

The study of the impact of *in situ* polymerisation with styrene or acrylates on water absorbability and swelling of thermomechanically densified poplar wood

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Abstract: *The study of the impact of in situ polymerisation with styrene or acrylates on water absorbability and swelling of thermomechanically densified poplar wood.* Black poplar samples, which were previously subjected to thermomechanical densification, were tested for an improvement on the field of water resistance. Series of samples were additionally thermally treated in a nitrogen atmosphere, and then series of densified only or densified and thermally treated samples were treated with monomer mixtures, containing styrene or acrylates, and co-monomers reactive toward cell wall of wood, followed by thermally induced radical polymerisation. All samples were tested by prolonged soaking in water, while volume swelling and absorbability were determined. Densified wood proved to be suitable for modification by *in situ* polymerisation. Thermally treated densified wood was found to be significantly more compatible with polymers used, as a decrease in its swelling was observed as dominant effect, while absorbability changes were less clear.

Keywords: *in situ* polymerisation, styrene, acrylates, wood absorbability, wood swelling

INTRODUCTION

Wood is a polymer composite composed mainly of cellulose, hemicelluloses and lignin (Krzysik 1978). They form cell walls, which are responsible for most of the physical and chemical properties exhibited by wood. Wood has been used for centuries as a building and engineering material. It possesses however several properties that negatively affect such applications. These include shrinkage and swelling of the wood, causing cracks and creating conditions for fungal growth (Krzysik 1978). The factor responsible for these phenomena is the interaction of wood material with water.

Various types of methods are applied to minimise these undesirable phenomena. It is possible to use chemical compounds that react with the cell wall causing its hydrophobisation (Rowell 2014) or mechanically protect against water access, e.g. by oiling wood or through the application of creosote (Shiraishi 2001). Filling the lumen with a polymer is another method of mechanical protection against moisture (Rowel 2005). Such a filling blocks the fastest way of transporting water within wood tissue. Direct polymerisation in lumen, called *in situ* polymerisation, is the best method of filling, as the method does not demand following solvent evaporation (Hill 2006).

As wood material is hydrophilic while most of the polymers, including vinyl and acryl ones, is hydrophobic, adhesion of the filling to cell wall is poor and some space can occur between them. It is possible to use substances, which on the one hand are able to become embedded into the polymer chain, and on the other hand chemically bind with wood (Li et al. 2013). In this study the method of *in situ* polymerisation using styrene and a mixture of acrylates was employed.

Wood modified in this way has greater dimensional stability and resistance to biotic agents (Li et al. 2013), with some mechanical properties such as bending strength and hardness being improved, as well (Sejati et al. 2017). In some methods, e.g. using furfuryl alcohol treatment wood also significantly changes colour, approaching the appearance of exotic species (Bartkowiak et al. 2015).

Polymers are macromolecular compounds, which are characterised by a kind of inhomogeneity, despite the fact that specific repeatability occurs in their structure. Unlike other compounds, they do not consist solely of the same molecules. They often do not have such a precisely defined chemical structure. Some of them can be used as additive in wood materials, especially as sealants, filling lumen in wood tissue.

Poly(butyl methacrylate) is a soft and flexible polymer (Ciabach 2001) while coatings are susceptible to dirt. Crosslinking undergoes when exposed to light which causes loss of solubility and is significant disadvantage from the viewpoint of polymer application. Poly(butyl methacrylate) is used in wood conservation as structurally consolidating agent (Lazzari and Chiantore 2000). Solutions of the polymer are used as wood adhesives or binder in wood putty for filling small defects.

Styrene is proposed as a cheap polymer precursor (Ermeidan et al. 2014), however its toxicity and carcinogenicity constitute severe problems (Weast and Grasselli 1989). Styrene is, in normal conditions, a colourless or slightly yellowish liquid with a characteristic, faint, unpleasant odour. On the other hand, styrene can be obtained with a good yield as the product of thermal depolymerisation of wastes, like expanded polystyrene packagings. This may be alternative source of styrene, in line with the principles of sustainable development. The same method of depolymerisation can be used to wood-styrene composites disposal. Styrene undergoes polymerisation quickly and easily (Rowel, 2005).

Paraloid B72 is a trade name of copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA) (Fig.1) at 70:30 ratio (Ciabach 2001). It is sold in two forms: as a 100% granulated resin and as a 50% solution in toluene. Paraloid B-72 is widely used for structural reinforcement of damaged wood items, with reduced strenght. This method is used, for example, in the conservation of historic wood (Ciabach, 2001).

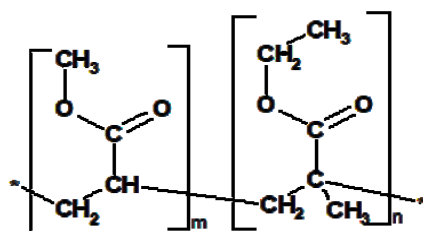


Figure 1. Paraloid B-72 polymer structure

Many compounds capable of reacting with wood are known, some of them, like isocyanates, are used in adhesives and varnishes. Styrene easily undergoes copolymerisation with maleic anhydride. Maleic anhydride, in turn, displays high reactivity to hydroxyl compounds, and can therefore react with alcohols and phenols present in wood (Fig. 2). Another type of reactive monomer is glycidyl methacrylate, capable of copolymerising with other acrylic monomers, at the same time its epoxy ring may be reactive towards wood (Fig. 3) but in this case the reaction often requires elevated temperature or the application of catalytic agents.

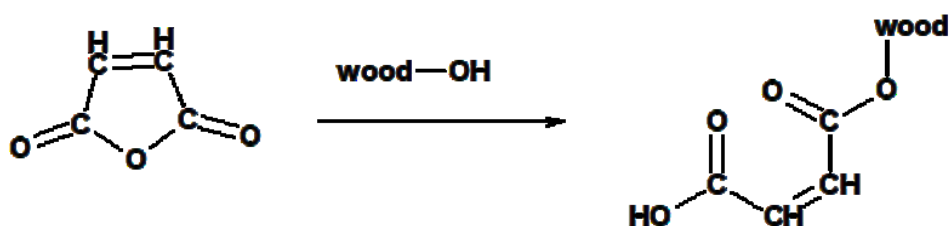


Figure 2. Maleic anhydride and its reactivity toward wood

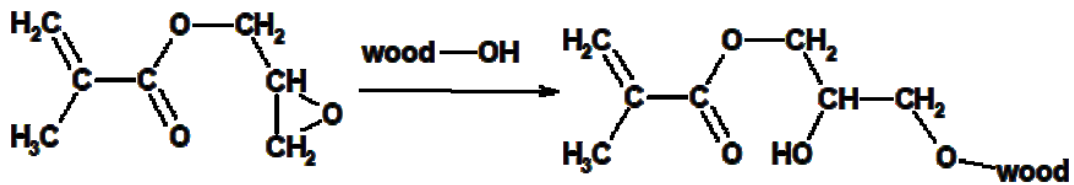


Figure 3. Glycidyl methacrylate and its reactivity toward wood

Aspen and poplar wood has relatively low durability or density, hence they are rarely used as a construction material for furniture and floors (Li et al. 2013). On the other hand, poplars, especially the fast-growing ones, achieve considerable annual growth and allow for obtaining large quantities of cheap material. Improving the quality of this material may cause new fields of application to emerge for poplar wood. Wood densification, which can be achieved by thermo-mechanical way is a promising method of its improvement. There are many reports on wood densification, e.g. alder, beech, birch, and pine wood veneer (Bekhta et al. 2017). Thermo-mechanical treatment was found to improve strength, surface properties (e.g. contact angle with water, roughness), and reduce equilibrium moisture content of wood as well (Vasconcelos and Del Menezzi 2013). Improvement of mechanical parameters was confirmed for black poplar wood as well (Ülker and Burdurlu 2016).

There is lack of reports connected to the modification of densified wood, especially of poplar, by *in situ* polymerisation in lumen. Due to changes in surface properties, interaction between polymer and wood cell wall may lead to different behaviour in contact with water. The aim of this study is to determine the improvement in water absorbability and dimensional stability of densified black poplar wood (*Populus nigra* L.), also additionally thermally treated, after *in situ* polymerisation with various monomers.

MATERIALS AND METHODS

Large samples (bars) were cut from a single board of black poplar wood (*Populus nigra* L.). The samples, of original dimension of 20×20×300 mm were subjected to densification at heated plate press at Versal sp. z o. o. company, as a part of the BIOSTRATEG2/298241/10/NCBR/2016 research project. Some of the samples were then thermal treated for 6 hours at 190 °C, in an atmosphere of nitrogen. Then the bars, both of densified only wood (DW) and thermally treated wood after densification (TTDW) were cut to 20 mm long samples, having dimensions about 20×20×6 mm, while thickness and width of the samples resulted from densification process, without further machining.

40 samples of densified wood (DW) and 40 samples of thermally treated densified wood (TTDW) were selected for the study. The samples were numbered, measured with accuracy to 0.01 mm and weighed with accuracy to 0.01 g. The samples were divided into 4 groups, dried at 105 °C to constant mass and subjected to *in situ* polymerisation. The samples were saturated with a solution of the following composition:

1. 115 cm³ of styrene and 1.85 g of maleic anhydride (MAN).
2. 2 cm³ of glycidyl methacrylate (GMA) in 115 cm³ of butyl methacrylate (BuMA).
3. 2 cm³ of glycidyl methacrylate (GMA) in 80 cm³ of ethyl methacrylate (EMA) and 35 cm³ of methyl acrylate (MA).

In each case, 0.25 g of benzoyl peroxide (BPO) initiator was dissolved as well.

The last two sample groups were the control one, consisting of the DW and TTDW samples respectively, but dried only, without monomer treatment and further polymerisation.

The sample groups destined for modification were placed in glass vessels and loaded with glass stopper to prevent floating. Appropriate monomer mixtures containing the initiator were poured into the vessels. Then the vessels with the samples were placed in a larger vacuum vessel and the air was evacuated using a vacuum pump for 30 minutes. The valve was then opened in the vacuum vessel to increase the pressure and fill up the pores in wood with

the monomers. After 30 minutes of soaking the process of air evacuation and pressure reduction was repeated. The next step involved removing the excess solution and placing the samples in polyamide pressure vessels, which were then hermetically sealed and placed in an oven. The samples were thermally hardened for 48 hours at 120 °C.

Then samples were removed from the oven and pressure vessels, and weighed to determine the weight percentage gain (*WPG*). *WPG* was measured based on the mass of the samples before polymerisation (m_d) and the mass of the samples after modification (m_m) using the following formula:

$$WPG = \frac{m_m - m_d}{m_d} \cdot 100 \%$$

Then the samples were placed in a vessel filled with water and loaded against floating. The samples were removed from water after 3, 11, 24, 48 and 100 hours of soaking, excess of water was removed by filter paper and then samples dimensions and mass were measured.

Water absorbability (*W*) was measured on the basis of the mass of the samples before soaking (m_0) and the mass of the same samples after soaking (m_w) based on the following formula:

$$W = \frac{m_w - m_0}{m_0} \cdot 100 \%$$

Swelling (K_V) was calculated on basis of the volume of the samples. Due to the wood densification process, it was not possible to determine the swelling in fixed anatomical directions of wood, so the calculations were limited to the volume before soaking (V_0) and the volume of the same samples after soaking (V_w) based on the following formula:

$$K_V = \frac{V_w - V_0}{V_0} \cdot 100 \%$$

RESULTS

The average density of densified poplar wood was $395.5 \pm 0.03 \text{ kg/m}^3$, and after thermal treatment the density dropped to $350 \pm 0.03 \text{ kg/m}^3$. This result indicates that the process of thermal treatment causes the densification to be partially inversed, probably due to interaction with steam or water contained in wood tissue.

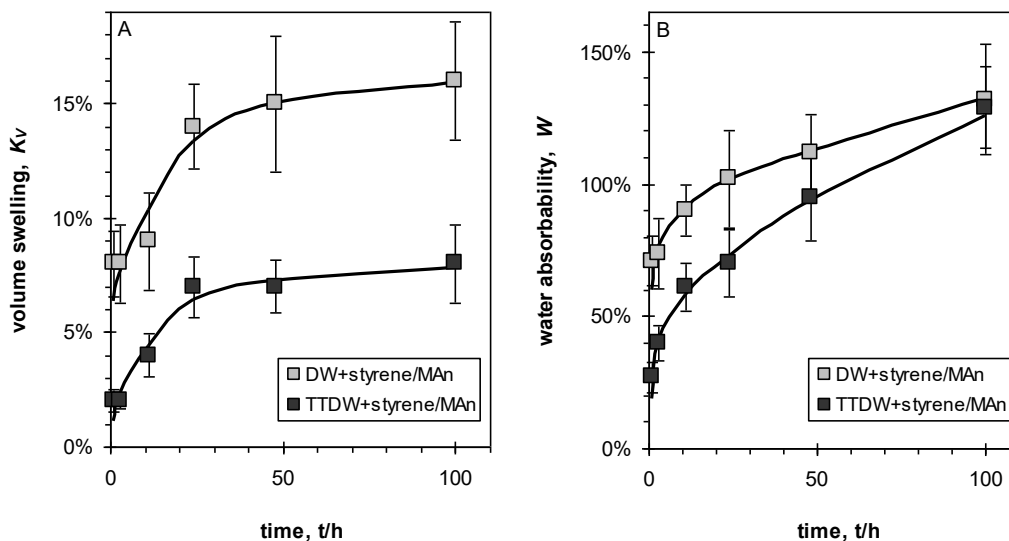


Figure 4. Swelling (A) and water absorbability (B) of wood treated with styrene/MAN

WPG averaged between 30 and 40 % for both DW and TTDW wood, thus thermal treatment of densified wood is supposed not to significantly influence its capacity of monomers used.

In the case of the control sample series, after 24 hours of soaking in water, the average swelling was found 15.5 % for DW and 9.7 % for TTDW, while average water absorbability 111 % and 76 % respectively. Figure 4 shows water absorbability and swelling found for the first series of modifications, using styrene and maleic anhydride. After the first hour of DW soaking, the water absorption was approx. 71%, while TTDW reached 27% at the same time. Swelling was found to be 8% and 2% respectively. Then, after 48 hours the absorption of water increased to 102% in the case of DW and 70% in the case of TTDW, while swelling increased to 14% and 7% respectively. The amount of water absorbed continued to increase, reaching 132% and 129%. The final swelling value was determined to be 16% for DW and 8% for TTDW. Over the entire experiment, TTDW swelling was about two times lower than DW one. The amount of water absorbed by DW increased twice as fast in the case of TTDW at the beginning, but after two days these values began to converge.

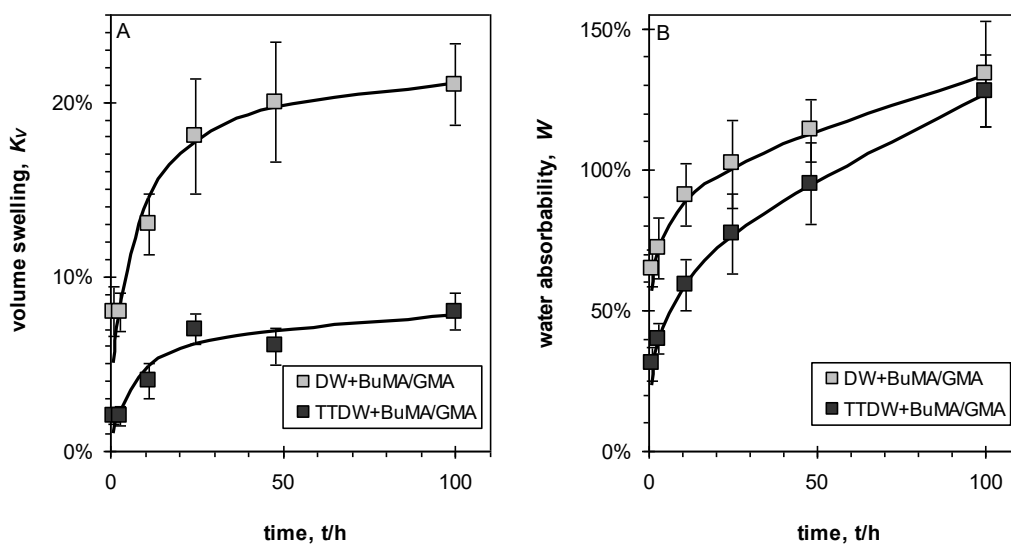


Figure 5. Swelling (A) and water absorbability (B) of wood treated with BuMA/GMA

In the Figure 5 water absorption and swelling are presented, which were determined for treatment with BuMA/GMA (modification No 2). Within the first hour of soaking, absorbed water amount was reached approx. 65% (DW) or 31% (TTDW). Swelling was found to be 8% and 2% respectively. After two days, absorption increased to 102% (DW) and 77% (TTDW), while swelling; increased to 14% and 7% respectively. Finally, the amount of water absorbed reached 134% and 128%, while swelling was 21% and 8%, respectively for DW and TTDW. In this case, the swelling value was twice as high for DW than TTWD as well. The values of absorbed water as in the first modification after 48 hours began to converge.

Figure 6 shows water absorption and swelling determined for treatment with the EMA/MA/GMA mixture (modification No 3). In this case the water absorption was approx. 55% (DW) and 30% (TTDW) after the first hour of soaking. Swelling at the level of 1% was found for both DW and TTDW. After two days, absorption increased to 117% for DW and to 94% for TTDW, while swelling increased to at the levels 14% and 6% respectively. In the end, the amount of water absorbed reached 165% and 137%, and swelling was 15% and 6% for DW and TTDW respectively. Initially, the swelling in both cases was the same and did not change after 5 hours of soaking; after 15 hours DW increased 10 times and then kept

gradually increasing. In this case, swelling of polymerised TTDW was the lowest among all the series tested.

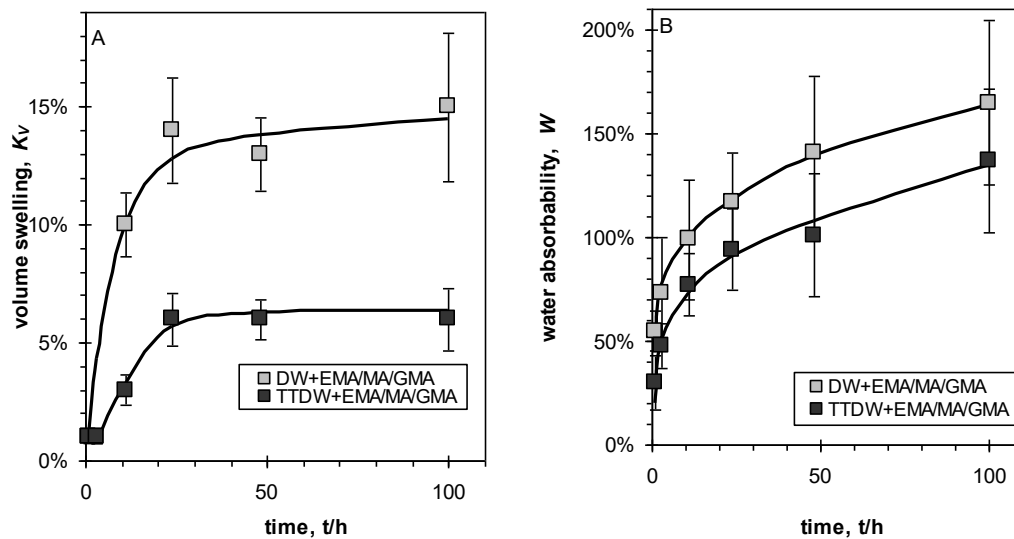


Figure 6. Swelling (A) and water absorbability (B) of wood treated with EMA/MA/GMA

In general, the tested methods of wood improvement demonstrated a great impact on the volume swelling of treated wood, while changes in water absorbability were found to be much lower. Strong interaction between cell wall and polymer can be thus concluded, reducing ability of wood to swell, in spite of still significant amount of water permeating into wood tissue. Changes in the swelling of densified wood were low in comparison to native wood of black poplar, which was investigated by Źmuda and Radomski (2018). At the same time, significant improvement of dimensional stability was found for densified and then thermally treated wood, as its swelling is about two time lower. The decrease in absorbability was observed mainly at the initial stage of soaking. This proves that the cell wall is still ready to interact with water. At the same time, the rate of change is strongly reduced, which can be linked to filling up the lumen with the polymer, and thus closing the fastest way of transporting water inside the wood. Such modified wood has a slightly lower water capacity and is more resistant to short-term exposure to wet conditions, but it is still able to adsorb and desorb water, providing a healthy indoor microclimate. On the other hand, its outdoor use is limited due to its relatively low dimensional stability, although it is much better than in the case of untreated wood (Li et al. 2010).

CONCLUSIONS

Based on the obtained results of the tests of treated wood, it can be concluded that the application of *in situ* polymerisation reduces the hygroscopicity of wood. The application of a mixture of acrylates improves the wood. However, better results were obtained with the use of styrene and maleic anhydride. The following particular conclusions can be drawn as well:

- Samples with higher WPG values were characterized by higher absorbability values on average.
- Wood modified with the *in situ* method displays greater dimensional stability, while the addition of maleic anhydride additionally enhances its properties.
- In this case, a strong time dependence was established, as the improvement of wood properties is high in a short period of time, but much lower in the case of long-term exposure.

- In all cases of tested modifications water absorption was found to be slightly lower in the case of densified and thermally treated wood samples, especially in a short period of time, than in densified wood. In contrast, the reduction of swelling for densified and thermally treated wood samples is much more conspicuous.
- It is worth subjecting densified wood to thermal modification, as such wood has a more aesthetically pleasing and desirable colour and can be used as an exotic wood imitation, while simultaneously achieving much better dimensional stability.

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Streszczenie: *Badanie wpływu polimeryzacji in situ z użyciem styrenu lub akrylanów na nasiąkliwość i pęcznienie zagęszczonego termomechanicznie drewna topoli czarnej (Populus nigra L.).* Próbki topoli czarnej poddano zagęszczeniu termomechanicznemu, a następnie przebadano je pod kątem poprawy odporności na wodę. Seria próbek została dodatkowo poddana modyfikacji termicznej w atmosferze azotu, a następnie próbki drewna tylko zagęszczonego oraz zagęszczonego i termowanego zostały zmodyfikowane metodą polimeryzacji mieszaniny monomerów, zawierających styren lub akrylany z dodatkiem komonomerów reagujących ze ścianą komórkową drewna. Wszystkie próbki badano przez długotrwałe moczenie w wodzie, określając spęcznienie objętościowe i nasiąkliwość. Drewno zagęszczone okazało się podatne na modyfikację metodą polimeryzacji *in situ*. Stwierdzono, że drewno zagęszczone i termowane jest znacznie bardziej kompatybilne z zastosowanymi polimerami, ponieważ zauważono silny spadek spęcznienia i mniej wyraźny spadek nasiąkliwości.

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