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# The effect of phenol-formaldehyde adhesive modification with fire retardant on the properties of birch plywood

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**Abstract:** *The effect of phenol-formaldehyde adhesive modification with fire retardant on the properties of birch plywood.* The study investigated how the modification of phenol-formaldehyde adhesive with a mixture of potassium carbonate and urea affect the properties of plywood. Based on the investigations of the viscosity, gel time and solid content of PF resin mixture containing various amounts of modifiers with various compositions it was found that modification led to major decrease in viscosity, caused the elongation of gelling time and reduced the solid content. In all variants modification of the resin led to significant improvement in plywood flammability evaluated on the basis of parameters such as: weight loss, time of ignition and burned area. The addition of fire retardant to the resin caused a decrease of shear strength. Composition of the modifier had a significant effect on bonding quality, however all plywood samples retained good values exceeding 1 N/mm$^2$ required by EN 314-2 (1993).

*Keywords*: fire retardant, plywood, impregnation

## INTRODUCTION

Birch plywood due to its very good mechanical properties have a wide range of applications in many industries. Similarly to other wood-based materials it is often used in the production of construction materials, furniture and floor (Bohm et al. 2012). Despite the very good mechanical properties resulting from its layered construction the application may be limited due to its susceptibility to inflammation. This results from the fact that the main raw material used for the production of plywood is combustible and characterized by a large number of oxygen atoms located in the chemical structures of wood main components (Mahr et al. 2012, Grześkowiak et al. 2016). To improve the flammable properties of wood based materials various types of fire retardants are commonly used in the industry. The application of these substances can considerably influence the fire parameters such as rate of combustion, heat release and flame spread (Grześkowiak 2012). In addition to increasing resistance to fire they should also be harmless to people and animals and shouldn't release toxic substances. Grexa et al. (1999) lists three ways to protect wood-based materials against fire including: chemical impregnation of wood, addition of flame retardant to an adhesive and application of chemicals on the surface of the materials. However, regardless of the impregnation method the protective agent should not adversely affect the properties of the materials. Dziurka et al. (2017) investigated the effect of method of introducing fire retardant on the properties of plywood. The addition of Fobos M4 led to decrease of the mechanical properties of plywood irrespective of the impregnation method but according to the authors the level of decrease was acceptable because plywood still met the requirements from the standard. Moreover, the addition of Fobos M4 reduced free formaldehyde emission. Treatment with ammonium sulfate and monoammonium phosphate as fire retardant also led to the considerable reduction of HCHO content (Demir et al. 2018). As reported by Borysiuk et al. (2011) the species of wood which veneer are made of are also important. Thus, the impregnation of beech veneer caused a decrease in the shear strength of plywood by about 20% and did not affect the bonding quality of plywood made of pine veneer. Bekhta et al. (2016) in their study confirmed that the standardized fire retardants for solid wood can be efficiently used for production of fire-resistant plywood and highlighted the capillary impregnation as the most effective treatment to achieve a good protection. Kawalerczyk et al. (2019) in their recent studies investigated the effect of veneer impregnation with a mixture of potassium carbonate and urea on the properties of plywood. Studies have shown that veneer protection did not affect the mechanical properties of water-resistant plywood glued with phenol-formaldehyde adhesive. Nowadays the achievements of nanotechnology are also used to improve the properties of wood materials. Łukawski et al. (2019) coated wood particles with aqueous dispersion of carbon nanotubes and it led to significant decrease of manufactured particle board thermal decomposition. Furthermore, Bueno et al. (2014) reported that the treatment of pine veneers with 3 wt% nano-$SiO_2$ aqueous dispersion can improve their fire behavior.

Due to the growing interest in improving fire properties of wood-based materials the aim of this study was to investigate the effect of phenol-formaldehyde adhesive modification with fire retardant on the fire behavior and bonding quality of manufactured water-resistant plywood.

## MATERIALS AND METHODS

The adhesive used for research purposes was the commercially available phenol-formaldehyde (PF) resin with the following characteristics: solid resin content of 48%, no. 4 Ford Cup viscosity of 153 s, gel time of 190 s at 130°C, pH 12.5, and density 1.22 g/cm$^3$. To adjust the viscosity of the adhesive mixture the commercially available mimosa filler (UT-10) was added. In order to improve fire behaviour of plywood the 30 wt% aqueous solutions of mixture of potassium carbonate and urea was added to PF resin in the amount and composition depending on the variant (Table 1).

**Table 1.** Composition of adhesive mixtures.

| Variant label | Amount of fire retardant | Weight ratio Urea : $K_2CO_3$ | UT-10 (g/100 g d.m. of resin) |
|---|---|---|---|
| 0 | - | - | 15 |
| 20.1 | 20% | 1:1 | 20 |
| 20.2 | | 1:2 | 20 |
| 30.1 | 30% | 1:1 | 20 |
| 30.2 | | 1:2 | 20 |

After the addition of the modifier and filler, the adhesive mixture was stirred in a magnetic stirrer (500 rpm, 5 min). In order to determine the properties of adhesive mixture the following tests were carried out: viscosity using a Brookfield DV-II + Pro viscometer, pH and solid content according to EN 1245 (2011) and EN 827 (2005), gel time at 130°C in accordance with PN-C-89352-3 (1996). The veneers with an average thickness of 1.5 mm and moisture content of 7% were glued with PF resin in the amount of 160 g/m$^2$. Prepared sets of three-layered plywood were pressed in laboratory press at 140°C for 4 min with the unit pressure of 1.4 MPa. To evaluate the effectiveness of fire protection the flammability test was carried out using modified French method (Soltani et al. 2016, Kawalerczyk et al. 2019). Plywood samples were placed on a tripod at 45° and a spirit burner with cotton wick was placed centrally under the sample. During the test the top of the flame was in direct contact with the sample. The duration of the test was 2 min and the time of ignition of the surface of the plywood was measured from the moment the specimens were exposed to fire. Based on the differences in the weights before and after test the weight loss (*WL*) was calculated:

$$WL = \frac{Wb - Wa}{Wb} \times 100\%$$

where: WL - weight loss, %

Wb – weight before the test, g

Wa – weight after the test, g

After two minutes the samples were cooled and then after removing the carbon layer the burned area was measured using a planimeter. The effect of the modification on the fire behaviour of plywood was evaluated on the basis of calculated Coefficient *Z:*

$$Z = \frac{Pz}{Pk} \times 100\%$$

where: Z - coefficient *Z*, %

Pk – burned surface of control samples, $cm^2$

Pz – burned surface of impregnated samples, $cm^2$

The evaluation of the protection quality was made on the basis of Coefficient Z values as follows: >75% - poor protection, 50-74% - average protection, <50% - good protection (Grześkowiak et al. 2016).

To assess bonding quality the shear strength ($f_v$) test was carried out in accordance to EN 314-1 (2004). Plywood samples were tested both after soaking in water at the temperature of 20°C for 24h (acc. 5.1.1. of EN 314-1) and after ageing test i.e. boiling in water for 4h, then drying in a laboratory oven at 60°C for 18h, re-boiling in water for 4h and cooling in water at 20°C for 1h (acc. 5.1.3. of EN-314-2).

## RESULTS

Curing properties and rheological behavior of both control and modified adhesive mixtures are shown in Table 2.

**Table 2.** Properties of adhesive mixtures.

| Variant label | Viscosity, m Pa s | pH | Solid content, % | Gel time, s |
|---|---|---|---|---|
| 0 | 1480 | 12.01 | 44.98 | 193 |
| 20.1 | 675 | 11.89 | 40.47 | 207 |
| 20.2 | 660 | 12.02 | 41.26 | 203 |
| 30.1 | 611 | 11.81 | 38.32 | 211 |
| 30.2 | 624 | 11.95 | 37.71 | 216 |

Based on the data presented in the Table 2 it can be concluded that modification of the resin caused a significant reduction in viscosity. The decreasing viscosity results in sinking excessively into the veneer and as a result the layer remaining on the surface is not sufficient to ensure good properties of the joint (Sellers 1989). The selection of the right type and the right amount of filler can regulate the viscosity of the adhesive mixture and consequently prevent the resin from sinking into the veneer. Therefore, in case of modified resin the amount of UT-10 filler added was increased. Regardless of the type and amount of modifier the modification didn't significantly affect the pH level of the mixtures. Moreover, the addition of fire retardant solution to the resin resulted in a longer gelling time. This is most likely caused by the decreasing solid content as a result of introducing an additional amount of water with the solution. Extending the gelling time is not beneficial from a technological point of view because the pressing cycle time should be as short as possible (Mirski et al. 2011).

On the basis of the data presented in Table 3 it can be concluded that the modification of PF resin with a mixture of potassium carbonate and urea led to the improvement of the flammable properties of plywood.

**Table 3.** Flammable properties of plywood.

| Parameter | 0 | 20.1 | 20.2 | 30.1 | 30.2 |
|---|---|---|---|---|---|
| Weight loss, % | 12.16<br>*0.41** | 8.98<br>*0.36* | 7.09<br>*0.74* | 7.45<br>*0.44* | 6.63<br>*0.71* |
| Time of ignition, s | 4<br>*0.5* | 9<br>*0.5* | 12<br>*0.8* | 11<br>*0.5* | 13<br>*0.8* |
| Burned area, $cm^2$ | 89.17<br>*3.07* | 65.49<br>*2.34* | 51.13<br>*3.13* | 53.76<br>*5.88* | 44.21<br>*1.21* |
| Coefficient Z | - | 73.44 | 57.34 | 60.29 | 49.58 |

*Standard deviation

The reduction of weight loss was achieved in all tested variants, however the largest reduction in mass loss was noted for the fire retardant addition in the amount of 30% having weight ratio 1:2 (Urea : $K_2CO_3$). Research have shown that increasing the amount of potassium carbonate in the mixture improves the effectiveness of the protection. Moreover, studies confirmed that reducing the concentration of the fire retardant aqueous solution have a negative effect on the protection of wood based materials (Wang et al. 2014). Delay of ignition time is a very desirable effect which is an important parameter for assessing the quality of the protection. In all variants of impregnated samples the ignition time was more than doubly elongated in comparison to the control samples. Similarly as in case of weight loss, the best results were obtained for variant 30.2. On the basis of the measured burned area and the calculated coefficient Z all variants of impregnation with the exception of 30.2 were classified as average protection. Variant 30.2 was defined as a good protection allowing the production of plywood with significantly better flammable properties.

The outcomes of shear strength ($f_v$) of both control and protected plywood are presented in Figure 1. As can be seen, all variants of adhesive modification caused a slight decrease of bonding quality of plywood.

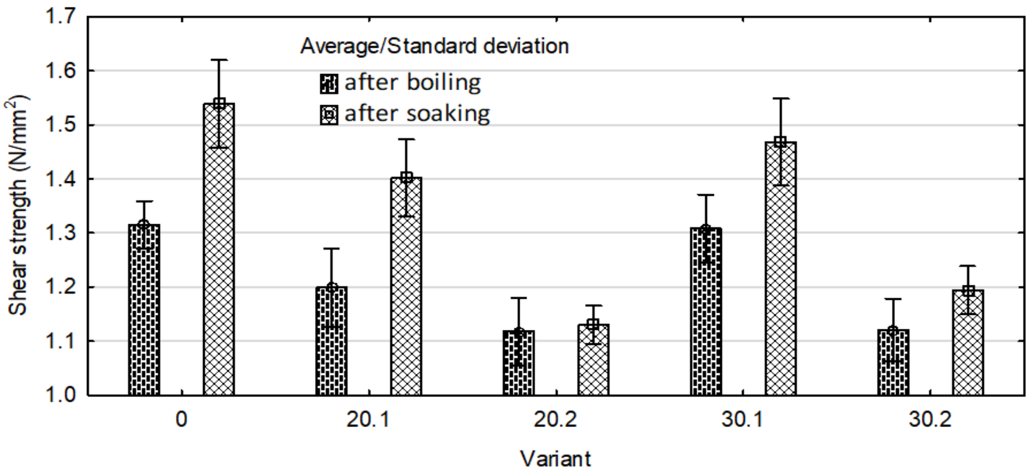


**Figure 1.** Shear strength of plywood.

The data included in Fig. 1 provide the evidence that increase of the amount of potassium carbonate in the mixture had a negative effect on bonding quality of plywood. The largest decrease in shear strength was noted for variants with components weight ratio 1:2 regardless of the amount of added fire retardant. The use of a mixture with the same weight ratio of urea and potassium carbonate led to slight decrease of shear strength in comparison to reference samples. The best results were obtained for the variant 30.1 where the decrease wasn't statistically significant. Despite the decrease in bonding quality, the shear strength of all plywood retained good values exceeding 1 $N/mm^2$ required by the standard.

CONCLUSIONS

1. The modification of PF resin with a mixture of potassium carbonate and urea had a significant effect on rheological behavior and curing properties of adhesive mixture. Introducing additional amount of water with aqueous fire retardant solutions led to elongation of gel time, decrease of viscosity and lowered solid content of the resin.
2. Each variant of the modification resulted in the improvement of the flammable properties of plywood. Addition of fire retardant to PF resin caused a delay in time of ignition and reduced weight loss and burned area.
3. Fire protection affected the bonding quality of plywood. However, it was found that shear strength of all plywood retained values exceeding 1 $N/mm^2$ as required by the EN 314-2 (1993).

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**Streszczenie**: *Wpływ modyfikacji żywicy fenolowo-formaldehydowej z wykorzystaniem środka ogniochronnego na właściwości brzozowej sklejki*. W pracy zbadano wpływ modyfikacji żywicy fenolowo-formaldehydowej z wykorzystaniem mieszaniny węglanu potasu i mocznika na właściwości wytworzonej sklejki. Na podstawie wyników badań mieszaniny klejowej zawierającej różne ilości modyfikatora o różnym składzie stwierdzono, że modyfikacja środka wiążącego spowodowała obniżenie jego lepkości, wydłużenie czasu

żelowania oraz zmniejszenie zawartości suchej substancji. W każdym z zastosowanych wariantów dodatek modyfikatora poprawił natomiast właściwości palne sklejki poprzez wydłużenie czasu zapłonu, zmniejszenie ubytku masy oraz powierzchni wypału. Modyfikacja żywicy PF wpłynęła negatywnie na wytrzymałość na ścinanie spoiny klejowej, jednakże wszystkie sklejki osiągnęły wartości przekraczające 1 N/mm$^2$ wymagane w normie EN 314-2.

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