Annals of Warsaw University of Life Sciences – SGGW
Forestry and Wood Technology No 110, 2020: 35-40
(Ann. WULS-SGGW, For. and Wood Technol. 110, 2020)

Swelling and water resistance of black poplar wood (*Populus nigra* L.) modified by polymerisation in lumen with styrene

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Abstract: *Swelling and water resistance of black poplar wood (Populus nigra* L.*) modified by polymerisation in lumen with styrene.* Polymerisation in lumen of black poplar (*Populus nigra* L.) was performed to improve wood properties related to interaction with water. Wood samples were modified with styrene or a mixture of styrene and maleic anhydride, using benzoyl peroxide as initiator. Polymerisation was conducted in closed vessels at a temperature up to 120 °C. Volume swelling and water absorbability of modified wood samples were measured. A significant decrease in the rate of water absorption was found, especially at the initial stage of soaking, resulting in 50 % decrease in volume swelling and 85 % decrease in water absorption.

Keywords: black poplar wood, absorbability, swelling, styrene, polymerisation in lumen

INTRODUCTION

Wood is one of the oldest engineering materials, which has been used for a variety of applications. Wood has applications in building, furniture, housewares, toys, weapons and paper (Xu et al. 2009; Li et al. 2011). One of the oldest uses of wood is generating heat through combustion, while novel technologies of bioenergy from wood are subjects of wide research (Zhu et al. 2016a; Zhu et al. 2016b). The properties of wood depend on its cell wall structure (Salmén and Burgert 2009), which is composed of lignin, cellulose and hemicelluloses structural polymers; thus wood tissue is defined as a biocomposite (Rowell 2005, Salmen and Burgert 2009, Paris *et al.* 2010). Although wood is widely used, unfortunately it has some disadvantages, such as susceptibility to fungi or some insects, flammability or a change of properties during ageing (Li *et al.* 2011). The most important disadvantage of wood is connected to its interaction with water, which leads to dimensional change (Hill 2006, Fu *et al.* 2012) and subsequently to deformation and cracking.

Chemical improvement of wood's water resistance is a subject of wide research on wood modification (Bach *et al.* 2005), including reactions with anhydrides (Hill and Mallon 1998a, 1998b; Hill and Jones 1999) or alkoxysilanes (Donath *et al.* 2004). One of the ways to change the properties of wood is to modify the cell wall with polymers such as styrene-acrylonitrile copolymers (Devi and Maji 2012), or polymerisation within wood pores, including grafted PMMA (Cabane *et al.* 2014), polyglycols (Trey *et al.* 2010), polyaniline (Trey *et al.* 2012) or phenol-formaldehyde resins (Furuno *et al.* 2004). Substances are introduced into the cell wall to fill in the free space, which makes it difficult for water to enter the cell wall. The introduction of polymers into wood can be achieved through vacuum saturation with a polymer solution or with monomers, followed by *in situ* polymerization. Polymer chains should be covalently attached to the cell wall for stable modification (Rowell 2005). One possible solution is to attach a monomer reactive to the wood in order to bind polymer chain with cell wall (Cabane *et al.* 2014).

Black poplar wood is not considered a valuable material for construction, furniture, passageways or floors. The modification of wood with styrene, investigated in this work, leads to an improvement of wood properties, such as reduced water absorption or increased dimensional stability. New uses of black poplar wood are expected to be available thanks to such modification.

MATERIAL AND METHOD

A single deck of black poplar wood (*Populus nigra* L.) was cut into samples of 30 × 20 × 20 mm, while the longest dimension was cut parallel to the grain. Moisture content in raw wood was 6.94% ± 0.25% (determined according to Krutul 2002). Density of wood was 372 kg/m^3 ± 18 kg/m^3 .The samples were sorted and divided into three groups of 10 samples each. Group 1 was filled with styrene and group 2 with a mixture of styrene and maleic anhydride. A reference group wasn't modified.

Styrene from Sigma-Aldrich (Poznań, Poland), maleic anhydride and benzoyl peroxide (initiator) from POCh (Gliwice, Poland) was used. All reagents were of analytical purity. 250 cm^3 of styrene was used in both modifications, while an addition of 5 g of maleic anhydride was applied in group 2. Prior to the treatment of the wood samples, 0.75 g of benzoyl peroxide was dissolved in styrene.

Detailed description of vacuum saturation, thermal induced polymerization and final curing was presented in our previous paper (Żmuda and Radomski 2019), along with a procedure of soaking in water and measuring water absorption and swelling. In this work, samples were tested after 1 hour, 8 hours, 16 hours, 1 day, 2 days, 3 days, 5 days, 7 days and 14 days of soaking.

RESULTS

For the group 1 of the samples (modification with styrene), the weight percentage gain (WPG) was 98% ± 11%, while for the group 2 (styrene-maleic anhydride) the WPG of 106% ± 10% was determined.

In the case of the reference group, strong absorbability and swelling was observed (Figure 1). After one hour of soaking, swelling of 6% and water absorption of 47% were measured. Then, swelling of 13% and water absorption of 83% were determined after 16 hours. After 3 days, the swelling reached 15%, while water absorption increased to 118%.

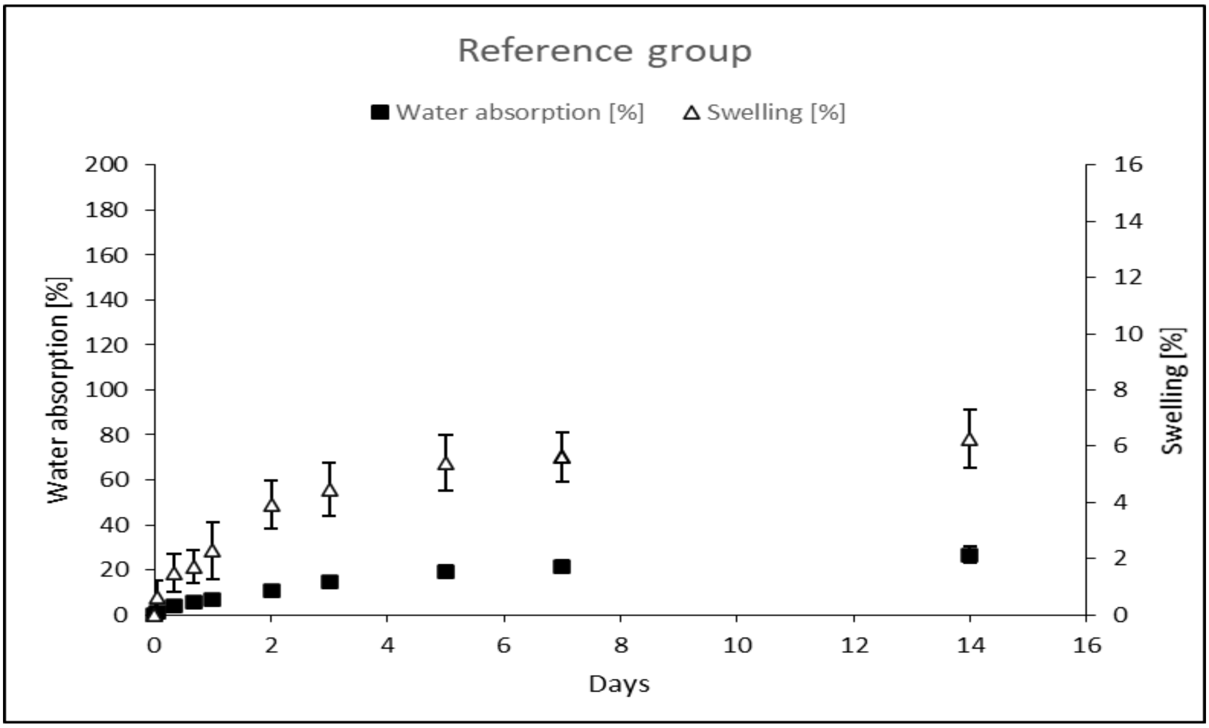

Figure 1. Swelling and water resistance for the reference group (without modification) – full time range

Further absorption was considered to takes place out of the cell wall, as a negligible increase of swelling was found in the next days of the experiment. The final value of the swelling was determined at 15%, and water absorption was at 170% after 14 days.

In the case of the group 1 of the samples (modification with styrene), a slight absorbability of the samples during the first hour was observed, along with low swelling, which was only 1% (Figure 2). After 24 hours water absorption rose up to 6%, which was still 15 times lower than the reference group, and swelling reached 3% was 5 times lover than reference group. After 5 days water absorption raised up to 17%, and swelling for 7%. Water absorption at the level of 25% and swelling of 7% were observed at the last measurement, which states absorbability 7 times lower than the reference and swelling 2 times lower. The swelling value in the whole test changes from a 6-fold to 2-fold difference for this series compared to the reference one. Water absorption value changes from 47 times to 7 times during the 14 days of the test.

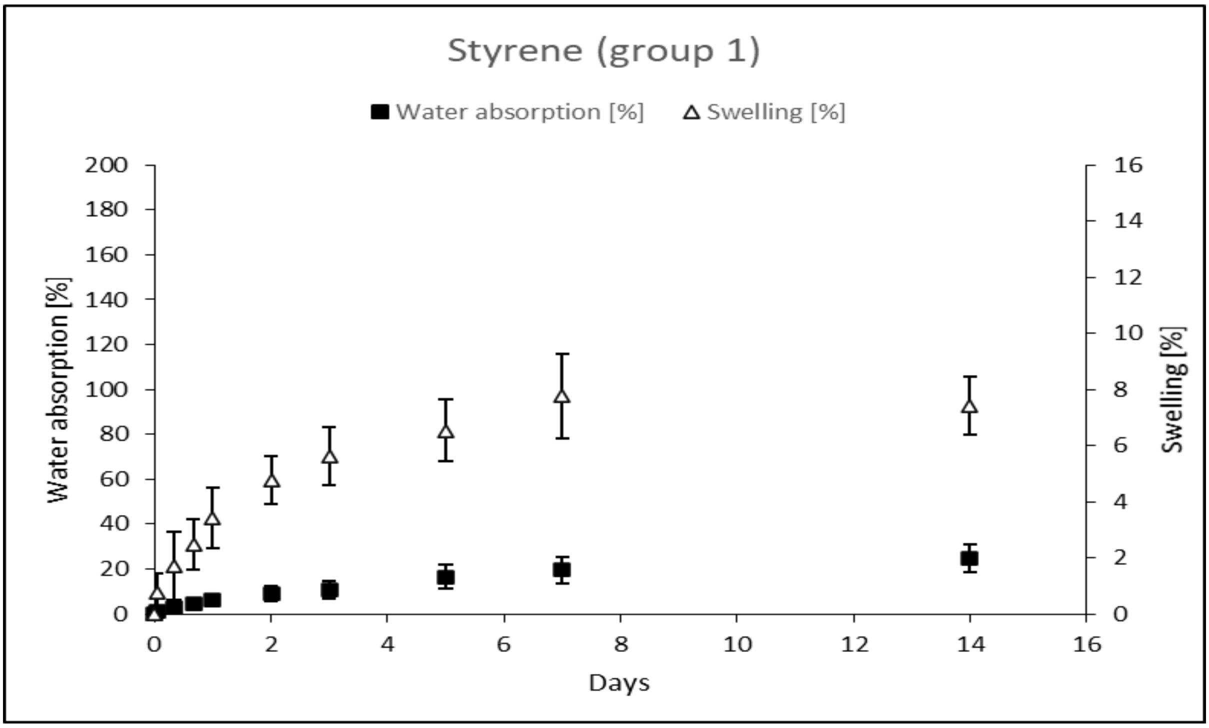

Figure 2. Swelling and water resistance for the Styrene group – full time range

In the case of the group 2 (modification with styrene-maleic anhydride mixture), the same increase in value was observed in the first hour (Figure 3). After 24 hours water absorption increased to 7%, which was noticeably higher then with styrene, but still 13 times lower than reference group.

In both modifications we received similar results after 14 days: absorbability of 25% for the group 1 and 27% for the group 2, while swelling was 7% and 6% respectively. In such a short period of time there are no differences between the two modifications. It is possible however, that with prolonged soaking would allow observing some differences. The modifications show considerable wood resistance to water, featuring lower absorption and swelling.

A slight difference in the amount of absorbed water between the two modifications, together with no significant difference in swelling degree, may be considered as an indication of cell wall not being modified in this way, while polymerization occurs in lumen.

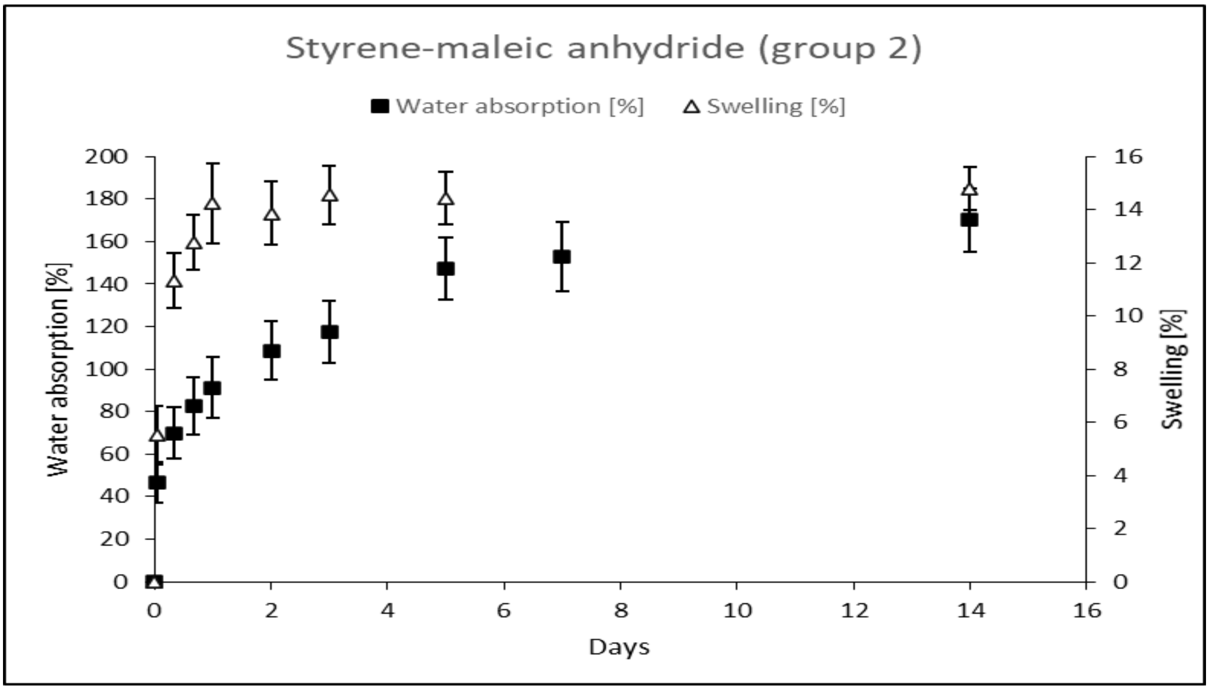

Figure 3. Swelling and water resistance for the Styrene-maleic Anhydride group – full time range

The polymer that gets through vacuum impregnation polymerizes and fills the cells lumen, thus less water can get into the cell's lumen. The cell wall can still absorb water at the same time, which leads to swelling.

CONCLUSION

The tests carried out show that:

1. Modification with styrene and maleic anhydride showed higher average WPG than modification with styrene alone, while the difference is not significant.
2. Both modifications showed similar absorbability and swelling of wood, while absorbability of the samples from the group 2 (modification with styrene-maleic anhydride) was still lower than the samples from the group 1.
3. The absorbability of modified wood is much lower than that of native wood, while swelling is only twice as low.
4. Further long-soaking studies and polymer-wood interaction studies are suggested to be useful.

ACKNOWLEDGEMENT. These investigations were conducted as a part of a research project founded by the National Centre for Research and Development BIOSTRATEG2/298241/10/NCBR/2016 "Intelligent systems for breeding and cultivation of wheat, maize and poplar for optimized biomass production, biofuels and modified wood."

REFERENCES

1. BACH S., BELGACEM MN., GANDINI A., 2005: Hydrophobisation and densification of wood by different chemical treatments. Holzforschung 59; 389–396.
2. CABANE E., KEPLINGER T., MERK V., HASS P., BURGERT I., 2014: Renewable and functional wood materials by grafting polymerization within cell walls, ChemSusChem 7 (4); 1020–1025.

3. DEVI RR., MAJI TK., 2012: Chemical modification of simul wood with styrene-acrylonitrile copolymer and organically modified nanoclay. Wood Sci. Technol. 46; 299–315.
4. DONATH S, MILITZ H, MAI C., 2004: Wood modification with alkoxysilanes. Wood Sci. Technol. 38; 555–566.
5. FU Y., LI G., YU H., LIU Y., 2012: Hydrophobic modification of wood via surface-initiated ARGET ATRP of MMA, Appl. Surf. Sci. 258 (7); 2529–2533.
6. FURUNO T, IMAMURA Y, KAJITA H., 2004: The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: a properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls. Wood Sci Technol 37; 349–361.
7. HILL C.A.S., 2006: Wood modification: chemical, thermal and other processes. Chichester: Wiley.
8. HILL C.A.S., JONES D., 1999: Dimensional changes in corsican pine sapwood due to chemical modification with linear chain anhydrides. Holzforschung 53; 267–271.
9. HILL C.A.S., MALLON S., 1998A: The chemical modification of scots pine with succinic anhydride or octenyl succinic anhydride. I. Dimensional stabilisation. Holzforschung 52; 427–433.
10. HILL C.A.S., MALLON S., 1998B: The chemical modification of scots pine with succinic anhydride or octenyl succinic anhydride. II. Reaction kinetics. J. Wood Chem. Technol. 18; 299–311.
11. KRUTUL D., 2002: Ćwiczenia z chemii drewna oraz wybranych zagadnień chemii organicznej. SGGW, Warszawa.
12. LI Y.F., LIU Y.X., WANG X.M., WU Q.L., YU H.P., LI J.A., 2011: Wood-polymer composites prepared by the in situ polymerization of monomers within wood, J. Appl. Polym. Sci. 119 (6); 3207–3216.
13. PARIS O., BURGERT I., FRATZL P., 2010: Biomimetics and biotemplating of natural materials. MRS Bull. 35; 219–225.
14. ROWELL R.M., 2005: Handbook of wood chemistry and wood composites. Boca Raton, FL: CRC Press.
15. SALMÉN L., BURGERT I., 2009: Cell wall features with regard to mechanical performance. A review COST Action E35 2004–2008: Wood machining – micromechanics and fracture, Holzforschung 63 (2); 121–129.
16. TREY S, JAFARZADEH S, JOHANSSON M., 2012: In situ polymerization of polyaniline in wood veneers. Appl. Mater. Interfaces 4; 1760–1769.
17. TREY S, NETRVAL J, BERGLUND L, JOHANSSON M., 2010: Electron-beam-initiated polymerization of poly(ethylene glycol)-based wood impregnants. ACS Appl. Mater. Interfaces 2; 3352–3362.
18. XU F.J., NEOH K.G., KANG E.T., 2009: Bioactive surfaces and biomaterials via atom transfer radical polymerization, Prog. Polym. Sci. 34 (8); 719–761.
19. ZHU H., LUO W., CIESIELSKI P.N., FANG Z., ZHU J.Y., HENRIKSSON G., HIMMEL M.E., HU L., 2016A: Wood-derived materials for green electronics, biological devices, and energy applications, Chem. Rev. 116 (16); 9305–9374.
20. ZHU H., FANG Z.Q., WANG Z., DAI J.Q., YAO Y.G., SHEN F., PRESTON C., WU W.X., PENG P., JANG N., YU Q.K., YU Z.F., HU L.B., 2016B: Extreme light management in mesoporous wood cellulose paper for optoelectronics, ACS Nano 10 (1); 1369–1377.
21. ŻMUDA E., RADOMSKI A., 2018: Water resistance and swelling of black poplar wood (Populus nigra L.) modified by polymerisation in lumen with acrylate polymers, Ann. WULS–SGGW, For. and Wood Technol. 104; 345–352

Streszczenie: *Pęcznienie i nasiąkliwość topoli czarnej (Populus nigra L.) modyfikowanej styrenem metodą polimeryzacji w świetle komórki.* Polimeryzacje w świetle komórki wykonano na gatunku topoli czarnej (*Populus nigra* L.) w celu poprawy jej właściwości związanych z oddziaływaniem woda-drewno. Próbki drewna zostały zmodyfikowane styrenem oraz mieszaniną styrenu i bezwodnika kwasu maleinowego z dodatkiem nadtlenku benzoilu, jako inicjatora. Następnie próbki poddano polimeryzacji w zamkniętych pojemnikach w warunkach podwyższonej temperatury do 120°C w celu utwardzenia. Na wykonanych próbkach zostały przeprowadzone następujące badania: WPG, spęcznienia objętościowego i nasiąkliwości. Pęcznienie objętościowe zmniejszyło częściowo swoje wartości. Stwierdzono znaczne zmniejszenie szybkości wchłaniania wody, zwłaszcza w początkowej fazie namaczania, co skutkowało 50% zmniejszeniem spęcznienia objętościowego i 85% spadkiem nasiąkliwości.

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