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Selected aspects of production and characterization of layered biopolymer composite bonded with a cellulose-based binder

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Abstract: *Selected aspects of production and characterization of layered biopolymer composite bonded with a cellulose-based binder.* This project aimed to study the possibility of using regenerated cellulose for gluing a layered composite. In the scope of research have been produced different variants of layered composite differ in wood species and pressing time. The produced composite has been characterized according to selected mechanical and physical properties. The prepared samples have been referred to as those bonded with industrial MUF resin. Obtained results proved that regenerated cellulose can be used as a bonding agent. Furthermore, the tests confirmed an improvement in mechanical and physical properties after the bonding of the regenerated cellulose.

Keywords: regenerated cellulose, plywood, bonding agent, MUF resin, layered composite

INTRODUCTION

The growing and expanding population contribute to the ever-increasing problem of mass production of new goods. In the case of wood-based materials, to limit this tendency, it is necessary to search for new adhesives among the existing, well-known, and available biobased products, instead of inventing new ones. Plywood is an important wood-based composite widely used in furniture and interior decoration (Song *et al.* 2016). There used to be mechanical binders which have now been replaced by adhesives (Örs *et al.* 2000). However, most of these adhesives release formaldehyde emissions, which has a negative impact on the living environment and terms of hygienic safety (Böhm *et al.* 2012).

Because of environmental concerns regarding the lack of biodegradability of synthetic thermoplastics, green alternatives are increasingly studied that should be both based on renewable resources and biodegradable. One of them is regenerated cellulose which is one form of natural cellulose.

The basic substance of cellulose polymers is natural cellulose, which is the basic material that builds plant tissue. Cellulose occurs in a natural form (wood, cotton fibers), in a partially modified form (paper, parchment, fiber), or a completely changed form, as a result of depriving it of its original fibrous structure (cellophane, viscose fiber). Regenerated cellulose is used, among others, for the production of foil (cellophane, tomophane) for packaging purposes.

Currently, there is very limited knowledge regarding regenerated cellulose and its application in wood technology, and the product is still being researched in many directions.

Regenerated cellulose fibers have been explored in particle board as a reinforcement material by Kowaluk (2014). Single-layer boards with a thickness of 10 mm and a density of 800 kg/m^3 and the addition of regenerated cellulose fibers in the range from 0 to 15% were used in the research. The results showed that the addition of regenerated cellulose fibers did not improve the mechanical and physical parameters of the panels produced and the fracture performance. It was found that an increase in the content of regenerated cellulose fibers in the range from 0 to 15%, causes a decrease in mechanical parameters, and the board density profile becomes flatter, thus reducing the breaking modulus, intensifying water absorption at the beginning of soaking, but then the water absorption decreases with time and the breaking work of the composite increases linearly and causes a 120% increase in work.

(Chang *et al.* 2016) tested the tensile strength of poplar plywood using high-density polyethylene (HDPE) film as a binder. The plywood was produced using hot pressing and then cold pressing. The results showed that the viscosity of the HDPE melted film gradually decreased with the temperature increase from 140°C to 180°C, and the mechanical properties of the plywood showed that the produced plywood meets the requirements for type II plywood specified in the standard (GB/T 9846.3 2004), HDPE resins penetrate the light of the rays of the vessels and the wood fiber near the joint, contributing to the mechanical anchoring and filling of the plywood with excellent bonding properties. With increasing HDPE dose, hot press temperature, and pressure, MP and EP showed a tendency to increase, while with increasing humidity the results were opposite.

Studies of compounds based on Silk Fibroin powders, SF sponge, SF film for medical applications have been studied by Sultan *et al.* (2022). Haemostasis is very important in all surgical procedures and the results have shown that they are very good properties of all the above-mentioned compounds which have been confirmed for medical applications. It was found to be a promising standard biomaterial in various forms such as powder, sponges, films, and adhesive/sealant in various hemostatic applications. SFs in various forms are used in many applications such as wound healing, drug delivery, and tissue engineering due to their excellent biocompatibility, less inflammatory response to host tissue, slow biodegradation rate, cost-effectiveness, and ease of use.

The aim of this work was to use regenerated cellulose as a bonding agent in plywood technology. In the scope of research, thin transparent sheets of regenerated cellulose have been prepared, and the set of plywood of different pressing times and their content has been produced in laboratory conditions. These plywood have been tested to characterize their selected mechanical and physical properties.

MATERIALS AND METHODS

The raw materials listed below were used to make the tested material:

- Ash *(Fraxinus excelsior* L.*)*, 725 kg/m^3 density, 0.55 mm thick, and beech *(Fagus sylvatica* L.*)*, 0.62 mm thick veneer, 772 kg/m^3 density; both 4.8% +/-0,2% moisture content
- Melamine – urea-formaldehyde (MUF) resin with 8% of melamine content; 10% w/w filler (wheat flour); ammonium nitrate (NH_4NO_3) as a hardener; curing time of glue mass at 100°C was about 88 s,
- Regenerated cellulose in the form of a 0.3 mm thick, transparent sheet

Three-layer plywood was created, which had three layers of biodegradable cellulose between each veneer. The samples were pressed in a high-temperature press (pressing temperature 220°C; unit pressing pressure 1 MPa) for 5 minutes and 15 minutes. After pressing, they were air-conditioned at 20°C and 65% humidity to weight stabilization.

Depending on the time of pressing and type of veneer, the samples were produced in six variants:

1. Ash veneer with regenerated cellulose, short press time - 5 minutes (A1)
2. Ash veneer with regenerated cellulose, long press time - 15 minutes (A2)
3. Beech veneer with regenerated cellulose, short press time - 5 minutes (B1)
4. Beech veneer with regenerated cellulose, long press time - 15 minutes (B2)
5. Ash veneer with melamine – urea-formaldehyde resin, press time 5 minutes (reference for ash; A0)
6. Beech veneer with melamine – urea-formaldehyde resin, press time 5 minutes (reference for beech; B0)

Determination of Modulus of Elasticity in Bending and of Bending Strength

The elasticity and strength in bending were carried out on a computer-controlled universal testing machine following an EN 310 (1993) standard on at least 10 samples in each variant.

Contact angle

The contact angle has been measured on the PHOENIX 300 goniometer (SEO Co. Ltd., South Korea), where the samples have been moistened with a drop of water. The test was repeated 4 times on each variant. The program was set to take 60 shots in 60 seconds. Pictures and results after 0, 15, 30, 45, and 60 seconds were used for the study.

Colour parameters

Colour parameters were tested on the X-Rite spherical spectrophotometer (CIELab system; X-Rite, Grand Rapids, Michigan, USA) on 10 samples per variant.

Total VOC emission (TVOC)

In the emission test chamber, a supersaturated solution of potassium carbonate (K_2CO_3) was used and at a temperature of 23°C +/- 0.5°C the relative air humidity was 44% +/- 1%. Other parameters of sample conditioning - as in EN 717-1 (2004). The TVOC emission test was carried out after 24 hours of conditioning the samples by analyzing the chamber air over three repetitions after 20 minutes each, with the use of JD-3002 Air Quality Tester (Dongguan Jinlide Electronic Technology Co., Ltd., Dongguan City, Guangdong Province, China). We adhered to the standards when it comes to air conditioning conditions for samples during the emission test.

Density profile

The density profile of samples was analyzed using a DA-X measuring instrument (GreCon, Alfeld, Germany). The measurement based on direct scanning X-ray densitometry was carried out with a speed of 0.05 mm/s across the panel thickness with a sampling step of 0.02 mm. Samples were cut into 50 mm × 50 mm nominal dimensions. No less than 3 samples of every composite type were used to test the density profile.

Statistical Analysis

Analysis of variance (ANOVA) and t-tests calculations was used to test ($\alpha = 0.05$) for significant differences between factors and levels, where appropriate, using IBM SPSS statistic base (IBM, SPSS 20, Armonk, NY, USA). A comparison of the means was performed when the ANOVA indicated a significant difference by employing the Duncan test. The statistically significant differences for the achieved results have been indicated in the Results and Discussion paragraph, whenever the data were evaluated.

RESULTS AND DISCUSSION

Determination of Modulus of Elasticity in Bending and of Bending Strength

The results of measurement of modulus of elasticity in bending of plywood bonded with the use of regenerated cellulose and melamine – urea-formaldehyde resin (references) are visualized in Figure 1. The results of measurement of bending strength of plywood bonded with the use of regenerated cellulose and melamine – urea-formaldehyde resin are visualized in Figure 2. The best elasticity and strength bending results were shown by sample B2 beech wood with a longer pressing time and has better results than the reference sample B0. The worst results were shown by sample B1 pressed beech in a shorter time. After bending samples B1 were delaminated on one side. Probably the reason may be too short a pressing time, during which the binder may not yet interblend into the veneer. Ash plywood samples have the opposite results to those of the beech plywood sample. Sample A0 has the best results than B1 and B2. When analyzing the mean values of modulus of elasticity, it should be said, that within the ash wood samples, all the achieved results have been statistically significantly different. The same was for beech wood samples. Also, between the samples of the same pressing time, but different wood species, the differences between mean values of modulus of elasticity have been statistically significantly different. For modulus of rupture, the only statistically significant differences were found between A1 and B1, as well as between A2 and B2. There were also significant differences between reference and A1 and B1 samples. Song *et al.* (2017) in research on the use of polypropylene film as a binder, obtained higher bending strength using the APTES modification than using the MAPP modification. Flexural strength and modulus of elasticity deteriorated when the dose was increased from 3 to 5%. According to other research (Kawalerczyk *et al.* 2019), the best bending strength was achieved by plywood glued with pumpkin and rye flour. On the other hand, the addition of coconut flour had a negative effect and caused a reduction in bending strength.

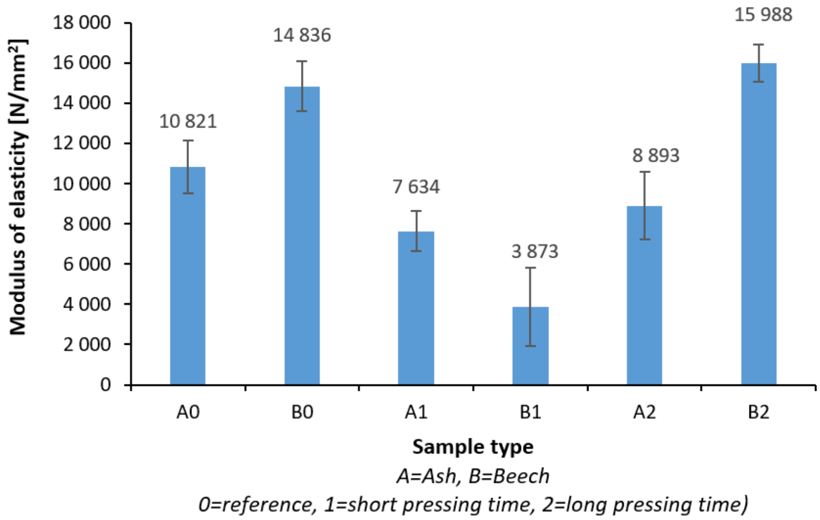

Figure 1. Modulus of elasticity of tested samples

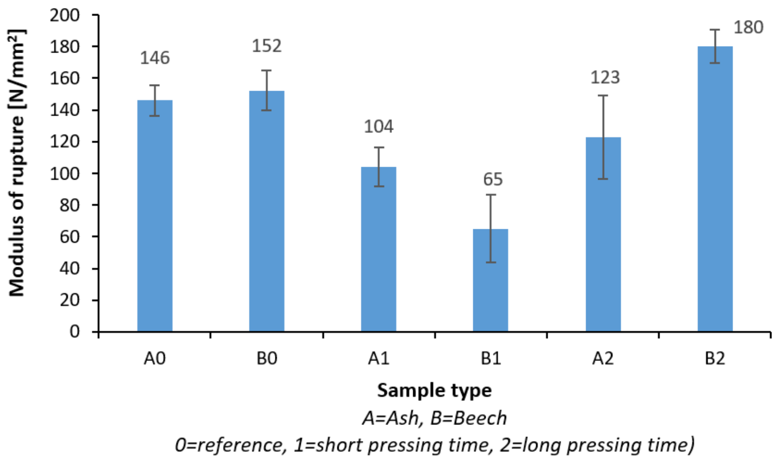

Figure 2. Modulus of rupture of tested samples

Contact angle

The results of the contact angle test are shown in Figure 3. The chart shows that the contact angle decreased with the increase of the time since the drop was placed. Two control samples, A0 and B0, were characterized by the fact that they spread over the test surface in a very short time. The three samples B2, B1, and A1 had a very similar contact angle, however, sample A2 had the highest contact angle and the contact angle did not change much with time. All cellulose samples, regardless of when they were pressed, are resistant in terms of their water repellent properties. They can find a special application where high water resistance is required. A similar observation has been made by Song *et al.* (2017), where the veneer was treated with a 3% modifier and a 0% modifier. The sample with the 3% modifier had a higher initial contact angle than the sample with the 0% modifier. With time, the contact angle decreased for the sample with the 0% modifier, but for the sample with the 3% modifier, the contact angle did not change much.

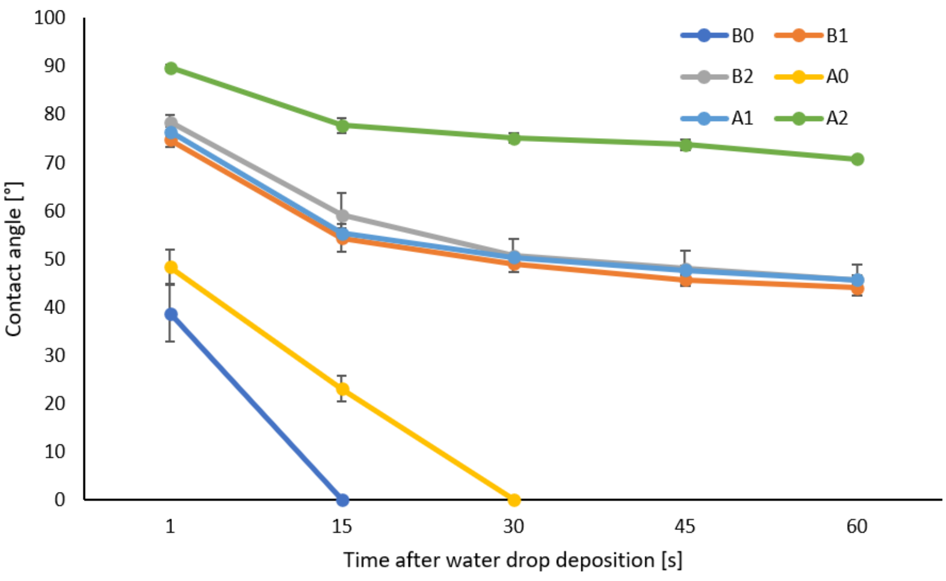

Figure 3. Contact angle on tested samples

Colour parameters

The results of the colour parameters test are shown in Figure 4. and Figure 6. The results of the colours of ash plywood are shown in the photos in Figure 5. and beech plywood is shown in Figure. 7. Based on the analysis of the obtained results, a significantly higher change of colour can be observed with an increase in pressing time. L- lightness decreases with longer sample pressing time. In the reference sample, the ash is lighter than the beech, but later, irrespective of the time, the brightness in the beech and ash became even. The a* greenness and redness do not change with increasing pressing time, but there are fewer of them in the reference sample. The *b** blueness and yellowness decrease with longer sample pressing time. There is more in the reference samples than in the short and long pressing time of the sample. Yamamoto *et al.* (2015) investigated the effect of annealing temperature on the color change of the veneer surface. Increasing the soaking temperature made the samples slightly darker (ie, L * decreased) and reddish (ie, a * increased). On the other hand, at 70°C, L * increased a lot and b * decreased. In research (Durmaz *et al.* 2019) during heat treatment, the wood of Scots pine darkened with increasing temperature and duration of heat treatment. These results showed that the color after heat treatment was darker due to oxidation and hydrolysis reactions during heat treatment (Korkut *et al.* 2008). Tuncer and Doğu (2018) mentioned that the color of the wood changes after heat treatment because the chemical components are degraded and extracts and other compounds are removed leading to a darkening of the color after heat treatment.

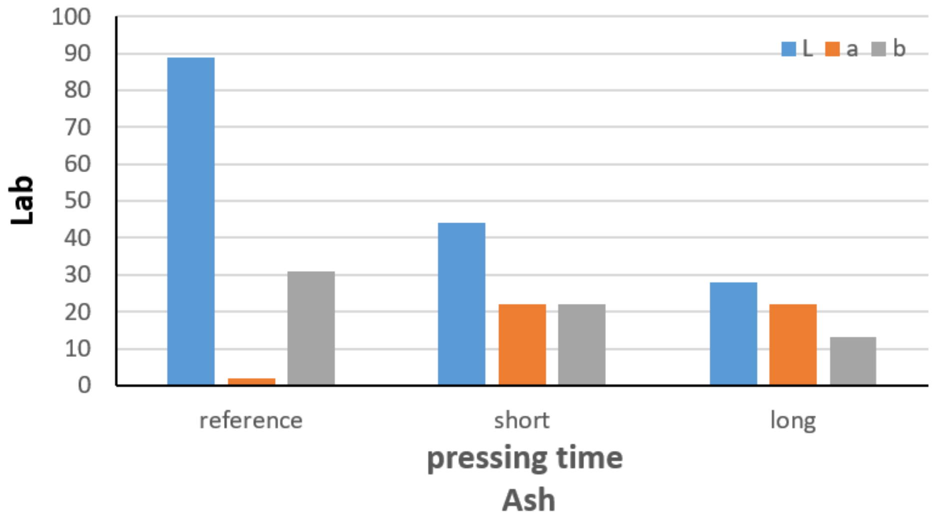

Figure 4. Colour parameters of ash plywood on tested samples

Figure 5. Color change in ash plywood

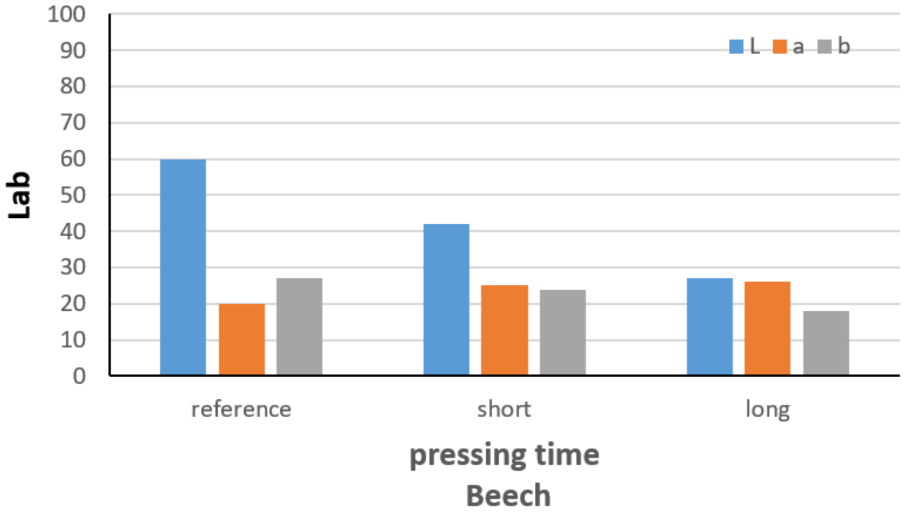

Figure 6. Colour parameters of beech plywood on tested samples

Figure 7. Colour change in beech plywood

Total VOC emission (TVOC)

The results of the total VOC emission test are shown in Figure 8.

The total VOC emission study showed that the total VOC emissions increase with the extension of the pressing time. Studies have shown that total VOC emissions for ash are higher than for beech. A similar observation has been made by Sivrikaya *et al.* (2019), where the Scots pine sapwood and heartwood have been thermally modified, and the VOC emissions have been evaluated. According to the cited research, the vacuum-heat treatment increased the sum of emitted compounds (TVOC) when heartwood samples were used. According to other research (Hyttinen *et al.* 2010), the VOC emissions significantly decrease after heat treatment, and the composition of emissions changes, as well.

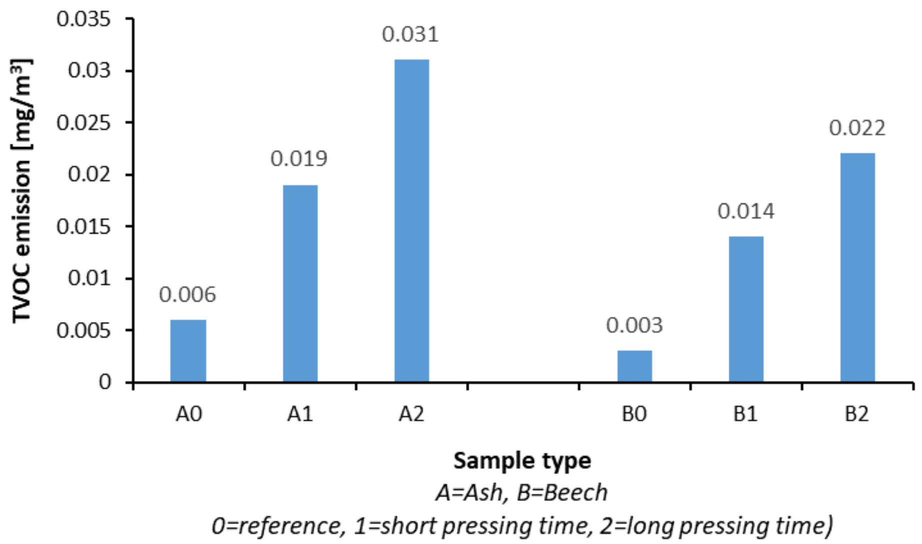

Figure 8. TVOC emission on tested samples

Density profile

The results of the density profile measurement have been displayed in Figure 9. As it can be seen, the presence of regenerated cellulose binder significantly influences the distribution of density over the composite thickness. When analyzing the ash composites (A0, A1, and A2), it can be found, that the bonding line density reaches the highest values, over 1100 kg/m^3 for the thickness of about 0.6 mm and 1.18 mm. It should be also mentioned here, that, despite the filler content in the glue mass, the binder impregnates the veneers. This fact is visible, because of the smooth change of the density of veneers to the higher density of binder. The same is for the beech reference composite (B0). With the increasing pressing time the thickness of the composites decreases, and, the density of veneers raise significantly. The highest density of bonding lines for cellulose binder is about 900 kg/m^3. These values have been reached for A2 composite at the thickness of 0.5 mm and 0.94 mm, and for B2 at the thickness of 0.62 mm and 1.14 mm. The compression of reference composites was 6.7% for ash (A0) and 11.8% for beech (B0). The higher compression of the composites pressed in 15 min, calculated as the difference between initial and final thickness, referred to as initial thickness, was found for ash (A2), and it was 58.8%, whereas for beech (B2) it was 55.7%. This can be caused by the density of veneers because the density of ash was about 6% lower than beech. It is well known, that wood of lower density can be more densified under the same parameters as the wood of higher density. It should be also mentioned here, that such a high compression (over 55%) was reached due to the fact, that the thermoplastic binder, which was used in research (regenerated cellulose) has been melted and partially transferred into the wood structure, what was also visible on the plots of density profiles. In research of the quality of the wood bonding depending on the method of applying the selected thermoplastic biopolymers by Gumowska and Kowaluk (2021) showed, that a significant increase in the density was noticed in the middle of composites thickness, in the bonding line. According to other research (Zeng *et al.* 2016), the density profile after 3 cycles of the three adhesive layers fluttered rapidly.

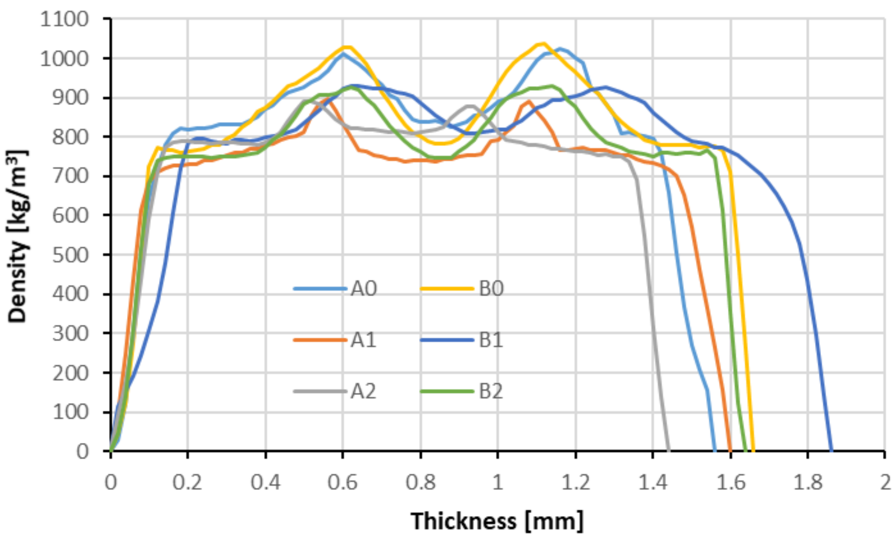

Figure 9. The density profiles of tested composites

CONCLUSIONS

According to the conducted research and the analysis of the achieved results, the following conclusions and remarks can be drawn:

1. Plywood bonded with regenerated cellulose exhibits very good mechanical properties when pressed by 15 min.
2. Of all the tested samples, the beech plywood bonded with regenerated cellulose and pressed for 15 min, had better properties during bending.
3. The most resistant to water absorption is ash plywood, also bonded with cellulose and pressed for 15 min.
4. The possibility of simultaneous bonding of composite materials and thermal modification of wood has been confirmed and demonstrated.
5. The application of regenerated cellulose binder for layered lignocellulosic composites production causes the impregnation of veneers and the higher density of face and core layers of bonded veneers.

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Streszczenie: *Wybrane aspekty wytwarzania i charakterystyka warstwowego kompozytu biopolimerowego wiązanego spoiwem na bazie celulozy*. Celem badań było określenie możliwości wykorzystania regenerowanej celulozy do klejenia kompozytu warstwowego. W ramach badań wykonano różne warianty kompozytu warstwowego różniące się gatunkiem drewna i czasem prasowania. Wytworzony kompozyt scharakteryzowano zgodnie z wybranymi właściwościami mechanicznymi i fizycznymi. Uzyskane wyniki dowiodły, że regenerowana celuloza może być stosowana jako spoiwo. Ponadto badania potwierdziły poprawę właściwości mechanicznych i fizycznych po użyciu regenerowanej celulozy w kompozytach warstwowych.

Słowa kluczowe: celuloza regenerowana, sklejka, spoiwo, żywica MUF, kompozyt warstwowy

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