of veneer impregnation on the fire protection properties of plywood are given in table 4. In the case of plywood with both PF and UF resin, the flammable properties were improved by the applied protection method.

Table 4. Flammable properties of plywood

Parameter	0PF	20PF	30PF	0UF	30UF
Mass loss [%]	11.20	6.23	4.39	10.51	3.91
	*0.85**	*0.32*	*0.43*	*0.44*	*0.48*
Time of ignition [s]	4	11	11	6	13
	0.5	*1.7*	*1.0*	*0.8*	*0.8*
Burned area [cm^2]	91.58	45.53	45.48	90.15	42.05
	2.42	*2.23*	*3.14*	*7.90*	*1.13*
Coefficient Z	–	49.71	49.66	–	46.64

*Standard deviation.

As indicated by the data in table 4, a reduction of mass loss was achieved in each of the tested variants. The best results were obtained with UF resin plywood, where the difference between the protected and non-protected samples was 63%. A slightly smaller reduction in mass loss was observed in the case of plywood with PF resin. The studies confirmed the finding that lowering the concentration of the aqueous impregnate solution has a negative effect on the quality of protection of wood-based materials [Wang et al. 2014].

The time of ignition, namely the time measured from the start of combustion to the time of sustained burning [Craft et al. 2008], is a parameter that to a large degree determines the effectiveness of fire protection. As expected, in the case of the protected samples, the ignition time was much longer than for the control samples (table 4). The longest ignition time was recorded in the case of plywood glued with UF resin, for which the time increased by 117% compared with the control sample. Although a slightly shorter ignition time was observed for PF resin plywood, it increased by as much as 175% compared with the unprotected samples. Unlike in the case of mass loss, lowering the fire retardant concentration had no negative impact on the recorded time of ignition.

Measurements of burned area showed that the least surface damage during combustion was sustained by the protected plywood with UF resin. A slightly larger burned area was measured for plywood with PF resin. However, in both cases the ratio of this area to the whole surface of the sample was improved by about 20%.

In the case of plywood with both UF and PF resin, impregnation had a negative impact on the bonding quality, evaluated on the basis of values of the shear strength (f_v) of the plywood (fig. 1).

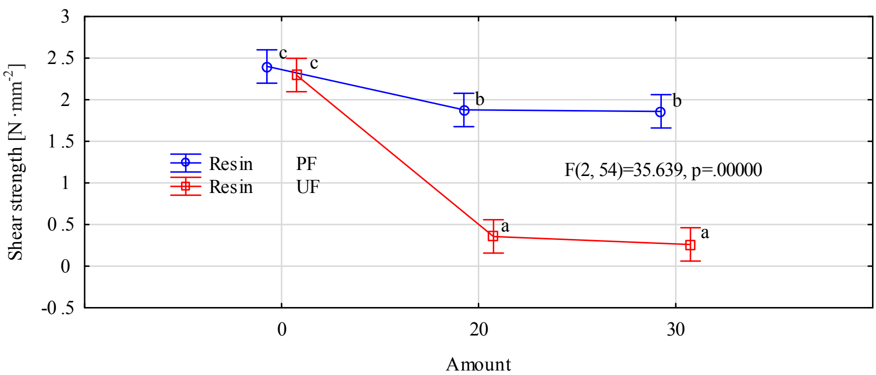

Fig. 1. Shear strength (f_v) of plywood

The tests revealed that in case of plywood made of unprotected veneers, the type of resin did not affect the results for shear strength. Samples with UF resin were tested dry and after soaking in water at (20 ±3)°C. Based on the results of the dry tests, it was found that bonding quality decreased by 22% compared with the control samples. The largest decrease in bonding quality was recorded for samples with UF resin soaked in water, and was as high as 89%. The shear strength of plywood with PF resin was also lowered after soaking, but irrespective of the concentration of the impregnating solution, the decrease was only approximately 21%. Waterproof plywood samples, as required by the EN 314-2 standard, were also tested after double boiling. As a result of this treatment, shear strength decreased by 48% and 19% respectively for 30% and 20% fire retardant concentration. It was found that the magnitude of the difference between results for the two fire retardant concentrations was not statistically significant. Despite the decrease in bonding quality, the shear strength of all plywood samples, except the wet samples with UF resin, retained good values exceeding 1 N/mm^2. The large decrease in the case of samples with UF resin tested wet was most likely caused by the pH of the fire retardant. Use of an alkaline impregnating agent impairs the process of UF resin condensation and hence leads to a significant decrease in shear strength [Zenkteler 1996].

Results of investigations concerning the effect of veneer impregnation on the modulus of rigidity and modulus of elasticity of plywood are given in table 5. Tests were performed both along (||) and across (⊥) the wood fibers.

Table 5. Modulus of elasticity (MOE) and modulus of rigidity (MOR) of plywood

Variant	MOE [N·mm^{-2}]		MOR [N·mm^{-2}]
	||	⊥	||
0PF	14031	1060	133.43
	*1275**	*180*	*13.99*
20PF	16271	1389	157.29
	2034	*142*	*25.91*
30PF	14769	1340	134.03
	2504	*183*	*17.74*
0UF	14378	1397	149.52
	2324	*110*	*21.59*
20UF	13820	1201	133.30
	2289	*124*	*18.91*
30UF	13877	1130	112.41
	2379	*147*	*16.50*

*Standard deviation.

The best results were obtained for PF resin plywood impregnated with 20% fire retardant solution. Bending strength was increased compared with the control samples by 18% along the fibers and 37% across the fibers. Similar findings were made for modulus of elasticity, which increased by 16% along and by 31% across the fibers (table 5). Moreover, impregnation of the veneer of PF resin plywood with 30% fire retardant solution also led to satisfactory results, especially for the properties determined across the fibers. In turn, the impregnation of veneers glued with UF resin seems to have a slight negative impact on the properties of the plywood. However, ANOVA statistical analysis (table 6) did not indicate an unequivocally negative impact of impregnation on the mechanical properties (MOR and MOE). The data in table 6 show that in the case of samples with UF resin, impregnation did not cause significant changes in these properties.

Table 6. Analysis of variance

	MOR ǁ MS=335.89 df=60	MOR ⊥ MS=19.077 df=54	MOR MS=185.82 df=114	MOE ǁ MS=3734E3 df=60	MOE ⊥ MS=20518 df=54	MOE MS=1975E3 df=114
0PF	A,B	A,B	B	A,B	A	B
20PF	C	C	C	B	B,C	B,C
30PF	A,B	B,C	B	A,B	B,C	C
0UF	B,C	A	B,C	A,B	C	B,C
20UF	A,B	A	B	A	A,B	B
30UF	A	A	A	A,B	A	A

A,B,C – homogeneous groups.

Conclusions

The results of the tests show that the impregnation of birch veneers with fire retardant based on potassium carbonate and urea significantly improved the flammable properties of the plywood, including mass loss, burned area and time of ignition.

Impregnation of the veneers had a negative impact on the bonding quality of the protected plywood. However, it was found that the shear strength of all plywood samples, except the wet samples with UF resin, retained good values exceeding 1 N/mm^2.

Veneer protection with the tested fire retardant does not affect the modulus of rigidity or modulus of elasticity of plywood with PF resin. Impregnation causes a slight decrease in these properties for plywood with UF resin, but statistical analysis shows that these changes are not significant.

The applied fire retardant enables the manufacture of water-resistant plywood (glued with phenolic resin) with improved fire protection and good mechanical properties.

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EN 827:2005 Adhesives – Determination of conventional solid content and constant mass solids content
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